

Article

Evaluation and Selection of the Primary Zeldovich Reaction Rate Constant for NO Formation in Marine Diesel Engines

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Abstract

Accurate prediction of nitrogen oxide emissions from marine medium-speed four-stroke diesel engines is crucial for meeting increasingly stringent environmental standards. This paper focuses on the evaluation and selection of the optimal rate constant for the first and most significant reaction of the extended Zeldovich mechanism within a specific simulation framework. A numerical engine model was developed and validated against experimental measurements of combustion pressure, power, and emissions at 81% of the Maximum Continuous Rating (MCR). The research analyzes the influence of thirteen distinct chemical reaction rate constants on the accuracy of nitric oxide concentration predictions under the assumptions and inherent structural limitations of the developed zero-dimensional multi-zone model. The results demonstrate that by carefully selecting these kinetic parameters, the numerical model's deviation can be reduced to just -0.93% . Crucially, these findings reflect the performance of alternative kinetic formulations within this specific diagnostic modeling framework rather than a fundamental investigation into the universal chemical kinetics of nitrogen oxide formation. By systematically examining the primary Zeldovich reaction through its pre-exponential factor, temperature exponent, and activation energy, this approach provides a reliable calibration framework that significantly improves the fidelity of this specific emission formation simulation without increasing computational complexity.

Keywords: fuel combustion; chemical kinetics; Zeldovich mechanism; nitric oxide; marine diesel engines

1. Introduction

The maritime industry is currently facing unprecedented pressure to reduce its environmental impact, driven by the International Maritime Organization (IMO) Tier III regulations and the recent enforcement of stricter Emission Control Areas (ECAs) [1,2]. Specifically, the implementation of the Mediterranean Sea SO_x ECA and the upcoming NO_x Tier III requirements in the Canadian Arctic and Norwegian Sea have forced operators to significantly restrict exhaust emissions [1]. Nitrogen oxides (NO_x) remain the most critical pollutant from marine diesel engines due to their severe impact on human respiratory health, acid rain formation, and ozone depletion [3–5]. While new technologies such as dual-fuel combustion of ammonia and diesel [6] and alternative biofuels [7] show promise, the conventional medium-speed four-stroke diesel engine remains the primary prime mover of global shipping, requiring highly accurate numerical models to evaluate and improve its emissions performance [8–11]. In addition to traditional engine testing, the



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emergence of digital twin frameworks for marine propulsion systems has intensified the need for high-fidelity yet computationally efficient combustion models [12].

The formation of nitric oxide (NO) in diesel engines is predominantly governed by the thermal mechanism proposed by Zeldovich [13]. This mechanism, often extended to include a third reaction involving the hydroxyl radical (OH), is very sensitive to the local temperature and concentration of chemical species in the combustion chamber [14,15]. Recent studies have highlighted that, although the pre-exponential multiplier ARC1 (Arrhenius Pre-exponential Factor) is crucial at high loads, the exponential multiplier AERC1 (Arrhenius Activation Energy Factor) maintains a significant influence throughout the operating range, which requires precise calibration for robust emission modeling [9,16]. For medium-speed direct injection engines, quasi-dimensional, crank-angle-resolved multi-zone models are widely utilized to predict NO formation [16,17]. However, accurate prediction depends largely on the precision of heat release rate (HRR) estimation [9,18,19] and the modeling of fuel dispersion and mixture formation [20,21].

At the core of the Zeldovich mechanism (Equation (1)) lies the first and rate-limiting reaction:



The reaction rate constant ($k_{1,f}$) effectively determines the overall rate of NO production [22,23]. Despite its importance, there is no universal consensus on the optimal value of ($k_{1,f}$) for the specific thermodynamic conditions found in marine diesel engines. Different sources suggest variations in the pre-exponential factor and activation energy, which can lead to significant deviations in emission predictions [15]. Comparative analyses of different reaction rate constants ($k_{1,f}$) suggest that deviations in NO predictions can exceed 10% depending on the kinetic set chosen, especially under conditions outside the design limits or at high loads [9,10,24].

The aim of this paper is to evaluate and select the most accurate rate constant parameters for the primary Zeldovich reaction of NO formation in a marine four-stroke medium-speed diesel engine. By performing a systematic comparative analysis of thirteen distinct sets of coefficients, this study identifies the configuration that yields the highest predictive accuracy when compared to experimental data. This approach establishes a reliable calibration protocol that improves emission simulation fidelity without the prohibitive computational cost of multi-dimensional fluid dynamics.

2. Legal Restrictions on Nitrogen Oxide Emissions

Air pollution is regulated by international and regional regulations on the control of emissions of harmful substances into the atmosphere. In addition to the framework provisions of the United Nations Convention on the Law of the Sea (UNCLOS), atmospheric pollution from marine vessels is specifically addressed by the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78). Annex VI of MARPOL entered into force on 19 May 2005, with retroactive application to marine engines and ships constructed on or after 1 January 2000. Subsequently, Resolution MEPC.176(58), which amended the 1997 Protocol to amend the MARPOL Convention, was adopted on 10 October 2008 and entered into force on 1 July 2010.

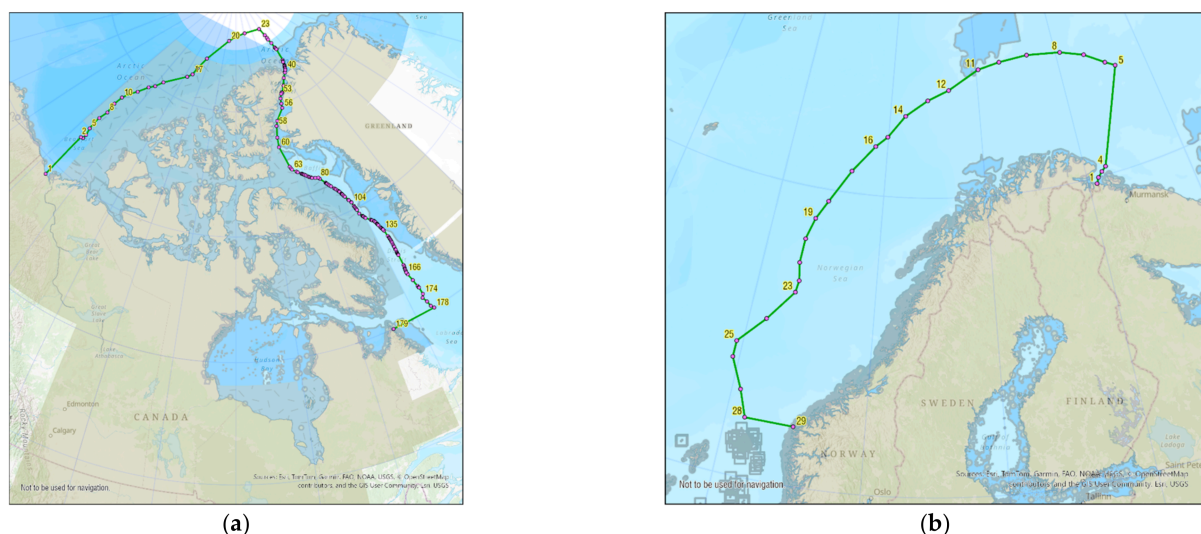
These amendments to Annex VI established two additional tiers of control for nitrogen oxide (NOx) emissions beyond the original Tier I limit. As detailed in Table 1 for medium-speed diesel engines, Tier II required a (NOx) emission reduction of approximately 15% relative to Tier I, while Tier III mandated a comprehensive 80% reduction compared to Tier I.

Table 1. Permissible NO_x emission limits for four-stroke medium-speed marine diesel engines based on ship construction dates.

Tier	Ship Construction Date on or After	130 < n < 2000
I	1 January 2000	$45 \cdot n^{-0.2}$, e.g., $1000 \text{ min}^{-1} = 11.3 \text{ g/kWh}$
II	1 January 2011	$44 \cdot n^{-0.23}$, e.g., $1000 \text{ min}^{-1} = 8.98 \text{ g/kWh}$
III	1 January 2016	$9 \cdot n^{-0.2}$, e.g., $1000 \text{ min}^{-1} = 2.26 \text{ g/kWh}$

The statutory requirements for nitrogen oxide (NO_x) emissions control apply to every marine diesel engine with a power output exceeding 130 kW installed on a ship, as well as to any engine exceeding 130 kW that underwent a major conversion on or after 1 January 2000, unless it can be demonstrated to the satisfaction of the Maritime Administration that the engine is an identical replacement. These regulations exclude marine diesel engines designated solely for emergency applications [4,9,10]. Table 1 outlines the specific emission limits applicable to the engine evaluated in this study, the Wärtsilä Corporation, Helsinki, Finland, 6L26A (1650 kW @ 1000 rpm), which underwent experimental testing.

Further regulatory tightening occurred during the 66th session of the IMO Marine Environment Protection Committee (MEPC) in 2014, resulting in amendments to MARPOL Annex VI, Regulation 13. Pursuant to IMO Resolution MEPC.271(69), ships operating within designated Emission Control Areas (ECAs) in North America or the US Caribbean Sea with a keel-laying date on or after 1 January 2016 must comply with Tier III standards. To address worsening climate impacts, the IMO has continuously expanded these protected zones. Notably, under regulations adopted at MEPC 82, the Canadian Arctic and the Norwegian Sea officially became active ECAs for both NO_x and SO_x emissions (Figure 1) [1,2].

**Figure 1.** Boundaries of new Emission Control Areas (ECAs): (a) Canadian Arctic (NO_x and SO_x); (b) Norwegian Sea (NO_x and SO_x).

Additionally, legislative updates targeting emission reductions across the Mediterranean basin remain imminent. In contrast to established ECAs in the North Sea and Baltic Sea, as well as newly designated zones across the North Atlantic, the Mediterranean ECA framework does not yet impose specific limits on nitrogen oxide (NO_x) emissions [3]. However, historical regulatory trends within active Emission Control Areas demonstrate that regional SO_x restrictions are rapidly followed by strict Tier III NO_x limits. For smaller vessels operating on short intra-ECA voyages, preparing marine operations for imminent NO_x abatement in this region requires the development of computationally efficient, pressure-driven diagnostic models before these statutory mandates enter into full force.

3. Simulation Model and Validation Procedure

The mathematical model accounts for the variable piston speed and its impact on the residence time of the cylinder charge at peak temperatures. By resolving the process every 0.5 °CA, the coupling between thermal conditions and chemical kinetics is accurately captured, which is essential for the time-dependent Zeldovich NO formation mechanism.

The Wärtsilä NSD 6L26A engine (1650 kW @ 1000 rpm) achieved 1669 kW on the test bench at 100% MCR and 1252 kW at 75%, showing that, according to the mathematical model, the achieved power was 81% MCR, which according to the master and chief engineer represents the most frequently used engine power during port operations. Although a single operating condition is presented, the model is built upon a high-fidelity, crank-angle-resolved approach (0.5 °CA resolution) rather than a simplified cycle-averaged estimation. This high resolution ensures that the coupling between the cylinder pressure, temperature, and the Zeldovich kinetics is physically consistent. As demonstrated in previous research [9,10], the underlying thermodynamic framework and the Wiebe-based heat release model have been extensively validated across various loads for this engine class, providing a robust foundation for the current investigation into kinetic rate constants.

A previously published scientific paper [10] provides a comprehensive analysis of the kinematics of the piston mechanism, and the calculation of the effective engine power from the recorded operational pressures in operation in order to determine the concentration of NOx in the exhaust emissions.

The simulation model for NOx emissions, implemented in Microsoft office LTSC Profesional 2019 Visual Basic Application, utilizes experimental pressure data obtained through the MarPrime Ultra system, incorporating fuel characteristics for stoichiometric calculations [3,10]. The analysis establishes a crank-angle-resolved multi-zone model based on cylinder pressure, which requires precise determination of combustion temperatures and air–fuel ratios for accurate prediction of NOx [9,10].

To calculate the stoichiometric amount of air required for the combustion of the injected fuel, the design characteristics of the engine and the chemical analysis parameters of the fuel must be entered into the program, as excess combustion air directly influences (NOx) production.

The fuel utilized by the engine during the pressure recording exhibits the properties outlined in Table 2.

Table 2. Marine engine fuel oil specification (ISO-F-DMA).

Characteristic Values	Unit	ISO-F-DMA
Kinematic viscosity @ 50 °C	mm ² /s	2.913
Density	kg/m ³	834.3
Lower heating value (LHV)	kJ/kg	42,940
Carbon	m/m	85.86
Hydrogen	m/m	13.78
Sulfur	m/m	0.033
Nitrogen	m/m	0.0019
Oxygen	m/m	0.32
Water	m/m	0.0

Atmospheric oxygen is consumed during both the normal combustion process and the formation of NOx. Since oxygen constitutes 23.2% by mass or 21% by volume of ambient air, the minimum theoretical mass of air required for complete combustion is determined according to Equations (2) and (3):

$$m_{O_2, \min} = \frac{8}{3} \cdot C + 8 \cdot H + S - O \quad \text{kg}_{\text{air}}/\text{kg}_{\text{fuel}}, \quad (2)$$

$$m_{\text{air,stoich}} = \frac{m_{\text{O}_2,\text{min}}}{0.232} = \frac{1}{0.232} \cdot \left(\frac{8}{3} \cdot C + 8 \cdot H + S - O \right) \quad \text{kg}_{\text{air}}/\text{kg}_{\text{fuel}}, \quad (3)$$

Combustion pressures were experimentally acquired using the MarPrime Ultra cylinder pressure indicator from Maridis GmbH, Rostock, Germany (Figure 2) [25]. This diagnostic system provides the development of cylinder pressures resolved at every 0.5 °CA.

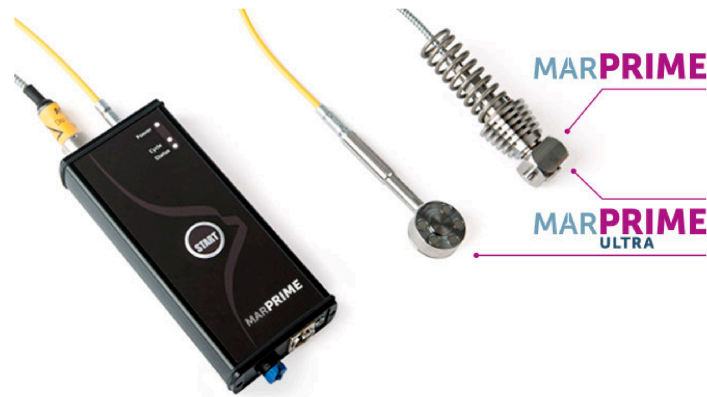


Figure 2. MarPrime Ultra cylinder pressure indicator: Device for recording combustion pressures, determining injection and valve opening times, and valve leakage with ultrasonic sensor.

The individual high-resolution pressure developments recorded for each of the six cylinders are illustrated in the p - α diagram in Figure 3. The tight overlapping of the traces confirms highly uniform combustion and stable fuel injection balancing across the entire cylinder bank. To streamline the subsequent thermodynamic evaluations and eliminate minor stochastic signal noise, the arithmetic mean of these combustion pressures was computed. The resulting averaged p - α diagram utilized as the primary diagnostic input is illustrated in Figure 4.

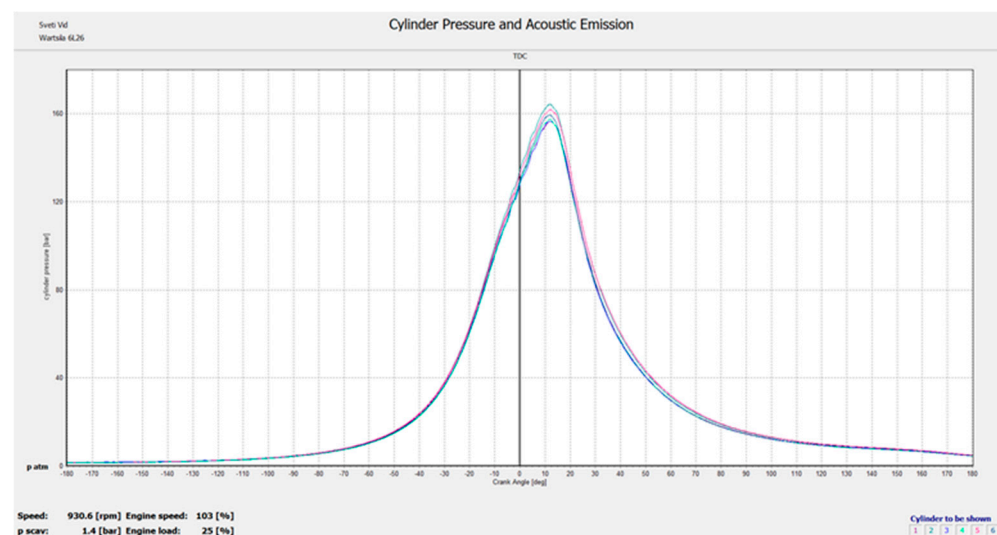


Figure 3. Display of combustion pressures on observed engine in p - α diagram.

Recording the indicated cylinder pressure remains one of the most reliable methods for diagnostic evaluation of the internal combustion engine working cycle. Even without an explicit forward simulation of pressure development, the recorded indicator diagram yields crucial thermodynamic data, including peak combustion pressure, peak temperature, their respective angular positions, and the maximum rate of pressure rise. The indicated engine

power (P_i) for a single cylinder is determined via Equation (4), utilizing the mean indicated pressure p_i from Equation (5) and the mean piston speed v_m from Equation (6) [9,10].

$$P_i = \frac{\pi}{4} \cdot d_c^2 \cdot p_i \cdot v_m \cdot \frac{1}{\tau}, \quad (4)$$

$$p_i = \frac{1}{s} \int_{x(\alpha_{\min})}^{x(\alpha_{\max})} p(x) dx = \frac{1}{2} \int_{\alpha_{\min}}^{\alpha_{\max}} p(x) \cdot \left(\sin \alpha + \frac{\lambda_m}{2} \cdot \frac{\sin 2\alpha}{\sqrt{1 - \lambda_m^2 \sin^2 \alpha}} \right) \cdot d\alpha, \quad (5)$$

$$v_m = \frac{2 \cdot s \cdot n}{60}. \quad (6)$$

When evaluating the final effective power and brake mean effective pressure, the mechanical efficiency of the engine (η_m) must be strictly accounted for, as specific emissions are legally regulated and expressed in grams per kilowatt-hour (g/kWh) effective brake power.

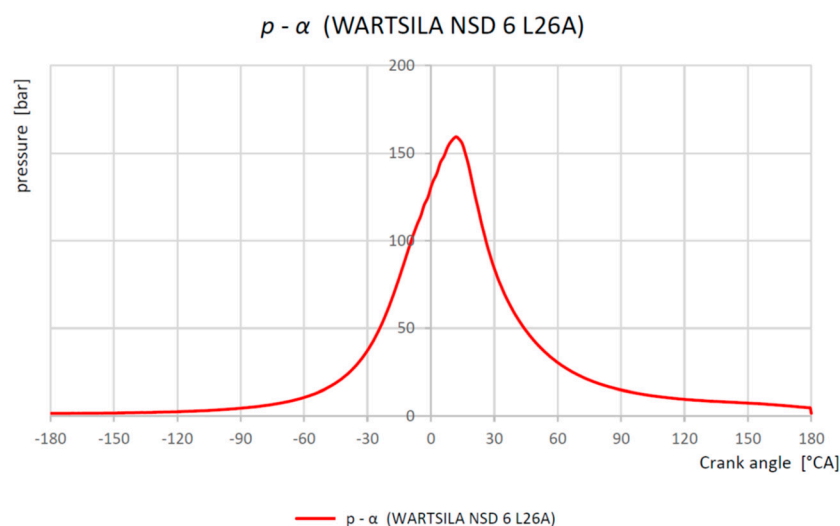


Figure 4. A display of the development of all cylinder's combustion pressures as an arithmetic mean.

Furthermore, calculating the actual working parameters requires quantifying the excess air ratio λ_{air} supplied to the cylinders to ensure complete fuel oxidation, as defined by Equation (7):

$$\lambda_{air} = \frac{m_{air,deliv}}{m_{air,stoich}} \quad (7)$$

Beyond the unburned oxygen trapped within the cylinder, the spatial and temporal development of local temperatures, particularly the peak combustion temperatures, plays a dominant role in thermal NOx synthesis [9,10].

Within internal combustion engines, prior to fuel injection, the cylinder charge consists entirely of fresh air, characterized by a specific gas constant 287 J/kgK.

However, following the start of injection, the cylinder medium transforms into a complex mixture of combustion products and residual gases. The corresponding evolution of in-cylinder temperatures and thermodynamic states is evaluated using Equations (8) and (9).

$$T = \frac{p \cdot V}{v_{air} \cdot R} \quad (8)$$

$$T = \frac{p \cdot V}{v_{air} \cdot R_{cp}} \quad (9)$$

The gas constant of the burned mixture depends directly on its local chemical composition. For standard marine distillate fuels, the compositional deviations are minimal and can be safely neglected for zero-dimensional evaluations. Thus, the specific gas constant of the combustion products (R_{cp}) is calculated with high engineering precision using Equation (10), yielding values in J/(kg · K) (10) [18,19]

$$R_{cp} = 287 + \frac{20.5}{m_{air,stoich} \cdot \lambda_{air}} \quad (10)$$

Impact of Rate Constant Variations on Emission Predictive Reliability

The systematic evaluation of different ($k_{1,f}$) sets in this study is not an iterative numerical tuning process but a fundamental investigation into the sensitivity of the thermal NO formation mechanism under real-world marine engine conditions. To minimize the inherent modeling uncertainties highlighted in engine combustion research, the mathematical formulation of the multi-zone framework is strictly derived from the validated diagnostic protocols established by [9,10].

Crucially, a clear distinction must be made between the theoretical predictive capabilities of the original framework and the specific diagnostic mode implemented in this study. In broader parametric research such as the foundational Ph.D. work in [9], empirical multi-zone Wiebe functions are useful for artificially modifying heat release profiles to evaluate how variations in fuel injection timing or compression ratios influence emissions. However, because the commercial Wärtsilä engine evaluated in this study was operating under fixed in-service conditions where geometric and operational parameters could not be altered, empirical Wiebe functions were completely omitted from the combustion core.

Instead, the thermodynamic state, mass burning rate, and subsequent multi-zone temperature histories are extracted directly from the high-resolution experimental cylinder pressure data (0.5 °CA step) recorded during the specialized quay-wall trial. The local temperature fields and the transient local excess air ratios (λ_{air}) within the reacting post-flame zones are directly calculated by solving the conservation of energy and mass equations simultaneously with the experimental pressure derivative ($dp/d\alpha$). Because the actual recorded (p/α) indicator diagram serves as the sole thermodynamic driver, the real-world ignition delay, the sharp kinetic premixed burning spike, and the subsequent diffusion combustion phase are inherently and fully captured by the model.

Furthermore, because the calculation step of 0.5 °CA is directly locked to the physical sampling resolution of the MarPrime Ultra diagnostic hardware, it eliminates the numerical grid-dependency risks typically associated with forward predictive simulations. Variations in the chemical kinetic rate constants of the Zeldovich mechanism exclusively affect the post-combustion emission chemistry and the rate of NO synthesis; they do not exert any feedback or altered physical effects on the underlying combustion development, heat release profiles, or engine performance indicators, preventing arbitrary numerical tuning across the thirteen evaluated kinetic sets.

Regarding the treatment of the reverse reaction within the extended Zeldovich framework, this study focuses strictly on the initial, high-temperature dominant phase of NO formation. In medium-speed marine diesel engines operating at high loads, the residence time at peak combustion temperatures is relatively short, and the process is characterized by a violent temperature drop during the subsequent polytropic expansion phase. Under these specific thermodynamic gradients, the forward reaction significantly outweighs the decomposition rate. As the cylinder volume expands, the chemical kinetics experience a phenomenon known as “thermal freezing”, wherein both forward and reverse reaction rates drop sharply, effectively locking the final NO concentration. Consequently, to maintain computational simplicity and high processing speed for real-time diagnostic engineering

applications, the instantaneous NO concentration in the reverse reaction rate calculation was neglected. This simplification is physically justified, as its numerical impact on the cumulative tailpipe emission values remains well within the acceptable engineering error margin for this engine category.

Contrary to arbitrary curve-fitting or iterative numerical optimization, this work performs a structured, systematic evaluation across thirteen fundamentally distinct kinetic paths established in the combustion literature. This parametric screening isolates the physical sensitivity of the rate constant under real-world engine conditions. However, from a methodological standpoint, it must be explicitly acknowledged that conducting this kinetic screening based on a single stable operational point (81% MCR) introduces inherent conceptual limitations. In an actual engine environment, the localized synthesis of NO is exponentially sensitive to micro-scale spatial fluctuations in temperature and species concentrations, which cannot be fully resolved by zero-dimensional or multi-zone diagnostic formulations. Therefore, the selection of the optimal kinetic parameter set should not be interpreted as a definitive, universal calibration of the fundamental Zeldovich constants, which are traditionally derived under strictly controlled laboratory conditions. Rather, it indicates which established literary dataset provides the highest predictive accuracy and minimizes cumulative engineering error when integrated into a real-time, high-resolution, pressure-driven diagnostic digital twin framework for this specific class of medium-speed marine propulsion units.

4. Modeling of NO_x Emissions in Exhaust Gases of Marine Four-Stroke Medium-Speed Engines

Pollutants in the exhaust gases of marine four-stroke medium-speed diesel engines are primary byproducts of the complex thermochemical combustion process. The final composition of these exhaust emissions is primarily dictated by the elemental composition of the fuel utilized, the local excess air ratio that remains unconsumed during the oxidation of the fuel oil, and the localized peak combustion temperatures. Furthermore, engine rotational speed constitutes a critical operational factor governing specific nitrogen oxide (NO_x) emissions. In medium-speed configurations, higher rotational speeds shorten the available physical time (residence time) for the high-temperature chemical kinetics to proceed, effectively limiting the accumulation of thermal NO. This operational dependency underpins the engine speed-based regulatory emission limits established by the IMO, as previously detailed in the statutory frameworks of Table 1.

4.1. Nitrogen Oxides

Due to the inherent characteristics of the heterogeneous combustion process in four-stroke medium-speed diesel engines utilizing distillate marine fuels, the global commercial fleet emits significant quantities of nitrogen oxides (NO_x). The term nitrogen oxides (NO_x) serves as a collective designation for the various oxides of nitrogen present in internal combustion engine exhaust, which are predominantly represented by nitric oxide (NO) and nitrogen dioxide (NO₂).

Within diesel exhaust streams, NO constitutes the primary component, accounting for approximately 70% to 90% of total nitrogen oxides (NO_x) by volume, while nitrogen dioxide (NO₂) comprises roughly 5% to 10% by volume. Conversely, nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), and dinitrogen pentoxide (N₂O₅) occur only in trace quantities.

From a toxicological perspective, nitrogen dioxide (NO₂) causes severe inflammation of the human respiratory tract, resulting in coughing, dyspnea, exacerbated asthma attacks, and heightened susceptibility to respiratory infections, while also acting as a primary precursor in photochemical smog formation. Nitrogen monoxide (NO) synthesized within

the engine cylinder is thermodynamically unstable under ambient conditions and readily oxidizes into nitrogen dioxide (NO_2). Conversely, in the presence of solar radiation at wavelengths shorter than 429 nm, $\lambda_s < 429$ nm, nitrogen dioxide (NO_2) undergoes continuous photochemical dissociation back into NO and a highly reactive oxygen radical (O). When performing experimental exhaust gas diagnostics on an engine test bench to verify compliance with international statutory standards, the analytical equipment quantifies the total cumulative concentration of both NO and nitrogen dioxide (NO_2) as the NO_x emission.

However, in accordance with international emission certification protocols, the total NO_x mass emission rate is calculated and officially expressed utilizing exclusively the molecular weight of nitrogen dioxide (NO_2).

The synthesis of NO_x during the working cycle is highly dependent on the local cylinder temperature, the availability of unconsumed oxygen within the post-flame zones, and the duration of these high-temperature states [9,10]. Within the combustion chamber, NO can be synthesized via several distinct pathways: the thermal (Zeldovich) mechanism, the prompt (Fenimore) mechanism, the nitrous oxide (N_2O) intermediate pathway, and the fuel-bound nitrogen mechanism [3,9,15,16,25].

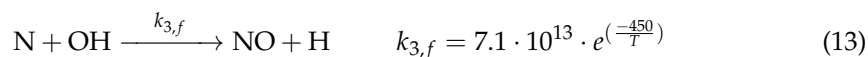
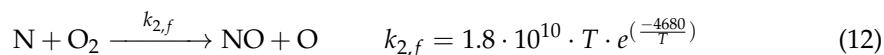
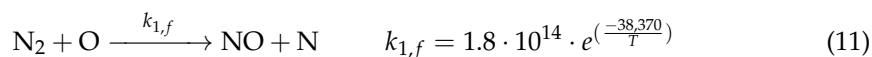
Although all these formation pathways contribute to the final exhaust composition, this investigation focuses strictly on the thermal NO mechanism. This focus is physically and mathematically justified because the thermal pathway overwhelmingly dominates at the elevated peak combustion temperatures characteristic of heavily loaded medium-speed marine engines. Furthermore, the contribution of the fuel-bound nitrogen mechanism is completely negligible due to the ultra-low nitrogen content (only 0.0019% m/m) of the certified ISO-F-DMA distillate fuel utilized in this study (Table 2), which lacks the complex chemical nitrogen chains required to initiate fuel- NO_x synthesis. Concurrently, the prompt (Fenimore) mechanism, which typically initiates within early, thin flame fronts under low-temperature, fuel-rich conditions, yields a minimal and statistically minor impact under the intense, high-temperature expansion environment (reaching peak localized states of 2211 K) dominant at 81% MCR. At these elevated thermal states, the formation rate of the thermal Zeldovich path is exponentially accelerated, accounting for over 90–95% of total NO_x and establishing itself as the sole governance metric for predictive diagnostic accuracy.

Thermal Nitrogen Monoxide (NO) Generation

To ensure low computational overhead and enable real-time processing capabilities for marine diagnostic software, the concentrations of the major chemical species and intermediate radicals involved in the nitrogen monoxide (NO) synthesis framework, specifically atomic oxygen (O), molecular oxygen (O_2), and molecular nitrogen (N_2), are determined utilizing explicit, analytically optimized algebraic formulations derived from the literature. While multi-species equilibrium models (such as 18-species or 33-species reaction matrices) solved via systems of algebraic equations are widely established and computationally accessible, this study evaluates a streamlined alternative specifically adapted to pressure-driven diagnostic environments. This simplification is thermodynamically justified by the elevated peak in-cylinder temperatures (reaching up to 2211 K), where the rapid initiation and dissociation rates of the fuel-air radical pool can be adequately captured by established algebraic correlations without requiring the iterative resolution of larger equilibrium matrices. This approach maintains an optimal balance between chemical consistency and processing speed, making it highly suitable for integration into on-board digital twin architectures.

The three elementary chemical reactions responsible for the thermal synthesis of nitric oxide within the cylinder are represented by Equations (11–13), which constitute

the classic Zeldovich mechanism extended to account for the contribution of the hydroxyl radical [13,14,21,26]:



Under the thermodynamic conditions prevailing within marine diesel engines, the chain reactions of the extended Zeldovich mechanism proceed at a significantly slower rate than the primary hydrocarbon oxidation reactions. Consequently, NO synthesis is governed strictly by chemical kinetics. Due to the highly localized nature of peak flame temperatures, coupled with the short residence times at these states during the expansion stroke, chemical equilibrium for the final NOx concentration is never achieved. Because thermal NO generation is exponentially sensitive to temperature, managing the maximum flame zone temperature represents the primary path for reducing final emissions. At core temperatures exceeding 1800 K, a local temperature reduction of approximately 70 K can diminish NO formation by up to 50%.

Within this kinetic framework, the forward rate constant ($k_{1,f}$) of the primary Zeldovich reaction (Equation (11)) serves as the absolute rate-limiting step, and its precision determines the overall reliability of the emission model. Applying the well-established steady-state approximation for the highly reactive nitrogen radical pool ($d[\text{N}]/dt \approx 0$), and focusing on the core high-temperature phase where initial forward kinetics strongly dominate over reverse decomposition reactions, the temporal evolution of the nitric oxide concentration is simplified to Equation (14) [26–28]:

$$\frac{d[\text{NO}]}{dt} \cong 2k_1[\text{N}_2][\text{O}] \quad (14)$$

The concentration of molecular nitrogen (N_2) is evaluated via Equation (15), where ($x\text{N}_2$) denotes the corresponding mole fraction of nitrogen within the trapped air charge [26–28]:

$$[\text{N}_2] = x\text{N}_2 \cdot \frac{p}{R \cdot T} \quad (15)$$

In Equation (14), (O) represents the concentration of atomic oxygen radicals, which can be evaluated through alternative equilibrium formulations. According to the framework established in the literature, the atomic oxygen concentration can be calculated via Equation (16) [26–28]:

$$[\text{O}] = \frac{K_C \cdot [\text{O}_2]^{0.5}}{(R \cdot T)^{0.5}} \quad (16)$$

The concentration constant (K_C), the molecular oxygen concentration (O_2), and the partial-pressure equilibrium constant (K_P) are determined through Equations (17)–(19) [26–28]:

$$K_C = R \cdot T \cdot K_P \quad (17)$$

$$[\text{O}_2] = x\text{O}_2 \cdot \frac{p}{R \cdot T} \quad (18)$$

$$K_P = 3.6 \cdot 10^3 \cdot \exp\left(-\frac{31,090}{T}\right) \quad (19)$$

To enhance numerical fidelity, an alternative formulation for the concentration constant [26] can be implemented via Equation (20) [26–28]:

$$K_C = 4.48 \cdot 10^3 \cdot e^{\left(-\frac{30,640}{T}\right)} \quad (20)$$

Alternatively, the oxygen radical pool can be tracked using the simplified kinetic formulation presented in Equation (21) [26–28]:

$$[O] = \frac{3.97 \cdot 10^5}{T^{0.5}} \cdot [O_2]^{0.5} \cdot \exp\left(-\frac{31,090}{T}\right) \quad (21)$$

Commercial exhaust gas analyzers record the cumulative concentration of nitric oxide directly in parts per million (ppm). To align the simulation results with the physical output of the diagnostic equipment and comply with international maritime emission certification protocols, the raw simulated NO concentration must be converted to dry volumetric parts per million and corrected to the statutory reference oxygen content of 13% as mandated by the IMO NO_x Technical Code 2008. This normalization accounts for arbitrary exhaust dilution and is executed Via Equation (22) [26–28]:

$$NO_{\text{ppm},13\%O_2} = [NO]_{\text{ppm,raw}} \cdot \left(\frac{20.9 - \varphi_{O_2,\text{ref}}}{20.9 - \varphi_{O_2,\text{meas}}}\right) = [NO]_{\text{ppm,raw}} \cdot \left(\frac{20.9 - 13}{20.9 - \varphi_{O_2,\text{meas}}}\right) \quad (22)$$

where $\varphi_{O_2,\text{meas}}$ represents the actual measured exhaust oxygen volume fraction (%), and $\varphi_{O_2,\text{ref}}$ is the statutory baseline reference oxygen level, legally fixed at 13.0% for marine diesel propulsion applications.

As introduced in the section titled Impact of Rate Constant Variations on Emission Predictive Reliability, Equation (22) treats the cumulative forward NO formation as the dominant metric for final emissions under these standardized reference conditions. Neglecting the instantaneous feedback of NO within the reverse decomposition pathways during this final step is a deliberate engineering simplification. Because the severe expansion stroke induces rapid thermal freezing of the chemical kinetics, the decomposition rate becomes negligible, allowing this standardized algebraic formulation to match experimental values within the strict margins required by maritime legislative frameworks.

4.2. Experimental Setup and Model Calibration Framework

Experimental data collection for marine engines in actual service presents significant logistical and operational challenges. Due to the nature of harbor tugboat operations, which involve frequent and rapid load fluctuations during port activities, the highly stable thermodynamic conditions required for high-fidelity combustion measurements are exceptionally difficult to maintain. To ensure data accuracy and reliability, the measurements for this study were performed under a specifically authorized trial. The vessel was granted special permission from port authorities to operate under a steady, high-load condition (81% MCR) by pushing continuously against the quay wall. This unique setup provided the necessary operational stability for capturing 0.5 °CA resolved cylinder pressure data, which would be unobtainable during standard maneuvering. Consequently, while the validation is legally and operationally restricted to this representative high-load point, it offers rare insights into the kinetic behavior of a medium-speed engine within its authentic maritime environment.

For the application of data in the developed simulation model, a four-stroke medium-speed diesel engine Wärtsilä NSD 6L26A was evaluated. The chief technical specifications of the prime mover are detailed below:

- Type: four-stroke medium-speed diesel engine with direct injection;

- Number of cylinders: 6, in-line engine;
- Cylinder diameter: 260 mm;
- Piston stroke: 320 mm;
- Firing order: 1-5-3-6-2-4;
- Maximum continuous power MCR: 1669 kW;
- Maximum continuous speed: 999 rpm;
- Fuel injection time: 14 before top dead center;
- Maximum mean indicated pressure: 1970 kPa;
- Maximum combustion pressure: 16,400 kPa;
- Brake specific fuel consumption BSFC: 199.5 g/kWh @ 100% MCR;
- Compression ratio: 17.5;
- Crankshaft radius to connecting rod length ratio: 0.2461.

The experimental diagnostics were recorded under the following ambient boundary conditions:

- Ambient temperature: 13 °C;
- Atmospheric pressure: 99.99 kPa;
- Relative humidity: 35%.

The NO_x concentration within the exhaust gas stream was measured utilizing a certified Testo 350 Maritime, Titisee-Neustadt, Germany emission analyzer system. To comply with the strict sampling protocols of the IMO NO_x Technical Code 2008, a heated stainless-steel sampling probe was rigidly installed into a designated sampling port on a straight section of the exhaust pipe, positioned 1.5 m downstream of the turbocharger turbine outlet to ensure a homogeneous, unstratified gas sample. The Testo 350 MARITIME system consists of a main analyzer unit containing electrochemical sensors and a gas conditioning assembly (Figure 5), which communicates directly with a handheld terminal interface used for real-time data acquisition (Figure 6). The system holds type-approval certifications from Det Norske Veritas (DNV) and Nippon Kaiji Kyokai (NK).



Figure 5. Testo 350 MARITIME main analyzer unit connected downstream of the turbocharger turbine outlet [29].

Figure 5 does not show the current measured values on the engine under test, but only a representation of the measuring device as promotional material.



Figure 6. Real-time display on the Testo 350 MARITIME handheld control unit during reading of NO_x and other pollutants in exhaust emissions.

The experimental test procedure was executed under strict steady-state monitoring. Once the harbor tugboat stabilized at the permitted 81% MCR quay-wall thermal load, the prime mover was run continuously for 45 min to ensure that all internal fluid temperatures, boost pressures, and exhaust thermal fields reached equilibrium. Following this stabilization window, cylinder pressure data from the MarPrime Ultra device and electrochemical emission logs from the Testo system were acquired simultaneously over a 15-minute operational period, providing the verified baseline value of 889 ppm (10.61 g/kWh).

These physical measurements were utilized to validate the thermodynamic sub-models and systematically select the most accurate kinetic rate parameters ($k_{1,f}$) for this engine class. To evaluate the mathematical sensitivity of the model without resorting to empirical curve-fitting or iterative tuning, a parallel multi-run parametric evaluation was conducted across thirteen distinct kinetic configurations. In each discrete simulation run, only the Arrhenius coefficients (pre-exponential factor, temperature exponent, and activation energy) for the rate-limiting Zeldovich step (Equation (11)) were switched, adopting the parameters established by the various authors listed in Table 3. All other underlying thermodynamic boundary conditions derived from the averaged p - α diagram (Figure 5) and Equations (8)–(10) were kept strictly constant. Following this stabilization window, cylinder pressure data from the MarPrime Ultra device and electrochemical emission logs from the Testo system were acquired simultaneously over a 15 min operational period, providing the verified baseline value of 889 ppm corrected to 13% O₂ (equivalent to 10.61 g/kWh).

These physical measurements were utilized to validate the thermodynamic sub-models and systematically select the most accurate kinetic rate parameters ($k_{1,f}$) for this engine class. Table 3 presents the comparative analysis. In accordance with physical measurement principles, the simulated ppm values are rounded to the nearest integer to reflect the realistic measurement uncertainty threshold of the certified maritime gas analyzer. Furthermore, the term “Error” has been replaced with “Relative Deviation” to precisely represent the numerical variance relative to the experimental baseline.

As compiled in Table 3, the multi-run simulation demonstrates that the numerical framework achieves an extremely low minimum deviation of just -0.93% when operating

under Configuration No. 6. This exceptional degree of predictive correlation strongly validates the model's reliability under high thermal loads. Remarkably, this optimal performance is achieved using the fundamental kinetic parameters proposed by Merker, Schwarz, Stiesch, and Otto [29], which are widely recognized as a benchmark in high-temperature combustion chemistry.

Table 3. Comparative parametric evaluation of thirteen distinct Zeldovich kinetic rate constants ($k_{1,f}$) against experimental marine engine data (experimental baseline: 10.61 g/kWh as 889 ppm at 13% O₂).

No.	$k_{1,f}$ (mol/cm ³ s)	NO (g/kWh)	NO Corrected to 13% O ₂ (ppm)	Relative Deviation (%)	Ref.
1	$k_{1,f} = 1.8 \cdot 10^{14} \cdot e^{(-\frac{38,000}{T})}$	12.21	1014	+14.01	[12]
2	$k_{1,f} = 6.68 \cdot 10^{12} \cdot T^{0.4} \cdot e^{(-\frac{37,707.29}{T})}$	11.17	927	+4.30	[16]
3	$k_{1,f} = 1.778 \cdot 10^{14} \cdot e^{(-\frac{38,370}{T})}$	10.15	843	−5.22	[21]
4	$k_{1,f} = 1.8197 \cdot 10^{14} \cdot e^{(-\frac{38,370}{T})}$	10.38	865	−3.07	[25]
5	$k_{1,f} = 1.82 \cdot 10^{14} \cdot e^{(-\frac{38,370}{T})}$	10.38	862	−3.07	[21]
6	$k_{1,f} = 1.8 \cdot 10^{14} \cdot e^{(-\frac{38,300}{T})}$	10.61	881	−0.93	[29]
7	$k_{1,f} = 1.63 \cdot 10^{14} \cdot e^{(-\frac{38,095}{T})}$	10.57	877	−1.30	[30]
8	$k_{1,f} = 1.58 \cdot 10^{14} \cdot e^{(-\frac{38,031}{T})}$	10.56	877	−1.39	[31]
9	$k_{1,f} = 1.8 \cdot 10^{14} \cdot e^{(-\frac{318,000}{R \cdot T})}$	10.88	903	+1.60	[32]
10	$k_{1,f} = 1.47 \cdot 10^{13} \cdot T^{0.3} \cdot e^{(-\frac{75,286.81}{R \cdot T})}$	10.50	872	−1.95	[33]
11	$k_{1,f} = 1.81 \cdot 10^{14} \cdot e^{(-\frac{38,400}{T})}$	10.18	845	−4.94	[34]
12	$k_{1,f} = 1.4 \cdot 10^{14} \cdot e^{(-\frac{37,900}{T})}$	9.95	826	−7.09	[35]
13	$k_{1,f} = 1.8 \cdot 10^{14} \cdot T^0 \cdot e^{(-\frac{76,300}{R \cdot T})}$	10.15	843	−5.22	[36]

Achieving this level of precision inside the highly complex and transient chamber environment of an operational marine propulsion unit reinforces the validity of the decoupled multi-zone approach. It proves that when paired with high-resolution experimental indicator data, simplified kinetic structures can successfully replicate complex emission behavior without massive computational demand.

It must be explicitly acknowledged, from a methodological standpoint, that validating a chemical kinetic screening based on a single operational point (81% MCR) introduces inherent conceptual limitations. In an actual engine environment, the localized synthesis of NO is exponentially sensitive to micro-scale spatial fluctuations in temperature and species concentrations, which cannot be fully resolved by zero-dimensional or multi-zone diagnostic formulations. Therefore, the selection of Configuration No. 6 (Merker et al.) in Table 3 should not be interpreted as a definitive, universal calibration of the fundamental Zeldovich constants. Rather, it indicates the optimal kinetic parameter set that minimizes cumulative engineering error when operating within a high-resolution, pressure-driven diagnostic digital twin framework for this specific class of medium-speed marine engines. Future research steps will expand this screening protocol to other four-stroke medium-speed engine platforms operating at alternative nominal speeds, as well as large two-stroke slow-speed commercial installations. This upcoming campaign aims to ascertain whether the Hanson and Salimian rate parameters maintain universal cross-platform fidelity or if alternative multi-zone scaling factors must be introduced for crosshead engine layouts.

5. Conclusions

In this study, systematic evaluation and selection of the primary Zeldovich reaction rate constant ($k_{1,f}$) were performed to enhance the predictive reliability of NO emission

frameworks in marine engineering. Based on the experimental and numerical investigations carried out under authentic in-service conditions, the following main conclusions can be drawn:

The findings and calibration protocols established in this study are strictly valid within the context of the developed mathematical model, including its inherent zero-dimensional multi-zone assumptions, simplifications, and boundary limitations. These results demonstrate the performance of alternative kinetic formulations within this specific diagnostic simulation framework and should not be interpreted as a fundamental investigation into the universal chemical kinetics of nitrogen oxide formation in diesel engines.

The developed zero-dimensional multi-zone prognostic model, operating with a high crank-angle resolution of 0.5 °CA, successfully captures the transient in-cylinder pressure and local temperature gradients. This high-resolution temporal resolution is vital for solving the highly temperature-sensitive thermal NO synthesis pathway.

The numerical framework demonstrated an exceptional level of correlation with physical test-bench data acquired under a stable, high-load tugboat operating regime at 81% MCR, which was uniquely accomplished and stabilized via a specialized quay-wall trial.

Through parametric sensitivity screening of thirteen distinct, scientifically established kinetic coefficient sets, the rate constant parameters proposed by Merker, Schwarz, Stiesch, and Otto [29] were isolated as the most precise configuration for this engine category, yielding a minimum numerical deviation of only −0.93%.

The results confirm that the precise selection of Arrhenius pre-exponential factors and activation energies is highly critical for emission modeling under the extreme peak cylinder pressures and thermal loads characteristic of marine prime movers within this modeling framework.

The verified diagnostic methodology provides marine engineers and researchers with a reliable, computationally efficient tool for evaluating and mitigating emissions. This framework is highly suitable for integration into real-time digital twin architectures aimed at ensuring compliance with strict IMO Tier III standards and operational demands within newly designated Emission Control Areas (ECAs).

Future research efforts will focus on expanding this kinetic selection protocol to at least two more four-stroke medium-speed engines and to two-stroke slow-speed engines. This upcoming campaign aims to systematically test the cross-platform universality of the identified Merker et al. [29] constants across different thermodynamic cycles and multi-zone scaling configurations, determining whether alternative scaling tools are required for crosshead engine layouts.

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Abbreviations

MCR	Maximum Continuous Rating
IMO	International Maritime Organization
ACR	Arrhenius Pre-exponential Factor
AERC	Arrhenius Activation Energy Factor
3D-CFD	3D Computational Fluid Dynamics
MARPOL	International Convention for the Prevention of Pollution from Ships
MEPC	Marine Environment Protection Committee
ECA	Emission Control Area
EGCS	Exhaust Gas Cleaning System
MGO	Marine Gas Oil
DNV	Det Norske Veritas
NK	Nippon Kaiji Kyokai
Latin Symbols	
C	Carbon mass fraction in fuel, kg/kg
H	Hydrogen mass fraction in fuel, kg/kg
S	Sulfur mass fraction in fuel, kg/kg
O	Oxygen mass fraction in fuel, kg/kg
$m_{O_2,min}$	Minimum theoretical mass of oxygen required for complete combustion, kg _{O₂} /kg _{fuel}
$m_{air,stoich}$	Minimum theoretical mass of oxygen required for complete combustion, kg _{air} /kg _{fuel}
$m_{air,deliv}$	Mass of delivered air, kg _{air} /kg _{fuel} ^l
p	Cylinder pressure, kPa
p_i	Mean indicated pressure, kPa
p_{ref}	Reference pressure for ideal gas volumetric conversion, kPa
P_i	Indicated engine power, kW
v_m	Mean piston speed, m/s
n	Engine rotational speed (revolutions), rpm
d_c	Cylinder diameter, m
s	Piston stroke, m
R	Universal gas constant, J/(kmol K)
R_{cp}	Specific gas constant of combustion products, J/(kg K)
T	Cylinder gas temperature, K
T_{ref}	Reference temperature for ideal gas volumetric conversion, K
V	Cylinder volume, m ³
$k_{1,f}$	Forward rate constant of the first Zeldovich reaction, cm ³ /(mol s)
$k_{2,f}$	Forward rate constant of the second Zeldovich reaction, cm ³ /(mol s)
$k_{3,f}$	Forward rate constant of the third Zeldovich reaction, cm ³ /(mol s)
K_C	Concentration equilibrium constant, (mol/cm ³) ^{Δn}
K_P	Pressure equilibrium constant, kPa ^{Δn}
x_{N_2}	Mole fraction of nitrogen, mol/mol
x_{O_2}	Mole fraction of oxygen, mol/mol
NO_x	Nitrogen Oxides (collective term for NO and NO ₂)
$[NO]$	Nitric oxide concentration, mol/cm ³
$[NO]_{ppm,13\%O_2}$	Normalized nitric oxide volumetric concentration corrected to 13% O ₂ , ppm
$[NO]_{ppm,raw}$	Raw simulated nitric oxide volumetric concentration, ppm
N_2O	Nitrous oxide
N_2O_3	Dinitrogen trioxide

N_2O_5	Dinitrogen pentoxide
Greek symbols	
τ	Number of strokes per engine cycle (for two-stroke cycle 2, for four-stroke cycle 4)
λ_m	Ratio of crank radius to connecting rod length
α	Crankshaft angle, °CA
α_{air}	Excess air ratio
λ_s	Solar radiation, nm
$\varphi_{O_2, meas}$	Actual measured exhaust oxygen volume fraction, %
$\varphi_{O_2, ref}$	Statutory reference oxygen level in exhaust gas, %

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