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NO formation in premixed flames of C_1–C_3 alkanes and alcohols

Graeme M.G. Watson, Philippe Versailles, Jeffrey M. Bergthorson*

Department of Mechanical Engineering, McGill University, Montreal, Quebec, Canada

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The influence of alkane and alcohol molecular structures on nitric oxide (NO) pollutant formation trends is investigated through the study of C_1–C_3 alkanes and alcohols in premixed stagnation flames at atmospheric pressure. The flame diagnostics consist of one-dimensional (1-D) Planar Laser-Induced Fluorescence (PLIF) for measurements of NO and CH concentrations, 1-D NO-LIF thermometry, and 1-D Particle Tracking Velocimetry (PTV) for the determination of flame reactivity and burning rates. The results show that alcohols produce less NO than their alkane equivalents. This behaviour is linked to the lower flame temperatures of alcohol flames and the tendency of alcohols to produce lower concentrations of the CH radical, due to inhibition of the formation of methyl groups. These trends are captured in the available thermochemical models; however, there are discrepancies regarding the formation pathways of NO and its intermediates which are linked to variability in model rate coefficients. Further adjustments to all of the thermochemical models are needed to accurately capture the nature of NO_x pollutant formation in premixed alkane and alcohol flames, and this experimental study provides target data for this effort.

1. Introduction

Nitrogen oxides, NO and NO_2, or NO_x, are common byproducts of combustion that cause serious, adverse environmental and health issues. NO_x emissions are, therefore, subject to increasingly stringent environmental regulations. This has resulted in renewed interest in the study of NO_x formation routes so that comprehensive thermochemical models can be developed to predict the formation and evolution of NO_x species in combustion systems, at different pressures, temperatures, and for varying compositions [1].

A data set can be compiled for C_1–C_3 alkane fuels from a number of experimental sources to determine characteristics relating to fuel oxidation and NO_x formation. These experiments include premixed flames [2,3], flow reactors [4,5], batch reactors [6,7], and shock tubes [7]. These studies have also aided in the development of comprehensive thermochemical combustion models (see, for example, [8–11]).

There is a need to extend this understanding to alcohol fuels. Alcohols are a class of biofuel which have a number of uses in transportation applications. When derived from biological feedstocks, these fuels have the potential to provide energy that is carbon-neutral and renewable. Methanol and ethanol have a long history of use as anti-knock additives in gasoline. Ethanol in particular is widely blended with gasoline, and as E10, E15 and E85, makes up a significant proportion of the total usage in the United States [12]. There is also interest in substituting conventional fuel sources with higher chain-length alcohols, propanol and butanol. These longer-chained alcohols have properties similar to conventional gasoline, and could potentially be used as drop-in replacements. There is also recent interest in using propanol as an additive in blended diesel fuels [13,14].

There is literature relating to the combustion properties of the alcohols: methanol, ethanol, and propanol. Reviews of the issues relating to biofuel production and use, including discussions of combustion chemistry, are in [15–17]. These fuels have been studied in a number of experimental configurations to determine combustion characteristics relating to fuel oxidation and reactivity. These include recent works in flames [18–23], flow reactors [24–26], batch reactors [27], and in shock tubes [28,29]. These studies have helped to develop hierarchical thermochemical combustion models for C_1–C_3 alcohols (see, for example, [8,24,29–33]).

Fundamental, comparative studies have determined differences between alkanes and alcohols with respect to fuel reactivity. [21,34] compared the flame speeds and extinction strain rates of C_1–C_4 alcohols and showed trends linked to carbon chain length and isomeric fuel composition. Similar reactivity behaviour has been observed by Noorani et al. [35] in the investigated ignition times of C_1–C_4 alcohols. The authors in [21,34] note that the burning characteristics (flame speed and reactivity) of long,

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* Corresponding author.
E-mail address: jeff.bergthorson@mcgill.ca (J.M. Bergthorson).

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straight-chained alcohols are, for a large part, similar to alkane fuels of equivalent chain length; however these characteristics diverge as the chain length is reduced. It is the presence of oxygen in the molecular structure of the fuels, found in an alcohol functional group, –OH, and its placement relative to secondary and tertiary C–H bonds which is responsible for these trends. This structural difference produces different pathways for the decomposition of the fuel producing a varied pool of oxygenated intermediates [15] and is thought to reduce the possible number of the CH-precursor methyl groups. Fuel-bound oxygen also affects stoichiometric ratios and typically lowers flame temperatures compared to hydrocarbons of equivalent chain length.

There are limited definitive data pertaining to the NO_x emissions potentials of alcohols relative to conventional fuels. Work has been done to investigate pollutant emissions at the system-level [13,14], but such evaluations are rendered difficult by the complexity of engine systems and by the numerous physical and chemical processes involved. The formation of NO_x from the burning of various oxygenated fuels, and its dependence on fuel structure, was addressed recently in a study by Bohon et al. [36]; however, a comprehensive survey of the phenomenon in alcohols of various chain lengths was not undertaken.

This study uses a comparative approach that uses fundamental premixed laminar flame experiments to study the relative differences in NO_x emissions between alkane and alcohol fuels. The current paper restricts its attention to C_1–C_3 alcohols and their respective alkane equivalents. A later article shall expand the study to C_4 fuels. The current understanding of how NO_x is produced comes primarily from studies of low-molecular weight fuels, especially methane [1,37,38]. Sutton et al. [39] have recently expanded these investigations to longer-chained, C_2–C_4 alkane fuels. However, while some data have been collected in isolated experiments for methanol [40] and ethanol [29], further work is needed to build an equivalent comprehensive data set for alcohol fuels. There is also interest in determining the relative emission performance of alcohols in comparison to conventional fuels, and these data are provided by a comparative approach.

This study carries out such comparisons in stagnation flames using the jet-wall experimental configuration. In this geometry, flames are hydrodynamically stabilized inside a stagnation flow profile created between an impinging-flow nozzle and a cooled stagnation wall. The configuration produces stable, lifted flames that are readily accessible by optical laser diagnostics, which allows for velocity, temperature and speciation profiles relevant for NO_x formation to be monitored unobtrusively throughout the flow field. The experimental configuration also offers a means of carrying out comparisons between experimental and simulated profiles under well-controlled conditions. All upstream and downstream boundary conditions can also be accurately specified, allowing the measurements to be directly compared to model predictions without the need for adjustments or extrapolation [41]. This methodology has, therefore, been shown to be a useful test-bed for NO_x formation studies, and for thermochemical model development and validation [42].

Stagnation flames offer other advantages compared to alternative burner-stabilized configurations for comparative NO_x studies. Due to the method of stabilization, these lifted flames are free from the influences of the burner boundaries. As such, burning rates, flame temperatures and species compositions are, to a first-order, only a function of the fundamental properties of the combustible mixture. This is in contrast to McKenna-type burners, in which flames are stabilized close to the burner face. In such burners, flame temperatures and mass burning rates are decoupled and manipulated independently by the temperature-stabilization method, due to the heat loss to the burner upstream of the flame. At atmospheric pressures and above, the location of these temperature-stabilized flames also prevents access to measure intermediate species inside the reaction zone, such as CH, using optical diagnostic methods.

The objective of this work is to carry out a comparative study of C_1–C_3 alcohols and alkanes to assess the current understanding of NO_x formation in these fuels. This is the first study to provide a comprehensive data set for this fuel range. The paper starts with a survey of the apparatus and diagnostic methods. Measurements of velocity, temperature, and NO and CH species concentrations are performed with 1-D Particle Tracking Velocimetry (PTV), 1-D NO-LIF Thermometry, and 1-D Planar Laser-Induced Fluorescence (PLIF) techniques, respectively. Results are then shown for the emissions of alcohols and alkane fuels, and are compared to determine differences in fuel-dependent emissions. This data is expected to be useful as optimization targets for future NO_x sub-model development and optimization. For this purpose, results are also compared to predictions from comprehensive thermochemical models to assess current model performance and to identify areas for further improvement.

2. Apparatus and methodology

The apparatus and methodology has been used extensively by this group for flame studies. A detailed discussion of the apparatus and its development can be found in previous papers [41–44].

A co-flow nozzle system, with an inner-nozzle diameter of 20 mm, is used to generate a jet of premixed fuel and air which impinges onto a stagnation-plate. The flow is shrouded with an inert co-flow of nitrogen or helium, depending on flame composition, to isolate the premixed flame from ambient oxygen. The nozzle-to-plate separation distance, normalized by the diameter of the nozzle, is approximately 1.25. This configuration produces a hydrodynamically-stabilized, laminar flame between the nozzle outlet and the wall, inside the diverging stagnation flow.

Simultaneous measurements of the fuel and air composition, the centreline velocity profile, and the inlet and wall temperatures permit accurate determinations of all upstream and downstream boundary conditions for the direct simulation of the flames with the 1-D hydrodynamic model of [45]. This apparatus uses a temperature-controlled (water-cooled) stagnation-plate wall that imposes a downstream heat loss on the flame. The plate temperature is held constant in each experiment near 350 K to prevent condensation on the plate surface and to inhibit surface reactions. This permits reliable predictions of the gas temperature profile in the hydrodynamic simulation of these experiments through a complete specification of all boundary conditions [42]. This is confirmed by measurements of the gas temperature profiles in the present work.

The oxidizer stream and gaseous alkane fuel flow rates are metered by Brooks thermal mass flow controllers (models 5850S and 5851S). The flow meters are calibrated using a Bios DryCal ML-500 dry-piston calibrator, giving a total uncertainty in each mixture flow rate of ±0.51% of the reading. Liquid alcohol mass flow rates are metered by a syringe pump (Chemyx Nexus 6000), which has a total rated uncertainty of ±0.35% of the reading. The fuel is then vaporized into the heated oxidizer stream by a Brooks Vaporizer DLI 750 system. In all, seven fuels (three alkanes and four alcohols, including the two isomers of propanol) are used in this study to determine NO formation trends with changing C_1–C_3 fuel structure. The mixture compositions are chosen to isolate thermal- and prompt-NO formation routes, which are dominant at stoichiometric and rich equivalence ratios, respectively. The total uncertainty of these mixture compositions is less than ±0.8% in equivalence ratio.

Care is taken to maintain a sufficient temperature throughout the fuelling system and nozzle assembly to eliminate fuel