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Additional Information

# Validity of the Livengood & Wu correlation and theoretical development of an alternative procedure to predict ignition delays under variable thermodynamic conditions

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## Abstract

A theoretical study about the autoignition phenomenon has been performed in this article. The hypotheses of the Livengood & Wu integral have been revised, concluding that the critical concentration of chain carriers is not constant. However, its validity under engine conditions has been justified. Expressions to characterize the temporal evolution of the concentration of chain carriers, as well as the critical concentration of active radicals and the ignition delay, have been obtained starting from the Glassman's model. A new expression to predict ignition delays under variable conditions has been developed and the results obtained with this expression have been compared with those obtained from the Livengood & Wu integral. Two different fuels have been studied: isooctane (as a gasoline surrogate) and n-heptane (as a diesel fuel surrogate). The new method to predict ignition delays un-

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der variable conditions has shown, in general, better results than the classic Livengood & Wu integral, but the inability of the Glassman's model to reproduce the negative temperature coefficient regime should be improved in future works.

*Keywords:* Livengood-Wu integral, ignition delay, autoignition modeling, CHEMKIN

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## 1. Introduction

Autoignition is the spontaneous combustion of an air-fuel mixture under certain thermodynamic conditions. It is a phenomenon with high relevance in the propulsive systems for transport media and, specifically, in internal combustion engines. In fact, autoignition is the operating principle of the start of combustion of compression ignition (CI) engines and it is a phenomenon to avoid in spark ignition (SI) engines, where it can cause catastrophic damages.

Autoignition is present in most of the operating principles of new combustion modes, such as Homogeneous Charge Compression Ignition (HCCI), Premixed Charge Compression Ignition (PCCI) and Reactivity Controlled Compression Ignition (RCCI). These new low-temperature combustion strategies are based on the autoignition of a reactive mixture, with a higher or a lower degree of homogeneity, in an environment with low oxygen content (much less than in the atmosphere) to reduce the maximum temperature reached in the cycle [1]. In this way, the soot and  $\text{NO}_x$  formation peninsulas, which can be seen in equivalence ratio - temperature diagrams, can be avoided [2]. Thus, these modes show virtually zero emissions of soot and  $\text{NO}_x$ , but high emissions of unburned hydrocarbons (UHC) and carbon monoxide (CO) [3].

19 The main challenge to implement these new combustion strategies in com-  
20 mercial engines is the lack of control over the autoignition process and over  
21 the heat release rate [4], whereby it is necessary to improve the knowledge  
22 about the autoignition phenomenon.

## 23 **2. Justification and objective**

24 There are several experimental facilities designed to study the autoigni-  
25 tion phenomenon. All of them are based on keeping an air-fuel mixture under  
26 certain thermodynamic conditions and measuring the time elapsed between  
27 the instant where these conditions are reached and the start of combustion,  
28 obtaining the ignition delay,  $t_i$ , of the mixture. It should be noted that these  
29 studies are not typically carried out in single-cylinder engines but in facilities  
30 like rapid compression machines or shock tubes [5, 6].

31 Rapid compression machines and shock tubes allow obtaining the ignition  
32 delay of a homogeneous air-fuel mixture under constant and full-controlled  
33 thermodynamic conditions [7]. However, the parameter of interest in applied  
34 studies is the ignition delay under variable conditions of pressure and tem-  
35 perature. In the frame of simulation and modeling, there are two different  
36 ways to obtain ignition delays under variable conditions:

- 37 • By employing a chemical kinetic mechanism.
- 38 • By employing a numerical method such as the Livengood & Wu inte-  
39 gral.

40 There is a great interest in simulating with accuracy the phenomena that  
41 takes place in the cylinder of an internal combustion engine. Computational

42 Fluid Dynamics (CFD) simulations are very useful at the design stage, since  
43 they reduce the number of experiments, prototypes and cost of developing  
44 a new engine. Computing time is the key parameter when CFD simulations  
45 are carried out, and it can be highly increased by linking the physical mod-  
46 els with detailed chemical kinetic mechanisms. This is the reason why the  
47 higher the spatial resolution, the simpler the chemical mechanism employed  
48 to solve the reaction paths. Thus, some CFD applications can be solved with  
49 simple numerical methods that characterize the autoignition and combustion  
50 processes with a quite reasonable computing time.

51 Although ignition can be reasonably predicted by using advanced CFD  
52 codes with detailed chemistry, the required computing time is too long to  
53 be solved in real time. Thus, simple numerical methods with very short  
54 computing time are the only ones that can be implemented in an engine  
55 control unit. Methods accurate enough allow improving the control of the  
56 engine by making it possible to take decisions in real time.

57 The Livengood & Wu hypothesis [8], also known as the Livengood & Wu  
58 integral or, simply, the integral method, allows to obtain ignition delays of  
59 processes under variable conditions of temperature and pressure by using  
60 the ignition characteristics under constant thermodynamic conditions, which  
61 are much easier to obtain. The expression proposed by these authors is the  
62 following:

$$\int_0^{t_i} \frac{1}{\tau} dt = 1 \quad (1)$$

63 where  $t_i$  is the ignition delay of the process and  $\tau$  is the ignition delay under  
64 constant conditions of pressure and temperature for the successive thermo-

65 dynamic states.

66 The Livengood & Wu integral assumes that the oxidation process during  
67 the ignition delay can be described by a single zero-order global reaction and,  
68 therefore, the reaction rate does not depend on time under constant thermo-  
69 dynamic conditions. Moreover, the authors assumed that the autoignition  
70 happens when a critical concentration of chain carriers is reached, being this  
71 critical concentration constant for a given air-fuel mixture. These hypotheses  
72 will be discussed in the following section.

73 This integral has been traditionally enunciated as a method to predict  
74 the occurrence of knock in SI-engines [9]. However, it has been extended to  
75 CI-engines as a way to predict the ignition delay of homogeneous air-fuel mix-  
76 tures as the ones used in HCCI engines [10]. The method has great interest  
77 for the prediction of autoignition due to its simplicity and low computational  
78 cost, but this simplicity is a consequence of the hypotheses assumed for its  
79 development.

80 The integral method has been used in several CFD studies as the model  
81 to predict the autoignition time. For example, Imamori et al. [11] coupled  
82 the Livengood & Wu integral with Star-CD and KIVA 3 to improve the  
83 performance of a low speed two-stroke diesel engine. And Li et al. [12]  
84 linked the integral method with the CFD code VECTIS to study the effects  
85 of heterogeneities on a two-stroke HCCI engine fueled with gasoline.

86 A new use of the Livengood & Wu integral is its implementation in an  
87 engine control unit. Several authors such as Ohyama [13], Rausen et al.  
88 [14], Choi et al. [15] and Hillion et al. [16] used the integral method to  
89 predict the start of combustion under HCCI conditions. This method can

90 be combined with other simple models to obtain global parameters of the  
91 combustion process allowing the control of the engine in real time.

92 Bradley et al. [17, 18] used the Livengood & Wu hypothesis to obtain the  
93 octane number of non-PRF fuels by predicting the ignition delay of PRF fuels  
94 under engine conditions, with the aim of relating the octane number with  
95 the ignition delay. Reyes et al. [19] measured the knock time of n-heptane  
96 and of a mixture of 50% n-heptane - 50% toluene in a constant volume  
97 vessel. Knock times, which correspond to ignition delays under variable  
98 thermodynamic conditions, were used with the Livengood & Wu integral  
99 to obtain correlations for the ignition delay under constant conditions,  $\tau$ .  
100 Finally, these correlations were used with the integral method to predict  
101 ignition delays under engine conditions. In fact, different correlations for  $\tau$   
102 have been proposed by several authors in order to take into account the effect  
103 of EGR or of the equivalence ratio, such as the works of Swan et al. [20] or  
104 Hoepke et al. [21].

105 Several authors have noted that the Livengood & Wu integral loses its  
106 validity under certain conditions [22]. When a two-stage ignition occurs, the  
107 integral method is not able to accurately predict any of the delays because it  
108 is based on a single global reaction mechanism that ignores the cool flames.  
109 Some of these authors as Liang and Reitz [23] or Edenhofer et al. [24] show  
110 the need to create simple algorithms, but more sophisticated than the integral  
111 method, to characterize the autoignition at low temperatures without using  
112 any chemical kinetic mechanism. However, few alternatives to the Livengood  
113 & Wu integral can be found in the literature.

114 Hernandez et al. [25] analyzed the validity of the Livengood & Wu in-

115 tegral by simulations performed with CHEMKIN for several fuels and with  
116 various chemical kinetics mechanisms. They proved that the predictions of  
117 the method are accurate if the fuel do not show two-stage ignition. These  
118 authors also proposed two different alternatives in order to predict the igni-  
119 tion delay of cool flames, one with better and other with worse results than  
120 the integral method. However, to the authors' knowledge, there is not any  
121 English written paper in which the validity of the Livengood & Wu integral  
122 is not only analyzed, but also justified. Moreover, most of the alternatives  
123 proposed to improve the integral method are based on the method itself or  
124 assume the same hypothesis, which are too simple. Expressions based on  
125 more sophisticated autoignition mechanisms are needed in order to extend  
126 the range of validity of the methods.

127 In this study the validity of different expressions to determine ignition de-  
128 lays under variable conditions is intended to be solved from a point of view  
129 of simulation and modeling. Simulations have been done for two different  
130 surrogate fuels with reactivities typical of diesel fuel and gasoline: n-heptane  
131 and isooctane, respectively. Despite the fact that more sophisticated surro-  
132 gate fuels for diesel and gasoline can be found in the literature, n-heptane  
133 and isooctane were chosen because extended and fully validated chemical  
134 kinetic mechanisms are available for both. Moreover, n-heptane, isooctane  
135 and their blends are primary reference fuels (PRF) employed to define the  
136 octane reference scale and they are widely used in the literature as surrogates  
137 of diesel and gasoline under engine conditions [26, 27].

138 Ignition delays and critical concentrations of chain carriers for isooctane  
139 and n-heptane are obtained under different conditions of pressure, tempera-



140 ture, equivalence ratio and oxygen mass fraction. The calculations are per-  
141 formed with the software of chemical simulation CHEMKIN. This software,  
142 which is developed by Reaction Design (ANSYS), is consolidated in the world  
143 of engineering investigations and the chemical kinetics mechanisms of several  
144 hydrocarbons are perfectly defined to be used with it. This study is a work  
145 based on simulation and modeling.

### 146 **3. Theoretical justification of the Livengood & Wu integral method**

147 The theoretical development performed to characterize the autoignition  
148 phenomenon is described in detail in this section. Expressions to charac-  
149 terize the temporal evolution of the concentration of chain carriers, as well  
150 as the critical concentration of active radicals and the ignition delay, have  
151 been obtained starting from the Glassman's model. Finally, this autoignition  
152 model is linked to the Livengood & Wu integral, highlighting the hypotheses  
153 assumed to obtain each expression and discussing their validity.

154 The Glassman's model [28] is a simple model to characterize the autoigni-  
155 tion phenomenon by a chain reactions mechanism. It is composed by the five  
156 following reactions:





157 where R and R' represent the reactants, CC represents the chain carriers,  
158 P and P' represent the main products of the combustion and P'' represents  
159 the partially oxidized products such as those formed by wall effects. In this  
160 model, reaction (R1) corresponds to the initiation reaction, (R2) is the chain  
161 reaction that promotes the progression of the autoignition process by the  
162 generation of chain carriers, (R3) is the propagation reaction and, finally,  
163 (R4) and (R5) correspond to the termination reactions: whereas in (R4) the  
164 other main product of the combustion is generated, in reaction (R5) partially  
165 oxidized products are formed due to an incomplete combustion because of  
166 lack of oxygen or quenching caused by wall effects.

167 The generation rate of the main products P and P' must stretch to infin-  
168 ity when the combustion starts. Under these conditions, the generation rate  
169 of the chain carriers CC must stretch to minus infinity (it has to be a disap-  
170 pearance rate). Since during the ignition delay there is a generation rate of  
171 chain carriers, which becomes a disappearance rate when combustion starts,  
172 ignition must happen when a maximum of concentration of chain carriers oc-  
173 curs. This maximum is known as critical concentration. With this concept,  
174 the autoignition delay phenomenon can be described as the accumulation  
175 of active radicals thanks to chain reactions, until a critical concentration is  
176 reached, at which time the ignition occurs.

177 The generation rate of chain carriers has the following expression accord-

178 ing to the Glassman's model:

$$\frac{d[CC]}{dt} = k_1[R] + (k_2(\alpha - 1) - k_4)[R][CC] - k_5[CC] \quad (2)$$

179 The chemical kinetic mechanism will be a chain reactions mechanism  
 180 if reaction (R2) introduces a multiplier effect on the generation of chain  
 181 carriers. This means that the global generation rate of chain carriers must  
 182 be higher than the generation rate corresponding to the initiation reaction.  
 183 Imposing this condition on equation (2), there is a critical value of  $\alpha$  from  
 184 which reaction (R2) is characterized as a chain reaction.

$$\alpha_{crit} = 1 + \frac{k_4[R] + k_5}{k_2[R]} \quad (3)$$

185 If  $\alpha$  is written as  $\alpha = \alpha_{crit} + \Delta\alpha$ , then, equation (2) can be rewritten as  
 186 follows:

$$\frac{d[CC]}{dt} = k_1[R] + \Delta\alpha k_2[R][CC] \quad (4)$$

187 Assuming that the concentration of chain carriers is always much smaller  
 188 than the initial concentration of reactants,  $[CC] \ll [R]$ ,  $[R]$  can be con-  
 189 sidered as a constant during the ignition delay period. Considering an air-  
 190 fuel mixture under constant conditions of temperature and pressure, the  
 191 previous differential equation can be integrated with the initial condition  
 192  $t = 0 \rightarrow [CC] = 0$  as follows:

$$\exp(tk_2\Delta\alpha[R]) = 1 + [CC]\frac{k_2}{k_1}\Delta\alpha \quad (5)$$

193 where  $\frac{1}{k_2\Delta\alpha[R]}$  is a characteristic time of the process and, therefore, it may  
 194 be proportional to the ignition delay. If  $\delta$  is defined as the corresponding  
 195 proportionality constant, the ignition delay  $\tau$  can be defined as follows:

$$\tau = \frac{\delta}{k_2\Delta\alpha[R]} \quad (6)$$

196 According to the above definition, Eq.(5) can be rewritten as follows:

$$\exp\left(\delta\frac{t}{\tau}\right) = 1 + \delta\frac{[CC]}{k_1[R]\tau} \quad (7)$$

197 Thereby, when  $t = \tau$  the start of combustion occurs and the concentration  
 198 of chain carriers is equal to the critical concentration. In this way, the critical  
 199 concentration of active radicals can be defined by the following expression  
 200 obtained from Eq. (7):

$$[CC]_{crit} = \frac{\exp(\delta) - 1}{\delta} k_1[R]\tau = (\exp(\delta) - 1) \frac{k_1}{k_2\Delta\alpha} \quad (8)$$

201 Eq.(8) can be combined with Eq.(7) in order to obtain an expression for  
 202 the temporal evolution of the concentration of chain carriers that depends  
 203 only on the ignition delay and the critical concentration:

$$\exp\left(\delta\frac{t}{\tau}\right) = 1 + \frac{[CC]}{[CC]_{crit}}(\exp(\delta) - 1) \quad (9)$$

204 It should be noted that ignition represents a discontinuity in the model. In  
 205 fact, the expression deducted for the generation rate of chain carriers loses its

206 validity: this reaction rate suffers a discontinuity and the fast decomposition  
 207 of the fuel by the consumption of active radicals starts. Thus, although  
 208 ignition happens when a maximum concentration of chain carriers occurs  
 209 (the critical concentration), the generation rate of chain carriers predicted  
 210 by the model at this instant is not equal to zero.

211 The ignition delay,  $\tau$ , and the critical concentration of chain carriers,  
 212  $[CC]_{crit}$ , can be correlated by Eq.(6) and Eq.(8), respectively. All the spe-  
 213 cific reaction rates and the value of  $\Delta\alpha$  have to be adjusted for each fuel.  
 214 Thus, the effect of pressure and temperature will be taken into account by  
 215 the characterization of each specific reaction rate. The effect of the equiva-  
 216 lence ratio will be taken into account with the concentration of fuel,  $[R]$ , and  
 217 with  $\Delta\alpha$ . Finally, the effect of the EGR rate cannot be directly taken into  
 218 account since the Glassman's model does not consider the oxygen concentra-  
 219 tion. However, the EGR rate can be reflected in  $\alpha$  since the multiplier effect  
 220 of the chain carriers depends, somehow, on the concentration of oxygen.

221 The exponential term in equation (7) can be approximated by a Taylor  
 222 series expansion, resulting in the following equation:

$$\sum_{n=1}^{\infty} \frac{1}{n!} \left( \delta \frac{t}{\tau} \right)^n = \delta \frac{[CC]}{k_1[R]\tau} \quad (10)$$

223 which can be truncated in the second term of the series (n=1) to obtain  
 224 simplified expressions for the concentration of chain carriers  $[CC]$ , their gen-  
 225 eration rate  $d[CC]/dt$  and the critical concentration  $[CC]_{crit}$ :

$$[CC] = k_1[R]t \quad (11)$$

$$\frac{d[CC]}{dt} = k_1[R] \quad (12)$$

$$[CC]_{crit} = k_1[R]\tau \rightarrow \frac{d[CC]}{dt} = \frac{[CC]_{crit}}{\tau} \quad (13)$$

Eq. (13) can be integrated for an evolution of the thermodynamic conditions assuming the critical concentration,  $[CC]_{crit}$ , as a constant, as follows:

$$\int_0^{[CC]_{crit}} \frac{d[CC]}{[CC]_{crit}} = \int_0^{t_i} \frac{dt}{\tau} \rightarrow 1 = \int_0^{t_i} \frac{1}{\tau} dt \quad (14)$$

where  $t_i$  is the ignition delay under variable conditions of temperature and pressure and  $\tau$  is the ignition delay for each thermodynamic state. Eq. (14) is known as the Livengood & Wu integral or, simply, the integral method [8].

Regarding the expression for the critical concentration (8), it depends on the ignition delay  $\tau$  and on the specific reaction rate  $k_1$ , which are functions of pressure and temperature. Thereby, the critical concentration of active radicals has not to be constant, as will be shown in section 5.

#### 4. Methods

The methods employed in this paper to analyze the validity of the Livengood & Wu integral are described in the following paragraphs.

A parametric study was carried out with CHEMKIN in order to study the accuracy of the integral method following these methods: for a certain case, the evolution of both the in-cylinder temperature and pressure is obtained by simulating the compression and expansion strokes without solving the chemical kinetics (under motored conditions). Then, the ignition delay,  $\tau$ , and the critical concentration,  $[CC]_{crit}$ , is obtained for each thermodynamic

244 state by simulating in a perfectly stirred reactor. The ignition delay under  
245 variable conditions is then calculated by using the integral method. Finally,  
246 the ignition delay under variable conditions is also calculated by simulating  
247 it in an internal combustion engine reactor and this value is compared with  
248 the one obtained from the numerical method.

249 As mentioned before, CHEMKIN is the software used to obtain the  
250 different ignition delays and critical concentrations. The version used is  
251 CHEMKIN-PRO. Curran's kinetic mechanism is used both for isooctane and  
252 n-heptane [29, 30]. This mechanism consists of 1034 species and 4238 reac-  
253 tions, and includes the chemical kinetics of the two hydrocarbons used in this  
254 investigation. Its validity has been checked in several articles [26, 27, 31] by  
255 comparison with experimental results.

256 The model used to obtain ignition delays under constant conditions and  
257 critical concentrations is a homogeneous closed reactor (perfectly stirred reac-  
258 tor, PSR), which works with constant pressure and uses the energy equation  
259 to solve the temperature temporal evolution. This model is the most ap-  
260 propriate to obtain ignition delays under certain pressure and temperature  
261 conditions [32]. The model used to obtain ignition delays under variable  
262 conditions, as well as the temperature and pressure profiles, is an adiabatic  
263 reciprocating internal combustion engine operating with homogeneous charge  
264 (IC-engine, closed 0-D reactors from CHEMKIN). The rod-to-crank ratio is  
265 equal to 3 and the volume at top dead center (TDC) is equal to  $20 \text{ cm}^3$ ,  
266 which are typical values in current engines. The piston starts at bottom  
267 dead center (BDC) and a complete engine revolution is simulated.

268 In this work the autoignition of the mixture is considered to be produced

269 when the concentration of  $\text{CH}_2\text{O}$  reaches a maximum, since formaldehyde is  
270 widely recognized as an autoignition tracer [33]. This means that when the  
271 critical concentration of formaldehyde is reached, the time corresponding to  
272 this instant will be considered as the ignition delay. Any active radical with  
273 chain behavior can be taken as chain carrier, e. g.  $\text{HO}_2$  or  $\text{H}_2\text{O}_2$ .

274 The maximum waiting time for the autoignition of the mixture has been  
275 set to 30 s, which provides accuracy enough in the calculations.

276 Finally, the ignition delay,  $\tau$ , and the critical concentration,  $[CC]_{crit}$ ,  
277 is obtained for each thermodynamic state with a  $\Delta t = 10^{-5} \text{s}$ , since it was  
278 found that smaller values of the time step result in changes in the predictions  
279 smaller than the selected  $\Delta t$ .

280 The performed parametric study was as follows:

- 281 • Fuel: isooctane (gasoline surrogate) and n-heptane (diesel fuel surro-  
282 gate).
- 283 • Initial temperature: 350 K and 400 K.
- 284 • Initial pressure: 0.1 MPa and 0.2 MPa.
- 285 • Equivalence ratio: from 0.5, 1 and 1.5.
- 286 • Oxygen mass fraction: 0.21 (low EGR rate) and 0.13 (high EGR rate).
- 287 • Compression ratio: 12 (SI-engine) and 18 (CI-engine).
- 288 • Engine speed: from 600 rpm to 5000 rpm at steps of 200 rpm.

289 Although equivalence ratios of 1.5 can seem uninteresting for practical  
290 applications, it must be taken into account that autoignition occurs under



291 rich local equivalence ratios in direct-injection engines [34]. This concept is  
292 known as *most reactive mixture fraction* and it arises due to the balance  
293 of reactivities between the fuel-air ratio distribution and the temperature  
294 distribution.

295 In this study, EGR was considered as the products of a complete com-  
296 bustion reaction between the fuel and dry air in which the amount of oxygen  
297 is the desired by the user. Thus, the EGR is composed by  $N_2$ ,  $O_2$ ,  $CO_2$  and  
298  $H_2O$  as it is explained in [35].

299 The same methods are followed to analyze the new procedure proposed  
300 by the authors in this paper.

## 301 **5. Results obtained from the Livengood & Wu integral and discus-** 302 **sion**

303 In this section, the validity of the integral method proposed by Livengood  
304 & Wu is checked and explained.

305 First, the most outstanding hypotheses assumed by the method are sum-  
306 marized to allow fast and easy references in the following paragraphs.

- 307 • Hypotheses of the Livengood & Wu integral method:
  - 308 – H1-LW: the oxidation process during the ignition delay can be  
309 described by a global 0-order chemical reaction.
  - 310 – H2-LW: the critical concentration of chain carriers at which the  
311 autoignition occurs does not depend on temperature and pressure.
  - 312 – H3-LW: the concentration of chain carriers increases linearly with  
313 time under certain given thermodynamic conditions of pressure

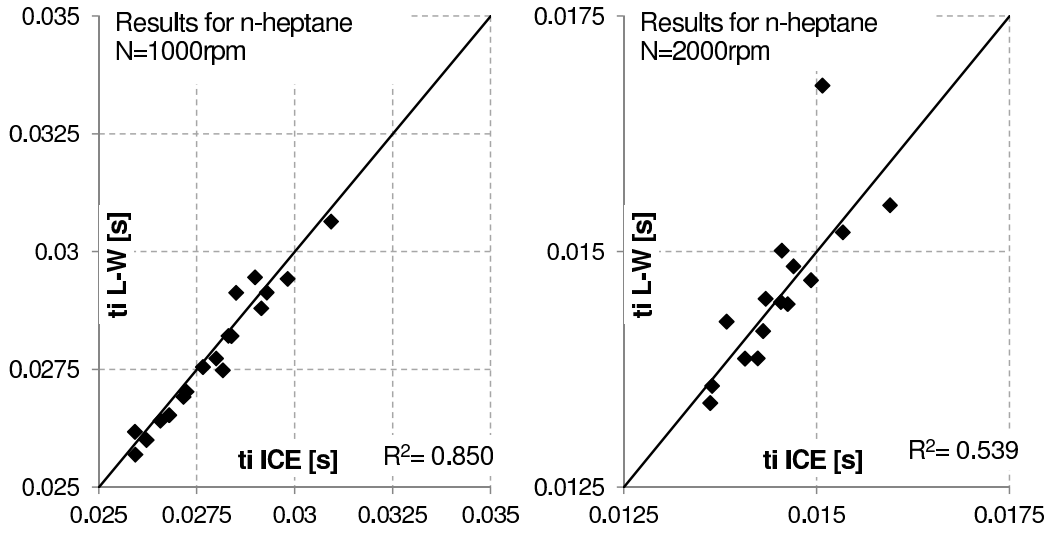


Figure 1: Ignition delay prediction versus simulated ignition delay for n-heptane at different engine speeds and under various initial conditions. Left.- 1000 rpm. Right.- 2000 rpm.

314 and temperature.

315 – H4-LW: the fuel molar fraction is approximately constant during  
 316 the ignition delay.

317 Fig. 1 and Fig. 2 show the comparison between the integral method and  
 318 the chemical kinetic simulation for n-heptane and isooctane, respectively, at  
 319 different engine speeds and under various initial conditions. Ignition delays  
 320 under variable conditions are represented: those obtained from the numeri-  
 321 cal method ( $L - W$ ) in the ordinates axis and those obtained from chemical  
 322 kinetic simulations ( $ICE$ ) in the abscissas axis. The line  $y=x$ , which rep-  
 323 represents a perfect match between the numerical method and the chemical  
 324 kinetic simulation, is plotted in all graphs. The coefficients of determination,  
 325  $R^2$ , have been calculated for each fuel, and their values can be seen in the

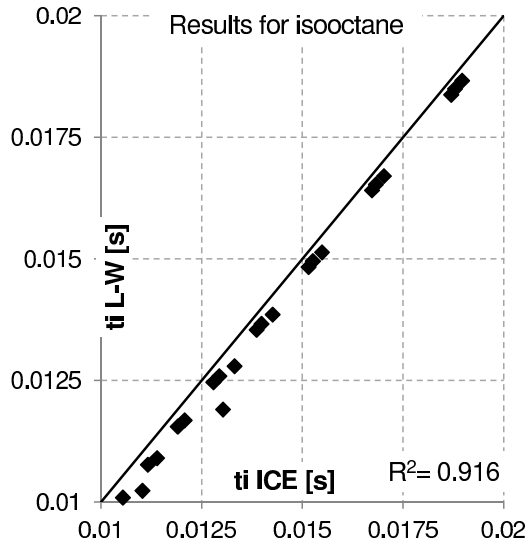


Figure 2: Ignition delay prediction versus simulated ignition delay for isooctane at different engine speeds and under various initial conditions.

326 corresponding figure.

327 The coefficients of determination for n-heptane are much worse than the  
 328  $R^2$  for isooctane. n-Heptane presents a high Negative Temperature Coeffi-  
 329 cient (NTC) zone, in which the reactivity decreases when the temperature  
 330 increases. This effect cannot be described by a global chemical reaction, as  
 331 assumed in the Livengood & Wu method, which causes erroneous predictions  
 332 in some cases that will be explained in detail below.

333 The percentage ignition delay deviation with relation to detailed chem-  
 334 istry predictions (or prediction deviation),  $\xi$ , was calculated in order to com-  
 335 pare more easily the prediction capability of the Livengood & Wu integral  
 336 method. This deviation is defined as follows:

$$\xi = \frac{ti_{LW} - ti_{ICE}}{ti_{ICE}} 100 \quad (15)$$

337 where  $ti$  represents the ignition time (ignition delay under variable condi-  
 338 tions). The subscript  $ICE$  represents a data obtained from a chemical sim-  
 339 ulation with CHEMKIN using a closed 0-D IC-engine reactor. Finally, the  
 340 subscript  $LW$  represents a data obtained from the Livengood & Wu nu-  
 341 merical method. Similarly, the difference between the ignition crank angles  
 342 obtained with the integral method and with the direct chemical kinetic simu-  
 343 lation was calculated. This difference is denoted as  $\Delta\theta = ICA_{LW} - ICA_{ICE}$ ,  
 344 where  $ICA$  represents the ignition crank angle and the subscripts follow the  
 345 same notation as for the ignition time.

346 Fig. 3 and Fig. 4 show these deviations for n-heptane under different  
 347 engine speeds, fuel/air equivalence ratios and oxygen mass fractions. As can  
 348 be seen in both figures, the higher the engine speed, the higher the prediction  
 349 deviation, i.e., the method is less accurate if the ignition occurs at crank angle  
 350 after TDC. This can be easily explained because a higher ignition crank angle  
 351 implies that a longer range of the  $\tau$  function is used, which results in a higher  
 352 cumulated error.

353 In Fig. 4 the method overpredicts the ignition times for lean mixtures  
 354 whereas it underpredicts the ignition delay for the other equivalence ratios.  
 355 This tendency only occurs when very pronounced effects of the NTC behavior  
 356 on the  $\tau$  function appear, since the NTC zone becomes less pronounced if  
 357 the fuel/air equivalence ratio is increased. Finally, if comparing Fig. 3 and  
 358 Fig. 4 it can be seen that the lower the oxygen mass fraction, the higher  
 359 the prediction deviation because the NTC zone becomes more pronounced

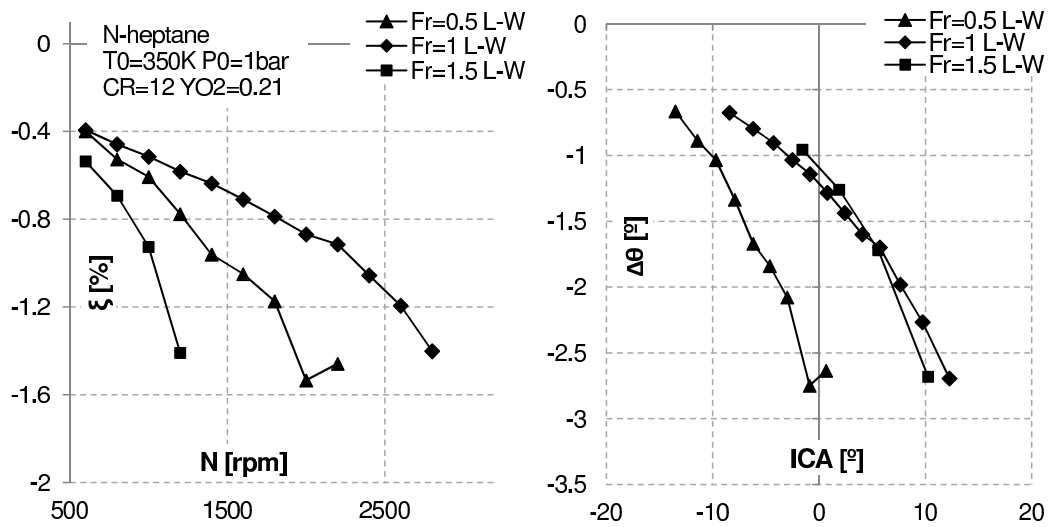


Figure 3: Prediction accuracy of the Livengood & Wu method for n-heptane and various engine speeds. The engine simulated has a compression ratio of 12 and an initial temperature, pressure and oxygen mass fraction of 350 K, 1 bar and 0.21, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

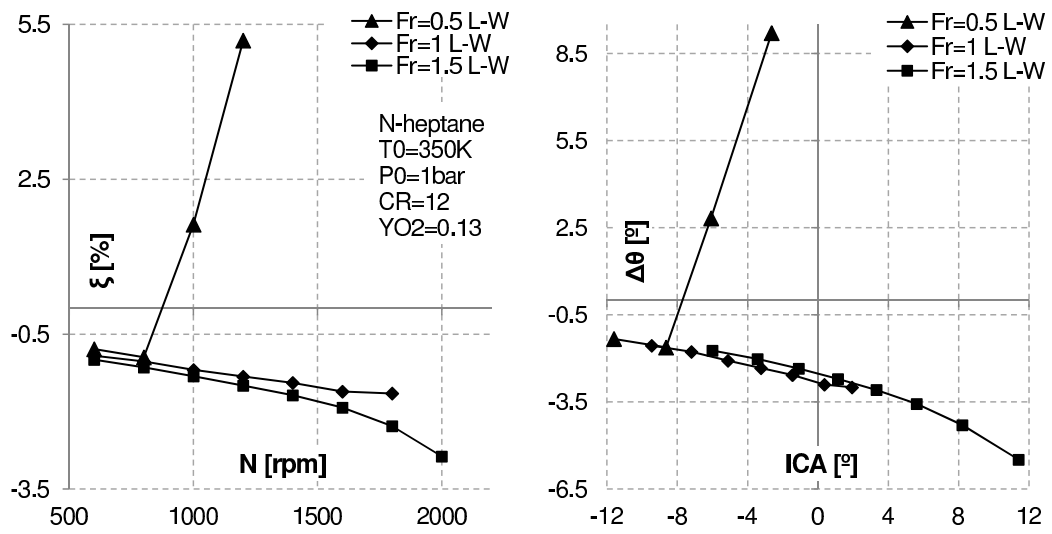


Figure 4: Prediction accuracy of the Livengood & Wu method for n-heptane and various engine speeds. The engine simulated has a compression ratio of 12 and an initial temperature, pressure and oxygen mass fraction of 350 K, 1 bar and 0.13, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

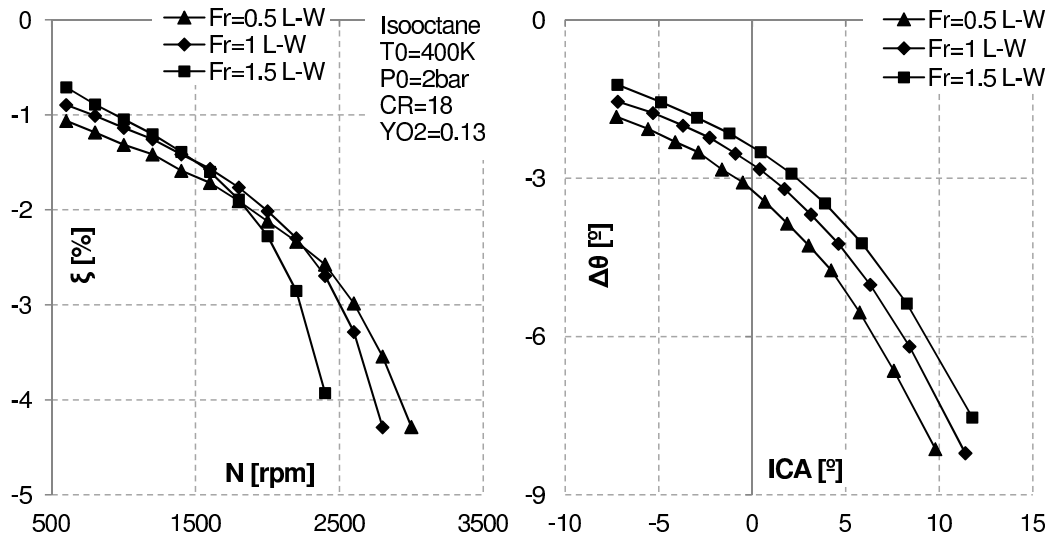


Figure 5: Prediction accuracy of the Livengood & Wu method for isooctane and various engine speeds. The engine simulated has a compression ratio of 18 and an initial temperature, pressure and oxygen mass fraction of 400 K, 2 bar and 0.13, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

360 if the oxygen proportion is reduced. This change of trend in the reactivity  
 361 of the fuel is the main cause of the lack of accuracy of the predictions, since  
 362 the integral method does not take into account the NTC behavior among its  
 363 hypotheses.

364 Fig. 5 shows the prediction deviation and the difference between ignition  
 365 angles by using the Livengood & Wu method for isooctane. The method  
 366 underpredicts the ignition delay. As said before, the higher the equivalence  
 367 ratio the smoother the NTC zone and better predictions are achieved. Once  
 368 again, the method is less accurate if the ignition occurs at higher crank angles  
 369 because of the accumulation of errors. Moreover, the deviation is higher for  
 370 n-heptane than for isooctane if the combustion starts at the same crank angle

371 under the same initial conditions (by varying the engine speed). This result  
372 is quite obvious because isoctane has a much smoother NTC zone than n-  
373 heptane. Besides, the NTC zone appears at lower temperatures and pressures  
374 for isoctane, so their effects affect much less to the numerical method.

375 Despite the fact that the prediction deviation reaches inadmissible values  
376 for combustions that start after TDC, the Livengood & Wu method can be  
377 used to predict ignition delays for combustions before TDC, which is the zone  
378 of interest of engines operating with premix charge.

379 The  $\tau$  function is presented in Fig. 6 and the  $[CC]_{crit}$  function is presented  
380 in Fig. 7. As can be seen, the critical concentration of chain carriers is not  
381 constant with pressure and temperature, as it is assumed by the Livengood  
382 & Wu method (hypothesis H2-LW). Furthermore, the NTC zone of both  
383 fuels can be usually crossed during the compression stroke. The authors  
384 assume that the discontinuity of  $\tau$ , which only appears in some cases, is a  
385 consequence of the chemical kinetic mechanism used. Despite the fact that  
386 the calculations were carried out with a detailed chemical kinetic mechanism,  
387 the transition between the low temperature regime and the NTC zone, as well  
388 as the transition between the NTC zone and the high temperature regime  
389 can result in discontinuities in the  $\tau$  function. Moreover, if the autoignition  
390 occurs just after the discontinuity the major contribution to the integral  
391 is made with this data, which can lead to unexpected deviations (e. g.  
392 Fig.4,  $Fr = 0.5$ ). Therefore, depending on the working conditions, the NTC  
393 behavior can be more or less pronounced and can be located earlier or later,  
394 affecting more or less to the prediction deviation.

395 Fig. 7 represents the evolution of the critical concentration of chain car-



396 riers (in dashed line) for certain engine conditions. Besides, the accumulated  
397 area of the Livengood & Wu integral (Eq. 14) is also represented for the same  
398 conditions. As can be seen, the largest contribution to the integral method  
399 is made in a narrow range of crank angle degrees. Thus, if the variation of  
400 critical concentration corresponding to the last 75% of the accumulated area  
401 of the integral method is plotted (solid length of the dashed line in Fig. 7), it  
402 is found that this variation is not large. Moreover, it can be checked that the  
403 critical concentration of chain carriers decreases with temperature whereas  
404 it increases with pressure. The relationship between pressure and temper-  
405 ature in an engine (simultaneous increase or decrease of both) causes that  
406 the net variation of the critical concentration is soft enough to validate the  
407 method. In fact, the pressure effect is, in general, dominant and the critical  
408 concentration of chain carriers increases during the compression stroke and  
409 decreases during the expansion stroke.

## 410 **6. Theoretical development of a new method to predict ignition** 411 **delays**

412 A new method to predict the ignition delay under variable thermody-  
413 namic conditions is developed in this section. This new procedure intends  
414 to improve the predictions obtained by the Livengood & Wu integral by  
415 rejecting some of its wrong hypotheses.

416 As it is explained in the first theoretical development, an expression for  
417 the time evolution of the concentration of chain carriers can be obtained  
418 from the Glassman's model (Eq. (9)). A process under variable conditions  
419 of pressure and temperature can be discretized as a series of thermodynamic

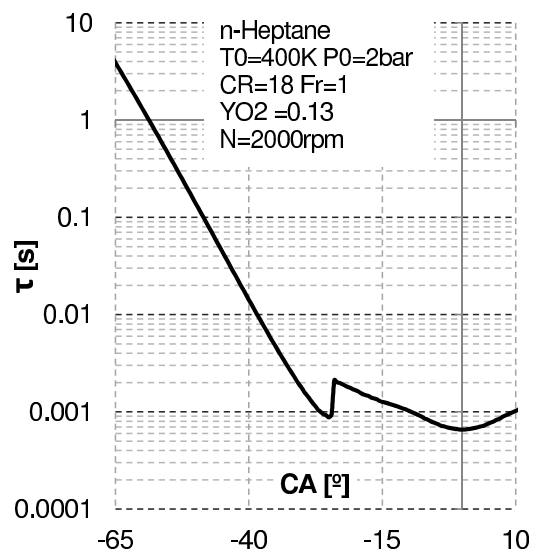


Figure 6:  $\tau$  function. The engine simulated is fuelled with n-heptane, it has a compression ratio of 18 and an initial temperature, pressure, fuel/air equivalence ratio and oxygen mass fraction of 400 K, 2 bar, 1 and 0.13, respectively.

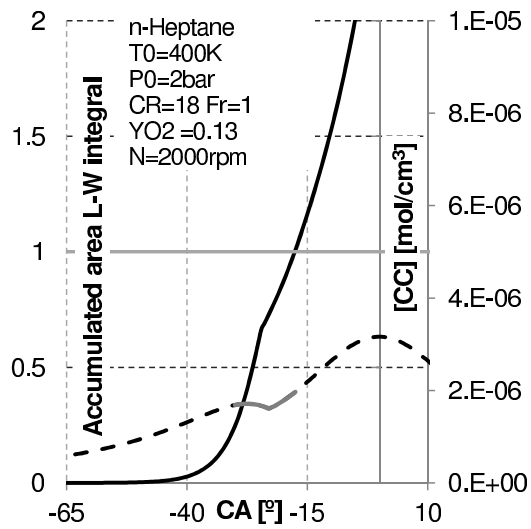


Figure 7: Accumulated area of the Livengood & Wu integral method (solid line) and critical concentration of chain carriers (dashed line), the variation of critical concentration corresponding to the last 75% of the accumulated area of the integral method is plotted in solid line. The engine simulated is fuelled with n-heptane, it has a compression ratio of 18 and an initial temperature, pressure, fuel/air equivalence ratio and oxygen mass fraction of 400 K, 2 bar, 1 and 0.13, respectively.

420 states that remain constant for a time  $\Delta t$ . The working air-fuel mixture  
 421 that has a concentration of chain carriers  $[CC]_j$  at instant  $j$  would reach the  
 422 same concentration of active radicals by staying at constant pressure  $P_j$  and  
 423 constant temperature  $T_j$  during a time  $t_{P_j, T_j}$  defined by Eq. (9):

$$t_{P_j, T_j} = \frac{\tau_j}{\delta} \ln \left( 1 + \frac{[CC]_j}{[CC]_{crit, j}} (exp(\delta) - 1) \right) \quad (16)$$

424 Thus, if the working air-fuel mixture stay under constant conditions  $P_j$ ,  
 425  $T_j$  for a time  $\Delta t$ , the concentration of chain carriers will be the amount  
 426 of active radicals cumulated at time  $j$  plus the amount of active radicals  
 427 generated from time  $t_{P_j, T_j}$  to time  $t_{P_j, T_j} + \Delta t$  following Eq. (9). Furthermore,  
 428 the concentration of chain carriers is not only affected by the generation of  
 429 new radicals during  $\Delta t$ , but also by the volume variation of the compression-  
 430 expansion process. Thus, the concentration of chain carriers at time  $j + 1$   
 431 can be obtained from the data at time  $j$  by the following equation:

$$[CC]_{j+1} = \left( \frac{[CC]_{crit, j}}{exp(\delta) - 1} \left( exp \left( \delta \frac{t_{P_j, T_j} + \Delta t}{\tau_j} \right) - 1 \right) \right) \frac{V_j}{V_{j+1}} \quad (17)$$

432 Which results in:

$$[CC]_{j+1} = \left( \left( \frac{[CC]_{crit, j}}{exp(\delta) - 1} + [CC]_j \right) exp \left( \delta \frac{\Delta t}{\tau_j} \right) - \frac{[CC]_{crit, j}}{exp(\delta) - 1} \right) \cdot \frac{V_j}{V_{j+1}} \quad (18)$$

433 If  $RCCC_j$  is defined as the ratio between the concentration of chain carri-  
 434 ers and the critical concentration (Relative Concentration of Chain Carriers)  
 435 at instant  $j$  ( $RCCC_j = [CC]_j / [CC]_{crit, j}$ ), the autoignition will occur when  
 436  $RCCC_j = 1$  and Eq. (18) can be rewritten as follows:

$$RCCC_{j+1} = \frac{[CC]_{crit,j}}{[CC]_{crit,j+1}} \frac{V_j}{V_{j+1}} \left( \left( \frac{1}{exp(\delta) - 1} + RCCC_j \right) exp \left( \delta \frac{\Delta t}{\tau_j} \right) - \frac{1}{exp(\delta) - 1} \right) \quad (19)$$

437 The details of how Eq. (19) is obtained from the Glassman's model can be  
 438 found in Appendix A.

439 This new method to obtain ignition delays under variable conditions is de-  
 440 fined as follows: if the evolution of pressure and temperature are known, the  
 441 evolution of the ignition delay under constant conditions  $\tau$  and the evolution  
 442 of the critical concentration  $[CC]_{crit}$  can be obtained. With them, the evolu-  
 443 tion of the parameter  $RCCC$  can be calculated. Finally, when  $RCCC_j = 1$ ,  
 444 this instant  $j$  will correspond with the ignition time and the ignition delay  
 445 will be found.

446 It should be noted that a wide database of critical concentrations and  
 447 ignition delays under constant conditions is easily obtainable with a detailed  
 448 chemical kinetic mechanism, which is impossible to be used in complex CFD  
 449 calculations. This database linked with Eq. (19) allow the obtaining of igni-  
 450 tion delays under variable conditions without spending too much computing  
 451 time in solving complex chemical kinetics mechanisms.

## 452 **7. Comparison between the RCCC-method and the Livengood &** 453 **Wu integral**

454 Ignition delays under variable thermodynamic conditions are obtained  
 455 with the RCCC-method following the same methods as the one described in  
 456 section 4. Then, the resulting predictions from both methods (Livengood &

457 Wu and RCCC-method) are compared. Finally, the challenges of this new  
458 procedure as well as the necessary improvements are discussed.

459 First, the hypotheses assumed by the RCCC-method are summarized to  
460 allow fast and easy references in the following paragraphs.

461 • Hypotheses of the RCCC-method:

462 – H1-RCCC: the oxidation process during the ignition delay can be  
463 described by five chemical reactions that do not take into account  
464 the NTC behavior (this method is deduced from the Glassman  
465 model, which do not reproduce the NTC zone).

466 – H2-RCCC: the fuel molar fraction is approximately constant dur-  
467 ing the ignition delay.

468 The main advantage of this new procedure is discarding the hypotheses of  
469 constant critical concentration of chain carriers and linear growth of the ac-  
470 tive radicals concentration under constant thermodynamic conditions, which  
471 are assumed by the Livengood & Wu integral. Moreover, since the method  
472 works with integrated equations there are not problems of calculation insta-  
473 bilities.

474 The percentage ignition delay deviation with relation to detailed chem-  
475 istry predictions (or prediction deviation),  $\xi$ , and the difference between the  
476 ignition crank angles obtained with the RCCC-method and with the direct  
477 chemical kinetic simulation,  $\Delta\theta$ , were calculated for the new procedure in  
478 order to compare more easily the prediction capability of both numerical  
479 methods. The definition of these two parameters can be revised in section 5.

480 The proportionality constant,  $\delta$ , is determined by searching the value that

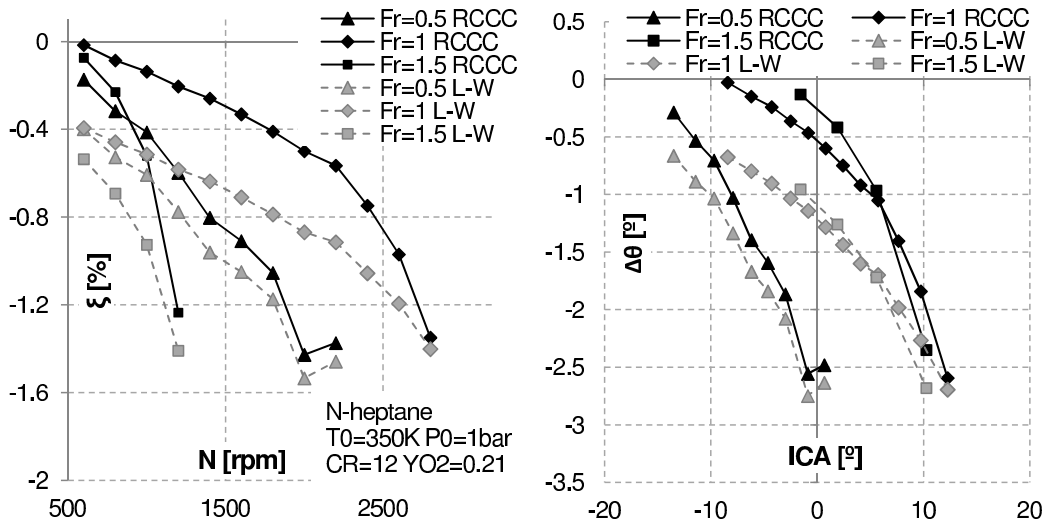


Figure 8: Prediction accuracy of both methods for n-heptane and various engine speeds. The engine simulated has a compression ratio of 12 and an initial temperature, pressure and oxygen mass fraction of 350 K, 1 bar and 0.21, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

481 optimizes the predictions. Obviously, this constant must be higher than zero,  
 482 since the ignition delay  $\tau$  cannot be negative. It was found that values of  $\delta$   
 483 higher than 1 result in earlier ignition delays, which implies worse predictions.  
 484 Besides, it was found that values of  $\delta$  equal or smaller than 1 result in the  
 485 same ignition delay, since the changes in the predictions are smaller than the  
 486 selected  $\Delta t$ .

487 Thus,  $\delta = 1$  has been selected, since any value in the interval  $(0 \ 1]$  has  
 488 physical sense and all of them result in the same predictions.

489 Fig. 8 and Fig. 9 show the prediction deviation and the difference be-  
 490 tween ignition angles for n-heptane under different engine speeds, fuel/air  
 491 equivalence ratios and oxygen mass fractions. Besides, Fig. 10 shows these

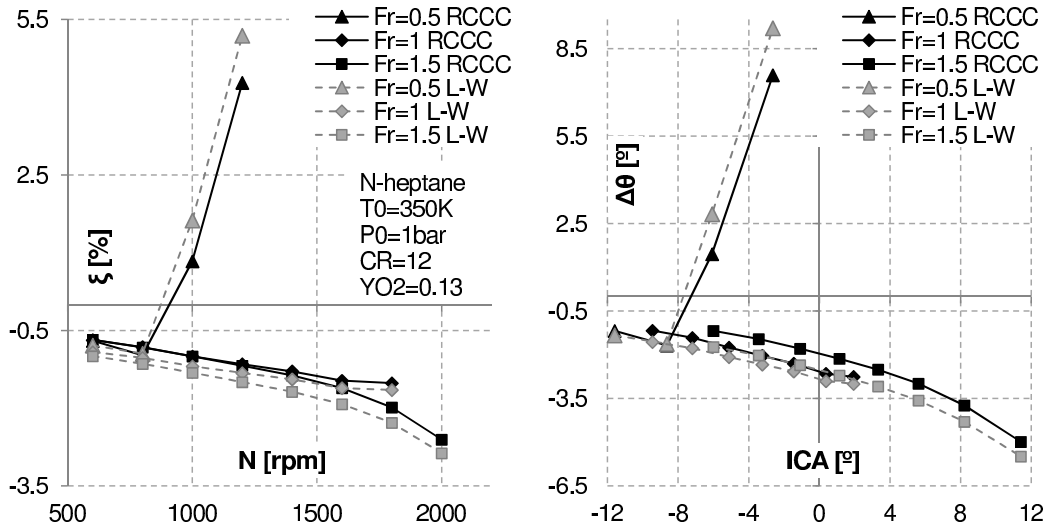


Figure 9: Prediction accuracy of both methods for n-heptane and various engine speeds. The engine simulated has a compression ratio of 12 and an initial temperature, pressure and oxygen mass fraction of 350 K, 1 bar and 0.13, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

492 deviations by using both methods for isoctane. As can be seen in the figures,  
 493 the prediction is better for the RCCC-method than for the Livengood & Wu  
 494 integral. This reduction in the prediction deviation by using the new proce-  
 495 dure proposed is caused by the assumption of a variable critical concentration  
 496 of chain carriers.

497 Fig. 9 shows that the new procedure also overpredicts the ignition times  
 498 for lean mixtures whereas it underpredicts the ignition delay for the other  
 499 equivalence ratios. As said before, this tendency only occurs when very  
 500 pronounced effects of the NTC behavior on the  $\tau$  function appear. Moreover,  
 501 it is found that better predictions could be achieved with the integral method  
 502 instead of with the RCCC-method when autoignition occurs near the NTC



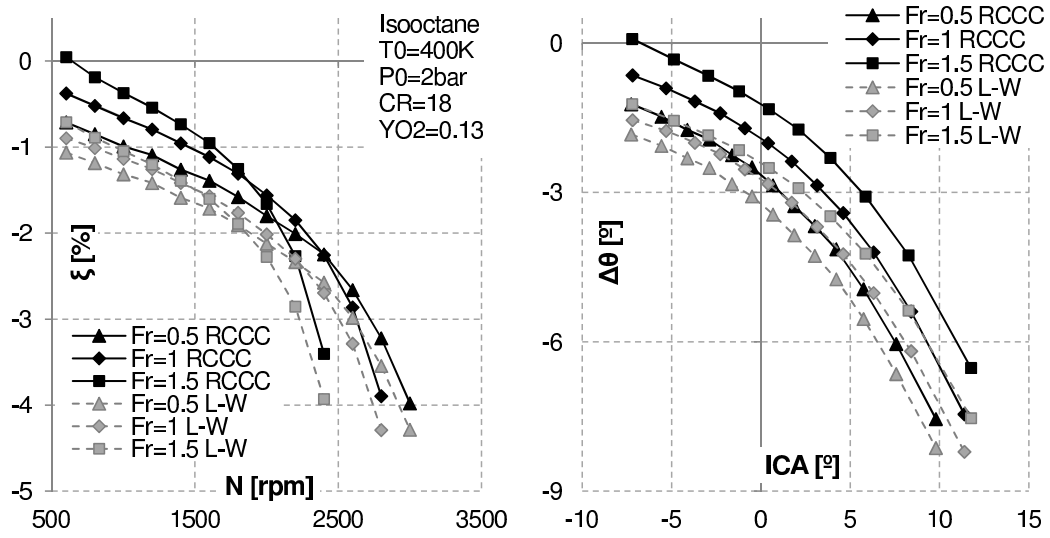


Figure 10: Prediction accuracy of both methods for isooctane and various engine speeds. The engine simulated has a compression ratio of 18 and an initial temperature, pressure and oxygen mass fraction of 400 K, 2 bar and 0.13, respectively. Left.- Prediction deviation. Right.- Difference in ignition crank angle.

503 zone, e.g. the case represented in Fig. 6 and 7. The authors think that this  
504 is caused by, in some degree, compensating errors in the Livengood & Wu  
505 method, since any of both methods do not take into account the NTC regime  
506 in their hypotheses.

507 Finally, it is interesting to analyze what happens when the mixture does  
508 not autoignite. In Fig. 11 the evolution of the critical concentration (dashed  
509 line) versus the evolution of the concentration of chain carriers (solid line)  
510 can be seen. Assuming that autoignition occurs when the critical concen-  
511 tration is reached, the RCCC-method predicts the start of combustion at  
512 31 CAD ATDC for this particular case, whereas this case does not present  
513 combustion in the direct chemical kinetic simulation. The RCCC-method,  
514 which derives from the Glassman's model, only takes into account the oxida-  
515 tion process during the ignition delay and it does not have any degeneration  
516 path for chain carriers. Analyzing the concentration of  $\text{CH}_2\text{O}$  (as an autoigni-  
517 tion tracer) as well as the heat release, it can be seen that the chemistry is  
518 frozen by the cooling effect of the expansion preventing the progress of the  
519 combustion process. Whereas the RCCC-method describes the frozen effect  
520 of the generation rate of chain carriers (just discarding the effect of volume  
521 on the concentration of chain carriers in Eq. 18), it is not able to predict if  
522 the thermodynamic conditions are appropriate to allow the decomposition of  
523 active radicals. However, if the predicted ignition occurs when the frozen ef-  
524 fect has already arisen, it can be concluded that the combustion process will  
525 not progress. For example, in Fig. 11 the dotted line represents the evolution  
526 of the concentration of chain carriers caused only by chemical effects. As can  
527 be seen, the critical concentration is achieved when the chemical paths are

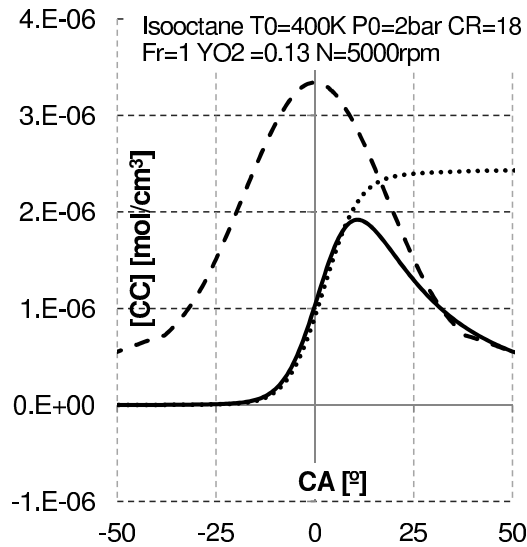


Figure 11: Accumulated concentration of chain carriers considering the effect of the expansion (solid line) and considering only chemical effects (dotted line) versus critical concentration (dashed line). The engine simulated is fuelled with isooctane, it has a compression ratio of 18 and an initial temperature, pressure and oxygen mass fraction of 400 K, 2 bar and 0.13, respectively.

528 frozen, therefore, combustion can not occur.

529 Despite the fact that the RCCC-method and the integral method works  
 530 properly in the range of interest for homogeneous-charge engines, a method  
 531 that takes into account the NTC zone of the fuel is needed in order to im-  
 532 prove the predictions. This new method can be developed following a similar  
 533 methods than the used in this paper, but starting from a simple autoigni-  
 534 tion model with NTC behavior. The authors are working on these methods,  
 535 which will be published in the near future.

536 **8. Conclusions**

537 In this work a new method to predict ignition delays under variable con-  
538 ditions from those obtained under constant conditions is developed. This  
539 method, which is named as the RCCC-method (Relative Concentration of  
540 Chain Carriers method), is theoretically deduced from the Glassman's au-  
541 toignition model and it shows, in general, better results than the Livengood  
542 & Wu integral method.

543 The following conclusions can be deduced from this study:

- 544 • The Livengood & Wu integral is valid despite the hypothesis of constant  
545 critical concentration for a temperature and pressure evolution. The  
546 largest contribution to the integral method is made in a narrow frame  
547 of crank angle degrees in which the assumption of constant critical  
548 concentration is not catastrophic.
- 549 • Since both methods are deduced from models that cannot reproduce  
550 the NTC zone, the more pronounced the NTC regime, the higher the  
551 prediction deviations. Thereby, prediction deviations increase if the  
552 oxygen mass fraction is decreased, the fuel/air equivalence ratio is de-  
553 creased or if fuels with lower octane numbers are used.
- 554 • The prediction deviation increases when the engine speed increases (for  
555 higher ignition crank angles) due to the accumulation of errors caused  
556 by taking more data of the  $\tau$  and  $[CC]_{crit}$  functions.
- 557 • When autoignition occurs in the NTC regime, better predictions can  
558 be obtained from the Livengood & Wu integral method due to, to some  
559 extent, a compensation of errors.

- 560 • The criterion used to define the autoignition should be reformulated in  
561 order to take into account ignitions after TDC. Not only the critical  
562 concentration of chain carriers must be reached, but also the thermo-  
563 dynamic conditions at this instant must allow the combustion progress,  
564 i.e., the chemical paths must not be frozen.
  
- 565 • A new method should be developed from a simple autoignition model  
566 that reproduces the NTC regime.

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574 **Notation**

<i>ATDC</i>	After top dead center
<i>BDC</i>	Bottom dead center
<i>CAD</i>	Crank angle degrees
<i>CC</i>	Chain carriers
<i>CFD</i>	Computational Fluid Dynamics
<i>CI</i>	Compression Ignition
<i>CR</i>	Compression ratio
575 <i>crit</i>	Referred to the critical concentration
<i>EGR</i>	Exhaust Gas Recirculation
<i>Fr</i>	Working equivalence ratio
<i>HCCI</i>	Homogeneous Charge Compression Ignition
<i>ICA</i>	Ignition crank angle
<i>ICE</i>	Referred to a data obtained from CHEMKIN using the internal combustion engine reactor

$k_i$	Specific reaction rate of reaction $i$
$L - W$	Referred to a data obtained from the Livengood & Wu integral
$N$	Engine speed
$NTC$	Negative Temperature Coefficient
$P_0$	Initial pressure
$PCCI$	Premixed Charge Compression Ignition
$PRF$	Primary Reference Fuels
$PSR$	Perfectly Stirred Reactor
$R^2$	Coefficient of determination
$RCCC$	Relative Concentration of Chain Carriers, referred to the new method proposed in this paper
<sup>576</sup> $RCCI$	Reactivity Controlled Compression Ignition
$SI$	Spark Ignition
$t$	Time
$T_0$	Initial temperature
$TDC$	Top Dead Center
$t_i$	Ignition time (ignition delay under variable conditions)
$UHC$	Unburned hydrocarbons
$V$	Volume
$Y_{O_2}$	Oxygen mass fraction
$\xi$	Prediction deviation
$\Delta t$	Time step
$\Delta\theta$	Difference between predicted and simulated ignition crank angles

	$\tau$	Ignition delay
577	$[X_i]$	Concentration of the species $X_i$

578 **Appendix A. Mathematical development for the RCCC-method**

579 The Glassman's model [28] is a simple model to characterize the autoigni-  
580 tion phenomenon by a chain reactions mechanism. It is composed by the five  
581 following reactions:



582

583 The generation rate of chain carriers has the following expression:

$$\frac{d[CC]}{dt} = k_1[R] + (k_2(\alpha - 1) - k_4)[R][CC] - k_5[CC] \tag{A.1}$$



584 The chemical kinetic mechanism will be a chain reactions mechanism if  
 585 reaction (R2) introduces a multiplier effect on the generation of chain carriers.  
 586 This means that the global generation rate of chain carriers must be higher  
 587 than the generation rate corresponding to the initiation reaction. Imposing  
 588 this condition on equation (A.1), there is a critical value of  $\alpha$  from which  
 589 reaction (R2) is characterized as a chain reaction.

$$\alpha_{crit} = 1 + \frac{k_4[R] + k_5}{k_2[R]} \quad (\text{A.2})$$

590 If  $\alpha$  is written as  $\alpha = \alpha_{crit} + \Delta\alpha$ , then, equation (A.1) can be rewritten  
 591 as follows:

$$\frac{d[CC]}{dt} = k_1[R] + \Delta\alpha k_2[R][CC] \quad (\text{A.3})$$

592 Assuming that the concentration of chain carriers is always much smaller  
 593 than the initial concentration of reactants,  $[CC] \ll [R]$ ,  $[R]$  can be con-  
 594 sidered as a constant during the ignition delay period. Considering an air-  
 595 fuel mixture under constant conditions of temperature and pressure, the  
 596 previous differential equation can be integrated with the initial condition  
 597  $t = 0 \rightarrow [CC] = 0$  as follows:

$$\exp(tk_2\Delta\alpha[R]) = 1 + [CC]\frac{k_2}{k_1}\Delta\alpha \quad (\text{A.4})$$

598 where  $\frac{1}{k_2\Delta\alpha[R]}$  is a characteristic time of the process and, therefore, it may  
 599 be proportional to the ignition delay. If  $\delta$  is defined as the corresponding  
 600 proportionality constant, the ignition delay  $\tau$  can be defined as follows:

$$\tau = \frac{\delta}{k_2 \Delta \alpha [R]} \quad (\text{A.5})$$

601 According to the above definition, Eq.(A.4) can be rewritten as follows:

$$\exp\left(\delta \frac{t}{\tau}\right) = 1 + \delta \frac{[CC]}{k_1 [R] \tau} \quad (\text{A.6})$$

602 Thereby, when  $t = \tau$  the start of combustion occurs and the concentration  
 603 of chain carriers is equal to the critical concentration. In this way, the critical  
 604 concentration of active radicals can be defined by the following expression  
 605 obtained from Eq. (A.6):

$$[CC]_{crit} = \frac{\exp(\delta) - 1}{\delta} k_1 [R] \tau = (\exp(\delta) - 1) \frac{k_1}{k_2 \Delta \alpha} \quad (\text{A.7})$$

606 Eq.(A.7) can be combined with Eq.(A.6) in order to obtain an expression  
 607 for the temporal evolution of the concentration of chain carriers that depends  
 608 only on the ignition delay and the critical concentration:

$$\exp\left(\delta \frac{t}{\tau}\right) = 1 + \frac{[CC]}{[CC]_{crit}} (\exp(\delta) - 1) \quad (\text{A.8})$$

609 OF:

$$[CC] = \frac{[CC]_{crit}}{(\exp(\delta) - 1)} \left(1 - \exp\left(\delta \frac{t}{\tau}\right)\right) \quad (\text{A.9})$$

610 Equation that is only valid under constant conditions of pressure and tem-  
 611 perature.

612 A process under variable conditions of pressure and temperature can be  
613 discretized as a series of thermodynamic states that remain constant for a  
614 time  $\Delta t$ . The working air-fuel mixture that has a concentration of chain carri-  
615 ers  $[CC]_j$  under variable thermodynamic conditions at instant  $j$  would reach  
616 the same concentration of active radicals by staying at constant pressure  $P_j$   
617 and constant temperature  $T_j$  during a time  $t_{P_j, T_j}$  defined by Eq. (A.9):

$$[CC]_j = \frac{[CC]_{crit,j}}{\exp(\delta) - 1} \left( 1 - \exp\left(\delta \frac{t_{P_j, T_j}}{\tau_j}\right) \right) \quad (\text{A.10})$$

618 that results in:

$$t_{P_j, T_j} = \frac{\tau_j}{\delta} \ln \left( 1 + \frac{[CC]_j}{[CC]_{crit,j}} (\exp(\delta) - 1) \right) \quad (\text{A.11})$$

619 Thus, if the working air-fuel mixture stay under constant conditions  $P_j, T_j$   
620 for a time  $\Delta t$ , the concentration of chain carriers will be the amount of active  
621 radicals cumulated at time  $j$  plus the amount of active radicals generated  
622 from time  $t_{P_j, T_j}$  to time  $t_{P_j, T_j} + \Delta t$  following Eq. (A.9). Furthermore, the  
623 concentration of chain carriers is not only affected by the generation of new  
624 radicals during  $\Delta t$ , but also by the volume variation of the compression-  
625 expansion process. Thus, the concentration of chain carriers at time  $j + 1$   
626 can be obtained from the data at time  $j$  by the following equation:

$$[CC]_{j+1} = \left( \frac{[CC]_{crit,j}}{\exp(\delta) - 1} \left( \exp\left(\delta \frac{t_{P_j, T_j} + \Delta t}{\tau_j}\right) - 1 \right) \right) \frac{V_j}{V_{j+1}} \quad (\text{A.12})$$

627 Which results in the following equation regarding the expression  $t_{P_j, T_j}$   
628 (Eq. (A.11)):

$$[CC]_{j+1} = \left( \left( \frac{[CC]_{crit,j}}{\exp(\delta) - 1} + [CC]_j \right) \exp\left(\delta \frac{\Delta t}{\tau_j}\right) - \frac{[CC]_{crit,j}}{\exp(\delta) - 1} \right) \cdot \frac{V_j}{V_{j+1}} \quad (\text{A.13})$$

629 If  $RCCC_j$  is defined as the ratio between the concentration of chain carri-  
 630 ers and the critical concentration (Relative Concentration of Chain Carriers)  
 631 at instant  $j$  ( $RCCC_j = [CC]_j/[CC]_{crit,j}$ ), the autoignition will occur when  
 632  $RCCC_j = 1$  and Eq. (A.13) can be rewritten as follows by dividing the  
 633 equality by  $[CC]_{crit,j}$ :

$$RCCC_{j+1} = \frac{[CC]_{crit,j}}{[CC]_{crit,j+1}} \frac{V_j}{V_{j+1}} \left( \left( \frac{1}{\exp(\delta) - 1} + RCCC_j \right) \exp\left(\delta \frac{\Delta t}{\tau_j}\right) - \frac{1}{\exp(\delta) - 1} \right) \quad (\text{A.14})$$

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