



Experimental study and modelling of NO_x formation in high pressure counter-flow premixed CH₄/air flames



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HIGHLIGHTS

- NO mole fraction profiles measured by LIF in high pressure lean CH₄/air flames.
- Three kinetic mechanisms: GDFkin[®]3.0_NCN, GRImech2.11 and GRImech3.0 are compared.
- Kinetic analysis to better understand the differences between the three mechanisms.
- Inclusion of the new prompt-NO formation pathway in the GRImech3.0 mechanism.

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ABSTRACT

Nitric oxide (NO) is an atmospheric pollutant responsible for the destruction of the ozone layer and the creation of photochemical smog. As a result, NO_x emissions from combustion sources are regulated in most industrialised countries. The need to control NO_x emissions while also promoting more efficient use of fossil energy resources requires a better understanding of combustion processes, especially the chemical kinetics of NO_x formation. NO formation in high-pressure flames is a research area of great practical interest as high pressure exists in practically all power-generation and propulsion engines and it is known that pressure influences the combustion chemistry. In the present work, NO mole fraction profiles were measured by Laser Induced Fluorescence in laminar high pressure (up to 0.7 MPa) counter-flow lean CH₄/air (E.R. = 0.7) flames. Inherent problems linked to the application of the NO LIF technique in high pressure environment were addressed. The experimental NO profiles were then compared with modelling using the OPPDIF code and the three detailed kinetic mechanisms: the GDFkin[®]3.0_NCN mechanism developed by Lamoureux et al. and the two mechanisms from the Gas Research Institute: GRImech 2.11 and GRImech 3.0. A kinetic analysis based on rate of production/consumption analyses was performed to better understand the differences between the three mechanisms. Finally, the GRImech3.0 mechanism was modified with three updated prompt-NO submechanisms proposed in the literature and the consequences on the N-containing species mole fractions predictions are discussed.

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1. Introduction

The combustion of fossil fuels (natural gas, coal, oil) leads to a number of pollutant emissions in the atmosphere. Among these pollutants (CO_x, SO_x, soot, etc.), nitrogen oxides NO_x (NO and NO₂) emitted from combustion sources are regulated in most industri-

alised countries. The need to control NO_x emissions requires a better understanding of combustion processes, especially the chemical kinetics of NO_x formation during combustion. The study of NO_x formation and destruction kinetics in high-pressure flames is a research area of great practical interest as high pressure exists in practically all power-generation and propulsion engines and it is known that pressure greatly influences the combustion chemistry. NO_x measurements in industrial combustion conditions are usually performed in the exhaust gases using gas analysers (chemiluminescence for NO_x). While this method provides global data, it does not enable the detailed study of NO_x formation mechanisms during combustion. Hence, experimental investigations within the combustion chamber (engine) or in laboratory flames are required. Most of the studies related to NO_x measurements in engines [1–6], or

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high pressure flames [7–9] have been performed using the non-intrusive Laser Induced Fluorescence (LIF) technique. However, NO LIF measurements in high pressure environments are perturbed by various spectral features: interferences with O₂ fluorescence bands (Schumann Runge B³Σ⁻–X³Σ⁻ bands), collisional broadening and shifting, and absorption by CO₂ and H₂O (laser attenuation and trapping). Several strategies have been proposed in the literature to minimise those perturbations. In particular, Bessler et al. [9] presented a relevant comparative study, based on previous work by their group [10–12], on the different excitation/detection strategies using the A–X(*v'* = 0, *v''* = 0,1,2) vibrational bands of NO for LIF measurements in CH₄/air flat flames stabilised at pressures up to 6 MPa. Their main conclusions were: (i) excitation on the A–X(0,0) band followed by detection on the A–X(0,1) and/or A–X(0,2) bands present the best performances in terms of selectivity and signal to noise ratio as long as the absorption and trapping phenomena are weak. The authors recommend this scheme in high pressure flames with small diameters; (ii) excitation on the A–X(0,1) band with collection over the A–X(0,2) and/or (0,3) bands gives relatively high fluorescence signals and has the advantage of reducing laser absorption and trapping effects, especially if the experiment requires long signal paths; (iii) excitation through the A–X(0,2) band with collection on the A–X(0,0) and/or (0,1) bands has been mainly employed for NO measurements in engines. Even if signals are weak, attenuation and interference problems are strongly reduced. NO measurements can be achieved for relatively high concentrations (>1000 ppm).

Most of the studies comparing experimental and modelled NO data in high pressure flames [8,13,14] use the well-known mechanisms from the Gas Research Institute: GRI_{mech} 2.11 [15] or GRI_{mech} 3.0 [16]. In the last decade, particular attention has been paid to the prompt-NO formation pathway and it has been demonstrated that the reaction CH + N₂ = HCN + N (known to be spin forbidden) [17] has to be replaced by the reaction CH + N₂ = NCN + H [18,19]. Recently, Lamoureux et al. revised the GDFkin[®]3.0_NCN mechanism [20] based on their extended experimental database (NO, CH, CN, NCN, HCN, NCO) in low pressure flames. To our knowledge, this mechanism has never been validated on NO in high pressure flames, except in our previous work [21] where its performance was tested by comparison with experiments from the literature [22] and other models (GRI_{mech} 2.11, 3.0 [15,16] and Konnov6.0 [23]).

In the present work, NO mole fraction profiles were measured by Laser Induced Fluorescence in laminar high pressure (up to 0.7 MPa) counter-flow lean CH₄/air (E.R. = 0.7) flames. Inherent problems linked to the application of the NO LIF technique in a high pressure environment were addressed. The excitation/detection scheme was carefully chosen, based on excitation and fluorescence spectra analysis, to limit interferences on NO LIF signals and a theoretical correction procedure is proposed to take into account the influence of spectral broadening and quenching on LIF signals when pressure increases. The experimental NO profiles were then compared with modelling using the OPPDIF code [24] and the three detailed kinetic mechanisms: GDFkin[®]3.0_NCN [20], GRI_{mech} 2.11 [15] and GRI_{mech} 3.0 [16]. To better understand the behaviour of these three mechanisms with respect to their predictions of NO formation in counter-flow flames at high pressure, a kinetic analysis was performed. The aim is to evaluate the relative contribution to the overall NO concentration from each of the four major NO formation pathways (thermal, prompt, N₂O and NNH). For this purpose, a sub-mechanism subtraction technique as well as rate of production and consumption analyses were used. Finally, as the GRI_{mech}3.0 mechanism still does not include the appropriate channel for the initiation reaction of prompt-NO (CH + N₂ = NCN + H), it was modified with three updated prompt-NO submechanisms proposed in the literature: Lamoureux et al. [20], Konnov [23] and Williams et al. [25]. The consequences

on the N-containing species mole fractions predictions are discussed.

2. Experimental set-up

2.1. High pressure facility

The high pressure facility used in this work was detailed previously in [26]. An overview is presented here. It consists of two twin counter-flow converging burners placed in a high pressure vessel, equipped with optical access for laser diagnostics. The burners are mounted on a vertical translation system and the distance between the nozzles can be manually adjusted by moving the top burner with respect to the bottom one. In the present study, the distance between the burners was fixed at 10 mm. Each burner is composed of two co-annular nozzles of 7 mm and 13 mm diameter, which were aerodynamically shaped according to a modified empirical calculation from Rolon [27], resulting in a nearly uniform velocity profile on their exit. A nitrogen coflow around the burner isolates the flame from the surrounding gases. The burners are cooled using a closed loop water circulation at a fixed temperature between 30 and 50 °C depending on the flame conditions to avoid water condensation at the burner surfaces. The pressure within the vessel is controlled with a pressure transducer coupled with a control valve. Gas flows are monitored by Brooks mass flow meters through a Labview program.

2.2. Flame conditions

Laminar lean (E.R. = 0.7) premixed CH₄/air flames (dilution ratio X(N₂)/X(O₂) of 3.77) were studied in this work. The pressure was varied from 0.1 to 0.7 MPa. Flame conditions are summarised in Table 1 together with adiabatic temperatures and predicted NO_x (NO + NO₂) mole fractions computed at thermodynamic equilibrium using STANJAN [28], as well as flame temperatures and laminar flame velocities computed for a free flame configuration using PREMIX [29] with both GRI_{mech}2.11 [15] and GRI_{mech}3.0 [16] mechanisms as well as the GDFkin[®]3.0_NCN mechanism [20].

Table 1 confirms that NO₂ mole fractions can be neglected compared to NO mole fractions. As mentioned in [26,30], depending on flame conditions, the gas velocity ratio between the upper and the bottom burners needs to be adjusted in order to keep the flames well centred between the burners. This ratio, noted β in [26,30] is equal to 1.05 for all the CH₄/air lean flames studied here.

2.3. LIF experimental set-up

The experimental set-up is presented in Fig. 1. The laser system consists of a frequency-doubled Nd-YAG pulsed laser (Quantel Brilliant B, repetition rate 10 Hz, 6 ns pulses) pumping a dye laser (Quantel TDL+). For NO excitation, a wavelength around 226 nm was obtained by mixing the frequency-doubled output of the dye laser (mixture of Rhodamine 590 and 610) with the residual infrared radiation from the Nd-YAG laser. The resulting laser beam near 226 nm has a diameter of 6 mm, and delivers a few milli-joules per pulse. The beam linewidth is 0.06 cm⁻¹ (Quantel specifications). Measurements in the linear fluorescence regime were made by reducing the beam energy per pulse to 100 μJ with a variable attenuator composed of a half-wave plate and a Glan-Taylor prism. Part of the laser beam is collected by a fast photodiode (Newport, 818-BB-22 model) in order to monitor the laser beam energy fluctuations. The beam is focused with a *f* = 350 mm lens inside the high pressure chamber, on the centre axis between the burners. The fluorescence signal is collected at right angle through a

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