

Measurements of laminar burning velocities and NO concentration in neat and blended ethanol and n-heptane flames.

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Introduction

The development of modern combustion technologies is mainly oriented towards searching for replacement fuels, or energy carriers, that offer alternatives to fossil fuels, commonly used in both automotive and stationary engines. Among the alternative fuels, more and more attention has been devoted to biofuels, which can be obtained from renewable energy sources, such as biomass. It is well known that combustion of biofuels contributes to the reduction of CO₂, that leads to the greenhouse effect [1].

Among biofuels that are gaining importance is ethanol. Although such fuel does not seem to be an ideal fuel due to the low heating value, it has attracted attention worldwide because of its potential use as an alternative automotive fuel [2]. As a matter of fact, ethanol-based fuels are increasingly popular in spark-ignition engines due to their high octane ratings and high heats of vaporization, or in compression ignition engines that use two-fuel systems for combined combustion of alcohol and diesel [3].

Combined with modern control systems of the combustion process, the use of ethanol should lead to lower emissions of harmful exhaust components while maintaining improved functional parameters of the engine. Indeed, so far, many experimental studies claimed that the ethanol-blended fuels reduce pollutant emissions compared to gasoline and/or diesel-fueled engine. Generally, in these studies, the reductions in the exhaust emissions have been associated with the oxygen content in ethanol, which improves combustion and provides significant reduction in CO, UHC and soot emissions, but it may adversely affect NO_x emissions [4]. In fact, many investigations have been carried out (e. g [4-7]) to understand the effect of ethanol usage on NO_x emissions. However, the results among different studies are not consistent: with increasing ethanol content, emission of NO_x have been reported to increase, decrease or remain unchanged when compared to pure gasoline or diesel fuels. The authors discussed some reasons for the observed behaviors but there are considerable inconsistencies in the explanations, which make fundamental understanding incomplete. Therefore, there is a need of additional studies to better understand the effects of physicochemical properties for new fuels/fuel blends on NO_x emissions.

Information in the literature is plentiful for engines related to the use of ethanol blends with gasoline or diesel, which are difficult to compare with each other. However, few systematic studies exist about the NO_x emissions of ethanol blends in fundamental experiments. In the literature, it is reported that flame speed could be an important factor that affects NO_x emissions. Indeed, as the flame speed of ethanol is higher than that of gasoline, it assists in completing the combustion at high speeds, which could result in higher NO_x emission for ethanol [4-6]. In this regard, van Lipzig et al. [8] acquired accurate data on laminar burning velocities of n-heptane, iso-octane, ethanol and mixtures of them with each other.

The objective of the present study therefore is to provide new accurate data on laminar burning velocity (S_L) and NO concentration for premixed laminar flames of n-heptane, ethanol, and a mixture of the two, at different conditions. The effects of fuel type and equivalence ratio have been tested, at constant temperature and pressure. The information obtained from this study

will help in understanding and predicting the implications of changes in fuel properties on NO emissions.

Experimental details

In the present work, the heat flux method for the stabilization of adiabatic premixed laminar flames on a flat flame burner has been used [9]. This method has been extensively used for measuring S_L of gaseous and liquid fuels. Detailed descriptions of the method and associated experimental uncertainties are given elsewhere [10].

The experimental setup consists of a heat flux burner (30 mm in diameter) made in brass. A 2 mm thick perforated plate with small holes (0.5 mm in diameter) is attached to the burner outlet. The burner head has a heating jacket supplied with thermostatic water to keep the temperature of the burner plate constant. During the experiments, this temperature was fixed at 368 K. The plenum chamber has a separate heating system supplied with water, which fixes the initial temperature (T_g) of the fresh gas mixture. In the present experiments T_g was fixed at 338 K because at standard conditions the maximum accessible equivalence ratio for ethanol + air flames is about 1.2 due to the vaporization limit, while at 338 K a wider range of equivalence ratios could be covered.

A mixing panel provides controlled flow of the vaporized fuel and air at the required equivalence ratio. The liquid fuel flow from the fuel reservoir, pressurized by nitrogen, is metered by a Cori-Flow liquid mass flow controller and fed to a Controlled Evaporator Mixer, both from Bronkhorst High-Tech. The required air flow, controlled by a calibrated gas mass flow controller, is also used as a carrier gas to facilitate vaporization. Neat fuels (n-heptane and ethanol) were used as delivered from Fisher Scientific in sealed bottles. Then, pure ethanol was blended with n-heptane in a ratio of 50 vol.%.

Laser-Induced Fluorescence (LIF) measurements of NO were made using a combined Nd:YAG and dye laser system. The second harmonic at wavelength 532 nm of the Nd:YAG laser (Brilliant B, Quantel) was used to pump the dye laser (Quantel TDL-90) operated on a Rhodamine 590/610 dye mixture. Conversion to ultraviolet (UV) wavelengths for NO excitation was achieved by means of frequency-doubling of the dye laser output beam followed by frequency mixing with the fundamental beam of the Nd:YAG laser at wavelength 1064 nm. The resulting output UV beam had pulse energies of 2.5-3 mJ and the linewidth of the beam was approximately 1 cm^{-1} . In order to improve focusing, the 225 nm laser beam was expanded using a telescope arranged with an $f=-150\text{ mm}$ lens and a $f=+300\text{ mm}$ lens. A prism directed the expanded laser beam across the centre of the burner surface at height 10 mm and an $f=+500\text{ mm}$ spherical lens focussed them beam at the position above the burner centre.

The laser was tuned to the $Q_2(26.5)$ transition of the $\text{NO } A^2\Sigma^+ \leftarrow X^2\Pi$ (0-0) band at wavelength 225.5 nm. The pulse energy used together with the beam focussing resulted in operation under saturated fluorescence, i.e. where the fluorescence yield becomes independent on collisional quenching, which facilitates determination of quantitative NO concentrations from the measured signal. The NO fluorescence was collected using an arrangement of two spherical lenses of focal length $f=+150\text{ mm}$ and $f=+300\text{ mm}$, by which the measurement volume, defined by the focussed laser beam, was imaged on the slit of a spectrometer (Shamrock SR-500i-A-R, Andor). A longpass filter (LP02-224R-25, Semrock) was mounted in front of the slit for suppression of background such as flame luminescence and residual scattered laser light. A photomultiplier tube (model H9305-01, Hamamatsu) was mounted at the spectrometer exit for signal detection. To further ensure detection of a pure NO signal, an additional slit was mounted at the spectrometer exit resulting in its operation as a monochromator. The exit slit resulted in detection of the (0-1) γ -band of the $A^2\Sigma^+ \rightarrow X^2\Pi$ NO transition, centred at wavelength 236 nm. The photomultiplier signal was registered by a digital oscilloscope (Wavejet Touch 354, Lecroy) and fluorescence signal traces were collected by averaging over 128 laser pulses. In addition to measurement made with the laser tuned to the $Q_2(26.5)$

resonance, corresponding data were recorded with the laser tuned to wavelength 225.58 nm off any NO resonance and for which no fluorescence was induced. The background measured at the off-resonance wavelength position was subtracted from the corresponding measurement made on the Q₂(26.5) resonance. The peak value after background subtraction represents a saturated fluorescence signal and was retrieved for further evaluation. The NO signal is converted into concentration values using a calibration measurement, in which the NO signal is measured for different levels of NO seeding in a $\Phi=0.7$ CH₄-air flame with negligible level native NO formed. The NO concentration can be expressed according to Eq. (1)

$$X_{NO,flame} = \frac{1}{C_{cal}} \cdot \frac{f_{cal}}{T_{cal}} \cdot \frac{T_{flame}}{f_{flame}} \cdot I_{LIF,flame} \quad (1)$$

where X_{NO} is the NO concentration, C_{cal} is a constant of proportionality determined from the calibration measurement, f the population of NO molecules in the probed energy level given by the Boltzmann distribution, $I_{LIF, flame}$ is the LIF signal and T the temperature. The flames stabilized on the heat flux burner were assumed to burn under adiabatic conditions and temperatures were thus set to adiabatic values. Population factors for these temperatures were obtained from the LIFBASE software.

Results

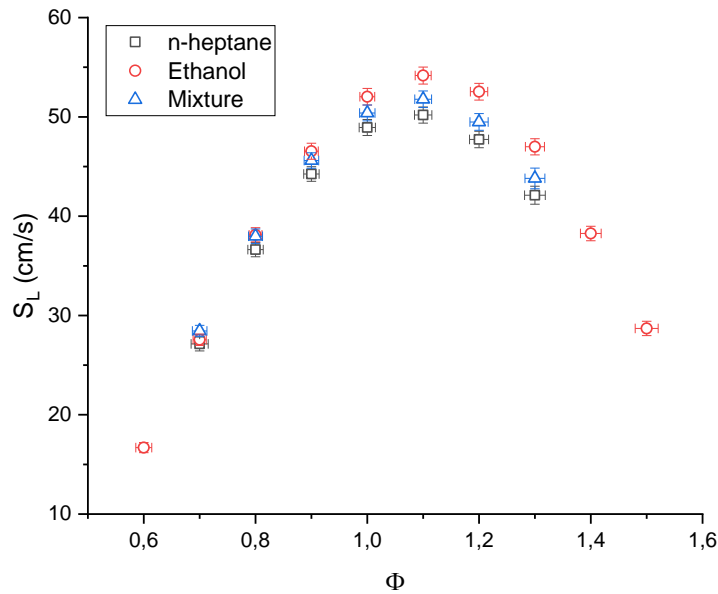


Fig. 1 - Experimental S_L as a function of Φ at $T_g = 338$ K and $P = 1$ atm. Black squares: n-heptane-air. Red circles: ethanol-air. Blue triangles: 50% ethanol/50% n-heptane-air.

Figure 1 shows a plot of S_L versus equivalence ratio (Φ) for ethanol, n-heptane and their mixture combusted with air at $P = 1$ atm and at a T_g of 338 K. Generally, the three datasets have the same trend as a function of the equivalence ratio and the maximum burning velocity is found at an equivalence ratio of 1.1. In particular, higher laminar burning velocities can be observed for the ethanol/air mixture. It has to be pointed out that, for the n-heptane mixtures (pure or blended with ethanol), due to flame instabilities, S_L have not been reported for equivalence ratios lower than 0.7 and higher than 1.3, as shown in Fig. 1. However, such instabilities have been observed to not influence NO concentration measurements.

Straightforward comparison of the laminar burning velocities of ethanol, n-heptane and their mixture + air flames measured in the present work with those obtained before is expected to confirm reproducibility of the heat flux experiments within the evaluated uncertainties. In this regard, the present results are in remarkably good agreement with the measurements of van Lipzig et al. [8], obtained under the same conditions.

The different combustive behavior of the three fuel mixtures is reflected in the NO distributions. As seen in Fig. 1 for S_L , also for NO measurements the behavior of the three datasets as a function of the equivalence ratio is similar, but the trend is the opposite. In particular, due to lower adiabatic flame temperature, the NO concentrations for the ethanol/air mixture are lower compared with the other mixtures. As expected, the NO concentration increases with equivalence ratio from the fuel-lean side and the maximum NO concentration is found at the stoichiometric condition for the three investigated mixtures. Above $\Phi = 1$, NO concentrations slightly decrease and then reach a plateau level with further increase of the equivalence ratio due to prompt-NO formation.

Conclusions

New accurate measurements of the adiabatic laminar burning velocities and NO concentrations of ethanol, n-heptane and a mixture of them have been reported. The results demonstrated similar trends as a function of the equivalence ratio for the investigated fuels. The ethanol/air mixture shows higher burning velocities and lower NO concentrations than the other two mixtures. The series of measurements are believed to be valuable data for validation of detailed kinetic models.

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