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Laminar flame speeds of pentanol isomers: An experimental and modeling study

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ABSTRACT

Long chain alcohols such as 1- and *iso*-pentanol are foreseen as a suitable replacement for ethanol, due to more favorable physical properties (higher energy density, higher boiling point and lower hygroscopicity). The present study presents high accuracy laminar flame speed measurements for *iso*-pentanol/air and 1-pentanol/air mixtures, at initial temperatures of 353 K, 433 K and 473 K, 1 bar pressure and equivalence ratios ranging from 0.7 to 1.5. Comparisons with previous measurements from the literature are also presented and the observed deviations are discussed in detail. The updated kinetic mechanism for alcohols combustion from the CRECK group at Politecnico di Milano is discussed and used for modeling purposes. For a more complete validation of the oxidation mechanism at high temperature conditions, modeling results are also compared with shock tube ignition delay times from the literature. This study extends the presently sparse and uncertain experimental database for high molecular weight alcohols oxidation in laminar flames, providing high accuracy and reliable experimental data of use for alcohols oxidation mechanism development and improvement.

1. Introduction

In order to decrease green-house gases and increase energetic independence, new combustion modes are currently being developed that will likely require fuel reformulation. Furthermore, regulations impose blending petroleum-based fuels with biofuels up to 20% [1]. Consequently, it is mandatory to study the impact of biofuel addition on fundamental combustion parameters and especially on pollutant emissions. Ethanol for example is widely used alone or blended with gasoline. However, ethanol is problematic due to both its source of supply and its pollutant emissions. Indeed, ethanol-gasoline and diesel blend engine-out emissions showed high concentration of carbonyl species (e.g., acetaldehyde). These compounds present an air quality concern since they are toxic and irritating, as well as being precursors of urban smog (e.g., free radicals, ozone. and peroxyacetyl nitrates) [2]. To overcome these two aspects, heavier alcohols, such as 1-pentanol and *iso*-pentanol, are foreseen as a suitable replacement for ethanol, constituting the next generation of biofuels. Moreover, pentanol isomers have several advantages compared to ethanol such as a higher energy density, a higher boiling point and a lower hygroscopicity [3]. Up to now, only few experimental studies were reported in the literature. Togbé et al. [4] studied 1-pentanol oxidation in a Jet Stirred Reactor (JSR) and in a 23.32 L combustion bomb. Flame speed results were presented and the unstretched laminar flame speed was derived using a non-linear relation. They also proposed a detailed chemical kinetic mechanism. Li et al. [3] measured laminar flame speeds of three pentanol isomers in a 5.35 L cylindrical vessel and used a linear relation to extrapolate the unstretched laminar flame speed. In a very recent work, Li et al. [5] have revised these data using the non-linear method. More recently, Heufer et al. [6] presented a detailed kinetic model for 1-pentanol oxidation validated against ignition delay time, speciation in JSR and laminar flame speed data. For *iso*-pentanol, a detailed kinetic model was presented by Dayma et al. [7] and validated against speciation data from JSR. Recently, Sarathy et al. [8] developed another detailed chemical kinetic model validated against shock tube and rapid compression machine ignition delay times, speciation from JSR and counterflow premixed flame speed data.

The primary objective of the present work is to obtain new experimental laminar flame speed data, with the best accuracy possible for *iso*-pentanol and 1-pentanol. Laminar flame speeds of

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iso-pentanol and 1-pentanol in air were measured, in a 56 L spherical bomb, at three initial temperatures 353, 433 and 473 K. The initial pressure was fixed at 1 bar and the equivalence ratios varied from 0.7 to 1.5.

The updated mechanism for alcohols combustion from CRECK group at Politecnico di Milano (POLIMI) is discussed in Section 4 and comparisons with experimental data are reported in Section 5. The high temperature mechanism is based on previous studies on alcohol fuels [9–13]. A lumped kinetic mechanism has been also developed to systematically describe the low-temperature oxidation of alcohols (1- and *iso*-butanol, 1- and *iso*-pentanol). The low temperature chemistry is beyond the scope of this study, thus it will be not discussed nor provided herein.

2. Experimental methodology

2.1. Experimental set-up

Laminar flame speeds were determined using a heated stainless steel spherical bomb made of two concentric spheres (Fig. S1 in Supplementary material). The internal sphere in which the combustion is taking place has an internal diameter of 476 mm. Between the two spheres, a heat transfer fluid heats the apparatus to the desired temperature and a thermal insulation ensures a homogeneous temperature (±0.8 K). The temperature is measured via a thermocouple on the side of the inner wall of the vessel. The maximum operating pressure is 50 bar and a piezo-electric pressure transducer (Kistler 601A) equipped with a flame arrestor is used to monitor the pressure during combustion.

The mixture is spark-ignited with two tungsten electrodes connected to a high voltage generator. High voltage and current probes are connected to an oscilloscope to measure both U and I signals and therefore calculate the energy delivered by the spark ($E = \int U.I$). The average energy delivered by the high voltage generator is 1.82 mJ with a standard deviation of 0.48 mJ. The spark triggers pressure, voltage, current, and camera measurements at the same time via the oscilloscope and a TTL generator. The spherical bomb is equipped with two opposite quartz windows (97 mm optical diameter, 50 mm thick). The visualization of the flame was obtained using a Z-shape Schlieren apparatus. A white continuous lamp is used to illuminate the flame via two lenses and two concave spherical mirrors. A high speed camera (PHANTOM V1610), with an acquisition rate of 25,000 images per second, records the Schlieren images of the growing flame. The frame size was fixed to a 768 × 768 pixels^2. More details can be found in [14]. A schematic of the Z-shape Schlieren configuration and the experimental setup is given in Fig. S2 of the Supplementary material.

Before the introduction of the mixture, the whole setup bomb and lines were evacuated using two primary pumps. The liquid fuels were chosen of relatively high purity: 1-pentanol (Sigma Aldrich Reagentplus® ≥99%) and *iso*-pentanol (Sigma-Aldrich anhydrous ≥99%). The manufactured bottles of liquid fuel were transferred under argon atmosphere on vial equipped with septum to avoid any adsorption of water vapor in the fuel. The air was chosen of well-defined composition (Air Liquide, grade alphagaz 2, purity >99.9999%) with following composition: 20.9% O_2+ 79.1% N_2.The mixtures were prepared directly in the bomb according to the following steps:

- the liquid fuel was firstly injected into the bomb with a syringe. The corresponding vapor pressure was measured using a capacitive pressure sensor (MKS-631) with a measurement range of 100 Torr. Each time, the vapor pressure was monitored in order to ensure that all the liquid has vaporized.
- the air was introduced in the bomb to the total pressure of 1 bar, the total pressure was then measured using a capacitive pressure sensor (MKS-631) with a measurement range of 1000 Torr.

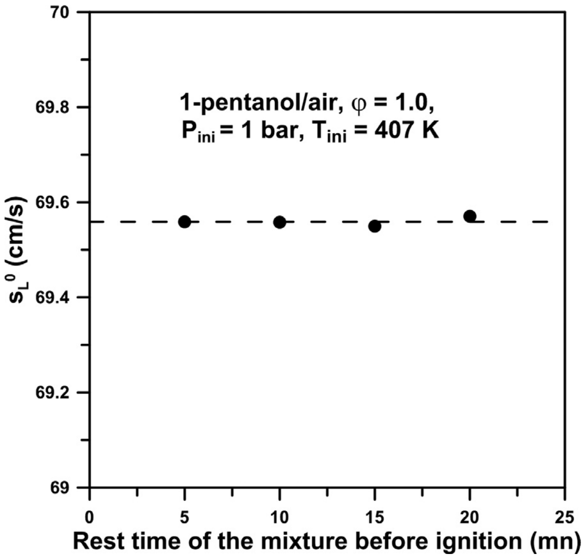

Fig. 1. Effect of the mixture rest time prior to ignition on $S_L°$ for stoichiometric 1-pentanol/air mixtures for an initial temperature of 407 K.

These high accuracy gauges have an accuracy of 0.5% and a precision of 10^{-2} Torr for the first one and 10^{-1} Torr for the second one. They are re-calibrated, in our laboratory, using a mercury U shape manometer with an accuracy of 0.01 Torr. The final accuracy on the equivalence ratio, $\Delta\varphi$, is ± 0.2% (Fig. 1).

After the admission of the mixture in the spherical bomb, the mixtures is allowed 5 min to rest before triggering the ignition. This time was considered as sufficient since increasing it up to 20 min did not show any effect on the measured $S°_L$ as it is shown in Fig. 3.

2.2. Laminar flame speed determination

2.2.1. Data acquisition and processing

The Schlieren images of the growing flame (Fig. 2a) have been processed using a home-made code based on Matlab® [15] to obtain the radius of the flame R_f as a function of time. For this typical run, 162 images are used to derive the laminar flame speed. For leaner or richer mixtures, the number of images used to derive the laminar flame speed is much higher than 162 images. For the slowest flames, around 375 images are typically used.

When the experiments are performed, it is important to characterize the shape of the flame during the propagation to ensure that no deformation is occurring due to either a misalignment of the electrodes or the beginning of buoyancy effects. Thus, for each processed image, a ratio is calculated to evaluate the shape of the detected flame contour when compared to an ideal circle. This ratio is called the sphericity and is defined as the ratio between the smallest radius and the largest radius of the flame contour, for each individual frame. When the flame contour matches a perfect round circle, this ratio is equal to 1.

The good sphericity of a flame depends on several parameters. The most important ones are: the alignment of the electrodes, the gap between the tips of the electrodes and the occurrence of buoyancy. In the present study special care has been taken to optimize the electrodes configuration (diameter and gap-distance) to minimize the flame-electrodes interactions, which can have a noticeable impact on the sphericity. This optimization aimed also to minimize the energy-deposition. Indeed, as explained by Halter et al.