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1 Understanding the Role of Soot Oxidation in Gaso- 2 line Combustion: a Numerical Study on the Effects 3 of Oxygen Enrichment on Particulate Mass and Num- 4 ber Emissions in a Spark-Ignition Engine

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Spark-Ignition Engine Simulations.*

12 Abstract

13 The production of increasingly clean engines has become imperative. More stringent
14 regulations for internal combustion engines are constantly proposed, and recent number-
15 based regulations have become a new challenge, since historically only a mass-based
16 regulation needed to be met. It is known that soot particles detectable at the exhaust
17 of an engine are the results of the competition between the formation of soot precursor
18 species and their oxidation. However, the attention is mainly focused on inhibiting soot
19 precursors formation, and much less research is dedicated at elucidating the benefits
20 achievable from enhancing soot oxidation rates. Soot oxidation can be enhanced by
21 increasing the in-cylinder oxygen content. Oxygenated fuels, which are often added to
22 gasoline in order to achieve more efficient combustion, can represent a possible way
23 for achieving this goal. However, chemical mechanisms are still uncertain for practical
24 fuels, and ambiguous results can be produced when the effect of oxygenated fuels on
25 gasoline engine combustion and soot emissions is considered. In the present study, 3-D
26 Computational Fluid Dynamics simulations were performed and the numerical results
27 were compared with existing experimental data, in which load increases were achieved by
28 pure oxygen addition within the intake manifold of a single-cylinder Spark-Ignition (SI)
29 engine. Studying the effects that an addition of 5% and 10% by volume (with respect
30 to air) of additional oxygen produces on the combustion process, allowed to provide
31 basic additional information on soot formation and oxidation, avoiding the uncertainties
32 associated with chemistry models. A semi-detailed soot model and a chemical kinetic

33 model, including poly-aromatic hydrocarbon formation, were coupled with the G-
34 equation flame propagation model for SI engine simulations and for predictions of
35 soot mass and particulate number density. Improvements in the modeling of gasoline
36 premixed combustion were achieved, as well. Specifically, different approaches in the
37 evaluation of the laminar flame speed of gasoline (which is a key factor for obtaining
38 reliable SI engine simulations) were critically compared and analyzed. The numerical
39 results showed aspects that were not possible to appreciate by only referring to the
40 experimental results on which this work was based. It was possible to observe that the
41 higher soot concentrations were located in regions characterized by lower temperatures
42 and lower OH concentrations. Oxygen addition favored a faster burning velocity and
43 produced higher in-cylinder temperatures. However, the production rates of both OH
44 radicals and soot precursor species resulted enhanced. The analysis of these concurrent
45 phenomena allowed to explain why in the experiments the soot mass per kg of fuel was
46 lower for the oxygenated combustion cases.

47 **1 Introduction**

48 The recent establishment of a limit on Particle Number (PN) concentration and more
49 stringent limits on Particulate Mass (PM) has increased the efforts putted worldwide
50 into better understanding the production mechanisms of particulate emissions [1–4].
51 More attention has been focused on developing new emissions reduction strategies, which
52 generally consist of the simultaneous implementation of new combustion techniques [5–7]
53 coupled with innovative control methods [8–10].

54 In this scenario, it is becoming conventional wisdom that gasoline Spark-Ignition
55 (SI) engines show a wider margin for further improve their efficiency and meet upcoming
56 stringent emission regulations, in comparison to Diesel engines [11, 12]. In fact, the
57 introduction of the high boost and downsizing techniques offers the potential to increase
58 power density and limit pumping and friction losses [13, 14]. Moreover, the gasoline
59 direct injection strategy has recently attracted great interest due to its capability
60 to further improve fuel economy and reduce gaseous emissions [15]. However, the
61 development of such technologies is far from being considered completely mature and
62 is challenging for engine designers [16, 17]. The main limitations are imposed by the
63 occurrence of abnormal combustion modes [18, 19], especially concerning the direct
64 injection technology applied to highly boosted downsized engines operating at low-speed
65 and high-load regimes [20–23].

66 Oxygen-enriched combustion has been widely studied in order to provide an addi-
67 tional alternative for turbo-charging, especially in the case of downsized SI engines.
68 An oxygen-enriched mixture can serve both as a booster to increase engine output
69 and as a combustion enhancer when the engine operates at low loads or in cold start

70 conditions. In fact, it has been pointed out that, adding oxygen can results in higher
71 power densities [24–27] low carbon monoxide and hydrocarbon emissions [27–29], as well
72 as it can reduce cold-start emissions [24, 30]. This because the addition of oxygen leads
73 to a decrease in the combustion phase, namely a more complete and quick combustion
74 is achievable [24, 28, 31], also due to less mixing and reaction irreversibilities [25].

75 Thus, oxygen addition, coupled with downsizing, can ensure a typical requirement
76 for a SI engine in terms of power, but with the advantage of employing a smaller
77 and lighter engine. By controlling the oxygen content, it is possible to optimize the
78 downsized operating mode due to the direct effect on the combustion process and
79 overall engine thermodynamics [24, 25]. However, oxygen-enriched combustion includes
80 some intrinsic drawbacks, that need to be accounted for, such as higher nitrogen oxides
81 emissions, higher in-cylinder and exhaust temperatures, and costs.

82 An alternative way to meet present emission requirements being considered by
83 several researchers consists in the use of alternative fuels, since it has been found
84 that fuel selection impacts the power output and exhaust emission of vehicles [23, 32].
85 Therefore, investigating the behavior of alternative fuels, as well as of their mixtures,
86 represents a practical mid-term solution for the automotive marketplace, until more
87 advanced technologies are available and become more economically attractive [33–37].

88 Oxygenated fuels represent an interesting choice and they are often added to gasoline
89 in order to achieve more efficient combustion. For example, alcohols, such as ethanol,
90 butanol, and their blends with gasoline are considered as valid alternative fuels and
91 have been extensively studied by many researchers [23, 38–41]. In particular, ethanol
92 has become an additive of choice for oxygenated fuels in many places around the
93 world [6, 23, 39, 40]. However, a number of other chemical compounds could be added
94 to the fuel to produce the desired effects [42]. For example, the use of gasoline containing
95 3 to 10 vol% of bioethanol is being promoted in many parts of the world [43]. Ethanol
96 has the potential to improve engine efficiency and to reduce harmful emissions when
97 used as the fuel in a spark-ignited engine [39, 41]. Kim et al. [40] highlighted that in
98 order to fully utilize the merits of ethanol, the fuel-blending ratio should be changed
99 according to the engine operating conditions. Other advantages include its high octane
100 number and its self-sustainability, since it is obtained from renewable energy sources [41].
101 However, the effect on particulate emissions is not well understood.

102 Chemical mechanisms are still uncertain for practical fuels, and ambiguous results
103 can be produced when the effect of oxygenated fuels on gasoline engine combustion is
104 considered [44–46]. To better assess the influence on engine performance and emissions,
105 it is necessary to developed well validated detailed kinetic models for combustion and
106 oxidation of the components of biofuels. In addition, as Tran et al. [44], when reviewed
107 the major detailed kinetic models already proposed in the literature, highlighted that
108 some of the most recent mechanisms can be very large in terms of the species and

109 reactions involved: for instance, the model of Harper et al. [47] for the oxidation of
110 n-butanol consists of 263 species and 3381 reactions and that of Herbinet et al. [48]
111 for the oxidation of methyl palmytate includes 30425 reactions and 4442 species. More
112 practical and reliable approaches should be taking into account in order to provide more
113 insight on this complex and comparatively new field, which particle characterization
114 from vehicle emissions is.

115 When the goal is reducing soot emissions, the common thought is that the best way
116 consists in inhibiting the formation of soot precursors. However, it must be highlighted
117 that soot emissions are characterized by two competing in-cylinder processes, namely
118 soot formation and soot oxidation. So that, soot oxidation rates can also have a strong
119 effect on soot emissions levels and improving the oxidation rate can result in beneficial
120 effects [49–52]. Therefore, it should not surprise that previous studies have shown that
121 reducing the formation of soot did not necessarily correlate with a reduction of soot
122 emissions [53], especially when the availability of oxidizers is reduced and hence the
123 oxidation process inhibited.

124 It is well known that temperature has a strong influence on chemical reaction rates.
125 In the case of soot, it has been observed that the rate of the reactions involved in soot
126 oxidation increase faster with temperature than those of the reactions responsible for
127 soot formation [54]. An interesting result pointed out by Gallo et al. [49] indicates that
128 global turbulence levels are not necessarily beneficial. By means of laser extinction
129 measurements carried out on an optical heavy-duty diesel engine, they found that
130 varying swirl and engine speed produced ambiguous trends. A possible explanation
131 provided in that work was based on the supposition that soot formation extremely
132 depends on local conditions, which means that turbulence needs to be increased at the
133 specific locations where soot is oxidized for obtaining appreciable effects.

134 In the present study, in order to provide additional basic information and, at the same
135 time, to avoid uncertainties from chemistry models, load increases in stoichiometric
136 SI engine combustion were achieved by pure oxygen addition as a first step. 3-D
137 Computational Fluid Dynamics simulations were performed and the numerical results
138 were compared with existing experimental data carried out by Catapano et al. [27], in
139 which 5% and 10% by volume of additional oxygen (with respect to air) was mixed with
140 gasoline within the intake manifold of a small single-cylinder Port Fuel Injection SI
141 engine. Different engine operating conditions were also considered for a more exhaustive
142 analysis.

143 For the numerical study, the KIVA3V Release 2 code, coupled with a Jacobian
144 Chemistry solver, SpeedCHEM, was used [55]. The semi-detailed soot model of Vish-
145 wanathan et al. [56] with Jiao and Reitz’s improvements [57] and a chemical kinetic
146 mechanism that includes iso-octane/n-heptane/toluene/PAH [58], were coupled with
147 the Discrete Particle Ignition Kernel model [59] and the G-equation flame propagation

148 model [60, 61] for the Spark-Ignition engine simulations and for predictions of soot mass
149 and particulate number density. In addition, a discrete multi-component fuel surrogate
150 approach was used to model the physical and chemical properties of real gasoline, as
151 proposed in [58]. A more accurate formulation for predicting the laminar flame speed
152 of gasoline, which is a vital scaling factor for a successful SI engine simulation, was
153 employed in the present work [62]. For achieving this purpose, different approaches
154 available in the literature for evaluating the laminar flame speed were compared and
155 critically analyzed.

156 Two different engine speeds were considered for the simulations, namely 2000 and
157 4000 rev/min, which were assumed to be representative, respectively, of low and high
158 engine speed regimes. In accordance with the experimental tests, beside the baseline
159 conditions, the effects of increasing the initial oxygen content by 5% and 10% were
160 investigated. For the low-speed case, the results were further analyzed to provided in-
161 cylinder soot distributions and to better understand the reasons for the experimentally
162 observed soot particle size distributions.

163 **2 Modeling approach**

164 The multi-dimensional KIVA-3V code developed at the Los Alamos National Labo-
165 ratory [63–65] was used for the present modeling work. In particular, the modified
166 version of KIVA-3V developed at the Engine Research Center (ERC) of the University of
167 Wisconsin-Madison was adopted and includes improvements in its ignition, combustion
168 and emission models.

169 The KIVA code was coupled with the SpeedCHEM code [55], where KIVA models
170 the fuel preparation, the governing equations for using conservation of mass, momentum
171 and energy, as well as species transport, and SpeedCHEM solves the gas phase fuel
172 chemistry. The chemistry solver is called for each cell and the fuel chemistry is modeled
173 using a kinetic reaction mechanism that contains the species and thermodynamic data
174 for a given fuel, as well as reactions and reaction rates information that describe the
175 oxidation process. Each computational cell is considered to be a Well-Stirred Reactor
176 (WSR), and the production rates for each species are calculated and used with the mass
177 fraction, density, and molecular mass to form new species based on the reactions in the
178 mechanism. Species concentration changes are returned to KIVA and these values are
179 used to calculate the energy release at each time step in the calculation.

180 The main sub-models used for the SI engine simulation are briefly described here,
181 together with the improvements made for a more accurate evaluation of gasoline flame
182 propagation, essential to correctly predict combustion phasing and in-cylinder pressure
183 evolution.

184 2.1 Spark-ignition model

185 In a SI engine the combustion process is initiated as a point-source ignition kernel by
 186 the triggering of the spark and then governed by the subsequent flame propagation
 187 phenomenon.

188 Although the early stage of ignition is important, it is not practical to resolve the
 189 process in detail in engine CFD simulations, because the typical grid-size and time step
 190 used is larger than that needed to describe this early stage of ignition precisely. Thus,
 191 a relatively simple sub-grid scale model is needed to simulate the early ignition process.
 192 In the present work, the growth of the ignition kernel is tracked by using the so-called
 193 Discrete Particle Ignition Kernel (DPIK) model developed by of Fan et al. [59] and
 194 improved by Tan and Reitz [61].

195 In the DPIK model, following a Lagrangian approach, the ignition kernel is repre-
 196 sented by particles that move radially outwards from the spark-plug electrodes. The
 197 kernel grows by keeping a spherical shape and its growth rate depends upon several
 198 parameters, i.e., the mixture strength, the turbulence intensity, the spark discharge
 199 energy, the gas temperature and pressure. Assuming the temperature inside the kernel
 200 to be uniform, the kernel growth rate is:

$$\frac{dr_{ker}}{dt} = \frac{\rho_u}{\rho_{ker}} (S_{plasma} + S_T), \quad (1)$$

201 where r_{ker} is the kernel radius, ρ_u is the local unburnt gas density, S_T is the turbulent
 202 flame speed, and ρ_{ker} is the gas density inside the kernel region. Based on the energy
 203 balance analysis of the ignition kernel thermodynamic system, the plasma velocity
 204 S_{plasma} is given as [61]:

$$S_{plasma} = \frac{\dot{Q}_{spk} \eta_{eff}}{4\pi r_{ker}^2 \left[\rho_u (u_{ker} - h_u) + p \frac{\rho_u}{\rho_{ker}} \right]}, \quad (2)$$

205 where \dot{Q}_{spk} is the electrical energy discharge rate, η_{eff} is the electrical energy transfer
 206 efficiency due to heat loss to the spark plug. $\eta_{eff} = 0.3$, as suggested by Heywood [66]
 207 is used in this study. ρ_u and h_u are the density and specific enthalpy of the unburnt
 208 mixture, respectively. ρ_{ker} and u_{ker} are the density and internal energy of the mixture
 209 inside the kernel.

210 To account for turbulent strain and curvature effects on the kernel flame, the
 211 unstretched laminar flame speed S_L^0 was multiplied by a stretch factor, following the
 212 form proposed by Herweg et al. [67] (cf. [59, 61]).

213 For the cells that do not contain the kernel flame particles, the chemical source
 214 terms are calculated by detailed chemistry based on the WSR assumption

215 **2.2 Transition from kernel growth to turbulent flame propa-**
 216 **gation**

217 The DPIK model is used when the flame is not significantly disturbed by the turbulence.
 218 However, when the kernel size exceeds a critical diameter, a the transition from the
 219 kernel growth model to the actual turbulent flame propagation calculation is required.
 220 This transition follows the criteria introduced by Liang and Reitz [68], and it is based
 221 on the local turbulent integral length scale, l , of the flow, viz.:

$$r_k \geq C_m l = C_m \cdot 0.16 \cdot \frac{k^{\frac{3}{2}}}{\varepsilon} \quad (3)$$

222 where k and e are the turbulent kinetic energy and its dissipation rate, respectively. C_m
 223 is the only model constant that needs to be tuned within the code used for the present
 224 work.

225 **2.3 G-equation model**

226 The G-equation model is than called for calculating the turbulent flame front evolution.
 227 Based on a flamelet approach, it assumes that the burnt and unburnt gases are separated
 228 by the flame brush, which is modeled as a 3-dimensional surface, defined by the equation
 229 $G(\mathbf{x}, t) = 0$. This surface divides the flow field into an unburnt region, $G < 0$, and a
 230 burnt gas region, $G > 0$.

231 The G-transport equation formulated by Peters [69], valid in both *thin reaction zone*
 232 and *corrugated flamelets* regimes, was adopted:

$$\rho \frac{\partial G}{\partial t} + \rho \mathbf{u} \cdot \nabla G = (\rho S_L^0) \sigma - (\rho D) \kappa \sigma, \quad (4)$$

233 where \mathbf{u} is the bulk fluid velocity of the unburnt mixture ahead of the flame front, ρ its
 234 density, S_L^0 the unstretched planar laminar flame speed, κ the flame curvature and σ is
 235 the turbulent to laminar flame surface area ratio or equivalently the flame speed ratio,
 236 i.e.,

$$\sigma = \frac{A_T}{A_L} = \frac{S_T^0}{S_L^0} = 1 + \frac{S_T^0 - S_L^0}{S_L^0} = |\nabla \tilde{G}| + \sigma_T, \quad (5)$$

237 and σ_T accounts for the turbulent contribution to the flame surface area ratio σ . More
 238 information about the terms appearing in Equations (4) and (5), as well as their
 239 derivation, can be found in [69].

240 Based on Equation (4), a set of Favre-averaged level set equations applicable to
 241 both regimes can be derived, including the equations for the Favre mean, \tilde{G} , and its
 242 variance, $\overline{G'^2}$, and a model equation for the flame surface area ratio σ_T . These equations,
 243 together with the Reynolds averaged Navier-Stokes equations and the $k - \epsilon$ turbulence
 244 modeling equations, form a complete set to describe premixed turbulent flame front

245 propagation [69]. Considering the Arbitrary Lagrangian-Eulerian (ALE) numerical
 246 method used in the KIVA code, the equation set, accounting for the change of \tilde{G} value
 247 due to the velocity of the moving vertex, \mathbf{u}_{vertex} [70], suitable for KIVA implementation,
 248 is:

$$\frac{\partial \tilde{G}}{\partial t} + (\tilde{\mathbf{u}} - \mathbf{u}_{vertex}) \cdot \nabla \tilde{G} = \frac{\bar{\rho}_u}{\bar{\rho}} S_T^0 |\nabla \tilde{G}| - D_T \tilde{\kappa} |\nabla \tilde{G}|, \quad (6)$$

249

$$\frac{\partial \widetilde{G''^2}}{\partial t} + \tilde{\mathbf{u}} \cdot \nabla \widetilde{G''^2} = \nabla_{\parallel} \cdot \left(\frac{\bar{\rho}_u}{\bar{\rho}} D_T \nabla_{\parallel} \widetilde{G''^2} \right) + 2D_T (\nabla \tilde{G})^2 - c_s \frac{\tilde{\varepsilon}}{\tilde{k}} \widetilde{G''^2} \quad (7)$$

$$\begin{aligned} \bar{\rho} \frac{\partial \bar{\sigma}_T}{\partial t} + \bar{\rho} \tilde{\mathbf{u}} \cdot \nabla \bar{\sigma}_T = \nabla_{\parallel} \cdot (\bar{\rho} D_T \nabla_{\parallel} \bar{\sigma}_T) + c_0 \bar{\rho} \frac{(-\mathbf{u}'' \mathbf{u}'') : \nabla \tilde{\mathbf{u}}}{\tilde{k}} \bar{\sigma}_T + \\ c_1 \bar{\rho} \frac{D_T (\nabla \tilde{G})^2}{\widetilde{G''^2}} \bar{\sigma}_T - c_2 \bar{\rho} \frac{S_L^0 \bar{\sigma}_T^2}{(\widetilde{G''^2})^{1/2}} - c_3 \bar{\rho} \frac{D \bar{\sigma}_T^3}{\widetilde{G''^2}}, \quad (8) \end{aligned}$$

250 where ∇_{\parallel} is the tangential gradient operator, \mathbf{u} the fluid velocity, \mathbf{u}'' the turbulence
 251 intensity, D_T the turbulent diffusivity, and c_s , c_0 , c_1 , c_2 , and c_3 are modeling constants
 252 (cf. Ref. [69]), \tilde{k} and $\tilde{\varepsilon}$ are the Favre mean turbulent kinetic energy and its dissipation
 253 rate from the RNG $k - \varepsilon$ model [71]. $\tilde{\kappa}$ is the Favre mean flame front curvature defined
 254 as

$$\tilde{\kappa} = \nabla \cdot \left(\frac{\nabla \tilde{G}}{|\nabla \tilde{G}|} \right). \quad (9)$$

255 **2.4 Primary heat release and species conversion within the** 256 **turbulent flame brush**

257 The information about the flame front position allows the calculation of the species
 258 conservation rate in the flame-containing cells and, consequently, the associated primary
 259 heat release at the flame front. In the code, a method based on the sub-grid scale
 260 unburnt/burnt volumes [60] was implemented for this purpose. Namely, the sub-grid
 261 scale volumes are tracked each time step based on the coordinate information of the
 262 cell vertices and the flame surface piercing points. The species density conversion rate
 263 then is expressed as:

$$\frac{\partial \rho_i}{\partial t} = \rho_u (Y_{i,u} - Y_{i,b}) \frac{A_{f,i4}}{V_{i4}} S_t^0, \quad (10)$$

264 where the $Y_{i,u}$ and $Y_{i,b}$ are the mass fractions of species i in the unburnt and burnt
 265 mixtures, respectively. A_f is the mean flame front area and V is the cell volume, $i4$ is
 266 the cell index used in the KIVA code.

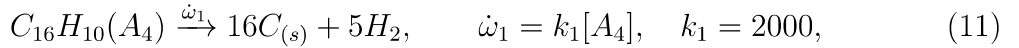
267 Chemical reaction mechanisms are applied to model the secondary heat release and
 268 pollutant formation within the diffusion flames behind the flame front. Specifically, a
 269 reduced chemical kinetic mechanism that includes iso-octane/n-heptane/toluene/PAH

270 (89 species and 506 reactions) [58] was used in this study for this purpose.

271 2.5 Semi-detailed soot model

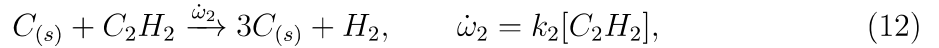
272 The semi-detailed soot model by Vishwanathan et al. [56], with Jiao and Reitz's
 273 improvements [57] was coupled with the above-mentioned chemistry mechanism, for
 274 accounting for the nucleation of soot particles from PAH. The smallest incipient particle
 275 size is assumed to start from 1.25 nm (size of 100 carbon atoms).

276 The soot particles, $C_{(s)}$, are assumed to be formed from the PAH species pyrene
 277 (A_4) via the reaction



278 where $[A_4]$ represents the concentration of A_4 in mol/cm^3 , and k_1 has units of $[1/s]$.

279 Once formed, the particles grow via the *Hydrogen Abstraction-C₂H₂ Addition* (HACA)
 280 mechanism:



281 where

$$k_2 = 9.0 \cdot 10^4 e^{-12100/T} \cdot \sqrt{S}, \quad \text{with } S = \pi d_p^2 N, \quad (13)$$

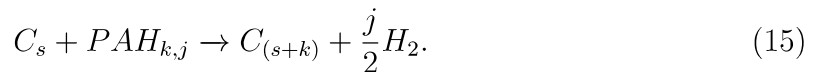
282 where S is the soot surface area per unit volume in $[1/cm]$, d_p is the particle diameter,
 283 and N is the soot number density in $particles/cm^3$.

284 The soot species density can be correlated with soot particle number density based
 285 on mass conservation in each computational cell, via.,

$$\left(\frac{\pi}{6} d_d^3 \rho_{C_{(s)}} \right) n = Y_{C_{(s)}} \rho V, \quad (14)$$

286 where $n = N \nabla$, is the number of particles in a cell, and V is the volume of the cell. $\rho_{C_{(s)}}$
 287 is the soot density for which the density of graphite ($2.0 g/cm^3$) is used throughout this
 288 study, and ρ is the ambient density, Y_{C_s} is the soot mass fraction.

289 In addition, soot growth is modeled via PAH condensation from



290 PAHs up to four rings ($A_1 \sim A_4$) are included in the current chemistry mechanism, and
 291 they also participate in the soot surface growth.

292 A decrease of particle number density is assumed to occurring during particle
 293 coagulation processes, which is modeled using the normal square dependence. The soot
 294 particles coagulate following:



Table 1: Considered steps in soot formation and oxidation. $C_{(s)}$ represents soot, $PAH_{k,j}$ is a PAH species with k carbon and j hydrogen atoms.

Step	Reactions
Soot inception	$C_{16}H_{10}(A_4) \rightarrow 16C_{(s)} + 5H_2$
Soot surface growth	$C_{(s)} + C_2H_2 \rightarrow 3C_{(s)} + H_2C_{(s)} + PAH_{k,j} \rightarrow C_{(s+k)} + \frac{j}{2}H_2$
Soot coagulation	$nC_{(s)} \rightarrow C_{(s)n}$
Soot oxidation	$C_{(s)} + 0.5O_2 \rightarrow CO$ $C_{(s)} + OH \rightarrow CO + 0.5H_2$

295 with

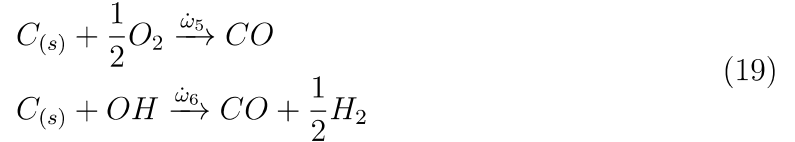
$$\dot{\omega}_3 = k_3 \left[\frac{\rho Y_{C_{(s)}}}{M_{C_{(s)}}} \right] [N]^{11/6} \quad (17)$$

296 and

$$k_3 = 2C_a \left(\frac{6M_{C_{(s)}}}{\pi \rho_{C_{(s)}}} \right)^{1/6} \left(\frac{6k_b T}{\rho_{C_{(s)}}} \right)^{1/2}, \quad (18)$$

297 where $M_{C_{(s)}}$ is the molecular weight of carbon, C_a the constant is the agglomeration
 298 constant with the value of 9.0 suggested by Leung et al. [72] used in this work. Generally,
 299 this step reduces the soot number density. k_b is Boltzmann's constant ($1.38054 \cdot$
 300 10^{-16} erg/K). It can be observed from Equations 17 and 18 that the soot coagulation
 301 rate depends on particle number density and the temperature in each CFD computational
 302 cell.

303 Oxidation occurs by O_2 and OH following:



304 where the reaction rates of O_2 and OH oxidation are $\dot{\omega}_5$ and $\dot{\omega}_6$, respectively.

305 All steps for soot formation and oxidation are summarized in Table 1.

306 The soot species density and soot number density are treated as passive species in
 307 the model, and their transport equations are represented as:

$$\frac{\partial M}{\partial t} = -\nabla \cdot (M \cdot \mathbf{v}) + \nabla \cdot \left(\frac{\mu}{SC} \cdot \nabla \left(\frac{M}{\rho} \right) + \varsigma M \frac{\mu}{\rho} \frac{\nabla T}{T} \right) + \dot{S}_M \quad (20)$$

308 where M stands for either soot species density ($Y_{C_{(s)}} \cdot \rho$) in g/cm^3 or soot number
 309 density (N) in $partiles/cm^3$. \mathbf{v} (cm/s) is the CFD gas-phase velocity, SC is the
 310 Schmidt number, μ is the fluid viscosity, T is the temperature of the CFD computation
 311 cell, and \dot{S}_M represents source terms.

312 Details of the steps of the soot model and the source terms for both soot species
 313 density and soot number density are described by Vishwanathan [56]. Additionally,
 314 source terms for ($A_2 \sim A_4$) PAH-surface-growth-assisted steps are also included in the

315 source terms, since they are considered in the current soot model [57].

316 It must be highlighted that in the present soot model the soot particles are assumed
 317 to be spherical and with a single possible size and number density allowed in each
 318 computational cell. In this way, the model is locally mono-disperse (on a cell basis).
 319 However, the soot diameter and number density can vary from one computational cell
 320 to another through the transport equations of both the soot species density and soot
 321 number density.

322 2.6 Gasoline modeling

323 As showed above, the prediction of the turbulent burning velocity plays an essential
 324 role in modeling SI engine combustion. The most crucial scaling factor that affects the
 325 reliability of the G-equation model is represented by the laminar flame speed, as can be
 326 inferred by the relationship that links the turbulent flame speed S_T^0 to the estimated
 327 value for the laminar flame speed S_L^0 in the G-equation model, namely:

$$\frac{S_T^0}{S_L^0} = 1 + I_P \left\{ -\frac{a_4 b_3^2}{b_1} \frac{\ell_I}{\ell_F} + \left[\left(\frac{a_4 b_3^2}{b_1} \frac{\ell_I}{\ell_F} \right)^2 + a_4 b_3^2 \frac{u' \ell_I}{S_L^0 \ell_F} \right]^{1/2} I_P \right\} \quad (21)$$

328 (specific information about the terms appearing in Equation (21) can be found in [68]).

329 The laminar flame speed is an intrinsic property of the fuel mixture, which therefore
 330 means that it is uniquely defined once the unburnt mixture composition, temperature
 331 and pressure are known. Encouraging progress has been made in developing detailed
 332 chemical kinetic models for its prediction, but such models are still extremely complex
 333 and require significant computational effort [73]. Thus, experimental-derived analytical
 334 correlations are preferred in engine practical simulations. Such empirical correlations are
 335 also more easily implemented in CFD codes than tabulated data. Their implementation
 336 allows to restrict the use of detailed chemical kinetics to the solely modeling of the
 337 post-flame and the end-gas chemistry, which does not require high resolution, thus
 338 saving computational time [74].

339 The most widespread used form for an empirical correlation is the so-called “power
 340 law” formula:

$$S_L^0(\phi, T_u, p_u) = S_{L0} \left(\frac{T_u}{T_0} \right)^\alpha \left(\frac{p_u}{p_0} \right)^\beta, \quad (22)$$

341 where S_{L0} is the velocity measured at $T_u = T_0$ and $p_u = p_0$ for a given equivalence ratio
 342 ϕ , and α and β are mixture strength-dependent terms.

343 One of the most widely used correlation having this form was derived by Metghalchi
 344 et al. [75] in 1982, from measurements carried out in a constant volume vessel for
 345 fuel-air equivalence ratios $\varphi = 0.8 \div 1.5$, over pressure and temperature ranges of
 346 $p_u = 0.4 \div 50 \text{ atm}$ and $T_u = 298 \div 750 \text{ K}$, for methanol, propane, iso-octane and

347 indolene. They found that the reference velocities S_{L0} could be fit by a second-order
 348 polynomial of the form:

$$S_{L0}(\phi) = 26.32 - 84.72(\phi - 1.13)^2. \quad (23)$$

349 The fuel-type independent exponents α and β were represented by the expressions:

$$\begin{aligned} \alpha(\phi) &= 2.18 - 0.8(\phi - 1) \\ \beta(\phi) &= 0.16 + 0.22(\phi - 1). \end{aligned} \quad (24)$$

350 In Equation (22) they considered $p_0 = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$, and recommended
 351 expressions for application in the ranges: $p_u = 1 \div 50 \text{ atm}$ and $T_u = 350 \div 700 \text{ K}$.

352 Although the Metghalchi et al. formulation [75] for the reference velocities S_{L0}
 353 has gained a lot of popularity (it has been used in many numerical studies, even in
 354 the case of fuels that were not those for which it was validated) has the drawback of
 355 predicting negative flame speeds for very lean or very rich mixtures. In addition it was
 356 not developed specifically for gasoline, so that the use of the value derived for iso-octane,
 357 as surrogate, can produce ambiguous results.

358 A practical solution to the intrinsic problem of that polynomial form, was proposed
 359 in 2006 by Liang and Reitz [68], who suggested the use of Gülder's correlation [76]
 360 (1984) for the room temperature burning velocity S_{L0} , which has the following form:

$$S_{L0}(\phi) = W \phi^\eta e^{-\xi(\phi-\sigma)^2}, \quad (25)$$

361 where W , η , ξ and σ are constants for a given fuel. In their study, Liang and Reitz [68]
 362 correlated the experimental data for iso-octane by Metghalchi et al. [75] within the
 363 range $\varphi = 0.65 \div 1.6$, obtaining the following expression for Equation (25):

$$S_{L0}(\phi) = 26.9 \phi^{-0.134} e^{-3.86(\phi-1.146)^2}. \quad (26)$$

364 The same coefficients for exponents α and β proposed by Metghalchi et al. for iso-
 365 octane [75] were used [68].

366 Liang and Reitz used the derived correlation for studying a stratified charge two-
 367 stroke gasoline engine, obtaining good agreement with measured data [68]. However,
 368 more recently, the same correlation was employed by Jiao and Reitz (2014) to simulate
 369 a four-stroke gasoline SI engine under premixed conditions [57], and the results were
 370 not as good as for the former case. In this study, to reproduce the characteristics of
 371 a EPA Tier II EEE gasoline, in the simulations, the fuel was modeled as a surrogate
 372 binary mixture of iso-octane and toluene. However, the ignition timing, as well as the
 373 equivalence ratio, were adjusted case-by-case in order to match the C/O ratio of the
 374 Tier II EEE certification and, mostly, for reproducing the experimental in-cylinder

375 pressure traces. The discrepancies were mainly attributed to the flame propagation
 376 speeds, which were not in accordance with the experimental values.

377 In the work by Liang and Reitz [68] pure iso-octane was used in the simulations, but
 378 it was not provided any chemical or physical specification related to the gasoline used in
 379 the experiments. It is hard to infer any general result regarding flame propagation from
 380 this study, because the working operation of the two-stroke DISI engine used in the
 381 work is heavily influenced by the mixture preparation and the spray-related processes.

382 In the case of the four-stroke Port Fuel Injection engine used in the work by Jiao
 383 and Reitz [57], in which fully-premixed conditions reign (and the combustion process is
 384 exclusively governed by the turbulent flame propagation phenomenon), it was necessary
 385 to adjust some parameters, in order to compensate the inaccuracies relying on the
 386 evaluation of the laminar flame speed. This depends upon the fact that the analytical
 387 correlation used for predicting the flame speed of commercial gasoline, was actually
 388 derived for iso-octane, which cannot be considered a reasonable surrogate of gasoline in
 389 terms of laminar flame speed.

390 More recently, Amirante et al. [62] (2017) proposed a specific formulation for
 391 gasoline. It was developed on the basis of experimental measurements obtained by
 392 several workers and available in the literature. The correlation has the “power law” form
 393 of Equation (22), with $p_0 = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$. The $S_{L0}(\phi)$ term is represented
 394 by using “Gülder’s exponential formulation” of Equation (25), and the data fitting
 395 produced the following expression:

$$S_{L0}(\phi) = 36.82 \phi^{-0.20} e^{-6.45(\phi-1.08)^2}. \quad (27)$$

396 For the exponents α and β a second-order polynomial fitting was proposed:

$$\begin{aligned} \alpha(\phi) &= 3.28\phi^2 - 7.52\phi + 5.93 \\ \beta(\phi) &= -0.925\phi^2 + 2.012\phi - 1.365. \end{aligned} \quad (28)$$

397 The latter polynomial form for α and β can better reproduce the influence of pressure
 398 and temperature on the lean and rich sides, in comparison to the linear expression
 399 proposed by Metghalchi et al. [75] and used by Liang and Reitz [68] and Jiao and
 400 Reitz [57]. This because Metghalchi et al.’s expression [75] was derived by considering
 401 only three different equivalence ratios near stoichiometric conditions [62].

402 Figure 1 shows a comparison between the results obtainable by employing the analyt-
 403 ical correlations developed by Amirante et al. [62] (Equations (27) and (28)), Liang and
 404 Reitz [68] (Equations (26) and (24)) and Metghalchi et al. [75] (Equations (23) and (24)).
 405 The comparison is made against data collected in two different studies, namely, the
 406 work by Sileghem et al. [77], who recently measured the laminar burning velocities for
 407 a gasoline Exxon 708629-60 using the heat flux method on a flat flame adiabatic burner

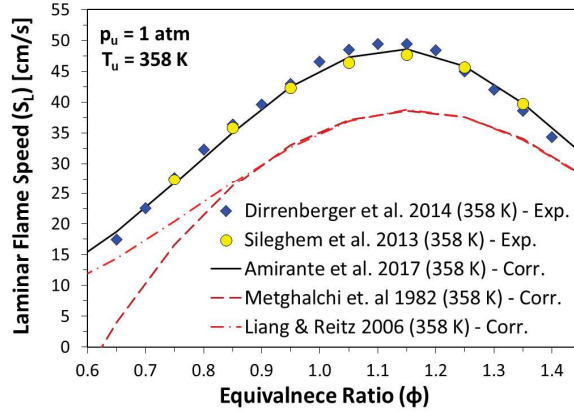


Figure 1: Comparisons between the effectiveness in reproducing experimental measurements of gasoline laminar flame speed of the analytical correlations by Amirante et al. [62], Liang and Reitz [68] and Metghalchi et al. [75].

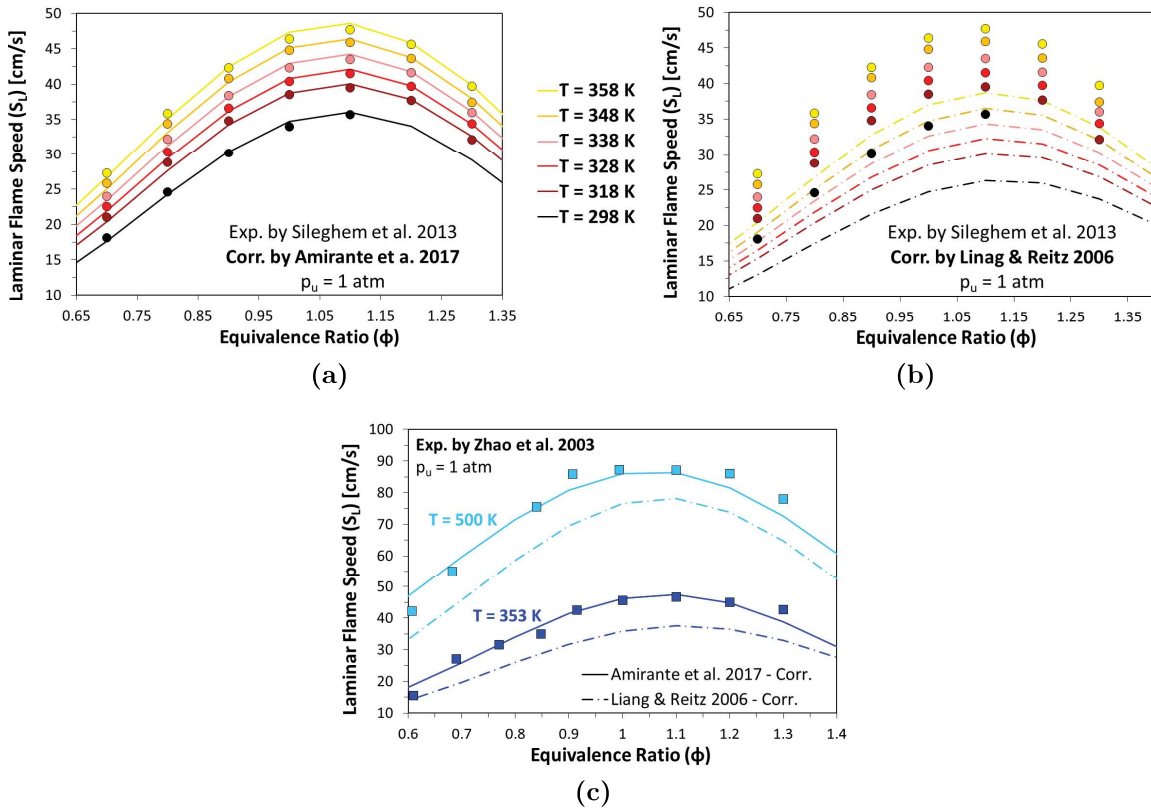


Figure 2: Improvements obtained by Amirante et al. [62] (solid lines), with respect to the correlation by Liang and Reitz [68] (dashed lines), in reproducing the laminar flame speed of commercial gasoline over a wide range of operating conditions. Comparison with the experiments by Sileghem et al. [77] (a) and (b); comparison with the experiments by Zhao et al. [78] (c).

408 and the data of Dirrenberger et al. [79], who used the same measurement method and
 409 found good agreement with the previous study. Figure 1 highlights the improvements
 410 made by Liang and Reitz [68] in avoiding negative flame speeds, but shows as well that
 411 the values derived for iso-octane are not suitable for reproducing the laminar flame

Table 2: Composition of the surrogate mixture of ten components used to model gasoline in the simulations.

Component	Mole fraction
nC ₇ H ₁₆	0.055399
nC ₁₀ H ₂₂	0.039687
C ₁₀ H ₂₂	0.019337
iC ₅ H ₁₂	0.411976
iC ₇ H ₁₆	0.130568
iC ₈ H ₁₈	0.074380
C ₇ H ₈	0.101062
mxylyene	0.062182
mcymene	0.073237
C ₆ H ₁₂	0.032171

412 speed of gasoline.

413 Figures 2a and 2b provide a comparison with other experiments carried out by
 414 Sileghem et al. [77] at different initial temperatures, confirming that the errors deriving
 415 from the use of the correlation of Liang and Reitz [68] cannot be acceptable. Figure 2c
 416 refers to the experiments by Zhao et al. [78] who used the stagnation jet-wall flame
 417 configuration and Particle Image Velocimetry for measuring the laminar flame speed of a
 418 commercial gasoline at higher temperatures than those investigated in the two previous
 419 works. The results underline the need of a dedicated formulation for calculating the
 420 laminar flame speed of gasoline.

421 Recently, Teodosio et al. [80] assessed the relative impact that different formula-
 422 tions for predicting the laminar flame speed of gasoline (including those developed
 423 by Metghalchi et al. [75] and by Amirante et al. [62]) can have on the prediction of
 424 the combustion process in a SI engine. The results highlighted the reliability of the
 425 formulation proposed by Amirante et al. [62], which produced trends really close to
 426 those obtained by a chemical kinetic solver.

427 In the present work, the analytical correlation developed by Amirante et al. [62]
 428 (Equations (27) and (28)) was implemented in the code for reproducing the flame speed
 429 of gasoline. The surrogate mixture of ten components reported in Table 2 was used for
 430 reproducing the chemical and physical properties of gasoline used in the experiments and
 431 whose specification are reported in [27], as provided by suppliers. This approach allowed
 432 to keep a constant composition of the surrogate fuel mixture used in the simulations,
 433 avoiding the need of varying any other parameter in order to match the experimental
 434 measurements.

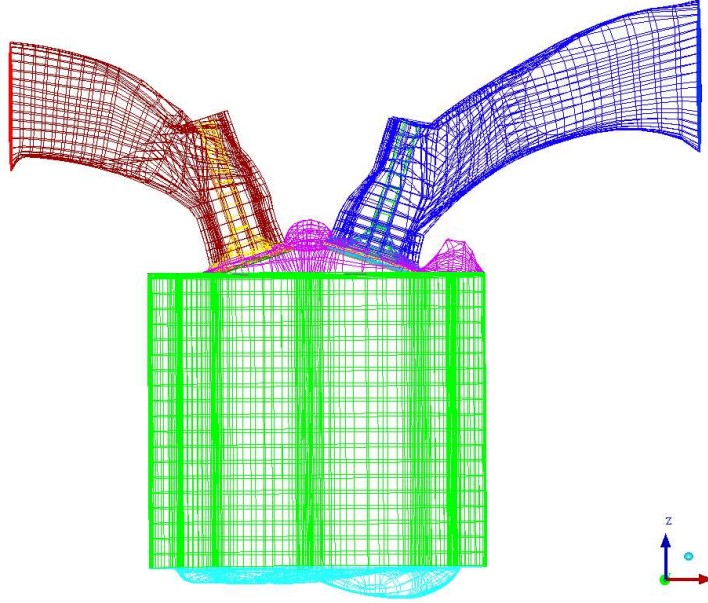


Figure 3: Computational mesh of the SI engine used in the experiments [27] with pent-roof and flat-top piston, 100,000 cells at BDC including intake and exhaust valves.

3 Numerical setup

Figure 3 shows the 3D computational mesh of the engine whose specifications are reported in Table 3.

A fully structured computational mesh, containing around 100,000 cells at Bottom Dead Center (BDC), including the intake and exhaust manifolds, was employed in the present study. Considering that about 20% of the total number of cells was used for the manifolds, it results that the mesh density within the cylinder was about 320 cells/cm^3 , with the majority of the cells located near the cylinder head and the bowl piston. This value was selected in accordance to the studies in which the main sub-models used in this work were validated, as well as, on the basis of the values adopted in previous studies based on the same version of the KIVA code.

In the work by Vishwanathan et al. [56], a mesh density within the cylinder of 80 cells/cm^3 , was sufficient for validating the soot model and obtaining good agreement

Table 3: Engine specifications.

Name	Units	Value
Cylinder volume	cm^3	250
Bore	mm	72
Stroke	mm	60
Compression ratio	None	10.5
Max power	kW	16 at 8000 rpm
Max torque	Nm	20 at 5500 rpm

Table 4: Operating condition specifications.

Engine speed [rpm]	O ₂ [%vol]	Spark Advance [CAD ATDC]
2000	0	-22.0
	5	-12.5
	10	-12.5
4000	0	-24.0
	5	-24.0
	10	-24.0

448 with the experiments. Liang et al. [81], in the work in which the G-equation model
 449 was coupled with detailed chemical kinetics, performed a successfully validation with
 450 a mesh density within the cylinder of about 200 *cells/cm*³. Singh et al. [82] used
 451 the combustion model developed by Liang et al. [68, 81] to simulate the combustion
 452 in a dual-fuel engine. In that study, a mesh density within the cylinder of about 40
 453 *cells/cm*³, ensured good results. Furthermore, the same version of the code used in the
 454 present study, was recently used in two works carried out by Jiao and Reitz [57, 58].
 455 In both studies, a mesh density within the cylinder of about 90 *cells/cm*³ produced
 456 more than satisfactory results. In all the considered case, a fully structured meshes was
 457 employed, as well.

458 On the basis of the analyzed cases, the mesh density value selected for the present
 459 study can be considered adequate, being it abundantly larger than those used in each
 460 of the above-mentioned works and the cells distribution comparable.

461 The initial in-cylinder mixture was assumed to be completely homogeneous, and
 462 the simulations started from intake valve closure (IVC). A value of 2.0 for the only
 463 model constant C_m that needed to be tuned was found to give the best results for the
 464 considered SI engine. It was kept constant for all the cases considered in this work.

465 In the experiments [27], 5% and 10% by volume of additional oxygen was mixed
 466 with gasoline within the intake manifold to explore loads higher than the wide open
 467 throttle case. All the tests were performed at steady state conditions and two engine
 468 speeds were investigated, namely 2000 and 4000 rpm. The list of the conditions and
 469 important engine settings considered in the tests are reported in Table 4. At 2000 rpm
 470 it was necessary reducing the spark-advance with oxygen addition, in order to avoid
 471 the onset of knocking phenomena in the experiments [27].

472 In-cylinder pressure and HRR traces obtained from the simulations were compared
 473 with the experimental measurements in order to validate the numerical results. Then
 474 the results were further analyzed to provide in-cylinder soot distributions and to better
 475 understand the reasons for the experimentally observed soot particle size distributions.

4 Results and discussion

Before simulating the considered fired cycles, a simulation without combustion was performed, in order to match experimental motored pressure traces and thus verify the information related to the compression ratio. The only available motored in-cylinder pressure trace was recorded at 2000 rpm. No data were available at 4000 rpm in this condition. Therefore, a simulation was performed at 2000 rpm, considering a compression ratio equal to 10.5, in accordance with the information provided in the experimental work by Catapano et al. [27], on which this study is based (cf. Table 3). The results are reported in Figure 4.

Figure 5 reports the in-cylinder pressure and HRR for the two engine speeds considered and illustrates that the effect of oxygen addition was to speed up the combustion process. At 4000 rpm the effects are more evident since these cases have similar combustion phasing (as previously mentioned, at 2000 rpm, it was necessary to delay the ignition timing to avoid knock). The faster combustion is ascribable to the higher burning velocity due to oxygen addition [24]. The lower N_2 content (which is an inert that lowers the flame temperature by absorbing heat without actively participating to the combustion), results in a higher local oxygen availability, contributing to the formation of a more homogeneous mixture that enhances the ignition as well as the flame propagation process.

The lower in-cylinder pressures obtained with 5% of additional oxygen at 2000 rpm, in comparison to the baseline case, are uniquely due to the spark-advance reduction by 9.5 CAD operated in the experiments to avoid knock (as reported in the work by Catapano et al. [27]) when oxygen was added at low speed (cf. Table 4). The spark-advance was kept constant when the amount of additional oxygen was increased from 5 to 10% by volume, for both the engine speeds. As a result, the in-cylinder pressure traces with 10% of additional oxygen resulted higher than those recorded with 5% of oxygen, at both low and high engine speeds, confirming that the in-cylinder

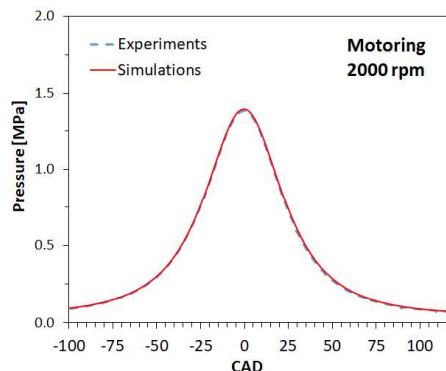


Figure 4: In-cylinder pressure trace during motoring conditions at 2000 rpm. Dashed lines: experiments [27]; solid lines: simulations.

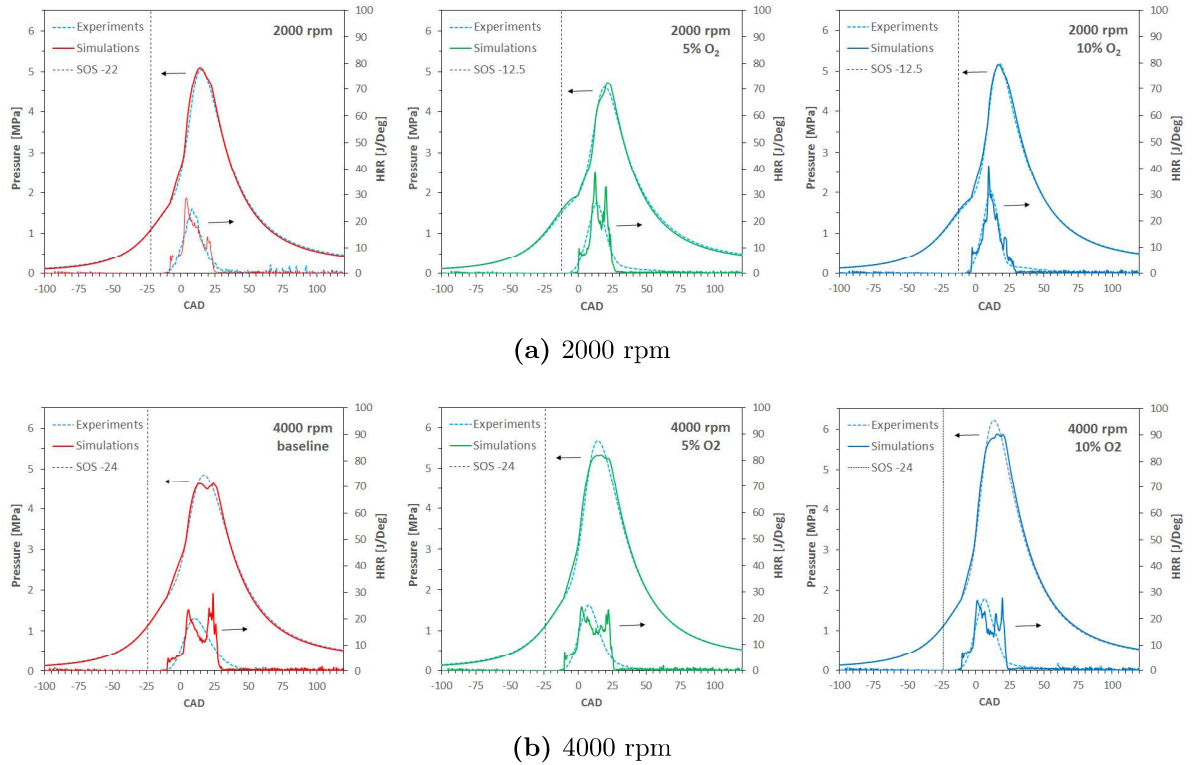


Figure 5: In-cylinder pressure and HRR traces at 2000 (a) and 4000 (b) rpm. Dashed lines: experiments [27]; solid lines: simulations; vertical dashed lines: Spark Advance.

503 pressure reduction with 5% of additional oxygen with respect to the baseline case at
 504 2000 rpm, can be uniquely ascribable to the spark-advance reduction performed in the
 505 experiments by Catapano et al. [27].

506 The above described trends are faithfully replicated by the simulations when the
 507 spark-advance and the additional oxygen amount are changed accordingly to the exper-
 508 imental tests. The comparison between the numerical simulations and the experiments
 509 is reported in Figure 5, as well. The overall results can be considered more than
 510 satisfactory. Very good agreement was obtained for the low speed case (Figure 5a),
 511 while some slight discrepancies were found for the high speed case (Figure 5b). These
 512 can be probably attributed to the absence of a crevice model.

513 In general, the absence of a crevice model results in an overestimation of the
 514 predicted in-cylinder pressure, as observed in many studies that compared measured
 515 in-cylinder pressure traces with those calculated without any crevice model, during
 516 motoring conditions [83, 84]. In light of this result, it is reasonable to suppose that the
 517 actual compression ratio in the experiments might have been slightly lower than the
 518 declared one (the information provided by engine’s manufacturers was not verified in
 519 the experimental work [27], since was not crucial in that circumstance).

520 However, it must also be considered that the engine speed plays a significant role
 521 in determining the piston-ring flows. Specifically, the more is the engine speed, the
 522 less is the influence of the crevice flow [83, 85]. Rakopoulos et al. [83] observed that

523 increasing the engine speed during motoring conditions produces a higher increase in
 524 the measured in-cylinder pressure than that observed in the simulations without a
 525 crevice model. Considering that the numerical results reported in Figure 4 matched the
 526 available experimental motored pressure trace at the lowest speed (namely, 2000 rpm),
 527 it derives that simulations at higher speeds (such as 4000 rpm) would underestimate the
 528 motored pressure peak, once compared with the experiments. When fired conditions
 529 are considered, these effects can be more relevant and can reasonably explain why the
 530 absence of a crevice model produced an underestimation of the in-cylinder pressure at
 531 the higher engine speeds.

532 The absence of a crevice region can also explain the presence of a second pressure
 533 bump after the main peak observed from the baseline case at 4000 rpm (left-hand plot
 534 in Figure 5b). In real conditions, a significant amount of unburned gas ahead of the
 535 flame flows into the top-land crevice and it has been calculated that the crevice flow
 536 reduces the instantaneous in-cylinder charge mass by as much as 6% [86]. About 80%
 537 of this trapped mass (about 5% of the total cylinder mass) eventually returns to the
 538 chamber and is burned during the later stages of combustion, when the temperature
 539 is much lower [86]. In the simulations, the absence of this zone (i.e., a model that
 540 simulates this phenomenon) has the result that all the in-cylinder fuel survives far
 541 the flame propagation and is oxidized at higher temperatures, resulting in a sudden
 542 increase of pressure and a faster HRR at the conclusion of the combustion phase. At
 543 lower speeds this behavior is less relevant and therefore the simulations show better
 544 agreement.

545 Figure 6 points out that for all conditions the effect of oxygen addition is to increase
 546 the IMEP. The increment is almost linear, namely adding 10% of oxygen results in a
 547 load increase of roughly 10% and this trend is well captured by the numerical model,
 548 especially for the low speed conditions. At 4000 rpm the IMEP increase is slightly
 549 overestimated due to the above-described crevice flow reasons. It must be noticed that
 550 stoichiometric conditions were kept during the experimental tests and therefore the

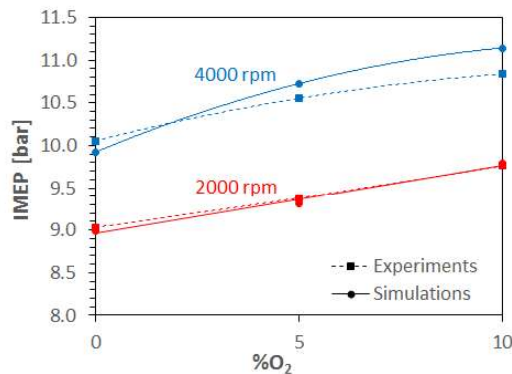


Figure 6: Load increase due to oxygen addition. Dashed lines: experiments [27]; solid lines: simulations.

551 increased IMEP values are ascribed to the larger amount of fuel that was injected, as is
552 inferable from the larger fuel consumption that was recorded for the cases with oxygen
553 addition.

554 The numerical model can be considered to have been successfully validated against
555 the experimental data and can be used for a deeper analysis of the results relating to
556 particle emission processes. In particular, the low-speed case, which showed the best
557 agreement, was chosen for further investigation on the combustion and soot formation
558 processes that are taking place within the engine. For sake of brevity, the two extreme
559 cases, namely 0 and 10% of oxygen, are compared.

560 Figure 7 illustrates the propagation of the flame front location as represented by the
561 $G=0$ (pink) surface after the transition from the kernel growth model to the turbulent
562 flame propagation model, as well as the temperature distributions (cross section on
563 x-z plane). The red particles in the center were used to represent the kernel surface.
564 The results indicate that combustion is due to flame propagation and that no auto-
565 ignition (knock) is observed. The burnt regions swept by the flame surface can be easily
566 distinguished from the unburnt regions.

567 The spark advance was delayed to avoid knock (Table 4) and therefore the turbulent
568 flame with 10% oxygen (right-hand side of Figure 7) starts to propagate later than
569 the baseline case. In the latter case, at -5°ATDC the transition from kernel growth
570 to flame propagation has already occurred, while in the higher-load case the kernel is
571 still growing. At TDC, in both cases, the turbulent flame is completely formed and
572 it propagates radially towards the cylinder walls with a quasi-spherical shape. The
573 fastest flame speed was found with oxygen addition, as can be inferred from the fact
574 that at 10°ATDC the flame front position is practically the same, even though the
575 spark was triggered 9 CAD later in the oxygen-enriched case. The two flames reach the
576 cylinder wall simultaneously at about 20°ATDC . Slightly higher temperatures in the
577 burned region are reached in a shorter time with oxygen addition, and in both cases
578 the lowest temperature is recorded near the spark-plug location, due to the particular
579 cylinder-head shape.

580 The average in-cylinder temperature evolution is reported in Figure 8(b), which
581 summarizes the results discussed in the previous figures and allows a comparison with
582 the average in-cylinder pressure and HRR traces (Figure 8(a)). Figure 8(c) shows the
583 time evolution of the soot mass per kg of fuel. When combustion begins, soot starts to
584 increase and the highest peak is recorded in correspondence with the higher in-cylinder
585 pressures and temperatures, just before the front flame reaches the wall. After that,
586 soot decreases and oxygen addition produces a lower specific value of soot mass at EVO.

587 In the next six figures the distributions of six variables of interest, i.e., mass fractions
588 of OH, C_2H_2 , A_4 , and soot, soot number density (PN) and particle size (D_p) are reported
589 to analyze the causes of the observed soot emission trends.

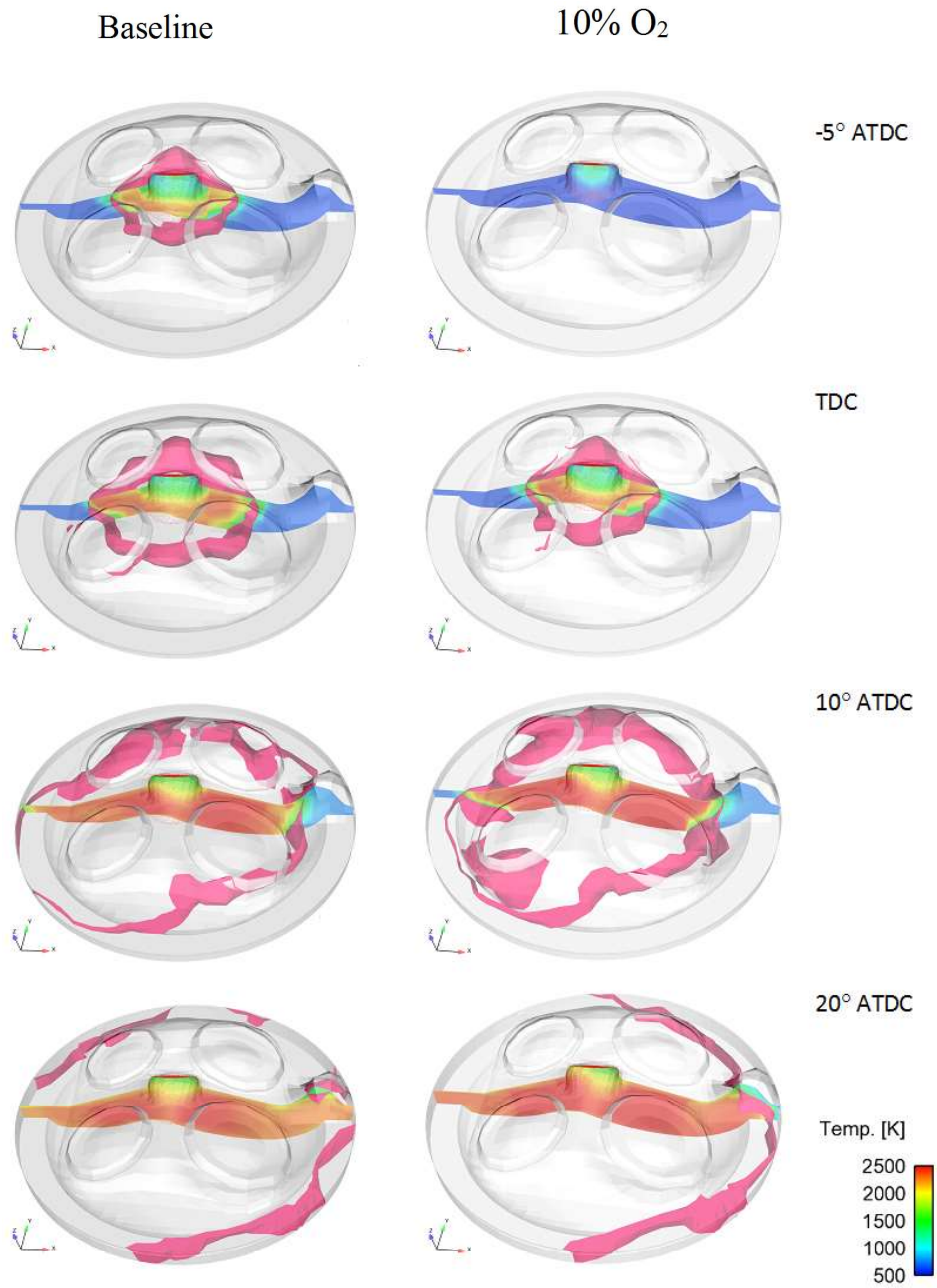
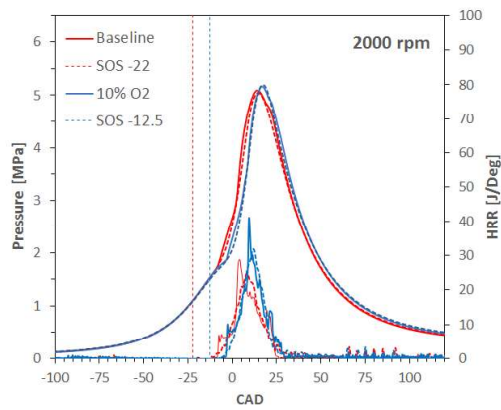
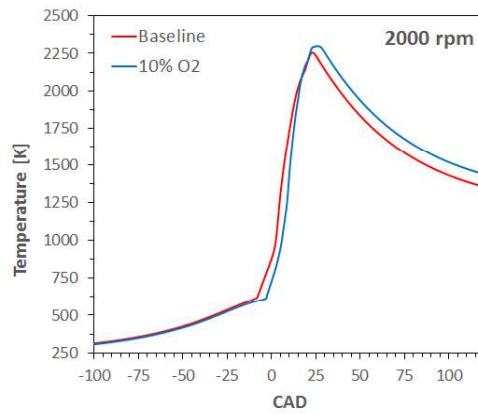


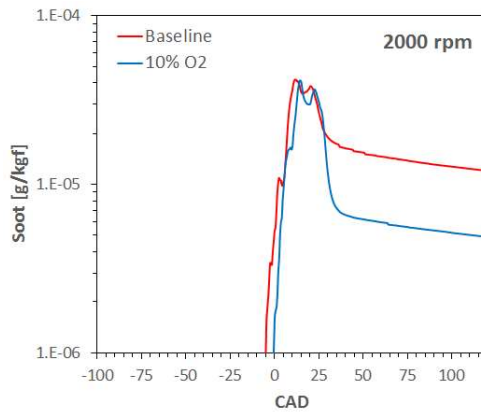
Figure 7: Evolution of in-cylinder turbulent flame and temperature field (plane x-z) for 2000 rpm case in the simulations. Red particles: kernel surface; pink surface: flame front.



(a)



(b)



(c)

Figure 8: In-cylinder time evolution of pressure and HRR traces (a). Temperature (b) and specific soot mass (c) in the simulations of the 2000 rpm cases. Dashed lines: experiments [27]; solid lines: simulations; vertical dashed lines: Spark Advance.

590 Figure 9 shows that the in-cylinder OH concentration increases in the region behind
591 the front flame and then start to decrease once the flame has reached the wall and
592 the temperatures are falling. In the central region, near the spark-plug location, low
593 OH concentration levels can be observed during the entire combustion process. At
594 20° ATDC, when the flame has reached the in-cylinder wall, the OH concentration is
595 larger for the high-load case of 10% of oxygen.

596 The OH concentration is crucial for the soot oxidation process, while soot inception
597 and surface growth depend on the in-cylinder concentration and distribution of the
598 soot precursors. In Figure 10 and Figure 11 is therefore reported the time evolution
599 of the mass fraction distributions of C₂H₂ and A₄, respectively, which are the most
600 abundant gaseous hydrocarbon species detectable in regions where soot is formed. The
601 highest values of their concentrations are recorded in the burned region, near the flame
602 front and where the temperatures are lower, namely near the spark-plug location, in
603 both cases. The mass fraction of these two species decreases after the flame, which is
604 responsible for their production, reaches the cylinder wall and sufficient residence time
605 at high temperatures is available in regions rich of OH radicals. In fact, at exhaust
606 valve opening time (120° ATDC) these precursor species are mainly found near the
607 center of the cylinder head due to the lack of OH radicals and the lower temperatures
608 (Figure 10(c) and Figure 11(c)). With oxygen addition, a slightly larger amount of
609 C₂H₂ and A₄ can be detected.

610 A competition between the increased concentration of species responsible for soot
611 generation and, at the same time, of OH radicals, which contribute to its oxidation,
612 explains the time evolution of the soot mass fraction reported in Figure 12. In other
613 words, higher soot mass fractions are seen near the fame front regions, where the
614 in-cylinder temperatures are higher and there is abundance of C₂H₂ and A₄, while in
615 the burnt regions, the oxidation process by OH radicals starts to take place, and thus
616 the soot mass fraction is reduced (Figure 12(a) and Figure 12(b)). Oxygen addition
617 enhances this aspect, increasing the production rates of both OH radicals and soot
618 precursor species and therefore, at 120° ATDC, the in-cylinder soot mass distribution
619 obtained with oxygen addition is comparable to the baseline case. Since stoichiometric
620 conditions were considered in both cases the soot mass per kg of fuel is lower for the
621 oxygenated combustion case, as previously shown in Figure 8(c).

622 From Figure 13 and Figure 14 it is also possible to observe that at TDC, soot
623 particles with larger sizes are located near the flame front (Figure 14(a)), where the
624 C₂H₂ and A₄ concentrations are higher, but the highest number density levels are
625 recored near the spark-plug location (Figure 13(a)), where the temperatures are not
626 high enough for a fast soot inception and growth process. At 120° ATDC the largest
627 part of the formed soot is composed of very fine particles.

628 These results are in perfect agreement with the experimental measured PSDs, shown

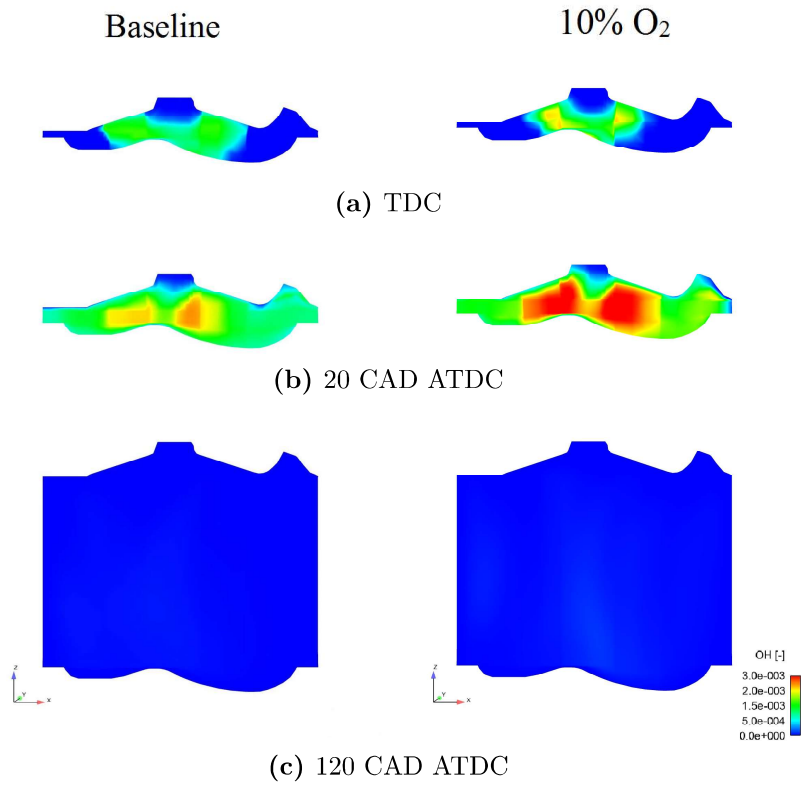


Figure 9: Time evolution of mass fraction distribution of OH radicals.

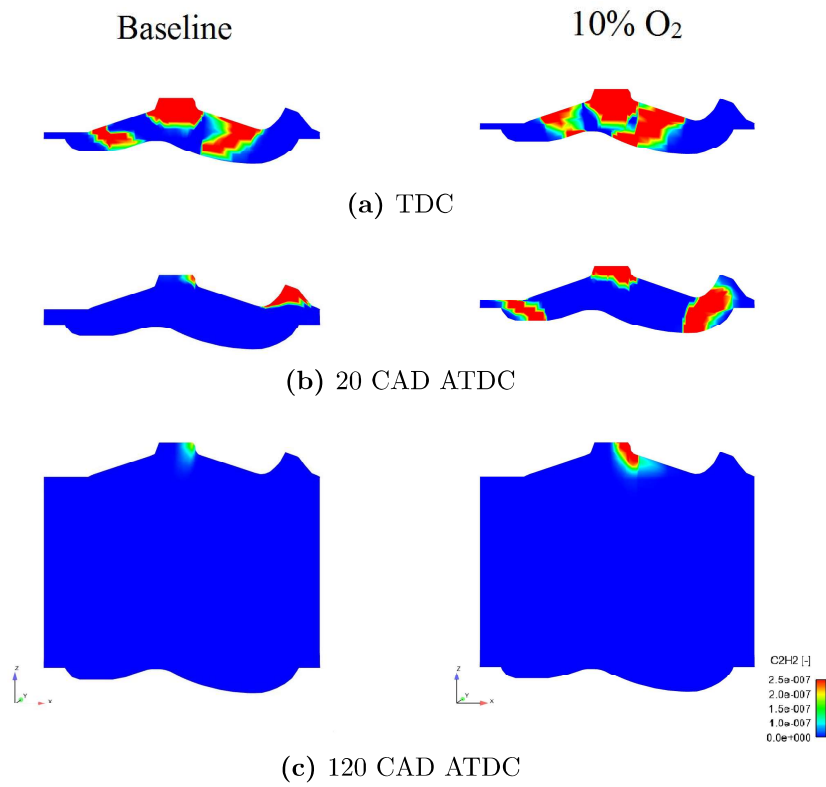


Figure 10: Time evolution of mass fraction distribution of C₂H₂.

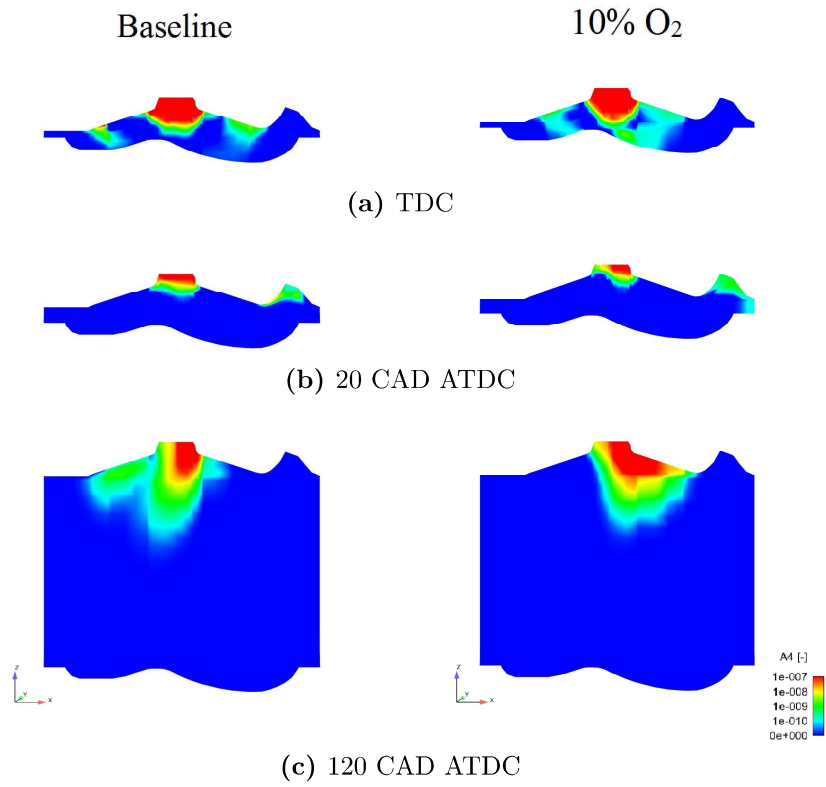


Figure 11: Time evolution of mass fraction distribution of A_4 .

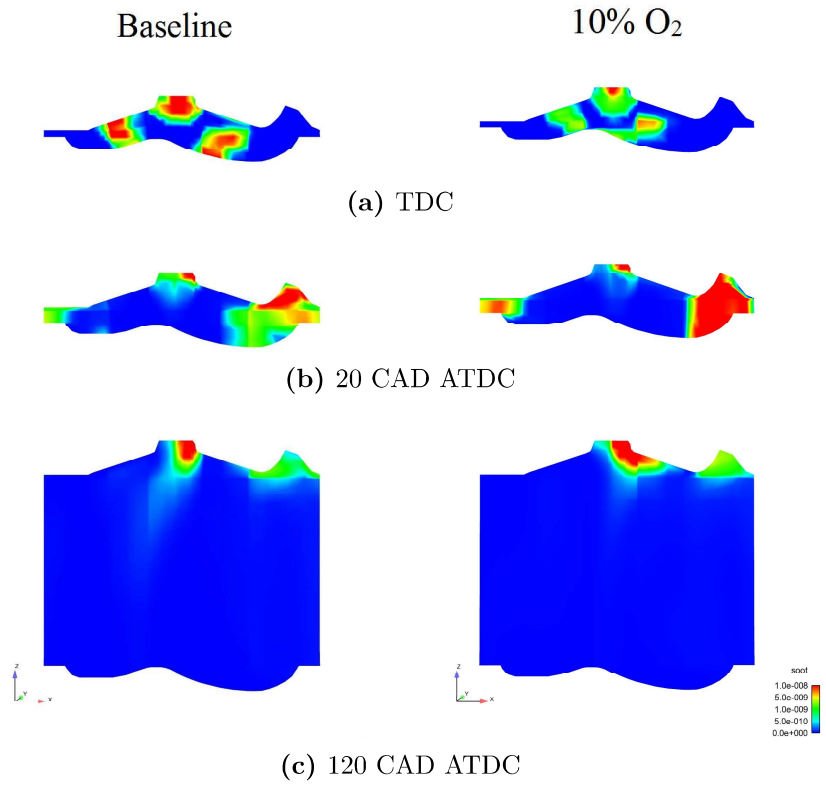


Figure 12: Time evolution of soot mass fraction distribution .

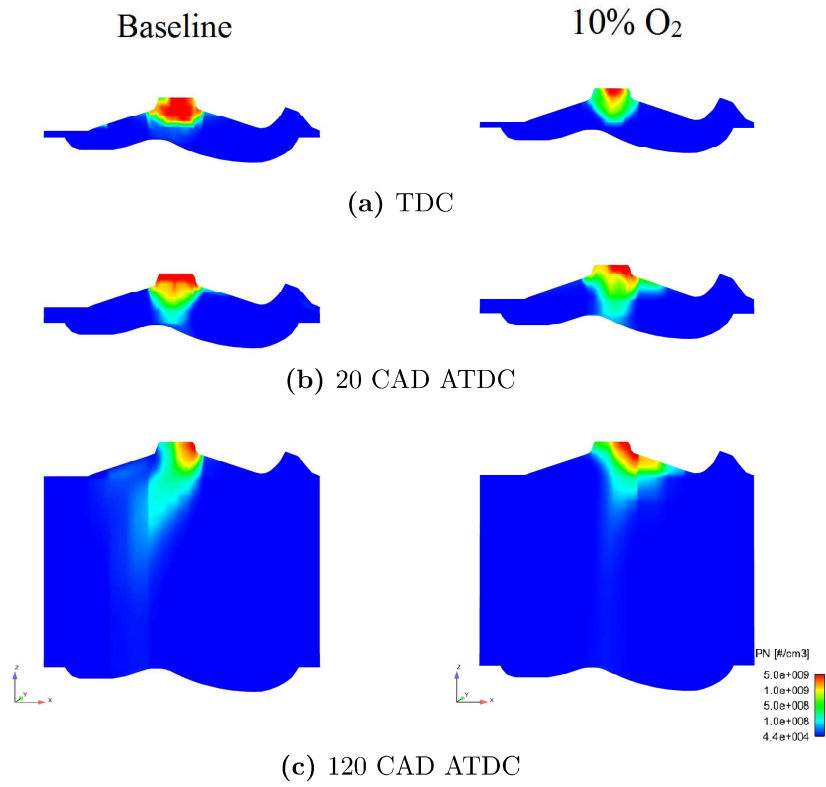


Figure 13: Time evolution of soot number density distribution.

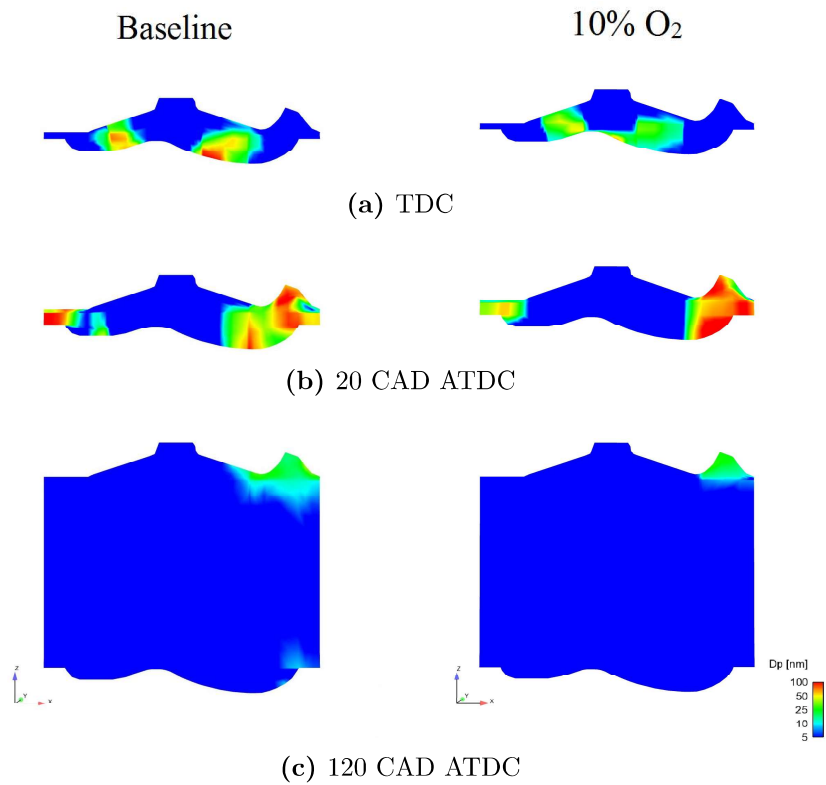


Figure 14: Time evolution of soot particle sizes distribution.

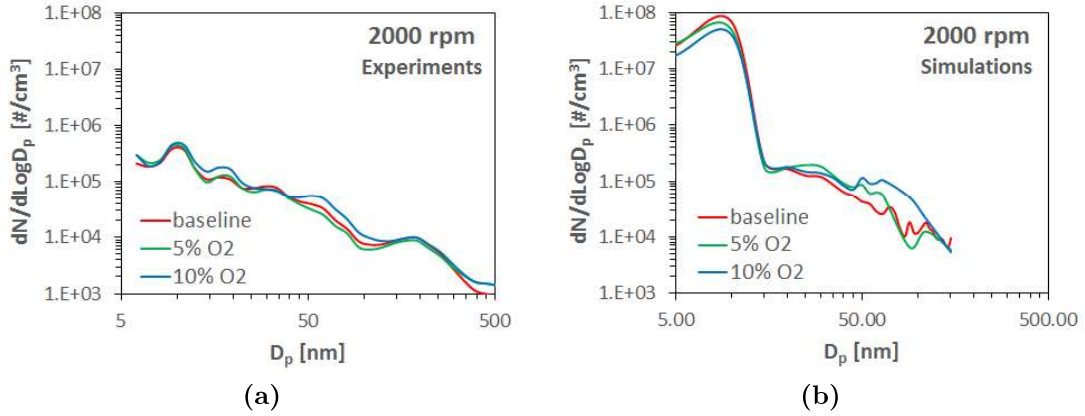


Figure 15: Experimental [27] (a) and predicted (a) PSD functions.

629 in Figure 15(a) and which pointed out that the load increase obtained by oxygen
 630 addition did not affect the granulometric distribution of the particles emitted from the
 631 engine at 2000 rpm. Computed PSDs are reported in Figure 15(a). The agreement with
 632 the experiments can be considered to be very good for particles with sizes larger than
 633 15 nm. The number of the finest particles is overestimated by the numerical model,
 634 but it must be considered that oxidation, which could occur in the exhaust, as well as
 635 physical soot transformation, i.e., due to the discharge process of the gasses from the
 636 combustion chamber into the exhaust pipe, or due to temperature conditions changing
 637 along the exhaust line or within the instrument can have strong effect on nucleation
 638 mode particles. This may explain the lower value detected by the particle sampler
 639 device within the exhaust pipe [2].

640 5 Conclusions

641 The present study analyzed the effect of a load increase on gasoline SI engine combustion,
 642 by means pure oxygen addition. 3-D Computational Fluid Dynamics simulations were
 643 performed and the numerical results were compared with existing experimental data, in
 644 which 5 and 10% by volume of additional oxygen was inducted with gasoline within
 645 the intake manifold of a SI engine to explore loads higher than the wide open throttle
 646 case. All the tests were performed at stoichiometric and steady state conditions and
 647 two engine speeds were investigated, namely 2000 and 4000 rpm. Such an approach
 648 provides additional basic information about oxygenated fuels and combustion, while
 649 avoiding still existing uncertainties relating to chemistry models.

650 The effect of oxygen addition was to speed up the combustion process and the
 651 induced increase in load was roughly linear with increased oxygen content. At 4000
 652 rpm the effects were more evident than at 2000 rpm, because in the latter case it was
 653 necessary to delay the ignition timing to avoid knock in the experiments. Very good
 654 agreement was obtained for the low speed case, while some discrepancies, which are

655 attributed to the absence of a crevice model, were found for the high speed case.

656 Further investigation on the combustion and soot formation processes was provided
657 at 2000 rpm. Oxygen addition produced a faster burning velocity and higher in-cylinder
658 temperatures. During the initial combustion stages, higher soot mass fractions were
659 seen near the fame front regions, where the in-cylinder temperatures were higher and
660 there was abundance of C_2H_2 and A_4 . Afterwards, the oxidation process by OH
661 radicals started to take place, and thus the soot mass fraction was reduced. At EVO
662 (120° ATDC) soot was mainly found in the center of the cylinder head due to the lack of
663 OH radicals and the lower temperatures that characterized this region. Oxygen addition
664 enhanced this aspect, increasing the production rates of both OH radicals and soot
665 precursor species and therefore, at 120° ATDC, the in-cylinder soot mass distribution
666 obtained with oxygen addition was comparable to the baseline case. However, since
667 stoichiometric conditions were considered in both cases the soot mass per kg of fuel
668 was lower for the oxygenated combustion case.

669 The results were in good agreement with experimentally measured PSDs and provide
670 confidence in the soot model in predicting soot emissions. In addition, the comparison
671 between measured and predicted PSDs showed very good agreement for particles with
672 sizes larger than 15 nm, but the number of the finest particles was overestimated by
673 the numerical model. This can be explained by considering oxidation process occurring
674 in the exhaust, which was not considered in the simulations.

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