Combustion properties of n-heptane/hydrogen mixtures

A. Comandini, K. Brialix, N. Chaumeix ICARE, CNRS Orléans, France

J. MacLean, G. Ciccarelli Department of Mechanical and Materials Engineering, Queen's University Ontario, Canada

1 Introduction

Current diesel engines use high levels of exhaust gas recirculation in order to decrease the combustion temperature and minimize the production of NOx. In addition, common rail high pressure fuel injection is used to produce a very fine fuel spray to reduce the production of soot and unburned hydrocarbons. In the latest diesel engines, the use of multiple fuel injections per cycle further reduces the amount of soot as well as the ignition delay time. The use of supplemental hydrogen gas mixed with diesel fuel has the potential to decrease these emissions. Concerning soot, the presence of hydrogen diminishes the carbonto-hydrogen ratio and enhances particle oxidation (higher concentrations of H/OH radicals and, for certain operating conditions, higher in-cylinder temperatures). Hydrogen-diesel fuel co-combustion also mitigates the effects of the over-mixing of diesel vapor with air which leads to compositions below the flammability limit and thus to significant portions of unburned hydrocarbons leaving the exhaust port. Indeed the presence of hydrogen favors the flame initiation even in areas of the chamber where the diesel fuel is deficient. Depending on the operating conditions and the percentage of H_2 in the fuel, NOx can also be reduced by lowering the combustion temperature. In order to further help the engine manufacturers to design solutions for a more-efficient implementation of this promising technology, the fundamental properties of the hydrogen-diesel fuels need to be carefully investigated. In particular, due to the complexity of the real fuels, surrogate mixtures composed of few compounds which mimic the chemical and physical properties of the real fuel are often used in order to simplify the CFD engine calculations. n-Heptane is the most common component used in surrogate formulations. The objective of this study is to analyze the effects of hydrogen addition to the fundamental combustion properties of large fuel surrogate components such as n-heptane.

2 Experimental and modeling techniques

Correspondence to: andrea.comandini@cnrs-orleans.fr

Spherical Bomb

The spherical bomb technique has been described in detail in previous publications [1],[2]. The bomb consists of a 56 liter spherical stainless steel vessel equipped with 4 quartz windows (100 mm optical diameter). Two tungsten electrodes are located along a diameter of the sphere for ignition at the center. The combustion process is monitored using two different diagnostics: pressure measurements using a piezo-electric pressure transducer (Kistler 601A) and flame visualization. The visualization was obtained via a single-pass schlieren system including a high-speed camera (Phantom v1610). The frame rate was fixed at 25000 fps. The synchronization between the different instruments allows the temporal correlation between the pressure increase and the flame diameter. A pressure increase between 0.5% and 0.9% of the peak was observed between the times corresponding to the first and the last images that were used for deriving the flame speed.

The flame radii were obtained by automated software (Canny method) as a function of time, and used to derive the unstretched laminar flame speed of the unburned gases. In particular, the non-linear relation by Ronney and Sivashinsky [3] was solved iteratively to obtain both the adiabatic unstretched gas speed of the burned gases relative to the flame and the Markstein length. The unstretched laminar flame speed of the unburned gases can be derived from the continuity equation. The maximum estimated error in the flame speed measurement due to uncertainties in the radii (± 1 pixel) is around ± 0.6 cm/s. Finally the estimated radiation-correction terms calculated based on the equation proposed by Yu et al. [4] is around 0.5 cm/s for all the experimental conditions.

Three different experimental datasets were obtained with the following percentage of H_2 in the fuel: 0%, 25%, and 50%. The mixtures were prepared directly in the vessel using the method of partial pressures,



Figure 1.Laminar flame speeds of nheptane/air. $T_{in} = 298$ K; $P_{in} = 101.3$ kPa: \times Dirrenberger et al. [5], \Box Huang et al. [6], Δ Davis et al. [7]. \bullet present work ($T_{in} = 294$ K; $P_{in} = 100$ kPa); \bigcirc p.w. normalized to 298 K.

introducing first the n-heptane component (Sigma Aldrich, 99.8% purity), then the hydrogen, if any (Alphagaz 1), and finally the laboratory dry air $(0.209 \text{ O}_2 + 0.791 \text{ N}_2)$. In order to minimize the uncertainty in the mixture preparation, the pressures were measured using capacitive manometers (MKS Baratron, Type 631) of different full scales according to the desired pressure range (100 Torr and 1000 Torr). Based on the precision of the capacitive manometers, the uncertainity in the mixture composition was 0.5%. The initial pressure and temperature in the spherical bomb were fixed respectively to 100 kPa and 294±1 K for all the experimental sets. In order to further confirm the validity of the experimental technique, the n-heptane/air measurements are compared to the measurements at room temperature and atmospheric pressure available in the literature (see Figure 1). Also provided in Figure 1 is the data after normalization to take into account the difference in initial temperature (294 K vs 298 K), pressure (100 kPa vs 101.3 kPa), and air composition. The normalization factors have been estimated

using kinetic modeling. The figure clearly shows that the present data closely agree with the recent measurements by Dirrenberger et al. [5] with a flat flame adiabatic burner.

Shock Tube

The shock tube has a 4.5 m long, 7.6 cm square cross-section driven-section and a 1.83 m long, 10.2 cm diameter driver. A 76.2 cm round-to-square transition section is included in the driven length. The double

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diaphragm technique was used to accurately obtain the desired shock Mach number. The diaphragm material is 2 mm thick, 1100 series aluminum, pressed with a four-petal shape to facilitate diaphragm opening (rupture pressure between 22.1 and 44.2 bar across the diaphragms). Three piezoelectric pressure transducers (PCB 113A24) are used to record the pressure inside the tube. The pressure transducers are located 4.04 m, 4.35 m, and 4.50 m (end plate) downstream of the diaphragm. A photodiode (Edmund Optics, S-050-H) with a 430±10 nm filter (Thorlabs, FB430-10) is attached to the end plate via an acrylic rod in order to detect luminescence from CH radicals. The onset of ignition can be determined by the rise in pressure and the appearance of CH radicals as measured by the photodiode. Ignition delay has been defined as the time between the arrival of the incident shock wave at the end plate and the onset of ignition. The fuel/air mixture is prepared in a separate mixing chamber using the method of partial pressures to combine n-heptane, hydrogen and air at the desired ratio. The auto-ignition of several blends of n-heptane/hydrogen/air mixtures has been studied behind reflected shock waves at a pressure of roughly 20 bar and for temperatures ranging from 700 to 1200 K.

Chemical kinetic modeling

Two reduced chemical kinetic schemes were tested against the laminar flame speed results, these include the models by Stagni et al. [8] and Cai and Pitsch [9]. The two models were validated against experimental results for n-heptane available in the literature. The present work includes the addition of hydrogen as a fuel component, thus the corresponding CO reactions were analyzed in detail. In particular, the model by Stagni et al. [8] does not contain the recombination reactions between two hydrogen atoms and two oxygen atoms as in the original CRECK model, thus such reactions were added for completeness. The addition of such reactions did not change the simulation results for the n-heptane experiments. The validation of the two models against experimental hydrogen/air data at room temperature and atmospheric pressure from the literature is presented in Figure 2. All the flame simulations have been performed using Cosilab



298 K; $P_{in} = 101.3$ kPa: × Kwon et al. [11], Dowdy et al. [12], O Tse et al. [13].

software, version 3.3.2 [10], solving the one-dimensional freely-propagating flame system. All the calculations were performed using multi-component transport properties, as well as including the Soret effect.

3 Results and discussions

The experimental results on the laminar flame speeds of n-heptane/air mixtures are reported in Figure 3a together with the simulations obtained with the two kinetic models. The blending of hydrogen with n-heptane leads to an increment in the laminar flame speed (defined as the difference between the laminar flame speed for the hydrogen/heptane and the heptane-only fuel), although the increment is substantial only when a large amount of H₂ is present. Figure 3b contains the experimental and modeling increments obtained with different H₂ additions. In particular, the experimental values were obtained from polynomial fits to the data in Figure 3a. The results indicate that the addition of 25% of hydrogen in the fuel mixture generates an average increase of only 3% in the speed (0.9 cm/s on average, with maximum increment of ~ 1.2 cm/s at $\phi \sim 1.1$, Figure 3b). On the other hand, the laminar flame speeds of the 50% C₇H₁₆ + 50% H₂/air mixtures are ~10% higher than the n-heptane case (3.3 cm/s on average). In this case, the maximum

increment is reached at $\phi \sim 1.2$, thus slightly shifted compared to the experiments with lower hydrogen mole fractions. From a modeling point of view, both models over-predict the current measurements (Figure 3a), although the error can be considered minimal (around 5% for the model by Cai and Pitsch [9] and between 6% and 14% for the model by Stagni et al. [8], with higher discrepancies at fuel-rich conditions). Independently from these considerations based on the measured profiles, both models are capable to reproduce quite accurately the effects of the addition of H₂, as shown in Figure 3b. In particular, the correspondence between the results obtained with the model by Cai and Pitsch [9] and the experiments is remarkable for both profiles. The only discrepancy appears at fuel-rich conditions, where the experimental profiles bend at lower equivalence ratios and thus the speed increments are slightly overpredicted. The effects of the H₂ addition on the experimental Markstein lengths (derived from the solution of the non-linear equation) were also considered, but no substantial differences were observed (data not shown). Thus the addition of hydrogen as a fuel component is not expected to change significantly the response of the flame to stretch.



Figure 3. a) Laminar flame speed of n-heptane/H₂/air mixtures. Fuels: □ 100% C₇H₁₆, △ 75% C₇H₁₆ + 25% H₂, ○ 50% C₇H₁₆ + 50% H₂. b) Increment of the flame speed compared to the n-heptane/air case for an addition in the fuel of: □ 25% H₂, ○ 50% H₂. Dashed lines: Cai and Pitsch model [9]; solid lines: Stagni et al. model [8].

The chemical kinetic models were also used to determine how the fuel composition influences the flame propagation. As expected, the main factor which leads to the increase in the flame speed with increased percentages of H_2 in the fuel is the formation of larger amounts of radicals (in particular H and OH). Such radicals diffuse towards the unburned gases leading to faster consumption of the n-heptane and a larger heat release rate. Although some of the pathways for the n-heptane consumption are more-or-less favored by the presence of additional radicals, the reactions which significantly affect the flame propagation remain unaltered by the presence of hydrogen.

Concerning the auto-ignition study, several blends have been investigated, air being the oxidizer. The mixture was defined as $\{(1-x) \%$ n-heptane $+ x \% H_2\} + air$, and three different equivalence ratios have been studied: 0.833, 1 and 1.25. The reflected shock pressure was chosen to be around 20 bar. These experiments have been simulated using the two aforementioned models by Cai and Pitsch [9] and by Stagni et al. [8]. Figure 4 gives an illustration of the variation of the ignition delay times versus the temperature inverse and of the effect of n-heptane substitution by hydrogen. The experimental data shows that the addition of hydrogen has almost no effect on the high temperature side of the curve, but is responsible for a longer delay, mainly in the negative temperature correlation (NTC) region; this effect

fades away in the low temperature zone as the temperature is decreased. This trend is observed for all three equivalence ratios investigated. These experimental results are in agreement with the findings of Frolov et al. [14].



Figure 4. Auto-ignition delay times of n-heptane/H₂/air mixtures for 3 different equivalent ratios and 20 bar: a) & d) ER=1, b) & e) ER=0.833, c) & f) ER=1.25. Fuels: \Box 100% C₇H₁₆, \triangle 80% C₇H₁₆ + 20% H₂, \bigcirc 50% C₇H₁₆ + 50% H₂, \Rightarrow 25% C₇H₁₆ + 75% H₂. Dashed lines: Cai and Pitsch model [9]; solid lines: Stagni et al. model [8].

The ignition delay time behavior is well reproduced by both models. Cai and Pitsch model underestimates the delays in the high temperature zone but reproduces very well the NTC region in the whole range of the study in terms of equivalence ratios, hydrogen content and temperature span. Stagni et al. model is able to reproduce the high temperature regimes and over-predicts the delays both in the NTC and the low temperature region. Cai and Pitsch model will be used in the very near future to highlight the chemical effects of the hydrogen addition in the reduced reaction rate in the NTC region.

4 Conclusions

This work is focused on the effect of blending n-heptane with hydrogen on combustion properties. Ignition delay times and laminar flame speeds of n-heptane/H₂/air mixtures have been experimentally determined using a shock tube and a spherical bomb. These data have been acquired over a large set of conditions to validate a suitable chemical kinetic mechanism in order to facilitate the detailed analysis of the role played by hydrogen in the n-heptane oxidation kinetics. This is the first mandatory step required

to predict the effect of diesel blending with hydrogen with regards to the emission of pollutants and the determination of the suitability of hydrogen addition in real engines.

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