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Theoretical development of a new procedure to predict ignition delays under transient thermodynamic conditions and validation using a Rapid Compression-Expansion Machine

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Abstract

An experimental and theoretical study about the autoignition phenomenon has been performed in this article. A new procedure to predict ignition delays under transient (i. e. variable) thermodynamic conditions has been developed starting from the Müller's chemical kinetics mechanism. The results obtained have been compared with those obtained from the Livengood & Wu integral method, as well as with direct chemical kinetic simulations. All simulations have been performed with CHEMKIN, employing a detailed chemical kinetic mechanism. The simulations have been validated in the working range versus experimental results obtained from a Rapid Compression-Expansion Machine (RCEM). The study has been carried out with n-heptane as a diesel fuel surrogate. The experimental results show a good agreement with the direct chemical kinetic simulations. Besides, better predictions of the ignition

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delay have been obtained from the new procedure than the ones obtained from the classic Livengood & Wu expression.
Keywords: RCEM, ignition delay, autoignition modeling, CHEMKIN

1. Introduction, justification and objective

The potential of new combustion modes, such as Homogeneous Charge Compression Ignition (HCCI), Premixed Charge Compression Ignition (PCCI) and others based on Low Temperature Combustion (LTC), for the simultaneous reduction of soot and NO_x has been widely proved in previous studies [1, 2]. These modes show virtually zero emissions of soot and NO_x, but high emissions of unburned hydrocarbons (UHC) and carbon monoxide (CO), by avoiding the soot and NO_x formation peninsulas, which can be seen in equivalence ratio - temperature diagrams [3]. The lack of control over the autoignition process and over the heat release rate are the main challenge to implement these new combustion strategies in commercial reciprocating internal combustion engines [4].

The ignition control is much more difficult under these conditions because of the absence of a explicit ignition-controlling event, such as a spark or an injection process when very reactive conditions are reached in the combustion chamber (near top dead center). Thus, the ignition is controlled by the chemical kinetics of the charge [5], which can be modified by adjusting the engine operating parameters, such as the Exhaust Gas Recirculation (EGR) rate and the inlet temperature. Therefore, it is necessary to improve the capability of predicting the autoignition event to properly modify the operating conditions of the engine and control the heat release.

Although ignition can be reasonably predicted by using advanced CFD codes with detailed chemistry, the required computing time is too long to be solved in real time. In fact, simple numerical methods with very short computing time are the only ones that can be implemented in an engine control unit. Low computing time methods with enough accuracy to predict ignition delays allow improving the control of the engine, since decisions in real time can be taken.

The Livengood & Wu hypothesis [6], also known as the Livengood & Wu integral or, simply, the integral method, allows obtaining ignition delays of processes under transient conditions of temperature and pressure by using the ignition characteristics under constant thermodynamic conditions, which are much easier to obtain both experimentally and by simulation. The expression proposed by these authors is the following:

$$\int_0^{t_i} \frac{1}{\tau} dt = 1 \tag{1}$$

where t_i is the ignition delay of the process and τ is the ignition delay under constant conditions of pressure and temperature for the successive thermodynamic states.

The Livengood & Wu integral assumes that the oxidation process during the ignition delay can be described by a single zero-order global reaction and, therefore, the reaction rate does not depend on time under constant thermodynamic conditions. The negative temperature coefficient (NTC) behavior cannot be modeled under this hypothesis. Moreover, the authors assumed that the autoignition happens when a critical concentration of chain carriers is reached, being this critical concentration constant with pressure and

temperature for a given air-fuel mixture.

Whereas this integral has been traditionally enunciated as a method to predict the occurrence of knock in SI-engines [7], it has been extended to CI-engines as a way to predict the ignition delay of homogeneous air-fuel mixtures as the ones used in HCCI engines [8]. A new use of the Livengood & Wu integral is its implementation in an engine control unit. Several authors such as Ohyama [9], Rausen et al. [10], Choi et al. [11] and Hillion et al. [12] used the integral method to predict the start of combustion under HCCI conditions. This method can be combined with other simple models to obtain global parameters of the combustion process allowing the control of the engine in real time. The integral method has great interest for the prediction of autoignition due to its simplicity and low computational cost. This simplicity is just a consequence of the hypotheses assumed for its development.

The validity of the Livengood & Wu integral under certain conditions has been wondered by several authors [13]. When a two-stage ignition occurs, the integral method is not able to accurately predict any of both delays because it is based on a single global reaction mechanism that ignores the cool flames. Some of these authors, as Liang and Reitz [14] or Edenhofer et al. [15], show the need to create simple algorithms, but more sophisticated than the integral method, to characterize the autoignition at low temperatures without using any chemical kinetic mechanism. However, few alternatives to the Livengood & Wu integral can be found in the literature.

Hernandez et al. [16] analized the validity of the Livengood & Wu integral by simulations performed with CHEMKIN for several fuels and with various chemical kinetics mechanisms. They proved that the predictions of

the method are accurate if the fuel do not show a two-stage ignition pattern. These authors also proposed two different alternatives, one with better and another with worse results than the integral method. However, most of the alternatives proposed to improve the integral method are based on the method itself or assume the same hypotheses, which are too simple. Expressions based on more sophisticated autoignition models are needed in order to extend the range of validity of the methods.

In this study the validity of an alternative procedure to determine ignition delays under transient conditions is intended to be solved. The study has been done with n-heptane, the reactivity of which is very similar to diesel fuel. Despite the fact that more sophisticated surrogate fuels for diesel can be found in the literature, n-heptane was chosen because extended and fully validated chemical kinetic mechanisms are avaliable for it. Moreover, n-heptane is a primary reference fuel (PRF) employed to define the octane reference scale and it is widely used in the literature as a diesel fuel surrogate under engine conditions [17].

Ignition delays and critical concentrations for n-heptane will be obtained under different conditions of pressure, temperature, equivalence ratio and oxygen mass fraction from calculations performed with the software of chemical simulation CHEMKIN. This software, which is developed by Reaction Design (ANSYS), is consolidated in the world of engineering investigations and the chemical kinetics mechanisms of several hydrocarbons are perfectly defined to be used with it. Finally, the numerical results are validated experimentally using a Rapid Compression-Expansion Machine (RCEM).

The structure of the paper is as follows: first, the experimental facili-

ties involved in the study are presented. Then, a new expression to predict ignition delays under transient conditions is theoretically developed. Afterward, the methodological approach is described, including the experimental methods, the chemical kinetic simulations, the predictive methods and the parametric study performed. Next, the chemical kinetic mechanism is validated by comparison with experimental results. Thereafter, the predictive methods are validated with the chemical simulations, since they cannot be compared with the experiments due to they are referred to a different stage of the autoignition process. Finally, the conclusions of this study are shown.

2. Experimental facilities

A RCEM is an experimental facility widely used in autoignition studies due to its capability to reproduce engine conditions [18]. It allows a detailed analysis of a single engine cycle of an internal combustion engine, including not only the compression stroke, but also part of the expansion stroke [19]. The RCEM available at CMT-Motores Térmicos is a quasi-standard experimental facility purchased by this laboratory, the results of which can be compared directly with those from other RCEMs produced by the same company.

A scheme of the RCEM is shown in Fig. 1. The RCEM is pneumatically driven and its pistons are hydraulically coupled. As it can be seen, it can be divided in two different zones, the experimentation zone and the driving zone. The experimentation zone is composed by the combustion chamber. The driving zone is composed by four different pistons. Piston 1, which is called pushing piston, is pneumatically driven and hydraulically coupled to

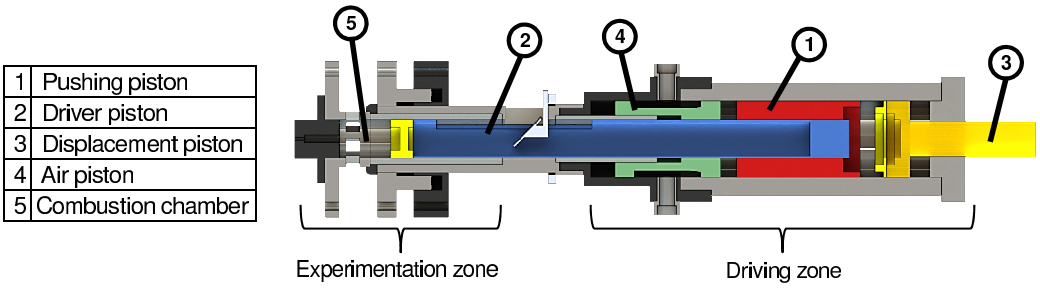

Figure 1: Rapid Compression Expansion Machine scheme.

piston 2, which is called driver piston and is directly connected with the combustion chamber. Piston 3 is hydraulically driven and it can be adjusted to select the compression stroke. Finally, piston 4 contains the compressed air that drives the machine. A detailled analysis about the operation principle of the RCEM can be found in Appendix A.

Bore	84	mm
Stroke	120 - 249	mm
Compression ratio	5 - 30	-
Maximum cylinder pressure	200	bar
Initial pressure	1 - 5	bar
Maximum heating temperature	393	K

Table 1: Technical characteristics of the RCEM.

The technical characteristics of the RCEM can be seen in Table 1. The pushing piston and the driver piston are instrumented with two AMO LMK102 incremental position sensors, which allow knowing the absolute position of each piston with a resolution of 0.01 mm and, therefore, the combustion

chamber volume. The combustion chamber is composed by three elements, the experimentation piston (mechanically connected to the driver piston), the liner and the cylinder head. The experimentation piston consists on a steel-made piston with 84 mm of bore and a quartz-made bowl with cylindrical shape, 46 mm of bore and 17 mm of depth, which allow the axial optical access. As the bowl is flat, the chamber can be recorded without any image distortion. Moreover, three quartz-made windows with rectangular shape are located in the liner to allow lateral optical access. Besides, the experimentation piston is provided with an electrical 80 W heater that allows varying the temperature of the bowl, and the cylinder head has four more electrical heaters of 180 W each, which are responsible for heating the cylinder walls. The walls temperature is measured by three thermoresistances PT1000 located in the cylinder head, in the piston and in the bowl. The intake and exhaust pipes are located in the liner of the combustion chamber. These ducts are designed to induce swirl motion to the gases admitted by the machine. The turbulence generated during the filling is enough to guarantee a homogeneous temperature in the chamber equal to the wall temperature, as demonstrated by some previous CFD calculations. The cylinder head is instrumented with a Kistler 6045A uncooled piezoelectric pressure sensor with a sensitivity of -45 pC/bar, which is coupled to a Kistler 5018 charge amplifier, and whereby the in-cylinder pressure is measured. Three Wika piezoresistive pressure sensors are avaliable to control the filling of the driving gas and of the combustion chamber with a resolution of 0.01 bar. The injection system is a common rail system composed by a BOSCH solenoid-commanded injector with a 7-hole nozzle and controlled by a EFS IPod power

driving module. This injection system has been characterized as explained in [20].

The acquisition system is a Yokogawa DL850V composed by one 10 MHz-12 bits module and five more 1 MHz-16 bits modules with two channels each. The acquisition frequency is fixed to 10 MHz, which is necessary to capture the pulses of the incremental position sensor. However, the in-cylinder pressure and the injection pressure are recorded at 1 MHz.

The RCEM is filled from an external tank that can be heated up to 520 K thanks to three electrical heaters of 1200 W each. The synthetic air is produced in the tank by a filling based on partial pressures where N_2, CO_2 and O_2 can be used. Besides, a syringe pump is available to allow the use of H_2O. A vacuum pump is used to ensure the no contamination of the mixture composition in this tank, nor in the RCEM charge. Finally, the synthetic air is analyzed by gas chromathography in a Rapid Refinery Gas Analyser from Bruker (450-GC) in order to know the exact composition and ensure the correct reproduction of the experiments in CHEMKIN.

3. Methodological approach

A parametric study was carried out in a RCEM in order to analyze the accuracy of a new method to predict ignition delays following this methodology: for a certain case, the evolutions of both the in-cylinder temperature and pressure are experimentally obtained under motoring conditions. Then, the ignition delay, τ, and the critical concentration, $[I]_{crit}$, are obtained for each thermodynamic state by simulating in a perfectly stirred reactor. The ignition delay under transient conditions is then predicted by using the new

procedure proposed in this paper and the Livengood & Wu integral method. Besides, the ignition delay under transient conditions is obtained experimentally and it is also calculated by simulating it in an internal combustion engine reactor (direct chemical simulation) solving the detailed chemical kinetics mechanism. Finally, the values obtained for the ignition delay from the direct chemical simulations are validated by comparing it with the experimental results, and the predicted ignition delays are compared directly with these simulations. The comparison between the experimental results and the predicted ignition delays is not possible since both are referred to diffrent stages of the autoignition process.

3.1. New predictive method

A new method to predict the ignition delay under transient thermodynamic conditions is obtained starting from the Müller's model [21]. This new procedure intends to improve the predictions obtained by the Livengood & Wu integral by avoiding some of its hypotheses.

The low-temperature chain branching mechanism is the dominant one in internal combustion engines (ICE) [22], since the evolution of the in-cylinder temperature covers a wide range below 1000 K during the ignition delay. Moreover, assuming that during the ignition delay the comsumption of oxygen is negligible, since the termination reactions are not very important, and as $[O_2] >> [F]$ and $[O_2] >> [I]$ (where F represents the fuel and I represents the typical intermediates of the low-temperature fuel decomposition), a constant oxygen concentration can be assumed. Considering an air-fuel mixture under constant conditions of temperature and pressure the following expression for the evolution of the concentration of chain carriers can be

obtained:

$$[I] = [I]_{crit}\frac{t}{\tau} \tag{2}$$

where $[I]_{crit}$ represents the critical concentration of chain carriers (maximum concentration of chain carriers, which defines the ignition time).

If a process under transient conditions of pressure and temperature is discretized as a series of thermodynamic states that remain constant for a time dt, the ignition time can be obtained as follows:

$$1 = \frac{1}{[I]_{crit,t_i}}\int_0^{t_i}\frac{[I]_{crit}}{\tau}dt \tag{3}$$

where t_i is the ignition delay of the process and τ and $[I]_{crit}$ are the ignition delay and the critical concentration of chain carriers under constant conditions of pressure and temperature for the successive thermodynamic states.

It should be noted that if the critical concentration of chain carriers is considered as a constant, Eq. 3 results in the Livengood & Wu integral.

The theoretical development performed to characterize the autoignition phenomenon is described in detail in Appendix B.

3.2. RCEM

The desired stroke of the machine is selected and the RCEM is heated up to the desired temperature. Two hours are needed in order to ensure a homogeneous wall temperature. The synthetic air-EGR mixture is prepared in the mixing tank. In this study, EGR was considered as the products of

a complete combustion reaction between the fuel and dry air in which the amount of oxygen is the one desired by the user, as it is explained in [23].

Vacuum is created in the combustion chamber before the filling. The fuel is injected into the combustion chamber at the start of the intake process to avoid problems of stratification or other inhomogeneities. The turbulence generated during the filling, as well as the long duration of the process (aproximately 40 s), are enough to guarantee a homogeneous environment in the chamber when the compression stroke starts.

The number of repetitions for each case to obtain a representative value of the ignition delay have been selected by the following criterion: the semi-amplitude of the confidence interval for the ignition delay with a level of confidence of 95% may be higher than the 1% of the ignition delay average. Thanks to the high repeatability of the machinen only five measurements are needed for each case.

In this work the autoignition of the mixture is considered to be produced when the time derivative of the pressure signal (which will be referred as pressure rise rate or, simply, pressure rise further on) reaches a maximum. Thus, the ignition delay in the experimental facility is defined as the time between the start of the rapid compression process and the instant in which the maximum pressure rise is obtained, as can be seen in Fig. 2.

Finally, the temperature profile is calculated for each experiment by applying the energy equation, since the pressure profile and the position of the piston are known. The heat losses are characterized by a model based on the Woschni correlation [24]. The calculation includes two additional models for deformations and leaks, both of them explained in [25, 26].

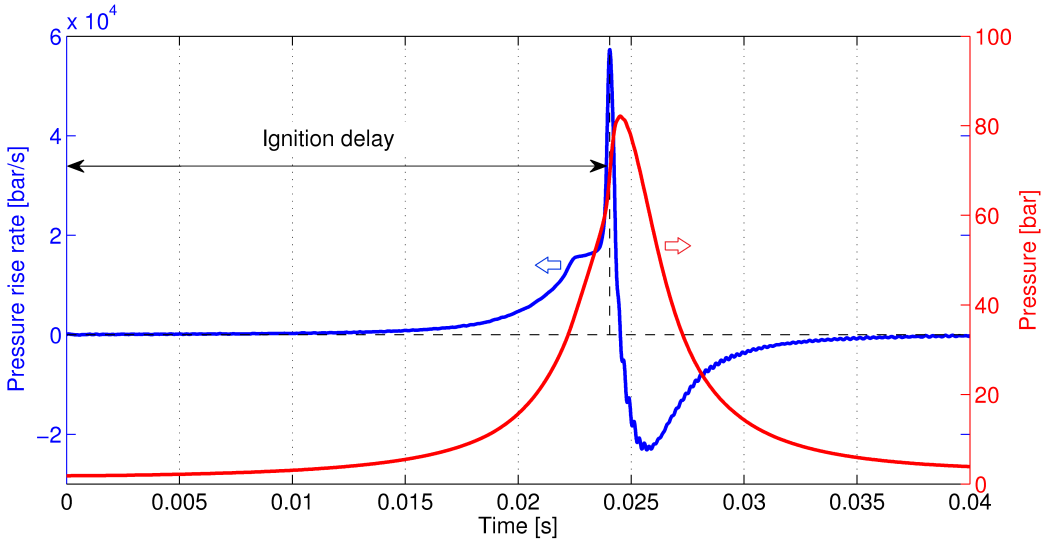

Figure 2: Ignition delay definition. The autoignition of the mixture is considered to be produced when the maximum pressure rise occurs.

3.3. CHEMKIN and chemical kinetic mechanisms

As mentioned before, CHEMKIN is the software used to obtain the different ignition delays and critical concentrations. The version used is CHEMKIN-PRO. Curran's kinetic mechanism is used for n-heptane [27]. This mechanism consists of 660 species and 2735 reactions and its validity has been checked in several articles [17, 28] by comparison with experimental results.

The model used to obtain ignition delays under constant conditions and critical concentrations is a homogeneous closed reactor (perfectly stirred reactor, PSR), which works with constant pressure and uses the energy equation to solve the temperature temporal evolution. This model is the most appropriate to obtain ignition delays under certain pressure and temperature

conditions [29]. Besides, working with constant pressure corrects, somewhat, the over-prediction of the pressure which is typical of this kind of reactor [30]. The autoignition of the mixture is considered to be produced when the concentration of CH_2O reaches a maximum, since formaldehyde is widely recognized as an autoignition tracer [31]. This means that when the critical concentration of formaldehyde is reached, the time corresponding to this instant will be considered as the ignition delay. This criterion is the most appropriate for the predictive methods, since they are based on it. Thus, a criterion based on a critical concentration of chain carriers has to be used in order to be consistent with the theoretical aspects of the predictive methods. Any active radical with chain behavior can be taken as chain carrier, e. g. HO_2 or H_2O_2.

The model used to obtain ignition delays under transient conditions is a reciprocating internal combustion engine operating with homogeneous charge (IC-engine, closed 0-D reactors from CHEMKIN). The volume profile as well as the heat loss profile are imposed in order to reproduce the RCEM conditions. The piston starts at bottom dead center (BDC) and a complete cycle of the RCEM is simulated. Two different criteria have be used to determine the ignition delay in this model. On the one hand, the autoignition is considered to be produced when the time derivative of the pressure signal reaches a maximum. This is the same criterion than the used in the experiments and, therefore, it allows comparing the simulated results directly with the experimental ones. On the other hand, the autoignition of the mixture is considered to be produced when the concentration of CH_2O reaches a maximum. Both criteria are used in the IC-engine model (direct chemical

simulations) in order to compare the simulation with both the experimental and the predicted (Livengood & Wu and the new integral proposed) results.

It should be noted that whereas the experimental ignition delays are based on a maximum pressure rise, ignition delays predicted by the numerical methods are based on a maximum concentration of chain carriers (by definition of the methods). Thus, ignition delays determined by both criteria can differ because they are referred to different events of the autoignition process.

Finally, the ignition delay, τ, and the critical concentration, $[I]_{crit}$, is obtained for each thermodynamic state with a Δt of $5 \cdot 10^{-5} s$. The criterion to select the working time step consists in choosing the one which relative deviation in ignition delay is, at most, two times the deviation caused by a time step. This means that the difference between the predicted and the simulated ignition delay should be lower than two time steps. This value of the time step is chosen because it represents an equilibrium between appropriate prediction accuracy and reasonable calculation time. Besides, the maximum waiting time for the autoignition of the mixture has been set to 3 s, which provides enough accuracy in the calculations.

3.4. Parametric study performed

The performed experimental study was as follows:

- Fuel: n-heptane.
- Initial temperature (T_0): 373 K and 383 K.
- Initial pressure (P_0): 0.134 MPa and 0.178 MPa.

- Compression stroke: 200 mm and 249 mm.
- Compression ratio (CR): 13, 15 and 17.
- Engine speed: 1000 rpm.
- Oxygen mass fraction (Y_{O_2}): 0.23, 0.16, 0.13 and 0.10.
- Equivalence ratio (Fr): from 0.27 to 1.45 depending on the oxygen mass fraction.

The maximum equivalence ratio is limited by the working oxygen mass fraction in order to avoid extremely violent combustions. The performed parametric study can be seen in Table 2.

Y_{O_2}	Fr	Y_{O_2}	Fr	Y_{O_2}	Fr	Y_{O_2}	Fr
0.23	0.27	0.16	0.41	0.13	0.50	0.10	0.88
	0.34		0.50		0.60		1
	0.41		0.83		0.70		1.20
	0.50		0.88		0.88		1.45
	0.55						

Table 2: Parametric study performed.

Although equivalence ratios of 1.5 can seem uninteresting for practical applications, it must be taken into account that autoignition occurs under rich local equivalence ratios in direct-injection engines [32]. This concept is known as *most reactive mixture fraction* and it arises due to the balance of reactivities between the fuel-air ratio distribution and the temperature distribution.

4. Results and discussion

4.1. Comparison between experimental and direct chemical simulation results (CHEMKIN)

Ignition delays obtained solving the n-heptane detailed chemical kinetic mechanism are compared with the experimental results as a method to validate the mechanism in the desired range.

As can be seen in Fig. 3 and Fig. 4, simulations reproduce with high accuracy not only the trends, but also the values of the experimental results. Ignition delay is defined in both cases as the time between the start of the compression process and the instant in which the maximum pressure rise occurs. As it is expected, the lower the oxygen mass fraction, the higher the ignition delay (Fig. 3). Besides, Fig. 3 also shows that ignition delays decrease when the compression ratio is increased, since the higher the compression ratio the higher the reached temperatures. Finally, because the reaction paths at low temperatures are dependant on radical species formed directly from the fuel, the richer mixtures have lower ignition delays than the leaner ones (Fig. 4).

The percentage deviation in ignition delay, ϵ, was calculated in order to compare more easily experimental and simulation results. This deviation is defined as follows:

$$\epsilon = \frac{t_{i,ICE} - t_{i,RCEM}}{t_{i,RCEM}} 100 \tag{4}$$

where t_i represents the time of ignition (ignition delay under transient conditions). The subscript ICE represents a data obtained from a chemical

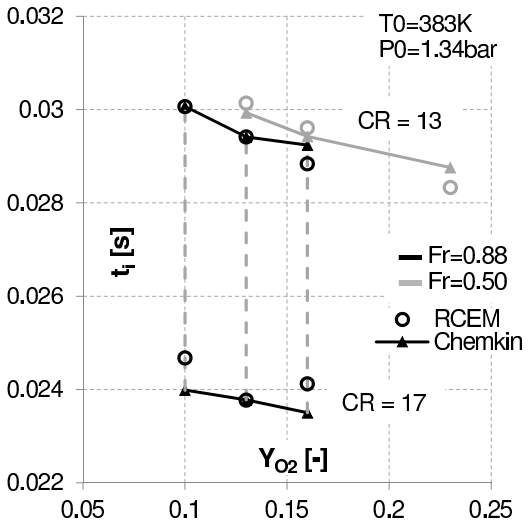

Figure 3: Ignition delay versus oxygen mass fraction at different equivalence ratios and compression ratios.

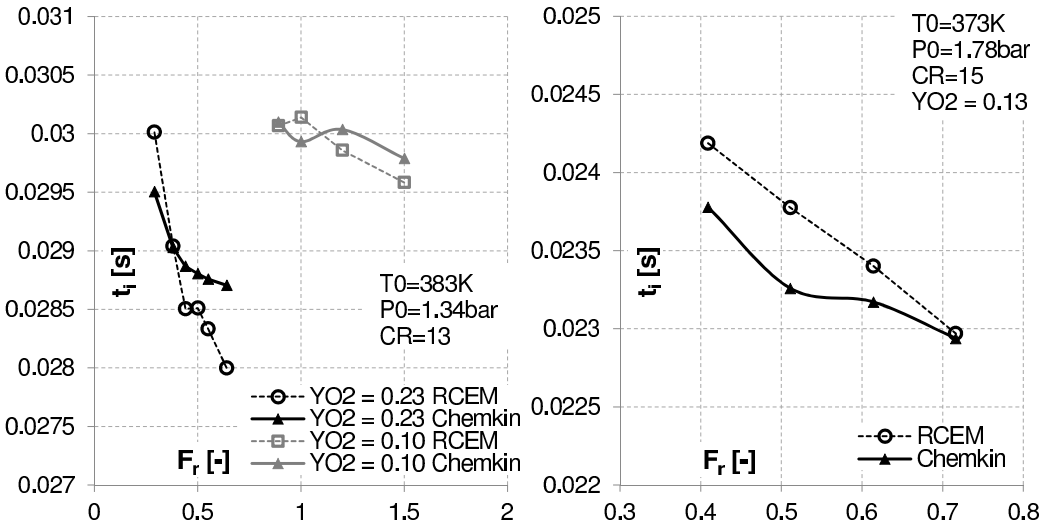

Figure 4: Ignition delay versus equivalence ratio at different oxygen mass fractions and compression ratios. Left.- Compression ratio = 13. Right.- Compression ratio = 15.

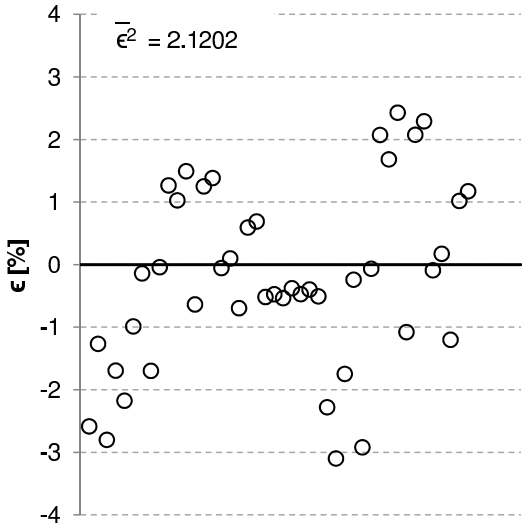

Figure 5: Percentage deviation in ignition delay. The mean square deviation, $\bar{\epsilon^2}$, shows a good agreement between both experimental and simulated results.

simulation with CHEMKIN using a closed 0-D IC-engine reactor. Finally, the subscript $RCEM$ represents a data obtained experimentally from the RCEM.

The ignition delay deviation is shown in Fig. 5 for all cases. The mean square deviation, $\bar{\epsilon^2}$, has been calculated and its value can be seen in the figure.

The results show that simulations are able to reproduce the experimental ignition delays with quite good accuracy. In fact, the confidence interval for the mean square deviation, $\bar{\epsilon^2}$, with a confidence level of 95% is equal to $[1.365, 2.875]$. Ignition delay deviations are caused partly by the chemical kinetic mechanism used and partly by the uncertainties in the calculation of the effective volume and the heat losses of the RCEM.

4.2. Comparison between the predictive methods and the direct chemical simulation

Ignition delays under transient thermodynamic conditions are obtained with the new proposed integral (Eq (3)), with the RCCC-method [33] and with the Livengood & Wu integral method. The resulting predictions from both methods are compared with the ignition delays obtained by the direct chemical kinetic simulation.

It should be noted that whereas the experimental ignition delays are based on a maximum pressure rise, $t_{i,dP2}$ (presented in Fig. 6, together with other important events of the ignition process), which represents the high temperature chemical stage, ignition delays predicted by the numerical methods are based on a maximum concentration of chain carriers, t_{i,CH_2O} (by definition of the methods). Thus, ignition delays determined by both criteria can differ because they are referred to different events of the autoignition process as can be seen in Fig. 6, where the normalized time derivative of pressure and the normalized mole fraction of CH_2O are plotted for a certain case. The most important events of a typical two-stage ignition are represented in the figure, as well as various possible definitions for the ignition delay.

As can be seen in Fig. 7 and Fig. 8, ignition delays can be predicted with high accuracy by the integral methods. Ignition delay is defined for all simulations as the time between the start of the rapid compression process and the instant in which the maximum concentration of CH_2O is reached, t_{i,CH_2O}. Thus, the trends of the ignition delay change regarding the experimental results, since the criterion to define this parameter is different.

The formation of CH_2O is controlled by the decomposition of the fuel to

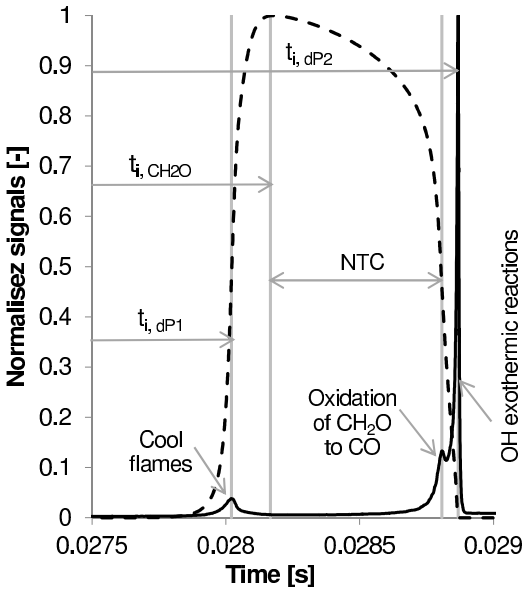

Figure 6: Important events of the ignition process and possible definitions of the ignition delay. The normalized time derivative of pressure (solid line) and the normalized mole fraction of CH_2O (dashed line) are plotted for a compression ratio of 13 and an initial temperature, pressure, equivalence ratio and oxygen mass fraction of 383 K, 1.34 bar, 0.50 and 0.23, respectively.

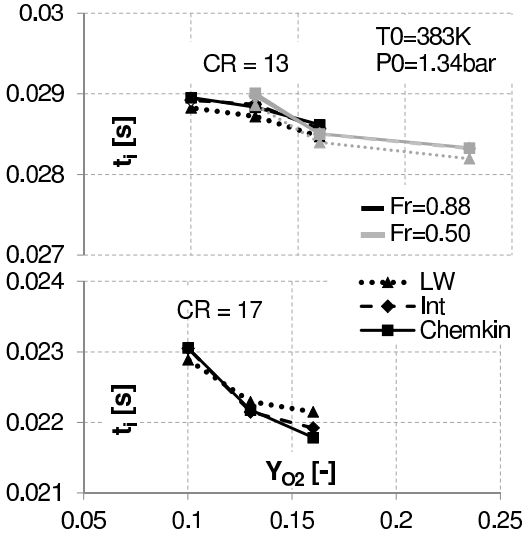

Figure 7: Ignition delay versus oxygen mass fraction at different equivalence ratios and compression ratios.

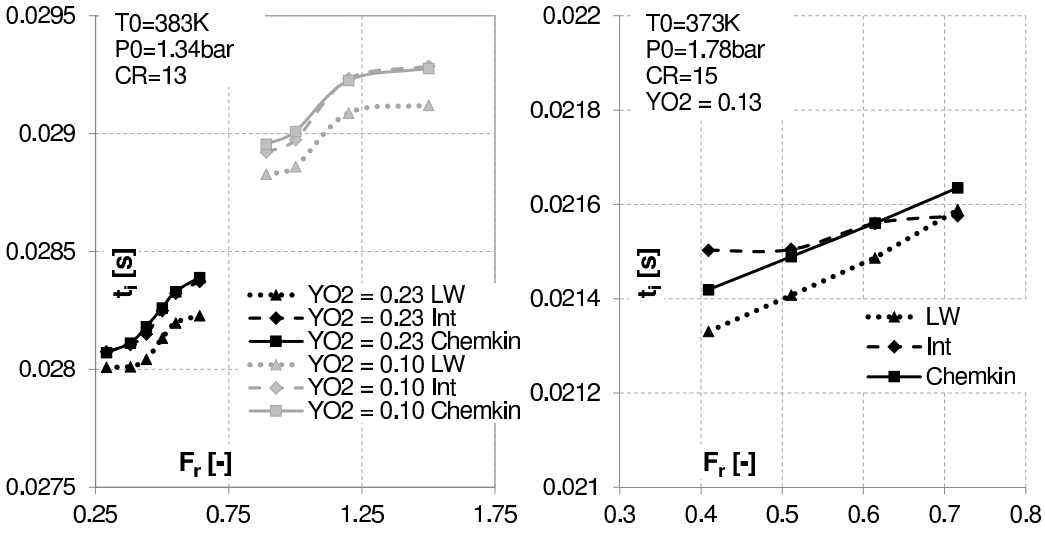

Figure 8: Ignition delay versus equivalence ratio at different oxygen mass fractions and compression ratios. Left.- Compression ratio = 13. Right.- Compression ratio = 15.

short chain hydrocarbons thanks to its combination with active radicals such as HO_2. These slight exothermic reactions cause the appearance of the cool flames. Besides, the maximum heat release of the cool flames coincides with the maximum generation rate of CH_2O.

Reactions that control the cool flames basically depend on temperature. Moreover, the higher the equivalence ratio or the lower the oxygen mass fraction, the higher the heat capacity of the gas mixture. Since a higher heat capacity means higher heat sink effect, the mixture with a higher heat capacity also undergoes (obviating chemical aspects) a slower temperature increase. Thus, a richer or a more diluted mixture leads to later cool flames and longer ignition delays $t_{i,dP1}$ and t_{i,CH_2O} (Fig. 7 and Fig. 8).

In the low-temperature chain branching mechanism, the decomposition of CH_2O is controlled by the decomposition of H_2O_2, which generates the necessary OH radicals for oxidizing the formaldehyde to CO. The decomposition of CH_2O define the transition between the NTC regime and the high temperature branch. In fact, the disappearance rate of CH_2O depends on the relevance of the NTC behavior. Besides, the NTC regime becomes less pronounced if the pressure, the oxygen proportion or the equivalence ratio are increased. Thus, a richer mixture or a less diluted mixture lead to a faster decomposition of CH_2O and a shorter ignition delay $t_{i,dP2}$, as shown in section 4.1.

It can be seen that the Livengood & Wu integral method underpredicts the ignition delay with respect to the direct chemical simulation. This integral method assumes that the critical concentration is constant and equal to the critical concentration at the ignition time. Since the critical concentra-

tion increases during the compression stroke of an engine, assuming it as a constant leads to shorter ignition delays (the integral increases more rapidly).

The percentage deviation in ignition delay (or prediction deviation), ε, was calculated in order to compare more easily the prediction capability of the methods. This deviation is defined as follows:

$$\varepsilon = \frac{t_{i,x} - t_{i,ICE}}{t_{i,ICE}} 100 \tag{5}$$

where t_i represents the time of ignition (ignition delay under transient conditions). The subscript ICE represents a data obtained from a chemical simulation with CHEMKIN using a closed 0-D IC-engine reactor. Finally, the subscript x representns one of the predictive methods. The data obtained from the Livengood & Wu numerical method are denoted by LW whereas the predictions obtained from the new proposed integral (Eq (3)) are denoted by Int.

The prediction deviation is shown in Fig. 9 in case of using both integral methods and for all cases. The results show that the predictive methods are able to reproduce the simulated ignition delays with high accuracy. The mean square deviation, $\bar{\varepsilon^2}$, has been calculated for the two integral methods and its value can be seen in the figure. In fact, the confidence interval for the mean square deviation, $\bar{\varepsilon^2}$, with a confidence level of 95% is equal to $[0.152, 1.238]$ for the Livengood & Wu integral method and to $[0, 0.178]$ for the new integral proposed.

The results of the RCCC-method will only be shown in the form of confidence intervals. They will not be presented in the different graphs for clarity reason, since they are very close to those of the integral method proposed

here, and the different lines would not be distinguishable. The confidence interval for the mean square deviation, $\bar{\varepsilon^2}$, with a confidence level of 95% is equal to $[0, 0.093]$ for the RCCC-method, which is very similar to the one obtained for the new integral proposed.

The new integral proposed by the authors in this paper takes into account the dependence of the critical concentration with pressure and temperature, discarding one of the hypotheses of the Livengood & Wu integral and leading to more accurate predictions. However, this new integral method also assumes that the autoignition process can be described by a zero-order global reaction. This is the main difference with the RCCC-method, in which both hypotheses are discarded at the expense of obtaining a numerical expression much more complex than the integral methods.

The similitude in predicted ignition delays between both methods implies that the generation rate of chain carriers during the ignition delay can be assumed as a zero-order reaction. Moreover, it also implies that the improvement in the predictions, comparing with the Livengood & Wu integral, are caused almost in exclusive by the assumption of variable critical concentration.

There are some points for which the Livengood & Wu integral method overpredicts the ignition delay and presents the highest prediction deviations. In general, these points correspond also to the highest prediction deviations for the new proposed integral method. In them, ignition occurs just in the transition between the high and the low temperature mechanism. Fig. 10 shows the τ function for one of these cases. Despite the fact that the calculations were carried out with a detailed chemical kinetic mechanism, the

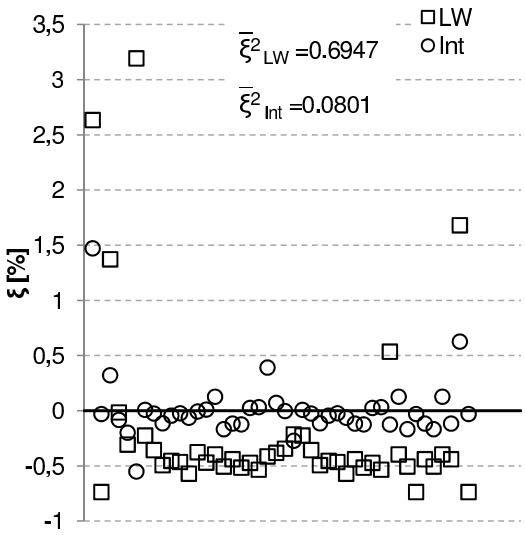

Figure 9: Percentage deviation in ignition delay. The mean square deviation, $\overline{\varepsilon^2}$, shows a good agreement between both predicted and simulated results.

transition between the low temperature regime and the high temperature regime can result in discontinuities in τ. In these cases, discontinuities appear in the interval in which the largest contribution to the integral is made, leading to higher prediction deviations. Moreover, these operating points also correspond to the highest deviations between the chemical simulations and the experimental results. According to the new integral method, this effect is not as dramatic as for the Livengood & Wu integral method since the variation of the critical concentration of chain carriers compensates the effect of the discontinuities in τ.

The Livengood & Wu method is also able to predict with quite accuracy ignition delays under transient conditions because the largest contribution to the integral is made in a narrow time range. This is the reason why the

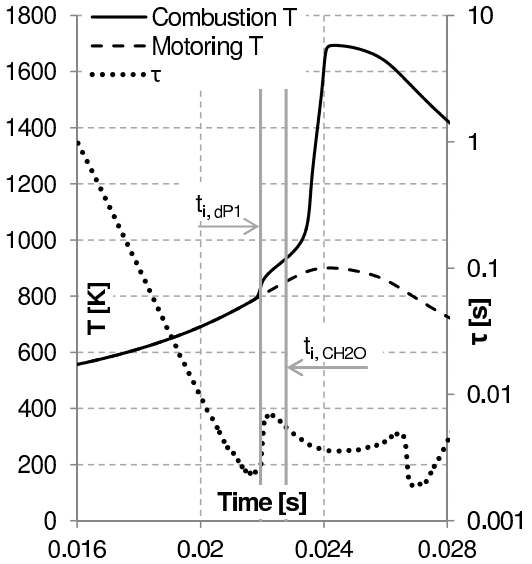

Figure 10: Combustion (solid line) and motoring (dashed line) temperatures and τ function (dotted line). The simulation has a compression ratio of 17 and an initial temperature, pressure, fuel/air equivalence ratio and oxygen mass fraction of 383 K, 1.34 bar, 0.60 and 0.13, respectively.

assumption of constant critical concentration does not invalidate the method at all. Moreover, it can be checked that the critical concentration of chain carriers decreases with temperature whereas it increases with pressure. The relationship between pressure and temperature in an engine (simultaneous increase or decrease of both) causes that the net variation of the critical concentration is soft enough not to invalidate the Livengood & Wu integral method, being the pressure effect dominant (the critical concentration of chain carriers increases during the compression stroke and decreases during the expansion stroke).

Finally, it should be noted that if the fuel does not present two-stage ignition or if it presents a very smooth (or inexistent) NTC zone, the different ignition delays are virtually the same and the predictive methods can be compared directly with experimental results.

5. Conclusions

In this work a new method to predict ignition delays under transient conditions from those obtained under constant conditions is developed. The method is theoretically deducted from the Müller's mechanism, but it can be obtained from other autoignition models following the same methodology than the described in this paper, and it shows better results than the Livengood & Wu integral method.

A detailed chemical kinetic mechanism has been validated in the working range versus experimental results obtained from a RCEM. Then, the new predictive method has been compared with the chemical simulations and with the Livengood & Wu integral.

The following conclusions can be deducted from this study:

- The predictive methods presented in this paper are based on the premise that autoignition occurs when the critical concentration of chain carriers is reached. Therefore, the predicted ignition delays will be referred to this criterion and the information used to obtain the predictions may be also referred to this criterion.

- Care should be taken in comparing the predictions obtained from the Livengood & Wu integral (and from the new integral method proposed) with experimental results, since both ignition delays could be referred to different stages of the combustion process.

- If the fuel does not present a two-stage combustion or if the NTC zone is very soft, all criteria to define the ignition delay are virtually the same and they can be compared with each other.

- If the autoignition occurs in the transition between the low and high temperature chain branching mechanism, the chemical kinetic simulation has shown the worst reproduction of the experimental results and the integral methods have also shown the worst predictions. But, in general, the detailed chemical kinetic mechanism is able to reproduce the experimental data with high accuracy, as well as the predictive methods are able to reproduce the chemical simulations.

- The trends of the ignition delay are different depending on the criterion used to define it. Cool flames are strongly dependant on temperature. Thus, the higher the equivalence ratio or the lower the compression

ratio and the oxygen content (higher EGR rate), the later the appearance of the cool flames. Besides, the low-temperature chain branching mechanism depends on radical species formed directly from the fuel. Therefore, the higher the equivalence ratio, the earlier the maximum pressure rise.

- A new method should be developed to predict ignition delays under other criteria. Using the Livengood & Wu method to predict ignition delays according to maximum pressure rise is not appropriate and can lead to bad predictions.

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Notation

a_{st}	Oxygen-to-fuel ratio under stoichiometric conditions
BDC	Bottom Dead Center
CFD	Computational Fluid Dynamics
CI	Compression Ignition
CR	Compression Ratio
$crit$	Referred to the critical concentration
EGR	Exhaust Gas Recirculation
Fr	Working equivalence ratio
$HCCI$	Homogeneous Charge Compression Ignition
ICE	Referred to data obtained from CHEMKIN using the internal combustion engine reactor

Int	Referred to data obtained from the new integral proposed in this paper
k_i	Specific reaction rate of reaction i
LW	Referred to data obtained from the Livengood & Wu integral method
LTC	Low Temperature Combustion
NTC	Negative Temperature Coefficient
P_0	Initial pressure
$PCCI$	Premixed Charge Compression Ignition
PRF	Primary Reference Fuels
PSR	Perfectly Stirred Reactor
SI	Spark Ignition
T_0	Initial temperature
TDC	Top Dead Center
t_i	Ignition delay under transient conditions
t_{i,CH_2O}	Ignition delay referred to the critical concentration of CH_2O
$t_{i,dP1}$	Ignition delay referred to the maximum pressure rise of the cool flames
$t_{i,dP2}$	Ignition delay referred to the maximum pressure rise
UHC	Unburned hydrocarbons
Y_{O2}	Oxygen mass fraction
ϵ	Percentage deviation in ignition delay between experimental and simulation results

	$\bar{\epsilon^2}$	Mean square deviation between experimental and simulation results
	ε	Ignition delay prediction deviation
	$\bar{\varepsilon^2}$	Mean square deviation of the predictive methods
	τ	Ignition delay under constant conditions of pressure and temperature

Appendix A. Description and validation of the RCEM

Rapid Compression Expansion Machines have the capability of replicating reasonably well the combustion process of reciprocating engines with fully controlled initial and boundary conditions and avoiding the complexities associated to engines [34].

The RCEM available at CMT-Motores Térmicos has some important features to perform various diagnostic studies under a wide range of experimental conditions: different compression ratios can be reached by varying the stroke and the clearance volume, axial and lateral optical accesses are available [35, 36] and the compression velocity can be varied in order to simulate different engine speeds. In a RCEM the expansion stroke of the piston can be also analyzed and most of the engine parameters can be calculated under real conditions, such as the heat release rate or the combustion efficiency. In this facility both homogeneous and heterogeneous (direct injection) mixtures can be tested, as well as new combustion modes such as the dual fuel technology [37, 38] or LTC [39]. Of course, the RCEM allows the study of autoignition of fuel-air mixtures under easily controlled and reproducible conditions in a

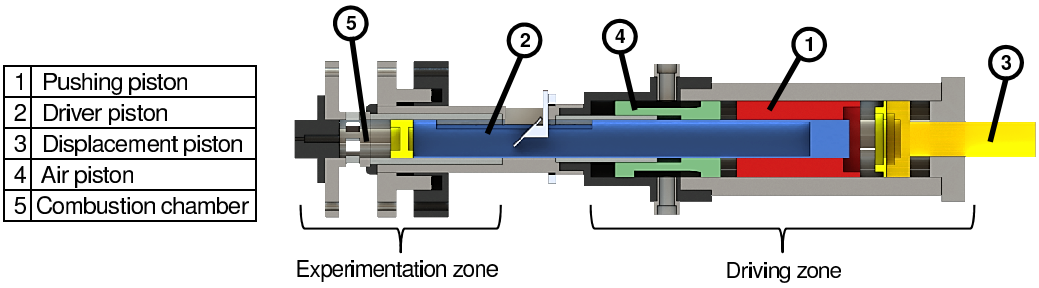

Figure A.11: Rapid Compression Expansion Machine scheme.

cleaner environment than in a traditional engine, without residual gases and with full control over the initial pressure and temperature, the volume and the trapped mass.

A scheme of the RCEM is shown in Fig. A.11. The RCEM is pneumatically driven and its pistons are hydraulically coupled. As it can be seen, it can be divided in two different zones, the experimentation zone and the driving zone. The experimentation zone is composed by the combustion chamber. The driving zone is composed by four different pistons. Piston 1, which is called pushing piston, is pneumatically driven and hydraulically coupled to piston 2, which is called driver piston and is directly connected with the combustion chamber. Piston 3 is hydraulically driven and it can be adjusted to select the compression stroke. Finally, piston 4 contains the compressed air that drives the machine.

First, the oil is pressurized by the driving gas, which is compressed air. The driver piston does not move because it is perfectly coupled to piston 3, avoiding contact between the pushing oil and the piston base. Then, pressure is established behind the driver piston by a bypass valve and it

starts to advance at low velocity in a process called slow compression. It should be noted that when the driver piston advances, the pushing piston must advance also in the opposite direction, keeping constant the volume of oil. In fact, both pistons are inertially balanced, leading to a process free of vibrations.

When the driver piston leaves the piston 3, it is suddenly accelerated and the rapid compression stroke starts. The driving air suffers an expansion process whereby its pressure and, consequently, the pushing oil pressure, are reduced. The piston stops when the pressure in the combustion chamber is high enough to compensate the pushing force and the inertia, defining TDC. Thereby, TDC is highly dependent on the operation conditions of the RCEM, which is completely different for engines. Moreover, there is a certain maximum driving pressure for each operating condition to avoid collision of the piston with the cylinder head, since in the RCEM there is not any mechanism as the rod-crank mechanism that fixes the maximum position of the piston. Once the piston reaches TDC, the pressure in the combustion chamber is higher than the pushing oil pressure and the expansion stroke starts. More details on the operation principle of the RCEM can be found in [40, 41].

This RCEM has been validated by comparison with the machine available at ETH-Zurich, using the results showed in [36]. In that study, Mitakos et al. studied the ignition delays referred to cool flames and referred to the high temperature heat release of different fuels under various conditions of temperature, equivalence ratio and EGR rate. The operating points of n-heptane have been reproduced with the RCEM available at CMT-Motores

YO2	0.23		0.17		0.11	
Fr	0.42	0.3	0.56	0.4	0.86	0.6

Table A.3: Operating points of Mitakos et al. reproduced in the RCEM of CMT-Motores Térmicos

Térmicos and the results have been compared with the published ones.

The corresponding operating points can be seen in Table A.3, with an initial temperature, pressure and stroke of 383 K, 1.34 bar and 249 mm.

In that case, the criterion to define the start of ignition delay is the time at which the piston is at 200 mm. Besides, the start of ignition is considered as the time at which the line that joins the 8% and the 25% of the maximum heat release rate crosses by zero. Finally, the start of ignition referred to the cool flames is considered as the time at which the line that joins the peak and the 50% of the maximum heat release rate of cool flames crosses by zero.

It should be taken into account that the RCEM available at ETH is the most similar to the one available at CMT. However, there are some constructive differences between machines that cause a difference in the combustion chamber volume and in some boundary conditions. Therefore, it is not possible to ensure the same pressure and temperature evolutions by reproducing the same initial conditions and command settings.

In Fig. A.12 the correlation between both RCEMs can be analyzed. The ignition delays obtained with the RCEM of CMT are plotted versus the ignition delays obtained at ETH. The line y = x, which represents a perfect match between values, has also been plotted in the figure. Finally, the coefficient of correlation R2 has been calculated between both machines and

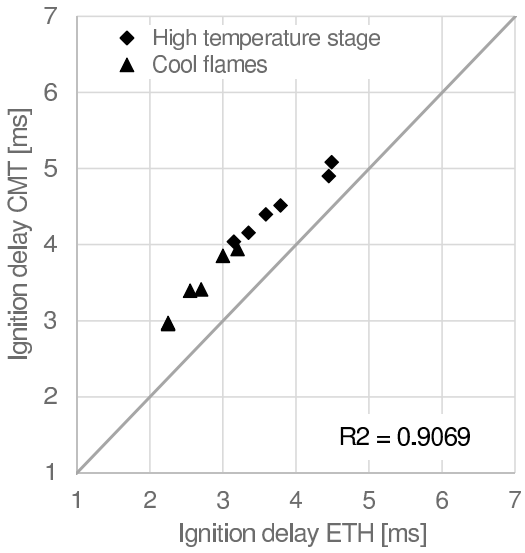

Figure A.12: Ignition delays obtained at CMT versus the corresponding values obtained at ETH. The coefficient of correlation between both machines has been calculated and its value is represented in the figure.

it is equal to 0.9069. As can be seen, the trends are perfectly reproduced at CMT. However, there is an offset between both results that is caused by the differences in dead volume and heat losses between machines. The fact that the differences in ignition delays are constant for all the experiments, which can be explained by constructive differences between RCEMs, allows the validation of the machine available at CMT-Motores Térmicos.

Appendix B. Theoretical development of a new expression to predict ignition delays

The theoretical development performed to characterize the autoignition phenomenon is described in detail in this section. A new method to pre-

dict the ignition delay under transient thermodynamic conditions is obtained starting from the Müller's model [21]. This new procedure intends to improve the predictions obtained by the Livengood & Wu integral by avoiding some of its hypotheses.

The Müller's model is a simple model to characterize the autoignition phenomenon of the n-heptane by a chain reactions mechanism. It is composed by four reactions, which can be extended to any hydrocarbon C_nH_m as follows:

$$F \xrightarrow{k_1} Q \tag{R1}$$

$$Q + a_{st}O_2 \xrightarrow{k_2} P \tag{R2}$$

$$F + 2O_2 \underset{k_{3b}}{\overset{k_{3f}}{\rightleftharpoons}} I \tag{R3}$$

$$I + (a_{st} - 2)\, O_2 \xrightarrow{k_4} P \tag{R4}$$

where a_{st} represents the oxygen-to-fuel molar ratio under stoichiometric conditions, which is equal to $n + m/4$. Besides, F represents the fuel, Q represents the typical intermediates of the high-temperature fuel decomposition, I represents the typical intermediates of the low-temperature fuel decomposition, and P represents the main products of the combustion.

In this model, reactions R1 and R2 correspond to the high-temperature reaction branch, where R1 represents the high-temperature dehydrogenation and the thermal cracking of the fuel. Reactions R3 and R4 correspond to the

low-temperature chain branching mechanism. R3 is the chain reaction that promotes the progression of the autoignition process by the generation of chain carriers. Finally, R2 and R4 correspond to the termination reactions. The NTC behavior can be modeled by introducing a backward reaction in R3.

The low-temperature chain branching mechanism is the dominant one in internal combustion engines (ICE) [22], since the evolution of the in-cylinder temperature covers a wide range below 1000 K during the ignition delay. Thus, if ignition delays under ICE conditions want to be predicted, reactions R1 and R2 can be obviated. Under these hypotheses the species conservation equations can be written as follows:

$$\frac{d[F]}{dt} = -k_{3f}[F][O_2] + k_{3b}[I] \tag{B.1}$$

$$\frac{d[I]}{dt} = k_{3f}[F][O_2] - k_{3b}[I] - k_4[I][O_2] \tag{B.2}$$

$$\frac{d[O_2]}{dt} = a_{st}\frac{d[F]}{dt} + (a_{st} - 2)\frac{d[I]}{dt} \tag{B.3}$$

where $[X]$ represents the concentration of the species X.

Moreover, assuming that during the ignition delay the comsumption of oxygen is negligible, since the termination reactions are not very important, and as $[O_2] >> [F]$ and $[O_2] >> [I]$, a constant oxygen concentration can be assumed. Therefore, the previous conservation equations can be simplified as follows (Eq. B.4 is derived from Eq B.3, and Eq. B.5 from B.2 and B.4):

$$[F] = [F]_0 - \frac{a_{st} - 2}{a_{st}}[I] \tag{B.4}$$

$$\frac{d[I]}{dt} = k_{3f}[O_2][F]_0 - \left(k_{3f}\frac{a_{st}-2}{a_{st}}[O_2] + k_{3b} + k_4[O_2]\right)[I] \tag{B.5}$$

where $[F]_0$ is the initial fuel concentration.

Considering an air-fuel mixture under constant conditions of temperature and pressure, the differential equation B.5 can be integrated with the initial condition $t = 0 \rightarrow [I] = 0$ as follows:

$$1 - \frac{k_{3f}\frac{a_{st}-2}{a_{st}}[O_2] + k_{3b} + k_4[O_2]}{k_{3f}[O_2][F]_0}[I] = exp(-t(k_{3f}\frac{a_{st}-2}{a_{st}}[O_2] + k_{3b} + k_4[O_2])) \tag{B.6}$$

where $\frac{1}{k_{3f}\frac{a_{st}-2}{a_{st}}[O_2]+k_{3b}+k_4[O_2]}$ is a characteristic time of the process and, therefore, it may be proportional to the ignition delay.

In order to simplify the expressions, the exponential term in Eq B.6 can be approximated by a Taylor series expansion. The series can be truncated in the second term, since $t(k_{3f}\frac{a_{st}-2}{a_{st}}[O_2] + k_{3b} + k_4[O_2]) \sim \frac{t}{\tau} < 1$ during the ignition delay, and Eq B.6 can be rewriten as follows:

$$[I] = k_{3f}[O_2][F]_0 t \tag{B.7}$$

When $t = \tau$ the concentration of chain carriers is equal to the critical concentration and the previous equation can be rewriten as follows:

$$[I] = [I]_{crit}\frac{t}{\tau} \tag{B.8}$$

equation that is only valid under constant conditions of pressure and temperature.

It should be noted that ignition represents a discontinuity in the model, since some hypotheses, as constant oxygen concentration, are no longer valid. In fact, the expression deducted for the generation rate of chain carriers loses its validity. Thus, although ignition happens when a maximum concentration of chain carriers occurs (the critical concentration), the generation rate of chain carriers predicted by the model at this instant is not equal to zero.

If a process under transient conditions of pressure and temperature is discretized as a series of thermodynamic states that remain constant for a time dt, the ignition time can be obtained as follows:

$$\int_0^{[I]_{crit,t_i}} d[I] = \int_0^{t_i} \frac{[I]_{crit}}{\tau} dt \rightarrow 1 = \frac{1}{[I]_{crit,t_i}} \int_0^{t_i} \frac{[I]_{crit}}{\tau} dt \tag{B.9}$$

where t_i is the ignition delay of the process and τ and $[I]_{crit}$ are the ignition delay and the critical concentration of chain carriers under constant conditions of pressure and temperature for the successive thermodynamic states.

It should be noted that if the critical concentration of chain carriers is considered as a constant, Eq. B.9 results in the Livengood & Wu integral.

The new integral presented in this paper can be obtained by applying a similar theoretical development to different autoignition models, e. g. the Glassman's model [42]. In [33], the authors propose an alternative method to predict ignition delays under transient conditions, the RCCC-method. Whereas the Livengood & Wu integral assumes that the critical concentration of chain carriers is constant and the production rate of active radicals can be assumed as a zero-order reaction, the new integral proposed in the present paper does not consider the critical concentration to be constant anymore, but still assumes a zero-order reaction for the chain carriers. Finally,

the RCCC-method discards both hypotheses, which might lead to a more accurate method. However, the simplicity of the new integral proposed and the small difference between the predictive accuracy of this method and the RCCC-method make Eq. B.9 a very attractive method.

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