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

D. Nativel, M. Barone, F. Gourmel, M. Idir, N. Chaumeix
ICARE, CNRS-INSIS, Orléans, France

1 Introduction

In order to decrease green-house gases and increase our energetic independence, new combustion modes are currently being developed that will likely require fuel reformulation. Furthermore, regulations impose blending actual fuels with biofuel 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. To overcome these two aspects, heavier alcohols, such as 1-pentanol and iso-pentanol, are foreseen as a suitable replacement for ethanol, they constitute the next generation of biofuels. Moreover, pentanol isomers have several advantages compared to ethanol such as a higher energy density and a lower hygroscopicity [2]. Up to now, only few experimental studies were reported in the literature. Togbe et al. [3] studied 1-pentanol oxidation in a 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 proposed also a detailed chemical kinetic mechanism. Li et al. [2] 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. More recently, Heufer et al. [4] presented a detailed kinetic model for n-pentanol oxidation validated against ignition delay time, speciation from JSR and laminar flame speed data. For the iso-pentanol, a detailed kinetic model was presented by Dayma et al. [5] and validated against speciation data from JSR. Recently, Mani Sarathy et al. [6] developed another detailed chemical kinetic model validated against shock tube and rapid compression machine ignition delay time, speciation from JSR and counterflow premixed flame speed data. The primary objective of the present work is to rigorously obtain new experimental data for iso-pentanol and 1-pentanol in a 56 L spherical bomb. Laminar flame speeds of iso-pentanol and 1-pentanol in air were measured at three initial temperatures 353, 433 and 473K. The initial pressure was 1 bar and the equivalence ratios varied from 0.7 to 1.5. The mechanism of 1-pentanol oxidation from Togbe et al. [3] was used to simulate laminar flame speeds of 1-pentanol/air mixtures.

2 Experimental methodology

Laminar flame speeds were determined using a heated stainless steel spherical bomb made of two concentric spheres. 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. Thermal insulation ensures a homogeneous temperature (±1 K). The temperature is

Correspondence to: damien.nativel@cnrs-orleans.fr

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) is used to monitor the pressure during combustion. The mixture is spark-ignited with two tungsten electrodes supplied by a high voltage generator. A 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 mixtures were prepared inside the spherical bomb using 1-pentanol (Sigma Aldrich Reagentplus® ≥ 99 %) or iso-pentanol (Sigma Aldrich anhydrous ≥ 99 %) and dry air (Air Liquide, alphagaz 2, 20,9% O_2 + 79,1% N_2). The introduction of air created turbulences that ensured a good mixing. Partial pressures of fuel as well as dry air were measured using capacitive manometers (MKS) of two different scales (133 and 1333mbar). According to the precision of the manometers, the mixtures were obtained with an accuracy of 0.2%. The spherical bomb is equipped with two opposite quartz windows (100 mm 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 25000 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 [7].

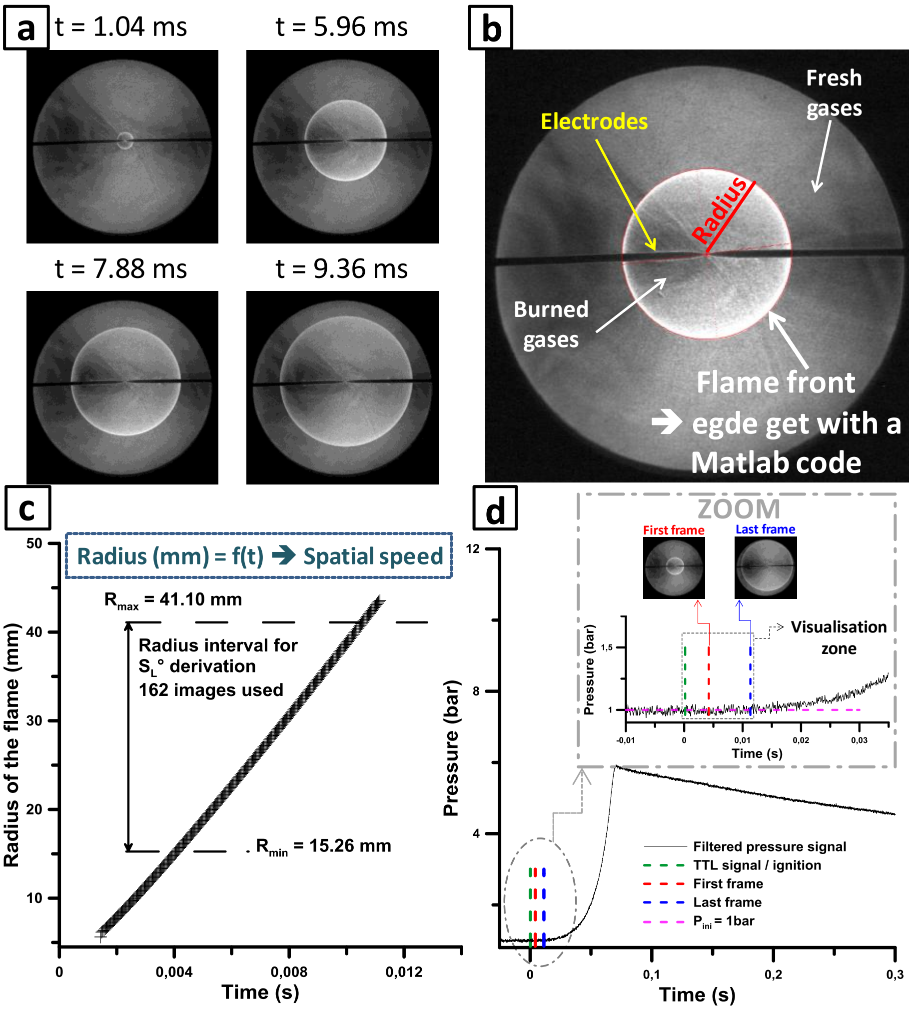


Figure 1: a) Typical propagation of the flame. b) Typical view of a Matlab process image. c) Radius of the flame as a function of time. d) Evolution of the pressure. The mixture studied here is the following: 2.84% i-$C_5H_{11}OH$/ 20.31% O_2 / 76.86% N_2 at initial temperature and pressure of 473K and 1 bar, respectively.

The images (figure 1a) are then processed using a home-made code based on Matlab to obtain the radius of the flame R_f as a function of time (figure 1b). Then, the spatial flame speed $V_S = dR_f/dt$ is determined from the measured radius (figure 1c). However, the spherical expansion of the flame has to be considered and consequently the presence of flame stretch in such experiments. Thus it is necessary to apply a stretch correction to the velocity either using a non-linear or a linear extrapolation. For this study, all the unstretched spatial flame speesd were extrapolated using the non-linear extrapolation from Ronney and Sivashinsky [8] between 15 mm and about 40 mm. The lowest radius was chosen to avoid any history from the ignition and the largest to avoid any pressure or wall effects. The Ronney and Sivashinsky equation is the following:

$$\left(V_S/V_S^0\right)^2 \ln\left(V_S/V_S^0\right)^2 = -2\left(L_b \cdot \kappa/V_S^0\right),$$

where V_S^0 is the unstretched spatial flame speed, κ the strech and L_b the Marstein length. L_b is a parameter characterizing the effect of the stretch on the flame propagation. Finally, considering that the evolution of the pressure inside the vessel is constant the simple equation $S_l^0 = \rho_u/\rho_b V_S^0$ is applied to link V_S^0 to the unstretched laminar flame speed S_l^0 where ρ_u and ρ_b are the unburned and burned density of the mixture, respectively. Indeed, after the observation of the flame expansion, the burnt volume is about 0.8% of the total volume of the vessel and the pressure remains constant during the visualization of the propagation of the flame as observed on the figure 1d. Therefore no effect of pressure is affecting its propagation.

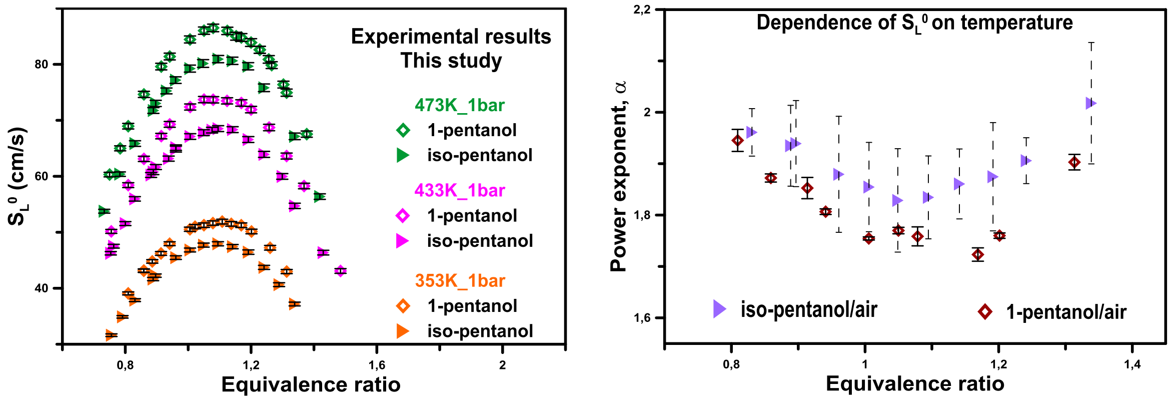
3 Results and discussion

3.1 Experimental results

During this study, three initials temperatures were carried out for each fuel, 353, 433 and 473K and the initial pressure was kept constant at 1 bar. Different equivalence ratio mixtures ($0.7 \le \varphi \le 1.5$) were tested. The study was stopped before the onset of the wrinkling of the flame. It is to be noted that particular attention was paid to the initial pressure and temperature, which can have a high impact on the laminar flame speed. Indeed, special care has been taken in performing these experiments in order to reduce the experimental error in laminar flame speed determination which is in this case around 1%. Many other parameters were checked such as: i) the composition of the dry air was well known; ii) all the pure fuels were opened under a glove-box fills with argon atmosphere, iii) the whole experimental set-up (lines and bomb) was well heated to avoid any condensation, iv) the processing procedure with the Matlab code was well respected (scale of the window checked by the code and manually, edges of the flame well detected); v) the calculation of the density of unburned and burned gas ρ_u and ρ_b calculated using COSILAB [9] software with the Equilibrium Calculations. As can be observed on figure 2a, the unstretched laminar burning velocity is maximum for all the mixtures just above stoechiometry ($1.05 \le \varphi \le 1.10$) and decreases with either increasing or decreasing equivalence ratios. The flame speed also increases with increasing the temperature as expected. However the impact of the temperature on S_l^0 depends on the equivalence ratio. Following the classical formulation [7], the exponent over the temperature can be deduced:

$$S^0_{l\,(T_i)} = S^0_{l\,(T_0)}\left(T_i/T_0\right)^{\alpha},$$

Where the subscript “0” refers to the values at reference conditions (353 K, 1 bar), “i” refers to the values at the expected conditions and α is the power exponent of the temperature dependence. This exponent α is derived at each equivalence ratio from our measurements and is plotted versus φ in figure 2b. Errors bars present uncertainties obtained by the least-squares procedure.



(a) (b)

Figure 2: a) Evolution of the laminar flame speed versus the equivalence ratio for 1-pentanol/air and iso-pentanol/air mixtures; b) Dependence of the exponent α on the equivalence ratio from experiments results.

On figure 3 are reported the Markstein lengths L_b' versus the equivalence ratio, where $L_b' = \rho_u/\rho_b\ L_b$. The figure 3a et 3b compare the Markstein length at three different temperature of iso-pentanol /air mixture and 1-pentanol air mixture respectively. For both mixtures, the temperature dependence can be noticed. L_b' increases with increasing the temperature. The figure 3c et 3d compare L_b' for iso-pentanol and n-pentanol at each temperature. Both fuels exhibit similar Markstein lengths over the whole studied domain both in terms of composition and initial temperature.

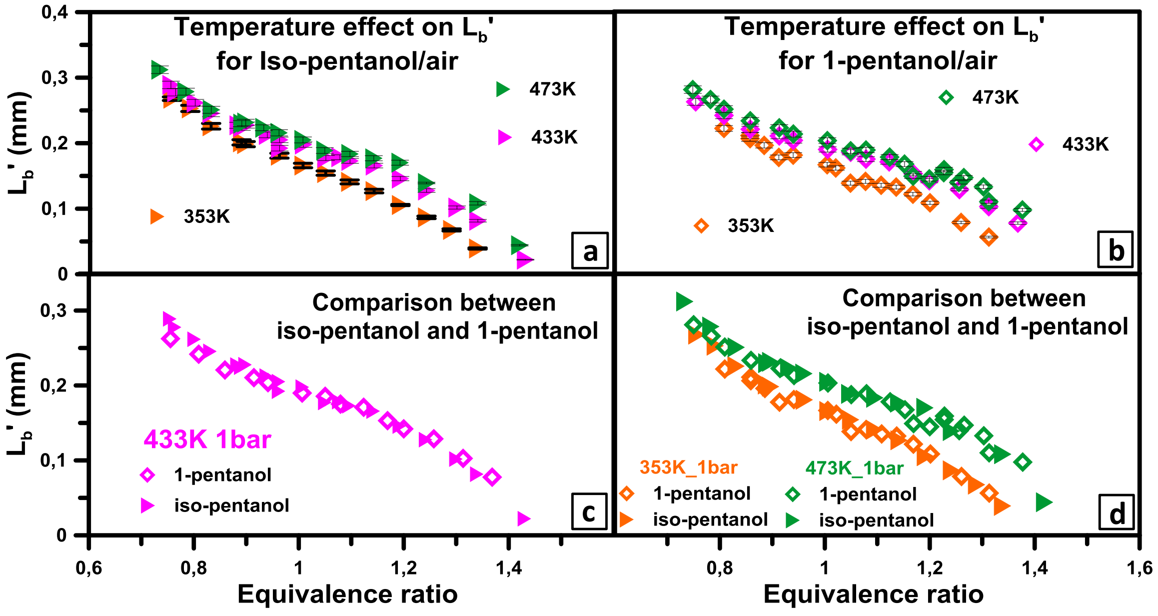
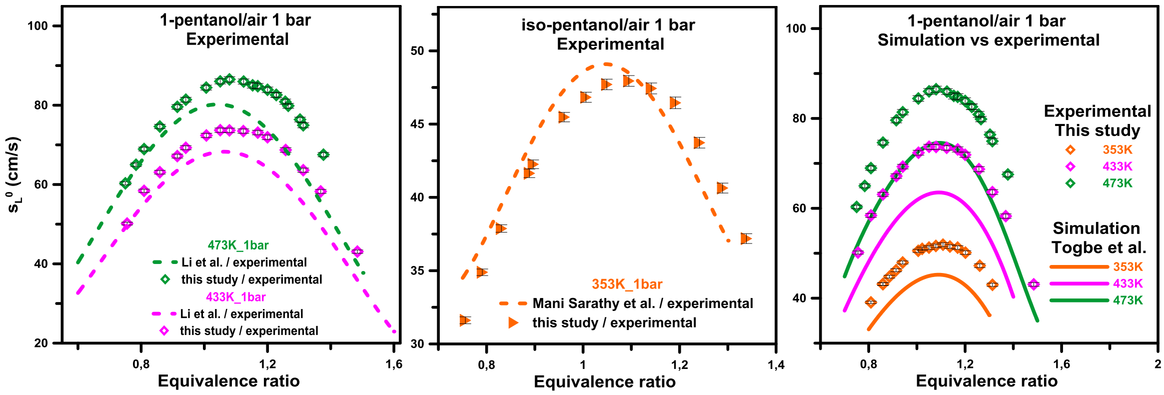


Figure 3: a) Comparison of experimental laminar flame speeds for 1-pentanol/air mixture with Li et al. [2]; b) Comparison of experimental laminar flame speeds for iso-pentanol/air mixtures with Mani Sarathy et al. [6]; c) Togbe et al. [3]predictions compared against experimental results for iso-pentanol/air mixtures]

3.1 Comparison with literature and modeling

The results of the 1-pentanol/air mixture at 433 and 473 K were compared to the data of Li et al. [2] on figure 4a. The data of Li et al. are in good agreement for very lean mixtures but start to be lower from 0.8 equivalence ratio. The large discrepancy between the results of Li et al. and the present study can be explained on the ground of many reasons. First of all, their combustion vessel is cylindrical with a volume of 5.35 liters and Li et al. observe the propagation of their flames until a radius of 25 mm. Consequently, the burnt volume is about 7.85% of the total volume of the vessel and the pressure does not remain constant anymore during the visualization of the propagation of the flame. Moreover, the wall-effect must be more important especially in a cylindrical shape inducing a reduction in the final value. Secondly the derivation method, Li et al. derived their flame speed with the linear method between 6 and 25 mm flame radius. Finally, the impact of the initial conditions such as initial temperature and air composition is also important but not reported in their paper.



(a) (b) (c)

Figure 4: a) Comparison of the experimental laminar flame speed for 1-pentanol/air mixture with Li et al. [2]; b) Comparison of the experimental laminar flame speed for iso-pentanol/air mixtures with Mani Sarathy et al. [6]; c) Togbe et al. [3] predictions compared against experimental results for iso-pentanol/air mixtures.

The experimental results of iso-pentanol/air mixtures at 353 K were compared with the data of Mani Sarathy et al. [6] obtained with the counterflow configuration (figure 4b). An overall good agreement between the predictions and the experimental results is observed. Just some minor discrepancies are observed. Indeed, the data seems shifted towards lean region. The modeling of the laminar flame speed of 1-pentanol/air mixtures at an initial pressure of 1 bar and temperature of 353, 433 and 473K have been performed using COSILAB software. Togbe et al. [3] detailed kinetic mechanism was used to simulate these experiments. The predictions of the model are, for all the tested temperature lower than the experimental data of this study (figure 4c). On the other hand, the global shape of the predictions seems to be the same as the experiments.

4 Conclusion

New values of laminar flame speeds at initial temperature ranging from 353 to 473K and 1 bar were rigorously obtained in a spherical bomb for two mixtures, iso-pentanol/air and 1-pentanol/air. From those experiments the temperature and the equivalence ratio dependence of S_l^0 was studied and the Markstein lengths were determined for each mixture. The experimental results of this study were compared to the literature (Li et al. [2] et Mani Sarathy et al. [6]). The simulation of the 1-pentanol/air mixture flame speeds was performed using the model of Togbe et al. [3]. The main conclusions are the following: 1) Laminar flame speeds of iso-pentanol/air and 1-pentanol/air mixture have a non-linear temperature dependence; 2) the Markstein lengths of each mixture are very close which indicate the same response to the stretch. From an engineering point of view, it means that the use of 1-pentanol on an engine would be more efficient considering that inside an engine the stretch is dramatically important. Thus, a 1-pentanol flame would be always faster than an iso-pentanol flame; 3) The experimental results of Li et al. are lower than the experimental data of this study from $0.8 \leq \varphi \leq 1.5$ (1-pentanol/air mixture) and the experimental results of Mani Sarathy et al. are in good agreement with the present study (iso-pentanol/air mixture); 4) The prediction of the Togbe et al. model underestimate systematically the experimental results of the present study for 1-pentanol/air mixtures. The next part of the modeling will be undertaken in the very near future (Heufer et al. model [4] for n-pentanol and Mani Sarathy et al. model [6] for iso-pentanol have to be tested).

Acknowledgements

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