Comprehensive modeling study analyzing the insights of the NO-NO$_2$ conversion process in current diesel engines

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Abstract:

Multiple researches have focused on reducing the NO$_x$ emissions and the greatest results have been achieved when lowering the combustion temperature by employing massive exhaust gas recirculation rates (LTC). Despite this benefit, a substantial increase in the NO$_2$ contribution to the NO$_x$ emissions has also been observed, which is the most harmful specie and is important for the design and positioning of the after-treatment devices. To understand how NO$_2$ behaves and how it contributes to the total NOx (NO$_2$/NO$_x$), not only under LTC but also for CDC conditions, a stepwise computational research study was performed with Chemkin Pro software, due to the complexity of isolating the different phenomena studied, to analyze: 1) general equilibrium conditions and 2) the influence of typical diesel engine phenomena (combustion and cooling effects) under non-equilibrium conditions.

The results obtained under equilibrium state confirm the theoretical guidelines established for the NO$_2$ formation process. When considering a combustion process (HCCI-like mode), the previous results were corroborated as well as the fact that only poor or slow combustion processes are responsible for the NO$_2$ formation. Additionally, it reflected a cyclic process between NO and NO$_2$, or in other words, it is suffice to just concentrate on NO to be able to predict NO$_2$. Finally, the results yield after analyzing some cooling effects, inherent to how diesel engines work (the expansion stroke, dilution of combustion products with the rest of in-cylinder charge and the one caused by wall impingement), reflect that: 1) the dilution effect explains the 10% of the NO$_2$/NO$_x$ ratio under CDC conditions and 2) the coupling of the dilution

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with the expansion stroke cooling effects can explain the NO_2 increase typical of LTC conditions. These results were also supported by some experiments performed in a single-cylinder diesel engine. Consequently, the cooling effect caused by dilution should be considered when modeling the NO_2 formation just like the expansion stroke.

Keywords: Low temperature combustion, conventional diesel combustion, NO_x emission, NO_2 formation, 0-D modeling, diesel engines.

Nomenclature:

A/F:	Air to fuel ratio	*CDC:*	Conventional diesel combustion
EGR:	Exhaust gases recirculation	*EPEFE:*	European Program on Emissions, Fuels and Engine Technologies
Φ:	Equivalence ratio	*GRI-Mech:*	Gas Research Institute chemical kinetic mechanism
HCCI:	Homogeneous Charge Compression Ignition	*LTC:*	Low temperature combustion
N:	Engine speed in rpm	*NO:*	Nitrogen monoxide
NO_2:	Nitrogen dioxide	*NO_{ini}:*	Initial nitrogen monoxide composition
NO_x:	Nitrogen oxides	*P:*	Pressure
PCCI:	Premixed Charge Compression Ignition	*P_{inj}:*	Injection pressure
PSR:	Perfectly Stirred Reactor	*T:*	Temperature
T_{ad}:	Adiabatic temperature	*Y_{O2}:*	Oxygen mass fraction

1.- Introduction:

Over the past two decades, the amount of exhaust gas pollutants emissions have been significantly decreased due to the severe emission legislation imposed in Europe with the well-known Euro Emission Standards, as it can be appreciated from Table 1. A similar situation can be found in other countries worldwide.

DIESEL PASSENGER CARS					
Emission Standard	Date	CO (g/km)	NOx (g/km)	HC+NOx (g/km)	PM (g/km)
Euro 1	July '92	2.72	-	0.97	0.14
Euro 2	January '96	1.0	-	0.7	0.08
Euro 3	January '00	0.64	0.5	0.56	0.05
Euro 4	January '05	0.5	0.25	0.3	0.025
Euro 5	September '09	0.5	0.18	0.26	0.005
Euro 6	September '14	0.5	0.08	0.17	0.005

Table 1.- Euro Emission Standards for diesel passenger cars.

Initially, the accomplishment of the standards was fulfilled by using after-treatment and engine control devices (by far less sophisticated than current ones) coupled with a fully optimized conventional diesel combustion (CDC). Currently, the restriction facing (Euro 5) and the next to come (Euro 6), implies the need to change the diesel combustion process itself in order to significantly reduce NO_x (the sum of NO, NO_2 and N_2O) emissions. Analyzing the equivalence ratio - temperature map, (see Figure 1 adopted from [1]), where the soot and NO formation regions are delimited, it's appreciable that the new research field has to focus on the left part of the diagram represented in the Figure. This area corresponds to low local temperature combustion and lots of research are now taking place developing and optimizing new combustion modes, which includes: homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI) and the mixing-controlled low temperature combustion (LTC).
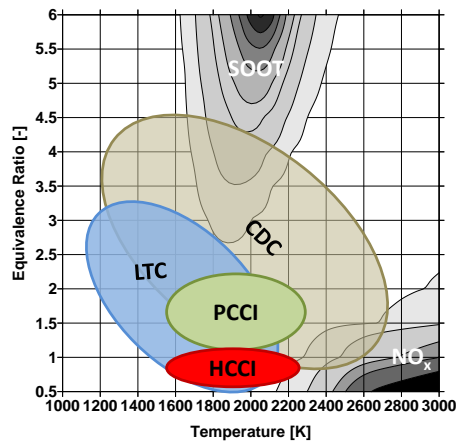
Figure 1.- Predominant ϕ-T working conditions for several new combustion modes [1].

Under these new combustion modes, interactions between hydrocarbons and NO_x are promoted due to the use of massive exhaust gas recirculation (EGR), main strategy to reduce pollutant emissions by diluting reactants with burnt gases. By doing so, leaner mixtures and lower combustion temperatures are reached affecting the NO_x formation process and composition. Regarding this latter aspect and even though the values differ between experimentalists [2, 3, 4], it has been generally observed that the proportion of NO_2 engine-out emissions increases above the typical range for CDC, i.e: 10% to 30% for different engine loads and engine speeds [5].

In order to understand the reasons of such important increase in the NO_2/NO_x ratio it is necessary to review the most important factors affecting the NO_2 formation. The first studies were focused on the field of gas turbines, domestic combustion appliances and probing samples and the results of these researches established the "guidelines" of the NO-NO_2 conversion process, which are:

- Different authors [6-13] reported how the NO_2 formation takes place due to a radical relaxation process mechanism as a consequence of the rapid cooling of hot combustion gas. This process achieves significant NO-NO_2 conversion throughout the HO_2 radical at low temperatures.

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- Hori et al. [9, 11] and Marinov et al. [12] confirmed the strong temperature dependency of the process, especially at low temperatures, and also showed that this process was greatly promoted by ultra-lean conditions and by the ability of the fuel to produce reactive radicals (O and OH). As the hydrocarbon chain gets larger and increases its saturation degree, higher is the conversion degree of the NO-NO$_2$ process.

- Bromly et al. [13] reflected the fact that a small amount of NO promotes the oxidation of the fuel at atmospheric pressure and for different gas inlet temperatures and different initial concentrations of ethylene, oxygen and NO. This phenomenon was named by Bromly et al. as "mutually sensitized oxidation of NO and fuel", and is believed to control the NO$_2$ emissions as a consequence of the fuel oxidation.

Nowadays, due to this substantial increase of the NO$_2$ emissions [14], the interest for this phenomenon is high and multiple studies have been developed focusing on exhaust-out [15-23] and engine-out emissions [24-32]. Concerning this latter group the main influence comes from the fuel's characteristics (i.e: blends and/or composition) and the influence of the combustion process. A priori, higher NO$_2$/NO$_x$ ratios are expected to be produced by the new combustion modes, characterized by lower combustion temperatures, than conventional diesel combustions.

Several authors [24-29] have analyzed the fuel's effect on the NO$_2$ formation process. To do so, they have considered different diesel compositions [24] and diesel blends (with hydrogen, injected in the intake manifold, and oxygenated fuels) [25-29]. Generally speaking, it can be assumed that fuels with high heating values and/or lower sulfur content will form less NO$_2$. This trend can be explained by higher combustion temperatures and higher cetane numbers (caused by the hydroprocessing procedure, employed in refineries, to diminish the sulfur content),

respectively. Also it has been concluded that the higher the oxygen content available in the fuel, lower is the NO_2 formation.

Regarding the combustion process [30-32], the most extended explanation for the new combustion mode, characterized by low combustion temperatures, is that such increase in NO_2 is formed by the reaction $NO+O_2=NO_2+O$ and afterwards this formed NO_2 cannot reconvert back to NO because of poor mixing and an overall slow combustion process [30-31]. This explanation has been contextualized in a HCCI combustion mode scenario. In the case of LTC diffusive combustion no further explanations have been developed besides the one proposed, in the early stages of the NO_2 research, in which it was the result of a mixing process between cold air/charge with hot combustion products.

Finally, it is also worth to mention that the starting point of the NO_2 formation relies on the production or the presence of NO. Therefore all the guidelines regarding this NO formation process [5, 33-36] must be also taken into consideration when analyzing the interactions between both species.

2.- Objectives and Methodology:

The aim of the present paper is to understand the substantial increase, in comparison with CDC, of NO_2 in the NO_x emissions when operating at LTC conditions. This study will be contextualized in HCCI and LTC diffusive combustion scenarios and the authors, with the information reviewed previously, will assume as reference values a NO_2 content, in the NO_x emissions, of 10% and 30% for CDC and LTC conditions, respectively. Even though it may seem that these values can influence the findings, the authors believe they are a good starting point because they are widely described in scientific literature. Nevertheless, the derived results will clearly reflect the differences between CDC and LTC conditions despite the reference values used, specially when characterizing LTC conditions.

For this purpose, two parametric studies (**constant and non-constant temperature conditions**) were performed at constant pressure (P = 10MPa) and assuming equilibrium and non-equilibrium (non-steady) states by using the EQUIL and the PSR modules of Chemkin-Pro [37], respectively. Finally, some of these results will be validated against real engine measurements.

The **constant temperature and equilibrium state analyses** were performed to check if the employed NO_x sub-mechanism captures the main behavior of the NO-NO_2 conversion process and quantify the NO_2/NO_x ratio under these unrealistic conditions. The temperature (T) will ranged from 1000K to 2400K, the equivalence ratio (Φ) from 0.2 to 1 and two different EGR rates (characterized by the oxygen mass fraction; Y_{O2} = 0.23 & 0.1) with two different initial concentrations of NO (NO_{ini}: 0ppm, and 200ppm) were used. The fact of choosing a Y_{O2} = 0.1 had two main purposes. The first of them is to characterize the LTC conditions in coherence with the criterion (Y_{O2} = 0.127) used by multiple researchers [38-39] and the second is to analyze the effect of massive EGR.

Note that the selected temperatures describe not only typical LTC combustion temperatures but also typical fuel-air mixture temperatures for LTC and CDC conditions. The Y_{O2} = 0.1 was achieved by diluting the air with combustion products (CO_2, H_2O and N_2) in the same proportions as in a stoichiometric oxidation reaction between diesel fuel surrogate and dry air. The two different concentrations of initial NO, chosen arbitrarily specially 200ppm, were achieved by removing the same amount of N_2 as the NO introduced. It is worth highlighting that even though these values have been established arbitrarily, the results of the present study will reflect that the significance of this parameter is minor, at least, in the authors' considered range (0-200ppm).

The combination of the Y_{O2} variable with NO_{ini} will illustrate realistic and fictitious cases, in diesel engines, to help understanding the influence of the different parameters. These are:

Case A.- Lack of EGR (Y_{O2} = 0.23, NO_{ini} = 0ppm)

Case B.- Air doped with NO (Y_{O2} = 0.23, NO_{ini} = 200ppm)

Case C.- Air highly diluted with EGR coming from low NO formation operational conditions (Y_{O2} = 0.1, NO_{ini} = 0ppm)

Case D.- Fictitious EGR (Y_{O2} = 0.1, NO_{inI} = 200ppm).

The **non-constant temperature** and non-equilibrium state simulations were performed for several working conditions contextualized in: 1) single-zone homogeneous combustion process, which resembles HCCI combustion mode and 2) several cooling effects predominant in internal combustion diesel engines. Despite the fact that both scenarios are very distinct, the fact that the second of them was considered was due to the conclusions obtained from the first one.

Other variables necessary to be taken into consideration to perform this research study, are: a diesel fuel surrogate and the chemical-kinetic mechanisms, which are described in the following paragraphs.

The diesel fuel surrogate chosen was n-heptane mainly due to its similar cetane number with typical European diesel fuel [41] but also because it is considered a highly efficient fuel for the NO-NO$_2$ conversion process following the Hori reasoning [12]. However, the main drawback of using this single component fuel surrogate is the fact that it discards the NO formation process by fuel's nitrogen content and by aromatics contribution. On the one hand, the extremely low contents of nitrogen in the refined liquid fuels used nowadays in the automotive industry makes this route insignificant. On the other hand, it is well known that a higher aromatic content causes an increase in NO_x emissions. Nevertheless, the study performed by the European Programme on Emissions, Fuels and Engine Technologies (EPEFE) [42] has demonstrated, on light duty diesel engines conformed to EU 1996 and based on the complete

European driving cycle, that emission limits only experienced a 3.4% reduction of NO_x with a reduction of aromatic content from 8% to 1%. Taking into account that the maximum threshold value for aromatic content in current fuels is 11%, it is presumable that this reduction percentage won't increase significantly. Nevertheless, this reduction was obtained for engines operating under CDC conditions and therefore the influence of aromatic content is expected to be even lower on the new diesel engines operating at LTC conditions. Consequently, the inclusion of aromatics in the present kinetic mechanism would just increase the computational cost without making a whole difference.

The employed chemical-kinetic mechanism was made up of the n-heptane oxidation mechanism [41] coupled with the NO_x formation sub-mechanism included in the GRI-Mech 3.0 mechanism [43]. This model describes extensively the NO_x formation/destruction process by taking into account the most important reactions dealing with the different NO_x formation pathways.

3.- Results and Discussion:

3.1.- NO_2/NO_x results for constant temperature analyses under equilibrium state at high pressure

In order to have a general overview of how the $NO-NO_2$ conversion process behaves, a parametric study assuming equilibrium state and summarized in Table 2, was performed across a wide temperature (1000K < T < 2400K) and equivalence ratio (0.2 < Φ < 1) range and at high pressure (P=10 MPa) for the four cases, described in the previous section.

Equilibrium and Non-Equilibrium states working conditions			
Φ range [-]	Y_{O2} [-]	Temperature Range [K]	NO_{ini} [ppm]
0.2 - 1	0.23; 0.1	1000 – 2400	0
0.2 - 1	0.23; 0.1	1000 – 2400	200

*Table 2.- Description of the different mixtures considered in the present study.*

The results for Case A (YO_2 = 0.23, NO_{ini} = 0 ppm) and Case C (YO_2 = 0.1, NO_{ini} = 0 ppm) are plotted in Figure 2a and 2b, respectively, as the percentage ratio between NO_2/NO_x (grams NO_2 * 100/grams NO_x).

a)   b)
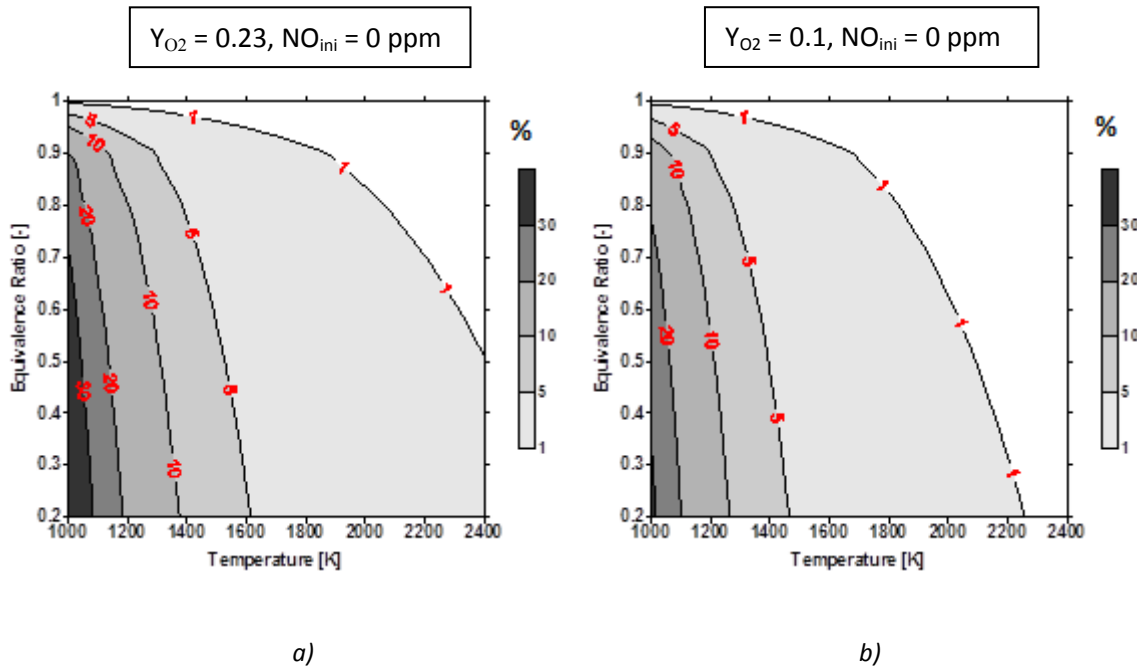
Figure 2.- Equilibrium results of the NO₂/NOx ratio as a function of equivalence ratio and temperature at high pressure (10MPa) and with n-heptane as diesel fuel surrogate; a) corresponds to Y_{O2} = 0.23 and NO_{ini} = 0, b) corresponds to Y_{O2} = 0.1 and NO_{ini} = 0 ppm.

These plots clearly reflect that the temperature is the predominant variable affecting the process and, in minor extent, the equivalence ratio. Furthermore, by comparing both figures, a reduction in the NO_2/NO_x ratio when the Y_{O2} variable is reduced can be observed, especially at low temperatures (T < 1400K): e.g. at T = 1200 K and Φ = 0.7 a 10% in NO_2/NO_x is obtained for the highly diluted scenario (Y_{O2} = 0.1) instead of a 15% for Y_{O2} = 0.23. At higher temperatures the differences remain similar, if relative values are considered, but are insignificant if considering absolute values (e.g: the greatest difference at 2000K corresponds to Φ = 0.2 and is from 1.5% to 2.3% for EGR and non-EGR conditions, respectively). This shows that a reduction in oxygen content reduces the influence of the conversion process either by: 1) reducing the production of NO, which further on, will be oxidized to NO_2, 2) by inhibiting the formation of key specie/s, or 3) a combination of both.

These same simulations were repeated but in this case with NO_{ini} = 200 ppm (Case B and Case D, respectively) and the results were plotted under the same axes in Figures 3a and 3b. As it can be observed by comparing them with Figures 2a and 2b, no differences are appreciated. This reflects that NO_{ini} has no influence when considering equilibrium conditions.

$Y_{O2} = 0.23$, $NO_{ini} = 200ppm$

$Y_{O2} = 0.1$, $NO_{ini} = 200ppm$

a)   b)
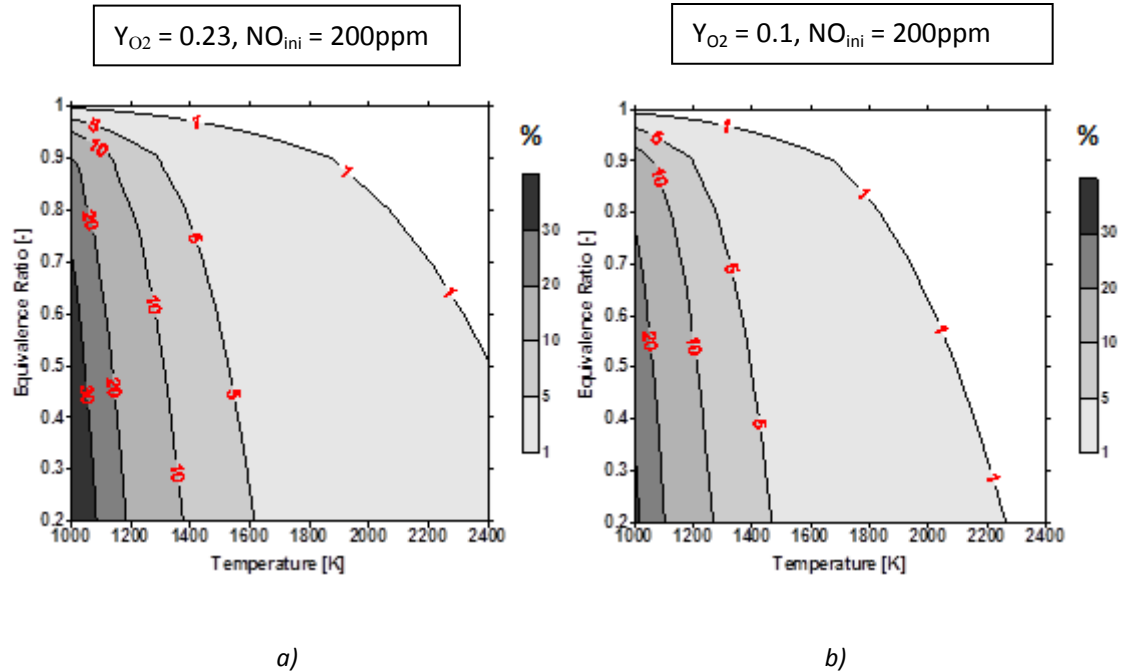
Figure 3.- Equilibrium results of the NO_2/NO_x ratio as a function of equivalence ratio and temperature at high pressure (10 MPa) and with n-heptane as diesel fuel surrogate; a) corresponds to $Y_{O2} = 0.23$ and $NO_{ini} = 200$, b) corresponds to $Y_{O2} = 0.1$ and $NO_{ini} = 200$ ppm.

These preliminary calculations illustrate when considering equilibrium conditions, higher NO_2/NO_x ratios are expected to be yield at lower temperatures and higher oxygen mass fractions while the initial concentration of NO has no relevancy. These findings are coherent with the $NO-NO_2$ guidelines reviewed in the Introduction section and therefore it can be said that this process is well described by the current NO_x sub-mechanism included in the GRI-Mech 3.0 mechanism. In addition the NO_2/NO_x ratios achieved are substantially lower than the values given in [5]: expected 30% NO_2 contribution for LTC conditions, where temperatures may range from 2000 K up to 2200 K and high amounts of EGR are employed, and 10% for CDC conditions, where temperatures are greater than 2200 K without or with minor EGR employment. These discrepancies can be easily explained by the fact that the diesel combustion process in internal combustion engines (ICE) is far from the equilibrium state.

3.2.- NO_2/NO_x results for non-constant temperature conditions under non-equilibrium state
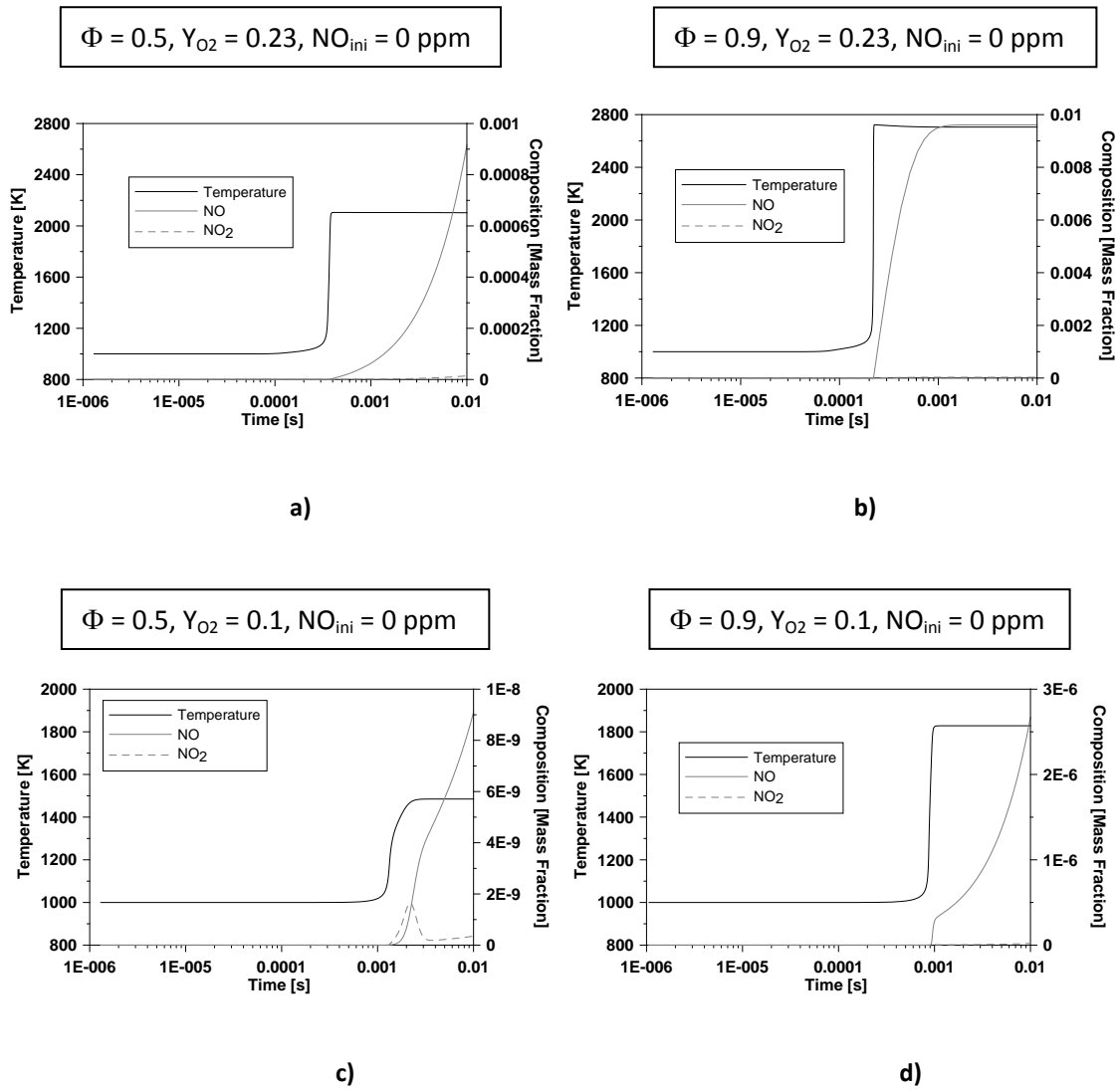
3.2.1.- Combustion process

The next step was to check if the combustion process is responsible for the described NO_2/NO_x values. For this purpose, the authors analyzed closely the time evolution of NO_2, NO and temperature, in four different situations, in the context of a single-zone homogeneous mixture combustion process (HCCI combustion mode) and with the following initial conditions: two different equivalence ratios ($\Phi = 0.5$ & 0.9) and an initial temperature (T_{ini}) of 1000K. In this scenario a third initial NO concentration, NO_{ini} = 40ppm, was chosen arbitrary in response to the need of analyzing the possible effects of this variable throughout the whole combustion process in a non-equilibrium state, see Table 3. The considered simulation time was of 10ms.

Combustion process simulation				
Φ [-]	T_{ini} [K]	Y_{O2} [-]	NO_{ini} [ppm]	Nomenclature from Section 2, depending on oxidizer conditions
0.5 ; 0.9	1000	0.23	0	Case A
0.5 ; 0.9	1000	0.1	0	Case C
0.5 ; 0.9	1000	0.1	40 ; 200	Case new ; Case D

Table 3.- Description of the different mixtures considered for the simulation of the combustion process.

In this subsection, the temporal evolution of the two species being studied have been plotted in Figures 4a, 4b, 4c and 4d. This will allow the authors to extract more observations from the combustion process than just that related with the NO_2/NO_x ratio.
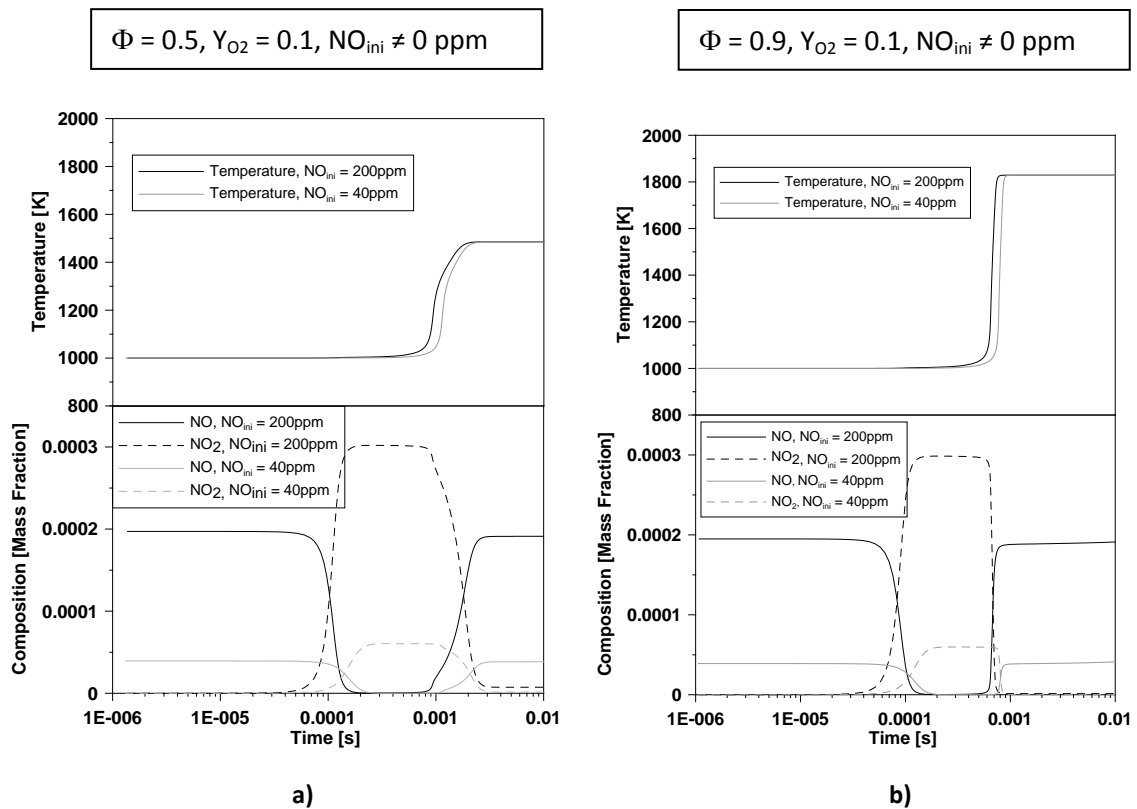
$\Phi = 0.5$, $Y_{O2} = 0.23$, $NO_{ini} = 0$ ppm

$\Phi = 0.9$, $Y_{O2} = 0.23$, $NO_{ini} = 0$ ppm

a)

b)

$\Phi = 0.5$, $Y_{O2} = 0.1$, $NO_{ini} = 0$ ppm

$\Phi = 0.9$, $Y_{O2} = 0.1$, $NO_{ini} = 0$ ppm

c)

d)

Figure 4.- Temperature and NO composition time evolution for several operational conditions simulating a constant pressure (P = 10MPa) HCCI combustion process at T_{ini} = 1000K: a) Φ = 0.5, Y_{O2}=0.23 and NO_{ini} = 0ppm, b) Φ = 0.9, Y_{O2}=0.23 and NO_{ini} = 0ppm, c) Φ = 0.5, Y_{O2}=0.1 and NO_{ini} = 0 ppm, d) Φ = 0.9, Y_{O2}=0.1 and NO_{ini} = 0ppm.

Despite the influence of the simulation time, it is observed that as the temperature increases the NO mass fraction increases while the NO_2 remains negligible for all the tested cases with the exception of Φ = 0.5, Y_{O2} = 0.1. In this case the amount of NO_2 is even higher than NO during the rapid temperature increase stage of the combustion process. Nevertheless, shortly after the temperature stabilizes, the NO_2 concentration starts to diminish rapidly. Despite this behavior it is important to note that both concentrations are negligible (< 0.01 ppm).

These results corroborate the ones obtained in the previous scenario and demonstrate that it is unlikely that the combustion process could generate the expected NO_2/NO_x increase unless under very poor combustion conditions for current diesel engines.

In Figures 5a and 5b the influence of the initial NO concentration is plotted. For both cases, these corroborate Bromly's findings [13], as NO_{ini} increases so does the ignition delay for a given equivalence ratio, and also highlights that the $NO-NO_2$ conversion process is cyclic and consisting in two stages: 1) conversion of NO to NO_2 and 2) re-conversion of NO_2 to NO.

Figure 5.- *Temperature and NO composition time evolution for several operational conditions simulating a constant pressure (P = 10MPa) HCCI combustion process at T_{ini} = 1000K: a)Φ = 0.5, Y_{O2}=0.1 and $NO_{ini} \neq$ 0 ppm, b)Φ = 0.9, Y_{O2}=0.1 and $NO_{ini} \neq$ 0ppm.*

In the first stage, all NO_{ini} is converted into NO_2 due to the formation of reactive radicals involved in the process and promoted at low temperatures. During this period higher NO_2 composition than NO_{ini} is achieved. However such increment is not a consequence of an additional NO_2 formation process, but instead is due to the higher molecular weight of NO_2 in

comparison with NO. This can be observed in Figure 6 where the time evolution of the molar fraction of both species is plotted.
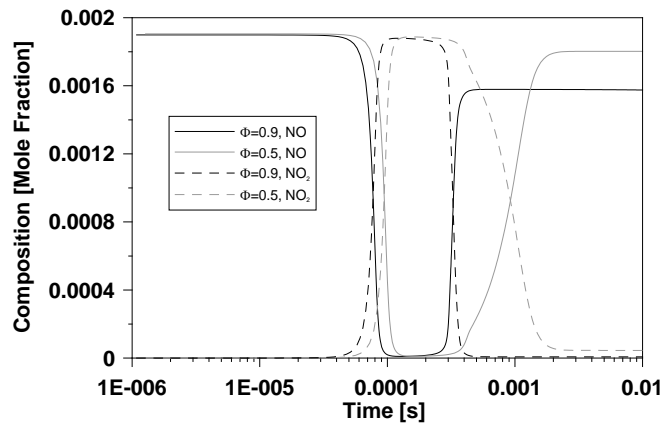
Figure 6.- Check of the influence of the molecular weight as the factor behind the greater NO2 composition in comparison with NO when representing the mass fraction of NO and NO$_2$.

As time evolves and the temperature increases, due to combustion, the NO$_2$ concentration diminishes in favor of NO (stage 2). The speed of this re-conversion is related with the combustion temperature reached: the higher the temperature, the higher the re-conversion. The final concentration of NO will strongly depend on the final conditions.

Consequently, the results from this scenario cannot explain, on its own, the increase from 10% to 30%, moving from CDC to LTC conditions, neither the 10% at CDC.

3.2.2- Effect of cooling processes on the NO-NO$_2$ conversion

The results from the previous scenarios seem to suggest that the increase in the NO$_2$/NO$_x$ ratio can be a consequence of the cooling effects inherent to the diesel engine operation: expansion stroke, the dilution effect of combustion products with fresh oxidizer stream remaining in the combustion chamber and due to wall impingement. Nevertheless, this latter effect won't be analyzed because the mass impinging the walls is so minor that it won't significantly influence the NO$_2$ formation.

To study their influence on the process, two different situations (corresponding to Case A and C described in the Objective and Methodology section) were analyzed employing the following procedure:

The influence of the expansion stroke on the NO_2 increase will be analyzed for two different engine speeds (N = 1000rpm and 2000rpm) using a straight forward procedure. This consists in determining the NO_2/NO_x ratio by using the single zone homogenous internal combustion engine module of Chemkin (ICE) and the engine characteristics summarized in Table 4. This ratio will be plotted as a function of time in concordance with the rest of the plots in the present paper.

Engine's Characteristic	Values
Stroke [m]	0.15
Bore [m]	0.12
Compression ratio [-]	14.4

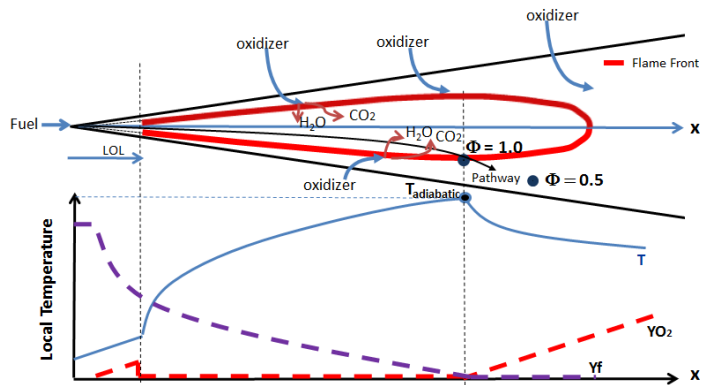*Table 4.- Engine's characteristics*

Figure 7. Schematic representation of the dilution phenomenon of the combustion products, generated in the flame front region, by the oxidizer stream and how it affects temperature, oxygen and fuel mass fraction.

The dilution effect will be contextualized in the diesel diffusion flame environment (see Figure 7) where its relevancy is greater than under HCCI combustion. This process will be simplified by considering adiabatic and constant pressure mixing phenomenon between: i) the combustion products (determined by assuming equilibrium conditions for Φ = 1 under the initial

conditions described by the two cases (A and C, as mentioned above)) and ii) the remaining

charge stream (assume to have a constant composition and at a substantially lower temperature

than the flame's temperature). Both the charge stream temperature and the mixing rate were

determined using the criterion of having an identical cooling speed than the dilution effect

(reference cooling curve), calculated using the two-stage Lagrangian model (TSL model) [44], for

two different injection pressures (P_{inj} = 500bar and 1500bar) and considering the spray's

baseline conditions summarized in Table 5. This 1-D spray modeling software is described in

great detail in Appendix A. Finally, it is worth to note that the authors are well aware that in the

flame front region the NO formation hasn't reached equilibrium. However, by doing so the

effect of the simulation time on the NO and NO_2 formation process is discarded.

Variables	Values
d_o [m]	$1.4 \cdot 10^{-4}$
ρ_f [kg/m^3]	830
ρ_a [kg/m^3]	20
T_a [m]	1000
T_f [K]	400
Fuel	n-heptane

Table 5.- Spray's baseline conditions.

To discard the reduction of NO and NO_2 as a consequence of the dilution effect due to

the entrainment of the charge stream the NO_2/NO_x ratio will be employed.

Figures 8a and 8b represent, for the non-EGR situation, the time evolution of the

temperature and the NO_2/NO_x ratio for the two studied phenomena: expansion stroke and

dilution by charge stream, respectively. Generally speaking, it can be observed that lower

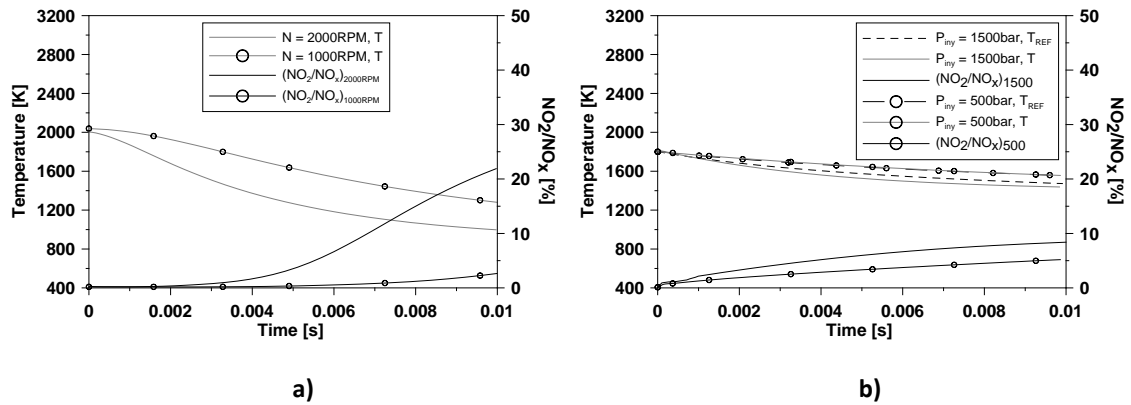temperatures yield higher NO_2/NO_x ratio.
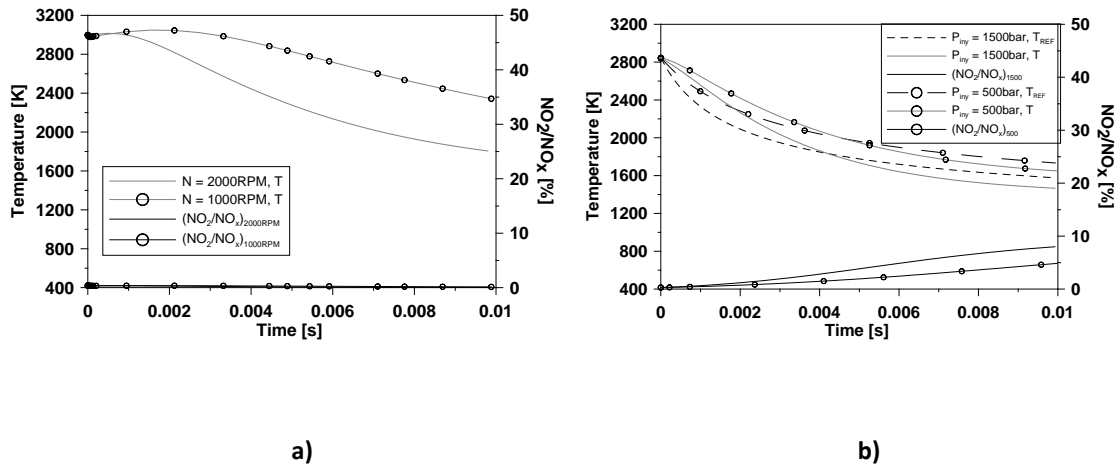
Figure 8.- Temperature evolution and NO$_2$/NO$_x$ ratio due to different cooling effects typical in diesel engines: a) expansion effect at two different engine speeds and b) dilution effects by considering two cooling speeds.

A closer analysis of the two plots reflects that under these conditions the cooling effect due to dilution could explain, by itself, the 10% NO$_2$/NO$_x$ ratio described in literature. Therefore it can be stated that the dilution effect will be the predominant factor to explain the ratio found in literature for these conditions. In contrast, it is evident from these plots that the expansion stroke is negligible independently of the considered engine speed.

The next situation resembles the use of high amounts of EGR from very low NO formation combustions (LTC) and/or engine working conditions, $Y_{O2} = 0.1$ and $NO_{ini} = 0ppm$.

Under these conditions, Figures 9a and 9b, lower combustion temperatures but higher NO$_2$/NO$_x$ ratios are reached. Therefore, once more, the results confirm that the NO-NO$_2$ conversion process is strongly enhanced at low temperatures. Additionally, it can be observed how the cooling effect due to the expansion stroke (highest engine speed) is not negligible in comparison with the rest of the results.

Figure 9.- Temperature evolution and NO$_2$/NO$_x$ ratio due to different cooling effects typical in diesel engines: a) expansion stroke at two engine speeds and b) dilution effects by considering two cooling speeds.

In this situation, with massive EGR, the results suggest that the increase in the NO$_2$ proportion could be explained by the combination of the cooling effects due to dilution and to the expansion stroke.

3.3.- Real engine measurement of NO$_2$/NO$_x$

Finally, measurements in a real single-cylinder engine were performed to quantify the proportion of NO$_2$ in the NO$_x$ emissions. The tested operating conditions are detailed in Table 6, whereas the engine's characteristics are described in the already presented Table 4. Regarding the operating conditions, it can be observed that a parametric study has been performed, changing the following parameters: the initial oxygen mass fraction, the engine speed (to modify the speed of the cooling effect associated to the expansion process) and the injection pressure (to modify the speed of the cooling effect associated to dilution).

|	Test #	1	2	3	4	5	6
O_2	[%]	12	12	12	17	17	17
N	[rpm]	1200	1200	1800	1200	1200	1800
P_{inj}	[bar]	2100	1300	2100	2100	1300	2100
A/F	[-]	19	19	19	19	19	19
P_{adm}	[bar]	2.53	2.53	2.53	1.42	1.42	1.42
m_f	[mg/cc]	90	90	90	90	90	90

Table 6. Conditions tested to validate the general trends observed in the present research

These results, plotted in Figures 10 and 11, corroborate the general trend observed throughout the research presented previously:

- For a given A/F ratio, an increase in EGR rate causes lower NO formation but greater proportion of NO_2 due to a reduction of oxygen content available to react.

- The engine speed is especially relevant for cases with massive EGR, Y_{O2} = 12%. An increase of this variable causes an increase in the NO_2/NO_x ratio. This is due to a quicker cooling process.

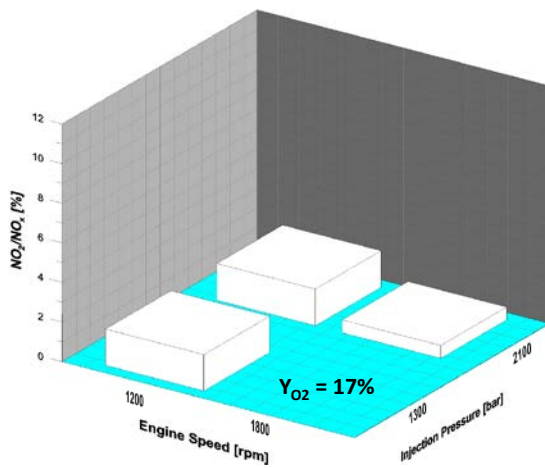- The injection pressure is not influence by the EGR rate. In both scenarios, the ratio is similar.
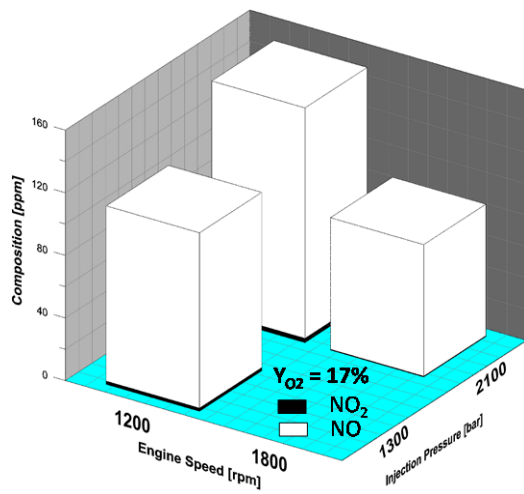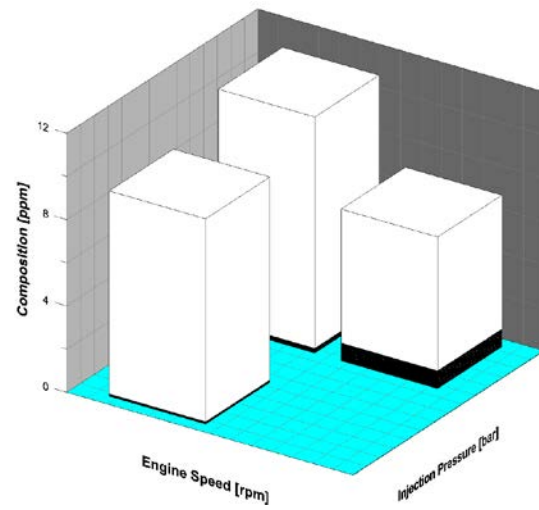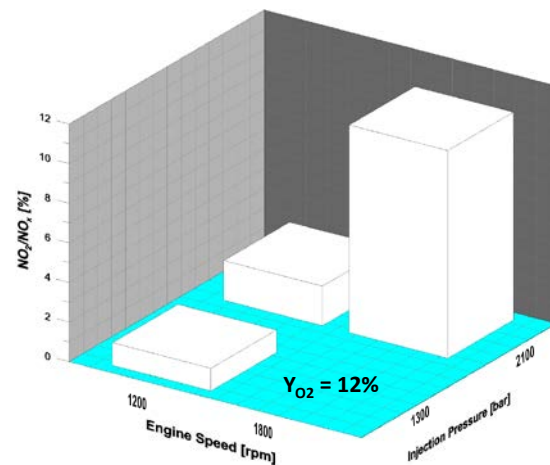
a)   *b)*

Figure 10. Quantification of the composition of NO and NO$_2$ in real engine experiments at different injection pressure, engine speed and oxygen mass fraction; a) 17%, b) 12%.

a)   *b)*

Figure 11. Quantification of the NO$_2$/NO$_x$ ratio in real engine experiments at different injection pressure, engine speed and oxygen mass fraction; a) 17%, b) 12%.

Finally it can be deduced then that high speed engines are prone to form less NO$_x$ but with a greater NO$_2$ content than other engines. This should be taken into consideration especially for the optimization of after-treatment devices.

4.- Conclusions:

After analyzing the results obtained, the conclusions that can be extracted from the present study are the following:

1.- Generally speaking, the NO_2 formation is a consequence of a cycling $NO-NO_2$ process which is strongly influenced by temperature and followed by oxygen mass content and simulation time and, to a minor extent, by the initial NO concentration.

2.- The equilibrium results illustrate that the NO_2/NO_x ratio are much lower than the well accepted range described in multiple combustion textbooks for CDC and for LTC combustion modes. However, when performing non-steady state simulations for the same working conditions it is appreciable that the NO_2/NO_x, for T < 1600K, is substantially greater than the equilibrium values. This suggests that low efficient combustion processes can indeed be responsible for the increase in the NO_2 formation.

3.- The non-equilibrium (non-steady state), non-constant temperature scenario confirms that the combustion process, by itself, is not responsible for the increase in NO_2 formation, from CDC to LTC conditions.

4.- Cooling effects (expansion stroke, dilution effect by oxidizer stream and wall impingement) enhance the $NO-NO_2$ conversion process increasing the NO_2 formation reaching the values described in the scientific literature.

a).- For CDC conditions the major contributor to the final NO_2/NO_x ratio is the dilution effect.

b).- For LTC conditions, the combination of the cooling processes due to the expansion stroke and the dilution effect are the main phenomena influencing the increase of NO_2 formation when moving from CDC to LTC.

c).- In both scenarios, CDC and LTC conditions, the cooling effect due to wall impingement can be discarded due to fact that the mass colliding is so minor that it won't significantly influence the NO_2 formation.

5.- The measurements performed in real engines not only have validated the results obtained in this research but also has highlighted that there is a big chance that high speed engines, under massive EGR recirculation conditions, are more prone to

produce higher NO_2 content than conventional engines even though less NO_X are formed.

6.- These cooling effects should be taken into consideration when modeling the NO_2 formation process.

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Appendix A: Two Stage Lagrangian model calculations

In this Appendix a detail description of the calculation performed with the TSL model is presented. The model requires the input of several variables in order to work, like: the air's composition (specially the initial oxygen mass fraction (Y_{O2ini})), the injection pressure (P_{inj}), the fuel and the air density (ρ_f and ρ_a, respectively), the fuel and the air temperature (T_f and T_a, respectively), the nozzle orifice diameter (d_o) and the fuel (n-heptane). All these variables with their corresponding values are summarized in Table A.1.

Variables	Values
d_o [m]	$1.4\cdot10^{-4}$
ρ_f [kg/m^3]	830
ρ_a [kg/m^3]	20
T_a [m]	1000
T_f [K]	400
Y_{O2ini} [mass fraction]	0.23 and 0.1
Fuel	n-heptane

Table A.1.- Summary of the inputs required and their values for the TSL model to work.

With these values, the equivalent diameter (d_{eq}) and the fuel's speed (u_o) is calculated applying equation A.1 and A.2, respectively.

$$d_{eq} = d_o \cdot \sqrt{\frac{\rho_f}{\rho_a}} \qquad (Eq.A.1)$$

$$u_o = \sqrt{\left(2 \cdot P_{inj} \cdot \frac{10^6}{\rho_f}\right)} \qquad (Eq.A.2)$$

Afterwards, the mixture's history along the axis and within time is possible to be determined by applying the Ricou and Spalding equation (Eq. A.3), for the entrainment rate for

non-reacting turbulent jets, and considering the momentum flux in the jet to be constant (Eq. A.4).

$$\frac{m}{m_o} = 0.32 \cdot \frac{x}{d_{eq}} \quad (Eq.A.3)$$

$$m \cdot u = m_o \cdot u_o \quad (Eq.A.4)$$

With these basic principles of the spray's theory and dividing the structure in two different zones (flame front and flame core), each one characterized by a perfectly stirred reactor (PSR), the temperature evolution is easily calculated. In the following plots the evolution for the two P_{inj} (500 and 1500bar), under the non-EGR and EGR situations (Y_{O2ini}: 0.23 and 0.1, respectively), are represented.
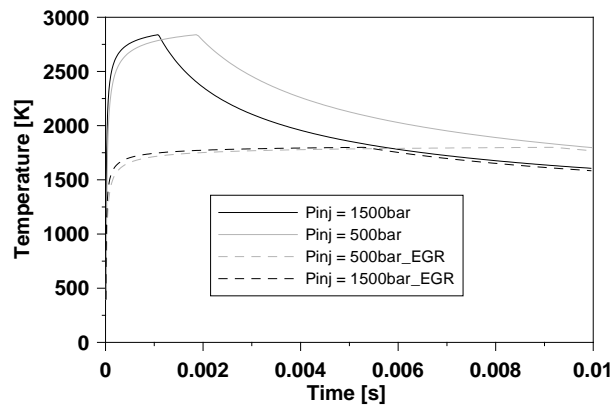
Figure A.1.- Temperature time evolution for a diesel spray under the four different working conditions.

These temperature curves are considered to be the reference cooling speed, depicted in discontinuous line in the text, for the cooling effect caused by the dilution of combustion products with fresh oxidizer stream.