

Study of prompt NO formation during methyl esters combustion in low pressure premixed flames

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Abstract

This work is focused on the study of the environmental impact of methyl esters used as biodiesel and concerns more particularly the kinetic of nitrogen oxides formation during the methyl esters combustion in flame conditions. The aim of this study is to test and optimize detailed kinetic mechanism for the prediction of NO formation during the oxidation of methyl butanoate (MB), a compound chosen as model for biodiesel. Structure analysis in laminar low pressure flames is performed by coupling laser diagnostic techniques (Laser Induced Fluorescence, LIF) and analytical techniques (Gas Chromatography, GC, and Fourier Transform Infrared Spectroscopy, IRTF). Experimental results will be compared to detailed kinetic mechanisms previously reported in the literature for MB oxidation.

Introduction

Due to the increase of demand for energy, concerns for the oxidation of fuels impact on environment and healthy have been reviewed since the late 90's. Concerning the reduction of pollutant emission due to transport, one option relies on the use of biodiesels that are typically derived from oil transesterification. Depending on the oil source (animal fat, vegetable oil, ...), biodiesel composition is wide. It consists mainly on esters with long alkyl chain (C12-C24) that can be more or less saturated. Biodiesel presents numerous advantages in comparison to fossil fuel. Among them, one can mention its renewable aspect, reduction of greenhouse gas emission, of particulate matter. NO_x emissions are often reported to be increased in comparison to classical diesel [1], but few studies show that the NO_x emission could be reduced [2] if the engine cycle are optimized to.

In engine gas exhaust, NO_x is predominantly NO. NO formation is attributed to 3 routes; thermal-NO, prompt-NO and fuel-NO. The fuel-NO is negligible since it is due to the oxidation of the nitrogen-containing species which are almost equal to zero in the fuel (fossil and bio-). Prompt-NO is due to the rapid reactions between N₂ and radicals CH and CH₂. It is expected to be more important in rich conditions, but is dependent on the fuel chemistry. Thermal-NO occurs at high temperature (1800K and higher) according to Zeldovich mechanism. Moreover, the timescales of thermal-NO formation are comparable to the residence time of the gas inside the engine. It is suspected that there is a competition between thermal-NO (at longer timescale) and prompt-NO formation (with the change of fuel composition). Recently, Hoekman and Robbins [3] reviewed the effects of biodiesel on NO_x emission. They mentioned different effects due to not only the fuel but the engine that could explain the NO_x increase. From chemical point of view, NO_x emission increases

with increasing the unsaturation (iodine value) but decreases with the increase of the length of the alkyl chain. From physical point of view, the lower compressibility and the higher viscosity of alkyl esters than diesel both yields an increase of the pressure rise and increase of the thermal-NO.

Because of the complexity of biodiesel not only in term of size of molecules but also in variety of molecules composition is complex, methyl butanoate (MB) that is the simplest methyl ester, is a good candidate to examine the chemical kinetics aspect of the ester oxidation. MB oxidation has been previously studied in numerous apparatus (jet-stirred reactor, opposed diffusion flames, flow tube, shock tube and rapid compression machine). From these experiments, different detailed mechanisms were validated [4,5,6]. However, none of them was validated against not only laminar low pressure flames but NO formation.

In the present work, NO formation was studied during MB oxidation in low pressure flames. Experimental conditions were selected to examine the prompt-NO formation exclusively. NO species and temperature profiles were measured in situ by using LIF techniques. Stable species profiles were measured after gas probe sampling by using analytical techniques such as GC and IRTF. Experimental results have been compared to species profiles calculated by using Premix code. For that purpose, detailed mechanisms available in the literature was updated with the NO_x chemistry extracted from Lamoureux et al. [7].

Experimental

Low pressure burner

Experiments were performed in laminar, premixed flames stabilized on a 6 cm diameter bronze water-cooled McKenna burner. The burner is vertically mobile in a stainless steel enclosure connected with a vacuum

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pump. The pressure is maintained at 5.3 kPa (40 torr) thanks to an automatic valve.

The mixture composition was regulated using three mass flow controllers for CH₄, O₂, MB and N₂. Liquid fuel (MB) is first vaporized at 353 K and the vapor phase is added to the gas mixture through a heated mass flow controller. 5 flame compositions have been considered with a constant total flow rate (320L/h) and nitrogen dilution equal to 65%. A stoichiometric CH₄/O₂/N₂ flame (for which the C/O ratio is equal to 0.25) is studied as reference flame (flame 1). MB fuel is substituted to CH₄ (with 20 and 50%) with respect to either the equivalence ratio (flames 2 and 3) or the C/O ratio (flames 4 and 5). Volumetric flow rates are listed in Table 1.

flame	CH ₄	MB	O ₂	N ₂	Φ	C/O
1	37.3	0.0	74.7	208.0	1.0	0.25
2	23.0	5.7	83.3	208.0	1.0	0.29
3	10.7	10.7	90.7	208.0	1.0	0.32
4	24.9	6.2	80.9	208.0	0.85	0.25
5	9.3	9.3	93.3	208.0	0.77	0.25

Table 1. Volumetric flow rates in standard liter per hour unit of the flames. Φ is the flame richness.

Laser diagnostics for NO detection at 225 nm

The laser system consists of a Quantel Nd:YAG laser pumping a dye laser. Wavelengths around 225 nm were provided after doubling the fundamental dye radiation pumped with the second harmonic frequency at 532 nm, and frequency mixing with residual 1064 nm. The 6 ns duration pulse had a bandwidth of around 0.7 cm⁻¹ at 225 nm.

The laser beam was introduced unfocused parallel to the burner surface and shaped using a horizontal slit of 1 mm height in front of the burner enclosure and parallel to the burner surface. The LIF signal was collected by a two-lens system and focused on the entrance slit of a 0.3-m monochromator. The entrance slit (250-μm width, 10-mm height) was parallel to the laser axis. The output slit was adjusted to obtain a collection bandwidth of 9 nm. The LIF signal in the linear regime was collected along the (0-2) band of NO around 246 nm and measured at the temporal peak. The fluorescence and laser intensity signals were simultaneously acquired and averaged a digital scope.

Gas sampling and analysis using IRTF and GC techniques

Stable species are quantified after gas probe sampling through a quartz microprobe (tip equal to 150 μm) by using either infrared transformed Fourier spectroscopy or Gas Chromatography equipped with TCD/FID detectors. Using GC, species are identified thank to mass spectrometry. In both GC apparatus, the column is PARABOND Q25. Gas lines are heated at 350K.

Results

Temperature profiles

Temperature profiles have been measured using NO-LIF thermometry in linear regime. Gas mixture was doped with 50 ppm of NO substituted to N₂. The excitation LIF spectrum was recorded scanning the wavelength from 225.45 to 225.75 nm, in the A²Σ⁺ ← X²Π(0-0) band. Wavelengths scan rate was fixed at 0.5 pm/s in the fundamental and signals were accumulated over 7 laser shots. LIF signal was corrected spectra from the laser fluctuations. At each HAB, the experimental LIF excitation spectrum was compared to simulated spectra from Lifbase. The temperature was determined from minimization of the residual between the experimental and simulated spectra according to a least mean square method. Meantime, temperature was determined by fitting the Boltzmann lines after correcting the LIF signal from the absorption Einstein coefficient and the level degeneracy. Figure 1 illustrates the temperature profile along HAB determined in the CH₄ flame (flame 1) according to both methods, showing the good agreement between them. Temperature in the burned gases reached nearly 1800 K in all flames. Close to the burner surface, temperature was measured using a type K thermocouple.

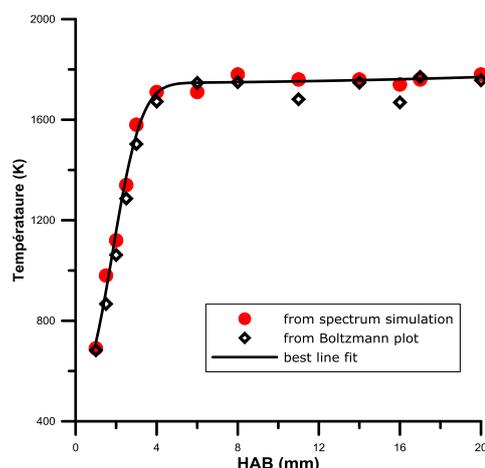


Fig 1. Temperature profiles in flame 1 determined either from Boltzmann plot or Lifbase simulated spectra.

Absolute NO species profiles measured in situ

NO species profiles were measured after exciting the Q₂(27) transition at 225.5 nm. Fluorescence signal was averaged over 500 laser shots. Owing the fact that the LIF signal is related to the population of the laser-excited levels, it is converted into NO mole fraction in arbitrary units after taking into account the temperature-dependence Boltzmann function. Absolute mole fraction of NO was determined equal to 12.4 ppm by using added species method where known amount of NO are substituted to N₂ in the CH₄ flame (flame 1). Absolute NO mole fractions profiles along HAB are plotted in Fig. 2. In all flames, the NO species profiles show a increase in the reaction zone and a plateau in the burned gases. At Φ=1, in presence of MB in the fuel mixture

there is a slight decrease (by 15%) of NO in comparison with the value measured in the CH₄ flame, but the substitution by 20% or 50% of MB in the fuel mole fraction does not affect the NO mole fraction in the burned gases. When the ratio C/O in the mixture is fixed equal to 0.25, the increase of MB in the fuel mixture yields a decrease of the NO mole fraction by 45 and 60%, with 20% and 50% of MB respectively.

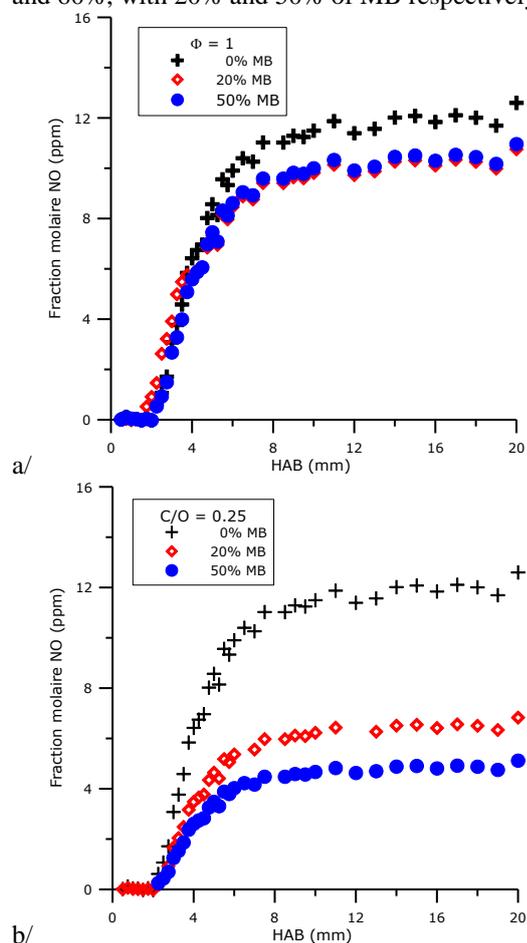


Fig 2. Absolute NO profiles in the CH₄/MB/O₂/N₂ flames a/ $\Phi=1$ (flame 1-3), b/ C/O=0.25 (flame 1 and 4-5). Gas flow rates in Table 1.

Species profiles after gas probe sampling

IR spectra obtained in the CH₄/MB flames reveal very complex structures in the reaction zone as shown in Fig. 3. MB exhibits a very congested spectrum that presents many interfering spectral range with CO, CH₄ or H₂O. However, spectra measured in the burned gases show very simple structures that are attributed as expected to CO, CO₂ and H₂O. Except for CO₂ (in wavenumber range 2394-2276 cm⁻¹), it is rather difficult to determine the species profiles along the distance above the burner since the spectral region for each species is more or less affected by interfering species in the reaction zone.

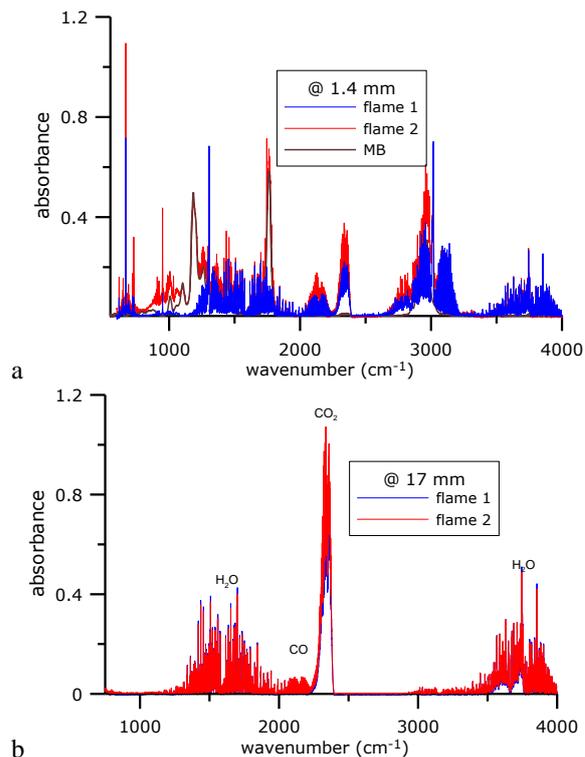


Fig 3. IR spectra measured in the gas probed in the flame 1 and 2, a/ at 1.4 mm b/ at 17 mm above the burner. MB diluted in N₂ spectrum is shown in a/.

Species measurements by GC apparatus are still under progress at the time of writing this communication. The major intermediate species due to oxidation of MB will be analyzed and quantified.

Discussion and comparison with modeling

Modelling computations were performed using the Premix code of the Chemkin-II package [8]. The kinetic analysis was essentially based on the rate of production and consumption and on the flux of N-atoms analysis. Computations were performed using experimental temperature profiles. The mass fluxes were computed with respect to the standard volumetric flow rates (Table 1). Two detailed kinetic mechanisms available in the literature were tested: Gail et al. [4] and Dooley et al. [5]. Since none of them included nitrogen chemistry, they were completed with the N-species sub-mechanism validated against prompt-NO formation in CH₄ or C₂H₂ flames [7]. Hereafter the 2 mechanisms will be referenced as GL and DL, respectively for [4] and [5].

Absolute mole fractions of NO measured at 20 mm above the burner are compared to those calculated by using either GL or DL mechanisms, Fig. 4. By using GL mechanism, calculated values are twice higher than the experimental results in the stoichiometric flames. Surprisingly, the simulated values are in good agreement with the experimental in the leaner conditions corresponding the CH₄/MB flames at C/O ratio = 0.25. Results issued from DL lies 25% below the experimental data in all flames.

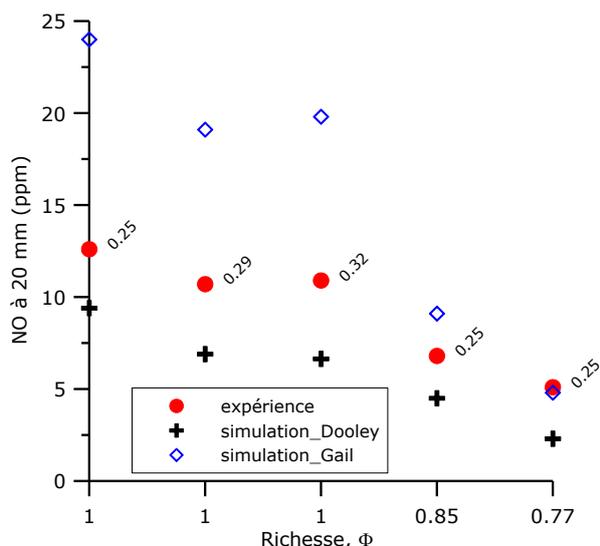


Fig 4. Absolute NO mole fraction at 20 mm. Comparison between experimental data and simulated by using DL and GL mechanisms. Labels refer to C/O ratio in the mixture.

Analysis of rate-of-production was performed for the 2 mechanisms. H-abstraction reactions of MB yield 4 isomers $C_5H_9O_2$ (MBMJ, MB2J, MB3J and MB4J, see fig. 5). The 2 major intermediates are MB2J and MB3J according to Gail, but MBMJ and MB2J according to Dooley. Moreover the reaction rate constant values in GL are even higher than in DL. Figure 5 shows the primary alkyl radical pathways in the reaction zone, according to ROP analysis performed in flame 3 at HAB = 3mm.

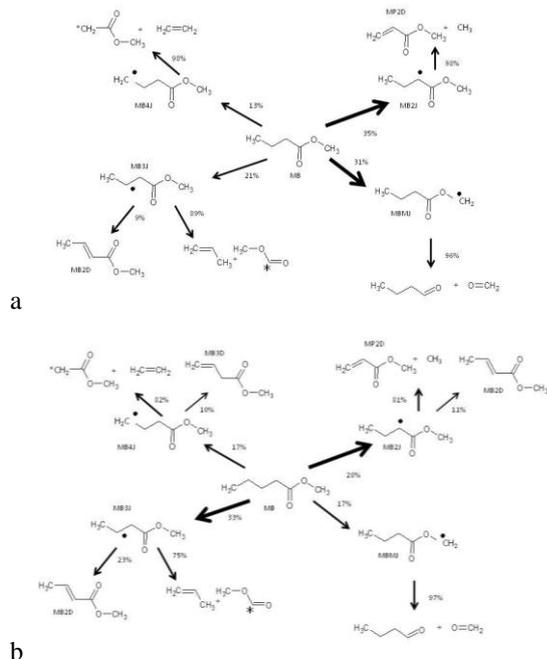


Fig. 5. MB oxidation pathways performed in flame 3 at HAB=3mm. a/ with DL mechanism, b/ GL mechanism.

Conclusions

In this work, NO profiles were obtained in different flames MB/ $CH_4/O_2/N_2$ stabilized at low pressure. NO species were measured by using LIF technique after probing the molecule at 225.5 nm and collecting the fluorescence signal at 245 nm. Temperature profiles in these flames were also measured by NO-LIF. Temperature was determined by a fitting procedure that consists to minimize the residual between the experimental spectrum and a calculated one (from Lifbase). Stable species will be measured by classical techniques such as IRTF and GC.

Experimental NO species profiles were compared to simulated ones by using 2 detailed mechanisms available in the literature [4, 5]. None of them were validated for NO formation. N-species chemistry extracted from a recent mechanism validated for prompt-NO formation [7] was implemented to these 2 mechanisms. It is shown that the mechanism that the mechanism of Gail et al. [4] overpredicts NO mole fraction in the burned gases by a factor of 2 in the stoichiometric flames, and the one derived from [5] underpredicts by 25% the experimental results. ROP analysis performed with the 2 mechanisms show that the relative reaction pathways are different one to each other.

Measurements of stable species will be continued. We should be able to improve the prediction of NO species. GC measurements will allow to obtain some of the first intermediate species (MB2D, MB3D, MP2D, CH_2O or propene, ...).

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References

- EPA420-P-02-001, 2002 "A comprehensive analysis of biodiesel impacts on exhaust emissions"
- McCormick RL. Effects of biodiesel on NOx emissions. National Renewable Energy Laboratory, 2005. Available on line: http://www.arb.ca.gov/fuels/diesel/altdiesel/060805mco_rnick.pdf
- Hoekman S.K., Robbins C., Fuel Processing Technology 96 (2012) 237-249
- Gail S., Thomson M.J., Sarathy S.M., Syed S.A., Dagaut P., Diévar P., Marchese A.J., Dryer F.L., Proc. Combust. Inst. 31 (2007) 305-311
- Dooley S., Curran H.J., Simmie J.M., Combust. Flame 153 (2008) 2-32
- Hakka M.H., Bennadji H., Biet J., Yahyaoui M., Sirjean B., Warth V., Coniglio L., Herbinet O., Glaude P.A., Billaud F., Battin-Leclerc F., Int. J. Chem. Kin 42 (2010) 226-2010
- Lamoureux N., Desgroux P., El Bakali A., Pauwels J.F., Combust. Flame 157 (2010) 1929-1941

⁸ R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, A
fortran program for modelling steady laminar
onedimensional premixed flames, Sandia report
SAND85-8240, 1985