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MODELING OF THE NITROGEN OXIDES FORMATION PROCESS APPLICABLE TO SEVERAL DIESEL COMBUSTION MODES

DOCTORAL THESIS

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TESIS DOCTORAL

MODELING OF THE NITROGEN OXIDES FORMATION PROCESS APPLICABLE TO SEVERAL DIESEL COMBUSTION MODES

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Resumen:

Como consecuencia de las exigentes legislaciones medioambientales actualmente en vigor, como las Euro Emission Standards en Europa, los investigadores e ingenieros se ven forzados a "re-desarrollar" el proceso de combustión diésel para hacerlo menos contaminante. Uno de los principales contaminantes y más dañinos para la salud son los óxidos de nitrógeno (NO_x) que están principalmente compuestos por: monóxido de nitrógeno (NO), dióxido de nitrógeno (NO_2) y trióxido de dinitrógeno (N_2O_3).

Centrándose en los NO_x generados en una combustión diésel, una de las técnicas más populares para mitigar su formación es mediante la dilución de la corriente oxidante con productos de la combustión, previamente generados. De este modo, al reducir la reactividad de la corriente oxidante se consigue una disminución considerable de la temperatura de combustión y por extensión de los NO_x. Sin embargo, dicha técnica causa nuevas interacciones físico-químicas entre los hidrocarburos y los NO_x así como principalmente un notable cambio en la estructura del chorro diésel. Es por ello necesario considerar las diferentes vías de formación de éstos para poder predecir su generación.

El hecho de considerar las diferentes vías de formación implica un incremento considerable de los recursos computacionales destinados a realizar las simulaciones, siendo en algunos casos inviable. Es por ello que el **objetivo principal de esta tesis consiste en: desarrollar herramientas capaces de tener en consideración todas estas vías sin incrementar de manera considerable el coste computacional.**

Para ello inicialmente se realiza una exhaustiva revisión bibliográfica en donde se repasan las diferentes herramientas desarrolladas para la predicción de los NO_x y se analizan sus puntos débiles. Éstos radican en simplificaciones de dudosa validez, que solamente tienen efectos positivos a altas y no a bajas temperaturas, o bien procesos demasiado tediosos y complejos para caracterizar los diferentes estados de una combustión. Posteriormente se diseña una metodología capaz de satisfacer el objetivo principal, basada en tres estudios. El primero permite profundizar en el proceso de formación de este contaminante a través de estudiar el incremento de la proporción de NO_2 en los NO_x debido a la recirculación masiva de estos productos. Por otro lado, los otros dos consisten en desarrollar diversas herramientas predictivas centradas exclusivamente en el NO, ya que como se dedujo del estudio anterior el NO_2 se forma principalmente a partir del NO a través de un proceso de enfriamiento. La primera de estas herramientas está basada en una correlación empírica que a modo de ecuación correctiva mejora la capacidad predictiva, especialmente en condiciones de recirculación masiva, del mecanismo más implementado mundialmente, mientras que la segunda se sustenta en tabular únicamente la velocidad de formación del NO y el NO en equilibrio en función de la temperatura y de la cantidad de oxígeno disponible inicialmente para reaccionar.

Finalmente para poder llevar a cabo estos estudios y cumplir con el objetivo principal se hace uso de un software comercial cinético-químico Chemkin, en su versión Professional, que sirve tanto de herramienta desarrolladora como de referencia.

Resum:

Com a conseqüència de les exigents legislacions mediambientals actualment en vigor, com les Euro Emission Standards en Europa, els investigadors i enginyers es veuen forçats a "re-desenvolupar" el procediment de combustió dièsel per a fer-lo menys contaminant. Un dels principals contaminants, i més nocius per a la salut, són els òxids de nitrogen (NO_x) que estan principalment composats per: monòxid de nitrogen (NO), diòxid de nitrogen (NO_2) i triòxid de dinitrogen (N_2O_3).

Centrant-nos en els NO_x generats en una combustió dièsel, una de les tècniques més populars per a mitigar la seua formació és mitjançant la dilució del corrent oxidant amb productes de la combustió, prèviament generats. D'aquesta manera, al reduir la reactivitat del corrent oxidant s'aconsegueix una disminució considerable de la temperatura de combustió i per extensió dels NO_x. En canvi, la mencionada tècnica causa noves interacciones fisicoquímiques entre els hidrocarburs i els NO_x així com, principalment, un notable canvi en l'estructura del doll de dièsel. Per a això cal considerar les diferents vies de formació d'aquests per a poder predir la seua generació.

El fet de considerar les diferents vies de formació implica un increment considerable dels recursos computacionals destinats a realitzar les simulacions, sent, en alguns casos, inviable. És per això que l'**objectiu principal d'aquesta tesi consisteix en: desenvolupar eines capaces de tenir en consideració totes aquestes vies sense incrementar de manera considerable el cost computacional.**

Per a això, inicialment, es realitza una exhaustiva revisió bibliogràfica on es repassen les diferents eines desenvolupades per a la predicció dels NO_x i s'analitzen els seus punts febles. Aquests radiquen en simplificacions de validesa dubtosa que, solament, té efectes positius a altes i no a baixes temperatures, o bé processos massa tediosos i complexos per a caracteritzar els diferents estats d'una combustió. Posteriorment es dissenya una metodologia capaç de satisfer l'objectiu principal, basada en tres estudis. El primer permet aprofundir en el procediment de formació d'aquest contaminant a través d'estudiar l'increment de la proporció d'NO_2 en els NO_x degut a la recirculació massiva d'aquests productes. D'altra banda, els altres dos consisteixen a desenvolupar diverses eines predictives centrades, exclusivament, en l'NO, ja que com es va deduir de l'estudi anterior l'NO_2 es forma principalment a partir de l'NO a través d'un procediment de refredament. La primera d'aquestes eines està basada en una correlació empírica que a mode d'equació correctiva millora la capacitat predictiva, especialment en condicions de recirculació massiva, del mecanisme més implementat mundialment, mentre que la segona es sustenta en tabular únicament la velocitat de formació de l'NO i l'NO en equilibri en funció de la temperatura i de la quantitat d'oxigen disponible, inicialment, per a reaccionar.

Finalment per a poder portar a terme aquests estudis i complir amb l'objectiu principal es fa ús d'un programari comercial cineticoquímic, Chemkin, en la seua versió Professional, que serveix tant d'eina desenvolupadora com de referència.

Summary

As a consequence of the stringent emission legislation worldwide, like the Euro Emission Standards in Europe, researchers and engineers are in the need of "re-developing" the diesel combustion engine in order to make it more environmentally friendly. One of the main and most harmful gaseous pollutants of diesel engines for automotive applications are the nitrogen oxides (NO_x), the sum of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and di-nitrogen monoxide (N_2O), which have been and continues to be significantly reduced.

Focusing on the engine-out NO_x emissions, the most popular technique to reduce their level consists in reducing the combustion temperature and the local equivalence ratio mixtures by recirculating high amounts of exhaust gasses back to the combustion chamber. This causes the dilution of the fresh oxidizer stream, causing a reduction in its reactivity, which in consequence causes a decrease in the combustion temperature and of NO_x. However, this technique influences new physical-chemical interactions between hydrocarbons and NO_x as well as a significant change in the diesel spray. Consequently it is necessary to take into consideration all the different NO_x formation routes in order to accurately predict this formation.

The fact of considering the different routes implies an increase in the computational cost of the simulations performed which in some cases makes them unaffordable. Therefore the **main objective of this thesis is to develop predictive tools capable of considering all these formation routes without increasing the computational costs.**

To do so, initially an exhaustive literature review was performed in which the author goes over the different predictive tools analyzing their weaknesses. These relie mainly in performing several simplifications, not always precise, which only have influence at high and not at low temperatures or instead by performing tedious and complex procedures to characterize the different combustion stages. Afterwards a methodology was design capable of satisfying the main objective based on three studies. The first one analyzes in detail the formation process of this pollutant by focusing on the increase of the NO_2 ratio in the NO_x emissions. The remaining two consist in developing different predictive tools focusing only on the NO specie, because as concluded from the previous one, all the NO_2 is formed from NO during a cooling process. The first of these tools is based on an empirical correlation which serves as a corrective equation improving the NO predictions, of the most extended mechanism (Thermal), specially in cases with massive recirculation of combustion products. The second relies in tabulating as a function of temperature, oxygen content available and pressure the reaction rate of the NO formation process as well as the NO formed considering equilibrium state.

Finally, in order to perform all these studies and accomplish the main objective a commercial chemical-kinetic software (Chemkin), in its professional version, was employed serving as a developing and a reference tool.

A mis padres (Pepe y Empar), mi hermano (Carles) y mi mujer (Maria José) que han sido piezas fundamentales para completar esta etapa de mi vida. Pero sobre todo a mi hijo Pau que me ha enseñado muchísimo.

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Table of Symbols:

Nomenclature	Definition
$Calc\left(\frac{Thermal\ NO}{Total\ NO}\right)$	Result of applying the empirical corrective correlation to the Thermal mechanism's prediction
$Calc\left(\frac{(Thermal\ NO)_{COR}}{Total\ NO}\right)$	Quantifies the effectiveness of the empirical corrective correlation applied to the Thermal mechanism's prediction
CDC	Conventional diesel combustion
EGR	Exhaust gas recirculation
EPEFE	European Programme on Emissions, Fuels and Engine Technologies
Φ	Equivalence ratio
FGM	Flamelet generated manifold
FPI	Flamelet propagation approach to the intrinsic low dimension manifold
GRI-Mech	Gas Research Institute chemical kinetic mechanism
HCCI	Homogeneous Charge Compression Ignition
ILDM	Intrinsic low dimension manifold
ISAT	In-situ adaptive tabulation
k	Variable characterizing the NO/NOeq time evolution
LTC	Low temperature combustion
m_{O2}	Oxygen mass
m_{oxid}	Oxidizer mass (oxygen + exhaust gas recirculation mass)
n	Engine speed in rpm

NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_{eq}	Nitrogen monoxide predicted under equilibrium state
NO_{ini}	Initial nitrogen monoxide composition
NO_{ref}	Reference nitrogen monoxide prediction (yield by solving the energy equation)
NO_t	Predicted nitrogen monoxide at a given time
NO_{t-1}	Predicted nitrogen monoxide in the previous time step
NO_{Th}	Nitrogen monoxide predicted only by considering the Thermal version of the RES-mech
NO_x	Nitrogen oxides
PCCI	Premixed Charge Compression Ignition
P_{inj}	Injection pressure
PSR	Perfectly Stirred Reactor
RES-Mech	Resulting mechanism from coupling Seizer's n-heptane oxidation mechanism with the GRI-Mech 3.0 mechanism in order to take into consideration the NO_x sub-mechanism.
T	Temperature
T_{ad}	Adiabatic temperature
T_{end}	Temperature reached at the end of the reaction
Thermal NO	Nitrogen monoxide predicted by the Thermal mechanism
T_{ini}	Initial Temperature
Total NO	Nitrogen monoxide prediction obtained from the RES-mech
TSL	Two-stage Lagrangian model

$(Y_{O2})_{atm}$	Atmospheric oxygen mass fraction
Y_f	Fuel mass fraction
Y_{O2}	Oxygen mass fraction
Y_{O2exc}	Oxygen mass fraction remaining after the combustion process has ended.
Y_{O2ini}	Initial oxygen mass fraction available to react and will be employed to describe the EGR rate considered.
Z	Mixture fraction
Z_r	Relative mixture fraction
Z_{st}	Stoichiometric mixture fraction

Chapter 1

Introduction

Content

1.1 Introduction

This chapter consists in two sections. The first one will contextualize the present research study while the second will outline the document structure to give the reader an overview of the different analyzed topics.

1.1.1.- Context of the study

As a consequence of the stringent emission legislation worldwide, like the Euro Emission Standards in Europe, researchers and engineers are in the need of "re-developing" the diesel combustion engine in order to make it more environmentally friendly. One of the main and most harmful gaseous pollutants of diesel engines for automotive applications are the nitrogen oxides (NO_x), the sum of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and di-nitrogen monoxide (N_2O), which have been and continues to be significantly reduced.

Focusing on the engine-out NO_x emissions, the most popular technique to reduce their level consists in reducing the combustion temperature and the local equivalence ratio mixtures by recirculating high amounts of exhaust gasses back to the combustion chamber. This causes the dilution of the fresh oxidizer stream and consequently a reduction in its reactivity.

However it has been also demonstrated that other major changes are implicitly related with the massive recirculation of exhaust gasses, like: a substantial change in the diesel spray structure and in the chemistry ruling the NO_x formation. Focusing on this latter aspect, in order to accurately predict the formation of this pollutant it is necessary to consider at least several formation routes (Thermal, N_2O routes and in some cases also the prompt mechanism) in contrast with just considering the Thermal mechanism, which was the common strategy to

predict NO_x emissions under conventional diesel combustion, where high combustion temperatures are reached. The fact of considering more than one formation mechanism is associated with an increase in the computational cost which in some cases can be unaffordable.

Multiple techniques have been developed to predict the amount of NO formed. These techniques have a parallel evolution with the development of the computer technology and with the know-how of the nitrogen chemistry in gas-phase combustion processes. In the present document two new methodologies associated with low computational cost are proposed in order to perform reasonably accurate predictions, when massive use of exhaust gas recirculation (EGR) is employed, and maintaining high accuracy under conventional diesel combustion conditions.

1.1.2.- Structure of the study

Initially, a literature review will be performed, in **chapter 2**, covering different aspects directly related with the topics listed previously and involved in the different researches performed in this Thesis. Some of these topics reviewed are: 1) the diffusion flame conceptual models used to explain the structure and phenomena involved in diesel sprays under conventional diesel conditions and low temperature conditions, 2) the chemical mechanisms describing the formation/destruction of NO_x and different methodologies used to predict the amount of NO_x formed.

Chapter 3 will briefly summarize this review highlighting the weaknesses found and establishing the objectives of the present Thesis. Furthermore, in this chapter a general overview of the methodology employed to achieve them will be outlined. In **chapter 4**, the methodology used in the present work will be described in great detail and justified on key issues, like: the employed fuel surrogate, the construction of the chemical kinetic mechanism (fuel oxidation mechanism and NO_x sub-mechanism) and how the mixing process is characterized. Furthermore, a brief outline will be presented of the main characteristics of the well-known and accepted chemical kinetic software which have been used in this research: Chemkin.

Once the objectives and the methodology have been well defined, **chapter 5** will deal with the first of the proposed objectives: understand the NO-NO_2 conversion process. Even though the NO_2 formation in diesel engines is in most cases negligible with respect to the NO formation, in others, it is not. The main goal of this chapter is to understand how this conversion process occurs. Depending on the findings it would be taken or not into consideration in the following modeling processes of the NO_x emissions formed after a combustion process.

Chapter 6 will be related with another of the established objectives; determine the predictive capability of the different formation routes under conventional diesel combustion conditions but specially under low temperature combustion conditions. In case there is a predominant route, this behavior will be enhanced in a low computational cost methodology. One way of doing this, employed in the present chapter, is through an empirical correlation obtained by assuming constant local conditions over a wide operational range (eg:

conventional and low temperature diesel combustion conditions). However in real combustion processes the main variables (temperature, pressure and species composition) are continuously varying with time causing the empirical correlation to loose certain degree of accuracy. Consequently, in **chapter 7** the author proposes a new low computational cost methodology based on tabulated chemistry, in particular focusing on the NO formation rate, to predict the formation of this pollutant.

Finally in **chapter 8** the main conclusions of the three research studies, described in chapters 5, 6 and 7, will be summarized and future works will be presented taking as starting point the knowledge acquired from the present researches.

Chapter 2

Literature review

Content

2.1 Introduction

Nitrogen oxides, NO_x, are one of the main and most harmful pollutants of combustion processes for human's health and they are made up of different species, like: nitrogen monoxide (NO), nitrogen dioxide (NO_2), dinitrogen oxide (N_2O), nitrogen trioxide (NO_3) and dinitrogen trioxide (N_2O_3). To reduce these and other emissions severe stringent environmental legislations have been widely implemented worldwide. In the case of Europe these are known as Euro Emission Standards (Table 2.1). Consequently, major efforts have been dedicated, in the research field, by original engine manufacturers (OEMs), research departments at universities and at research institutions to understand the formation of the NO_x emissions in a diesel combustion process.

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 2.1.- Euro Emission Standards for Diesel Passenger Cars.

2.2 NO_x formation context

2.2.1 Conventional diesel combustion conditions

The first Euros where achieved by engine control and simple after-treatment devices which mitigated the NO_x emissions generated inside the diesel engine (engine-out NO_x emissions) when operating at conventional diesel combustion conditions (CDC). These conditions are based on a mixing controlled combustion, which generates a diesel diffusion flame, which is characterized mainly by: high combustion pressures, close to stoichiometric fuel-air mixtures, none or minor use of exhaust gas recirculation (EGR) and high combustion temperatures (T_{ad} > 2700K).

This diffusion flame has been research topic for multiple scientists (Chiu et al [1], Faeth [2], Kamimoto and Bae [3], Dec [4] and Flynn et al [5]) and several conceptual models were proposed, making use of various visualization techniques. The most recent one and extended, despite the presence of some uncertainties, is the Dec's model [4]. This model, illustrated in Figure 2.1, is referred to a "developed" reacting diesel fuel jet during the mixing controlled burn.

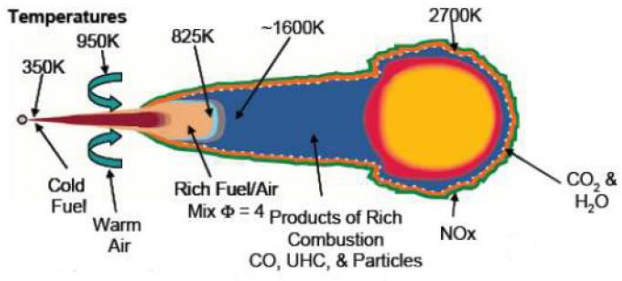

Figure 2.1.- Dec's conceptual model

Generally speaking, the flame structure can be divided into two main regions: inert zone (region between the nozzle orifice and the reactive zone of the flame, characterized by the lift-off length and where fuel's atomization and evaporation as well as air entrainment

occurs, just like in an evaporative and non-reactive spray) and reaction zone. The latter zone can be divided into two regions: premixed combustion and diffusion combustion. The premixed combustion region is located immediately after the inert zone. In it, all the oxygen entrained to the diesel spray, in the previous region, is consumed and therefore inside the diffusive flame the oxygen concentration is null. Corresponding to Dec's asseverations, the combustion products generated from the fuel-rich premix combustion are the origin for the formation of the soot precursors. On the other hand, the diffusion combustion zone corresponds to the area delimited by the flame's perimeter. In this flame perimeter two zones are distinguished by Dec: an internal zone (where partial combustion products, un-burned fuel and soot are commonly present) and an external region (NO_x formation is observed). This formation process takes place around a relatively thin sheath surrounding the exterior of the diffusion-burning interface, where the ideal NO_x formation conditions for the thermal route, can be encountered: high temperature and high presence of oxygen and nitrogen. Once the NO_x have been formed it can diffuse both into and away from this region.

In this context the 65% of the NO_x in the tail pipe is created as a consequence of the previously described process [4] and its composition is mainly 90% NO and 10% NO_2 even though it can vary up to 70%:30%, respectively, depending on the engine loads and engine speeds [6].

Focusing on the formation process of the NO specie, under these conditions, the Thermal or Zeldovich mechanism is undoubtedly the main route. This mechanism was initially postulated by Zeldovich [7] in the early 40s, and it consists of two reactions (R.1 and R.2) which describe the NO formation as a result of the competing dissociation process between oxygen and nitrogen due to the high temperatures reached during combustion. Three decades after, Lavoie [8] extended this mechanism, with a third reaction and consequently it was renamed as the extended Zeldovich mechanism. This latter reaction, which reduces its relevancy as the equivalence ratio increases, explains the oxidization of the N (released by R.1) by the OH radical. Note that in order to simplify the nomenclature extended Zeldovich mechanism and Thermal mechanism will be synonyms in the present document.

$$N_2 + O \leftrightarrow NO + N \quad \text{(R. 1)}$$

$$N + O_2 \leftrightarrow NO + O \quad \text{(R. 2)}$$

$$N + OH \leftrightarrow NO + H \quad \text{(R. 3)}$$

In the case of the formation of NO_2, initially, the combustion process (in the flame front) will generate combustion products, including NO, which as they diffuse downwards from the flame front region will mix with cold air/charge causing the oxidation of NO to NO_2 [6]. This reasoning is in coherence with the theoretical "guidelines" established by several authors [9-16] whom studied the phenomenon in gas turbines, domestic combustion appliances and probing samples. These guidelines are:

- The NO_2 formation takes place due to a radical relaxation process mechanism as a consequence of the rapid cooling of hot combustion gasses. This process

achieves significant NO-NO_2 conversion throughout the HO_2 radical at low temperatures.

- Hori et al. [9-10] and Marinov et al. [11] 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. [12] 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 as "mutually sensitized oxidation of NO and fuel", and is believed to control the NO_2 emissions as a consequence of the fuel oxidation.

All of these principles are coherently put together in the following mechanism consisting on the following reactions, R.4 – R.6. Note that R.7 takes into consideration the formation of the HO_2 radical at low temperatures.

$$NO + HO_2 \leftrightarrow NO_2 + OH \quad \text{(R.4)}$$

$$NO_2 + H \leftrightarrow NO + OH \quad \text{(R.5)}$$

$$NO_2 + O \leftrightarrow NO + O_2 \quad \text{(R.6)}$$

$$H + O_2 + M \leftrightarrow HO_2 + M \quad \text{(R.7)}$$

2.2.2 Low temperature diesel combustion conditions

However, to accomplish the new stringent Euro 5, currently facing, and the future ones the engineers and researchers are on the need of re-developing the diesel combustion process. Cleaner diesel combustion processes can be mainly achieved by: 1) operating with homogeneous fuel-oxidizer mixtures and/or 2) by reducing the combustion temperature (T_{ad} < 2200K). This will shift the combustion process to the left hand side of the Φ – T map, see Figure 2.2.

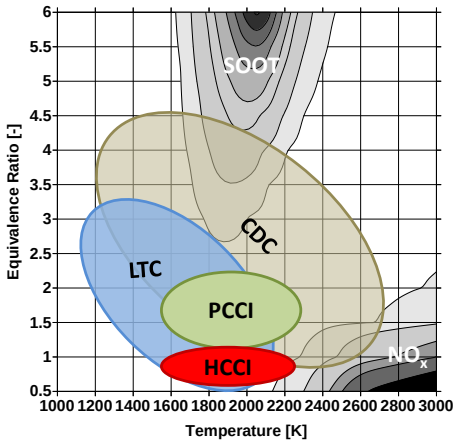

Figure 2.2.- Predominant ϕ-T working conditions for several new combustion modes [17].

Regarding homogeneous fuel-air mixtures, several modes have been developed and are currently on the conceptual stage or, in the best of the cases, in the optimization stage prior to be introduced in production engines. Some of these modes and their characteristics are [18]:

- Homogeneous Charge Compression Ignition (HCCI): The main characteristic withstands in the fact that is a combustion process of a fully homogeneous premixed mixture, the main advantages of which are: high combustion efficiency, low NO_x and low soot formation. The homogeneous mixture is achieved by injecting the fuel in the intake manifold or prior to the compression stroke. As the compression stroke continues to progress the in-cylinder temperature and pressure rises until it auto-ignites the mixture. This type of combustion has lower local temperatures than conventional combustions, therefore reducing NO_x emissions. On the other hand, to reduce soot emissions fuel-lean mixtures, associated to low temperature, are used. Nevertheless it has important drawbacks that need to be minimized prior to their commercialization: high unburned hydrocarbons and CO emissions, the complexity of controlling auto-ignition and minimize the mixture impinging into the wall. In Figure 2.3 a schematic comparison of this combustion mode with the diesel combustion is presented.

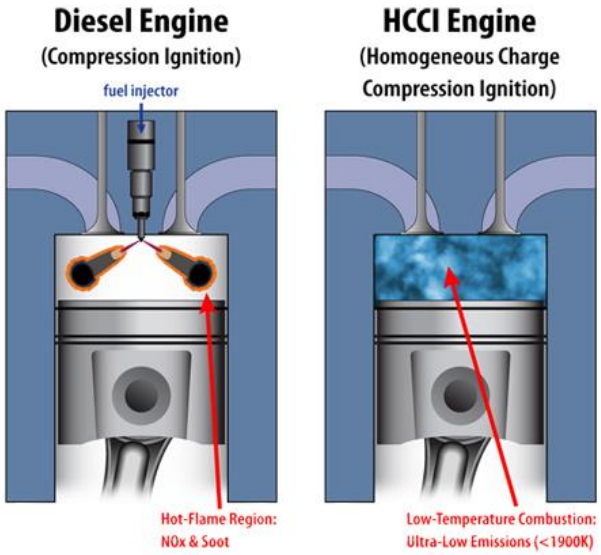

Figure 2.3.- Schematic comparison between a diesel and a HCCI combustion processes [19]

- Premixed Charge Compression Ignition (PCCI): Combustion mode similar to the previous one but the fuel is injected in the early stages of the compression stroke. A prototype engine was presented by Iwabuchi et al [19] in 1999 which reduced NO_x emissions without increasing soot. However high unburned hydrocarbons emissions and fuel specific consumption were observed.

With respect to reducing combustion temperature, this can be achieved by burning leaner fuel mixtures and/or by diluting the oxidizer stream with combustion products recirculated back to the combustion chamber. This latter one is the predominant strategy, is known as exhaust gas recirculation (EGR), and its main principle is to reduce the reactivity of the fresh oxidizer stream (normally fresh air) by mixing it with combustion products, which are substantially less reactive.

The proliferation of these combustion strategies strongly demands a new conceptual model of the diesel spray structure, under these new conditions, to help understand the phenomena involved. In a parallelism with the CDC scenario, several research studies [21-23] were performed using high EGR rates and injecting very early in the compression stroke of heavy [21] and light duty engines [22]. The main results reflected a low soot and NO_x formation process, typical of low temperature combustions, because other findings were incoherent when put together.

However, a study performed by Musculus [23], in a heavy duty engine at an engine speed (n) of 1200rpm, is the one that clarified this structure. The results were summarized in "an extension of Dec's model" for LTC combustions, see Figure 2.4.

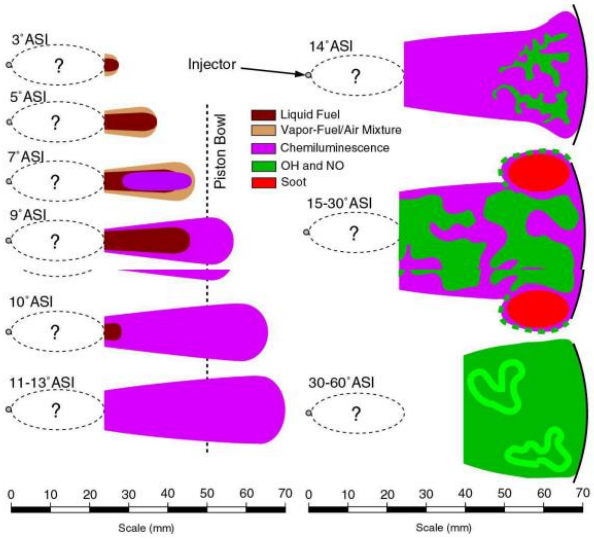

Figure 2.4.- Schematic representation of a diffusion flame's structure under low temperature conditions [23].

Besides the evident difference in the spray structure there are also different phenomena involved in comparison with those occurring under CDC conditions. The first of them is the appearance of the cool flame at 10º after start of injection (ASI). This phenomenon lasts for 1º ASI and at the end of its heat release and after the end of the fuel injection, the fuel is completely vaporized, even the one remaining near the injector (<25mm). The second is related with the NO_x formation process which takes place in the final stages of the combustion process. In contrast with the CDC conditions, these are produced in the inner region of the spray where the equivalence ratio can vary from 1.5 to 0.5.

This latter fact confirms a change in the chemistry influencing the NO_x formation process. The most obvious is the loss of relevance of the thermal mechanism in favor of the prompt [24] and the N_2O mechanisms under fuel-rich and fuel-lean mixtures, respectively. The increase in relevancy of this latter mechanism was confirmed by Amnèus [25] and Kung [26].

Even though N_2O is highly unstable and is very improbable to exist in the exhaust of combustion systems, Lavoie et al. [8] and Turns [27] developed several chemical-kinetic mechanisms for this specie. In the case of Lavoie's version it proceeds through reactions R.8, R.9 and R.10 while Turns' through R.8, R.11 and R.12. Independently of the mechanism, both are significant at temperatures below 1800K and for fuel-lean mixtures combustions, $\Phi < 0.8$.

$$N_2O + O \leftrightarrow NO + NO \quad \text{(R.8)}$$
$$N_2O + O \leftrightarrow N_2 + O_2 \quad \text{(R.9)}$$
$$N_2O + H \leftrightarrow N_2 + OH \quad \text{(R.10)}$$
$$N_2O + M \leftrightarrow N_2 + O + M \quad \text{(R.11)}$$
$$N_2O + H \leftrightarrow NO + NH \quad \text{(R.12)}$$

The prompt mechanism was proposed by Fenimore [24] when he observed that other reactions, besides those included in the thermal mechanism, were relevant in the NO

formation under fuel-rich combustion processes and little with temperature. This mechanism is much more complex than the previous ones, as it can be observed in Figure 2.5 [28], and therefore it is continuously being complemented with new reactions [29], even though most of them are not applicable when considering typical diesel engine working conditions.

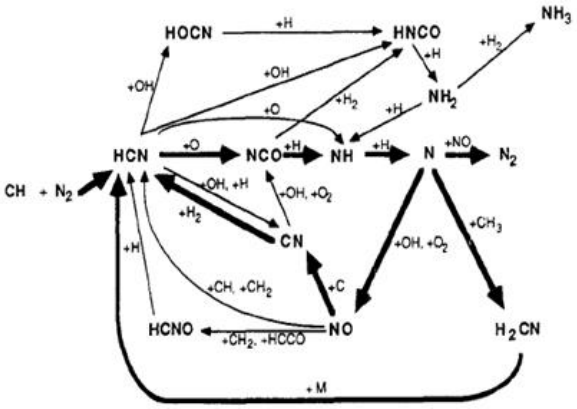

Figure 2.5.- Prompt mechanism scheme [28].

Generally speaking, it is based on the fact that hydrocarbon radicals react with molecular nitrogen (N_2) to form cyano compounds (HCN, HOCN, NCO, HNCO and CN) mainly through the following reaction: $CH + N_2 \leftrightarrow HCN + N$. Afterwards these species are rapidly converted to other intermediate species which react with radicals (H, O and OH) to form NO, or, with amines to form N_2.

Other phenomenon, less obvious, is the NO_x reburning process which is enhanced by the massive use of EGR and takes place not only in the inner region of the diesel flame but also in the flame front.

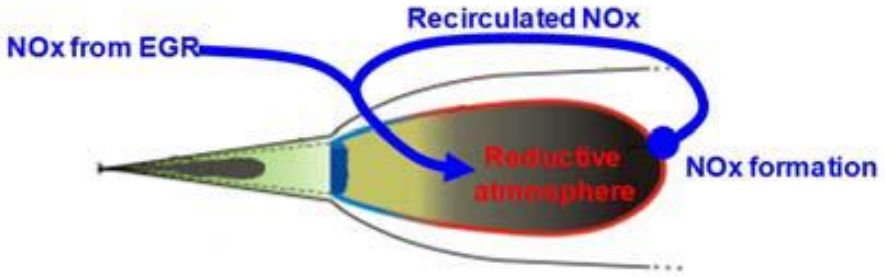

Figure 2.6.- Scheme of the phenomenology of NO_x re-burning process inside a diesel jet due to the re-entrainment of combustion products under high load working conditions in diesel engines and due to the employment of EGR [30].

Studies performed in real diesel engines, considering the employment of EGR under conventional combustion conditions, already reflected that this mechanism should be taken into account to improve the NO_x prediction for diesel engines [30-31]. As it can be appreciated from Figure 2.7, as the NO_x concentration increases in the intake manifold so does in the exhaust manifold. However, once a certain concentration is surpassed, a reduction in the NO_x emitted is plausible.

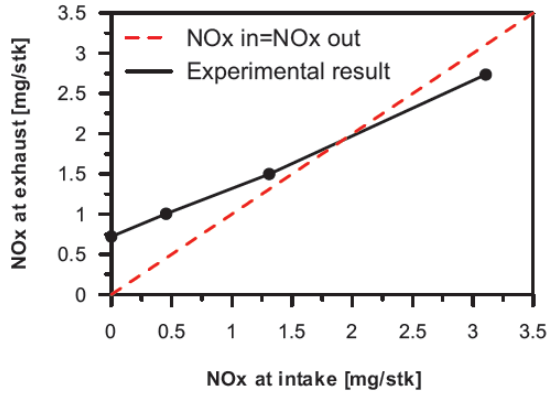

Figure 2.7.- NO_x amount at the exhaust vs NO_x amount at the intake [30].

This process was originally proposed and afterwards applied in boilers where the NO_x emissions were significant. In a study performed by Glarborg et al. [33] it was observed that for a temperature range between 800-1500K, the reactions R.13 and R.14 were relevant to reduce the NO emissions, when using methane as fuel and other types of fuels, respectively. Moreover, this latter reaction also has a significant effect on the NO formation, when poor mixing is encountered.

$$CH_3 + NO \leftrightarrow HCN + H_2O \quad \text{(R.13)}$$

$$HCCO + NO \leftrightarrow HCNO + CO \quad \text{(R.14)}$$

Even though these findings were observed for laboratory conditions, the results agreed with the studies performed by Meunier et al [34] and Dupont and Williams [35], making it extrapolable to the internal combustion engine (ICE) scenario. In the next figure, Figure 2.8, the different possible pathways in which NO reburning may occur are represented.

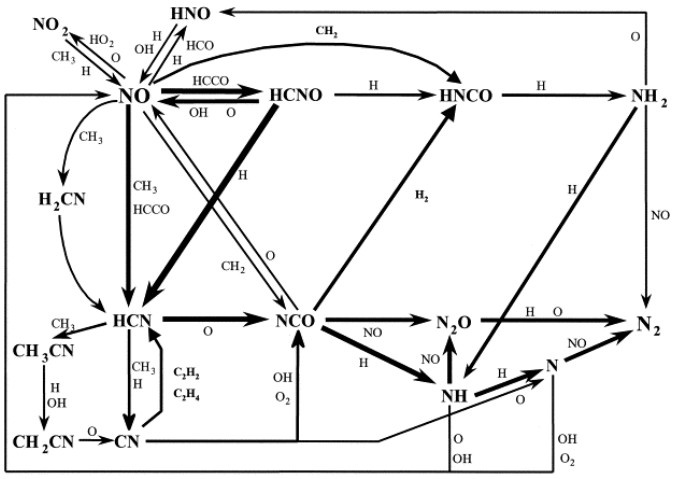

Figure 2.8.- NO_x destruction route through the hydrocarbon re-burning mechanism [36].

Finally, in this LTC scenario several authors [37-39] have observed a substantial increase of NO_2, even though these values vary between experimentalists. No further explanations have been presented to the scientific community besides the extended reasoning, built under CDC conditions, that such increase is related with the poor combustion and mixing of hot combustion products with cold oxidizer stream.

2.3 Modeling the NO_x emissions

As it can be concluded from the previous section, the diesel combustion process is becoming more complex each time in order to accomplish the most stringent Emissions Standards. Consequently, in order to accurately predict the NO_x engine-out emissions, detailed chemistry and physics must be considered.

In the following lines a review will be performed focusing on the most popular predictive tools under steady (i.e: equilibrium conditions) and non-steady state (i.e: taking into consideration the influence of chemical-kinetics) scenarios for modeling NO_x emissions. From a chemical point of view a similar classification, as in Hernández [40], will be used and complemented with more recent methodologies. On the other hand, regarding the combustion modeling the review will concentrate in those tools used to simulate the physics involved in premixed auto-ignition (diesel HCCI) and diffusion diesel combustion (diesel spray) scenarios when performing 1-D and 0-D simulations.

2.3.1 Chemical modeling of NO_x emission

2.3.1.1Equilibrium conditions

When considering steady state conditions, normally, the equilibrium state is assumed. In this case, several authors (Olikara [41], Nightingale [42], Way [43] and Agrawal [44]), have developed different predictive tools capable of being employed in ICE.

All are based on the equilibrium constants method to calculate the corresponding species' concentrations. This method implies the selection of the corresponding equilibrium reactions and solving, by an iterative procedure (e.g: Way's procedure[43], Gauss-Jordan [45], Newton-Raphson method [46] and Gauss-Siedel [47]), a system of equations made up of:

- One mass balance equation for each atomic element present (eg: C, H, O and N in a CHON system).
- (Number of species – number of different atomic elements considered) equations based on equilibrium reactions.

The main drawback of this method relies in the strong dependence of the chosen reactions and the accuracy of their Arrhenius constants. To overcome this important inconvenient, NASA developed a model [48]which is only dependent on the chemical species considered and is based on minimizing Gibbs Free Energy and in the chemical potential procedure. This model is included in Chemkin software [49] and will be widely employed in the present document.

2.3.1.2 Considering Chemical Kinetics

When considering non-steady state conditions, all variables are time dependent. This fact may affect considerably the computational cost making the simulation even unaffordable in some cases. This problem is substantially enhanced in the case of analyzing turbulent combustion, typical of ICE. In order to mitigate such effect some predictive tools have been developed based on the following assumptions:

- Equilibrium considerations of simplified chemical-kinetic scheme
- Empirical or quasi-empirical correlations
- Partial equilibrium assumption
- Detailed chemical kinetic schemes

2.3.1.2.1 Equilibrium considerations of simplified chemical-kinetic scheme

Equilibrium assumptions are normally employed to calculate the thermal NO (NO_{TH}) formation process, for non-steady state conditions, by considering the extended Zeldovich and the N_2O mechanisms. The most relevant methodology was proposed by Lavoie et al. [8] which assumes that O_2, O, OH and H are at equilibrium because the formation rate of these species are substantially greater than for NO, N and N_2O. Additionally, N_2 is also considered to be in equilibrium because its concentration is much greater than any of the three key species. With these considerations, the formation rate of NO, N and N_2O can be calculated applying the following equations:

$$\frac{1}{V}\cdot\frac{d([NO]\cdot V)}{dt} = -\alpha(\beta R_1 + R_2 + R_3 + 2\alpha R_6) + R_1 + \beta(R_2 + R_3) + 2\gamma R_6 \quad \textbf{(Eq. 1a)}$$

$$\frac{1}{V}\cdot\frac{d([N]\cdot V)}{dt} = -\beta(\alpha R_1 + R_2 + R_3) + R_1 + \alpha(R_2 + R_3) \quad \textbf{(Eq. 1b)}$$

$$\frac{1}{V}\cdot\frac{d([N_2O]\cdot V)}{dt} = -\gamma(R_4 + R_5 + R_6 + R_7) + R_4 + R_5 + \alpha^2 R_6 + R_7 \quad \textbf{(Eq. 1c)}$$

where α is $[NO]/[NO]_{eq}$, β is $[N]/[N]_{eq}$ and γ is $[N_2O]/[N_2O]_{eq}$ and R1-R7 are the reactions considered by Lavoie in its methodology [8].

Some variations of the present procedure have been encountered by: Komiyama and Heywood [50], Nightingale [42], Bowman [51] and Kyriakides et al [52]. These are mainly related with neglecting the effect of the N_2O pathway or even by discarding all reactions except: $N+NO=N_2+O$ and $N+O_2=NO+O$, [53-54]. By doing so, the previous equation (Eq. 1a) simplifies significantly into equation 2 (Eq. 2), reflecting the strong influence of the temperature on the process.

$$\frac{d(NO)}{dt} = 2K_{b1}\frac{3.6x10\text{^}3}{(RT)^{1/2}}\exp\left(\frac{-31090}{T}\right)[O_2]_{eq}^{\frac{1}{2}}[N_2]_{eq} \quad \textbf{(Eq. 2)}$$

Where K_{b1} is the backward reaction constant of reaction 1 (R.1), R is the universal constant of the ideal gas law and T is the system's temperature.

2.3.1.2.2 Empirical or quasi-empirical correlations

Multiple empirical correlations have been developed as a NO_x predictive tool based on the different formation routes.

With respect to the thermal NO, predominant in CDC conditions, in-cylinder parameters (capable of describing the evolution of the combustion process) and/or the flame temperature data (dependent on the air temperature and the oxygen concentration) have been related to this mechanism to predict the NO engine-out emissions. Some of the most popular in-cylinder parameters employed are: the temperature distribution, the pressure and the heat release rate. Some correlations worthy to list in order to illustrate a general overview are:

- Hountalas et al [55] considered a semi-empirical model based on the in-cylinder temperature distribution.
- Several authors [56-60] described a simplified semi-empirical NO_x formation model based on the in-cylinder pressure. With this parameter, their model was able to calculate the adiabatic temperature and therefore predict the NO emissions.
- Hegarty et al [61] presented a semi-empirical model for dynamic NO modeling. In this case the model was dependent on a coefficient, related with engine speed and torque.
- Others [62-63] have proposed a predictive model based on the heat release rate. To predict the NO formation, at each instant of the combustion process, the instantaneous adiabatic flame temperature and the combustion products mass, which is dependent on the heat release, are required. Moreover it can be said that the adiabatic flame temperature can be correlated with the engine speed as observed by several authors: Duffy et al. [64]and Uludogan et al. [65].

The NO formation rate corresponding to the prompt and the fuel-nitrogen content mechanisms is also commonly calculated using empirical correlations. The most popular one, referred to the prompt mechanism (NO_{pr}), relates the amount formed with the number of carbons the fuel molecule has [34], [66-67]. This is expressed by equation (Eq. 3):

$$\frac{d[NO]_{pr}}{dt} = f_{pr} \cdot T^{\beta} \cdot K_{pr}[O_2]^a[N_2] \cdot [fuel]^b \exp\left(-\frac{E_a}{RT}\right) \quad \textbf{(Eq. 3)}$$

where f_{pr} is the correcting factor which depends on the equivalence ratio of the mixture and the type of fuel.

Another empirical correlation, less accurate than the previous, was developed by Miller et al. [68]. In it, the NO_{pr} is function of the equivalence ratio and the pressure, Eq.4.

$$[NO]_{pr} = f \cdot (Fr) \cdot p^{0.5} \cdot [NO]_{eq} \quad \textbf{(Eq. 4)}$$

Even though the fuel-nitrogen content mechanism is not considered in the present document it is worth noting some empirical correlations, like: Fenimore [24], Bazari [69], and De Soete [70]. All of them are based on the fact that nitrogen fuel, when it reacts, is converted into an intermediate specie which will in turn react with NO or with an oxygenated intermediate specie to yield N_2 or NO, respectively.

Another relevant field of study to calculate the engine-out NO emissions is to develop skeletal or reduced chemical kinetic schemes applicable to ICE. Two of the most important works performed in this field were: Way [43] and Keck et al. [71]. In the first of them, the author proposed a method to calculate the composition of the different species involved by considering partial equilibrium conditions, or in other words, the quickest reactions were considered to have reached the equilibrium while the slowest were considered to be kinetically-controlled. In contrast, [71], only considered the reactions including a third body (M) to be kinetically-controlled. The effectiveness of both procedures was significant. Way's methodology reduced significantly the computational costs without reducing the accuracy of the results and the one proposed by Keck yield great results for conventional diesel combustion conditions, T > 2500K. However, for typical LTC temperatures (T < 2200K), significant differences were observed. As a result, the authors conclude that not only the reactions including third body should be considered kinetically-controlled but others too.

Other authors (Miller [68] and Zabetta and Kilpinen [72]) have also proposed chemical-kinetic mechanisms based on the partial equilibrium assumption. Miller et al [68] developed a super-extended Zeldovich mechanism capable of predicting with 90% accuracy the NO emitted under rich and lean mixtures instead of the 50% of the extended Zeldovich mechanism for certain working conditions. Moreover, this mechanism is compatible with the Lavoie methodology [8] which has been explained previously.

In [72] a reduced mechanism, accounting for the heterogeneity of the diesel combustion process, was constructed to predict NO_x formation (considering thermal and N_2O intermediate route) and with the objective of being implemented in CFD codes. In this case, O, OH and H radicals where assumed to be in equilibrium conditions while N_2O, N, NH and HNO

were considered to be in steady state. The results were more accurate than the previous model included in the CFD code.

Considering these principles, multi-zone or multi-stage thermodynamic models have also been proposed by: Merker [73] and Zanforlin [74]. The first author developed a two zone (flame front and burnt zone) model to calculate the NO formed in direct injection diesel engines. It uses the partial equilibrium simplifications to distinguish between sufficiently quick reactions, predominant in the flame front region and the sufficiently low speed reactions, considered to be kinetically-controlled and typical of the burnt zone. This model consists of a total of 25 reactions of which 5 were considered to be in equilibrium and the rest kinetically controlled, including the NO reactions. It is worth mentioning that neither thermal NO nor prompt NO, formed in the flame front region, were considered.

In [74] a step further was taken by constructing a three stage model which not only dealt with the chemical-kinetic process but also with the mixing process. The first stage, mixing-controlled, corresponds to the full conversion of the fuel molecule into intermediate species, H_2 and CO. The second and third stage, both kinetically-controlled and considering partial equilibrium conditions, describes the conversion of CO into CO_2 and H_2 into H_2O, respectively. The results reflected that the delay times (DT) were longer than those measured, especially with late injection, if the combustion process was assumed to be fully kinetically controlled. Instead, considering a turbulent mixture model, closer values will be achieved with the inconvenience of having a higher computational cost. On the other hand, the pressure and heat release values were similar to measured values, due to the partial equilibrium simplifications.

Finally, Hernández [40] developed a predictive NO_x model, applicable to ICE, in which equilibrium and kinetic considerations were compared using a chemical kinetic mechanism of 29 species and 63 reactions. The author observed that similar results with respect to NO were obtained, between both considerations, at high temperatures. In contrast, as the temperature decreases, the kinetics gain relevancy and significant differences appear. Furthermore, predicting NO with the Lavoie methodology [8] under-predicts the engine-out NO formation.

2.3.1.2.3 Detailed chemical kinetic scheme.

As concluded from the previous subsection, the fact of reducing the combustion temperature causes an increase in the relevance of the chemical kinetics in detriment of equilibrium and partial equilibrium assumptions reviewed previously. This is the case of LTC conditions where massive EGR rates are employed, altering the spray's structure and its chemistry, see Section 2. Consequently detailed mechanisms are nowadays required to accurately predict the NO formation.

In the last two decades, in parallel with the development of the computational science field, multiple detailed chemical kinetic mechanisms have been proposed to describe not only the formation processes of the NO_x and other pollutants but also the oxidation chemistry of fuel surrogates.

Currently, the most detailed chemical kinetic mechanism describing the NO_x formation process is the one included in the GRI-Mech 3.0 [75] and consists of 325 reactions and 53 species. Furthermore, multiple authors have proposed additional formation routes (NCN [76-78], NNH [79-80] and stepwise [81-82]) which complement the existing ones or are totally new. Of all of them, some are clearly not applicable to the ICE scenario, but others, require further studies and validations prior to their inclusion in well accepted mechanisms.

With respect to the fuel surrogate, the Curran mechanism [83] is the most popular detailed mechanism for n-heptane (which is an appropriate fuel surrogate for diesel). This detailed mechanism, 544 reactions and 2446 species, describes the oxidation chemistry of the n-heptane at high and low temperatures and over a broad pressure range important for internal combustion engines.

However this detail implies a substantial increase of the computational cost. This fact has caused the development of several procedures which its main objective resides in simplifying detailed mechanisms in order to reduce the calculation time without sacrificing the predictive accuracy. Some of these tools are: direct relationship graphing (drg) [84-85], lumping [86], sensitivity analysis [33], in-situ adaptive tabulation (ISAT) and the intrinsic low dimension manifold procedure (ILDM).

Due to the fact that in the present thesis a storage/retrieval procedure is going to be proposed to predict the NO formation, special attention will be paid to the ISAT [87] and the ILDM procedures [88]. They were the origin of tabulated chemistry and were developed in the spray's structure research field because the equilibrium or partial equilibrium simplifications were not applicable o weren't applied correctly. Generally speaking, they are based on a look-up table generated by simulating, in this case, the combustion process under very simplistic assumptions which demand low computational resources. Once generated, the system can now be simulated under more complex considerations, like turbulent combustion, and instead of coupling the chemical-kinetic solver with the physics solver, demanding high computational resources, the information can be obtained from the tabulated table.

From their origins, these tools have been continuously improved by modifying the original algorithm [89], proposing different versions [90-93], defining new approaches (flame propagation of ILDM, FPI, [94-95] and the flamelet generated manifold, FGM [96-97], or even developing new tools (specially artificial neural networks [98-100]) based on the storage/retrieval technique. These facts reflect the current interest for these procedures in different environments, like: combustion problems ([101-103]), chemical engineering [104-106], solid mechanics [107], control [108], etc….

2.3.2 Combustion modeling to predict NO_x emissions.

With respect to the combustion modeling there are multiple tools which can be employed depending on what is the main interest of the research study, i.e: if interested in studying the chemistry of the NO_x formation in CDC and LTC, like is the case, it is more profitable to focus on 0-D or even 1-D simulations than to perform a CFD, where simpler kinetic mechanism are considered in order to make affordable the calculations.

Focusing on 1-D simulations, the two-stage Lagrangian model was developed to mainly predict the NO_x [100], [110-111] and soot emissions [112-113] in diesel sprays with a low computational cost. Proposed by Broadwell [100] to calculate temperature and composition in a stationary, turbulent and non-premixed spray, it is based on simplifying the flame structure in two regions: flame front and flame core. Each of them is characterized by a perfectly stirred reactor (PSR) which move in parallel, exchanging mass between them, as they move downstream the stationary spray (see Figure 2.9).

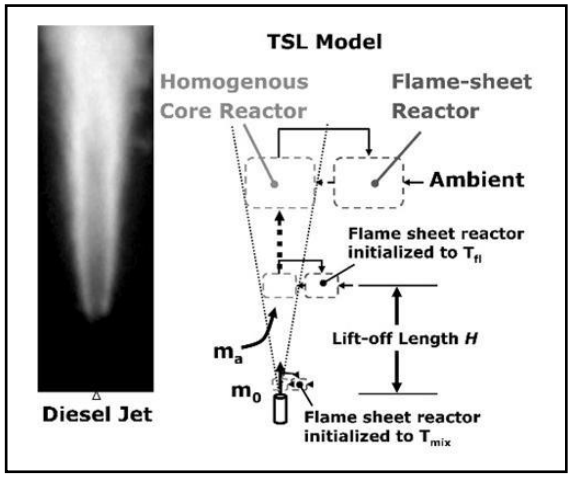

Figure 2.9.- Schematic representation of the how the two-stage Lagrangian model (TSL model) simplifies the diesel flame in two regions: flame core and flame front [109].

On the other hand, when considering 0-D simulations [114-117] it is worth distinguishing between single and multi-zone models. In this case, the main interest resides in analyzing the proper combustion process and therefore due to the low computational cost detailed chemical kinetics can be used. Several authors [118-122] have used them for comprehensive and predictive experimental studies (HCCI combustion). Generally speaking, it is well accepted that the multi-zone model predicts more accurately the experimental results, than the single zone, mainly because it takes into consideration the spatial distribution of temperature and composition in the cylinder [123]. On the other hand, the single zone model is the best tool to perform parametric studies to analyze the influence of chemical kinetics and different variables on the combustion process with an acceptable accuracy degree [124].

2.4 Summary

All the ideas presented along this chapter can be summarized as follows:

Due to the stringent emissions legislation the diesel combustion process is being “re-developed” by researchers and engineers in order make it more environmentally friendly. Focusing on the NO_x emissions, which is one of the predominant pollutants and the most harmful, the most popular technique employed to mitigate its formation is to recycle exhaust gasses back to the combustion chamber in order to dilute the oxidizer. This will cause a

reduction in the reactivity of this stream and therefore a reduction in the combustion temperature.

However an important drawback of a massive recirculation of these products is that it modifies considerably the structure of the diesel spray and the chemistry of the NO_x formation process. This causes the need to take into consideration detailed chemistry (all the formation routes) and physics in order to accurately predict NO_x formation.

Focusing on the tools developed, till now, to predict the formation of this pollutant, two main groups can be identified: 1) equilibrium assumption or 2) consideration of the chemical kinetics effect (non-equilibrium). As it can be deduced, the first ones assume equilibrium conditions of all or some of the species involved in the process. The main advantage of them resides in the low computational cost required but, on the other hand, they are very simplistic and poor results are obtained for low temperature combustion conditions. The second group strongly depends on the size and detail of the chemical kinetic mechanisms. In some cases, for detailed chemistry, the computational cost is so important that it makes the simulations unaffordable. In this case some tools, based on tabulated chemistry, have been developed and are currently proliferating in different versions. Even though they seem to be the solution for using detailed chemistry with low computational cost they are complex to understand, tedious to build the tabulated tables on which they are based and require huge amounts of memory.

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Chapter 3

Thesis Approach

Content

3.1 Introduction

The following chapter will be organized in three different sections. The first section (Section 3.2) will identify the opportunity areas as a result of the weakness of different aspects found in the related scientific literature review and outlined in Chapter 2. Sections 3.3 and 3.4 will describe the established objectives of the thesis and will review the employed methodology, respectively.

3.2 Summary of the literature review

As it can be concluded from the previous chapter, the diesel combustion process is becoming more complex each time in order to accomplish the most stringent Euro Emissions Standards. The predominant technique is based on reducing the combustion temperature and the local equivalence ratio by recirculating high amounts of exhaust gasses (EGR) back into the combustion chamber (low temperature combustion conditions, LTC). This change in the main characteristics of the combustion process not only alters the spray's structure, as observed by Musculus [1], but also its NO_x chemistry by increasing the relevance of the chemical kinetics and the influence of other formation routes, compared with conventional diesel combustion conditions (CDC), where high combustion temperatures were reached and the thermal mechanism was significantly predominant.

Besides the chemical changes described previously, the interaction of massive EGR with hydrocarbons enhance other processes related with these pollutants, like: increase in NO_2 proportion in the NO_x emissions and the NO_x reburning phenomenon.

Consequently, in order to accurately predict the NO_x engine-out emissions detailed NO_x chemistry (which takes into account all the formation/destruction routes) and physics must be considered.

3.3 Thesis objectives

Considering this detailed chemistry and physics to accurately predict the NO_x emissions involves a substantial increase in the computational cost which in some cases makes unaffordable the predictive simulations.

Therefore, the main objective of the thesis consists in setting the basis for developing a low computational cost tool capable of predicting the NO_x formation, over CDC and LTC conditions, independently of contextualizing it in a premixed auto-ignition or in a diffusion diesel combustion process.

In order to accomplish this main objective, several other secondary objectives have been established to enhance the comprehension of the NO_x formation/destruction process in both scenarios (CDC and LTC):

1.-Understand the NO-NO_2 conversion process and the contribution of the NO_2 to the NO_x engine-out emissions.

2.- Relate under CDC and LTC conditions the NO prediction of the thermal mechanism, the most implemented one, with the NO prediction of all the NO formation mechanisms coupled together. However, previously the predictive capability of the different formation routes will be determined under these conditions.

3.- Characterize the NO formation rate as a function of equivalence ratio (Φ), initial temperature (T_{ini}) and oxygen mass fraction (Y_{O2}).

3.4 Description of the methodology

The achievement of the main objective will depend on a recompilation of the different NO_x formation routes, described in the previous chapter, followed by the accomplishment of the secondary objectives.

Initially a detailed study of the NO_2 formation process (**chapter 5**), will determine the need to account for NO and NO_2 species or only concentrate in the NO specie in the following studies.

After determining which specie/s to take into account, in **chapter 6** the different NO_x formation routes will be tested individually, with special attention to the thermal mechanism, in order to study their contribution degree with respect to the total NO formation process for CDC and LTC (Y_{O2} < 12.7%[1]) conditions. Furthermore an empirical predictive tool will be

[1] Criterion used in several research studies (see references [1-4]) to consider low temperature combustion conditions.

developed based on the contribution degree results. Finally, due to some weaknesses in the empirical predictive tool, a new tool will be developed using detailed chemistry and based on the tabulated chemistry principles (**chapter 7**).

A general overview of the methodology employed in this document to achieve the described objectives is schematically represented Figure 3.1.

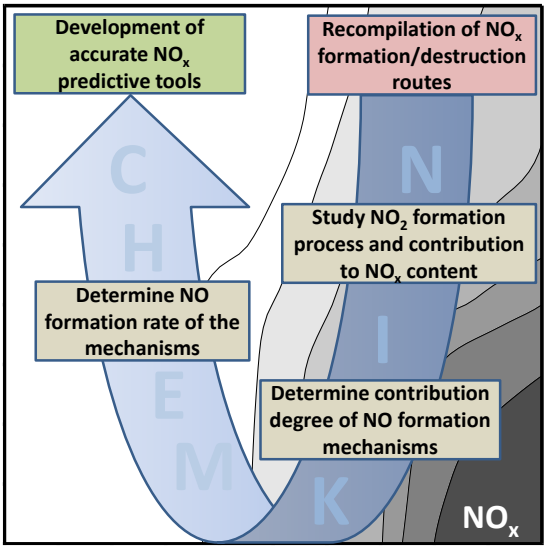

Figure 3.1.- General scheme of the applied methodology for the present Thesis.

Finally, all these studies will be performed using Chemkin Pro software [5], considering the n-heptane as the diesel fuel surrogate and using the chemical mechanism conformed, by the author, after coupling the Seizer et al. [6] and the GRI-Mech 3.0 [7] mechanism in order to take into account all the NO_x formation routes.

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Chapter 4

Tools

Content

4.1 Introduction

In the following chapter the different general tools used to achieve the main objectives of the present thesis are going to be described in detail and arranged in different sections. Initially, a general overview of the main procedure used throughout the research, described in this document, will be presented in the introduction (Section 4.1), followed by the description of the procedure used to model the combustion process (Section 4.2) and to characterize the diesel fuel surrogate and the NO_x formation processes (Section 4.3). Finally, other relevant tools, worth of describing, will be presented in Section 4.4 while other minor procedures employed, e.g: for a specific study, will be commented in the corresponding chapter.

Generally speaking, the main tool used to perform the different studies, described in this document, was a worldwide and well established chemical-kinetic software known as Chemkin [1], in particular the Professional version. This software can manage from simple thermodynamic calculations (determine chemical equilibrium), to analyses of chemical kinetics (shocktubes, sensitivity analysis and rate of production) and 0-D simulations in different contexts, like: gas-gas and gas-surface reactions.

In the present thesis, all the research will be contextualized in the gas-gas phase (resembling the conditions found in the combustion chamber of internal combustion diesel engines) and related with: 1) equilibrium calculations and 2) 0-D simulations to predict NO_x formation and study the combustion process.

On one hand, determining the equilibrium composition will be of special interest for normalization purposes (NO/NO_{eq}), or in other words, it will allow comparing results yield under very distinct conditions. It will be calculated using a procedure, included in the software, which is exclusively dependent on the considered species in contrast with others which are dependent on the chemical reactions [2] . The main inconvenience of these latter ones rely in the fact that the results will depend on the reactions considered as well as the Arrhenius values assigned to each of them. Moreover, depending on the number of reactions involved, the computational cost of these calculations can be significant. Instead, the previously mentioned procedure, developed by Reynolds [3], only depends on the species considered and that is possible due to the coupling of the chemical potentials procedure with the minimization of Gibbs free energy [1]. The key factor of this procedure is undoubtedly the chemical potentials, which remain constant for an element independently of the molecule in which it is found, e.g: the chemical potential of nitrogen will be the same independently of being in the form of the diatomic molecule (N_2) or in the NO molecule.

On the other hand, 0-D simulations were performed in order to: 1) develop a predictive tool and 2) check the accuracy of the developed tool by using the Chemkin results as reference. In the first case, as its name suggests, the 0-D simulations will be used to develop new low computational cost methodologies capable of improving the accuracy of future NO_x emissions predictions in the context of this research thesis: ***low temperature combustion modes where the relevancy of the thermal mechanism has diminished, compared with high temperatures, in favor of other formation routes***. This will be achieved by considering constant pressure and temperature conditions for non-steady state simulations. This means that, with the exception of pressure and temperature, the rest of the considered variables (species' composition, volume, thermodynamic properties of the system, etc….) will be time dependent. In contrast, when used as a reference tool, constant pressure conditions and solving the energy equation (temperature not constant) will be considered for non-steady state simulations.

To be able to perform all these calculations the software requires several inputs, like: 1) the characterization of the combustion phenomenon and 2) the chemical characterization of the reactants (diesel fuel surrogate and oxidizer) and pollutants (NO_x). Even though in the next sections each of them will be explained in detail, describing the information content included, it is worth to briefly describe how this software works, see Figure 4.1.

Initially the user introduces the reaction mechanism and its corresponding thermodynamic database into Chemkin which compiles the information making sure that all the elements, species, reactions and thermodynamic data are coherently described following established rules. Afterwards the user needs to select from a built-in library the reactor which best describes the physical characteristics of the combustion process to be modeled and specify the initial conditions (pressure, temperature relative equivalence ratio, etc…). Lastly,

depending on the reactor selected the corresponding solver will perform the calculations which after being post-processed will yield the final results for the corresponding simulation.

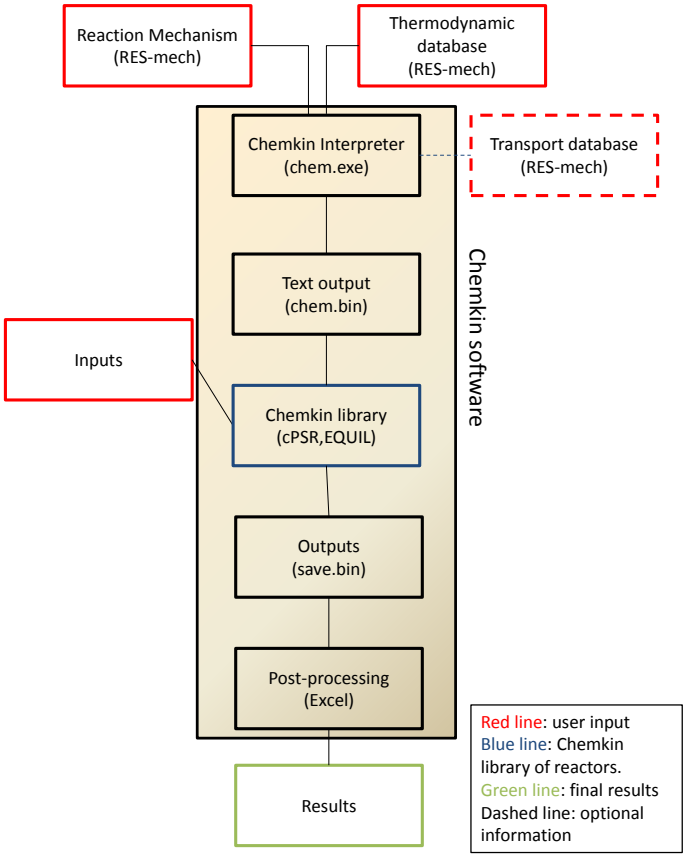

Figure 4.1.- Schematic representation of how the Chemkin software works

4.2 Modeling of the diesel combustion process

As mentioned previously, the studies performed in the present thesis are contextualized in analyzing the combustion, diesel-like, and the NO_x formation processes from a chemical point of view. To do so, with the lowest possible computational cost, the combustion process should be 0-D modeled. In this context several models, based on reactors, are available and depending on the main characteristics of the combustion process one or another should be selected.

These 0-D reactors can be mainly classified in two different groups depending on: homogeneous and inhomogeneous mixture.

For homogeneous mixtures, the simplest reactor is the perfectly stirred reactor (PSR) which besides assuming that the combustion process is due to a homogeneous mixture it also considers that it is controlled by the mixture's chemistry. Consequently, the main purpose of this reactor is to study the influence of the chemistry in the combustion process. Additionally, two more sophisticated versions of this reactor are the single-zone and the multi-zone internal combustion engine, typical in commercial softwares dealing with combustion modeling. Their reason of being is to couple the chemical analysis with how the engine's constructive

parameters influence the combustion process. The predominant difference between them relies in the number of zones in which the combustion chamber is divided into. Each of these zones will be considered as a PSR reactor with or without interactions with the surrounding regions.

For inhomogeneous mixtures, the partially stirred reactor (PaSR) is commonly employed. It considers the possibility that the combustion is controlled by turbulence or due to a combination of turbulence and mixture's chemistry. In order to mathematically define these factors several variables have been developed, like: the mixing time and the reaction time [1]. The mixing time is a measure of the turbulence degree and is described by the ratio between the kinetic energy (κ) and the dissipation rate (ε) found in the energy-containing eddies, while, the reaction time will be normally determined by the time difference between the simulation and the mixing time. Note that considering an infinitely fast mixing time (close to zero) will transform an inhomogeneous mixture into a homogeneous one and consequently a PaSR reactor into a PSR.

Besides these main characteristics, both reactors can be complemented by assuming:

- Opened or closed, or in other words, interacting or isolated from it's surroundings, respectively.
- Adiabatic or non-adiabatic conditions.
- Constant pressure or constant volume conditions.

Taking into account all the previous facts and the context of this thesis, the closed PSR reactor (cPSR) was selected. This selection has been corroborated by Zheng [3] and by the multiple studies performed using this reactor [5-12]. In his study, Zheng pointed out that the cPSR is the most effective in capturing detail chemical kinetics and basic thermodynamic events. Consequently, this makes it ideal for conceptual or fundamental combustion studies controlled by chemical kinetics, like is the case.

Additionally, this reactor will be complemented by assuming constant pressure and adiabatic conditions and depending if used as a reference tool or as a development tool the energy equation will be solved or not, respectively. By considering constant pressure conditions, the pressure over-prediction, typical of this reactor, will be discarded, while assuming adiabatic conditions will cause a NO_x over-prediction due to an over-estimation of the temperature, directly related with the NO_x formation process at high temperatures. Nevertheless, this thesis is contextualized as a conceptual study where qualitative trends will be analyzed. In the case of promising results the next step should then be to consider non-adiabatic conditions.

Finally, it is worth noting that the cPSR reactor has a low computational cost due to the simplicity of the mass and the energy balance equations governing it, and even though all calculations will be done internally, by the software, it is worth listing them:

- Mass balance

Accumulation Rate = (Inflow Rate + Recirculation Rate) – Outflow Rate + Generation Rate

$$\frac{d}{dt}(\rho V)^{(j)} = \sum_{r=1}^{N_{inlet}(j)} \dot{m}_{i}^{*(j)} + \sum_{r=1}^{N_{PSR}} \dot{m}^{(r)} \cdot R_{rj} - \dot{m}^{(j)} + \sum_{m=1}^{M} A_m^{(j)} \sum_{k=1}^{K_g} \dot{s}_{k,m}^{(j)} W_k$$

(Eq. 4.1)

where j is the reactor number (varying from j = 1 to N_{PSR}), ρ is the mass density, V is the reactor volume, $\dot{m}^*$ is the inlet flow rate and $\dot{m}$ is the outlet mass flow rate. $N_{inlet}(j)$ is the number of inlets for each reactor j, while N_{PSR} is the total number of reactors modules in the reactor network. R_{rj} is the fraction of the outflow of reactor r that is recycled into reactor j. A_m is the surface area of the m^{th} material defined within the reactor, $s_{k,m}$ is the molar surface production rate of the k^{th} species on the m^{th} material per unit of surface and W_k the molecular weight of the corresponding specie. There are k_g gas-phase species and m materials.

For the cPSR reactor, neither inflow nor outflow stream exist and therefore m* = m = 0 simplifying the previous equation to Equation 4.2.

$$\frac{d}{dt}(\rho)^{(j)} = \sum_{m=1}^{M} A_m^{(j)} \sum_{k=1}^{K_g} \dot{s}_{k,m}^{(j)} W_k \qquad \textbf{(Eq. 4.2)}$$

- Energy balance

Energy accumulation rate = Energy Rate in inflow – Energy Rate in outflow + Heat Rate added to system + Work Rate by system.

$$\frac{dU_{sys}^{(j)}}{dt} = \sum_{i=1}^{N_{INLET}(j)} \dot{m}_{i}^{*(j)} \sum_{k=1}^{K_g} (Y_{k,i}^{*} h_{k,i}^{*})^{(j)} + \sum_{r=1}^{N_{PSR}} \dot{m}^{(r)} R_{rj} \sum_{k=1}^{K_g} (Y_k h_k)^{(r)}$$
$$- (\dot{m} \sum_{k=1}^{K_g} Y_k h_k)^{(j)} - Q_{loss}^{(j)} + Q_{source}^{(j)} - P^{(j)} \frac{dV^{(j)}}{dt}$$

(Eq. 4.3)

where the total internal energy U_{sys} consists of the internal energy of the gas, and walls. Q_{loss} is the net heat flux directed out of the reactor. Q_{loss} can either be specified directly as a constant or can be specified in terms of a constant heat transfer coefficient, h_t, and ambient temperature applying the convective heat transfer equation. The term P(dV/dt) represents the work done by the control volume on the external world. Finally, Y_k is the mass fraction of the k^{th} species.

With the same reasoning as the one described in the last paragraph of the previous bullet and considering the adiabatic conditions (Q_{loss} = 0), the Equation 4.3 will be simplified to Equation 4.4.

$$\frac{dU_{sys}^{(j)}}{dt} = Q_{source}^{(j)} - P^{(j)} \frac{dV^{(j)}}{dt} \qquad \textbf{(Eq. 4.4)}$$

4.3 Chemical-kinetic characterization of the diesel fuel surrogate and nitrogen oxides (NO_x)

4.3.1.- Diesel fuel surrogate

Petroleum based commercial fuels are normally composed of multiple components whose concentration may vary substantially depending on the origin of the crude-oil. Multiple efforts have been employed in the task of requiring a normalized composition of automotive fuels in order to optimize the combustion process inside the internal combustion engines (ICE) and standardize the research in the combustion modeling field.

Regarding the combustion modeling scope, where this thesis is relevant, it is very common to employ fuel surrogates to perform the corresponding analyses. A fuel surrogate is a chemical reactant or a mixture of several of them which characterize the desired fuel by having similar key physical and reactive properties. Some of the most important properties when determining, in this case, the best surrogate are summarized in Table 4.1:

Property	Units	Description	Diesel combustion scenario
Cetane number (CN)	-	The capability of a fuel to auto-ignite. The higher the number the higher the tendency to auto-ignite.	The auto-ignition process is the key phenomenon in diesel combustion and therefore is related with the combustion process. Around 54 is the CN of diesel.
Flame temperature (T_{ad})	K	Maximum temperature reached after an isobaric and adiabatic process	Involved in the combustion process. High relevance with the NO_x process as it is strongly influenced by temperature.
Higher Heating Value (HHV)	kJ/kg	Energy released by the fuel after an oxidation reaction and considering that the water produced is in liquid state.	Related with the combustion process. Measures how much energy is going to be released when the fuel burns and consequently the amount of work capable of being produced.
Lower Heating Value (LHV)	kJ/kg	Energy released by the fuel after an oxidation reaction and considering that the water produced is in vapor state.	Related with the combustion process. Measures how much energy is going to release when the fuel burns and consequently the amount of work capable of being produced.

Table 4.1.- Key physical and reactive properties to determine the most appropriate diesel fuel surrogate in the combustion modeling field.

Even though major efforts have been performed in the pursue for determining and employing appropriate diesel fuel surrogates [13], in the practice, they will normally become imposed by the availability of well-established chemical kinetics mechanisms, the combustion mode willing to analyze and the associated computational cost.

Focusing on the diesel field, the most extended fuel surrogate is pure n-heptane, a saturated linear hydrocarbon made up of 7 carbon and 16 hydrogen atoms (see Figure 4.2), with a cetane number similar as the European diesel fuel. However, the main drawback of using this single component fuel surrogate instead of others like: mixtures of n-heptane and toluene (the 50:50 is the most popular) and the mixture made up of 70% decane and 30% 1-methylnaphthalene (IDEA fuel), is the fact that the mixture formation process, after fuel evaporation, is not the same as for the diesel fuel due to drastic differences in the liquid properties and it discards the NO formation process due to the aromatics' content.

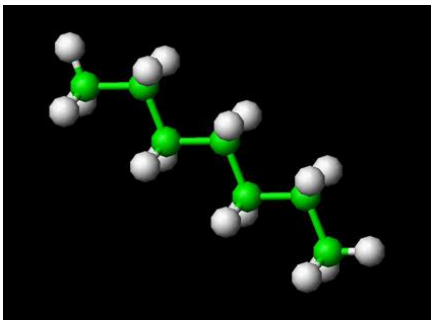

Figure 4.2. Structure of the n-heptane molecule. The green spheres symbolize carbon atoms and the white spheres represent hydrogen atoms.

Nevertheless, none of these inconveniences will influence the results obtained in the present work due to the following considerations:

a) The extremely low contents of nitrogen in the refined liquid fuels used nowadays in the automotive industry makes this route insignificant.
b) 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) [15] 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% (current maximum threshold value in mass fraction units) to 1%. Even though this reduction was obtained for engines operating under CDC conditions it is expected to be similar for the new diesel engines operating at LTC conditions. However the impact will be substantially lower because less NO are formed due to lower combustion temperatures.
c) Lastly, most of the studies performed in this work will be performed in the idealized context of homogeneous mixtures but the most important of all, the predicting tools resulting from this research studies are characterized using temperature or NO composition making it independent of the mixture process efficiency.

Consequently, in the present thesis, no aromatics will be taken into consideration and only the Seiser's et al. mechanism [16] will be employed. This mechanism is a simplified version of the well extended Curran mechanism [17], which describes the well-known n-heptane oxidation, and demands a lower computational cost than the detailed mechanism. This mechanism is made up of 159 species and 1434 reactions, which accounts for the oxidation of n-heptane at low and high temperatures.

4.3.2.- NO_x formation chemical kinetic mechanism.

Another aspect which is determinant when analyzing pollutant emissions, is the chemical kinetic characterization of the pollutant formation process. Regarding the automotive industry, in particular diesel fuelled engines, the main pollutants found in the exhaust gases and therefore legislated, are: CO, CO_2, HC + NO_x, NO_x and PM. In Europe the environmental

laws are known as Euro Emission Standards and their threshold values as well as their implementation date are summarized in Table 2.1.

Focusing on the NO_x emissions, which is the sum of several species (NO, NO_2 and N_2O), they have been drastically reduced from the first Euro implemented in 1992 till nowadays due to how harmful they are for the human beings' health.

In order to study their behavior multiple chemical kinetic mechanisms have been constructed by including, in more or less detail, all the well-known NO formation/destruction routes, described in Chapter 2. One of the most popular due not only to the number of routes considered but also to the multiple validation studies performed, is the NO_x sub-mechanism included in the GRI-Mech 3.0 mechanism [18]. Even though it has been fully optimized for the methane oxidation process (major component of natural gas), it has also been used in conjunction with other fuel surrogates, like: n-heptane [19].

4.3.3.- Resulting chemical-kinetic mechanism (RES-mech).

From the information provided in the previous sections, the resulting mechanism is made up of the Seiser and the GRI-Mech 3.0 mechanisms. A similar mechanism was used by the Engine Research Center (ERC) at Wisconsin to improve their reduced NO_x mechanism [19].

In order to check its appropriateness to perform the studies described in this document, it was compared in key aspects (auto-ignition delay times, adiabatic temperature and equilibrium NO composition) with the Curran and the Seiser mechanisms. Note that the first of them (described in Chapter 2) is the detailed n-heptane mechanism, well-established in the scientific community, while the second is the result of simplifying it in search of reducing computational costs. In contrast, comparisons couldn't be done with the diesel fuel surrogate developed by the Integrated Diesel European Action (IDEA) program [13] neither with the ERC mechanism [19] due to its unavailability.

The first key aspect analyzed was the auto-ignition delay, determinant parameter for a diesel fuel surrogate, for two different equivalence ratios (Φ = 0.5 and Φ = 1), over a wide temperature range (800K < T_{ini} < 1400K), constant pressure (P=10MPa) and with and without exhaust gas recirculation (EGR). Note that throughout the whole document the EGR rate will be characterized by the initial oxygen mass fraction variable (Y_{O2ini}) and the composition of the different constituents in the oxidizer stream, when EGR is employed, will be determined with the mathematical procedure presented in Appendix A.

The results obtained using the cPSR reactor and ΔT = 200K, criterion used to define the mixture's ignition, were plotted in Figures 4.3a and 4.3b. This criterion was selected because the modeled combustion processes, in this thesis, resembled homogeneous charge compression ignition (HCCI) combustions. Under these conditions the cool flame phenomenon becomes relevant and in order to capture this effect Bounaceur [20] proposed this temperature change. Note that there are other criteria also available (ΔT = 400K, peak concentration of key specie, inflexion point of the temperature curve).

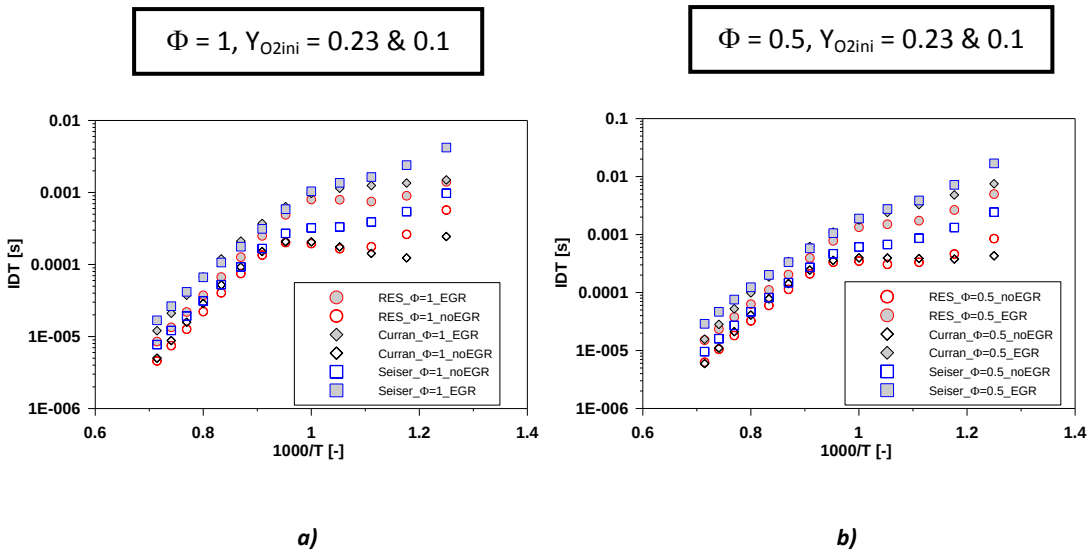

Figure 4.3.- Comparison of the auto-ignition delay times of the resulting mechanism (RES-mech) against those yield by the Curran and Seiser mechanisms, both directly related with the RE-mech, in which: a) Φ =1 for Y_{O2ini} = 0.23 and 0.1 and b) Φ = 0.5 for Y_{O2ini} = 0.23 and 0.1.

For the non-EGR cases, independently of the relative equivalence ratio, the results reflect that the RES-mechanism has similar IDT values, for T_{ini} > 900K, with those obtained by the Curran mechanism. However, for T_{ini} < 900K, differences start to appear between this two as the equivalence ratio tends to unity. In the case of the Seiser mechanism, greater differences are observed as the initial temperature decreases. This fact suggests that including the whole GRI-Mech mechanism improves the capability of the RES-mechanism to capture the cool flame phenomenon in the low temperature region.

For the cases with massive EGR (Y_{O2} = 0.1), the RES-mechanism has slightly lower IDT values in comparison with the other two, which in this case are almost identical, in the high temperature region (T_{ini} > 1200K) and for both relative equivalence ratios. However, as the temperature descreases the differences tend to decrease with respect to the Curran mechanism and increase with the Seiser mechanism.

In summary, the resulting mechanism is more similar to the Curran than to the Seiser mechanism, in which it is based on. Additionally, the observed differences in the low and high temperature regions for the non-EGR and EGR scenarios, respectively, will have minor impact in the internal combustion diesel engine context (the fuel-air mixture's initial temperature isn't so low neither so high for each of the corresponding scenarios). Moreover, it is worth noting that the computational cost of the RES-mechanism is substantially lower than for Curran.

The other two key aspects analyzed are closely related with the NO_x formation process, like: the adiabatic temperature (T_{ad}) and the amount of NO formed at equilibrium state (NO_{eq}). With respect to the NO_{eq}, only the NO_x sub-mechanism of the GRI-mech 3.0 was included in both. The conditions considered for these simulations are the same as for the previous analysis (800 < T_{ini} < 1400K, Φ: 0.5 & 1 and Y_{O2ini}: 0.1 & 0.23).

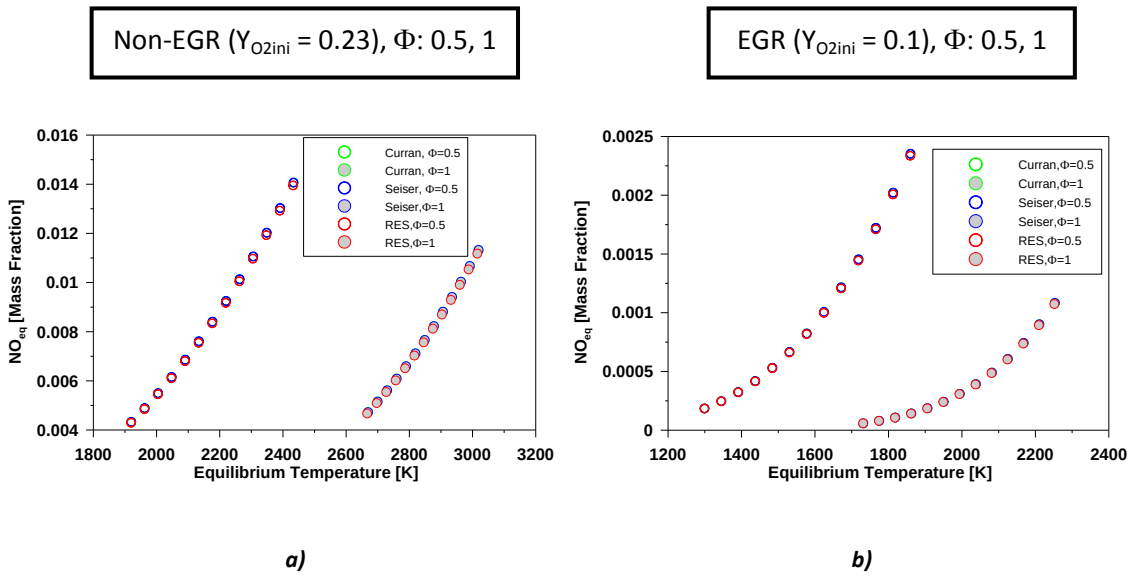

Figure 4.4.- Comparison of the equilibrium temperature and NO formation between the different mechanisms using pure n-heptane mixtures at 10MPa.

By representing the NO_{eq} as a function of T_{ad} both parameters can be compared in a single plot for each scenario (Y_{O2ini}: 0.23 & 0.1), Figures 4.4a and 4.4b. The results confirm that no differences are observable between the different mechanisms analyzed.

This fact, in addition with the previous conclusion, referred to IDT behavior, allows the author to conclude that the resulting chemical-kinetic mechanism is appropriate to perform the corresponding research studies.

Finally, different versions of this mechanism will be created, specially in Chapter 5, to study the contribution degree of each of the NO routes to the total NO formation (described by all the routes coupled together). Each of them will be named after the NO route taken into consideration, e.g: RES_{TH}-mechanism is referred to the coupling of the n-heptane oxidation mechanism (Seiser et al. mechanism) with exclusively the NO thermal route. Consequently, a total of four versions were created: RES_{TH} (thermal), RES_{PR} (prompt), RES_{N2O} (N_2O intermediate) and RES_{TOTAL}(all of the previous mechanisms coupled together).

4.4 Other relevant tools

Another tool which has been used extensively in the present research has been the Two-stage Lagrangian model (TSL model) which was originally developed by Broadwell and Lutz [21[22]. Generally speaking, this low computational cost model allows: 1) analyzing the physical behavior and the chemical phenomena involved in diesel sprays and 2) calculating the composition and the temperature of a non-premixed, turbulent spray in stationary conditions. This can be achieved based on the mixing-controlled hypothesis and in simplifying the spray structure in two regions: flame core and flame front.

As it can be appreciated in Figure 4.5, each of them is described by boundary conditions, according to the spray's theory, and characterized by a particular chemical reactor.

Despite the fact that several reactor combinations are possible, the most cost effective, without reducing its accuracy, is the 2 perfectly stirred reactors scheme (PSR).

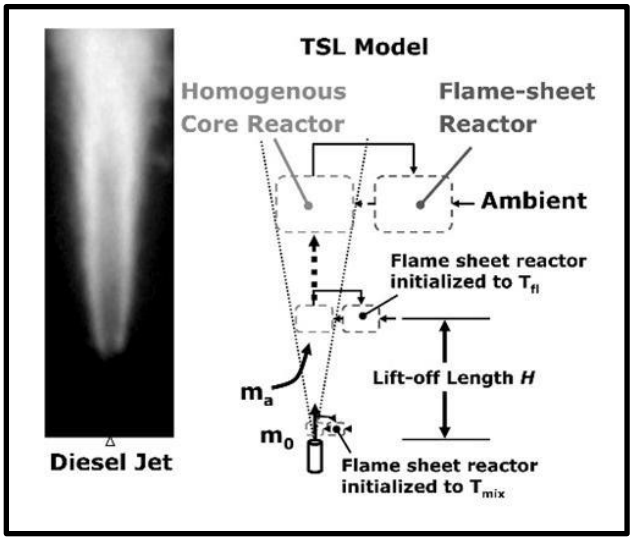

Figure 4.5.- Schematic representation of the how the two-stage Lagrangian model (TSL model) simplifies the diesel flame in two regions: flame core and flame front [22].

Several researches [22-27] have been performed with this tool demonstrating its versatility, due to the multiple physical phenomena the model can consider, even though the most relevant to the present document is [22]. In it, the authors illustrate how this tool can be effectively applied to comprehend the NO_x formation process, despite the fact that such formation mainly occurs in the outer region of the flame front.

4.4.1.-Two Stage Lagrangian model methodology (TSL-model)

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}) in case of dilution with EGR), 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 of course the fuel's oxidation chemical kinetic mechanism (RES-mechanism).

With these variables, the equivalent diameter (d_{eq}) and the fuel's speed (u_o) is calculated applying equations 4.5 and 4.6, respectively.

$$d_{eq} = d_o \cdot \sqrt{\frac{\rho_f}{\rho_a}} \qquad \textbf{(Eq. 4.5)}$$

$$u_o = \sqrt{(2 \cdot \Delta P / \rho_f)} \qquad \textbf{(Eq. 4.6)}$$

Afterwards, the mixture's history along the axis and within time is possible to be determined by applying the Ricou and Spalding equation (Eq. 4.7), constant entrainment rate

of non-reacting turbulent jets, and considering the momentum flux in the jet's axial directions to be constant (Eq. 4.8).

$$\frac{m}{m_o} = 0.32 \cdot \frac{x}{d_{eq}} \quad \textbf{(Eq. 4.7)}$$

$$m \cdot u = m_o \cdot u_o \quad \textbf{(Eq. 4.8)}$$

With these basic principles of the spray's theory and the fact that the model divides the structure in two different zones, flame core and flame front, the temporal evolution of parameters, like: the temperature, mixture fraction, the gas composition and the flame length, are easily calculated with a reasonable computational cost. It is worth noting that each region is characterized by a perfectly stirred reactor (PSR) and mass exchange exists between them. Initially, the transfer towards the flame front of the gas in the spray's surroundings as well as the combustion products, generated in the flame front region, towards the flame core will become imposed by the equation 4.7 (Eq. 4.7), which is function of the axial position. While the amount of mass recycled back to the flame front (B), from the flame core, in order to maintain the stoichiometric conditions, typical of the flame front region, will be function of the entrainment rate and the fuel concentration in the flame core region. This amount can be calculated with the following formula, Eq. 4.9:

$$B = \frac{Z_{st} - Z_{\infty}}{Z_h - Z_{st} + \varepsilon} \quad \textbf{(Eq. 4.9)}$$

where Z_{st} is the stoichiometric mixture fraction, Z_{∞} is the air's mixture fraction, Z_h is the mixture fraction corresponding to the flame core region and ε is a very small constant value to prevent singularity when $Z_h = Z_{st}$, or in other words, to prevent singularity when the flame front region is reached.

Finally, the model can be complemented by considering phenomena like: buoyancy, radiation, etc… Nevertheless none of these were considered in this conceptual study due to the negligible influence on the spray behavior (buoyancy) or due to the lack of rigorous data to compare with (radiation effect).

4.4.2.-Apparent Combustion Time model (ACT-model)

This model [28] was developed at CMT-Motores Térmicos and is made up of a combination of physical models together with the simplification and parameterization of some specific aspects, including the chemical kinetics for pollutants prediction. Some of these models are:

1.- Thermodynamic model: the First Law of Thermodynamics, applied to a single zone, to determine the cylinder pressure and temperature. Some of the most relevant parameters are: combustion chamber volume, heat transfer to the wall using Woschni correlation, injected fuel mass and heat release during combustion.

2.- Mixing model: based on the principles of turbulent gas jets it can be classified between a zero dimensional and a 1-D. It does not predict in detail the spray behavior but it has access to the local conditions through the mixing model. It also accounts for several effects, such as: the influence of heat release on the entrainment rate, the swirl influence, the injected fuel/jet element trajectory and transient processes, etc…

3.- Ignition delay and combustion model: The ignition delay model is based on a simplification and parameterization of a complete n-heptane chemical kinetics description from the Shell model [29]. The combustion model is controlled by the in-cylinder gas/fuel mixing process: the fuel mass will be burned when it reaches stoichiometric conditions, and this will be determined by the mixing model.

4.- NO_x formation model: only considers the three chemical reactions forming the extended Zeldovich mechanism.

In the present document this model will be employed to check the accuracy of the developed predictive tool with results obtained in real engines operating in diesel diffusion like combustion.

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Appendix A: Calculation of oxidizer stream composition for cases with EGR dilution.

The oxidizer stream entering the engine by the intake manifold can be just air, which in this case the oxygen mass fraction will be approximately 0.23, or air diluted with recirculated exhaust gases (EGR). In this latter case the composition of the oxidizer stream can vary drastically depending on multiple variables affecting the EGR, like: amount of exhaust gases recycled, equivalence ratio, initial fuel/air mixture temperature, combustion temperature, pressure, time, engine speed, etc…

Consequently, in an attempt of simplifying the calculations to determine this composition the following procedure has been employed throughout the whole document. This is mainly based on two premises: 1) assuming that the EGR stream is made up of the combustion products O_2, N_2, CO_2 and H_2O in the same proportions as those pertaining to a stoichiometric oxidation reaction between the fuel (n-heptane) and the oxidizer (dry pure air) and 2) establishing the initial oxygen mass fraction in the oxidizer stream.

The procedure starts by calculating the composition of the EGR stream which will correspond to the products of the stoichiometric oxidation reaction between n-heptane and dry pure air (composition in mass fraction: 0.23 of oxygen and 0.77 of nitrogen). In order to do so it is necessary to identify and balance the corresponding reaction. Once the proportions of the different species (O_2, N_2, CO_2 and H_2O) have been calculated, the amount of EGR to be recycled (m_{EGR}) was determined using equation A1 (Eq. A1) after establishing the desired initial oxygen mass fraction (Y_{O2ini}) for the oxidizer stream

$$\mathbf{Y_{O2ini}} = \frac{(\mathbf{m_{O2}})_{\mathbf{air}} + (\mathbf{m_{O2}})_{\mathbf{EGR}}}{(\mathbf{m_{O2}})_{\mathbf{air}} + (\mathbf{m_{N2}})_{\mathbf{air}} + (\mathbf{m})_{\mathbf{EGR}}} \qquad \textbf{(Eq. A1)}$$

where $(m_{O2})_{air}$ and $(m_{N2})_{air}$ corresponds to the oxygen and the nitrogen mass present in the air, respectively. Furthermore $(m_{O2})_{EGR}$ is the oxygen mass remaining in the EGR stream and which is directly related, by the proportion of oxygen in the EGR stream determined by a stoichiometric combustion, with $(m)_{EGR}$ which is the mass of EGR required for the desired Y_{O2ini} and the only unknown in the present equation.

Finally, the oxidizer stream composition was obtained by applying equations Eq. A2, Eq. A3 and Eq.A4 to each of the species involved

$$\mathbf{m_i} = (\mathbf{m_i})_{\mathbf{air}} + (\mathbf{m_i})_{\mathbf{EGR}} = (\mathbf{m_i})_{\mathbf{air}} + (\mathbf{m})_{\mathbf{EGR}} * (\mathbf{Y_i})_{\mathbf{EGR}} \qquad \textbf{(Eq. A2)}$$

$$\boldsymbol{m_{oxid}} = \sum_{\boldsymbol{i=O2,N2,CO2,H2O}} \boldsymbol{m_i} \qquad \textbf{(Eq. A3)}$$

$$(\mathbf{Y_i})_{\mathbf{oxid}} = \frac{\mathbf{m_i}}{\mathbf{m_{oxid}}} \qquad \textbf{(Eq. A4)}$$

where i symbolize each of the species (O_2, N_2, CO_2 and H_2O) involved in the process. Then $(m_i)_{air}$, $(m_i)_{EGR}$ and m_i are the mass, of specie i, in the air and in the EGR stream as well as the total mass, respectively. Finally, $(Y_i)_{EGR}$ is the mass fraction, of specie i, in the exhaust gas recirculation and $(Y_i)_{oxid}$ is the mass fraction, of the specie i, in the oxidizer stream.

Chapter 5

Insights about the NO-NO_2 conversion process in current diesel engines

Content

5.1 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 2.1. A similar situation can be found in other countries worldwide.

Initially, the accomplishment of the standards was fulfilled by using simple after-treatment and engine control devices 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. One of the most promising techniques relies on recycling, back to the combustion chamber, high amounts of combustion products in order to reduce the combustion's temperature and the local relative equivalence ratio. This action causes to move away from the soot and NO_x peninsula and the development of new combustion modes, like: homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI) and the mixing-controlled low temperature combustion (LTC), as it can be appreciated from Figure 2.2.

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 [1-3], it has been generally observed that the proportion of NO_2 increases above the typical range for CDC, i.e: 10% to 30% for different engine loads and engine speeds [4].

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 [5-12], 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.

Hori et al. [8], [10] and Marinov et al. [11] 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. [12] 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 a substantial increase of the NO_2 emissions [13], the interest for this phenomenon is high and therefore further studies have been developed focusing on it. Besides the effect of the oxidation catalyst (NO-NO_2), which undoubtedly can contribute to enhance these emissions, two other main contributors are the new combustion modes and the fuel (different blends or even composition).

Regarding the first of them, the most extended explanation for such increase is that in these combustion processes more NO_2 is formed by the reaction $NO+O_2=NO_2+O$, due to low temperatures, and afterwards this formed NO_2 can no longer react again to form NO because of poor mixing and a slower combustion process overall [14-15]. 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.

With respect to the fuel, several authors [16-19] have analyzed its effect on the NO_2 formation process. To do so, they have considered different diesel blends (with hydrogen, injected in the intake manifold, and oxygenated fuels) and diesel composition. 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.

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 [4], [20-23] must be also taken into consideration when analyzing the interactions between both species.

5.2 Objectives and Methodology

The aim of the present research study is to understand the substantial increase, in comparison with CDC, of NO_2 in the NO_x emissions when operating at LTC conditions. This will be contextualized in HCCI and LTC diffusive combustion scenarios and the author, 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.

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 [24], respectively.

The **constant temperature condition 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 simplistic conditions. Indistinctively of considering equilibrium and non-equilibrium states, the temperature (T) ranged from 1000K up 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. For the non-equilibrium state the considered simulation time (τ) was 1ms and 10ms.

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 5.1.- Description of the different mixtures considered in the present study.

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. 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_{inl} = 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. Due to the big differences in the applied methodology between both scenarios and in order to improve the comprehension, a detailed description of the particular characteristics of each of them will be performed under the corresponding section of the present document.

Apparently, these scenarios may seem to lack of any relationship between them, however, they will evolve from one to the other in accordance with the results analyzed and in pursue of the main objective of the present thesis.

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 [25] but also because it is considered a highly efficient fuel for the NO-NO_2 conversion process following the Hori reasoning [11]. 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. Nevertheless, as described in the previous chapter, Chapter 4, the effects of these species will be negligible justifying the employment of pure n-heptane.

The employed chemical-kinetic mechanism (RES_{TOTAL}-mech) was made up of the n-heptane oxidation mechanism [26] coupled with the NO_x formation sub-mechanism included in the GRI-Mech 3.0 mechanism [27]. 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 [20][20-23].

5.3 Results and Discussion

5.3.1.-NO_2/NO_x results for constant temperature analyses under equilibrium and non-equilibrium states 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, was performed across a wide temperature (1000K < T < 3000K) and equivalence ratio (0.2 < Φ < 1) range and at high pressure (P=10 MPa) for the four cases, described in the previous section.

The results for Case A (Y_{O2} = 0.23, NO_{ini} = 0 ppm) and Case C (Y_{O2} = 0.1, NO_{ini} = 0 ppm) are plotted in Figure 5.1a and Figure 5.1b, respectively, as the percentage ratio between NO_2/NO_x (grams NO_2*100/grams NO_x).

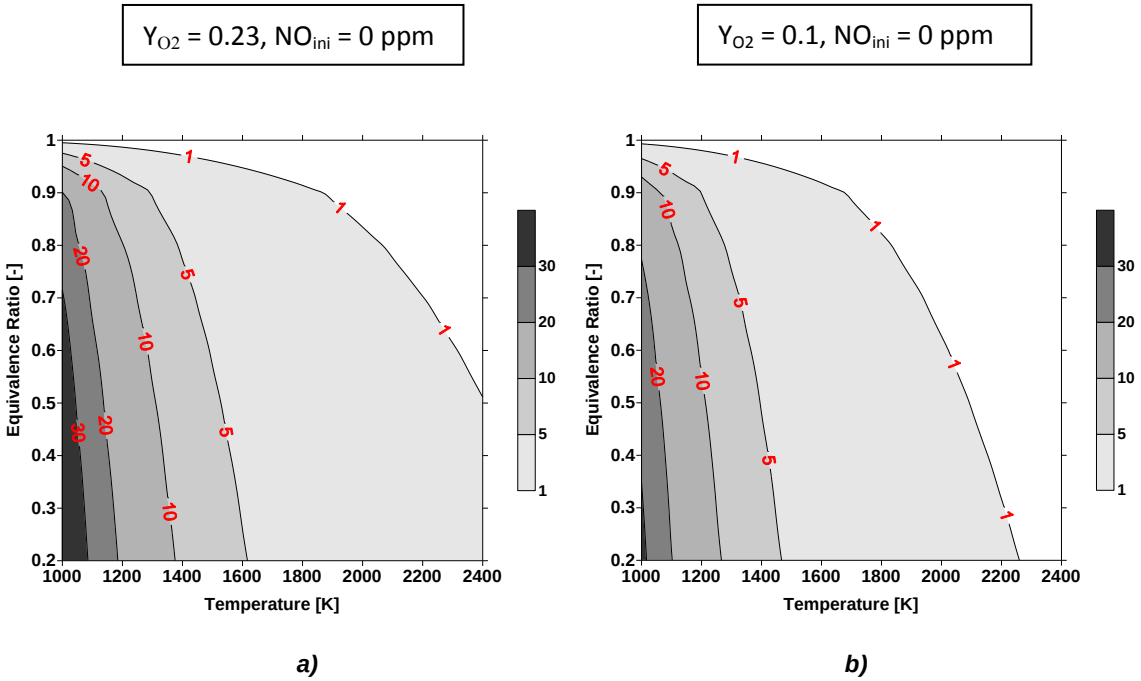

Figure 5.1.- Equilibrium results of the NO_2/NO_x ratio as a function of equivalence ratio and temperature at high pressure (10MPa) and with n-heptane as diesel fuel surrogate; a) corresponds to Y_{O2} = 0.23 and NO_{ini} = 0, b) corresponds to Y_{O2} = 0.1 and NO_{ini} = 0 ppm.

These plots clearly reflect that the temperature is the predominant variable affecting the process and, in minor extent, the equivalence ratio. Furthermore it can be observed, from

comparing both figures, a reduction in the NO_2/NO_x ratio when the Y_{O2} variable is reduced, especially at low temperatures (T < 1400K), e.g: at T = 1200 K and Φ = 0.7 a 10% 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 Figure 5.2a and Figure 5.2b. As it can be observed by comparing them with Figure 5.1a and Figure 5.1b, no differences are appreciated. This reflects that NO_{ini} has no influence when considering equilibrium conditions.

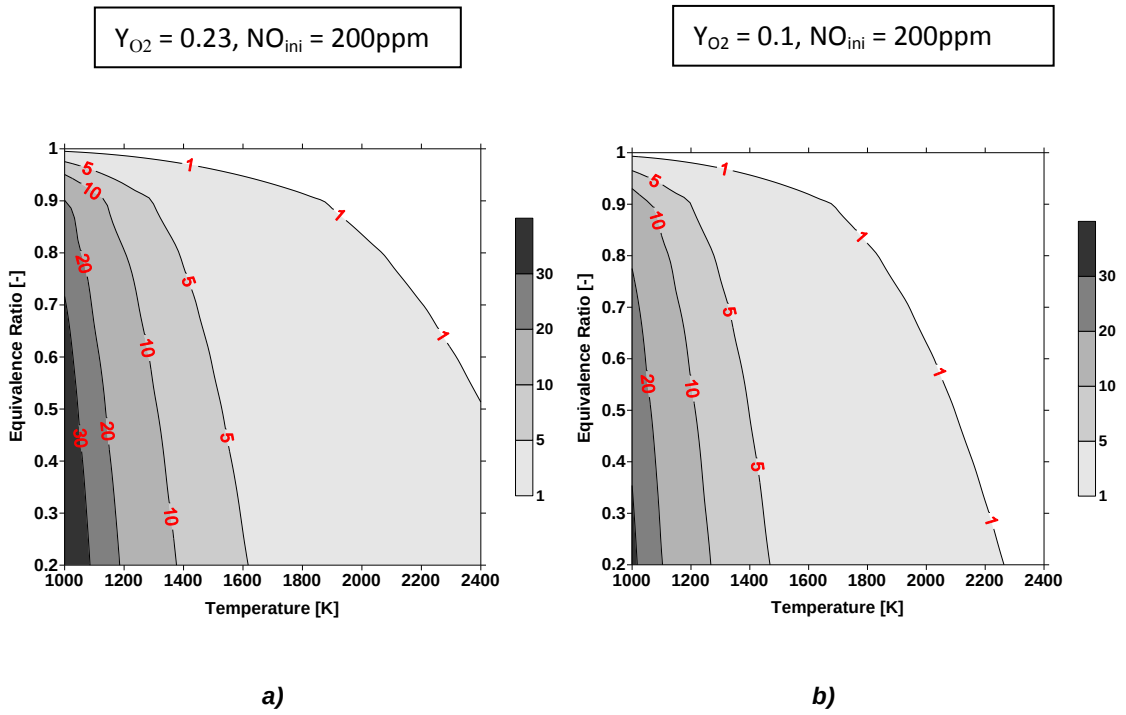

Figure 5.2.- Equilibrium results of the NO_2/NO_x ratio as a function of equivalence ratio and temperature at high pressure (10 MPa) and with n-heptane as diesel fuel surrogate; a) corresponds to Y_{O2} = 0.23 and NO_{ini} = 200ppm, b) corresponds to Y_{O2} = 0.1 and NO_{ini} = 200ppm.

These preliminary calculations illustrate that 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. Moreover it also reflects that the NO_2/NO_x ratios achieved are substantially lower than the values given in [4]: 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 is far from the equilibrium state.

Therefore, non-equilibrium, constant temperature simulations were performed for the four cases and considering two simulation times (1ms and 10ms). These simulation times are coherent with diesel combustion time scales in internal combustion engines. The results were plotted under the same axes, as shown in Figure 5.3 and Figure 5.4.

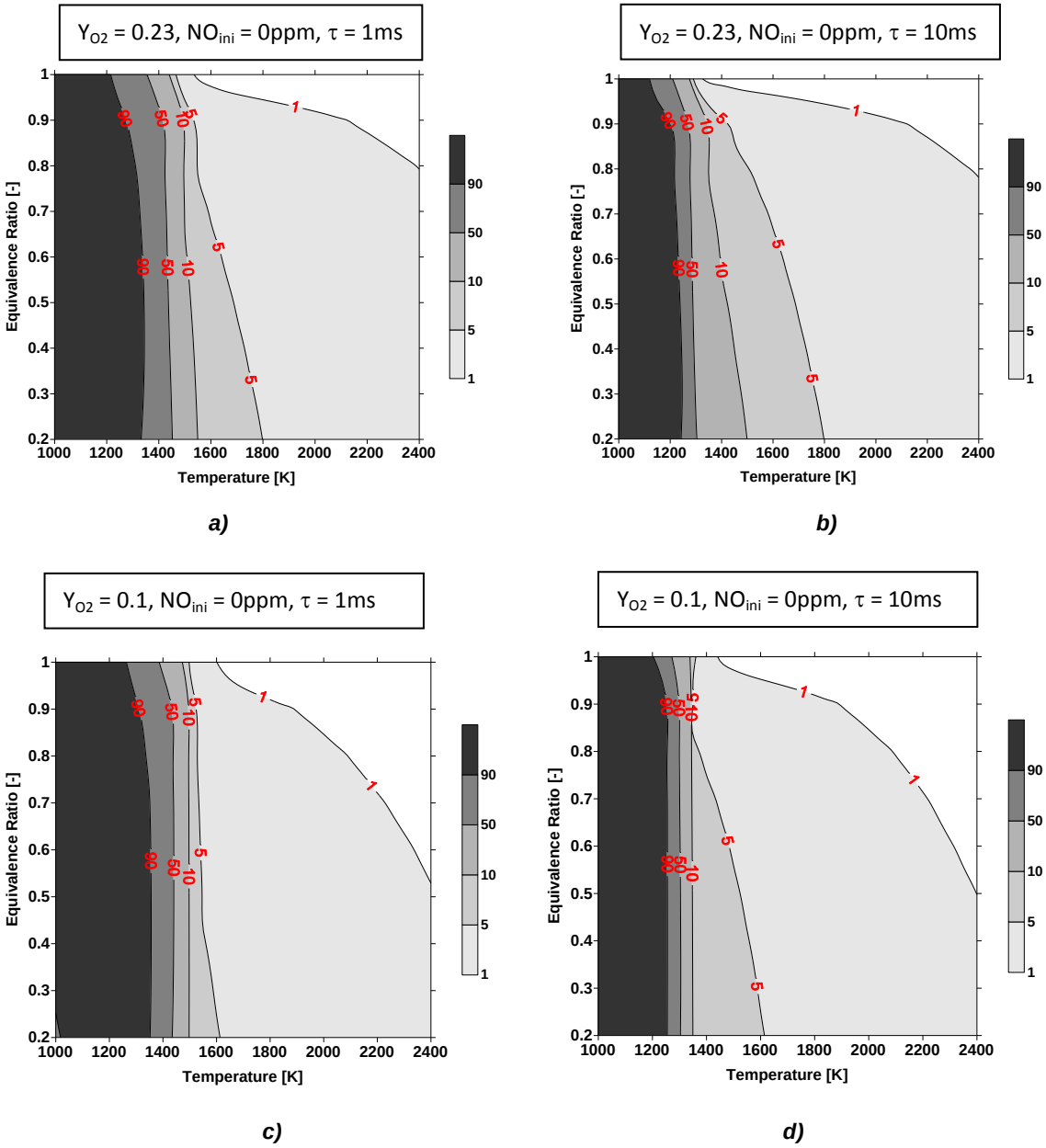

Figure 5.3.- Non-equilibrium results of the NO_2/NO_x produced as a function of equivalence ratio, temperature, oxygen mass fraction and simulation time at high pressure (10MPa) and with n-heptane as diesel fuel surrogate; a) Y_{O2} = 0.23, NO_{ini} = 0 ppm and τ = 1ms, b) Y_{O2} = 0.23, NO_{ini} = 0 ppm and τ = 10ms, c) Y_{O2} = 0.1, NO_{ini} = 0 ppm and τ = 1ms and d) Y_{O2} = 0.1, NO_{ini} = 0 ppm and τ = 10ms.

In Figure 5.3a, Figure 5.3b, Figure 5.3c and Figure 5.3d, despite the considered oxygen mass fraction and simulation time the general trends obtained in the equilibrium calculations were confirmed: determinant role of the temperature and, in a minor extent, the oxygen mass fraction on this process. Additionally, these results continue to be far from the target values, but they reveal (when compared with results under equilibrium conditions, i.e: Figure 5.a - Figure 5.d vs Figure 5.a-Figure 5.b) that the NO_2-NO reconversion process is slow specially for low temperatures (T<1300K), as the equilibrium values of the NO_2/NO_x ratio have not been reached yet after 10ms independently of the oxygen mass fraction considered.

Finally, to check if NO_{ini} still has negligible influence on the NO_2/NO_x ratio the same simulations were performed but with NO_{ini} = 200ppm. The results are summarized in Figure 5.4a and Figure 5.4b.

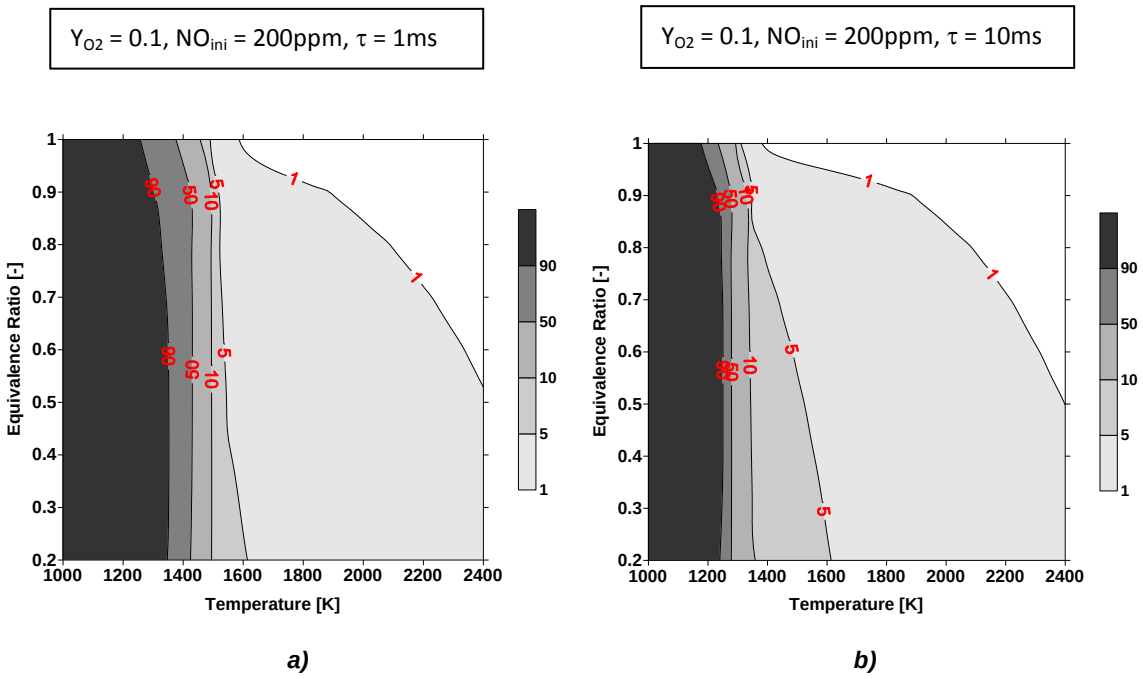

Figure 5.4.- Non-equilibrium results of the NO_2/NO_x produced as a function of equivalence ratio, temperature, oxygen mass fraction and simulation time at high pressure (10MPa) and with n-heptane as diesel fuel surrogate; a) Y_{O2} = 0.1, NO_{ini} = 200 ppm and τ = 1ms, b) Y_{O2} = 0.1, NO_{ini} =200 ppm and τ = 10ms.

Consequently, coupling the previous results (equilibrium state assumption) with the latter ones (non-equilibrium conditions) it can be said that the 10% and 30% ratio for CDC and LTC conditions, respectively, are far from being explained under these conditions. Moreover, it seems as if these values could only be reachable under extremely low temperatures, only reached in very unfavorable diesel combustion conditions. Nevertheless, to check these affirmations a more profound analysis of the combustion process will be performed assuming non-constant temperature conditions under non-equilibrium state.

5.3.2.-NO_2/NO_x results for non-constant temperature conditions under non-equilibrium state.

5.3.2.1.- Combustion process

To assure that the combustion process is not responsible for the described NO_2/NO_x values, the authors analyzed closely the time evolution of NO_2, NO and temperature, for four cases, in the context of a single-zone homogeneous mixture combustion process (HCCI combustion mode) and with the following initial conditions: two different equivalence ratios (Φ: 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 responds to the need of analyzing the possible effects of this variable throughout the whole combustion process in a non-equilibrium state, see Table 5.2. The considered simulation time was of 10ms.

In this subsection, the temporal evolution of the two species being studied will be plotted. This will allow the author to extract more observations from the combustion process than just that related with the NO_2/NO_x ratio.

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

Comparing Figure 5.5a, Figure 5.5b, Figure 5.5c and Figure 5.5d, 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 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 temperature increase characteristic 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).

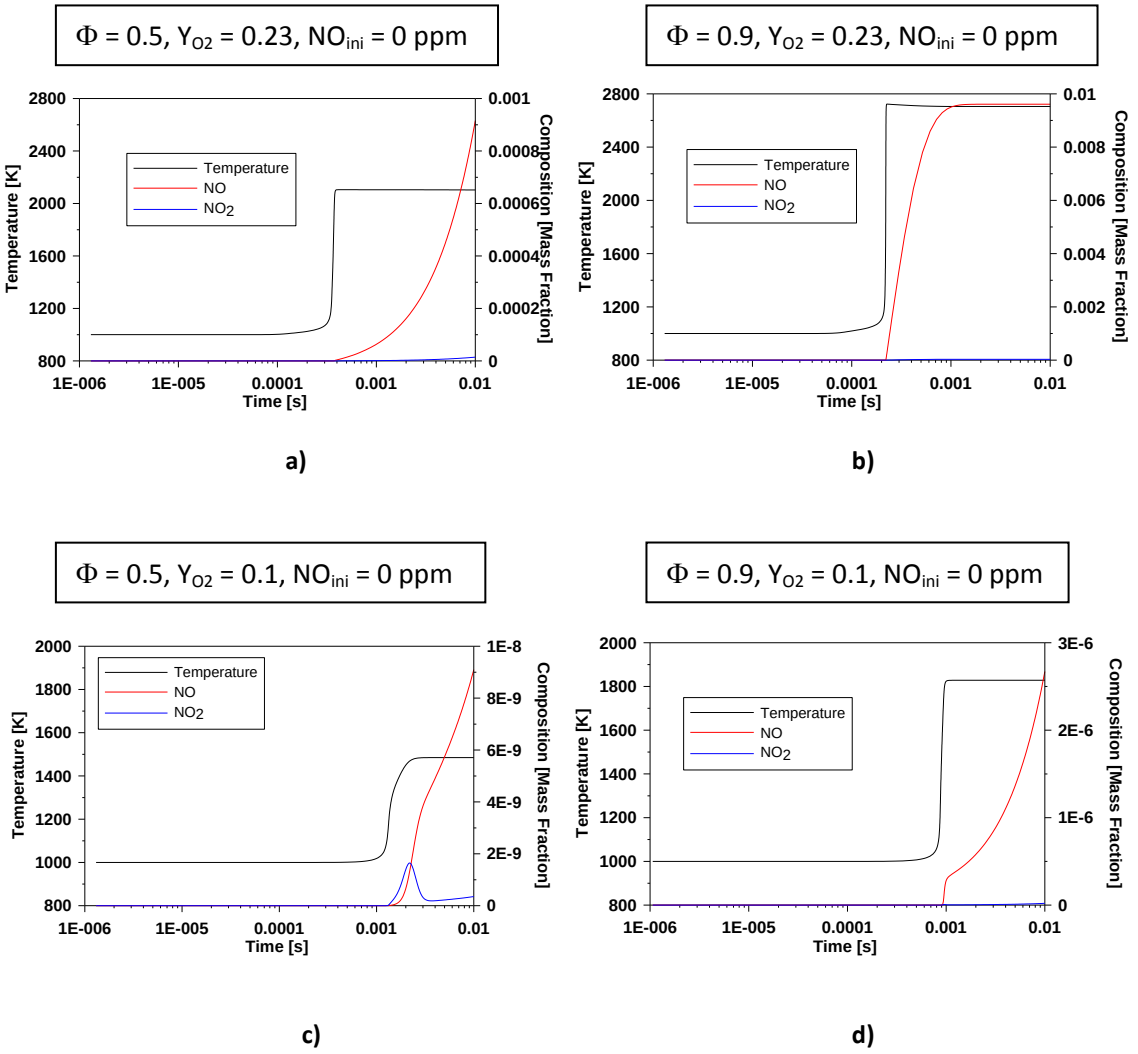

Figure 5.5.- Temperature and NO composition time evolution for several operational conditions simulating a constant pressure (P = 10MPa) HCCI combustion process at T_{ini} = 1000K: a)Φ = 0.5, Y_{O2}=0.23 and NO_{ini} = 0ppm, b)Φ = 0.9, Y_{O2}=0.23 and NO_{ini} = 0ppm, c) Φ = 0.5, Y_{O2}=0.1 and NO_{ini} = 0 ppm, d) Φ= 0.9, Y_{O2}=0.1 and NO_{ini} = 0ppm.

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 very poor combustion conditions (combustion temperature lower than 1600K), for current diesel engines, are considered. This observation seems to suggest that any combination of mixing process efficiency, fuel-air mixture temperature and equivalence ratio, engine design, EGR rates, slow combustion process, etc… which will generate low combustion temperatures will enhance the NO-NO_2 conversion process.

Despite these results and the fact that the initial NO concentration has no influence on the NO_2/NO_x ratio at the end of the simulation time, as concluded from the previous subsection, the author decided to consider EGR conditions with NO_{ini} = 200ppm. Figure 5.6a and Figure 5.6b show that the NO-NO_2 conversion process is cyclic, independently of the

equivalence ratio considered and the combustion temperature, and made up of two stages: 1) conversion of NO to NO_2 and 2) re-conversion of NO_2 to NO. The final concentration of NO will be NO_{ini} or higher depending on the fact that the considered experimental conditions enhance or not the NO formation.

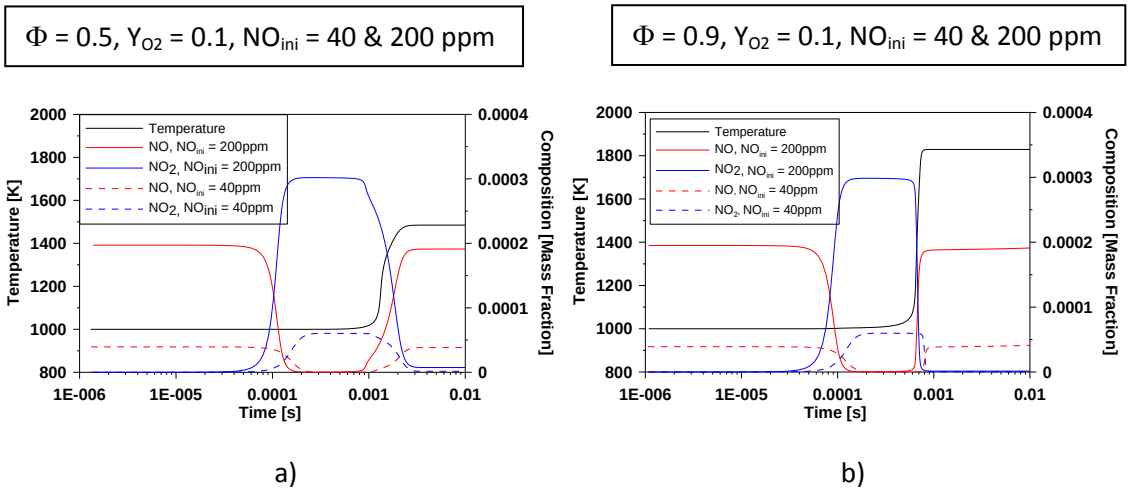

Figure 5.6.- Temperature and NO composition time evolution for several operational conditions simulating a constant pressure (P = 10MPa) HCCI combustion process at T_{ini} = 1000K: a) Φ = 0.5, Y_{O2}=0.1 and NO_{ini} = 200 ppm, b) Φ = 0.9, Y_{O2}=0.1 and NO_{ini} = 200ppm.

In the first stages of the process all NO_{ini} is converted into NO_2 due to the low temperatures, responsible for enhancing the formation of reactive radicals involved in the conversion process. 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 (checked by comparing between the molar fractions).

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 conversion.

To confirm if the previously described behavior is dependent on NO_{ini}, the latter simulations were repeated by arbitrarily considering NO_{ini} = 40ppm. To make easier the interpretation, the results were normalized using the NO_2/NO_x ratio and plotted in Figure 5.7 with the other two cases (NO_{ini} = 200ppm and 0ppm).

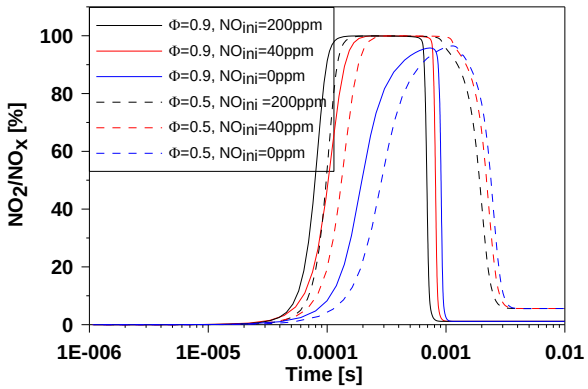

Figure 5.7.- Influence of the NO_{ini} variable on the NO_2/NO_x ratio on a single-zone homogeneous combustion process.

These results reflect identical trends for a given Φ and illustrates a cyclic process in which the main influence of NO_{ini} relies in the ignition delay time: as the initial NO composition increases, the ignition delay is reduced. This corroborates the findings of Bromly et al.[12] but in this case at high pressures. Also confirms that lower combustion temperatures, which in this scenario (temperature is not constant) is directly related with Φ and Y_{O2}, yields higher ratios and therefore in agreement with those plotted in Figure 5.4a and Figure 5.4b (1ms and 10ms, respectively).

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.

However another way to reach low temperatures in an internal combustion diesel engine is due to cooling effects caused by: the expansion stroke, the dilution effect of combustion products with fresh oxidizer stream remaining in the combustion chamber and due to wall impingement.

5.3.2.2.- 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 previously mentioned. 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 5.3. This ratio will be

plotted as a function of time in concordance with the rest of the plots in the present document.

Engine's Characteristic	Values
Stroke [m]	0.1
Bore [m]	0.08
Compression ratio [-]	17
Connecting rod length [m]	0.18
Engine speed [rpm]	2000
Vdisp [m^3]	5.03E-04
Vcc [m^3]	3.14E-05
P_BDC [bar]	1
T_BDC [K]	340

Table 5.3.- Engine characteristics.

- In contrast the dilution and the wall impingement effects were contextualized in the diesel diffusion flame environment, because the relevancy of them under HCCI combustion is negligible, using a more complex procedure. Their initial conditions, or in other words, the combustion products formed in the flame front region, will be determined by assuming equilibrium conditions for Φ = 1 under the initial conditions described by the two cases (A and C, as mentioned above) . It is worth to note that the author is 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.
    - The dilution effect of the combustion products was characterized by a fresh oxidizer stream, with constant composition and temperature (substantially lower than the flame temperature) throughout the whole simulation time, and considering adiabatic mixing and constant pressure conditions. Both the oxidizer 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) [28], for two different injection pressures (P_{inj} = 500bar and 1500bar) and considering the spray's baseline conditions summarized in Table 5.4.

This 1-D spray modeling software computes the average temperature and composition in a steady, non-premixed turbulent jet. This is achieved based on the mixing-control hypothesis and simplifying the spray structure in two different regions, flame front region and flame core, each characterized by a perfectly stirred reactor (PSR).

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 5.4.- Spray's baseline conditions.

- For the wall impingement effect, a brief cool down of the combustion products was considered followed by a sudden temperature drop, typical of this phenomenon. The initial cool down will correspond to the dilution of the combustion products by the oxidizer stream and therefore the same reasoning as described previously will be applied. However, due to the difficulty of determining accurately the temperature drop of the combustion products when colliding with the chamber wall, two proportionality degrees ($\Delta T = -T_{ad}/3$ and $-2 \cdot T_{ad}/3$) between the combustion temperature and the temperature drop will be arbitrarily considered. The author would like to emphasize that the present thesis is a comprehensive study of the NO-NO_2 conversion process.

In contrast with the previous non-constant temperature and non-equilibrium scenario, the NO_2/NO_x ratio will be employed to discard the reduction of NO and NO_2 as a consequence of the dilution effect of the entrainment of oxidizer stream and because it is the parameter which is being compared with literature results.

The first situation corresponds to non-EGR (Y_{O2} = 0.23) and the oxidizer stream temperature as well as the mixing rate will be established to have a similar cooling speed as the reference curve.

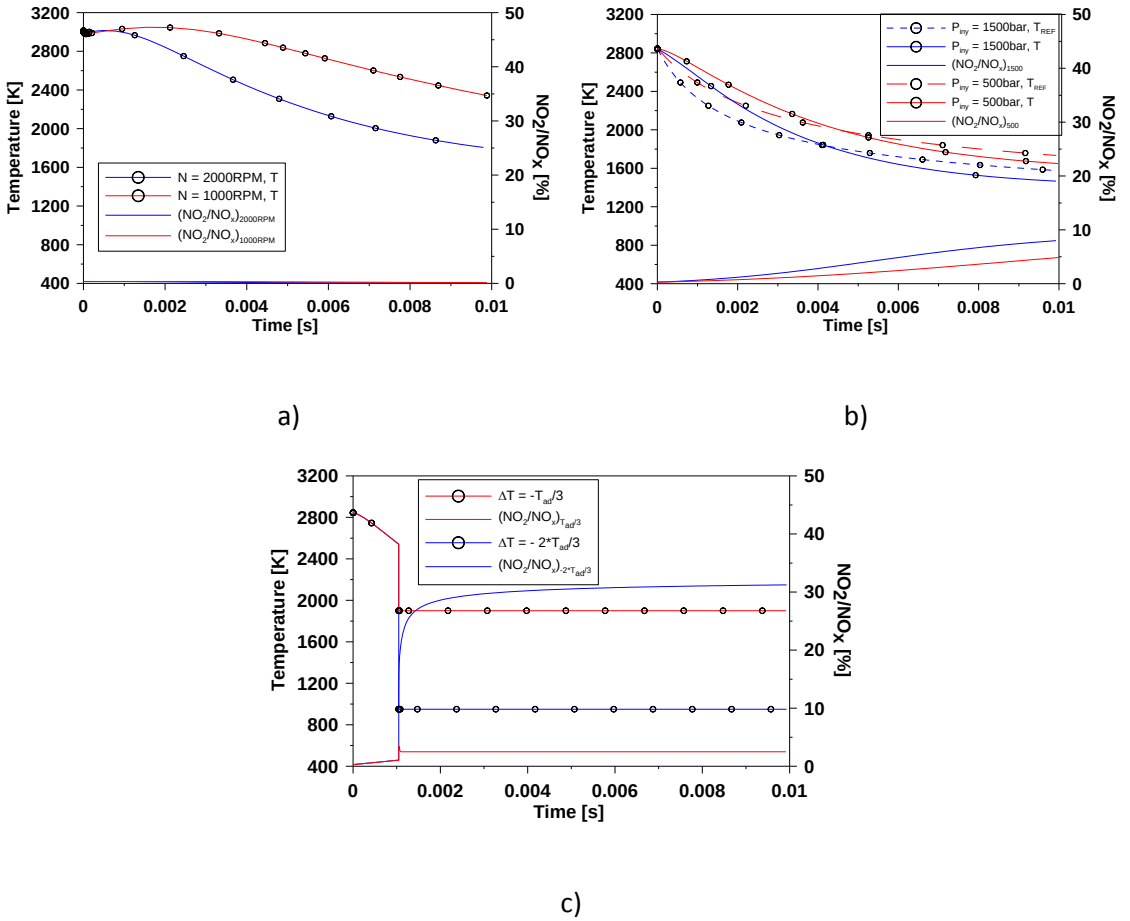

Figure 5.8.- Temperature evolution and NO$_2$/NO$_x$ ratio due to different cooling effects typical in diesel engines: a) expansion effect at two different engine speeds, b) dilution effects by considering two cooling speeds and c) wall impingement considering two temperature drops.

Figure 5.8a, Figure 5.8b and Figure 5.8c represent the time evolution of the temperature and the NO_2/NO_x ratio for the three studied phenomena: expansion stroke, dilution by oxidizer stream and wall impingement, respectively. Generally speaking, it can be observed that lower temperatures yield higher NO_2/NO_x ratio.

A closer analysis of the three plots reflects that under these conditions the cooling effect due to dilution and to wall impingement could explain the 10% NO_2/NO_x ratio described in literature by itself. However, in the case this latter phenomenon occurs, the amount of mass colliding with the wall is so minor that it won't justify it. 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. Applying the same reasoning as in the previous situation, the initial temperature of the oxidizer stream and the mixing rate were fixed to reproduce the reference cooling speed.

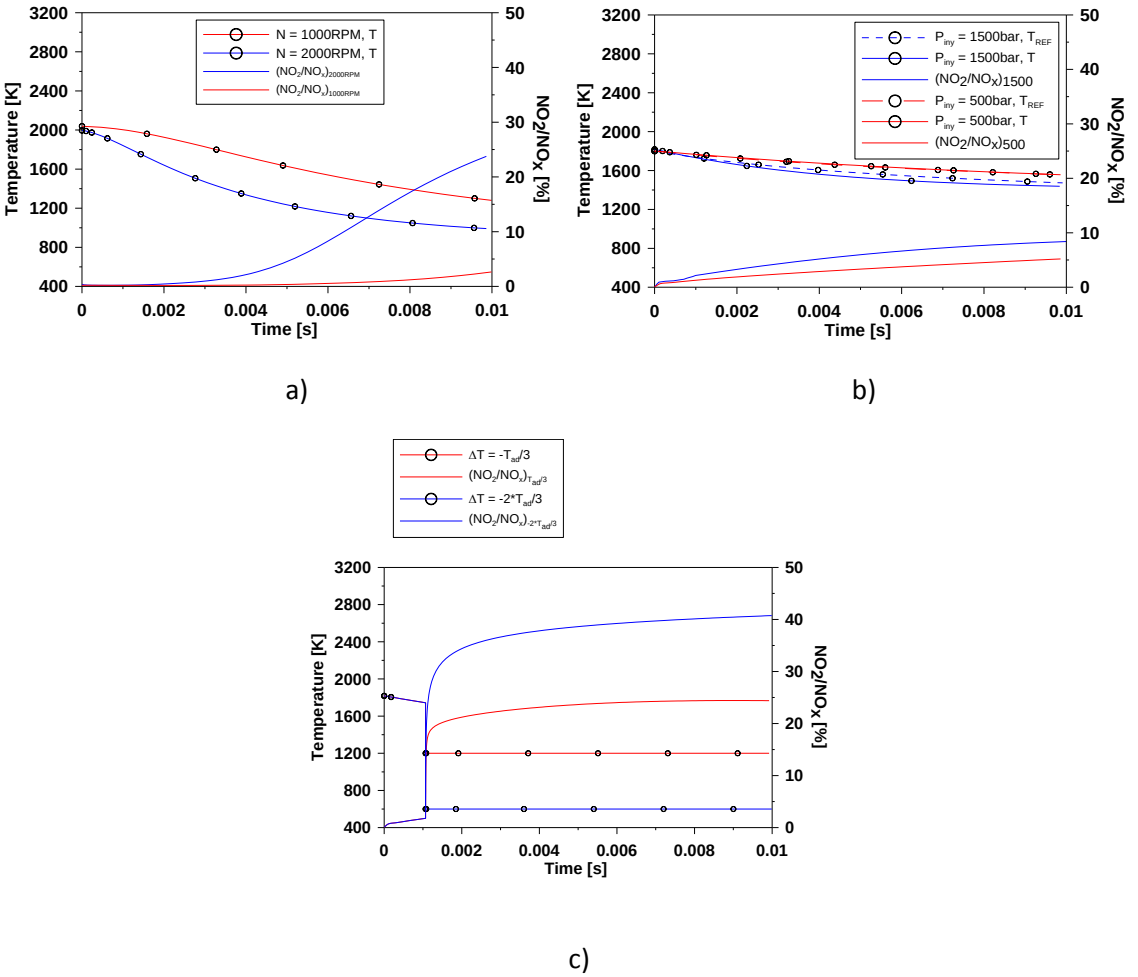

Figure 5.9.- Temperature evolution and NO_2/NO_x ratio due to different cooling effects typical in diesel engines: a) expansion stroke at two engine speeds, b) dilution effects by considering two cooling speeds and c) wall impingement for two temperature drops. Initial temperature and composition correspond to a single zone homogeneous combustion process with high EGR rate (Y_{O2} = 0.1).

Under these conditions Figure 5.9a, Figure 5.9b and Figure 5.9c, lower combustion temperatures are reached, due to the dilution of fresh air with EGR, but higher NO_2/NO_x ratios. 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.

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. Even though the wall impingement can by itself explain such increase, the amount of mass colliding is so minor it won't justify it.

5.4 Conclusions

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

a. Generally speaking, the NO2 formation is a consequence of a cycling NO-NO2 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.
b. The equilibrium results illustrate that the NO2/NOx 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 NO2/NOx, 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 NO2 formation.
c. The non-equilibrium (non-steady state), non-constant temperature scenario confirms that the combustion process, by itself, is not responsible for the increase in NO2 formation, from CDC to LTC conditions.
d. Cooling effects (expansion stroke, dilution effect by oxidizer stream and wall impingement) enhance the NO-NO2 conversion process increasing the NO2 formation reaching the values described in the scientific literature.
e. For CDC conditions the major contributor to the final NO2/NOx ratio is the dilution effect followed by the wall impingement. Even though this latter phenomenon yields high ratios, specially as the temperature drop becomes greater, the probability of occurring this event or even the amount of flame colliding with the wall is minor.
f. 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 NO2 formation when moving from CDC to LTC.
g. These cooling effects should be taken into consideration when modeling the NO2 formation process.

5.5 Summary

One of the most common pollutants generated in diesel engines, under conventional combustion conditions (CDC), are the nitrogen oxides (NO_x) which are composed mainly of NO, NO_2 and N_2O. Multiple researches have focused on reducing them and the greatest results have been achieved when lowering the combustion temperature by employing massive exhaust gas recirculation rates (LTC). Despite this benefit, it has also been observed a substantial increase in the NO_2 contribution to the NO_x emissions.

To analyze the reasons of such increase it is crucial to understand how NO_2 behaves and its contribution (NO_2/NO_x) not only under LTC but also for CDC conditions. In this context a stepwise research study was designed considering, initially, general equilibrium conditions and

finishing by analyzing the influence of typical diesel engine phenomena (combustion and cooling effects) on this specie.

The general results obtained under equilibrium conditions confirm the theoretical guidelines established for the NO_2 formation process. Afterwards, when considering a non-steady state homogeneous combustion process (HCCI-like mode), the previous results were corroborated as well as the fact that poor or slow combustion processes are responsible for the NO_2 formation. Additionally, it reflected a cyclic process between NO and NO_2. Finally, three cooling effects, inherent to how diesel engines work, were analyzed also assuming non-steady state conditions: the one associate to the expansion stroke, the one caused by the dilution of hot combustion products with the rest of in-cylinder charge and the one caused by wall impingement. Despite the dependency on the simulation time, the results corroborate that the dilution effect explains the 10% of the NO_2/NO_x ratio characteristic of CDC conditions but not the 30% or higher of the LTC diffusive combustion scenario. In this latter case, it is the combination of the cooling effects due to the expansion stroke and the dilution effect which yield similar values. Consequently, these cooling effects must be taken into consideration when modeling the NO_2.

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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]	$1.4 \cdot 10^{-4}$
ρ_f [kg/m^3]	830
ρ_a [kg/m^3]	20
T_a [K]	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 A1 and A2, respectively.

$$\boldsymbol{d_{eq} = d_o \cdot \sqrt{\frac{\rho_f}{\rho_a}}} \qquad \textbf{(Eq. A1)}$$

$$\mathbf{u_o = \sqrt{(2 \cdot \Delta P \cdot 10^6 / \rho_f)}} \qquad \textbf{(Eq. A2)}$$

Afterwards, the mixture's history along the axis and within time is possible to be determined by applying the Ricou and Spalding equation (Eq. A3), for the entrainment rate for non-reacting turbulent jets, and considering the momentum flux in the jet to be constant (Eq. A4).

$$\mathbf{\frac{m}{m_o} = 0.32 \cdot \frac{x}{d_{eq}}} \qquad \textbf{(Eq. A3)}$$

$$\mathbf{m \cdot u = m_o \cdot u_o} \qquad \textbf{(Eq. A4)}$$

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 closed perfectly stirred reactor (cPSR), 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.

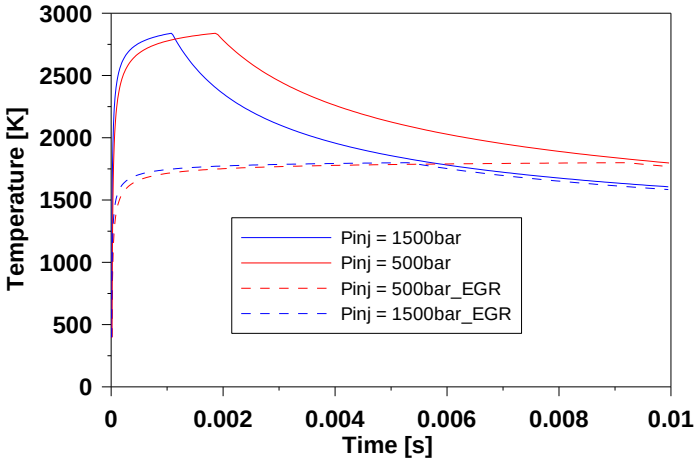


Figure A.1.- Temperature time evolution for a diesel spray under the four different working conditions.

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.

Chapter 6

Evaluation of the Thermal NO Formation Mechanism under Low Temperature Diesel Combustion Conditions

Content

6.1 Introduction

Until now, the diesel engines worked under CDC conditions, mainly characterized by high local temperatures and equivalence ratios and behaving as summarized in Dec's conceptual model [1], schematically represented in Figure 2.1, which is the most widely

accepted. Even though other authors [1-5] have worked on the topic, for the past two or three decades, it wasn't until the optical measuring tools got improved that it was possible to configure this suitable model.

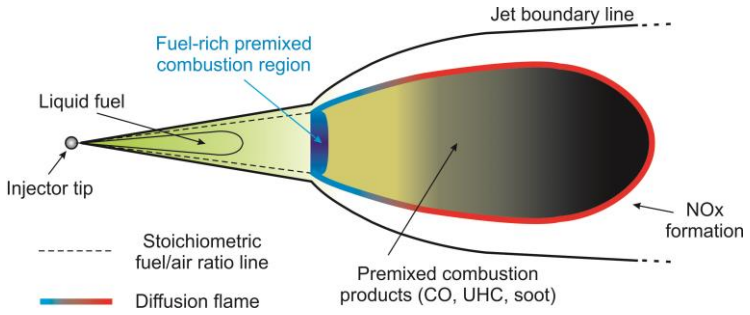


Figure 6.1.- Stabilized diffusive flame scheme based on Dec's diffusive flame conceptual model.

In contrast, the new combustion modes, characterized by LTC diesel conditions, remain mainly unknown due to the youth of these modes and to the complex chemical and physical processes involved. However, a recent study performed by Musculus [6] has started to reveal some interesting guidelines referred to the diesel spray structure under these conditions and summarized as "an extension of Dec's model", as the proper author names it.

Due to the uncertainty degree still remaining in this field a possible way to deal with this lack of knowledge is to extrapolate the well-known principles of CDC to LTC. In the present study a simplified version of Dec's model is going to be used as reference, illustrated in Figure 6.1, in order review the different processes involved in the NO formation phenomenon, at CDC conditions.

Using this model as scientific guideline will help understand the processes, simplifications and evolution of the fuel mass fraction (Y_f) (defined as a function of mixture fraction (Z)), oxygen mass fraction (Y_{O2}), temperature (T) and NO formation rate as the flame progresses.

The process starts when liquid fuel, injected into the combustion chamber at a temperature of 350K approximately, starts to suffer atomization (break up of droplets into smaller ones) and mixing phenomenon with entrained hot air, located inside the combustion chamber, due to the momentum flux with which has been injected. Both processes cause an increase in the fuel's temperature, enhancing the fuel's evaporation till it reaches the evaporative liquid length (L_{liq}). From this distance on, the vapor continues to mix with air, from the surroundings, until it reaches the auto-ignition conditions causing a fuel rich premixed combustion reaction at a distance from the nozzle known as lift-off length (LOL). This reaction causes the formation of small hydrocarbon chains (C_2H_2, C_2H_4, C_3H_3), partially burned products (CO), temperature increase and consumption of all the oxygen entrained previously.

Next, the different products enter the internal zone of the diffusive flame where it continues to mix with burned gases coming from the flame front. At this point, no oxygen is present due to the diffusive flame front, located around the flame's perimeter, which prevents it from entering. The lack of oxygen implies the lack of energy release in this region, even though the temperature continues to raise due to the mixing process with hot combustion products.

When these products reach the flame front, the remaining hydrocarbons and unburned products are completely burned, with the presence of oxygen, under stoichiometric conditions. This causes the release of the remaining energy still stored in the hydrocarbons and unburned products, increasing the temperature up to 2700-3000K in classical combustion conditions. Is beyond this region where the NO formation mechanisms are activated due to the presence of fuel, high temperatures and high content of oxygen. However, the NO formation process under LTC conditions is likely to be formed throughout the jet cross-section, in the same relatively hot, oxygen available environments, where OH exists. Even though the NO formation scenario changes from LTC to CDC conditions, it is worth to mention that the results obtained from the present study show its independence on a particular scenario, LTC or CDC.

Therefore, to study the formation of this pollutant, from a physical point of view, we must focus on all those variables and processes involved in diffusive flame combustion, like: oxygen content (Y_{O2}) and the influence of the local temperatures.

Besides understanding the physical principles, the chemical processes are gaining in importance. Several have been the authors that have tried to study the chemical-kinetic aspects of the NO formation process. These investigations have concluded with several well-known chemical models classified in two main groups: based in kinetic schemes and based in chemical equilibrium hypothesis. Most of the models used nowadays are based in the latter principle and are mainly applicable for CDC conditions. The most important ones are briefly described in the following paragraphs.

The thermal mechanism was first postulated by Zeldovich in 1946 [7] and is nowadays the most extended one in commercial CFD softwares for emission studies. It has a strong temperature-dependence and describes the formation of nitric oxides from the oxidation of atmospheric nitrogen, at relatively high temperatures, in fuel-lean environments [8]. An additional elementary reaction is often added in what is called the extended or modified Zeldovich mechanism. This last mechanism takes into account the NO formation due to oxygen and hydrogen radicals.

The Prompt mechanism was reported by Fenimore [9] and considers the NO formation by the reaction of atmospheric nitrogen with hydrocarbon radicals in fuel-rich regions to form cyano compounds and amines. These are then converted to intermediate compounds that ultimately form NO. The reaction where hydrocarbon radicals react with atmospheric nitrogen is the rate limiting and the primary path, as it is believed that 90 percent of NO prompt formed is via HCN.

The N_2O intermediate mechanism [10-11] considers the NO formation due to high pressures and lean fuel conditions and with a third body reactant. The mechanism starts by the formation of N_2O from atmospheric nitrogen.

The fuel contribution mechanism [8], [10-11] considers that NO is formed by the nitrogen bound in the fuel. Usually it is assumed to proceed through the formation of HCN and/or NH3 which are oxidized to NO while being competitively reduced to N_2.

Even if all these mechanisms have their relevance in predicting the amount of NO formed under certain conditions, the predominant one for CDC characteristics is the thermal mechanism [12-17]. This mechanism offers scientists and engineers the opportunity to accurately predict, up to 90 percent of the amount of NO formed with low computational cost.

On the other hand, when working at LTC conditions the Thermal mechanism loses accuracy [13-16] and [18] and others start to gain relevance, like Prompt and/or N_2O intermediate mechanisms, depending on different authors. Therefore new predictive tools, which take into account the widest possible range of operational conditions, are strongly required.

6.2 Objectives and Methodology

The main objective of this chapter is to relate the thermal mechanism, which is the most extended one, with the total NO formed under CDC and LTC conditions. This relationship could be used as a corrective tool capable of improving the thermal's prediction in those conditions where the mechanism is not fully predominant without increasing the computational cost.

Consequently, a preliminary study was performed to confirm the predominance of the Thermal mechanism over the rest of the NO formation mechanisms for a wide range of working conditions (CDC and LTC). It is worth noting that the prompt mechanism wasn't analyzed individually, in contrast with the N_2O route, because under the conditions considered in the present chapter this mechanism is not expected to be a significant contributor. Moreover, it is conferred by multiple NO formation/destruction processes in constant development and closely related between making it very complex to properly isolate it.

In order to achieve these objectives two parametric studies were designed and executed using Chemkin Pro version [19].

Focusing initially in the secondary objective, the analyses were performed assuming **constant pressure and temperature conditions** over a wide range of relative mixture fractions (Z_r[2]) and temperatures values. Furthermore, three different simulation times (1ms, 10ms and 1s) and two different oxygen mass fractions (Y_{O2}) were considered. In Table 6. are summarized all the considered conditions.

[2] Mixture fraction and relative mixture fraction are explained in great detail in Reference [23].

Zr	T [K]	Y_{O2}	Mechanisms
0.2 – 1	1000 - 2000K	0.23	Thermal and N_2O intermediate
0.2 – 1	1000 - 2000K	0.1	Thermal and N_2O intermediate

Table 6.1.-Summary of the conditions considered to perform the preliminary study to analyze the contribution degree of the two test mechanisms.

In contrast, to accomplish the main objective, it consisted in **varying the final reaction temperature (T_{end}) by modifying Y_{O2} in the fuel-air mixture for a given fixed local condition[3], described by:** Z_r, constant pressure (P) and initial reaction temperature (T_{ini}).

In Figure 6.2 all the fixed local conditions considered are plotted reflecting the expected flame temperature for a particular oxygen mass fraction and initial temperature. These were obtained assuming the equilibrium hypothesis, in order to remove the time effect on the combustion process, and hence using the equilibrium module, of the Chemkin Pro package, under constant pressure and enthalpy conditions. Additionally, the circles were depicted using 12.7% of oxygen mass fraction as delimiting value.

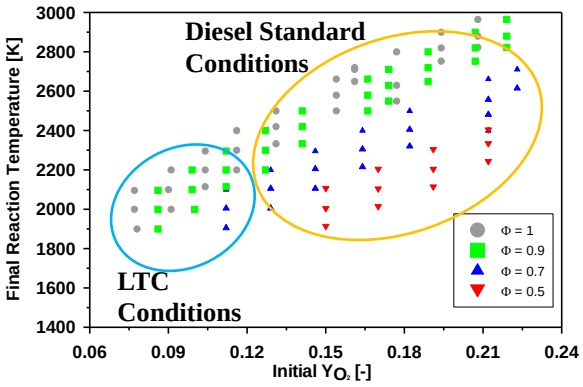


Figure 6.2. End temperature as a function of initial oxygen mass fraction of all the considered working conditions characterized by Φ and T_{ini}. Calculations were performed using the equilibrium module of the Chemkin Pro package, considering constant pressure and enthalpy.

Furthermore, detailed definitions of each of these variables are presented in Table 6.2. Special attention must be paid to:

- The T_{ini} variable; these values corresponds to the temperature given by the mixture of the injected fuel and the entrained hot air, if extrapolated to the Dec's conceptual model. This means that the fuel-rich premixed combustion process is neglected, due to the lack of NO formation at this stage.

[3] When it comes to characterize the physical phenomenon behind the NO formation mechanisms, inside a diffusive flame, two possible scenarios can be considered. The first one implies the use of continuously varying conditions, like in real diesel sprays processes, and the second one consists in considering fixed local conditions. In the present study the second scenario was considered.

- Characterization of the physical phenomenon behind the NO formation mechanisms inside a diffusive flame; 1) continuously varying conditions, like in real diesel sprays processes, yielding realistic results but with a very high computational cost or 2) considering fixed local conditions and consequently simplifying substantially the simulations. In the present study the second scenario was considered and a perfectly stirred reactor (PSR) was employed.

It is worthy to highlight that even though all of these simplifications, may seem to trivialize the present study, making it irrelevant for any practical applications, as it gets developed it will reflect interesting conclusions independently of this methodology.

Additional variables required to run the current studies are: a diesel fuel surrogate and a chemical-kinetic model.

The diesel fuel surrogate chosen was n-heptane mainly due to its similar cetane number with typical European diesel fuel [24]. 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. Nevertheless, as described in Chapter 4, the contribution of these species is negligible justifying the usage of neat n-heptane.

The employed chemical-kinetic mechanism was made up of the Seizer et al n-heptane oxidation mechanism [25] coupled to the GRI-Mech 3.0 mechanism [26] which includes the most complete NO_x formation/destruction mechanisms. This resulting mechanism was named as RES-mech (181 species and 1581 reactions) and different versions were constructed and named depending on the mechanism included in it (thermal, N_2O pathway and Total). The prediction yield by the Total version of the RES-mech, under the different studied conditions, was used as reference.

6.3 Results and Discussion

6.3.1.- Evaluation of the different NO formation mechanisms

In Figure 6.3 and Figure 6.4 the contribution degree of the different NO formation routes will be represented as a function of temperature and relative mixture fraction, for Y_{O2} = 0.23 and 0.1, respectively. In both scenarios different simulation times (1ms, 10ms, 1s) were analyzed. Note that this contribution degree will be quantified as the ratio between the analyzed mechanism and the total NO (e.g: NO_{TH}/NO_{TOTAL} and the NO_{N2O}/NO_{TOTAL}).

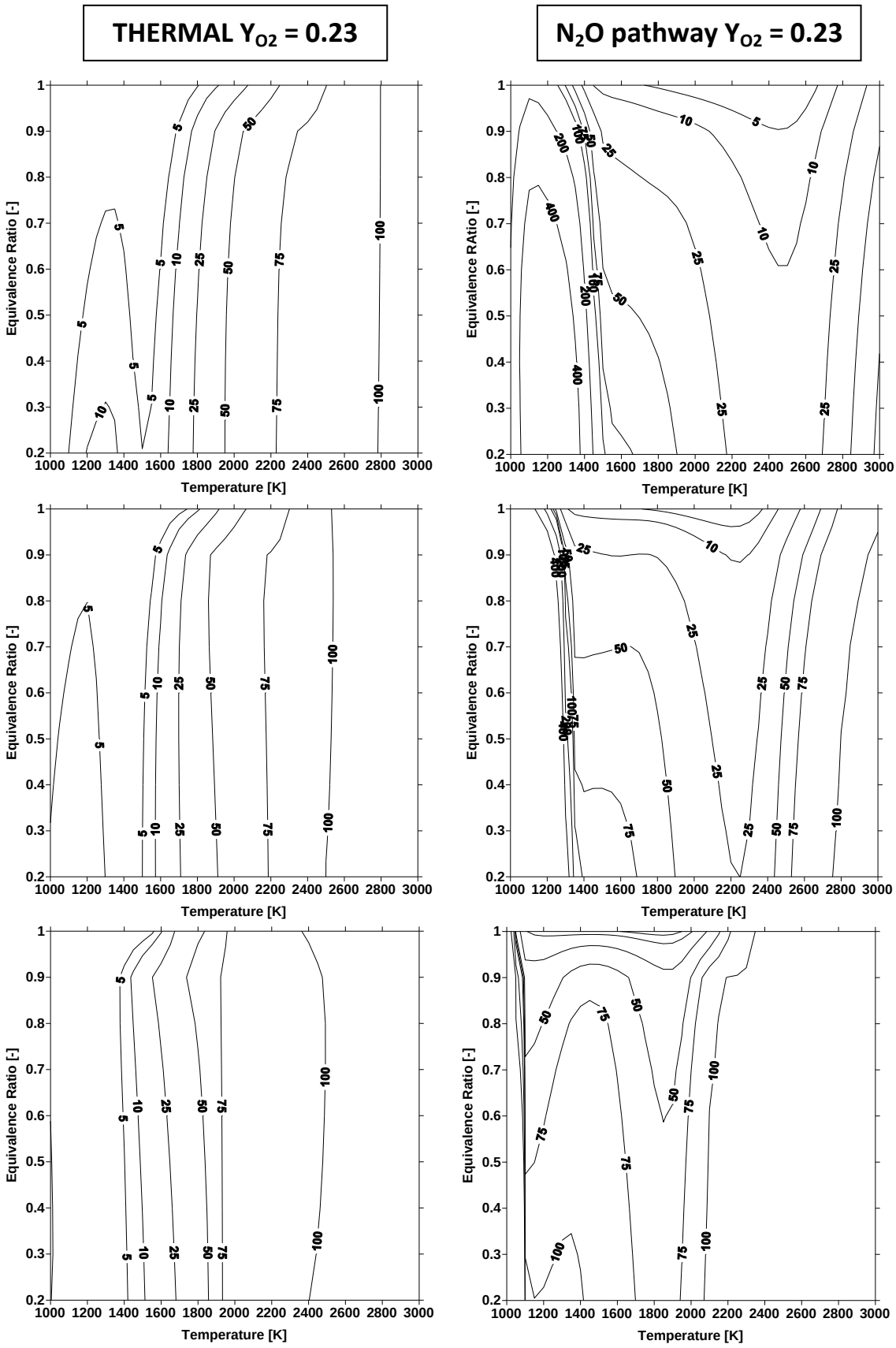


Figure 6.3.-Contribution degree of the Thermal and the N_2O mechanisms as a function of temperature and equivalence ratio for three different simulation times (1ms, 10ms and 1s) and without EGR.

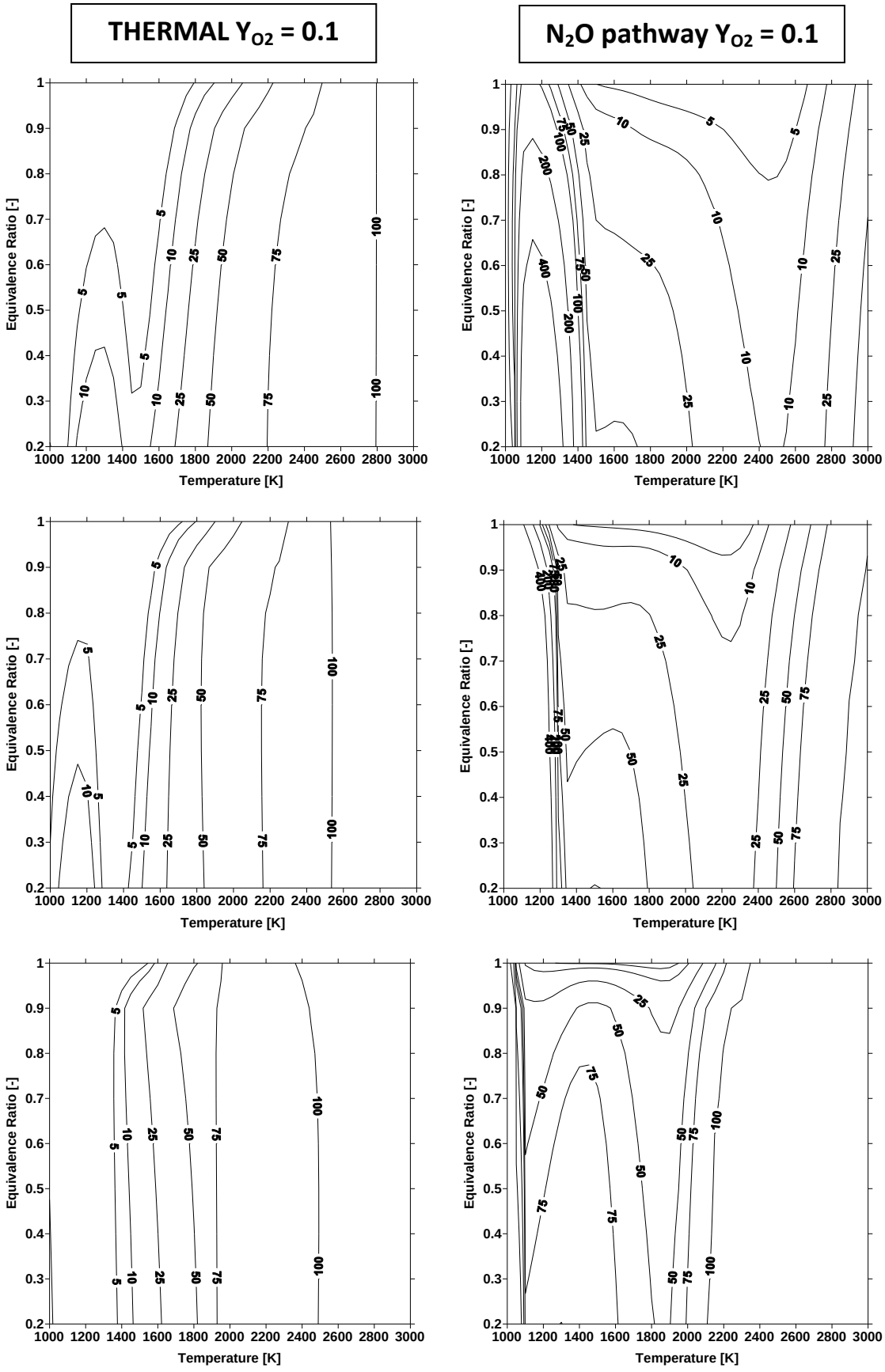


Figure 6.4.-Contribution degree of the thermal and the N_2O mechanisms as a function of temperature and equivalence ratio for three different simulation times (1ms, 10ms and 1s) and massive EGR.

Generally speaking the results reflect the direct relationship between the simulation time and the oxygen content with the contribution degree for both mechanisms and in the two scenarios (Y_{O2} = 0.23 and 0.1). This first observation is in coherence with the fact that as time evolves the equilibrium conditions, where the composition of NO is the same despite the mechanism being analyzed, are being approached or are close to them at lower temperatures. Consequently, higher ratios are observed at lower temperatures. The second observation agrees with the reasoning that the amount of oxygen available is key to the formation of this pollutant, specially through the N_2O intermediate pathway. It is worth to highlight that the amount of NO formed by the two studied mechanisms don't sum up to the NO formed by the Total version. This can be explained due to two facts: 1) the prompt mechanism is not directly considered and 2) all the mechanisms have to converge to a given NO value, corresponding to the equilibrium composition, which is independent of chemical kinetics.

Focusing individually in each mechanism the results corroborate the findings well described along the scientific literature. These can be summarized in:

1. The thermal mechanism is a formation route which is strongly dependent on temperature, mainly at high temperature (T > 1900K), where it becomes predominant (NO_{TH}/NO_{TOTAL} > 50%). Thus it is considered as the main formation mechanism in internal combustion engines, specially under CDC conditions where higher influence is observed.
2. The N_2O mechanism instead is more dependent on the relative mixture fraction than on temperature. For leaner mixtures higher contribution degree is observed for all temperatures even though at very low temperatures, T < 1400K, substantially higher NO is formed by the N_2O route than when considering all the mechanisms together. This observation could suggest the influence of the NO-NO_2 conversion process in this region. Additionally, it can be observed that there is a temperature, depending on the simulation time considered, which acts as a symmetry plane. This is probably illustrating the differences in formation rate between the Thermal and N_2O mechanisms in the mid and high temperature regions.

From this study it is plausible that the Thermal mechanism reduces substantially its influence till the point that it is inadmissible to just consider it in order to perform accurate NO predictions.

6.3.2.- Individual Results.

Initially, three random cases were selected (Table 6.2) to study the contribution degree of the two mechanisms involved in the study. In order to do so, individual simulations of the different RES-mech versions: *thermal, N_2O* and *Total*, were performed for a characteristic combustion time of 1.0ms.

Cases	Z_r	T_{end} [K]	Y_{O2} [-]	Y_f [-]	$NO_{version\ All,\ \tau = 1ms}$ [ppm]
Case A	1	2200	0.09	0.026	66.9
Case B	1	2400	0.116	0.033	756.7
Case C	0.7	2200	0.129	0.025	254.8

Table 6.2.-Summary of the values used for the parametric study performed.

This combustion time was chosen based on two complementary criteria:

1. Equilibrium conditions or close to them for the majority of the studied local conditions, in the present study. This fact is corroborated in Figure 6.5, where the whole NO formation processes of all the studied conditions are plotted. Despite the differences in speed, it is observed from this plot that by using this criterion the great majority of the tested local conditions are in equilibrium state or close to it.

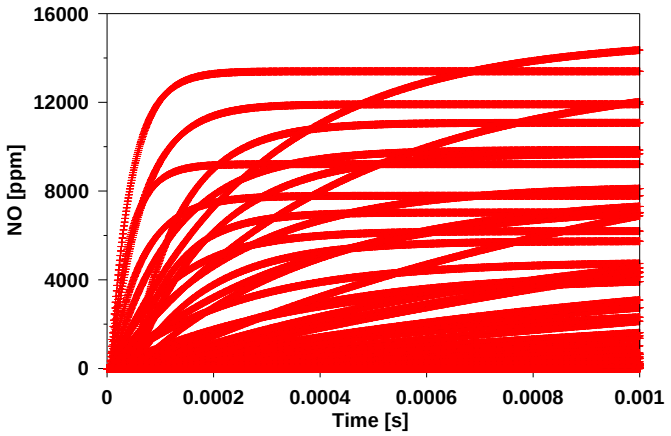


Figure 6.5.- Time evolution of the thermal NO formation mechanism for all the local conditions tested in the present study.

2. Realistic combustion process time scale of a fuel parcel in the NO formation region of a diffusion flame.

The next step was to plot the results obtained. The first figure, (Figure 6.6a) illustrates the differences in prediction between the Thermal and the Total mechanisms for the three cases with different Z_r and T_{end}.

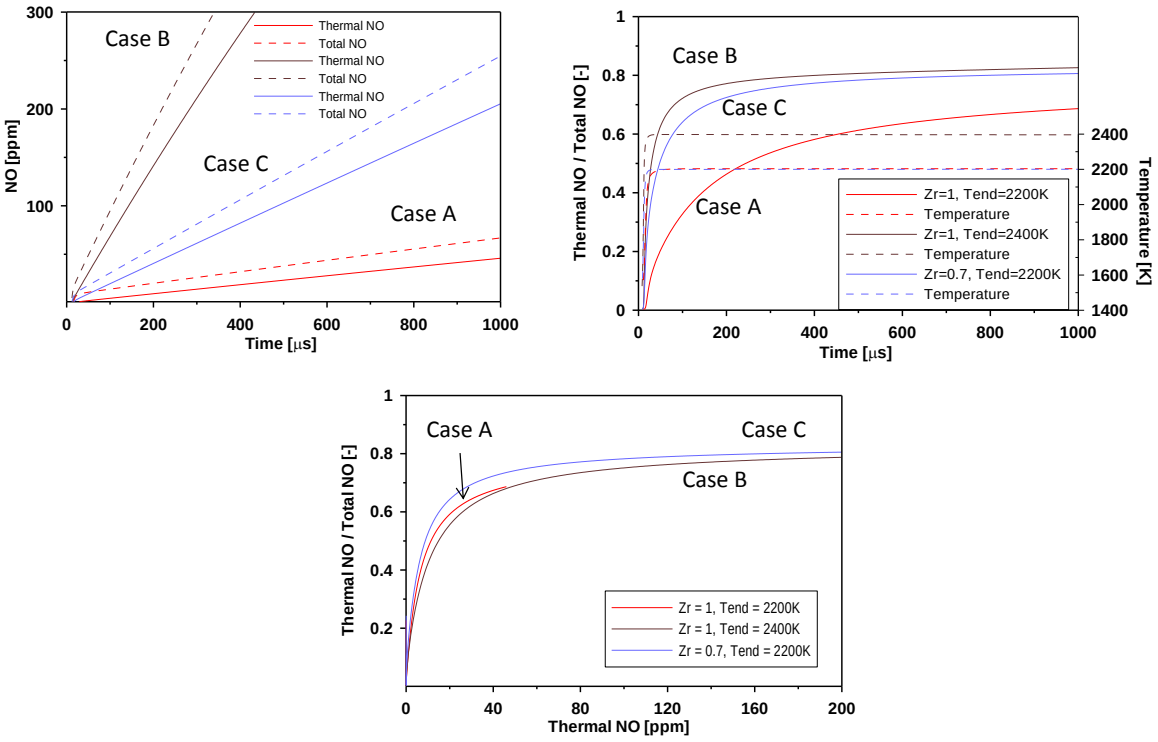


Figure 6.6.- a) Effect of the Zr and Tend on the amount of NO formed, considering Thermal and Total mechanisms. c) Time evolution of the Thermal's contribution degree to the Total NO prediction and temperature evolution. d) Relationship between the thermal NO and thermal NO / Total NO for the three cases.

These were plotted using a continuous and a dashed line, respectively. From this plot several interesting ideas can be extracted. The first one is referred to the time factor, which is very relevant in this process due to the different observed trends between cases. The second one is the T_{end} variable, which seems to be the main parameter affecting the NO formation, even though these conditions are located inside the LTC region.

In order to compare more representatively the different trends observed in the previous figure the NO_{TH}/NO_{TOTAL} was plotted as a function of time and the amount of NO predicted by Thermal mechanism, in Figure 6.6b and Figure 6.6c, respectively.

As it can be observed, the despair trends seen in the previous figure turn into similar behaviors despite the differences in temperature evolution between them. Generally speaking, all three cases start with a low initial Thermal contribution degree and temperature. As the combustion process evolves, both variables increase rapidly, especially temperature, converging to a constant value. Focusing on Cases B and C both have very similar Thermal contribution degree evolution but different temperature evolution.

On the other hand, if the whole transient process (0 - 1ms) is characterized as a function of Thermal NO, see Figure 6.6c, all cases show identical behaviors despite the differences between the temperature evolution of the three cases, as seen previously. Such common trend reflects the existence of a relationship between both variables (thermal NO / Total NO vs thermal NO) that is independent of the considered working conditions, time

variable and temperature evolution. If this relationship is confirmed for the rest of the cases it can be very useful for modeling purposes. Finally, it is worthy to highlight that Case A, red line, finishes much earlier than the others. The reason is due to the working conditions, represented in this case, which aren't convenient for NO formation throughout the Thermal mechanism, and consequently, less than 60ppm of NO is predicted.

6.3.3.- Global Results

The rest of the cases were plotted under the same axes, Figure 6.7, to confirm the relationship between thermal NO prediction and its contribution degree to the Total NO prediction. As expected, when the time variable is discarded, identical behaviors were observed independently of the Zr and T_{end} variables. The parametric study was enlarged by varying T_{ini} from 1400K to 1300K and afterwards to 1200K. In all cases identical trends were observed even though higher Zr have lower thermal contribution due to a minor influence of the prompt mechanism.

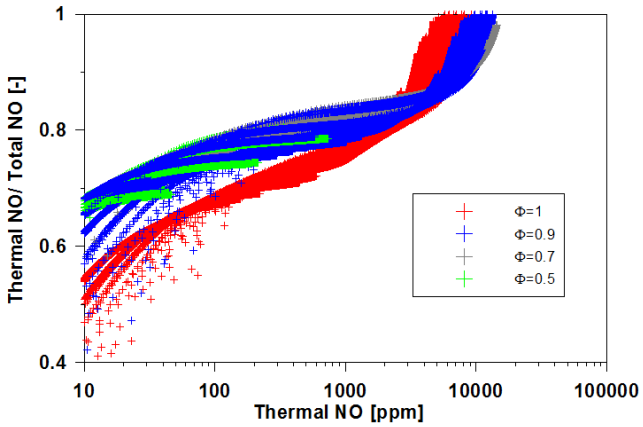


Figure 6.7.-Whole evolution of the thermal's contribution degree for all the studied conditions using n-heptane as diesel fuel surrogate.

Nevertheless, this plot corroborates the existence of such relationship, over a wide range of working conditions, independently of the combustion stage. To relate both variables, a polynomial fit was calculated and drawn, see Figure 6.8. The fit obtained corresponds to a fourth degree polynomial equation with an R^2 of 0.967 and was denoted as **corrective correlation**.

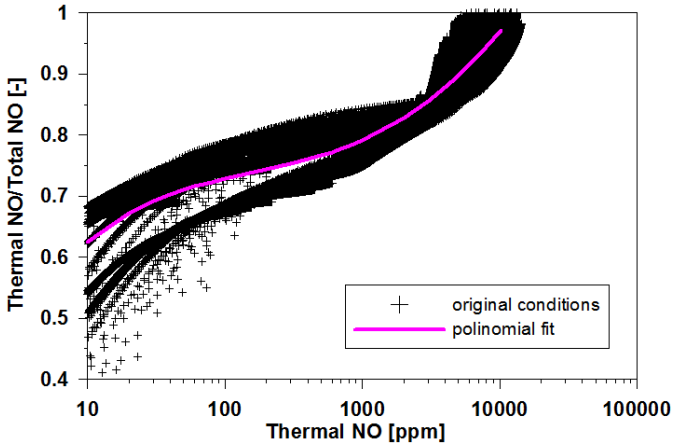


Figure 6.8.-Empirical polinomial fit characterizing the thermal's contribution degree as a function of the amount of NO predicted by the thermal mechanism

$$y = 0.2596 + 0.5840 \cdot log(x) - 0.2688 \cdot \log(x)^2 + 0.0522 \cdot \log(x)^3 - 0.0261 \cdot \log(x)^4$$

(Ec.1)

Where y = $(NO_{TH}/NO_{TOTAL})_{calc}$ and x = NO_{TH} [ppm].

The corrective correlation, (Ec.1), can be used to improve the NO predictions, by just using the Thermal NO formation mechanism, which has a low computational cost and is highly implemented in CFD softwares.

To check the effectiveness of this equation a new variable ($(Total\ NO)_{CORR}$/Total NO) was defined and the corrective correlation was applied throughout the whole evolution of the NO formation process for all the analyzed local conditions, or in other words, at each instant of the NO evolution for every studied condition. This effectiveness was plotted versus the Thermal mechanism's prediction in Figure 6.9.

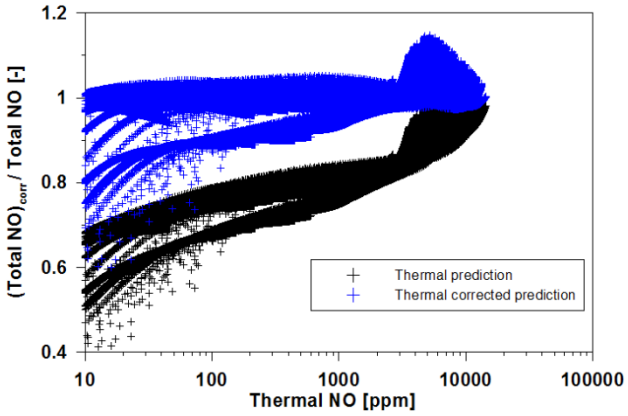


Figure 6.9.- Comparison between the thermal mechanism's predictive capability, before (black) and after (blue) applying the corrective correlation to the whole NO evolution for all studied conditions. The fuel employed was n-heptane.

Generally speaking it can be appreciated from Figure 6.9 a substantial improvement of the predictive capability after applying Ec. 1, as the $((Total\ NO)_{CORR}\ /Total\ NO)$ coefficient is close to unity throughout the whole NO range. This means that applying the corrective correlation to the thermal mechanism's prediction yields similar values as if all three mechanisms were used to predict the NO formation.

Detailed analysis of this plot reveals that for low NO formation conditions (e.g: like LTC conditions) the predictive capability has been substantially improved even though high dispersion is observed. Instead, for intermediate and high NO formation conditions, (> 100ppm), the predictive capability of this methodology is extremely good and presents lower dispersion.

The profound analysis of the results obtained seems to yield a main fact: "the thermal mechanism is related with the Total NO by a law which is applicable to any local condition, described by T_{end}, Z_r, Y_{O2}, and for any instant in the NO formation process independently of the combustion stage". Consequently, this generality improves substantially the predictive capability of the thermal mechanism and can be easily implemented in current CFD and chemical-kinetic softwares to closely predict NO formation with no additional computational cost and seems to be extrapolable to the real NO formation process in a diesel spray where continuously variable conditions are involved.

In order to check the degree of applicability of this promising finding, distinct conditions (purple) to the original ones (black), used to construct Eq.1, were considered: temperature ($T < 1200K$), simulation time ($\tau = 10ms$), pressure ($P = 50bar$), other fuel (methane) and in continuously varying conditions (diesel spray context). In each of these scenarios, with the exception of the temperature and for the diesel spray context, only the low and high threshold values ($Z_r = 1$ and 0.5 and T_{ini} =1200 and 1400K) of the original data were analyzed. In contrast for the temperature case, Z_r was equal 1 and 0.5 for all the new T_{ini} (T_{ini}: 1100, 1000, 900 and 800K) and for the spray scenario two different situations were simulated with EGR ($Y_{O2} = 0.23$) and with massive EGR ($Y_{O2} = 0.1$).

6.3.3.1.- Temperature (T < 1200K):

Four new initial temperatures were selected, while the rest of the variables were maintained the same. As it can be observed from Figure 6.10, there is a clear differentiation between the lean and the stoichiometric mixture. This is a clear symptom of the influence of other NO formation mechanisms on the results. Nevertheless, a substantial improvement is observed in both cases when correcting with Eq. 1 the thermal's contribution. The accuracy degree is between 90% and 110% for the vast majority of the cases. In comparison with the results yield by the original conditions higher over prediction is observed, for Z_r = 0.5, and the high dispersion at low NO formation condition is maintained.

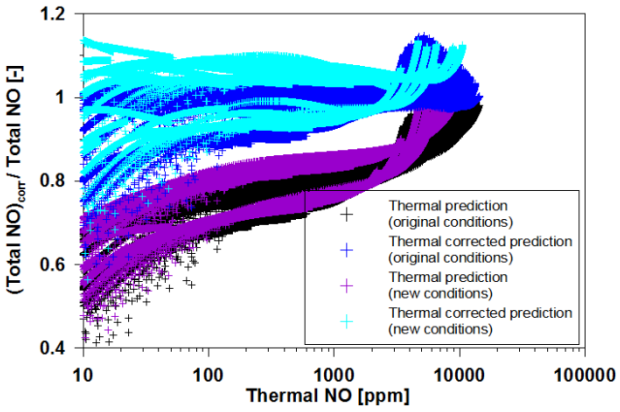


Figure 6.10.- Comparison between the thermal mechanism's predictive capability for the new considered temperatures before (purple) and after (cyan) applying the corrective correlation to the whole NO evolution for all studied conditions. The fuel employed was n-heptane

6.3.3.2.- Simulation time (τ = 10ms):

Now the simulation time was increased in an order of magnitude, up to 10ms. The results plotted in Figure 6.1 reflect a slight reduction in its contribution degree. Focusing on the slowest processes, this can be explained by: 1) increase of the simulation time causes more NO to be formed, shifting slightly to the right the purple curve, 2) the formation rate of both mechanism are despair, as expected on the other hand. Depending on how much combustion process has developed, in each of them, this difference in NO formed can be greater or smaller, affecting the thermal's contribution degree and being more visible in the plot due to its displacement to the mid NO formation region.

Even though there is an increase in the predictive accuracy, after being corrected, it is not as good as in the previous case, between 80% and 120%. The fact of having higher over-prediction in the high NO formation region will be discussed further on.

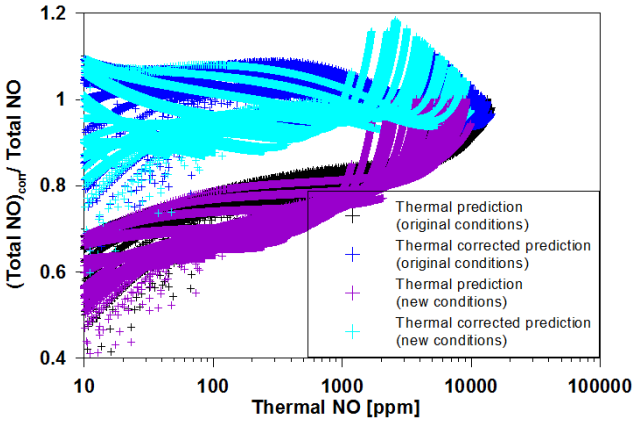


Figure 6.11.- Comparison between the thermal mechanism's predictive capability for the new considered simulation time, before (purple) and after (cyan) applying the corrective correlation to the whole NO evolution for all studied conditions. The fuel employed was n-heptane.

6.3.3.3.- Pressure (P = 50bar):

A substantial lower pressure was tested and as a result lower NO is formed. Despite the fact that an improvement in the accuracy is observed for all the tested conditions, after the thermal contribution is corrected, better results are obtained for leaner than for richer mixtures. Furthermore it can be observed how the difference between them has increased. This is a direct consequence of the influence, in these latter mixtures, of the prompt mechanism, which is more pressure dependent than any other analyzed mechanisms.

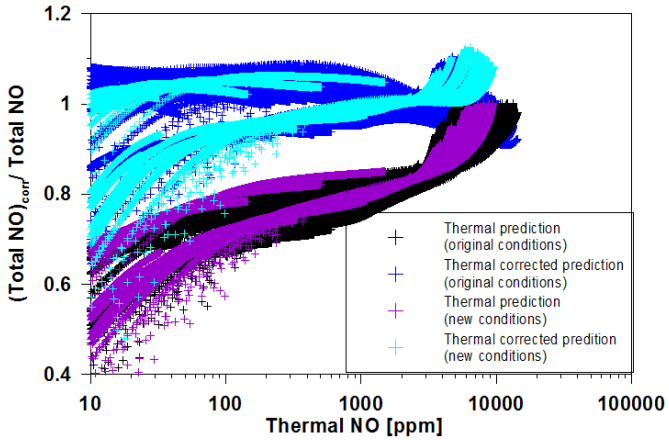


Figure 6.12.- Comparison between the thermal mechanism's predictive capability for a different pressure, before (purple) and after (cyan) applying the corrective correlation to the whole NO evolution for all studied conditions. The fuel employed was n-heptane.

6.3.3.4.- Other fuel (methane)

As it can be appreciated from Figure 6.3, very small differences appear when comparing the thermal mechanism's contribution for both fuels. The slightly lower values for methane can be related with the lower heating value of this fuel. This causes lower combustion temperatures and therefore lower influence of the thermal mechanism. These minor differences are afterwards observed when the corrective correlation is applied.

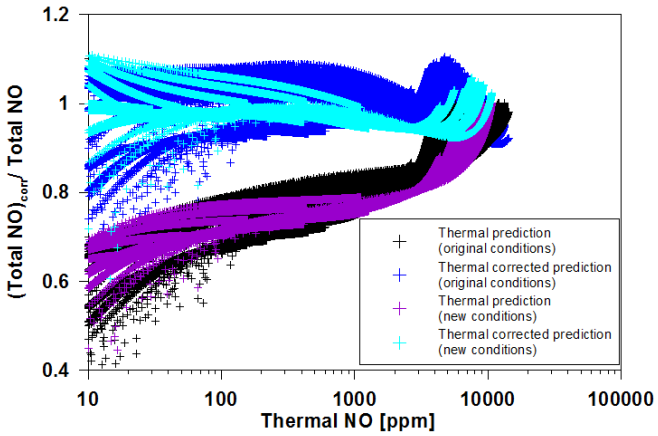
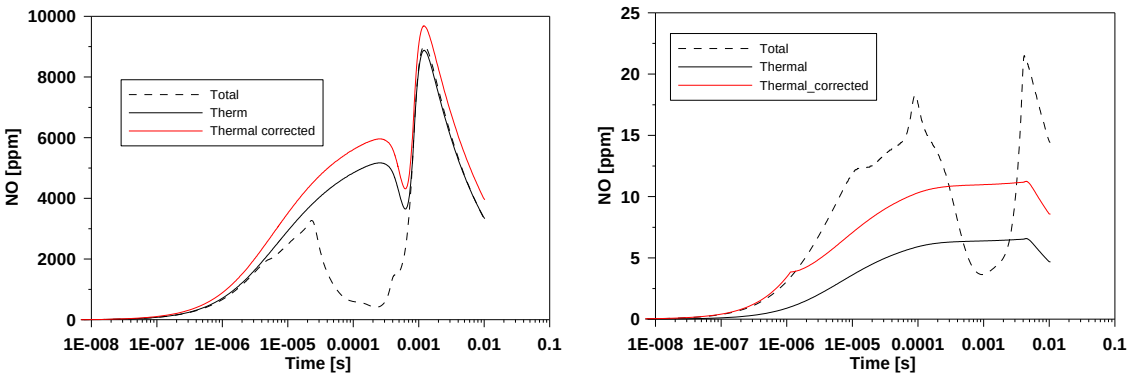


Figure 6.13.- Comparison between the thermal mechanism's predictive capability for the new fuel considered, before (purple) and after (cyan) applying the corrective correlation to the whole NO evolution for all studied conditions. The fuel employed was methane.

6.3.3.5.- Continuously varying conditions (diffusion diesel combustion process):

Finally, this corrective empirical tool was tested in a scenario where variables like temperature, equivalence ratio, composition, etc… are continuously varying along the axial axis. In order to obtain the evolution of NO_{TH} and NO_{TOTAL}, the two-stage Lagrangian model (TSL) [26] was employed. Further information regarding this model can be obtained in the chapter 4.

Afterwards the corrective tool was applied using a straightforward procedure and the results where plotted in Figure 6.4a and Figure 6.4b. The plot for Y_{O2} = 0.23 illustrates an over-prediction in the region of interest (near flame front and in the post-combustion region).



a) ***b)***

Figure 6.14.- Comparison between the Total NO prediction (dotted line) with the thermal NO prediction (solid black line) and the thermal corrected curve (red solid line) for non-EGR and for massive EGR conditions using n-heptane as diesel fuel surrogate.

In this case no corrective action is suggested. Meanwhile for the situation where massive EGR is being employed the results are very poor. Clearly this corrective tool is not applicable when massive EGR is being employed under continuously varying conditions.

Recompiling all of the previous results, it is worth noting two common trends: 1) the corrective correlation clearly improves the thermal's prediction even though in despair manners and 2) the over-prediction typical of the very low and high NO formation regions which are found in all the plots, independently of the conditions considered (even in the ones used to build the polynomial fit). These effects are a consequence of this fit which doesn't take into account the completeness degree of the NO formation process. In other words, the polynomial fit will yield the same result for a given value of thermal NO independently of how close or how far it is from equilibrium conditions (i.e: it is not the same to have 20ppm of thermal NO for a process where 200ppm are expected to be formed when equilibrium is reached than 25ppm).

Additionally, if comparing the last scenario, described in section 6.3.3.5, with the others it can be noted that in the diesel spray context there are no differences between the thermal and the total NO predictions while in the others there is a significant difference. Extrapolating these findings to different combustion modes, these results seem to suggest that when predicting NO formation in diffusion diesel combustion process, just considering the thermal mechanism is as good as taking into account all the formation routes coupled together. On the opposite side, when predicting NO emissions in premixed auto-ignition combustion processes the choice of the formation mechanism is a relevant to increase the accuracy degree of the predictions.

6.4 Conclusions

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

a. The results obtained in the preliminary study are in good agreement with the well documented results in the scientific literature. At high temperature, typical of CDC combustions, the thermal mechanism is the predominant independently of the relative equivalence ratio. However, for lower temperatures, typical of LTC combustion scenarios ($Y_{O2} \leq 12.7\%$), this mechanism reduces its contribution due this reduction in combustion temperature even though it continues to be predominant. In the case of N_2O it is observed how its influence increases as the fuel-air mixture becomes leaner. However, no relevant studies are available in the scientific literature to compare the results obtained in the present study. This is the reason of being of the present study especially when new combustion modes, characterized by LTC conditions, are being developed as a consequence of the stringent emission standards worldwide.
b. Only considering the thermal mechanism to predict NO formation in the new combustion modes characterized by low temperatures combustions or even by leaner mixtures is not appropriate for accurate simulations. The coupling of this mechanism with others, like Prompt and N_2O intermediate, increases the accuracy of the NO prediction but also the computational cost.
c. The relationship obtained between thermal NO prediction and thermal NO/Total NO ratio, under very simplified conditions, yields a law which seems to be applicable to any local condition, described by T_{end}, Z_r, Y_{O2}, and for any instant in the NO formation process independently of the combustion stage.
d. However when considering distinct conditions to the ones employed to build the equation, and even though this law clearly improves the predictive accuracy in all the regions (low, mid an high NO formation) the results reflect high dispersion and high sensitivity to changes.
e. The main drawback of this tool is that it doesn't consider the completeness degree of the NO formation process. In other words, for a given thermal NO value, this fit will yield the same results independently of how far or how close it is from the equilibrium conditions. As expected, the closer the NO formation stage is to equilibrium conditions, the minor the difference between thermal NO and Total NO and therefore lower corrective degree is required than when considering early stages of the formation process.

6.5 Summary

Over the past two decades, the amount of exhaust gas pollutant emissions has been significantly reduced due to the severe emission legislation imposed in most of the countries worldwide. Initial strategies just required the employment of simple after-treatment and engine control devices, however, as the restrictions become more stringent these strategies

are evolving in the development of different combustion modes, specially characterized by having low temperature combustion characteristics (LTC).

These new working conditions demand the need to check the suitability of the current NO predictive models which coexist nowadays under conventional diesel combustion characteristics (CDC), paying closer attention to the thermal mechanism. In order to do so, a common chemical-kinetic software was employed to simulate, for n-heptane and methane fuels, fixed local conditions (CDC and LTC) described by: constant pressure, relative mixture fraction, oxygen mass fraction and initial and final reaction temperature.

The study reflects a common trend between all the studied cases, independently of the considered local conditions, making it applicable to more complex situations like real NO formation process in diesel sprays. This relationship was characterized by a 4^{th} degree polynomial equation capable of substantially improving the NO prediction by just using the thermal NO predictive model.

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Chapter 7

New 0-D Methodology for Predicting NO Formation under continuously varying temperature and mixture composition conditions

Content

7.1 Introduction

The development of new diesel combustion modes characterized by low combustion temperatures, to minimize the NO_x emissions, has caused to diminish the relevancy of the thermal mechanism with respect to the total NO_x formation. This is mainly due to the low combustion temperatures and the leaner fuel-oxidizer mixtures in combustion processes and in diesel sprays as a consequence of changes in its structure.

As expected, a substantial reduction in the combustion temperature will undoubtedly cause a reduction of NO_x due to the thermal route. This fact was analyzed by Desantes et al. [1] for conventional diesel combustion (CDC) and low temperature combustion (LTC) conditions. These latter conditions were defined assuming a similar criteria to the one used by Musculus [2], i.e. adiabatic combustion temperature lower than 2200K. In this work the authors corroborated that the thermal mechanism reduces its relevancy to a 40%-60%, independently of the fuel (n-heptane or methane) and the relative equivalence ratio considered ($0.5 < \Phi < 1$).

Besides the effect that leaner mixtures have on the thermal route, by lowering the combustion temperature, it also modifies the chemistry of the NO formation process and therefore other pathways like the N_2O intermediate [3-5] can become relevant in the premixed auto-ignition diesel combustion (i.e: HCCI diesel combustion) and in the diffusion diesel combustion (i.e: diesel spray) scenarios. Combustion of leaner mixtures are employed, in LTC conditions, to achieve low combustion temperatures with little exhaust gas recirculation (EGR) and therefore mitigate the important drawbacks associated with the employment of massive EGR. These conditions cause the N_2O pathway to gain in importance as several authors have already demonstrated (Ammneus [6], Kung [7]). In the case of diesel sprays, Musculus [2] observed that the NO_x were formed inside the fuel spray where the variation of local conditions reflect a leaner mixture ($0.5 < Z_r < 1.5$) in comparison with CDC conditions summarized in Dec's model [8]. This fact corroborates that the N_2O route gains relevancy, under these conditions, but also the need of taking into account the prompt mechanism [3, 5, 10-11], which is relevant when $Z_r > 1$.

Independently of the scenario being analyzed, it seems clear the need to take into consideration not only the physical phenomena behind these processes but also all the pathways involved in the NO_x chemistry in order to accurately predict the emissions of this pollutant and especially when the threshold value is so low and still continues to be reduced.

This asseveration is undoubtedly associated with a substantial increase in the computational costs of the corresponding simulations. Some authors [12-23] have focused on reducing it by creating new computational tools based on: constrain equilibrium [13-15], partial-equilibrium assumptions [16][12], computational singular perturbation [17] and tabulated chemistry [18-23]. Multiple procedures have been developed relaying on this latter concept. Initially, Pope [18] developed the in-situ adaptive tabulation methodology (ISAT) which was the first attempt to tabulate the chemistry. It consisted in characterizing the thermochemical state of a mixture, at any time and point, by the mass fraction of a number of species, the enthalpy and the pressure variables. However, this methodology derived to the intake low dimension manifold procedure (ILDM) [19] which simplified the reduction of the

chemical schemes and therefore the generation of look-up tables. However its main inconvenience is the low accuracy at low temperatures, where higher manifold are required. To solve this inconvenience, the flame propagation of ILDM approach (FPI) [20]-[21] was developed as well as the flamelet generated manifold (FGM) [22-23]. Even though these latter ones are used nowadays, the great inconvenience of all these tools is considering assumptions of uncertain generality and accuracy, the tedious task of determining the key species and parameters to describe the mixture thermodynamically, the construction of the tables where the different species' concentrations are summarized and which require huge memory resources, and the degree of knowledge required to understand the fundamentals on which these computational tools are sustained on.

Another way to reduce computational cost focuses on simplifying the physics involved in the process and concentrate in the chemistry aspect by employing complete mechanisms, including high number of species and reactions. Commonly, this is achieved mainly by reducing the number of dimensions to be considered, e.g: 1-D and 0-D models. Regarding the 0-D models, the most extended approaches are related to: single-zone homogeneous in-cylinder conditions [24], two-zone [25] and multi-zone combustion models [26]. As Zheng pointed out in [27] even though the single zone cannot be used to obtain results referred to spatial distribution they are more efficient in capturing the detailed chemical kinetics and the basic thermodynamic events. This fact is corroborated by the extensive use of this approach in several research studies ([27-31]) to analyze how the combustion and the pollutant emissions formation processes are affected by different operating conditions, characterized by: pressure, intake temperature, exhaust gas recirculation rate and fuel chemistry.

In this context, the author believes that there is undoubtedly a great potential in the combination of tabulated chemistry with the usage of 0-D models to perform fast and accurate parametric studies for theoretical research in the combustion field. In order to reduce the drawbacks associated with the tabulated chemistry the author will just concentrate on NO and instead of tabulating the concentration or composition they will focus on the reaction rate.

7.2 Objectives and General Methodology

7.2.1.- Objectives

The scope of this study is to develop a new methodology, based on the coupling of tabulated chemistry with 0-D models, capable of accurately predicting the NO formation trends under **continuously varying conditions of temperature (T)** (like in homogeneous premixed combustion process) **or of temperature and relative mixture fraction** (Z_r) (like in heterogeneous diffusion diesel spray), like in combustion processes and real diesel sprays respectively. Moreover, this tool should be able to run independently of any specialized commercial chemical kinetic software and without the need of advanced modeling knowledge.

7.2.2.- General methodology

To achieve the established objective a three-stage procedure was employed in which the Chemkin Pro software [32] was used to construct the proposed methodology (first stage) and to check its effectiveness in predicting the NO formation due to a combustion process (second stage). The third and final stage consisted in checking the effectiveness of the methodology in diesel sprays. In this case the two-stage Lagrangian model (TSL) [33] and the apparent combustion time model (ACT) [34] were employed.

This methodology was developed using n-heptane as the diesel fuel surrogate and the chemical kinetic mechanism resulting from the coupling of the Seizer et al. mechanism [35] and the NO_x sub-mechanism included in the GRI-Mech 3.0 [36]. It consists of 181 species and 1583 reactions and will be denoted as RES_{TOTAL}-mechanism, following the nomenclature used in Chapter 4.

The fuel surrogate chosen was n-heptane due to its similar cetane number with typical European diesel fuel and its popularity in simplified modeling of diesel combustions [37]. The use of this single component fuel surrogate can have a priori the drawback of discarding the process of NO formation by fuel contribution, due to the lack of nitrogen and aromatics content, in n-heptane. Nevertheless, as described in Chapter 4, the effects of these species will be negligible and therefore the employment of neat n-heptane is fully justified.

7.3 Detailed description of the proposed methodology

In the next section the developed methodology will be explained in detail focusing on the theoretical principles and hypothesis considered, as well as on how it works.

7.3.1.- Theoretical principles

In the following lines a brief review of how some key variables (temperature, relative mixture fraction, time, EGR rate and pressure) influence the NO prediction will be performed focusing on a stationary diesel spray, even though, it would be also extensible to other combustion scenarios, like: homogeneous charge compression ignition (HCCI). In this latter context the variation along the axis will have to be replaced by a temporal evolution.

- Temperature (T): Parameter which varies, along the axial coordinate, from the fuel's temperature to the combustion's temperature, reached at the flame front region, and then decreases. This is due to a sequence of processes such as: premixed combustion, mixing phenomena with combustion products formed in the flame front region, diffusion combustion and dilution of the combustion products by remaining fresh oxidizer. The temperature reached at the flame front will undoubtedly determine the formation of this pollutant in the region where most NO is expected to be formed.
- Relative mixture fraction (Z_r): Variable which describes the fuel-air ratio in a particular mixture and key factor to the NO chemistry. It diminishes along the

axial coordinate, distinguishing three main regions; fuel-rich (Z_r > 1), stoichiometric (Z_r = 1) and fuel-lean conditions (Z_r < 1). In each of these regions a different NO formation route is predominant.

- Time (t): The time variable strongly influences the NO chemistry as a consequence of the time dependence of the two previous key parameters. Moreover, the proper initial working conditions influence the time evolution of these parameters.
- Exhaust gas recirculation rate (EGR rate): This variable influences indirectly the NO chemistry by reducing the combustion temperature as a consequence of diluting the oxidizer stream with combustion products which are less reactive. Therefore it determines the initial oxygen mass fraction (Y_{O2ini}) available to react. This last characteristic will be used to define the EGR rate of the different cases presented along the whole research study.
- Pressure (P): This variable has a minor impact on the NO chemistry and it can be considered to remain constant throughout the whole diesel spray. In the case of combustion scenario, the pressure varies due to the compression, combustion and expansion effects. However, lots of simulations consider it constant in order to study the chemical processes, like in the present thesis.

All this information is schematically summarized in Figure 7.1, using a generic diesel spray structure. Note that instead of representing Z_r, which is dependent of the oxygen and the fuel content, the author have decided to plot Y_{O2} and Y_f, which are two more intuitive parameters, to illustrate how these reactants vary throughout the diesel spray structure.

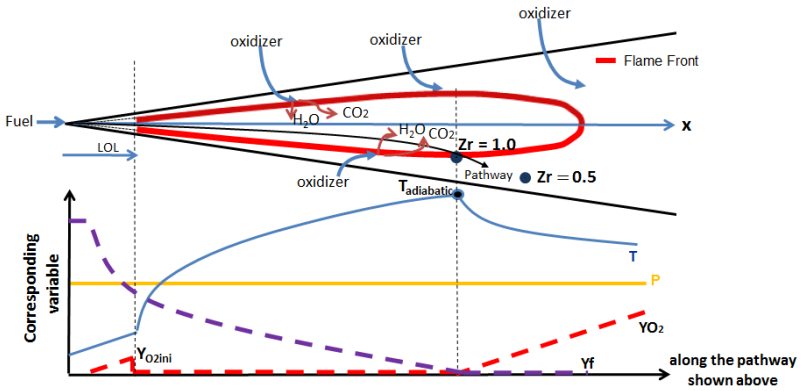


Figure 7.1.-Schematic representation of the evolution of key parameters, like: temperature, fuel and oxygen mass fraction and pressure, along the axial axis of a generic diesel spray.

From the previous review it is plausible that Zr and EGR rate are both closely related to the oxidizer stream, specially with the oxygen content. Therefore several authors, like Peters [38] and Payri [39], in an attempt to agglutinate both variables in one, have come up with a mathematical expression, like the following:

$$Y_{O2exc} = Y_{O2ini} * (1-Z_r) \quad \text{(Eq.1)}$$

where Y_{O2exc} is the oxygen excess mass fraction, Y_{O2ini} quantifies the content of oxygen available initially in the combustion chamber and Zr describes the fuel-air relative mixture fraction.

This definition is going to be employed in the present study because it reduces the degrees of freedom related to the characterization of diesel sprays and combustion processes. To confirm that this variable really achieves the desired role, a parametric study (varying Z_r between 0.2 and 1) was performed for two different EGR rates (Y_{O2ini}: 0.23 and 0.1). In order to discard the effect of the initial conditions on the temporal evolution of NO, equilibrium state was considered for two given temperatures, 1500K and 2500K. These temperatures were selected to analyze the behavior of Y_{O2exc} under two premises:

- Close to typical combustion temperatures in different combustion modes, like: low temperature combustion (LTC), 1800K ≤ T ≤ 2200K, and conventional diesel combustion (CDC), T > 2200K.
- With the temperature range previously described, the thermal mechanism can mask the "real" behavior of the tested variable due to the strong temperature dependency. Consequently, the 1500K temperature value was chosen to mitigate this effect while respecting the first premise.

The results obtained from the EQUIL module of Chemkin Pro were plotted in Figure 7.2a and Figure 7.2b. These illustrate that identical NO_{eq} values are achieved, at a given $Y_{O2exc,}$ for both cases and therefore corroborating that this parameter can be used to relate Zr and EGR rate (Y_{O2ini}) with a single variable.

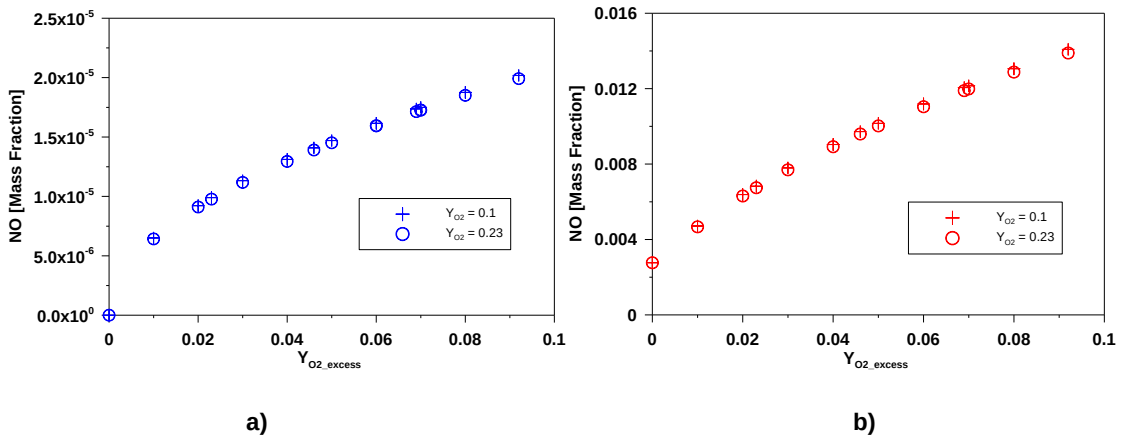
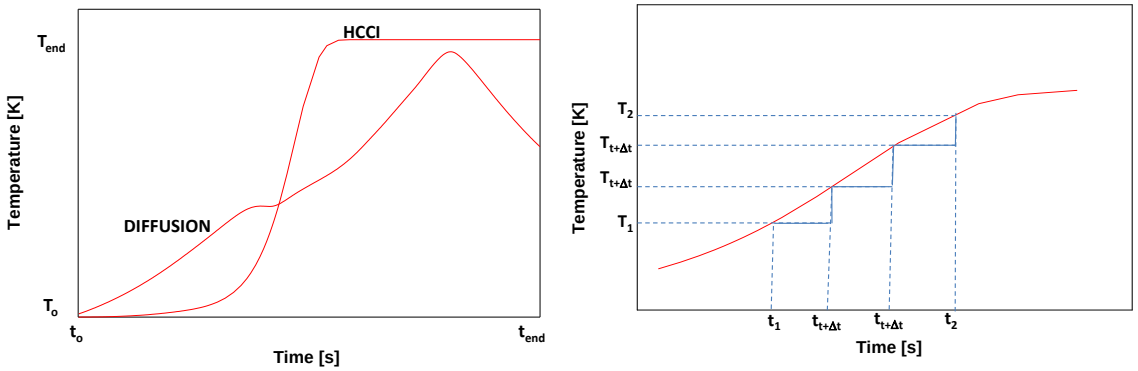


Figure 7.2.- Comparison of the NO values for a given excess oxygen mass fraction determined by different relative equivalence ratios and initial oxygen mass fraction (used to characterize the EGR rate), at equilibrium conditions and for two temperatures, a) 1500K and b) 2500K.

7.3.2.- Description of the hypothesis and the methodology's development procedure

After reviewing the key variables related to the NO formation process, the author realized that T and Y_{O2exc} where the predominant parameters and to a lesser extent P. Therefore the following hypothesis was considered: **the NO evolution, for a giving initial condition, can be determined with just the temporal evolution of temperature, pressure and Y_{O2exc} variables. This evolution can be reproduced by the concatenation of a finite number of infinitesimally small processes at constant T, Y_{O2exc} and P, indistinctively of considering the premixed auto-ignition diesel combustion or the diffusion diesel combustion scenario**. This idea is summarized in Figure 7.3a and 7.3b.



a) *b)*

Figure 7.3.- a) Typical temperature time evolution of two different combustion processes, b) zoom of a region of any of the two previous temperature evolutions to illustrate the hypothesis used to develop the proposed methodology.

Non-steady state simulations using the closed perfectly stirred reactor module from Chemkin Pro were performed to obtain the temporal evolution of NO (NO(t)) at constant T, Y_{O2exc} and P conditions. The considered simulation time was of 1s to guarantee an effective future characterization of all the studied conditions, including the slowest ones. Additionally, in an attempt of minimizing the number of simulations required, only the non-EGR scenario was taken into account. It is easily demonstrable, using equation 1, that by doing so all the other EGR rates are also being indirectly considered.

Afterwards, to make comparable all the studied conditions, a normalization process was encountered in which NO(t) was normalized by the corresponding NO equilibrium composition (NO_{eq}). These equilibrium values were stored in a look-up table as a function of T, Y_{O2exc} and P. Finally the resulting evolution was characterized by an exponential fit equation similar to those applicable to chemical reactions which behave as a pseudo first order reversible reaction (Eq.2), see Figure 7.4. In Appendix A a demonstration of how this equation describes this evolution is presented.

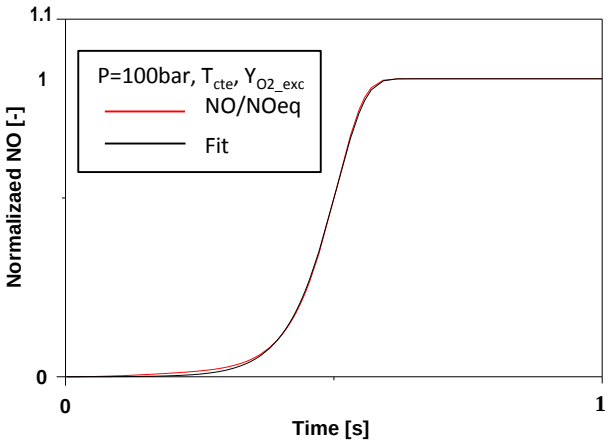


Figure 7.4.- Temporal evolution of normalized NO and its fit for a given temperature, pressure and oxygen excess mass fraction.

$$\frac{NO}{NO_{eq}} = 1 - \exp(-k * t) \qquad \textit{(Eq. 2)}$$

where NO is the amount of this pollutant predicted at a certain time, NO_{eq} is the amount of NO formed in equilibrium state for the corresponding working conditions, k is a constant value which characterizes the NO/NO_{eq} evolution and t is the elapsed time. The k value will be tabulated in a second look-up table function of T, Y_{O2exc} and P.

The great advantage of this fit mainly relies in three factors:

- Has its scientific rigourosity supported by the theoretical principles of the chemical kinetic science [40].
- The whole normalized temporal evolution is described by just one variable, k, which can be stored in a look-up table as a function of T and Y_{O2exc} (Figure 7.4).
- The equation in its differential form (Eq. 3), employed to concatenate the sequential processes, is simple and requires low computational cost. In Appendix B, the mathematical demonstration of how equation 3 is achieved from its predecesor, equation 2, is summarized.

$$\mathbf{NO_t} = \mathbf{NO_{t-1}} + \mathbf{k} * \left(\mathbf{NO_{eq}} - \mathbf{NO_{t-1}}\right) * (t_t - \mathbf{t_{t-1}}) \quad \textbf{(Eq. 3)}$$

Where NO_t is the NO calculated at each considered time (t), NO_{t-1} is the calculated amount of NO in the previous time step and k is the empirical exponential fit constant. The NO composition at equilibrium conditions for a

given T, P and Z_r is denoted as NO_{eq} and (t_t-t_{t-1}) is the considered time step, which can be constant or variable.

The resulting look-up tables from the described procedure are represented in figures, Figure 7.5a and Figure 7.5b for a given pressure. The first plot corresponds to the NO_{eq} values and it seems to be in contradiction with the well extended observation that they increase with the relative equivalence ratio, up to 0.8 approximately, and then diminish as the relative equivalence ratio continues to rise [41]. These discrepancies are due to the fact that in the present study the calculations were performed assuming constant pressure and temperature conditions (because of the reasons discussed above) instead of constant pressure and enthalpy (which is the most reasonable assumption generally speaking). In the first of scenario (constant P and T) the oxygen and nitrogen concentrations are determinant and therefore: the leaner the mixture, with respect to fuel, the greater the amount of NO formed. However, in the second (constant P and H), the predominant variable is the mixture fraction which strongly influences the equilibrium temperature. As Z_r increases, up to 0.8 approximately, the equilibrium temperature increases and so does the amount of NO formed. Nevertheless, from 0.8 to 1, the equilibrium temperature continues to rise but the NO slowly diminishes because of the decrease in oxygen availability.

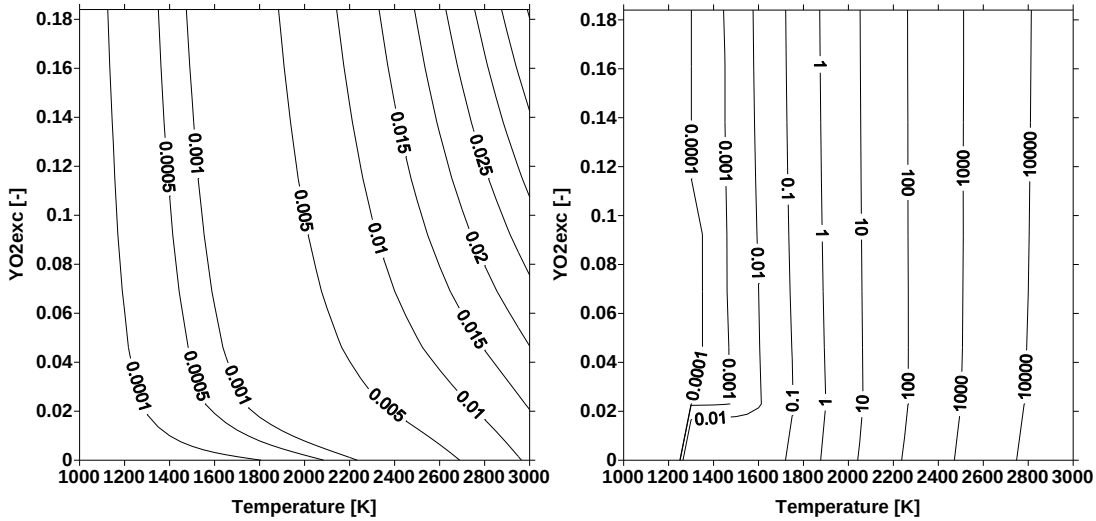


Figure 7.5.- Results yield from the constant temperature characterization process of NO formation over the considered operational range for n-heptane as diesel fuel surrogate and at 10MPa; a) NO equilibrium composition, b) the k values characterizing the normalize NO formation rate.

The results summarized in Figure 7.5b are coherent with the chemical kinetic principles (higher temperatures cause an increase in reaction rates leading to higher k values) and with the chemistry ruling the NO formation process. At high temperatures (T > 1800K) the thermal mechanism, strongly dependent on this parameter, is the predominant formation route. This explains the vertical iso-k lines in this region. As the temperature decreases (T < 1800K) so

does its contribution in favor of the prompt and the N_2O pathways. This explains the slight curvature of the iso-k lines and the observed distortions for $Y_{O2exc} < 0.05$.

Finally, the predicted NO formation trend will be determine by applying equation 3 which is dependent on these two constants.

7.3.3.- Implementation of the developed methodology

With the k and the NO_{eq} tables generated and in coherence with the theoretical principles ruling the NO chemistry, the methodology can be implemented and checked.

Initially, the Chemkin software [32] and the TSL model [33] were used as reference tools, in the combustion and the diesel spray context, to obtain: T(t), $Y_{O2exc}(t)$ and the NO time-evolution (NO_{REF} (t)) for a given initial working condition, described by P, Y_{O2ini} and T, respectively.

The information provided by these tools will be the input variables to determine the k and the NO_{eq} values from the look-up tables. Substituting these values into equation 3 and knowing the time step, given also by the reference tools, the predicted NO trend (NO_{MET}) is obtained. In this case, the index "MET" stands for present methodology, or in other words, the methodology proposed in the present chapter. This trend will be compared with NO_{REF} to check the accuracy of the proposed methodology.

7.4 Results

In this section the predictive capability of the proposed methodology will be presented and analyzed by comparing it with NO_{REF} under continuously varying temperature conditions (e.g: homogeneous premixed auto-ignition diesel combustion process, as described later) and in a continuously varying temperature and relative mixture fraction conditions (e.g: diffusion diesel spray scenario). In both scenarios non-EGR and EGR cases will be studied.

7.4.1.- Continuously varying temperature conditions

A constant pressure homogeneous combustion process was simulated with Chemkin and defined by the following initial working conditions presented in Table 7.1, as a representation of CDC and LTC conditions. Special attention was paid to the time interval between 1ms and 10ms, which is in accordance with the time scale of LTC and CDC combustion processes in current internal combustion diesel engines.

Zr	T_{ini} [K]	Y_{O2ini}	T_{end} [K]
0.9	1000	0.23	2786
0.7	1000	0.23	2430
0.9	1000	0.1	1900

Table 7.1.- Summary of the working conditions used to check the accuracy of the predictive methodology under continuously varying temperature conditions.

In Figure 7.6a and Figure 7.6b, it can be observed, for the three studied cases, the temperature evolution (T(t)) and the NO trend (NO_{REF}) as well as the predicted evolution yield by the proposed methodology (NO_{MET}). The plots reflect a reasonable accuracy for all cases even when equilibrium conditions haven't been reached. Nevertheless, it is worthy to note that in the non-EGR cases the methodology over-predicts the NO formation, while in the massive EGR case there is under-prediction, specially at the beginning.

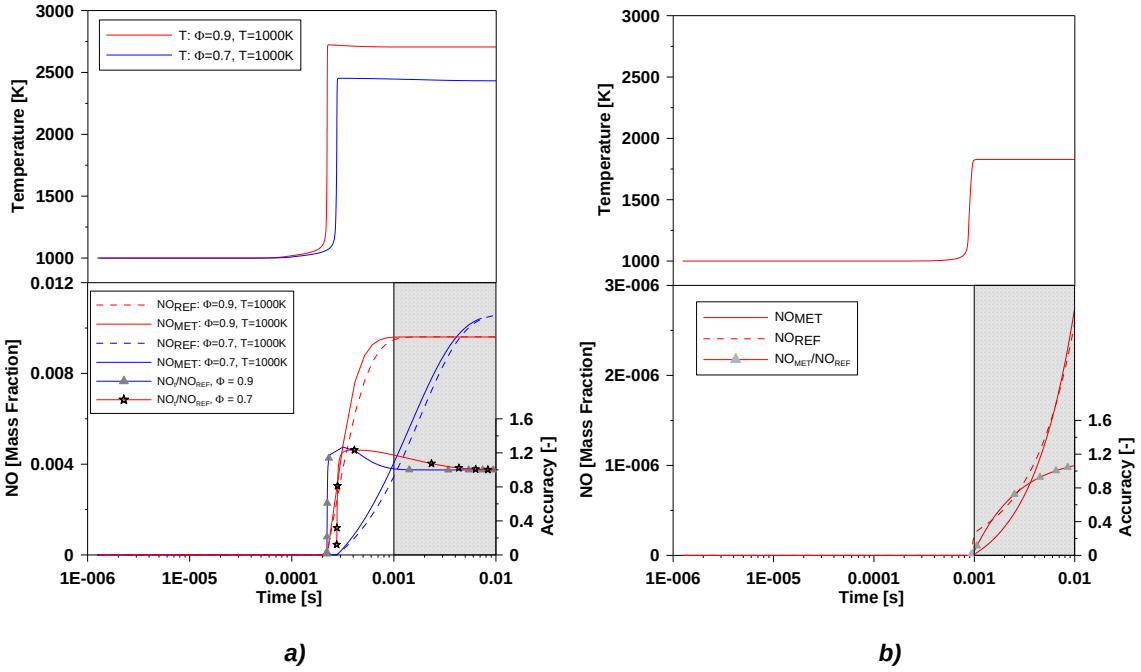


Figure 7.6.- Comparison between the NO predicted by the proposed methodology (NO_{MET}) and from Chemkin Pro by solving the energy equation and considering the whole NO_x sub-mechanism (NO_{REF}), for: a) Φ=0.7 and 0.9, Y_{O2ini}=0.23 at T_{ini}=1000K and b) Φ=0.9 and Y_{O2ini}=0.1 at T_{ini} =1000K, with n-heptane at 10MPa of pressure. The shaded area corresponds to the NO formation process time scale in current internal combustion diesel engines.

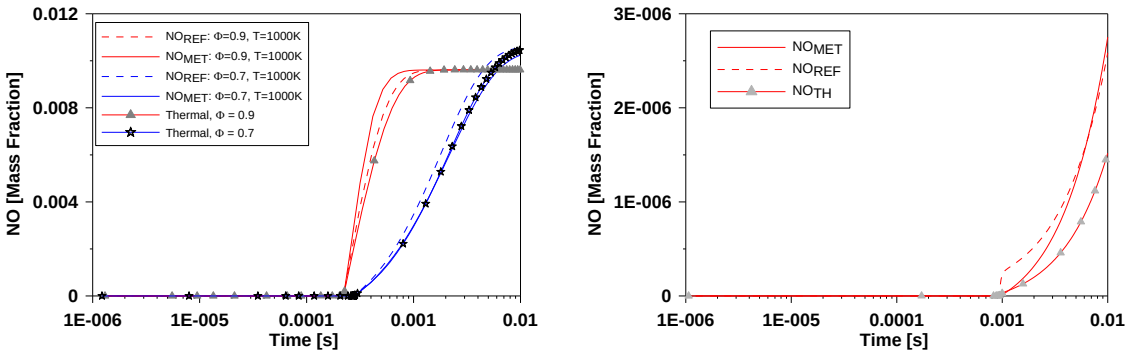
These two observations can be consequence of:

- The k-values, characterizing the speed in which the NO/NOeq process evolves at a given temperature, are characterized by assuming a fresh fuel-oxidizer mixture. Therefore this methodology doesn't take into consideration the loss of reactivity, between time steps, due to the presence of intermediates and combustion products. This is specially relevant for high speed processes.
- The temporal evolution of the NO process, at low temperatures and at very early stages of the process ($t < 1 \cdot 10^{-6}$s), has a poor exponential behavior due to: an initial minor NO formation process, which is not negligible, prior to the major production stage. Consequently, this will undoubtedly reduce the prediction accuracy.

A way to resolve this latter drawback could be to characterize the minor and the major NO formation processes independently. However, the author believes that there is no need for

this tedious work because the time scales ($t \approx 1 \cdot 10^{-8}$s), in which this minor formation occurs, is negligible for engine purposes.

Finally, due to the fact that the previous results reflect certain inaccuracy at some stages of the combustion process, the author decided to compare the NO_{MET} results against the predictions yield by just considering the Thermal mechanism (NO_{TH}), which is extensively used, in order to account for any improvement in predictive capability (see Figure 7.7a and Figure 7.7b). For Z_r close to the stoichiometric value, in the non-EGR case (Figure 7.7a), both procedures have a similar accuracy degree even though the thermal prediction is slightly better. However, as Z_r diminishes, the predictive capability of the proposed methodology is substantially better. This is in accordance with the fact that the thermal contribution to the total NO formation process decreases as the mixture becomes leaner in fuel content. For the massive EGR case (see Figure 7.7b), where low combustion temperatures are reached, the developed methodology is substantially more accurate than just considering the thermal route.



a) ***b)***

Figure 7.7.- Comparison between the NO predicted by just considering the thermal route (NO_{TH}), the proposed methodology (NO_{MET}) and from Chemkin Pro by solving the energy equation and considering the whole NO_x sub-mechanism (NO_{REF}), for: a) Φ=0.7 and 0.9, Y_{O2ini}=0.23 at T=1000K and b) Φ=0.9 and Y_{O2ini}=0.1 at T=1000K, with n-heptane at 10MPa of pressure. The shaded area corresponds to the NO formation process time scale in current internal combustion diesel engines.

These results show that the proposed methodology is a tool worth to be consider, under this homogeneous premixed auto-ignition diesel combustion, when performing qualitative predictions and studying the NO formation trends for non-EGR and EGR cases (even when assuming massive dilution, Y_{O2ini} = 0.1). As expected, in the latter scenario, this tool is much more accurate than the predictions yield by the thermal route and quicker than considering all the relevant NO formation routes in commercial chemical-kinetic softwares. Furthermore it also corroborates some of the findings of chapter 6 which illustrated that in premixed auto-ignition combustion processes there are substantial differences between predicting with the thermal or considering all the formation routes coupled together. This enhances the reason of being of a methodology like the one proposed which takes into consideration all the formation routes without increasing the computational cost.

7.4.2.- Continuously varying temperature and mixture's composition conditions

To check the accuracy of the proposed methodology under these continuously varying conditions, the TSL model was used to simulate the behavior of a diffusion diesel spray with the baseline conditions listed in Table 7.2 [42][41]. Under this scenario two cases were selected, non-EGR (Y_{O2ini} = 0.23) and massive EGR rate (Y_{O2ini} = 0.1), summarized in Table 7.3. Additionally, validation studies were performed with real engine-out NO_x emissions obtained for a wide range of operational conditions, covering LTC and CDC combustions, running the engine under diffusion diesel combustion characteristics (see Table 7.4 for more details regarding the engine's characteristics). Further details of the validation process will be presented in the corresponding sections.

Parameter	**Value**
Pressure [MPa]	10
Fuel	n-heptane
Nozzle orifice diameter [μm]	100
Injection velocity [m/s]	630
Fuel density [kg/m^3]	613

Table 7.2.- Summary of the baseline conditions considered in the TSL model.

Cases	**T_{oxi} [K]**	**T_{fuel} [K]**	**P [Mpa]**	**Y_{O2ini} [-]**
Case non-EGR	1000	300	10	0.23
Case EGR	1000	300	10	0.1

Table 7.3.- Summary of the considered conditions for the two studied cases.

Engine's Characteristic	**Values**
Stroke [m]	0.15
Bore [m]	0.12
Compression ratio [-]	14.26
Connecting rod length [m]	0.225
Inyector	**Values**
Num. Orifice	8
Diam. Orifice [mm]	0.1
Angle between sprays [º]	140

Table 7.4.- Summary of the engine's and the inyector's geometric specifications used for the two studied cases.

In Figure 7.8a and 7.8b the temporal evolution of T and Z_r (top row) are plotted as well as the NO_{REF} (bottom row) for both cases. Furthermore the stoichiometric condition (Z_r = 1),

typical of the flame front region, is depicted by a discontinuous line limiting the fuel-rich (left hand side) and the fuel-lean regions (right hand side).

These results agree with the theoretical principles ruling diesel sprays, under CDC [[8] and LTC conditions [2], and the Z_r value was used to calculate the corresponding Y_{O2exc}. It is worthy to highlight that the decrease in the amount of NO is due to dilution effects caused by the mixing of oxidizer with the combustion products as they move downstream from the flame front region.

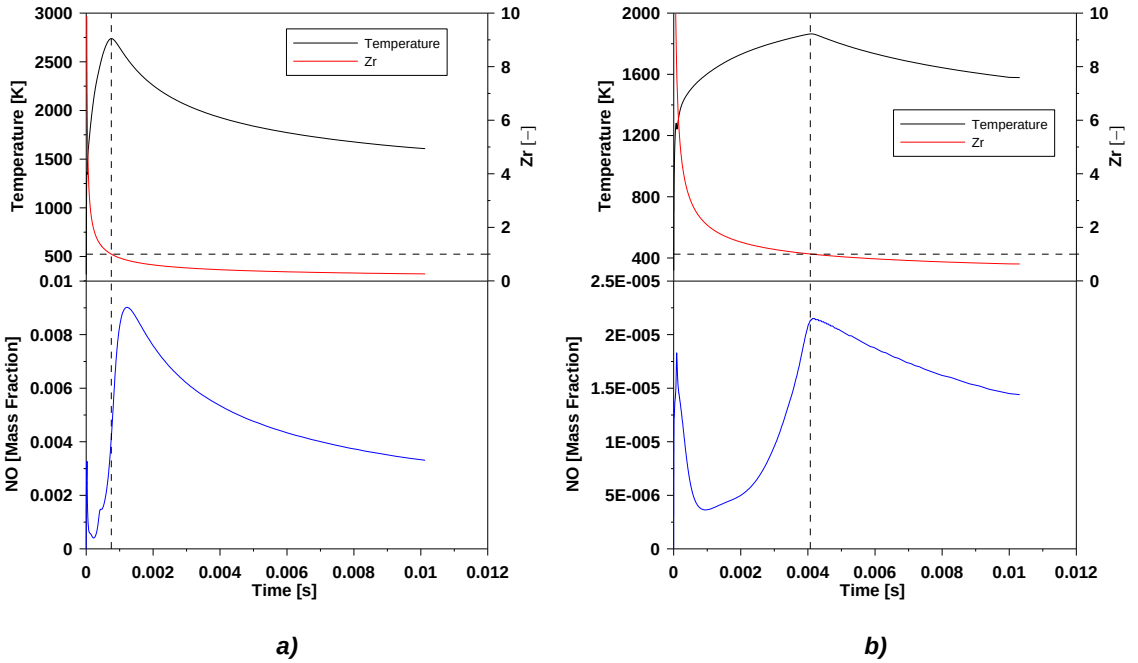


Figure 7.8.- Temperature, mixture fraction and NO evolution along the axial axis of a diesel spray simulated by the TSL model baseline conditions summarized in Table 7.2. a) Non-EGR case (Y_{O2ini}=0.23) and b) massive EGR case (Y_{O2ini}=0.1).

Despite the fact that the proposed methodology is built focusing on this latter region, because higher amounts of NO are expected to be formed and where the reburning effects are not expected, it was validated in two different contexts: focusing on the post-combustion region (as originally intended) and considering the whole evolution of the spray structure in the axial coordinate.

7.4.2.1.- Focusing on the post-combustion region

In this first context special attention will be paid to the post combustion region and therefore the starting point will be the flame front region (Z_r = 1) and the initial amount of NO will be determined by the TSL model. Additionally, the dilution effect will be considered as the ratio between the total mass of the flame core reactor at two consecutive time steps instead of with the fuel's mass. By doing so, the methodology requires less computational resources.

The results obtained were plotted with their homologous, from the TSL model, in Figure 7.9a and Figure 7.9b. These are reasonably accurate for both cases even though higher

accuracy is obtained for the massive EGR case. This observation can be explained by the fact that for the non-EGR case the starting NO composition, corresponding to Z_r = 1, is not the highest value and therefore there is still some more NO formation, prior to the dilution effect. This reflects the fact that the dilution effect near the flame front region is minor. However, in the latter case (e.g: massive EGR), due to poor NO formation conditions (low combustion temperatures) the predominant effect is dilution near the flame front region. Consequently the NO formed in this region is approximately the maximum value and therefore higher accuracy in the NO predictions are achieved.

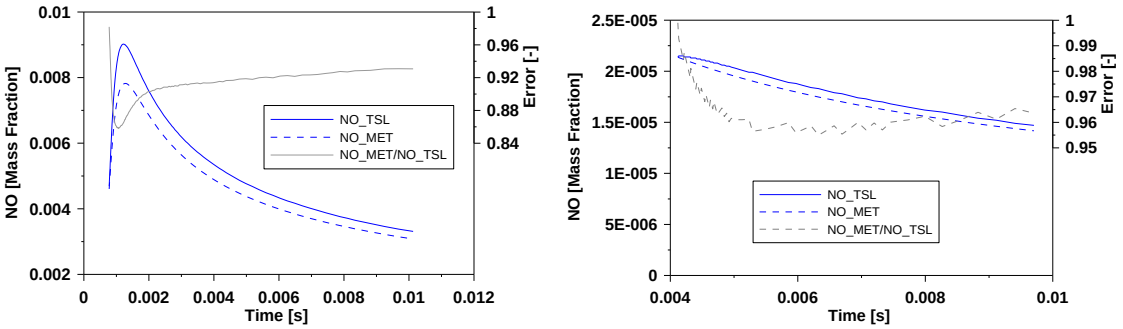


Figure 7.9.- Comparison between the NO predicted by the proposed methodology (NO_MET) and by the TSL model considering the whole NO_x sub-mechanism included in GRI-Mech 3.0 (NO_TSL), in the post-combustion region of a diesel spray, for: a) Y_{O2ini} = 0.23 and b) Y_{O2ini} = 0.1, with n-heptane at a pressure 10MPa.

From these results, the methodology is sufficiently accurate to perform not only qualitative but also quantitative predictions of NO formation in this region.

To confirm the previous observations, this methodology was validated against real engine-out NO_x emissions. These were obtained during experimental tests where the amount of oxygen, in the intake, was varied from 10% to 17% for low and medium loads. This engine worked based on diffusion diesel combustion principles and its geometrical specifications as well as those of the inyector are summarized in Table 7.5.

Engine's Characteristic	**Values**
Stroke [m]	0.15
Bore [m]	0.12
Compression ratio [-]	14.4
Inyector	**Values**
Num. Orifice	7
Diam. Orifice [mm]	0.19
Angle between sprays [º]	120

Table 7.5.- Summary of the engine's and inyector's geometric specifications.

Despite the fact that the these emissions are predominantly NO and NO_2 and this methodology only takes NO into consideration, it has been concluded in Chapter 5 that it is suffice to just consider this specie to perform accurate NO_x predictions. With this in mind the ACT model [34], developed at CMT-Motores Térmicos Department, was used with the current tabulated tables instead of the originals. When comparing with real engine-out NO_x emissions with simulated predictions, Figure 7.10a, it is clear that this methodology considerably under-predicts the formation of this pollutant in the LTC region (low NO formation) while for the CDC conditions (high NO formation) the accuracy is high. In order to confirm if this trend is due to the methodology or to the ACT model, the same predictions were repeated with the original tables. From Figure 7.10b it can be observed that: 1) this under-prediction is inherent to the proposed methodology and 2) the trend yield by the proposed methodology is as expected (higher NO formation than the thermal mechanism).

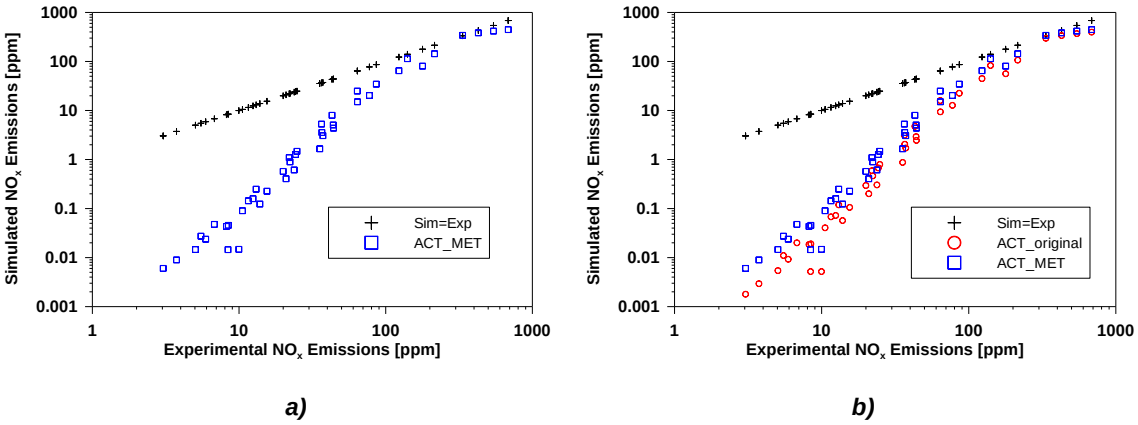


Figure 7.10.- Comparison between the experimental and the simulated NO_x emissions using ACT.

7.4.2.2.- Whole evolution of the spray structure in the axial coordinate

Finally, the author has tried to predict the NO formation process throughout the whole diesel spray, including the inner region (where $Z_r > 1$ and therefore the Y_{O2exc} is zero), employing the same methodology as in subsection 7.4.2.2 but slightly modified. Generally speaking, these modification consists in initializing the NO calculation by assuming $NO_{ini} = 0$ and taking into account the transfer of NO, formed in the flame front region, into the flame's core.

In order to consider this latter phenomenon in the simplest possible way, the author has decided to assume equilibrium conditions, even though this is not true in reality, throughout the whole flame front. Therefore the amount of NO formed will be equal to NO_{eq} (already tabulated) for $Y_{O2exc} = 0$ (stoichiometric conditions, $Z_r = 1$) and for a given T_{ad}. Consequently, the adiabatic combustion temperature (T_{ad}), the only unknown, was tabulated as a function of initial mixture's temperature (T_{ini}) and the initial oxygen mass fraction (Y_{O2ini}),

see Figure 7.11. Therefore, in this particular case, three tabulated tables will be considered plus the dilution effect typical of the post-combustion region.

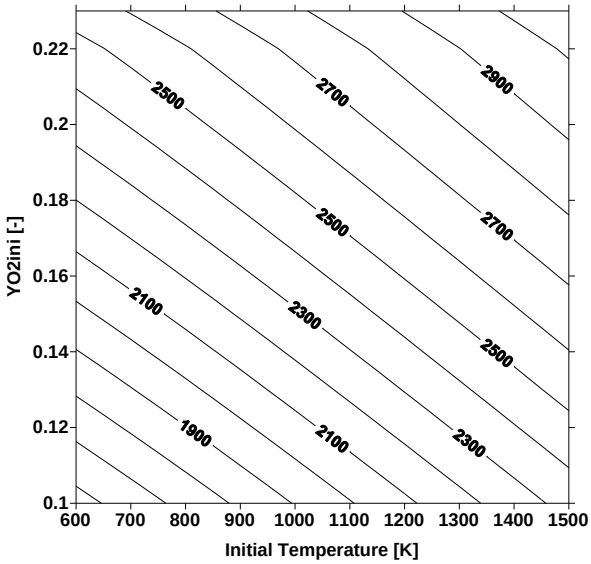
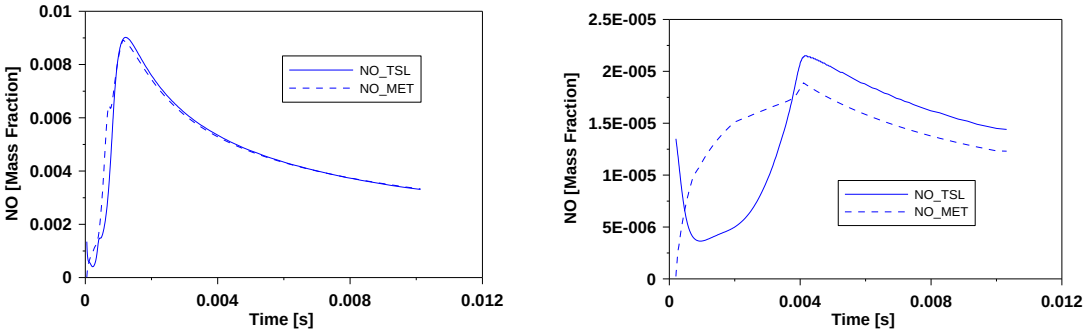


Figure 7.11.- Tabulated adiabatic combustion temperature as a function of initial mixture's temperature and initial oxygen mass fraction.

In Figure 7.12a and Figure 7.12b the results yield using this version of the proposed methodology are plotted. As expected, in both cases there is a considerable over-prediction in the inner region of the spray because the reburning phenomenon is not characterized due to the number of variables affecting the process. However this over-estimation rapidly diminishes as the flame front and the post combustion regions are reached. As a matter of fact, for the non-EGR case the accuracy is very high while for the massive EGR case the prediction reflects a reasonable accuracy (85%).



a) ***b)***

Figure 7.12.- Accuracy between the NO predicted by the proposed methodology (NO_MET) and by the TSL model considering the whole NO_x sub-mechanism included in GRI-Mech 3.0 (NO_TSL), in the inner region of a diesel spray, for: a) Y_{O2ini} = 0.23 and b) Y_{O2ini} = 0.1, with n-heptane at a pressure 10MPa.

These results suggest that the methodology is accurate enough to perform not only qualitative but also quantitative predictions of NO formation.

Finally a validation process similar to the one performed in 7.4.2.1 was encountered. In this case, the ACT model was slightly modified to consider the transfer of the NO, formed in the flame front, into the flame core. If plotting in Figure 7.13 the measured NO_x emissions versus the simulated predictions it is plausible that the accuracy is reasonable independently of LTC or CDC combustion conditions. However when compared with the original tables of ACT the results are very similar. This fact points out that the thermal mechanism is as accurate as considering all the NO formation routes to predict NO_x emissions in this context, "considering the transfer of NO in a diffusion diesel combustion process". This fact corroborates not only the findings of chapter 6, where no differences in NO prediction where found for diffusion diesel combustion processes, but also the findings of chapter 5, which one of the main conclusions was the fact that to perform accurate NO_x emissions it is suffice to just consider NO and not NO and NO_2 (which are the predominant species).

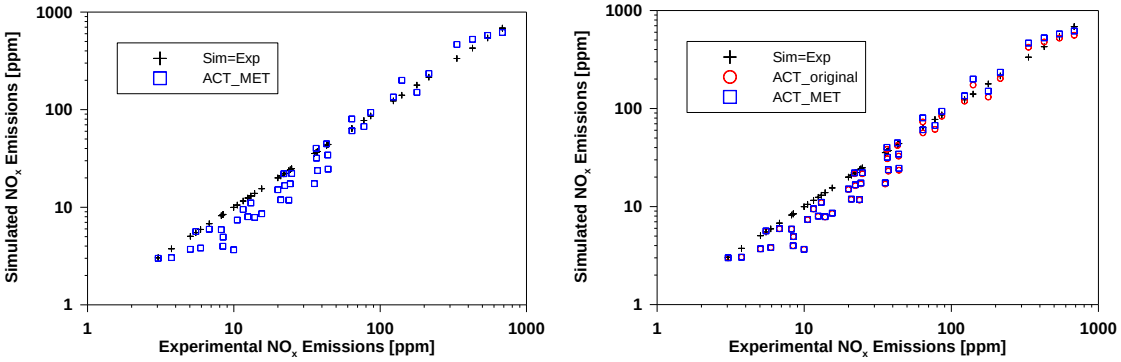


Figure 7.13.- Comparison between the experimental and the simulated NO_x emissions using a modified version of ACT to take into account the transfer of the NO, formed in the flame front, into the flame core.

7.5 Conclusions

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

a. The NO_x sub-mechanism employed from the GRI-Mech 3.0 mechanism can be considered as a first order reversible reaction for the vast majority of the studied conditions. Only at very low temperatures (T < 1300K) and independently of the equivalence ratio, this simplification is little effective.
b. The k-values obtained are in accordance with the chemistry ruling the NO formation process. They reflect that the thermal mechanism is the predominant route at high temperatures, vertical iso-k lines, and as the temperature decreases so does its predominance in favor of the prompt and the N_2O routes. This causes the iso-k lines to slightly curve or get distorted.

c. The hypothesis in which the present methodology is based on was satisfactorily validated in the homogeneous premixed auto-ignition diesel combustion process (e.g: HCCI diesel combustion) and in the diffusion diesel combustion (e.g: diesel spray) scenarios. The methodology reproduces, even when massive EGR is considered, the temporal evolution of NO with a reasonable accuracy, in the HCCI combustion context, and very accurately in the spray field. Consequently, the author believes that the 0-D low cost methodology proposed in the present chapter has enough favorable arguments to be considered for future simulations.
d. Regarding the heterogeneous diesel diffusion combustion mode context and independently of CDC or LTC conditions, no differences appear between the predictions yield by the thermal route or by all the formation pathways coupled together, specially when considering the transfer effect, into the flame core, of the NO generated in the flame front region.

7.6 Summary

The development of new diesel combustion modes characterized by low combustion temperatures, to minimize the NO_x emissions, has caused a noticeable change in the diesel spray's structure and in the NO_x chemistry, gaining relevance the N_2O and the prompt routes in detriment of the thermal mechanism. Therefore to accurately predict the NO_x emissions detailed chemistry and physics must be taken into account with the consequence of computational cost increase.

The author proposes in the current study a new predictive methodology associated to low computational cost, where detailed chemistry and simplified physics are considered. To diminish even more the computational cost, the chemistry was tabulated as function of temperature and oxygen excess mass fraction (parameter which effectively couples the equivalence ratio and the EGR rate). Furthermore, this tool has been developed with the objective of being applicable in **continuously varying temperature conditions** (e.g: homogenous charge compression ignition diesel combustion mode) and in **continuously varying temperature and mixture fraction conditions** (the diesel spray context).

The results reflect the fact that this tool can be applicable in both contexts to perform, at least, qualitative predictions.

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Appendix A: Mathematical demonstration of how the NO_x sub-mechanism behaves as a pseudo first order reversible reaction

In the present research study, the author has obtained an empirical fit equation (Eq.A1), which corresponds to a first order reversible reaction, to characterize the NO/NO_{eq} temporal evolution at constant pressure and temperature conditions and considering the whole NO_x sub-mechanism included in the GRI-Mech 3.0 chemical-kinetic mechanism. Consequently, this fact seems to suggest that the whole sub-mechanism can be treated as a first order reversible reaction.

$$\frac{NO}{NO_{eq}} = \left(1 - e^{-k \cdot t}\right) \qquad \textbf{(Eq. A1)}$$

To confirm such finding, the author will try to demonstrate that the fit equation can be achieved by applying the chemical-kinetic science.

Initially, the type of reactions considered in the NO_x sub-mechanism can be written, in a general manner, as:

$$aA + bB = cC + dD \qquad \textbf{(Eq.A2)}$$

and characterized by k_f and k_b which correspond to the forward and backward reaction constants, respectively. Note that A, B, C and D each stand for a chemical specie and a, b, c and d are the corresponding stoichiometric coefficients. The equal sign symbolizes that the reaction is reversible, which means, it can occur forward (yielding the species C and D) or backwards (yielding the species A and B).

The reaction rate law, for a pseudo first order reversible reaction, can be expressed by Eq. A3 and the variation in concentration for reactant A and product C can be described as Eq. A4 and Eq. A5, respectively.

$$\frac{dC}{dt} = k_f[A] - k_b[C] \qquad \textbf{(Eq.A3)}$$

$$[A] = [A_o] - ax \qquad \textbf{(Eq.A4)}$$

$$[C] = [C_o] + cx \qquad \textbf{(Eq. A5)}$$

Where $[A_o]$, $[C_o]$, [A] and [C] are the initial and final moles of the chemical specie A and C, respectively and x is a latent variable which describes the conversion degree.

Substituting Eq. A4 and A5 into Eq. A3 will yield the following expression (Eq. A8):

$$\frac{dC}{dt} = C * \frac{dx}{dt} \quad \textbf{(Eq. A6)}$$

$$K_c = \frac{k_f}{k_b} \quad \textbf{(Eq. A7)}$$

$$\frac{dx}{dt} = \frac{1}{C}(k_f([A_o] - ax]) - \frac{k_f}{K_c}([C_o] + cx)) \quad \textbf{(Eq. A8)}$$

Simplifying this latter equation by defining a new constant (Eq. A9) and rearranging it with basic algebra, the following expressions are yield:

$$\mathbf{cte} = \mathbf{A_o} - \frac{\mathbf{C_o}}{\mathbf{K_c}} \quad \textbf{(Eq. A9)}$$

$$\int_0^{\mathbf{x}} \frac{\mathbf{C \cdot dx}}{(\mathbf{cte} - \mathbf{ax} - \frac{\mathbf{cx}}{\mathbf{K_c}})} = \int_0^{\mathbf{t}} \mathbf{k_f \cdot dt} \quad \textbf{(Eq. A10)}$$

$$\int_0^{\mathbf{x}} \frac{\mathbf{C \cdot dx}}{(\mathbf{cte} - \mathbf{x} \cdot \left(\mathbf{a} + \frac{\mathbf{c}}{\mathbf{K_c}}\right))} = \int_0^{\mathbf{t}} \mathbf{k_f \cdot dt} \quad \textbf{(Eq. A11)}$$

Renaming what is inside the brackets, multiplying the x variable, with Eq. A11 and solving the integral in both sides will result in Equation A13.

$$\mathbf{cte_2} = \mathbf{a} + \frac{\mathbf{c}}{\mathbf{K_c}} \quad \textbf{(Eq. A12)}$$

$$-\frac{\mathbf{C}}{\mathbf{cte_2}} \cdot [\ln(\mathbf{cte} - \mathbf{cte_2} \cdot \mathbf{x}) - \ln(\mathbf{cte} - \mathbf{0})] = \mathbf{k_f \cdot t} \quad \textbf{(Eq. A13)}$$

Re-arranging with basic algebra:

$$\mathbf{x} = \frac{\mathbf{cte} \cdot (\mathbf{1} - \mathbf{e}^{-\mathbf{cte_2} \cdot \mathbf{k_f} \cdot \mathbf{t}})}{\mathbf{cte_2}} \quad \textbf{(Eq. A14)}$$

To solve for the equilibrium conditions two procedures, which yield the same result, can be used indistinctively. The first of them is to calculate x_{eq}, with Equation A15, assuming that t tends to ∞ and the second is to apply the condition that at equilibrium $\frac{dx}{dt} = 0$ and proceed in a similar way as previously. In this case, to simplify the calculations, the first procedure will be employed.

$$\mathbf{x_{eq}} = \frac{\mathbf{cte} - \mathbf{0}}{\mathbf{cte_2}} = \frac{\mathbf{cte}}{\mathbf{cte_2}} \quad \textbf{(Eq. A15)}$$

Dividing x by x_{eq} and substituting x by NO and redefining the power coefficient, as described in Eq. A16, will result in Eq. A17.

$$\mathbf{k = cte_2 \cdot k_f} \qquad \textbf{(Eq. A16)}$$

$$\frac{\mathbf{NO}}{\mathbf{NO_{eq}}} = \frac{\mathbf{cte}\cdot(\mathbf{1}-\mathbf{e}^{-\mathbf{k}\cdot\mathbf{t}})/\mathbf{cte_2}}{(\frac{\mathbf{cte}}{\mathbf{cte_2}})} = \left(\mathbf{1}-\mathbf{e}^{-\mathbf{k}\cdot\mathbf{t}}\right) \qquad \textbf{(Eq. A17)}$$

As it can be appreciated, Eq. A17 is identical to Eq. A1. This confirms that the whole NO_x sub-mechanism can be treated as a pseudo first order reversible reaction for the tested conditions.

Appendix B: Mathematical demonstration of how the equation in which the methodology is based on is yield from the fit equation

In the following appendix the mathematical demonstration of how equation (Eq. B0) is obtained from the fit equation (Eq. B00) is described.

$$\mathbf{NO_t = NO_{t-1} + k * \left(NO_{eq} - NO_{t-1}\right) * (t_t - t_{t-1})} \quad \textbf{(Eq. B0)}$$

$$\mathbf{\frac{NO}{NO_{eq}} = 1 - \exp(-k \cdot t)} \quad \textbf{(Eq. B00)}$$

Both equations have a common starting point, equation B1 (Eq. B1). Rearranging it with basic algebra, equation B2 (Eq. B2) is obtained:

$$\mathbf{\frac{dNO}{dt} = k \cdot (NO_{eq} - NO)} \quad \textbf{(Eq. B1)}$$

$$\mathbf{dNO = k \cdot \left(NO_{eq} - NO\right) \cdot dt} \quad \textbf{(Eq. B2)}$$

Differentiating both sides of equation B2 between two consecutive time steps will yield equation B3 which is identical to equation B0. On the other hand integrating equation B2 throughout the boundary conditions used in the characterization process will yield equation B4.

$$\boxed{\mathbf{NO_t - NO_{(t-1)} = k * \left(NO_{eq} - NO_{t-1}\right) \cdot (t - t_{t-1})}} \quad \textbf{(Eq. B3)}$$

$$\mathbf{\int_0^{NO} \frac{dNO}{(NO_{eq} - NO)} = k * \int_0^t dt} \quad \textbf{(Eq. B4)}$$

If the resulting equation of this integration procedure, (Eq. B5), is rearranged mathematically and multiplied both sides by the inverse of natural logarithm, the equation B6 will be obtained.

$$\mathbf{-\left[\ln\left(NO_{eq} - NO\right) - \ln\left(NO_{eq} - 0\right)\right] = k \cdot (t - 0)} \quad \textbf{(Eq. B5)}$$

$$\mathbf{\frac{NO_{eq} - NO}{NO_{eq}} = \exp(-k \cdot t)} \quad \textbf{(Eq. B6)}$$

Finally, further algebraically rearrangements will yield equation B7 which is identical to the fit equation (Eq. B00).

$$\boxed{\mathbf{\frac{NO}{NO_{eq}} = 1 - \exp(-k \cdot t)}} \quad \textbf{(Eq. B7)}$$

Chapter 8

Conclusions and Future Works

Content

8.1 Introduction

In this last chapter of the Thesis a recompilation of all the relevant conclusions obtained from each of the research studies will be presented together with the most relevant aspects of the corresponding methodology. Finally future works will be proposed taking as starting point the knowledge acquired during the performance of this work.

8.2 Conclusions

The fact of making more environmentally friendly the diesel combustion process, to accomplish the most stringent emission standards, causes major physical and chemical changes in comparison with conventional diesel combustion processes. Regarding the chemical changes, in order to accurately predict engine-out NO_x emissions under low temperature combustion conditions requires the employment of detailed chemistry. However this fact is associated with a substantial increase in the computational cost which in some cases makes unaffordable the predictive simulations.

Therefore, the main objective of the Thesis consists in setting the basis for developing a low computational cost tool capable of predicting the engine-out NO_x formation, over CDC and LTC conditions, independently of considering a premixed auto-

ignition diesel combustion process (i.e: diesel HCCI combustion mode) or in the diffusion diesel combustion process (i.e: diesel spray context).

In order to accomplish this main objective, several other secondary objectives have been also established to enhance the comprehension of the NO_x formation process in both scenarios (CDC and LTC):

1. Understand the NO-NO_2 conversion process and the contribution of the NO_2 to the NO_x engine-out emissions.
2. Determine the predictive capability of the different NO formation routes in CDC but specially in LTC.
3. Characterize the NO formation rate as a function of equivalence ratio (Φ), initial temperature (T_{ini}) and oxygen mass fraction (Y_{O2}).

8.2.1.- Understand the NO-NO_2 conversion process and the contribution of the NO_2 to the NO_x engine-out emissions

In the present research study the NO-NO_2 conversion process was profoundly analyzed using as reference the typical values described in several comprehensive combustion textbooks, 10% and 30%, to describe conventional (CDC) and low temperature combustion (LTC) conditions, respectively.

A stepwise methodology was employed, in which the Chemkin Pro software played a major role, considering two main scenarios: non-EGR and massive EGR. For both, initially, equilibrium conditions were analyzed followed by homogeneous combustions and by studying the cooling effects of several phenomena implicitly involved in the normal operation of diesel engines (e.g: expansion stroke, dilution of hot combustion products with cold charge and wall impingement).

The conclusions obtained are:

- Generally speaking, the NO_2 formation is a consequence of a cycling NO-NO_2 conversion 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.
- 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 very low combustion processes can indeed be responsible for the increase in the NO_2 formation.
- 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.
- Cooling effects (expansion stroke, dilution of hot combustion products with cold charge and wall impingement) enhance the NO-NO_2 conversion process

increasing the NO_2 formation reaching the values described in the scientific literature.

- For CDC conditions the major contributor to the final NO_2/NO_x ratio is the dilution effect followed by the wall impingement. Even though this latter phenomenon yields high ratios, specially as the temperature drop becomes greater, the probability of this event to occur or even the amount of flame colliding with the wall is minor.
- 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.

- To accurately predict the NO_x emissions it is sufficient to just consider the NO specie instead of NO and NO_2, which are by far the predominant ones. This is relevant to reduce computational cost and the main reason why the following studies were only focused on NO.

8.2.2.- Determine the predictive capability of the different NO formation routes in CDC but specially in LTC.

From the previous conclusions, in this next research study the predictive capability of the different NO formation routes were analyzed under CDC and LTC conditions using Chemkin. In order to do so a parametric study was designed assuming **constant pressure and temperature conditions** over a wide range of relative mixture fractions (Zr) and temperatures values. The main conclusion from this preliminary study was:

- At high temperature, typical of CDC combustions, the thermal mechanism is the predominant independently of the equivalence ratio. However, for lower temperatures, typical of LTC combustion scenarios ($Y_{O2} \leq 12.7\%$), this mechanism reduces its contribution due this reduction in combustion temperature even though it continues to be predominant.

The next step consisted in analyzing this relevancy of the thermal mechanism in both scenarios by performing a second parametric study where **the final reaction temperature (T_{end}) was varied by modifying Y_{O2} in the fuel-air mixture for a given fixed local condition, described by: Zr, constant pressure (P) and initial reaction temperature (T_{ini})**.

The main conclusions obtained from this study were:

- The relationship obtained between t*hermal NO* prediction and t*hermal NO/Total NO* ratio, under very simplified conditions, yields a law which seems to be applicable to any local condition, described by T_{end}, Zr, Y_{O2}, and for any instant in the NO formation process independently of the combustion stage.
- However when considering distinct conditions to the ones employed to build the equation, and even though this law clearly improves the predictive accuracy in all the regions (low, mid and high NO formation), the results reflect high dispersion and high sensitivity to changes.

- The main drawback of this tool is that it doesn't take into consideration the completeness degree of the NO formation process. Consequently, the corrective equation will yield the same result for a given thermal NO prediction independently of how far or close it is from equilibrium conditions. As expected, in this latter situation, the difference between thermal NO and total NO is substantially lower than in an early stage of the NO formation process.

8.2.3.- Characterize the NO formation rate as a function of equivalence ratio (Φ), initial temperature (T_{ini}) and oxygen mass fraction (Y_{O2}).

As a consequence of the main drawback of the previous methodology a new tool was developed based on tabulated chemistry and assuming the following hypothesis: "***the NO evolution, for a giving initial condition, can be determined with just the temporal evolution of temperature, pressure and Y_{O2exc} variables. This evolution can be reproduced by the concatenation of a finite number of infinitesimally small processes at constant T, Y_{O2exc} and P, indistinctively of considering the diffusion diesel combustion process (i.e: diesel spray) or the premixed auto-ignition diesel combustion scenario (i.e: HCCI diesel combustion mode)***."

Non-steady state simulations were performed to obtain the temporal evolution of NO (NO(t)) at constant T, Y_{O2exc} and P conditions. Afterwards this evolution was normalized, by the corresponding NO composition at equilibrium state (NO_{eq}), and characterized by an exponential fit (k). Hence this procedure yields two variables, k and NO_{eq}, which will be tabulated in two tables as function of temperature and oxygen excess mass fraction. Note that this last parameter was used in order to agglutinate the equivalence ratio and the EGR rate in one unique variable. Finally, Equation 1, which only depends on the two tabulated variables (NOeq and k), was employed to concatenate the infinitesimally small processes at constant T, P and Y_{O2exc}.

$$\mathbf{NO_t} = \mathbf{NO_{t-1}} + \mathbf{k} * \left(\mathbf{NO_{eq}} - \mathbf{NO_{t-1}}\right) * (\boldsymbol{t_t} - \mathbf{t_{t-1}}) \qquad \boldsymbol{Eq.1}$$

Where NO_t is the NO calculated at each considered time (t), NO_{t-1} is the calculated amount of NO in the previous time step and k is the empirical exponential fit constant. The NO composition at equilibrium conditions for a given T, P and Zr is denoted as NO_{eq} and (t_t-t_{t-1}) is the considered time step, which can be constant or variable.

This methodology was tested under continuously varying temperature conditions (premixed auto-ignition diesel combustion) and under continuously varying temperature and mixture's composition (diffusion diesel combustion process) with the following main conclusion:

- The hypothesis in which the present methodology is based on was satisfactorily validated in both scenarios. In both cases the methodology

reproduces, when massive EGR is considered, the temporal evolution of NO with an accuracy degree greater than just considering the thermal mechanism and without increasing the associated computational cost. Moreover, the accuracy when non-EGR is employed remains very high.

When validating it with experimental NO_x emissions, for LTC and CDC conditions, of a real diesel engine, running under diffusion diesel combustion characteristics, two important lessons were learned:

- In the case of not considering the inwards transfer of the NO, formed in the flame front, into the flame's core, the results yield have a low accuracy degree and substantial differences in prediction are observed between the formation mechanisms, for LTC conditions. Nevertheless, as the combustion temperature increases, so does the accuracy. Instead the differences between the predictions of the different NO formation mechanisms reduce considerably even reaching very similar values.
- On the other hand, if this transfer effect is considered, the results are substantially more accurate to the experimental results but no differences are observed between the predictions of the two formation mechanisms. This is observed independently of considering LTC or CDC conditions.

These findings illustrate that the selection of the NO formation mechanism, to perform future simulations, is relevant for premixed auto-ignition diesel combustion processes while for the diffusion diesel combustion context this is not true. Consequently, it can be stated that simulating with the thermal mechanism, in the diffusion diesel combustion context, is as a good as considering all the formation routes. This fact has a high relevancy with respect to the computational costs of a simulation process.

Finally it is worth highlighting that the combination of all of these conclusions coupled with the findings observed in the previous studies, part of this Thesis, and considered in this methodology help to set the basis to develop a low computational cost tool capable of predicting engine-out NO_x emissions accurately, achieving the main objective of the present document.

8.3 Future works

With these findings as starting point, some future works which are worth developing are:

- Characterization of the complex reburning process taking place inside the diffusion flame. This phenomenon is strongly influenced by multiple parameters. Consequently, the same number of characterization procedures as variables considered should be faced. Furthermore it is complex to determine the appropriate reactors' setup to encounter effectively this phenomenon.
- Increase the scope of the tool by extrapolating it to other fuels, like: gasoline and bio-fuels. This latter one will become relevant in the next years due to the

progressive increase, legislated by a European norm, of its content in the conventional fuels. Consequently new chemical kinetic mechanisms will be required.

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