NOx Reduction in Diesel-Hydrogen Engines Using Different Strategies of Ammonia Injection

M.I. Lamas 1, *, C.G. Rodriguez 2

1 Naval Sciences and Marine Engineering Department, Universidade da Coruña, 15403 Ferrol, Spain
2 Norplan Engineering S.L., 15570 Narón, Spain; c.rodriguez.vidal@udc.es
* Correspondence: isabellamas@udc.es; Tel.: +34-881013896

Received: 19 February 2019; Accepted: 28 March 2019; Published: 1 April 2019

Abstract: In order to reduce NOx emissions in internal combustion engines, the present work analyzes a measurement which consists of injecting ammonia directly into the combustion chamber. A commercial compression ignition engine fueled with a hydrogen-diesel blend was studied numerically. It was verified that the flow rate shape in which the ammonia was injected, particularly rectangular, triangular, or parabolic, as well as the injection duration had an important influence on NOx reduction. A 11.4% improvement in NOx reduction, corresponding to an overall reduction of 78.2% in NOx, was found for parabolic injection shape and 1º injection duration. The effect on carbon dioxide, carbon monoxide, and hydrocarbon emissions, as well as brake-specific consumption, was negligible.

Keywords: CFD; NOx; hydrogen; ammonia; engine.

1. Introduction

Nowadays, it is very important to reduce emissions in internal combustion engines as well as the dependency on fossil fuels. The current concerns about the limitation of fossil fuels and pollution are strong incentives for finding alternative sources. In this regard, both hydrogen and ammonia constitute promising fuels because these may be produced from alternative sources [1]. Since ammonia and hydrogen are carbon-free, they do not produce carbon dioxide (CO2), carbon monoxide (CO), unburned hydrocarbons (HC), nor particulates. Ammonia and hydrogen are also sulphur-free, and consequently, the emissions of sulphur oxides (SOx) are also negligible, since these depend on the sulphur content in the fuel [2–5]. In internal combustion engines, ammonia-hydrogen blends complement their properties since ammonia is characterized by a narrow flammability range, high ignition energy, low combustion velocity, and high auto-ignition temperature. On the other hand, hydrogen presents a wide flammability range, low ignition energy, high combustion velocity, and lower auto-ignition temperature [6,7]. Besides, hydrogen can be obtained directly from ammonia [8–11]. Some investigations [12–15] proposed hydrogen as a promoter to speed up diesel-ammonia combustion. Technologically, the most employed option is to inject ammonia into the intake air. Boretti [16] analyzed several injection procedures in a dual fuel ammonia-hydrogen engine and concluded that the most adequate option is to inject ammonia into the intake air. Sahin et al. [17] analyzed ammonia injection into the intake air of a small engine and obtained advantages regarding efficiency and CO2 emissions, but at expenses of increments in NOx, HC, and CO. Reiter et al. [18] also employed injection of ammonia into the intake air of an engine and obtained a noticeable reduction in soot emissions but at the expense of increments in NOx, HC, CO, and consumption. The authors indicated that the increment in NOx emissions is mainly produced by ammonia oxidation. Nevertheless, they obtained that when less than 40% of the fuel energy is provided by ammonia, NOx emissions are lower than for a diesel engine because the substitution by ammonia lowers the combustion temperature and thus reduces the thermal NOx formation mechanism. Another
ammonia fumigation study was developed by Gill et al. [19], who injected ammonia and hydrogen into the intake air of a diesel engine and obtained reductions in consumption and CO₂ emissions as well as increments in HC and NOₓ emissions.

Hydrogen usually increases NOₓ emissions, especially at high loads, due to the high temperatures reached in the combustion chamber [20–22]. This constitutes an important problem, since the transport sector, especially internal combustion engines, is considered the major source of NOₓ formation worldwide [23,24]. The production of NOₓ from oxygen and nitrogen in the air is a problem associated to the combustion of fuels, and its reduction has been investigated for a long time. As a possible solution to reduce NOₓ, hydrogen allows internal combustion engines to operate under ultra-lean combustion and thus under low-temperature combustion and lower NOₓ emissions, but at the expense of reducing efficiency noticeably [25–27]. Other procedures to reduce NOₓ emissions in internal combustion engines can be briefly summarized in primary and secondary measures. The latter consist of removing NOₓ from the exhaust gases by downstream cleaning techniques, while the former consist of reducing NOₓ produced during combustion by reducing the concentrations of oxygen and nitrogen as well as controlling the temperatures reached in the combustion process. The high price of after-treatment systems has promoted primary measures. In hydrogen engines, several techniques have been documented in the literature, such as modification of the injection parameters, reduction of the compression ratio, exhaust gas recirculation (EGR), water injection, etc.

As another measure to reduce NOₓ emissions in hydrogen-ammonia engines, several authors proposed to inject ammonia directly into the cylinder during the expansion stroke. As this is a novelty and recent technology, the literature about direct ammonia injection is still scarce. One can refer to Miyamoto et al. [28], who analyzed a diesel engine and showed that NOₓ emissions can be reduced by up to 60% by optimizing the injection timings. Larbi and Bessrorur [29] also found a substantial reduction in NOₓ emissions by injecting ammonia directly into the combustion chamber. Lamas et al. [30] verified that ammonia injection is much more efficient than water injection to reduce NOₓ.

Against this background, it can be concluded that an extended amount of literature has been developed on the applications of ammonia and hydrogen as fuels. Nevertheless, the research about direct ammonia injection into the combustion chamber as a NOₓ reduction measure is still scarce. The present paper proposes a CFD (Computational Fluid Dynamics) model to analyze NOₓ reduction in an internal combustion engine fueled with a hydrogen-diesel blend. Particularly, this work analyzes the commercial compression ignition engine MAN D2840LE V10. The process of NOₓ reduction from ammonia injection directly into the combustion chamber was analyzed. Since ammonia is toxic, it is important to avoid un-reacted ammonia to slip into the atmosphere. For this reason, several injection shapes and durations were analyzed in order to optimize NOₓ reduction and thus reduce ammonia slip.

2. Materials and Methods

The MAN D2840LE V10 analyzed, Figure 1, is a four-stroke, turbocharged, and direct injection engine. Table 1 summarizes the main technical specifications.
Figure 1. Engine analyzed in the present work.

Table 1. Technical specifications at 100% load.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>320</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>1500</td>
</tr>
<tr>
<td>Number of cylinders</td>
<td>10</td>
</tr>
<tr>
<td>Cylinder displacement volume (cm³)</td>
<td>18270</td>
</tr>
<tr>
<td>Bore (mm)</td>
<td>128</td>
</tr>
<tr>
<td>Stroke (mm)</td>
<td>142</td>
</tr>
</tbody>
</table>

The photograph in Figure 2 illustrates the combustion chamber at the piston head. The computational grid is shown in Figure 3. A deforming mesh was employed in order to implement the movement to the piston and valves. Figure 3a represents the tri-dimensional grid at the bottom dead center and Figure 3b represents the AA cross section. All elements are hexahedral, and the mesh size was refined around the valves in order to adapt properly to their opening and closing. Several meshes with different elements and sizes were tested to verify the adequacy of the mesh.
Figure 2. Piston head of the engine studied in the present work.

Figure 3. Computational mesh at bottom dead center. (a) Tri-dimensional view; (b) AA section.

The open software OpenFOAM was employed for the simulations. A new in-house solver based on C++ language was programmed. The solver is based on the RANS (Reynolds-averaged Navier–Stokes) equations of conservation of mass, momentum, and energy, Equations (1–3).

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) = 0 \tag{1}
\]

\[
\frac{\partial}{\partial t} (\rho u_i) + \frac{\partial}{\partial x_j} (\rho u_i u_j) = -\frac{\partial p}{\partial x_j} + \frac{\partial}{\partial x_j} \left( \mu + \frac{\tau_{ij}}{\sigma} \right) - \rho u_i u_j \tag{2}
\]

\[
\frac{\partial}{\partial t} (\rho H) + \frac{\partial}{\partial x_j} (\rho u_i H) = \frac{\partial}{\partial x_j} \left( \mu + \frac{\tau_{ij}}{\sigma} \right) + S_{rad} \tag{3}
\]

In the equations above, \( \rho \) is the density, \( \tau_{ij} \) is the viscous stress tensor, \( \sigma \) is the turbulent Prandtl number, \( \mu \) is the turbulent viscosity, and \( H \) is the total enthalpy, computed by the sum of the enthalpy of all species. The enthalpy of each species was computed by

\[
h_k = \int_{T_{ref}}^{T} c_{p,k} dT + h^0_k(T_{ref,k}) \tag{4}
\]

where \( c_{p,k} \) is the specific heat of species \( k \), and \( h^0_k \) is the formation enthalpy at the reference temperature \( T_{ref,k} \).

The term \( S_{rad} \) in Equation (3) is a source to include radiation heat transfer. The P1 radiation model was employed, according to which the radiative source term for the enthalpy equation is:

\[
S_{rad} = aG - 4a\sigma T^4 \tag{5}
\]

where \( a \) is the absorption coefficient, 0.2 [31], and \( G \) is the incident radiation, obtained by the following transport equation:

\[
\nabla \cdot \left( \frac{1}{3a} \nabla G \right) - aG + 4a\sigma T^4 = 0 \tag{6}
\]

A common procedure to model the Reynolds stresses, \( -\rho \overline{u_i u_j} \), is the Boussinesq hypothesis to relate the Reynolds stresses to the mean velocity gradients, Equation (7).
where $\delta_i$ is the Kronecker delta ($\delta_i = 1$ if $i = j$ and $\delta_i = 0$ if $i \neq j$), which is included to make the formula applicable to the normal Reynolds stresses for which $i = j$. Lamas and Rodriguez [32]. The turbulent viscosity was modeled by the $k$-$\varepsilon$ turbulence model, according to which $\mu_i = \rho C_{\mu_i} k^2/\varepsilon$. The $k$-$\varepsilon$ turbulence model implements two additional transport equations, one for the turbulence kinetic energy, $k$, Equation (8) and a further one for its dissipation rate, $\varepsilon$, Equation (9).

\[
\frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_i} (\rho k u_i) = \frac{\partial}{\partial x_i} \left( \mu_i \frac{\partial k}{\partial x_i} \right) + 2 \mu_i S_{ij} S_{ij} - \rho \varepsilon \tag{8}
\]

\[
\frac{\partial}{\partial t} (\rho \varepsilon) + \frac{\partial}{\partial x_i} (\rho \varepsilon u_i) = \frac{\partial}{\partial x_i} \left( \mu_i \frac{\partial \varepsilon}{\partial x_i} \right) + C_{\varepsilon} \frac{\varepsilon}{k} \left( 2 \mu_i S_{ij} S_{ij} - C_{\varepsilon} \rho \frac{\varepsilon^2}{k} \right) \tag{9}
\]

In the equations above $S_{ij}$ is the rate of deformation tensor, $C_{\mu_i}$ and $C_{\varepsilon}$ are constants and the terms $\alpha_i$ and $\sigma_i$ represent the turbulent Prandtl numbers for $k$ and $\varepsilon$, respectively. The default values were assumed for the model constants, $C_{\mu_i} = 0.09$, $C_{\varepsilon} = 1.00$, $\alpha_i = 1.30$, $C_{\varepsilon} = 1.44$, and $C_{\varepsilon} = 1.92$.

Regarding the simulation of fuel droplet breakup, the Kelvin-Helmholtz and Rayleigh-Taylor breakup models [33] were employed, and the heat-up and evaporation of the droplets was modeled by the Dukowicz model [34].

In order to solve the chemical kinetics, several additional equations must be added to the model. Given a set of $N$ species and $m$ reactions, Equation (10), the local mass fraction of each species, $f_i$, can be expressed by Equation (11).

\[
\sum_{i=1}^{N} \nu_{ij} M_i \xrightarrow{k_{ij}} \sum_{i=1}^{N} \nu_{ij} M_i, \quad j = 1, 2, \ldots, m \tag{10}
\]

\[
\frac{\partial}{\partial t} (\rho f_i) + \frac{\partial}{\partial x_i} (\rho u_i f_i) = \frac{\partial}{\partial x_i} \left( \mu_i \frac{\partial f_i}{\partial x_i} \right) + S_i \tag{11}
\]

In the equations above, $\nu_{ij}$ are the stoichiometric coefficients of the reactant species $M_i$ in the reaction $j$, $\nu_{ij}$ is the stoichiometric coefficients of the product species $M_i$ in the reaction $j$, $S_i$ is the turbulent Smidth number, and $S_i$ is the net rate of production of the species $M_i$ by chemical reaction, given by the molecular weight multiplied by the production rate of the species, Equation (12),

\[
S_i = MW_i \frac{d[M_i]}{dt} \tag{12}
\]

where $MW_i$ is the molecular weight of the species $M_i$ and $[M_i]$ its concentration. The net progress rate is given by the production of the species $M_i$ minus the destruction of the species $M_i$ along the $m$ reactions

\[
\frac{d[M_i]}{dt} = \sum_{j=1}^{m} \left\{ (\nu_{ij} - \nu_{ij}') \left[ k_{gj} \prod_{k=1}^{i} (M_k)^{\nu_{kj}} - k_{bj} \prod_{k=1}^{i} (M_k)^{\nu_{kj}} \right] \right\} \tag{13}
\]

where $k_{gj}$ and $k_{bj}$ are the forward and backward reaction rate constants for each reaction $j$. 
A reaction mechanism was programmed in the solver by integrating three kinetic schemes: combustion, NO\(_x\) formation, and NO\(_x\) reduction. Regarding NO\(_x\) reduction, the model of Miller and Glarborg [35], based on 24 species and 134 reactions, was employed. This model was validated with experimental results elsewhere [36], verifying that it reproduces the experimental trends with a reasonable accuracy. Regarding NO\(_x\) formation, the so-called extended Zeldovich mechanism is usually employed in CFD to characterize NO\(_x\) formation. This model is based on seven species and three reactions [37,38], listed in Appendix A.

Since the goal of the present work was to study NO\(_x\), several NO\(_x\) formation mechanisms were developed and validated with experimental results using 100% diesel fuel. Gasboard-3000 (Wuhan Cubic) series gas analyzers were employed to characterize the composition of the exhaust gas, particularly Gasboard-3030 for HC and Gasboard-3000 for NO, CO, and CO\(_2\). This gas analyzer provides NO instead of NO\(_x\), but the numerical model and numerous experimental analyses [39] indicated that NO\(_x\) is primarily NO. The extended Zeldovich model was compared to those of Mellor et al. [40], based on six reactions and eight species; Zabetta and Kilpinen [41], based on 10 reactions and 11 species; and Yang et al. [42], based on 20 species and 43 reactions, listed in Appendix B. The results obtained by these kinetic models at several loads and 1500 rpm are shown in Figure 4. This figure indicates that these models provide a satisfactory correspondence between numerical and experimental NO\(_x\) trends. Particularly, the extended Zeldovich model provides a 13.9% average error, while Mellor et al. [40] achieve 9.2%, Zabetta and Kilpinen [41] 8.1%, and Yang et al. [42] 5.8%. The \(R^2\) resulted in 0.955, 0.958, 0.959, and 0.962 for the extended Zeldovich, Mellor et al. [40], Zabetta and Kilpinen [41], and Yang et al. [42] models, respectively. According to this, the model of Yang et al. [42] was used for the computations in the remainder of the present paper.

![Figure 4. NO\(_x\) emissions experimentally and numerically obtained.](image)

Regarding the combustion mechanism, the simplest procedure is to assume that the kinetics are so fast that chemical species remain at equilibrium [30,36,43]. This hypothesis is commonly used in CFD taking into account the high temperatures reached during combustion, which promote fast kinetics. Nevertheless, a kinetic scheme is more accurate than the equilibrium hypothesis since the warming in the expansion process of an engine and dilution with the excess air elongate the time needed to achieve equilibrium. For instance, in the case of CO and HC, one of the sources of formation are warm regions that are not able to burn properly. In this case, the chemical equilibrium hypothesis leads to overestimating the levels of these species. For this reason, a chemical kinetic model was employed in the present work. Particularly, Ra and Reitz’s [44] model, based on 131 reactions and 41 species, was chosen. HC, CO, and CO\(_2\) emissions as well as brake-specific fuel
consumption at different loads and 1500 rpm are represented in Figure 5. This figure shows that a reasonable agreement was obtained, since the average error was 6.2%, 6.9%, 4.1%, and 3.8% for HC, CO, CO₂, and brake-specific fuel consumption (BSFC), respectively. Several reasons are responsible for the discrepancies between the numerical and experimental results obtained in Figures 4 and 5. Numerical techniques introduce inevitable errors due to the hypotheses assumed and the discretization on both the domain and governing equations. The RANS equations are time-averaged equations and the k-ε is a turbulence model that reproduces, as accurately as possible, the fluid flow. The P1 model for radiation, Kelvin-Helmholtz and Rayleigh-Taylor models for breakup, and Dukowicz model for heat-up and evaporation of the droplets are also models which reproduce, as accurately as possible, the physical mechanisms. Besides, the kinetic models employed are simplifications of the tens of species and hundreds of reactions involved in the chemistry of combustion. More accurate turbulence models such as LES (Large Eddy Simulation) or DNS (Direct Numerical Simulation) are too computationally expensive, as is the simulation of the hundreds of reactions involved. With the advancement of computational resources, it is expected that in the near future it will be possible to employ more accurate turbulence models and more chemical reactions within a reasonable computational time.

Regarding the simulation of fuel droplet breakup, the Kelvin-Helmholtz and Rayleigh-Taylor breakup models [33] were employed, and the heat-up and evaporation of the droplets were modeled by the Dukowicz model [34].

Figure 5. HC, CO, and CO₂ emissions as well as brake-specific fuel consumption (BSFC) experimentally and numerically obtained.

3. Results and Discussion

Once the numerical model was validated, it offered an efficient, cheap, and fast method to analyze the performance and emissions of the engine. In the present work, the model was employed to analyze several injection rate shapes, particularly rectangular, triangular, and parabolic. Before that, it was necessary to determine a proper NH₃/NOᵢ volumetric ratio, where NOᵢ is the NO concentration in the exhaust gas without ammonia injection. Figure 6 represents the NOₓ reduction as well as the ammonia slip in the exhaust gas against the NH₃/NOᵢ ratio using a rectangular ammonia injection shape, start of ammonia injection 43.2° after top dead center at the end of compression stroke, and 10° injection duration. This figure shows that more NOₓ reduction is obtained as NH₃ is increased. Due to the toxicity of ammonia, it is important to maintain low values of un-reacted ammonia slip to the exhaust. For this reason, a value of 2 was employed as a threshold for NH₃/NOᵢ in the remaining discussion of the present paper. Values between 2 and 3 are considered appropriate as well, since NOₓ reduction levels off around 3. A value greater than 3 provides few improvements in NOₓ reduction but a considerably higher amount of un-reacted
ammonia slips into the atmosphere, since ammonia slip analyses showed a noticeable increment with an increasing NH\textsubscript{3}/NO\textsubscript{i} ratio.

![Graph showing NO\textsubscript{x} reduction against the NH\textsubscript{3}/NO\textsubscript{i} ratio. Start of ammonia injection 43.2º, 10º injection duration, rectangular injection shape.]

**Figure 6.** NO\textsubscript{x} reduction against the NH\textsubscript{3}/NO\textsubscript{i} ratio. Start of ammonia injection 43.2º, 10º injection duration, rectangular injection shape.

Once the quantity of ammonia was determined, another important parameter to study was the shape of ammonia injection. The injection shapes indicated in Figure 7 were analyzed. These are rectangular, triangular, and parabolic. These three injection profiles refered to NH\textsubscript{3}/NO\textsubscript{i} = 2 and 10º injection duration. At 1500 rpm, 10º injection duration corresponded to 0.0011 s.

![Graph showing ammonia injection rates analyzed.]

**Figure 7.** Ammonia injection rates analyzed.

The results for these three shapes are indicated in Figure 8, which illustrates the NO\textsubscript{x} reduction against the start of ammonia injection using a 10º injection duration. This figure indicates that the instant start of ammonia injection has a noticeable effect on the NO\textsubscript{x} reduction. The reason is that the process of NO\textsubscript{x} reduction using ammonia is only efficient in a narrow temperature range. Consequently, in an internal combustion engine, it is too critical to determine the start of ammonia injection due to the variation of the in-cylinder temperature with the crankshaft angle. For the parameters analyzed in Figure 8, the maximum NO\textsubscript{x} reduction was obtained at start of ammonia injections 43.2º, 45.8º, and 42.9º after top dead center at the end of compression stroke for rectangular, triangular, and parabolic injection shapes, respectively. The corresponding NO\textsubscript{x} reductions were 68.3%, 66.8%, and 71.1% for rectangular, triangular, and parabolic injection shapes, respectively. The reason which explains these differences is that high temperatures promote ammonia to oxidize to NO instead of reacting with NO, while at lower temperatures, the reduction reactions become slow and un-reacted ammonia can be emitted. According to this, the ammonia must be injected progressively from 0 to a maximum value and then decrease to 0 again. The parabolic shape is the shape that adapts more properly to this tendency while the triangular shape is
the most different. Regarding brake-specific consumption and other emissions, such as CO, HC, and CO₂, it was verified that the effect was negligible.

Figure 8. NOₓ reduction against the start of ammonia injection for rectangular (green color), triangular (red color), and parabolic (blue color) injection shapes using 10º injection duration.

Another interesting parameter to analyze is the injection duration. Figure 9 shows the NOₓ reduction against the duration of ammonia injection. In order to obtain these data, the ammonia injection was equally shortened at start and end, using the same quantity of ammonia injected. The maximum NOₓ reduction obtained was 78.2%, corresponding to the parabolic shape at 1º injection duration. As can be seen in Figure 9, as the duration of ammonia injection was shortened, the NOₓ reduction increased. The reason is that lower injection durations facilitate the supply of ammonia at the optimum crankshaft angle and thus at the optimum in-cylinder temperature. On the other hand, longer injections deviate more from the optimum crankshaft angle and thus from the optimum in-cylinder temperature to reduce NOₓ. Particularly, from the data obtained from Figure 9, the NOₓ reduction improved from 66.8% for the triangular shape with 10º injection duration to 78.2% for the parabolic shape with 1º injection duration; i.e., a 11.4% NOₓ improvement was obtained. Another conclusion that can be obtained from Figure 9 is that the differences between rectangular, triangular, and parabolic shapes become smaller as the injection duration is reduced. The reason is that at shorter injection rates the ammonia is only injected at the optimum crankshaft angle and the injection duration is so short that the shape has a negligible influence. In practical applications, the injection rate can be shortened to the technically feasible level. Regarding brake-specific consumption and other emissions, such CO, HC, and CO₂, it was verified that the effect was negligible.
Figure 9. NOx reduction against the duration of injection for rectangular (green color), triangular (red color), and parabolic (blue color) injection shapes.

4. Conclusions

This paper analyzes the capability of ammonia to reduce NOx in a hydrogen-diesel engine. The motivation comes from the importance of the reduction of NOx emissions which are usually produced when hydrogen is added to internal combustion engines, and the increasingly stringent NOx restrictions. A CFD model was developed to analyze the commercial engine MAN D2840LE V10.

Since ammonia is toxic, it is important to optimize NOx reduction, minimizing the un-reacted ammonia slipping into the atmosphere. According to this, a NH3/NOx proportion around 2 was considered adequate. It was verified that the NOx reduction process using ammonia is highly dependent on the in-cylinder temperature. According to this, several ammonia injection shapes (rectangular, triangular, and parabolic) and durations (from 1° to 10°) were analyzed. The most appropriate case provided a 78.2% NOx reduction using a parabolic injection shape and 1° injection duration. On the other hand, the worst case analyzed provided a 66.8% NOx reduction using a triangular shape and 10° injection duration. As the injection duration is reduced, the differences between rectangular, triangular, and parabolic shapes become practically negligible. In practical applications, the injection rate can be shortened to the level that is technically feasible. For instance, in the present engine, which runs at 1500 rpm, 1° crankshaft angle corresponds to 0.00011 s. Current electromagnetic or solenoid injectors have longer response times but some piezo-injectors are able to switch on and off in tens of microseconds. These short injections provide practically identical results for rectangular, triangular, and parabolic injection shapes.

The main contribution of the present paper is that it provides a cheap and fast tool for studying NOx reduction in internal combustion engines. This tool constitutes an alternative to expensive and laborious experimental tests. It can be employed to study the influence of parameters such as the exhaust and intake pressures, number and position of injectors, nozzles, injection pressure, cam profile design, compression ratio, etc.

In future works, the goal is to employ this numerical model to study other engine operation conditions and other emission reduction procedures, such as water addition, common rail, exhaust gas recirculation, etc. Furthermore, further important work is needed to develop more tests in this and other engines in order to obtain a more complete validation of the numerical model.

Funding: This research received no external funding.

Acknowledgments: The authors would like to express their gratitude to Talleres Pineiro S.L., sale and repair of marine engines, as well as to Norplan Engineering S.L., and recommend the courses on CFD with OpenFOAM and C++ applied to OpenFOAM available at www.technicalcourses.net.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Reaction equations of the Zeldovich mechanism. The rate coefficients are in the form
\( k_j = AT^b e^{-E_0/T} \) (Table A1).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (cm(^3)/mol s)</th>
<th>b</th>
<th>E(_0) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N(_2) + O ⇄ NO + N</td>
<td>1.800-10(^{14})</td>
<td>0</td>
<td>38370</td>
</tr>
<tr>
<td>2 N + O(_2) ⇄ NO + O</td>
<td>1.800-10(^{10})</td>
<td>1</td>
<td>4680</td>
</tr>
<tr>
<td>3 N + OH ⇄ NO + H</td>
<td>7.100-10(^{13})</td>
<td>0</td>
<td>450</td>
</tr>
</tbody>
</table>

Appendix B

Reaction equations of the Yang et al. [42] mechanism. The rate coefficients are in the form
\( k_j = AT^b e^{-E_0/T} \) (Table A2).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (cm(^3)/mol s)</th>
<th>b</th>
<th>E(_0) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N(_2) + O ⇄ NO + N</td>
<td>1.800-10(^{14})</td>
<td>0.0</td>
<td>38370</td>
</tr>
<tr>
<td>2 N + O(_2) ⇄ NO + O</td>
<td>1.800-10(^{10})</td>
<td>1.0</td>
<td>4680</td>
</tr>
<tr>
<td>3 N + OH ⇄ NO + H</td>
<td>7.100-10(^{13})</td>
<td>0.0</td>
<td>450</td>
</tr>
<tr>
<td>4 N(_2)O + O ⇄ 2NO</td>
<td>6.900-10(^{13})</td>
<td>0.0</td>
<td>13400</td>
</tr>
<tr>
<td>5 N(_2)O + O ⇄ N(_2) + O(_2)</td>
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</tr>
<tr>
<td>6 N(_2)O + H ⇄ N(_2) + OH</td>
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<td>7600</td>
</tr>
<tr>
<td>7 N(_2)O + N \overset{2}{\leftrightarrow} 2N(_2) + O</td>
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</tr>
<tr>
<td>8 N(_2)O + N ⇄ NO + N(_2)</td>
<td>1.000-10(^{13})</td>
<td>0.0</td>
<td>10000</td>
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<tr>
<td>9 N(_2)O + NO ⇄ NO(_2) + N(_2)</td>
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<td>0.0</td>
<td>25000</td>
</tr>
<tr>
<td>10 N(_2)O + O \overset{2}{\leftrightarrow} NO + NO(_2)</td>
<td>6.000-10(^{14})</td>
<td>-1.5</td>
<td>4985</td>
</tr>
<tr>
<td>11 NO(_2) + O ⇄ NO + O(_2)</td>
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<td>0.0</td>
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<tr>
<td>12 NO(_2) + H ⇄ NO + OH</td>
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<td>740</td>
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<tr>
<td>13 NO(_2) + NO(_2) \overset{2}{\leftrightarrow} 2NO + O(_2)</td>
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<td>13500</td>
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<tr>
<td>15 NO + HO(_2) ⇄ NO(_2) + OH</td>
<td>2.089-10(^{12})</td>
<td>0.0</td>
<td>-240</td>
</tr>
<tr>
<td>16 NO + N \overset{2}{\leftrightarrow} N(_2)O + NO(_2)</td>
<td>2.300-10(^{14})</td>
<td>0.0</td>
<td>18000</td>
</tr>
<tr>
<td>17 N(_2) + O \overset{2}{\leftrightarrow} 2NO</td>
<td>2.730-10(^{13})</td>
<td>0.0</td>
<td>53800</td>
</tr>
<tr>
<td>18 NO + O \overset{2}{\leftrightarrow} N + O(_3)</td>
<td>2.700-10(^{14})</td>
<td>-1.0</td>
<td>63140</td>
</tr>
<tr>
<td>19 NO(_2) + O \overset{2}{\leftrightarrow} N + O(_3)</td>
<td>3.700-10(^{14})</td>
<td>-0.5</td>
<td>40280</td>
</tr>
<tr>
<td>20 NO + O \overset{2}{\leftrightarrow} O + NO(_3)</td>
<td>6.000-10(^{14})</td>
<td>-1.5</td>
<td>8000</td>
</tr>
<tr>
<td>21 N(_2) + HO(_2) ⇄ NO + HNO</td>
<td>5.925-10(^{10})</td>
<td>0.5</td>
<td>21550</td>
</tr>
<tr>
<td>22 N + OH \overset{2}{\leftrightarrow} NH + O</td>
<td>1.290-10(^{14})</td>
<td>0.0</td>
<td>2165</td>
</tr>
<tr>
<td>23 N + H(_2) ⇄ NH + H</td>
<td>1.320-10(^{15})</td>
<td>0.0</td>
<td>11230</td>
</tr>
<tr>
<td>24 N + H(_2)O ⇄ NH + OH</td>
<td>3.590-10(^{15})</td>
<td>0.0</td>
<td>18430</td>
</tr>
<tr>
<td>25 NH + OH ⇄ NO + H(_2)</td>
<td>1.600-10(^{12})</td>
<td>0.56</td>
<td>755</td>
</tr>
<tr>
<td>26 NH + O \overset{2}{\leftrightarrow} NO + H</td>
<td>5.000-10(^{13})</td>
<td>0.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
27. $\text{NH} + \text{OH} \leftrightarrow \text{HNO} + \text{H}$  
28. $\text{NH} + \text{O}_2 \leftrightarrow \text{HNO} + \text{O}$  
29. $\text{HNO} \leftrightarrow \text{H} + \text{NO}$  
30. $\text{HNO} + \text{OH} \leftrightarrow \text{NO} + \text{H}_2\text{O}$  
31. $\text{HNO} + \text{H} \leftrightarrow \text{NO} + \text{H}_2$  
32. $\text{HNO} + \text{O} \leftrightarrow \text{NO} + \text{OH}$  
33. $\text{NH} + \text{NO} \leftrightarrow \text{N}_2\text{O} + \text{H}$  
34. $\text{N}_2\text{O} + \text{NH} \leftrightarrow \text{N}_2 + \text{HNO}$  
35. $\text{NO}_2 + \text{NH} \leftrightarrow \text{HNO} + \text{NO}$  
36. $\text{N} + \text{H}_2\text{O} \leftrightarrow \text{NH} + \text{OH}$  
37. $\text{N} + \text{HO}_2 \leftrightarrow \text{NH} + \text{O}_2$  
38. $\text{NO} + \text{HO}_2 \leftrightarrow \text{HNO} + \text{O}$  
39. $\text{HNO} + \text{NO} \leftrightarrow \text{N}_2\text{O} + \text{OH}$  
40. $\text{HNO} + \text{N} \leftrightarrow \text{NO} + \text{NH}$  
41. $\text{HNO} + \text{HNO} \leftrightarrow \text{2NO} + \text{H}_2$  
42. $\text{NH} + \text{N} \leftrightarrow \text{N}_2 + \text{H}$  
43. $\text{NH} + \text{N}_2 \leftrightarrow \text{N} + \text{H} + \text{N}_2$  

References


40. Mellor, A.M. *Skeletal Mechanism for NOx Chemistry in Diesel Engines*; SAE Tech Pap 981450; SAE International: Warrendale, PA, USA, 1998; doi:10.4271/981450.