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PLIF measurements of non-thermal NO concentrations in alcohol and alkane premixed flames

Myles D. Bohon[a,b,*], Thibault F. Guiberti[b], William L. Roberts[b]

[a] Chair of Fluid Dynamics, Technische Universität Berlin, 10623 Berlin, Germany
[b] Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

There exists interest in using alcohols as renewable, lower emission fuels. It has been observed that alcohol flames generally produce lower concentrations of NO emissions and the cause of these reductions is attributable to a number of mechanisms. This work therefore investigates the relative contributions to total NO formation in alcohol fueled flames, relative to comparably sized alkane flames. Measurements of quantitative NO PLIF were conducted in two common premixed configurations: a conical, Bunsen-type flames and a lower peak temperature burner-stabilized McKenna flat flame. Additionally, these flames were modeled using a detailed NO_x chemical mechanism and investigated to understand the primary contribution pathways to non-thermal NO formation. From this analysis, it was observed that alcohol fueled flames produced as much as 50% less non-thermal NO than alkanes. However, under lean conditions the non-thermal contributions increased to about 80–90% of those observed in alkanes due to a greater contribution to non-thermal NO in both alcohol and alkane flames from non-hydrocarbon radical related mechanisms.

1. Introduction

With increasingly stringent regulations on combustion emissions, increasing emphasis is placed on utilizing alternative sources of energy while also reducing overall emissions. One strategy which combines both features is the increased usage of alcohols as fuels. Available from carbon-neutral sources and renewable, alcohols have also been observed to produce lower emissions of NO_x [1,2]. It is therefore important to gain a better understanding of the mechanisms through which NO_x is produced in alcohol flames, how that production compares with more traditional alkane flames, and whether these reductions can be achieved in mixtures of the alcohols with other fuels.

NO_x formation has been studied for a relatively long time. In this time, a number of mechanisms have been identified as sources of NO_x in flames [3]. In general, these sources of NO_x can be attributed to four primary categories of mechanisms: Thermal, Prompt, Fuel, and Minor. A detailed description of each of these categories is beyond the scope of this work, especially as several excellent sources examining these mechanisms in detail already exist. Therefore this work will only present a high-level overview of these mechanisms and how they relate to the current work, while interested readers are directed to the selected list of works referenced below.

The most broadly applicable mechanism to NO_x formation is through the Thermal mechanism. This mechanism is controlled by the reaction of N_2 with atomic oxygen, with the resulting nitrogen atoms further contributing to NO formation by reaction with other oxidizing radicals. Due to the high activation energy of the nitrogen triple bond, this reaction requires high temperatures and is typically active in the post-flame. Additionally, this mechanism is often considered relatively slow and decoupled from the fuel oxidation [3]. Consequently, this mechanism is largely independent of the fuel chemistry (apart from the flame temperature).

The Prompt mechanism is so called due to the rapid rate at which NO was formed in the flame front which was faster than could be accounted for by the Thermal mechanism alone [4,5]. This mechanism is initiated through the fixation of nitrogen by hydrocarbon radicals, HC. Consequently, the Prompt mechanism is strongly coupled to the fuel oxidation process. It was ultimately shown that CH and CH_2 are the primary initiating species for the Prompt mechanism [6] with CH as the most significant initiating radical through reaction below [7].

$$CH + N_2 \rightleftharpoons NCN + H \tag{1}$$

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[*] Corresponding author at: Chair of Fluid Dynamics, Technische Universität Berlin, 10623 Berlin, Germany.

E-mail address: mdbohon@gmail.com (M.D. Bohon).

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The resulting NCN then forms NO or N through reactions [8]

$$NCN + O \rightleftharpoons CN + NO \tag{2}$$

$$NCN + OH \rightleftharpoons HCN + NO \tag{3}$$

$$NCN + H \rightleftharpoons HCN + N \tag{4}$$

$$NCN + O_2 \rightleftharpoons NCO + NO \tag{5}$$

In summary, the controlling issues of the Prompt mechanism are: 1) the CH concentration and how it is established, 2) the rate of nitrogen fixation, and 3) the rates of interconversion among fixed nitrogen fragments [3]. Accurately predicting these features remains a significant hurdle to predicting NO_x formation, however work continues to improve the ability to predict NO formation through this pathway [9].

The Fuel mechanism is dominated by the presence of nitrogen within the fuel. Such fuel-nitrogen is commonly present in coal combustion [3], and can be a significant source of NO_x in the combustion of such fuels. In this work however, there is a negligible amount of nitrogen in the fuel and this mechanism will therefore not be considered further.

The final category is (perhaps poorly) called Minor. This category is grouped as a collection of mechanisms which can be significant contributors to NO_x under certain conditions and negligible at others. The first mechanism considered here is the NO-HCN-Reburn mechanism by which NO_x is recycled by reaction with HC back to HCN, the fate of which is either to reform NO or to be converted back to N_2 [10–13]. The second mechanism involves the reaction of forward diffusing NO with the hydroperoxyl radical HO_2 to form NO_2. Through reaction with H and O, NO_2 is also converted back to NO [14–16]. The balance of this reaction is particularly important in alcohol flames due to an abundance of HO_2. The final mechanism of consideration here is ultimately a combination of reactions involving N_2O [17] and NNH [18–20]. These two species can be significant contributors to NO_x, especially in the absence of significant HC radicals. A more detailed survey of this H/N/O reaction set is available in Klippenstein et al. [21]. As both N_2O and NNH sub-mechanisms proceed through a strongly coupled initiating process, the approach here will be to combine them into a single mechanism called NNX.

One of the first works examining NO_x formation specifically in alcohol fuels is from William's group. Li and Williams [1] studied laminar, premixed methanol flames with a relatively small set of experimental measurements of NO concentrations. They also studied the influence of the addition of H_2O, N_2, CO_2, and Ar [2]. In both works, lower formation of NO was observed, with the majority of the NO formation attributed to the Thermal Mechanism. Saxena and Williams [22] later extended this work to include ethanol, however an experimental measurements remained limited.

Chung et al. [23] conducted a comparison of iso- and n-butanol isomers with butane in stagnating premixed flames. A reduction in the levels of NO was observed for most butanol isomers, except for iso-butanol. These reductions were attributed to reductions in both the Prompt and Thermal mechanisms. Watson et al. [24,25] also investigated C1–C4 alkanes and alcohols in similar stagnating premixed flames. They measured simultaneous NO and CH PLIF and observed a scaling of the formation of NO with respect to the concentration of CH in the flame front, especially when the CH is appropriately scaled by the residence time in the flame front.

The objective of this work is two-fold. The first objective is to understand and compare the formation of NO through laminar, premixed alcohol and alkane fueled flames in two common configurations. The complex interaction between the different formation mechanisms with the oxidation of the fuel is not yet clearly understood for alcohols. Toward this aim, the different NO formation regimes within the flame will be observed and the relative contribution between the thermal and non-thermal mechanisms to total NO formation will be quantified. The use of two different burner configurations – one with nearly adiabatic conditions and another with significantly reduced peak temperatures due to heat loss – will further highlight the differences between the NO_x formation regimes. The second objective is to provide an empirical dataset against which improvements in detailed NO_x chemical mechanisms can be modeled. In addition to providing such a dataset, an analysis of the estimated contribution to non-thermal NO formation from several mechanisms is conducted in order to understand the mechanisms by which reductions of NO_x formation in alcohol flames are achieved.

2. Experimental methods

2.1. Experimental set-up

This work examines alcohol and alkane flames in two different premixed configurations: a Bunsen-type conical flame and a McKenna burner stabilized flat flame. The conical flame burner is composed of a contoured nozzle with a 10 mm diameter exit and a surrounding nitrogen shroud. The flat flame burner is composed of a 6 cm diameter McKenna burner with a stainless steel porous plug and a surrounding nitrogen shroud. The flames in the flat flame burner have previously been investigated by the authors [26]. This previous work measured the concentration of NO in the far field of the flat flame using probed gas sampling and modeled the flames using a temperature profile measured by 2λ OH PLIF combined with thermocouple measurements. The two lines for the 2λ thermometry used were the $P_1(7)$ and $Q_2(11)$ transitions of the $A^2\Sigma^+ \leftarrow X^2\Pi(1,0)$ OH band (285.088 and 285.157 nm, respectively), with a line separation energy of $\Delta\varepsilon_{12}$ of 2046 K. This pair provided a good temperature sensitivity over the temperature range of 1200–2000 K [27,28]. Additional information regarding the temperature measurements is available in Appendix A. The current work aims to expand on this previous work with non-intrusive NO PLIF and by comparison with a flame with less heat loss to the burner surface. It should be noted that these 2λ OH PLIF thermometry measurements were conducted separately from the NO PLIF measurements discussed in Section 2.2, and the two techniques were not applied simultaneously.

Both burners are supplied with premixed fuel and air using an in-house pre-vaporizing system, shown in Fig. 1. The vaporization system was composed of a series of three heated and insulated steel mixing vessels. The primary vaporization occurs in the first vessel. Here, an air atomizing nozzle uses preheated air to spray the liquid alcohol into the vessel. The temperature and flow rate of the atomizing air varied, depending on the fuel type and flow rate. Generally, the total atomizing air flow represented around 15–20% of the total combustion air. This rich mixture is then ducted through a distributed series of tubes into another settling tank, into which the remainder of the combustion air is injected. Within this tank and the final following tank, the mixture is brought to its final equivalence ratio and temperature. The gaseous alkanes were injected into this final tank when used. From here, the mixture is directed to the burner through a temperature controlled line. Both burners were insulated and temperature controlled to the target temperature. The recirculating fluid in the McKenna burner was replaced with oil and recirculated through a heat exchanger to also maintain the target temperature. Both burners were able to maintain very steady and consistent operation for many hours during testing. Gas flow rates were controlled by Brooks thermal mass flow controllers, and the liquid fuel flow rate was controlled by a Brooks coriolis mass flow controller. All controllers had been