Measurements of the auto-ignition of *n*-heptane/toluene mixtures using a rapid compression machine

R. Di Sante *

Sloan Automotive Laboratory, M.I.T., 77 Massachusetts Avenue, Cambridge, MA 02139, USA

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ABSTRACT

Ignition delay times of undiluted stoichiometric *n*-heptane/toluene mixtures have been measured in a rapid compression machine (RCM) for pure *n*-heptane and for an increasing concentration of toluene by liquid volume (25–100%) in the mixture, mainly at two different molar densities (150 and 180 mol/m^3). Initial pressures and temperatures were varied respectively in the 0226–0298 bar range and in the 299–352 K range, in order to allow compressed pressures and temperatures respectively in the 7.95–10.38 bar range and in the 710–814 K range.

No ignition was observed for pure toluene due most probably to the variation of the final temperature and pressure in the combustion chamber during the very long ignition times of pure toluene at the experimental conditions considered in this work. The ignition delay variation at fixed temperature and the relative variation of the two-stage ignition times are reported. It is shown how the mixture behavior seems to be governed by the *n*-heptane chemistry for low toluene amount, while an increase of toluene concentration causes longer ignition delay times.

Numerical modeling of the experiments with a recent Lawrence Livermore chemical mechanism for surrogate fuels shows that the results agree fairly well in the case of low and mid proportion of toluene by liquid volume. The single-zone model has allowed to extend the temperature range of investigation, showing that the low temperature range is the most influenced by the presence of toluene.

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1. Introduction

The study of hydrocarbon fuel ignition characteristics is of fundamental importance for the understanding of several phenomena related to internal combustion (IC) engines. Particular attention has been recently devoted to high pressure, intermediate temperature ignition characteristics of hydrocarbons which are encountered in real engines. Such information is needed to understand the operation of homogeneous charge compression ignition (HCCI) engines which is dependent on the auto-ignition characteristics of the employed fuel, and also of the knock phenomenon in SI engines. HCCI engines, in particular, are a subject of great interest in recent studies as they allow to reduce both particulate matter (PM) and nitrogen oxides (NO_x) emissions still assuring high performances [1,2]. Their operation rely completely on the fuel ignition time and combustion rate, and one method to control the combustion is the use of fuel mixtures [3].

In order to get a significant insight in the auto-ignition mechanisms of primary reference fuels (PRF) and non-PRF fuels the ignition delay τ as a function of temperature, pressure and mixture composition needs to be experimentally and theoretically studied. This type of information does not exist for practical fuels at conditions relevant to auto-ignition in IC engines [4], due to the difficulty of analyzing and establishing the combustion mechanisms especially in the case of complex mixtures where aromatics and paraffins are simultaneously present. A great deal of work is therefore necessary to understand the auto-ignition chemistry of practical fuels at a fundamental level. A start could be made with simple fuels like toluene/*n*-heptane mixtures (TRF fuels) which behave more like practical fuels than iso-octane/*n*-heptane mixtures (PRF fuels) [4]. Moreover, the amount of aromatics in commercial gasoline ranges from around 20% to 50% and toluene is the main component.

Besides the pioneering work of Halstead et al. [5], TRF fuels containing both toluene and *n*-heptane, have been studied in these years using shock tubes [6,7], HCCI engines [8–14] and rapid compression machines [3,15].

In [6], which is reported as the first experimental work on TRF fuels, the ignition delays for a mixture of *n*-heptane and toluene (35/65% by liq. volume) in air (equivalence ratio, $\varphi = 0.3$ and 1) at pressures of 10, 30 and 50 bar were investigated in a high-pressure shock tube. At lower temperatures no ignition was measured at 10 bar though.

* Present address: University of Bologna, DIEM – Departement of Mechanical, Nuclear, Aeronautical and Metallurgical Constructions, II Faculty of Engineering, via Fontanelle 40, 47100 Forlì, Italy.

E-mail address: raffaella.disante@unibo.it

Hartmann et al. [7] measured the ignition delay times of TRF fuels at φ = 1.0 and 0.5, at a pressure of 40 bar in a shock tube, with the aim of evaluating the influence of toluene as a tracer in laser induced fluorescence (LIF) experiments, therefore considering low concentrations of toluene in the investigated mixtures (mainly up to 20%). They were able to observe that the negative temperature coefficient (NTC) behavior almost disappears with increasing toluene proportions, while low concentrations (below 10%) of toluene have a negligible influence on the mixture ignition delay.

Andrae et al. [9] investigated the auto-ignition of TRF fuels both theoretically and experimentally using a HCCI engine and modeling the experiments with a single-zone adiabatic model and detailed chemical kinetic models. In a subsequent study [10], experimental data from shock tubes (mainly from [6]) and HCCI tests were used to validate a detailed kinetic mechanism describing the auto-ignition behavior of TRF fuels; while in [11] Andrae et al. developed a semi-detailed mechanism for TRF fuels adding skeletal mechanisms for n-heptane to a detailed toluene submechanisms. The model was validated against ignition delay times measured in a shock tube, a rapid compression machine and a HCCI engine.

In [12], Bradley and Head conducted a study on the relation between octane numbers and the autoignition delay times of non-PRF fuels in a single-cylinder engine at different temperatures and pressures and equivalence ratio of 0.25. They observed that the delay times of non-PRF fuels tend to increase more than those of PRFs as the pressure increases and the temperature decreases.

Dubreuil et al. [13] performed experiments on TRF fuels in a jet stirred reactor (JSR) under diluted conditions at 10 atm and in a HCCI engine in order to study the effect of NO addition and of variable rates of exhaust gas recirculation (EGR) on the ignition delay times.

In [14] the auto-ignition of PRFs, TRFs and diesel fuel was investigated in a HCCI engine varying the initial temperature, the equivalence ratio and the compression ratio. From a comparison with pure toluene it was found that aromatics have the strongest inhibiting effect on the ignition delay time and that the initial temperature plays a relevant role in this sense.

Very few experimental results from rapid compression machines are currently available in the literature on TRF fuels where both n-heptane and toluene are simultaneously present.

Tanaka et al. [3] conducted experiments in a rapid compression machine with complex fuels (cyclic paraffins, olefins and aromatics) showing that the ignition delay and the burn rate can be independently controlled using various fuel mixtures and additives. The combustion characteristics of various toluene standard fuels (TSFs) were studied for lean mixtures (φ = 0.4), at an initial temperature of 318 K, an initial pressure of 0.1 MPa and a compression ratio of 16.

Vanhove et al. [15] studied the oxidation and auto-ignition of five undiluted stoichiometric mixtures containing toluene in a RCM below 900 K and at a compression ratio of 9.5. Among them, they considered a 1/1 toluene/n-heptane blend and compared the ignition delay times obtained in this case to those of pure n-heptane. At around 4 bar and between 600 and 950 K, they reported that the ignition delay trend of the TRF fuel did not deviate substantially from the auto-ignition of pure n-heptane. However, the influence of increasing the compressed pressure, which is kept at 4 bar in this work, is not investigated. No modeling was attempted either.

The goal of this work is to measure the auto-ignition time of stoichiometric n-heptane/toluene mixtures in a rapid compression machine at high pressure (around 10 bar), systematically varying the amount of toluene in the fuel. The temperature dependence of paraffins (e.g. n-heptane) exhibits a negative temperature coefficient (NTC) region. That of an aromatic (e.g. toluene) does not. The presence of the NTC region is of particular interest because

the temperature range of such region (at 750–900 K) overlaps the end gas temperature in a SI engine, and hence the NTC behavior has a strong influence on the knock sensitivity of the fuel. Since practical fuels contain substantial amount of paraffins and aromatics, studying the auto-ignition properties of such mixture is of practical interest. Expected results consist in the attenuation of the NTC region while increasing the amount of toluene in the mixture.

A single-zone model is also developed using the CHEMKIN software (version 4.0.1 [16]) with Lawrence Livermore detailed mechanisms. In the case of pure n-heptane, the detailed mechanism version 2 [17] is employed. For modeling the combustion of the n-heptane/toluene mixtures, a reaction mechanism developed for a surrogate gasoline composed of iso-octane, n-heptane, 1-pentene, toluene and methyl-cyclohexane is adopted [18]. The toluene oxidation scheme for this mechanism is described in [19].

2. Experimental apparatus and procedures

A new RCM was built at MIT [20] based on the Thornton design [21] and modified to allow accurate measurements of binary fuels in this work. A schematic is shown in Fig. 1 and the essential features are reported in [20]. The new machine was designed to include the possibility of optically accessing the combustion chamber, in order to perform also soot formation studies by line-of-sight optical measurements through four fused silica windows [20] and imaging studies through a transparent cylinder head.

Two pistons (hydraulic and pneumatic) are connected and move together to compress the mixture in the combustion chamber. The hydraulic chamber is filled with silicon oil while the pneumatic chamber is initially vented to the atmosphere. After the introduction of the fuel and air mixture, the oil is compressed by a high-pressure gas (N_2). Pressure is then applied at the back of the pneumatic piston to balance pressure in the hydraulic chamber. The ratio between the piston areas is approximately 5–6 pneumatic to 1-hydraulic. Pressure in the hydraulic chamber is suddenly released and in this way the piston is fired, propelled by the compressed driving gas (N_2) behind the pneumatic piston. The gas is introduced with a large pipe from a reservoir (not shown in Fig. 1) that is around 50 times larger than the displaced volume in the pneumatic chamber so that no significant drop in the driving force occurs during the piston traveling. The piston starts to decelerate significantly when the pin of the hydraulic piston enters the grove, close to the end of the compression stroke. As the clearance between pin and groove is only about 0.7 mm, the back pressure buildup is large, causing the velocity to decrease from 30 m/s to 5 m/s in about 4 ms.

The piston is locked in its final position by the high pressure driving gas at the end of the compression stroke. In this condition a constant volume combustion takes place by preventing piston rebound. Driving pressure usually do not exceed 200 psi which results in approximately 15 ms compression time. For the given driving pressure the piston is prevented from bouncing back if the combustion chamber pressure is below 110 bar.

The combustion chamber is cylindrical with 5.08 cm bore. The initial piston position can be adjusted by suitable spacers (not shown in Fig. 1) so that the compression stroke varies from 15.24 cm to 20.32 cm which corresponds to compression ratios between 12.5 and 16.5. The value used in this work is the maximum allowed.

The compressed temperature T_c may be obtained from the measured compressed pressure P_c and the initial condition P_i and T_i via the isentropic relation:

$$\int_{T_i}^{T_c} c_p(T) \frac{dT}{T} = R \ln \left(\frac{P_c}{P_i} \right) \tag{1}$$
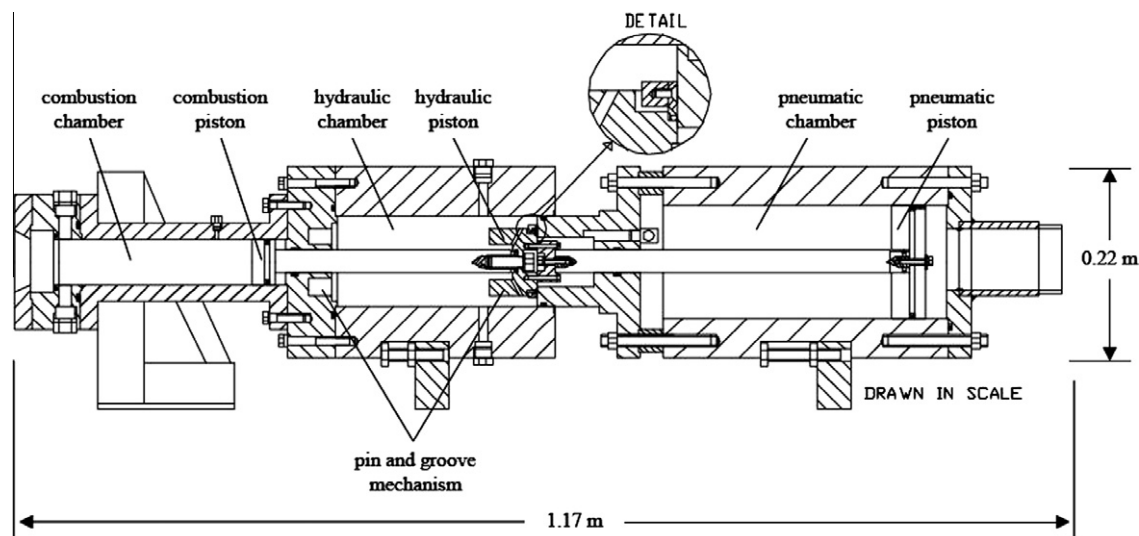
Fig. 1. Schematic of the RCM.

Here, $c_p(T)$ is the heat capacity per mole of the mixture at temperature T, and R is the universal gas constant.

An estimation of the compressed pressure before the experiment was obtained considering the flow in the crevice volume and gave a good correlation with the actually measured pressure at the end of the compression stroke.

A schematic of the setup used for mixture preparation is shown in Fig. 2.

The lines and fuel tanks are evacuated before introducing the mixture components. The vacuum pressure as well as the partial pressures of the vaporized fuels are checked using a Baratron 622A pressure transducer with accuracy of 0.1 Torr. The second tank was added specifically for studying the binary fuel mixtures considered in this work. This setup, with two separate fuel tanks, allows accurate measurement of the partial pressure of each fuel and the complete vaporization before the mixing phase. In this work, the proportion between the two fuels is indicated relative to the liquid phase, at ambient temperature, this means that the individual fuel mole fraction in the vapor phase is different and corresponds to its partial pressure at the initial conditions considered.

The combustion chamber, which is actually the mixing tank in the setup, the connecting lines and the fuel tanks are all heated and their temperature is controlled in two ways. The temperature of the lines and tanks is above the due point of the each fuel in the mixture at its partial pressure. The temperature in the combustion chamber is adjusted and monitored via special PID controllers in order to meet the initial test conditions.

In this way fuels were fully vaporized before being introduced in the combustion chamber. A 10 min interval was allowed before each compression for the mixture to become homogeneous and equilibrate with the temperature of the chamber. During this period, the system pressure (and thus the temperature) was monitored through the Baratron transducer to make sure that it stabilised. Good repeatability in the tests confirmed that the initial conditions were reproducible and that therefore the mixture was acceptably homogeneous and at least the core temperature did not vary from one run to the following. However, these issues will be further discussed in the following sections.

The combustion characteristics considered in this paper were determined from the analysis of the pressure time histories measured inside the combustion chamber using a Kistler pressure transducer.

Hydrocarbons like n-heptane present a characteristic two-stage ignition behavior. Defining the ignition delay t_i as the time at which the pressure increase is small with respect to the maximum pressure reached after the combustion (P_{max} in Fig. 3) may be misleading, as the second stage induction time t_2 (see Fig. 3) may induce a similar pressure rise. It was found that in all cases, defining the ignition delay as the time from the end of compression to the 20% of pressure rise was sufficient to assure that the actual combustion began. t_1 and t_2 are the two stage induction times defined as shown in Fig. 3. Figure 3 also shows the reference pressure trace, measured in case of an unreactive mixture under equivalent conditions.

3. Results and discussion

The set of experiments reported in this paper consisted of the study of stoichiometric toluene/n-heptane mixtures with the following proportion of toluene by liquid volume (at ambient temperature): 0%, 25%, 50%, 75%, 100%. Increasing toluene content approaches better the real situation as for example gasoline with RON around 95 do not contain high amount of n-heptane. An oxygen/nitrogen mixture (1:3.773 by mole) was used as air surrogate to achieve the desired compressed temperature. The compressed densities (150 and 180 mol/m^3) corresponded approximately to pressures in the 7.95–10.38 bar range.

In general, the repeatability of tests with pure n-heptane is excellent. For example, in the case of pure n-heptane at 711 K compressed temperature and 9.57 bar compressed pressure, the repeatability in the ignition delay time measurement was ±0.14 ms (±1.6%, with a confidence level of 95%). While the repeatability remained actually constant when changing the initial conditions of pressure and temperature, it decreased when increasing the amount of toluene in the mixture. This effect is due to two major phenomena acting simultaneously: the ignition delay time becomes longer changing the average conditions inside the chamber due to heat losses and, less importantly, the effect of possible inhomogeneities is increased. Heat loss effects have been discussed in Section 3.5.

3.1. Effect of the initial temperature

Ignition delay times measured for pure n-heptane were compared to those obtained by Griffiths et al. [22] and Silke et al.
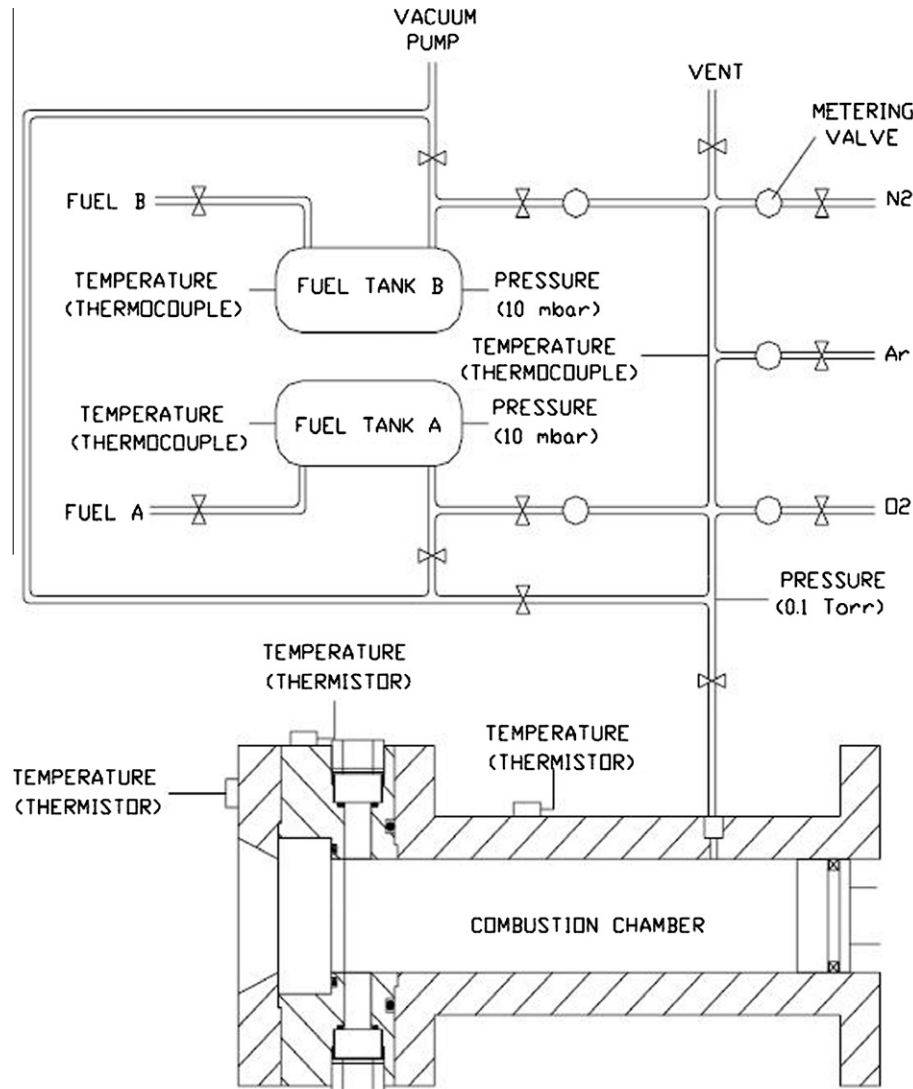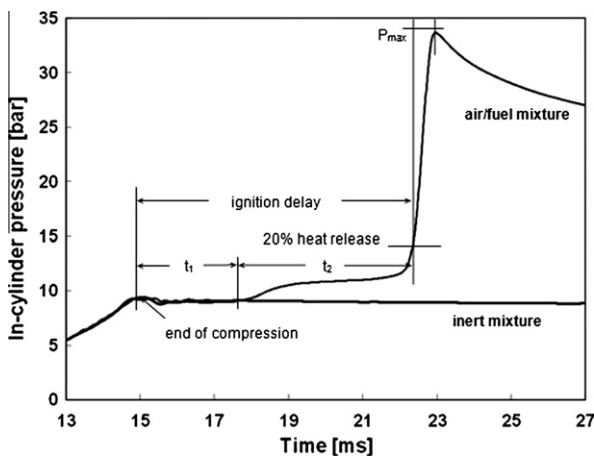
Fig. 2. Mixture preparation setup.

Fig. 3. Definition of ignition delay time in two-stage ignition.

[23] using stoichiometric *n*-heptane fuel mixtures in "air" at a compressed gas pressure of about 10 atm, in the temperature range 640–960 K. The comparison is shown in Fig. 4. Results agree

fairly well, especially with those of Silke et al. Keeping the mole density constant rather than the compressed temperature in this study means that discrepancies are likely to increase with the temperature. Also, as stated by Silke et al. as well, aerodynamic differences make the transferability of data from one RCM to another problematic.

In any case, in a RCM the study of pure *n*-heptane has to be carefully conducted as ignition delay times can be lower than a few milliseconds and, as a consequence, chemical reactions are more likely to start before the end of compression. The same analysis needs to be extended to all mixtures considered in this work though, as the problem may arise due to the nature of the RCM itself as observed in the past (see [24] for example).

In order to assess whether chemical reactions took place during the compression stroke the single-zone model developed using the CHEMKIN software (version 4.0.1 [15]) with Lawrence Livermore detailed mechanisms (described in [16] and in [17] for pure *n*-heptane for *n*-heptane/toluene mixtures respectively) was used assuming constant and variable volume relationships in an adiabatic environment. In the first case, initial conditions corresponded to the compressed pressure and the relative temperature calculated using Eq. (1), while in the second case simulations were started 5 ms before the end of compression. Anticipating by 5 ms
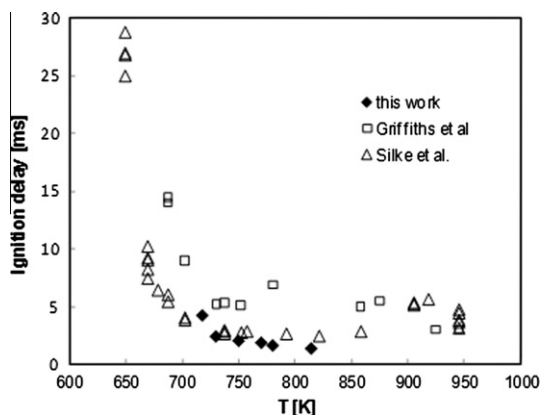
Fig. 4. Comparison between ignition delay times for stoichiometric *n*-heptane/air mixtures investigated in this study in the range 9.57–10.40 bar and in the studies of Griffiths et al. [22] at 10 atm and of Silke et al. [23] at 10 atm.

Fig. 5. Ignition delay times for *n*-heptane/toluene mixtures (n-C_7H_{16}/$C_6H_5CH_3$/N_2/O_2, φ = 1; initial conditions: 299–334 K, 0.274–0.298 bar; compressed temperature: 710–773 K; compressed pressure: 9.79–10.4 bar; molar density: 180 mol/m^3).

Fig. 6. Ignition delay times for *n*-heptane/toluene mixtures: variation with toluene proportion at fixed core temperature (compressed temperature: 721–771 K; molar density: 180 mol/m^3).

the starting of the simulations was sufficient in most cases, as the majority of the pressure rise took place in that time frame during the compression stroke. In this way it could be observed that the constant volume assumption overestimates ignition delay times when they are shorter than 2 ms, due therefore to pre-end of compression reactions. In the current study, ignition delay times were in almost all cases longer than 2 ms and therefore this phenomenon could be considered negligible.

The maximum compressed temperatures experimentally possible were limited by the initial temperature and the actual RCM compression ratio. Using a nitrogen/oxygen mixture as air surrogate, a maximum initial temperature of 363 K and a compression ratio of 16.5, the calculated maximum compressed temperature is around 860 K for pure *n*-heptane, for example. In practice, the existence of the crevice volume (3.1% of the total combustion chamber volume) and the fact that the core volume expands during the compression stroke due to contraction of the boundary layer gas (cooled by the machine wall), make the compressed pressure lower than expected and therefore the maximum compressed temperature was actually slightly above 800 K.

For the compressed pressure range considered in this work, a significant part of the NTC region is in the temperature range which can be experimentally achieved. As it will be seen in Section 3.5, the validated single-zone model was used to numerically predict ignition delay times above this range.

3.2. Effect of the increase in toluene content

At a fixed molar density (pressure) and constant temperature at the end of compression, increasing the toluene concentration makes the mixture more resistant to auto-ignition.

In Fig. 5, the ignition delays at 180 mol/m^3 molar density (pressures in the 9.79–10.4 bar range) are reported for different compressed temperatures and toluene concentrations. At fixed compressed temperature, the trend of ignition delay time is shown in Fig. 6, always at 180 mol/m^3. It can be seen that the lower the temperature, the stronger the variation in ignition delay. The trend changes from being linear at the highest compressed temperature considered in the diagram (771 K) to be almost quadratic at the lowest (721 K).

Toluene and *n*-heptane have a very different reactivity so *n*-heptane is expected to dominate somehow the kinetics of the mixture. But it seems that a lower content of *n*-heptane determines a change in the ignition behavior of the mixture which is not directly proportional. Moreover, the presence of toluene appears to modify the ignition delay time trend in the NTC region with respect to pure
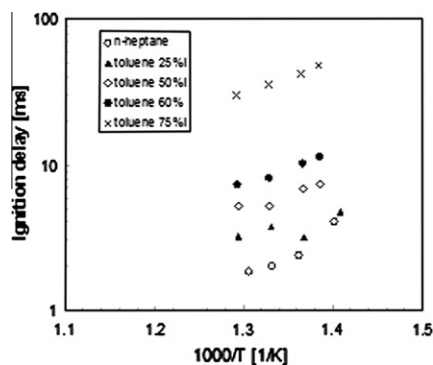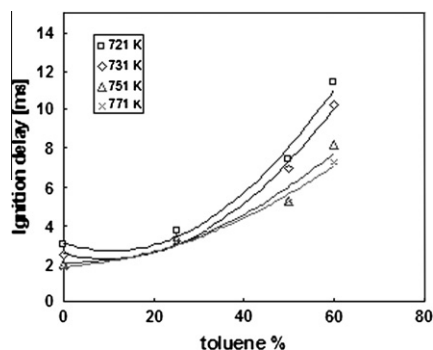
n-heptane. As it will be seen in Section 3.5, these considerations seem also confirmed by the single-zone model using the Lawrence Livermore mechanism for surrogate fuels.

At 75% concentration of toluene, the ignition delay times become too long (more than 20 ms) for the post-compression conditions to be considered constant. Data is in this case affected by higher uncertainty due to heat loss effects which become too relevant to be neglected, as it will also be shown in Section 3.5.

As mentioned, the repeatability of the data in the case of pure *n*-heptane was ±1.6%. Higher values were calculated for 50% (±3.4%) and 60% (±5.4%) toluene proportion in the mixture.

Pure toluene did not auto-ignite in any of the planned conditions. Golovitchev and Ogink [25] calculated that under stoichiometric conditions, at temperatures lower than 800 K and a pressure of 15 bar (conditions similar to those considered in this study) the auto-ignition of pure toluene is longer than 1 s. The explanation for the lack of ignition of pure toluene is therefore that both the temperature and the pressure after compression become so low that conditions are not anymore favorable to auto-ignition. Roubaud et al. [26] also showed with measurements in a RCM that toluene did not ignite at around 900 K compressed temperature and compressed pressures below 17 bar.

3.3. Effect of the molar density

Tests were repeated in the same conditions as before at 150 mol/m^3 molar density (compressed pressures in the 7.95–9.16 bar range). In general, all ignition delay times are longer either for the pure hydrocarbons or for the *n*-heptane/toluene mixtures (Fig. 7).
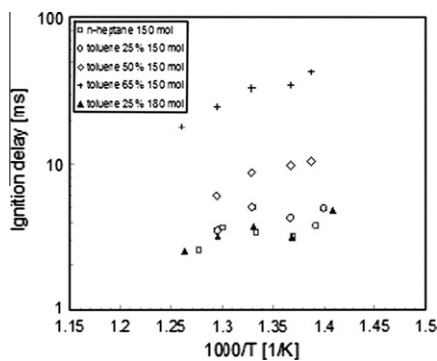
Fig. 7. Ignition delay times for *n*-heptane/toluene mixtures (n-C_7H_{16}/$C_6H_5CH_3$/N_2/O_2, φ = 1; initial conditions: 299–352 K, 0.226–0.272 bar; compressed temperature: 710–814 K; compressed pressure: 7.95–9.16 bar; molar density: 150 mol/m³).

In the case of pure *n*-heptane, it is evident from Fig. 7 that under these conditions the results superimpose to those measured for lower amount of toluene in the mixture (25%) at the higher molar density considered (180 mol/m³). Conditions are slightly different, as the compressed pressure changes. But this result suggests that for a low toluene content, chemistry kinetics seems to be governed by the most reactive component (*n*-heptane in this case) confirming the observations of Vanhove et al. [15] for example. However, for higher toluene content, ignition delays are longer than those expected for pure *n*-heptane under similar conditions of pressure and the smoother curve trend in the NTC region do not reflect *n*-heptane behavior at same pressure.

Further tests were conducted to assess the effect of varying the molar density and the results are shown in Fig. 8, where the compressed temperature was fixed at 751 K and the toluene concentrations considered were 0%, 25% and 50%. Again, increasing in toluene amount produces a quadratic trend for the ignition delay times. Higher molar density reduces the ignition delay times in a way that appears mostly proportional. It can be observed from Fig. 8 that until 180 mol/m³ the effect of adding toluene to the mixture appears to increase the effect of the molar density. On the contrary, the latter does not produce a relevant change in the ignition delay time of pure *n*-heptane at low temperature until it reaches the value of 220 mol/m³, for which the ignition delay time is around 2 ms. This is probably due to the fact that the NTC region tends to become smoother at higher pressure and as a result all ignition delay times are generally lower in the whole temperature range [17].

3.4. Variation of the first stage induction time

In Fig. 9 the first stage induction time t_1 is reported for different temperatures together with the total ignition delay time for com-
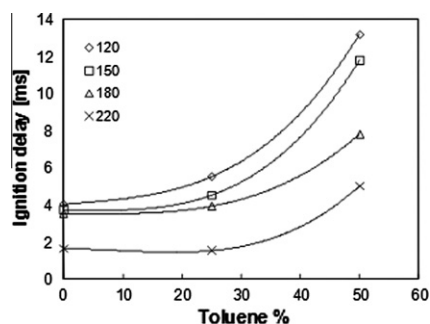

Fig. 8. Ignition delay times for *n*-heptane/toluene mixtures: variation with toluene proportion at variable molar density (compressed temperature: 751 K; molar densities in mol/m³).

parison. In all cases, the first stage ends when the gas temperature reaches 750–780 K. For pure *n*-heptane quite similar result was achieved by Curran et al. [17]. They conducted detailed kinetic studies observing that the first ignition is mostly associated with ketohydroperoxide species decomposition and the first stage ends when the temperature reaches a level where the equilibrium of the $R\cdot + O_2 = R\dot{O}_2$ reactions begin to shift toward dissociation at about 800–900 K and, as a result, the low-temperature reaction paths are shut-off.

Also, the duration of the first stage with respect to the overall ignition delay time becomes shorter when the toluene concentration is increased. This is due to the fact that toluene does not present any two-stage ignition behavior, so its presence has actually no effect on the first stage induction time but only on the overall ignition delay, while the first stage induction time is reduced due to the lower amount of *n*-heptane.

3.5. Comparison between experiments and modeling results

A single-zone modeling approach was used assuming therefore spatial uniformity of mixture and no temperature stratification across the chamber volume. The use of this approach implies that three major assumptions are made: (i) an adiabatic core exists and determines the ignition delay time, (ii) no significant reaction takes place before the end of compression and (iii) heat transfer is negligible during the ignition delay time.

Regarding the first assumption, it is established from previous studies that a constant temperature core establishes in a RCM after compression [27] and very recently, Mittal et al. [28] have demonstrated that despite of some quantitative discrepancy, the zero-dimensional modeling approach is deemed satisfactory from the viewpoint of the total ignition delay simulation.

In the case of this RCM, a CFD (Computational Fluid Dynamics) analysis was performed using the KIVA-3 code [29] under non-reactive conditions to evaluate thermal non-uniformities which could be most likely induced by the turbulent nature of the rapid compression. The model, the details of which are described in [30], showed that the temperature field inside the combustion chamber depends mainly on two parameters: the stroke and the crevice volume. In order to contain the vortex which interacts with the cold walls boundary layer, a large crevice volume is required. For shorter stroke the temperature distribution becomes more uniform keeping the same crevice volume, as a smaller vortex is generated. For the RCM used in this study, it is demonstrated that given the stroke and the compression time, a five time increase in the crevice volume would allow to contain the vortex entirely. As a result, the maximum temperature and pressure are slightly lower than those expected by theory. However, results also showed that there is a core containing approximately the 80% of the mass which is at the same temperature, while the 13% of the mass is at a lower temperature very close to the wall (where the boundary layer is mostly around 0.7 mm) and the remaining 7% is contained in the crevice. Therefore, it is considered that the core temperature is sufficiently representative of the thermal environment of the combustion chamber and determines the ignition delay time.

Reactivity during compression has been discussed in Section 3.1, concluding that for ignition delay times longer than 2 ms, it can most likely be neglected.

The effects of heat loss at the end of compression were also evaluated. In fact, the compressed pressure and temperature in the combustion chamber of a RCM tend to drop after the piston reaches the end of the compression stroke and during the ignition delay time, due to heat transfer effects. Using the pressure drop measured in the case of an unreactive mixture under equivalent conditions (see, for example, Fig. 3), it was possible to determine
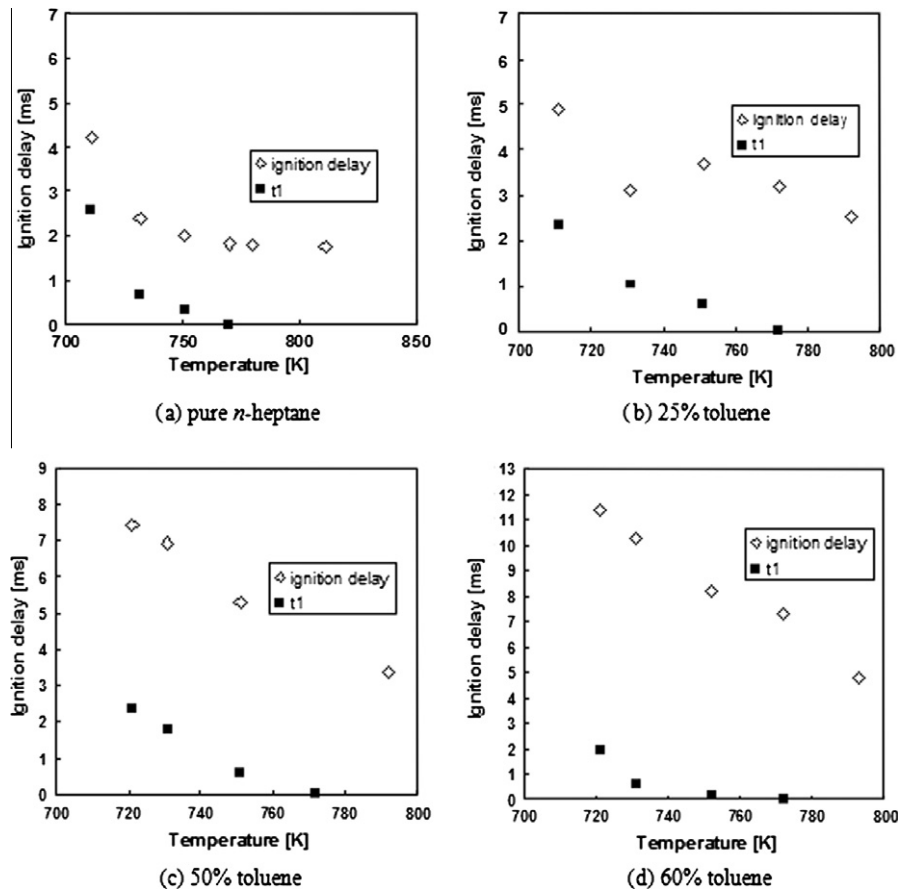
Fig. 9. First stage induction times for n-heptane/toluene mixtures (n-C$_7$H$_{16}$/C$_6$H$_5$CH$_3$/N$_2$/O$_2$, φ = 1; initial conditions: 299–334 K, 0.274–0.298 bar; compressed temperature: 710–773 K; compressed pressure: 9.79–10.4 bar; molar density: 180 mol/m^3).

the relative temperature drop and also the volume change due to it. Taking into consideration post-compression conditions calculated from the experimental estimation of the pressure drop, and comparing the results obtained in this case to the constant volume case, a good agreement was obtained when the ignition delay time did not exceed 20 ms. Above this value, the constant volume assumption underestimates the ignition delay time due to heat transfer effects.

Since the large majority of the data obtained in this work lies between 2 and 20 ms, simulations were carried out using a constant volume approach with the measured compressed pressure and the temperature calculated using Eq. (1) as the initial conditions.

To model n-heptane behavior, the detailed mechanism version 2 from Lawrence Livermore [17] was used. The model has been already validated successfully against experimental data and in this case also, the agreement between model and experimental results is fairly good, as shown in Fig. 10.

The Lawrence Livermore mechanism for surrogate fuels described in [18] was instead used for modeling n-heptane/toluene mixtures. It is a reaction mechanism developed for the following selected constituents: iso-octane, n-heptane, 1-pentene, toluene and methyl-cyclohexane, for which the model used for toluene oxidation is described in [19].

Figure 11 shows the comparison between numerical and experimental data for increasing amount of toluene in the mixture. In all cases, results agree fairly well. For the high toluene concentration (60%), the ignition delay times are numerically underestimated. This is still more evident for higher toluene proportions and, as said before, it is due to the fact that for long ignition delay times
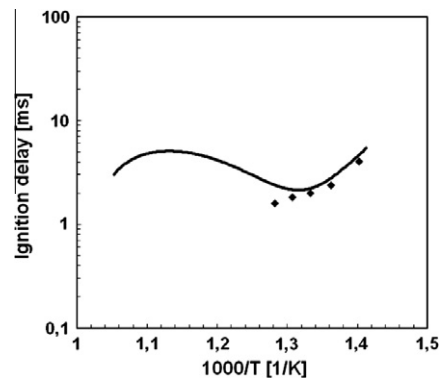

Fig. 10. Comparison between numerical and experimental ignition delay times for pure n-heptane (n-C$_7$H$_{16}$/N$_2$/O$_2$, φ = 1; core temperature: 711–956 K; compressed pressure: 8.11–11.7 bar; molar density: 180 mol/m^3).

(tenth of milliseconds) pressure and temperature values after the end of compression and during the ignition delay itself tend to decrease due to heat loss effects.

The overall behavior demonstrated in Fig. 6 for fixed temperatures and changing charge proportions is quite well confirmed numerically, as shown in Fig. 12. The curve trend tends to become linear as the temperature increases, while at low temperature it is rather a second-order curve.

In order to extend the temperature range and overcome the experimental limit values, simulations were carried out above the maximum test temperature. Also, since the experimental
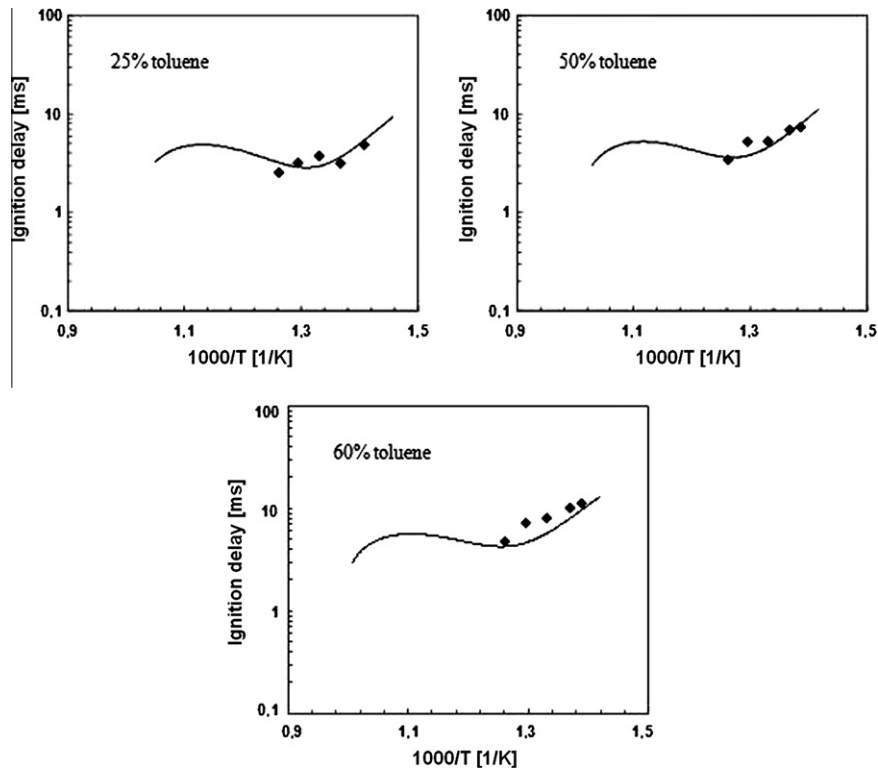
Fig. 11. Comparison between numerical and experimental ignition delay times for *n*-heptane/toluene mixtures (*n*-C$_7$H$_{16}$/ C$_6$H$_5$CH$_3$/N$_2$/O$_2$, φ = 1; molar density: 180 mol/m^3).
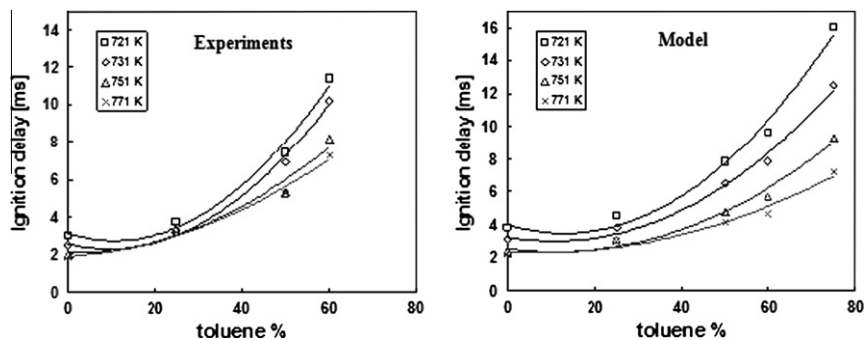

Fig. 12. Ignition delay times for *n*-heptane/toluene mixtures: variation with toluene proportion at fixed compressed temperature (compressed temperature: 721–771 K; molar density: 180 mol/m^3).
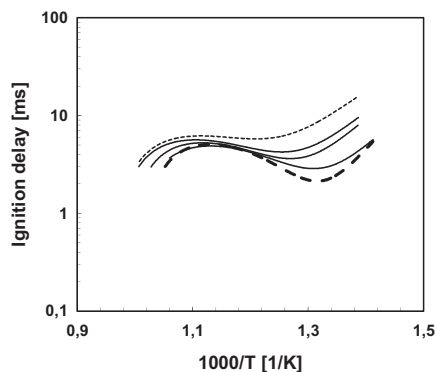

Fig. 13. Computed ignition delay times for *n*-heptane/toluene mixtures: pure *n*-heptane (dotted line), increasing concentration of toluene (25%, 50% and 60%, from lower to upper solid line) and mixture with 75% of toluene (dotted line).

values for the highest concentration of toluene (75%) were affected by heat losses, the validated model was used also to predict

ignition delay times without heat transfer effects. As it can be seen from Fig. 13, above 800 K calculations showed that the effect of adding toluene to the mixture is not marked. This result is in fair accordance with the findings of Hartmann et al. [7] and Vanohve et al. [15], that the most important differences between binary mixtures, and also therefore those obtained by changing the relative proportions of the single fuels, are in the NTC coefficient features which prove sensitive to the chemical structure of the fuel itself.

While the ignition delay values stay fairly constant the curve tends to become smoother, somewhat like the case of PRF fuels.

4. Conclusions

In this paper, ignition delay times of stoichiometric *n*-heptane/ toluene mixtures have been measured in a rapid compression machine for increasing concentration of toluene.

A new RCM was built and modified to realize controlled combustion under engine like conditions and the test conditions were

accurately set and monitored thus allowing an overall good test repeatability.

Results showed that the toluene/*n*-heptane mixture behavior is actually governed by the *n*-heptane chemistry for low toluene amount in the mixture, while for increased toluene concentration (50–70%) the effect of its presence becomes relevant at low temperatures. In particular, the ignition delay becomes longer and the data trend versus temperature smoother. The effect of toluene is also more marked for higher molar densities and tends to reduce the overall duration of the first stage induction time.

Numerical modeling of the experiments with a recent Lawrence Livermore chemical mechanism for surrogate fuels showed that the experimental results agree fairly well under the investigated conditions and allowed to extend the temperature range of investigation to intermediate temperatures and to prove that the NTC region is actually the most influenced by the presence of toluene, while above 800 K no additional proportion of toluene produces significant modifications to the ignition delay times, in good agreement with few other studies reported in the literature.

Acknowledgments

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