Autoignition of n-decane and multi-component surrogates of kerosene in an optical Rapid Compression Machine

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1 Introduction

Increasingly drastic environmental constraints are imposed to aeronautic engines manufacturers. A way to increase thermal efficiencies of aeronautic turbomachines is to take advantage of the Humphrey cycle. In this respect, constant volume combustion based on premixed or partially premixed combustion was investigated in several studies, see for instance [1, 2]. In particular, in the approach of Labarrere et al. [1], end-gas autoignition should rather be avoided, whereas autoignition is the core of the so-called shockless explosion combustion concept [2]. In the both cases, a good knowledge of autoignition behavior of aeronautic fuels is required. Last decades, numerous research efforts were devoted to the definition of surrogate fuels able to represent both physical and chemical properties of kerosene. The present work aims at characterizing the autoignition delays of single and multi-component surrogates initially developed for combustion applications. An optical RCM fitted with a flat piston is used to this purpose, which is well adapted as these fuels usually present a positive temperature coefficient (PTC) in typical RCM conditions. The results are compared to kerosene measurements available in the literature in order to evaluate the representativeness of these surrogates in terms of autoignition.

2 Experimental device

Experiments are performed with a RCM facility developed at PPRIME institute. Conditions at the end of compression (Top Dead Center - TDC) are varied by changing the diluent gas composition. In this study, the volumetric compression ratio is set to $\varepsilon = 9$. The RCM piston is flat with a square section and rounded corners. The top of the chamber is fitted with four quartz perpendicular windows, providing an optical access to the full dead volume along a direction normal to the cylinder axis. The walls, cylinder head, intake pipes, valves and pressure sensors are heated. A three-zone regulated heating system is used for the cylinder and a single zone regulator for the gas intake system (378 K). Temperature was measured along the cylinder axis with a bare bead K thermocouple in quiescent mixture [3]. The three-zone regulation system was set

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both (i) to obtain a monotonic temperature evolution within the cylinder (maximum at the cylinder head), and (ii) to homogenize the temperature field, with values ranging from 344 K close to the piston to 360 K near the cylinder head.

Gaseous mixtures are prepared following the partial pressure method. The RCM chamber and feeding lines are first placed under vacuum. The fuels are then vaporized in the chamber using microliter syringes and a septum. For multi-component kerosene surrogates, a mixture of liquid fuels is injected. Mixtures are prepared with high purity grade commercial chemicals: n-decane (Merck, > 99%), n-propylbenzene (Merck, > 98%), n-propylcyclohexane (Sigma-Aldrich, > 98.5%), n-dodecane (Merck, > 99%), iso-octane (Sigma-Aldrich,> 99.75%), 1,2,4-trimethylbenzene (Merck, > 98%), 1,3,5-trimethylbenzene (ACROS Organics, > 98.5%). Pressure is measured with 0.1 mbar accuracy using a 0-1300 mbar MKS Baratron 631 capacitive sensor heated up to 470 K. The volume of liquid fuel injected and the resulting fuel pressure are compared to check full vaporization is obtained. Then, an oxidizer premixture of $O_2/N_2/CO_2$ with 21% of oxygen mole fraction is preheated in a pipe and then admitted through the same intake system. One hour is waited before starting the compression experiment to ensure sufficient homogenization of the fuel-oxidizer mixture in the RCM cylinder. We checked both identical ignition delays and broadband chemiluminescence records were obtained for rest times of 45 min, 1 h, 1.5 h and 2 h. Initial pressure in the RCM is checked just before running each compression test. Pressure evolution is recorded at 100kHz using a Kistler 6125CU20 piezoelectric sensor coupled to a 5018A amplifier. For more details, please refer to [4,5].

3 Results

The autoignition of both single and multi-component kerosene surrogates is considered: n-decane and the surrogates of Dagaut et al [6] and MURI2 [7] are chosen for this work. The surrogate of Dagaut et al. is composed of 74% *n*-decane, 15% *n*-propylbenzene and 11% *n*-propylcyclohexane (% vol.). Composition of the MURI2 surrogate is 40.4% n-dodecane, 29.5% iso-octane, 7.3% 1,3,5-trimethylbenzene and 22.8% n-propylcyclohexane, (% vol). Ignition delays are measured as the time between the local pressure maximum at the end of compression (Top Dead Center – TDC) and the time corresponding to the maximum rate of pressure rise. The same criterion is used for the first stage ignition delay: the cool flame occurrence is detected using the local maximum rate of pressure rise.

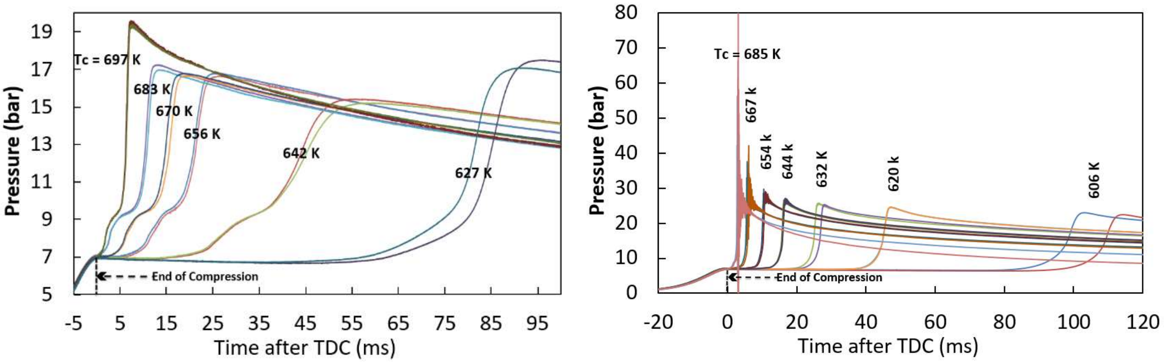

Figure 1. Pressure traces measured with n-decane/$O_2/N_2/CO_2$ mixtures at P_{TDC} = 7 bar. $\Phi = 0.5$ (left), $\Phi = 1$ (right).

Autoignition of n-decane is first investigated for both stoichiometric and lean mixtures ($\Phi = 0.5$), with two different pressure values at TDC: 7 and 15 bar. Figure 1 reports the pressure traces measured for the lowest pressure condition for different adiabatic core temperatures at TDC [4]. In agreement with previous studies, the rate of pressure rise during the second stage of ignition increases with temperature, e.g. with shorter ignition delays. Furthermore, the pressure traces clearly evidence the occurrence of the cool flame for the lean mixture. In the stoichiometric case, the first stage delay is not reported as it is difficult to detect the cool flame by pressure means: only a smooth and low pressure rise is observed a few milliseconds before the second stage of ignition. This behavior was unexpected as the cool flame clearly appears in the pressure traces reported by Kumar et al. [8] in similar conditions with a creviced piston. Further investigations were performed using simultaneously double-pulse planar laser induced fluorescence (PLIF) with excitation at 355 nm – the setup is described in [4] - and high frequency OH* chemiluminescence in these conditions. The formaldehyde PLIF images confirmed the cool flame occurs at the onset of pressure rise in small regions near the cylinder head, see Fig. 2b). Even if our pressure traces differ from that reported by Kumar et al. in similar conditions, the phenomena are identical: the small size of these cool flame regions just make the pressure rise lower and its detection more difficult in these particular conditions with our flat piston RCM. Furthermore, it is worth noticing these diagnostics, along with broadband chemiluminescence records, confirmed no particle preignition occurred in this work, whatever the fuel. The smooth pressure rise is rather attributed to a reactive front initiated close to the cylinder head, e.g. close to the first cool flame kernels, and which propagates downwards see Fig. 2a). As it propagates, the unburned mixture is compressed and finally autoignites close to the piston at the end of the combustion process. This behavior is observed for a large temperature range, leading to different propagation speed at the onset of the second stage. This vertical propagation results from the initial temperature gradient, which is supposed to persist and to be reinforced in the hot core zone by the quasi-1D compression flow observed during compression stroke in this zone [9]. In that case, auto-ignition occurs in the hottest region (PTC behavior) and propagates following the ignition delay gradient. More detailed analyses and discussions about the phenomena and their interaction with the flat piston aerodynamics can be made with the optical diagnostics evoked above, but this is avoided here for the sake of brevity. Discussion will be focused on ignition delay measurements, therefore the important point is that autoignition first occurs in the hot core zone. Therefore adiabatic core hypothesis can be used to analyze the results in the PTC region, even for relatively long delays as suggested in [5].

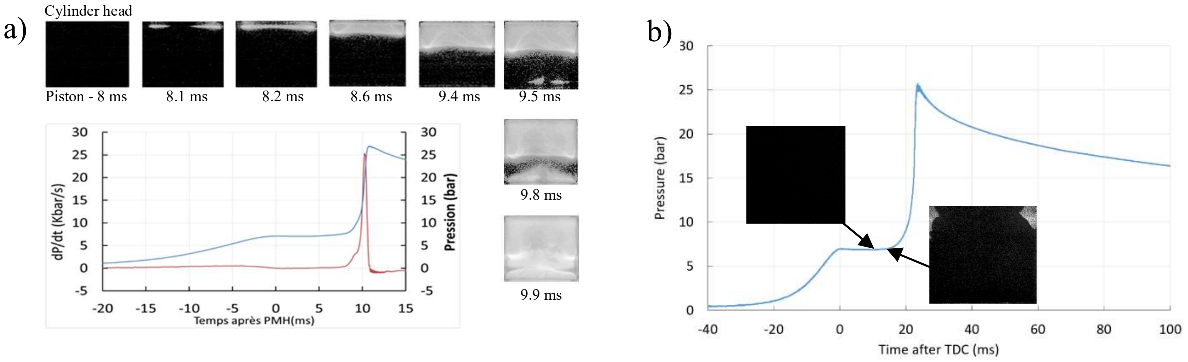

Figure 2. Typical images recorded using OH* chemiluminescence at $T_{PMH} = 654$ K(left) and CH_2O planar laser induced fluorescence with double-pulse 355 nm excitation at $T_{PMH} = 633$ K (right). $P_{TDC} = 7$ bar, n-decane/O_2/N_2/CO_2, $\Phi = 1$.

Figure 3 a) displays the ignition delays obtained for the first (τ_1) and second stage ($\tau_1 + \tau_2$) of autoignition, reported respectively with hollow and full symbols. Each symbol corresponds to a single experiment, and a relatively low scattering of ignition delay is obtained. As expected, ignition delays increase when the mixture is getting leaner or when pressure decreases, see for instance [8]. The data feature an exponential dependence of ignition delay (ID) to 1000/T, where T is the adiabatic core temperature at TDC. In other words, a constant global activation energy is obtained for each condition, provided that the delay is lower than 100 ms. This is not the case above this threshold (ID >100 ms), at $\Phi = 1$ and $P_{TDC} = 7$ bar, which may result from the failure of the adiabatic core hypothesis. An exception is also observed for the lean mixture at 7 bar: in that case, a PTC behavior is still observed but global activation energy decreases at the highest temperatures, as they are approaching the NTC region. For this mixture, τ_1 is relatively close to the second stage ignition delay ($\tau_{1+}\ \tau_2$), as relatively low temperatures are considered. Meanwhile, figure 3a shows τ_1 does not significantly vary with pressure for the lean mixture.

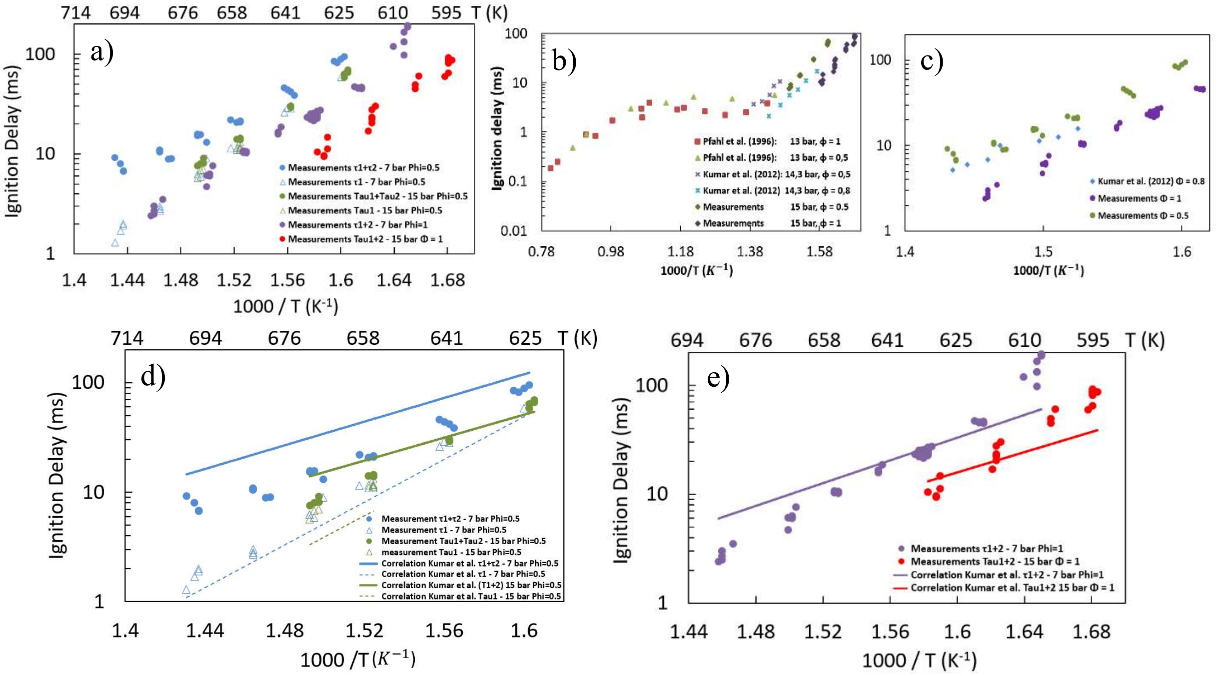

Figure 3. Ignition delays as a function of adiabatic core temperature at TDC for n-decane/O_2/N_2/CO_2, mixtures. $\Phi = 0.5$; $\Phi = 1$; $P_{TDC} = 7$ and 15 bar (a). Comparison to the literature is reported in subplots b) and c), and to the correlation of Kumar et al. [8] in subplots d) and e).

These data are compared to the results of Kumar et al. in Fig. 3 b) at 15 bar and c) at 7 bar. The correlation provided by this group of authors is reported as well in subplots d) and e). At high pressures, second stage ignition delays measured in our RCM are in good agreement with the shock tube measurements of Pfahl et al. [10] at $\Phi = 0.5$. For the stoichiometric case, temperature ranges of our measurements are closer to that obtained by Kumar et al. in a creviced piston RCM, even if there is no overlap. Extrapolation of their data suggests slightly shorter delays are measured in our flat piston RCM for the same temperatures. This may result from the faster compression performed by the RCM of Kumar et al.: pressure increases from $P_{TDC}/2$ to P_{TDC} in about 4 ms in [8] while 10 ms are needed with our machine, see Fig.1. In Fig.3c), the measurements at 7 bar show the delays measured by Kumar et al. at $\Phi = 0.8$ are included in the region delineated by our data at $\Phi = 0.5$ and 1. This confirms the relatively good agreement between the two datasets. The comparison between our data and the correlation fit proposed by Kumar et al. is consistent for stoichiometric mixtures. Nevertheless, the global activation energy seems to be underestimated by the correlation even for relatively short delays. This may be caused by the different compression durations.
0D numerical computations with detailed chemical kinetics and compression history are planned to confirm this hypothesis. In lean conditions ($\Phi = 0.5$), similar cool flame delays τ_1 are measured for 7 and 15 bar.

At 7 bar, they agree with the correlation values, nevertheless delays are slightly underestimated at 15 bar.

In conclusion, a fairly good agreement is obtained between the experimental dataset and the literature. Moreover, the RCM and the chosen protocol can be considered as validated for characterizing autoignition of liquid fuels with relatively low volatility such as n-decane. This is also the case for kerosene surrogates, which is the concern of the next paragraph. Finally, it is worth noticing the measurements performed with n-decane at stoichiometry complement the study of Kumar et al. [8], as this group of authors rather targeted their experiments at higher pressures, and on non-stoichiometric conditions.

Characterization of multi-component kerosene surrogates is performed in terms of ignition delays. The results obtained for stoichiometric Dagaut surrogate mixed with $O_2/N_2/CO_2$ are reported in Fig. 4 a) and b). Unlike n-decane, pressure traces at $P_{TDC} = 7$ bar and $\Phi = 1$ display a clear two-stage ignition behavior, but only for short delays. The figure displays as well high rates of pressure rise leading to pressure oscillations, e.g. knocking combustion. Fig. 4b) reports the corresponding ignition delays: they are divided by a factor of about three when pressure changes from 7 to 15 bar. Again, activation energy seems to be constant for a given pressure value, expect for ID>100 ms. This suggests adiabatic core simulations should be avoided for these highest delay values. The novelty of these results is underlined: to the authors knowledge, auto-ignition of this surrogate was only tested at much higher temperatures, by comparing directly delays obtained from simulation to commercial kerosene measurements [6].

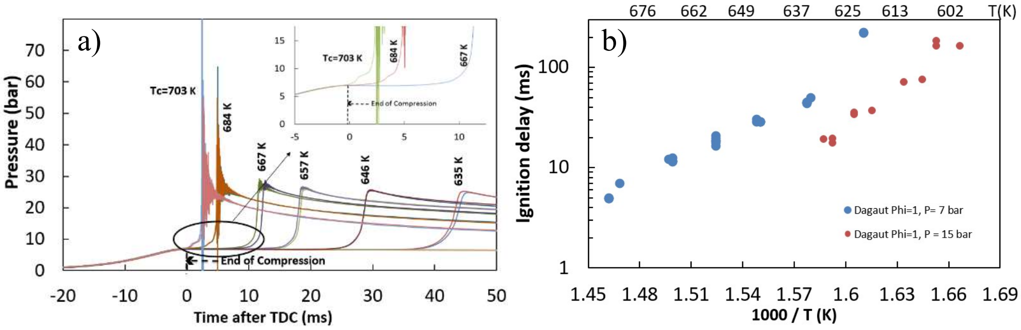

Figure 4. Pressure traces (left) and ignition delays (right) of stoichiometric mixture of Dagaut surrogate with $O_2/N_2/CO_2$, at $P_{TDC} = 7$ bar and 15 bar.

Finally, measurements performed for stoichiometric MURI2 – $O_2/N_2/CO_2$ mixtures are reported in Fig. 5. Delay measurements published in the literature for different kerosenes are reported as well in Fig 5.b). Global activation energies are similar for the three surrogates, but significant differences of the second stage ignition delay $\tau_1+\tau_2$ are reported, reaching up to a factor about four for the same temperature. This is consistent with the chemical structure of the surrogates, n-decane is a linear alkane and is prone to autoignition. Dagaut et al. surrogate is mostly composed of n-decane and also a part of aromatics, which increases the delays. The MURI2 surrogate contains a significant part of both linear and aromatic hydrocarbons, but it also includes 29.3% of isooctane, leading to a higher resistance to autoignition.

Large discrepancies are reported as well in Fig. 5b) for different kerosene fuels at 7 bar and low temperatures. In particular, significantly shorter ignition delays are measured for the natural gas derived fuel S8 at TDC temperatures lower than 690 K. These delays are in relatively good agreement with that of n-decane. This is consistent with the high cetane number reported in the literature for this S8 fuel. Second stage ignition delays are reported for other kerosenes at 7 bar in near stoichiometric conditions. They are relatively close together (Jet-A1[11], Jet-A [12], and Jp8[12]). In that case, MURI2 is the most representative kerosene surrogate in terms of ignition delays. This is consistent with the good agreement reported by Dooley et al. [7] between the MURI2 surrogate and the jet-A POSF4658 in stoichiometric conditions at $P_{TDC} = 21.7$ bar.

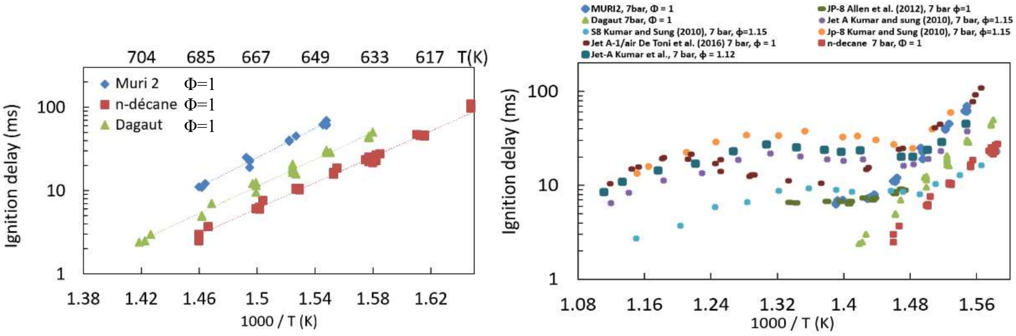

Figure 5. Ignition delay measurements: comparison of different surrogates at P_{TDC} = 7 bar, close to stoichiometry.

Conclusion

Autoignition of single and multi-component kerosene surrogates is characterized at low temperatures in a flat piston RCM. Significant differences in ignition delays are observed between the different surrogates. The measurements either provide new data, confirm or complement the databases already published. Additional experiments are planned to strengthen the dataset with n-decane. Further comparisons using 0D computations with detailed kinetic schemes will be done. The effects of the machine design, and in particular of compression history and temperature heterogeneities, will be quantified using numerical results and optical measurements.

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