

NO_x Formation in Low-pressure Flames of Oxygenated Cyclic Ether Compounds

N. Lamoureux, L. Giarracca, L. Gasnot, P. Desgroux

1. lab. PC2A, Université de Lille, UMR8522/CNRS, Lille, France

General aspects

In order to limit the Green House Gas (GHG) emissions, biofuels are commonly presented as an alternative to traditional fossil fuels. In addition to the “traditional” biofuels (DME, ethanol, ...) which have an interest on an industrial scale, there are some derivatives of the lignocellulosic biomass that attract the attention of researchers for their possible use as innovative and advanced biofuels. Among these derivatives products, the cyclic ethers arouse particular interest due to their physical properties (similar to gasoline). The main benefit of the biofuel use is the decrease of the GHG emissions. Recently, few studies have been conducted to better understand their oxidation at laboratory scale (ignition delays in shock tube or in Rapid Compression Machine (RCM), laminar flame velocities, species speciation in RCM, low-pressure flat flames or in jet-stirred reactor). From these experimental works, detailed chemical kinetic models have been developed and validated. The rare studies carried on the NO_x formation have shown contradictory tendencies about the NO_x emissions.

The present work is focused on the study of the impact of the furanic compounds oxidation on NO_x emission. The NO_x chemistry is well-known to be issued from three main routes; thermal-NO, prompt-NO and NO-reburning. Regarding the adiabatic flame temperature of oxygenated compounds which tends to be lower than the one of the pure hydrocarbon compounds [1], the thermal-NO formation is expected to decrease when the fuel is blended with biofuel. Regarding the prompt-NO formation and the NO-reburning consumption, the detailed chemistry and the interconnection with the fuel chemistry is more complex. The prompt-NO is initiated by the reaction between CH radicals and N₂ yielding NCN+H. The NO-reburning also occurs at relative low temperature, and experimental works have shown that the efficiency of the NO reduction depends on the secondary fuel [2,3]. Previous experiments conducted in low-pressure flames of CH₄/MB/O₂/N₂ and C₂H₂/O₂/N₂ [4,5] have highlighted that the NO inception zone is the centre of competition between the formation (CH+N₂) and consumption (HCCO+NO) processes of NO.

The aim of this study is to test detailed kinetic mechanisms for the prediction of NO formation during the oxidation of furan (F) and tetrahydrofuran (THF). The work is performed in low-pressure flames. Chemical structure analyses were performed by using laser diagnostic techniques (Laser Induced Fluorescence (LIF) and Cavity Ring-Down Spectroscopy (CRDS)) and by using Gas Chromatography (GC). Considering two detailed mechanisms [6,7] recently validated for the furan and the THF oxidation, experimental results are compared to simulated species profiles. The NO species profiles were simulated by coupling the NOMEcha2.0 model previously validated in our team [9] to the fuel oxidation mechanisms.

Experimental setup

The premixed flames were stabilized on a McKenna burner in low pressure conditions (5.33 kPa) under slightly rich equivalence ratio of 1.2. The first flame is a reference flame of $\text{CH}_4/\text{O}_2/\text{N}_2$. In the two other flames, 50% of the methane is substituted by the cyclic ether (F or THF), keeping constant the equivalence ratio. The total gas flow rate was fixed to 5 L/min for each flame. The experimental setup was previously described in [4]. The species mole fraction profiles as function of the height above the burner (HAB) were obtained by moving the burner that is mobile in the vertical direction. Stable species were sampled through a quartz microprobe (with an angle of 30° and an orifice diameter of $250\text{ }\mu\text{m}$) and analysed on real-time. The gas sampling is compressed at about 300 torr before being injected and analyzed by using two GC apparatus. The first one is coupled to a mass spectrometer allowing for the species identification. The second one is coupled to FID/TCD detectors allowing for the species mole fraction quantification as function of the HAB. In situ measurements of CH and NO were performed by using LIF. Absolute quantification of the relative NO and CH profiles was performed by NO addition in the cold mixture, and by using CRDS for the CH radicals. Temperature profiles were determined by using NO-LIF thermometry.

Modeling

Two detailed kinetic mechanisms for the furan and the THF oxidation were considered in the present work. Both of them have been validated from the low-moderate to the high temperature, considering extensive experimental database (ignition delays, species speciation, laminar flame velocities). The first one (named Tran) [6] is devoted to the unsaturated furanic oxidation, and the second one (named Fenard) [7] is devoted to the saturated furanic oxidation. However, the oxidation reaction pathways of both cyclic ethers (F and THF) present wide common routes which allow simulating the species profiles in our flames conditions. These models were coupled with the NOMecha2.0 sub mechanism validated for the prompt-NO formation. Additionally the GDFkin3.0+NOMecha2.0 model (named GDFkin) was used to simulate the species profiles in the case of the reference flame, in order to identify the capability of the furanic models to predict the methane oxidation. Calculations have been performed with the LOGEsoft package (LOGEresearch, version v.1.10.0) [8]. As the present work is ongoing, the temperature profile was measured in the methane flame only, and used as user-temperature profile for the three flames simulation.

Main results

Regarding the experimental results obtained for the CH and NO species, it is shown that the presence of furan with respect to the methane flame increases the peak mole fraction of CH by 4 %, and the NO mole fraction in the burned gases by 9%. On the contrary, the THF substitution decreases the CH peak mole fraction by 24 % and the NO mole fraction in the burned gases by 42%.

The experimental species mole fraction profiles as function of HAB were compared to the simulated ones obtained with the two examined mechanisms (Tran and Fenard). Using both mechanisms, the predicted species profiles are found in globally good agreement with the experimental ones. In the methane flame, the simulated CH peak mole fractions obtained with GDF or Fenard are found in good agreement with the experimental one, as shown in Fig. 1. Contrary to the simulated peak mole fraction obtained with Tran, which is found 70% lower than the experimental one. Thanks of the good ability of Fenard to predict the CH mole fraction profiles in the case of the methane flame, the nitrogen chemistry was focused on the coupling of this model with NOMecha2.0. Figure 2 shows the experimental NO mole fraction

profiles obtained in all flames, compared to the simulated ones obtained with the Fenard+NOMecha2.0 model. In the case of the reference flame, the simulated NO profile obtained with GDFkin is 9% higher than the one obtained with Fenard+NOMecha2.0. However, the present model fails to predict the increase (or decrease) of the NO profile observed with the Furan/Methane flame (or THF/Methane flame) with respect to the one measured in the reference flame.

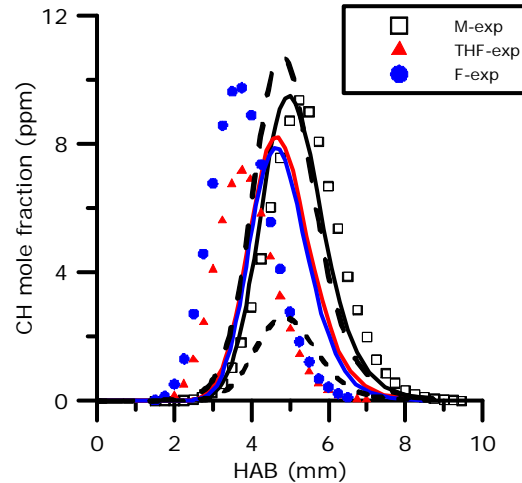


Fig. 1. Experimental and simulated CH mole fraction profiles. Symbols; experimental values, lines; simulated profiles with the corresponding color (lines: Fenard, dotted line: Tran (in the methane flame only), dashed line: GDFkin).

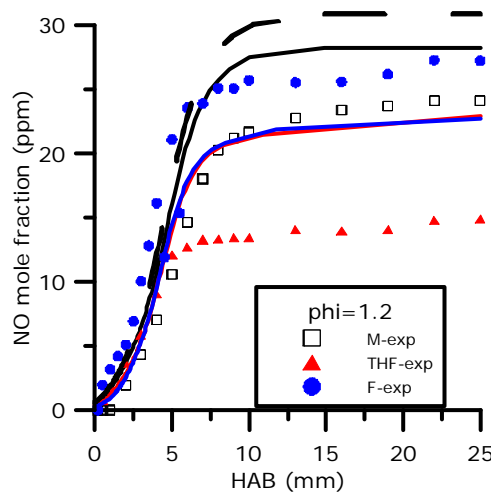


Fig. 2. Experimental and simulated NO mole fraction profiles. Symbols; experimental values, lines; simulated profiles with the corresponding color (lines: Fenard, dashed line: GDFkin in the methane flame only).

The preliminary analyses of the reaction pathways indicate that in the inception zone of the NO profiles, reactions relevant to the processes of the NO-reburning are important in the presence of furanic species. This is partially due to the increase of the C_2H_2 mole fraction with respect to the methane flame. As recently shown in the case of the NO formation in the acetylene flames, ketenyl radicals ($HCCO$) are formed in large amount from the acetylene oxidation and favour the reaction pathway following the sequence ($HCCO$, $HCNO$, $HNCO$, NH_2 , NH , NO) [5]. Because of the increase of the C_2H_2 peak mole fractions ($F > THF \gg M$), this sequence is activated in the presence of the furanic species. The pathway through the reactions

$\text{HCO} + \text{NO} = \text{HNO} + \text{CO}$, and $\text{HNO} + \text{H} = \text{NO} + \text{H}_2$ is also activated, especially in the furan/methane flame where the furan oxidation with OH yields promptly formaldehyde and HCO. However, we cannot explain the decrease of the NO formation in the case of the THF/methane flame which deserves further investigations.

Acknowledgments

This work is a contribution to the CPER research CLIMIBIO. The authors thank the Hauts de France Région and the French Ministère de l'Enseignement et de la Recherche for their financial support to this project.

References

- [1] P.-A. Glaude, R. Fournet, R. Bounaceur, M. Molière, Adiabatic flame temperature from biofuels and fossil fuels and derived effect on NO_x emissions, *Fuel Process. Technol.* 91 (2010) 229–235.
- [2] P. Dagaut, F. Lecomte, Experiments and Kinetic Modeling Study of NO-Reburning by Gases from Biomass Pyrolysis in a JSR, *Energy Fuels*. 17 (2003) 608–613.
- [3] Y. Shu, F. Zhang, H. Wang, J. Zhu, G. Tian, C. Zhang, Y. Cui, J. Huang, An experimental study of NO reduction by biomass reburning and the characterization of its pyrolysis gases, *Fuel*. 139 (n.d.) 321–327.
- [4] M.D. Sylla, N. Lamoureux, L. Gasnot, Impact of methyl butanoate oxidation on NO formation in laminar low pressure flames, *Fuel*. 207 (2017) 801–813.
- [5] N. Lamoureux, L. Gasnot, P. Desgroux, Quantitative NH measurements by using laser-based diagnostics in low-pressure flames, *Proc. Combust. Inst.* (2018).
- [6] L.-S. Tran, Z. Wang, H.-H. Carstensen, C. Hemken, F. Battin-Leclerc, K. Kohse-Höinghaus, Comparative experimental and modeling study of the low- to moderate-temperature oxidation chemistry of 2,5-dimethylfuran, 2-methylfuran, and furan, *Combust. Flame*. 181 (2017) 251–269.
- [7] Y. Fenard, A. Gil, G. Vanhove, H.-H. Carstensen, K.M. Van Geem, P.R. Westmoreland, O. Herbinet, F. Battin-Leclerc, A model of tetrahydrofuran low-temperature oxidation based on theoretically calculated rate constants, *Combust. Flame*. 191 (2018) 252–269.
- [8] LOGESoft, LOGEResearch, <http://logesoft.com/>.
- [9] N. Lamoureux, H. El Merhubi, L. Pillier, S. de Persis, P. Desgroux, Modeling of NO formation in low pressure premixed flames, *Combust. Flame*. 163 (2016) 557–575.