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Selective catalytic reduction systems for ammonia combustion in heavy-duty engines-a modelling study

Exhaust Gas Aftertreatment Solutions & CCS

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ABSTRACT

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This study employs catalytic surface kinetic modelling of the NOx reduction efficiency, using ANSYS Chemkin-Pro, for a range of fuel-air equivalence ratios and diverse driving conditions such as cold starts. The simulation has a transient inlet flow into a perfectly stirred reactor model. The NO molar conversion results obtained will be experimentally validated utilizing a fixed catalytic bed reactor. This presentation discusses the results obtained from this modelling study. The reductive effect of unburned NH3, H2 and HC in the exhaust on catalytic systems has not been considered altogether in any one study, so this will be tested under both fuel-lean and rich conditions.

The University of Sheffield is leading this research project in collaboration with industrial partners, Eminox Limited and Interkat Catalyst GmbH, specialists in exhaust after-treatment system design and catalyst manufacture. The boundary conditions were finalised in collaboration with industrial partners to facilitate application in existing vehicle fleet with minimum modifications.

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1 INTRODUCTION

The use of low-carbon fuels, such as ammonia (NH_3) and hydrogen (H_2), either individually or in combination with diesel, has been investigated as a means to decarbonize combustion fuels, yielding both promising results and significant challenges. This research has garnered substantial attention from both industry and academia, focusing on understanding the combustion behaviour of these alternative fuel blends in compression ignition (CI) engines. Additionally, there is a strong emphasis on elucidating the mechanisms of nitrogen oxide (NO_x) formation, particularly nitrous oxide (N_2O), to facilitate the development of effective exhaust after-treatment systems for next-generation nitrogen- and hydrogen-based fuel technologies.

While significant attention has been given to dual-fuel (DF) combustion using NH_3, research on exhaust after-treatment systems for NH_3 and its blends in CI engines remains limited. A critical issue is the increased N_2O emissions observed during NH_3 combustion, which are negligible in conventional diesel combustion. Furthermore, the combined reductive effects of unburned NH_3, H_2, and hydrocarbons (HC) in the exhaust on catalytic treatment systems have not been comprehensively examined in prior studies. Addressing this gap is essential for the development of efficient after-treatment strategies for NH_3-based fuel systems.

This research aims to advance the understanding of NH_3 combustion and its exhaust characteristics through a two-pronged approach. Gas-phase kinetic modelling, performed using ANSYS Chemkin-Pro software, investigates the mechanisms of NO_x formation, with a particular focus on N_2O emissions, under varying conditions such as air-fuel equivalence ratios (Φ), fuel injection timings and durations, inlet gas temperatures and pressures, fuel energy shares, engine speeds, and compression ratios. A direct injection (DI) model, newly integrated into Chemkin-Pro, effectively simulates DF combustion kinetics and predicts engine-out exhaust gas composition under a range of driving conditions, including cold starts and variable speeds. Surface kinetic modelling complements this analysis by examining the deNO_x reactions occurring on catalyst surfaces, with a focus on NO_x reduction efficiencies in the presence of unburned NH_3 and H_2 emissions, and increased water vapour.

1.1 NH_3 and H_2 as fuels for CI engines

Alternative fuels, such as NH_3 and H_2, have garnered significant attention due to their carbon-free molecular structure, which ensures the absence of CO_2, CO, unburned hydrocarbon (UHC), and soot in combustion products [1]. However, H_2 faces practical challenges, most notably its low volumetric energy density, which imposes constraints on on-board storage and significantly increases its cost [2]; [3]. To address these limitations, H_2 carriers like NH_3 offer an effective alternative, mitigating storage issues while retaining the advantages of H_2combustion.

Despite its promise, NH_3 presents challenges of its own. Its low reactivity and reduced flame propagation speed (s_L) result in incomplete combustion, with approximately 20% of injected NH_3 escaping as unburned fuel [4]. Furthermore, NH_3 is highly toxic, with an occupational exposure threshold of 300 ppm, necessitating treatment before being released into the atmosphere [5]; [6]. Hence, the suboptimal fuel properties of NH_3 present challenges for its direct use as a primary fuel, particularly in heavy-duty applications where CI engines are preferred over spark-ignition engines due to their superior efficiency and adaptability. However, the presence of residual NH_3 in the exhaust can be utilized as a reductant for NO_x emissions in catalytic treatment systems [7].

Numerous experimental studies have investigated pure NH_3 combustion, exploring approaches such as increasing compression ratios, preheating intake gases to temperatures above 422 K, and using NH_3-air premixed charges injected at the end of the compression stroke to rapidly raise in-cylinder temperatures and ignite the main NH_3 injection. However, the consensus among researchers is that complete combustion of NH_3 without supplemental carbon-based combustion promoters remains unachieved [1]; [8]. As a result, a dual-fuel (DF) combustion strategy is widely recommended to enable effective utilization of both NH_3 and H_2 in CI engines.

1.2 DF combustion of NH_3 with diesel

NH_3 is most commonly introduced into engines as a gaseous mixture with air through the intake manifold, while a small amount of pilot fuel is directly injected into the cylinder to ignite the NH_3-air mixture [9]. Experimental studies, such as that conducted by [10] have demonstrated that up to 85% of diesel can be replaced with NH_3 on an energy basis. However, the study also revealed that a minimum substitution of 36% NH_3 is required to achieve greenhouse gas (GHG) emissions lower than those of diesel, owing to the production of N_2O, particularly under fuel-lean conditions where N_2O formation is prominent. While dual-fuel (DF) combustion of NH_3 exhibits lower thermal efficiency compared to pure diesel combustion [11], it offers significant reductions in CO_2 emissions and has proven to be an effective approach for facilitating NH_3 combustion in CI engines.

1.3 NO_x emissions in NH_3 combustion

The production of NO_x during combustion is influenced by several factors, including the maximum in-cylinder temperature, oxygen concentration in the combustion zone, the residence time of gases in the flame, the nitrogen content in the fuel, compression ratio (CR), engine speed and load, ignition timing, and thermal dilution [12]; [2]; [5]; [35]; [13]. Numerous studies have demonstrated techniques for minimizing NO_x emissions by modifying the combustion process, such as lowering flame temperature, altering the air-fuel ratio (AFR), and adjusting flame stoichiometry [14]. For example, combustion of NH_3 under fuel-rich conditions and at high pressures has been shown to effectively reduce NO_x emissions, as these conditions limit both temperature and oxygen availability [15]. Additionally, delaying fuel injection timing can decrease the combustion temperature and reduce the fraction of N_2 that undergoes ionization to form thermal NO_x, while optimizing the mass flow rate of fuel further aids in minimizing emissions of fuel [16]; [17].

The trade-off between NO and unburned NH_3 emissions in NH_3 combustion has been examined extensively. [1] formation results from high combustion temperatures, whereas unburned NH_3 emissions are associated with low combustion temperatures. Thus, a simultaneous reduction in both NO and NH_3 emissions is necessary to enable the effective use of NH_3 as a fuel. Studies on NH_3-air mixtures by [18]; [19]; [15] suggest maintaining the equivalence ratio ϕ near 1.1 to balance NO_x and NH_3 emissions. While NO concentrations peak under slightly fuel-lean conditions (ϕ=0.9), they become negligible at ϕ=1.3, where unburned NH_3 emissions increase significantly.

In diesel engines, NO_x emissions typically consist of 90–95% NO and 5–10% NO_2. However, NH_3 combustion produces N_2O at temperatures slightly lower than those required for thermal NO_x formation ($T < 1,300$ K), which are commonly encountered in NH_3-fueled engines. Although N_2O emissions are comparatively low, they pose a significant environmental concern due to their high global warming potential (GWP), which is 276 times that of CO_2, and their ability to react with atmospheric ozone (O_3), depleting it and forming additional NO.

1.4 Post-Combustion NO_x emissions control

Oxidation catalysts are employed to convert HC, CO, and NO in the engine-out exhaust gas into H_2O, CO_2, and NO_2. The NO_2 formed subsequently oxidizes particulate matter (PM) trapped in the diesel particulate filter (DPF) to CO_2 and is simultaneously reduced to NO. Reduction catalysts, on the other hand, predominantly utilize NH_3 as a reductant to convert NO_x into N_2 and water vapor. The effectiveness of catalytic NO_x conversion is influenced by several parameters, including the concentrations of NO_x, water vapor, and O_2, as well as the residence time and temperature. Moisture content below 2.5% in exhaust gas has been shown to decrease catalytic treatment efficiency, while higher levels of moisture were initially believed to have negligible effects on NO conversion [20]. However, subsequent studies revealed that H_2O affects both the efficiency and stability of the denitrification process. When H_2O concentrations exceed those of NO and NH_3, a weak film forms at the catalyst's active sites, increasing mass transfer resistance and temporarily reducing catalytic activity. Additionally, H_2O contributes to the destruction of the catalyst structure and promotes the formation of hydroxyl species. These hydroxyl species can react with NH_3 to form ammonium bisulphate (NH_4HSO_4) or ammonium sulphate $(NH_4)_2SO_4$, which can block catalyst pores or cover active sites, leading to reversible inactivation [21].

Higher O_2 concentrations have been observed to enhance NO conversion efficiency [22]. However, at high gas hourly space velocities[1] (GHSV), the residence time for NH_3 to diffuse to active sites on the catalyst decreases, reducing catalytic performance and increasing NH_3 slip. Furthermore, as catalyst temperature rises, NH_3 saturation levels decrease, leading to an increase in NH_3 slip [35].

Studies investigating catalyst requirements for DF combustion in CI engines remain limited. For instance, research by [12] and [23], has primarily focused on systems using H_2 as the main fuel. The EGT of an NH_3-n-heptane DF CI engine differs significantly from that of a diesel-fired engine, particularly due to the presence of high water vapor levels

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[1] Gas hourly space velocity (GHSV) refers to the ratio of the exhaust gas flow rate passing through the catalyst block (m^3/h) and the total volume of the catalyst block in the catalyst chamber (m^3).

2 METHODOLOGY

2.1 NH_3-diesel DF combustion

The gas-phase kinetic modeling of NH_3-n-heptane combustion was simulated using ANSYS Chemkin-Pro 2022 R2 software, employing the Direct Injection (DI) model with dual injectors to predict engine-out exhaust gas characteristics. In this model, fuel is injected at a constant rate, with each injection event treated as a separate inlet activated at a specified start of injection (SOI) timing.

The reduced single component n-heptane (n-C_7H_{16}) reaction mechanism, developed by the University of Wisconsin Engine Research Centre has been validated under both constant volume and engine conditions. This mechanism is widely accepted for modeling pure diesel combustion in DI engines [24]; [25]. N-heptane serves as a surrogate fuel for diesel due to its similar physicochemical properties and chemical reactivity, as demonstrated in studies by [26]; [27]; [28]; [5]; [29]; [30].

For NH_3 combustion, the Tian mechanism has proven effective in accurately predicting NO_x emissions from NH_3-air flames, particularly at high NH_3 fractions [31]. Thermodynamic data for eight temperature-dependent liquid properties, such as density, specific heat capacity (C_p), critical temperature (T_c), heat of vapourization, vapour pressure, surface tension, viscosity, and thermal conductivity was added for NH_3. NH_3-n-heptane DF reaction mechanism is derived by combining the NH_3 mechanism with the reduced n-heptane mechanism using ANSYS Workbench, eliminating duplicate reactions and redundant species, as described by [32].

The combined reaction mechanism was validated, by obtaining the ignition delay time (IDT) of a 40% NH_3/60% nC_7H_{16} mixture at 10 bar, Φ=1, and 18.37% O_2, as an equivalence of time at which OH radical concentration peaked, using a 0-D closed homogeneous reactor model, under constant-pressure conditions across a wide temperature range of 700-1400 K. The modeled IDT, defined as the time at which OH radical concentration peaked, was compared with experimental IDT data from shock tube experiments under identical conditions reported in the literature [28], as a function of temperature. The comparison shown in figure 2.1 indicates a slight over-prediction of IDT.

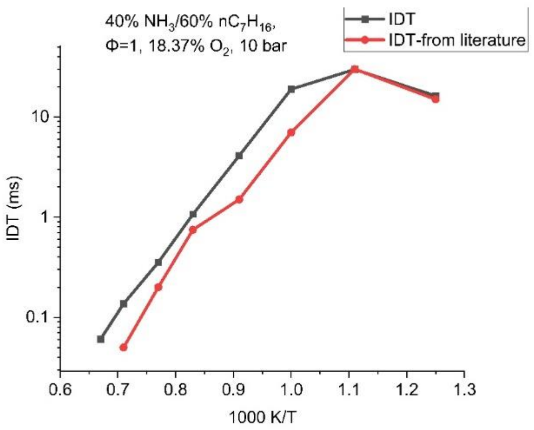

Figure 1. Comparison of modelled IDT with experimental shock tube IDT from the literature [28] for a 40% NH_3/60% nC_7H_{16} mixture at 10 bar, Φ=1, and 18.37% O_2 concentration.

In DF combustion, a premixed mixture of NH_3 and air is introduced first, followed by a pilot injection of n-heptane near before top dead center (bTDC). A short injection duration of around 2°CA was selected, as numerical studies on NH_3-H_2-diesel DF combustion by (Lamas and Rodriguez, 2019) found that a similarly short injection duration of 1°CA resulted in the largest NO_x reduction. In this study, the CR was varied between 13, 16, and 17, while engine speeds of 900, 1200, and 1500 rpm were considered.

The simulation divides the combustion cylinder into zones, representing spray parcels or individual reactors. Zone 1 initially contains no liquid fuel and shares the same gas composition and temperature as the air zone (ANSYS, 2022). Each spray parcel comprises droplets with similar attributes. Zone 1 represents engine start-up conditions, zone 180 corresponds to steady combustion at a constant speed or load, and zone 361 simulates engine shutdown.

2.2 Post-combustion treatment

Ansys Chemkin-Pro 2022 R2 software is utilized for surface kinetic modeling of exhaust after-treatment systems in CI engines using the perfectly stirred reactor (PSR) model. This approach enabled the prediction of exhaust gas characteristics and NO_x reduction efficiency by coupling gas-phase and surface kinetics. The PSR model assumes well-mixed reactor contents, where reaction rates dominate over mixing processes, and treats the system as adiabatic, with no heat loss assumed in the calculations.

Several assumptions underpin the modeling of homogeneous reactors in this framework. First, mass transport to the reactor walls is considered infinitely fast, making the relative importance of surface and gas-phase reactions dependent solely on surface-to-volume ratios and reaction rates, rather than transport constraints. Second, flow through the reactor is characterized by a nominal residence time, determined by the flow rate and reactor volume.

In this simulation, gas-phase reactions are neglected because surface conversion reactions dominate. Catalytic conversion of NO_x, CO, and UHCs is modeled using a Pt/Rh catalyst surface reaction mechanism designed for three-way catalysts, as described by [33]. The mechanism distinguishes between two types of adsorption sites: Pt(S), denoted as (S), and Rh(S1), denoted as (S1). It is specifically valid for a 75% Pt and 25% Rh ratio, as the activation energies dependent on surface coverage are scaled accordingly.

Within the three-way catalyst, C_3H_6 oxidation occurs on Pt sites, where species like O_2, C_3H_6, H_2, H_2O, CO_2, and CO are first adsorbed, followed by desorption, and surface reactions of oxidation of C_3H_5 to OH and C. On Pt sites, NO is reduced, while on Rh sites, NO reduction and CO oxidation occur simultaneously.

Table 1. Catalyst parameters

Parameter	Value
Catalyst composition	75% Pt and 25% Rh three-way catalyst
Catalyst reactor volume	1,400 cm^3
Reactive (internal) surface area	59,000 cm^2
Initial temperature of engine out	296.15 K
Pressure	1 atm
Initial inlet flow rate of engine out	$1.71 * 10^{-3}$ kg/s

The initial conditions for the converter system are assumed to represent air prior to the exhaust gas entering the system. Surface site fractions are estimated based on an understanding of surface conditions or through initial mechanism testing, with a uniform site distribution assumption. For the platinum portion of the catalyst, O(S) is specified as the dominant site, while CO(S1) is specified for the rhodium portion, each set to 1.0 to define the initial catalyst surface conditions.

The gas inlet, termed "engine-out," includes mole fractions for CO, NO, UHC, and O_2, derived from combustion modelling, with N_2 representing the balance of the gas composition. C_3H_6 is used as a chemical surrogate for UHCs. The simulation duration is set to 100 seconds, with a maximum solver time step of 1 millisecond, solution output intervals of 10 seconds, and data-saving intervals of 1 second. Only the maximum ammonia energy share (AES) of 89% has been evaluated, as it yielded optimal emissions performance and indicated work output.

Table 2. Mole fraction of engine-out exhaust to catalyst reactor

Engine conditions	Mole fraction of engine-out exhaust to catalyst reactor							
	N_2	NO	CO_2	CO	CH_4	H_2	H_2O	O_2

CR= 16, 1200 rpm, phi=1, zone 1	0.6795	0.0001	0.0467	0.0182	0.0000	0.0378	0.2178	0.0000
CR= 16, 1200 rpm, phi=1, zone 181	0.6893	0.0000	0.0447	0.0000	0.0000	0.0433	0.2226	0.0000
CR= 16, 1200 rpm, phi=1, zone 361	0.7120	0.0031	0.0691	0.0010	0.0000	0.0014	0.2140	0.0000
CR= 16, 1200 rpm, phi=1, avg zone	0.6797	0.0002	0.0471	0.0180	0.0000	0.0371	0.2179	0.0000
CR= 13, 1200 rpm, phi=1, avg zone	0.6806	0.0003	0.0495	0.0156	0.0000	0.0388	0.2152	0.0000
CR= 17, 1200 rpm, phi=1, avg zone	0.6798	0.0002	0.0467	0.0183	0.0000	0.0370	0.2179	0.0000
CR= 16, 900 rpm, phi=1, avg zone	0.6798	0.0002	0.0469	0.0181	0.0000	0.0370	0.2180	0.0000
CR= 16, 1500 rpm, phi=1, avg zone	0.6802	0.0003	0.0473	0.0177	0.0000	0.0374	0.2171	0.0000

3 RESULTS AND DISCUSSION

3.1 NH3-n-heptane DF combustion

For NH_3 DF combustion, the CR is varied between 13, 16, and 17 at an engine speed of 1200 rpm. These CR values are commonly employed in similar numerical studies, such as [28]. The results indicate that lower CRs produce higher NO emissions, with zone 361 generating more NO across all tested CRs, as illustrated in Figure 2.

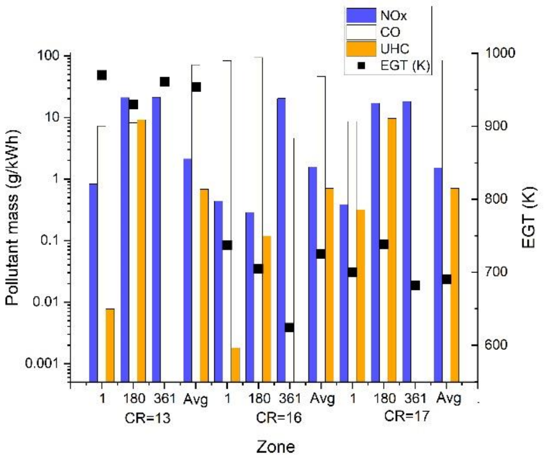

Figure 2. Comparison of pollutant concentration and EGT as a function of zone and CR value from

89% NH_3-n-heptane DF combustion at constant engine speed of 1200 rpm and stoichiometric conditions. Zone 1 represents an engine-start, zone 180 in NH_3-n-heptane combustion represents combustion at a constant speed or load, and zone 361 represents an engine stop.

Engine speed is varied at 900, 1200, and 1500 rpm. Higher speeds result in increased NO emissions, correlating with a rise in EGT, as shown in Figure 3. Across all speeds, zone 1 is the primary contributor to CO and H_2 emissions. The indicated work output reaches its maximum value at the highest tested speed of 1500 rpm.

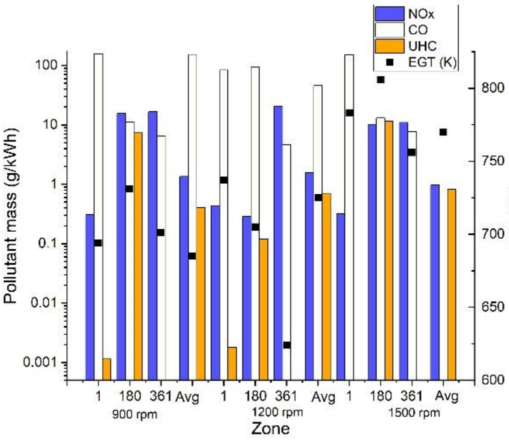

Figure 2. Comparison of pollutant concentration and EGT as a function of zone and engine speed from 89% NH_3-n-heptane DF combustion at constant CR of 16 and stoichiometric conditions.

3.2 Post-combustion treatment

Molar conversion of C_3H_6, NO, CO, and CO_2, X_{C3H6}, X_{NO}, X_{CO}, and X_{CO2} is calculated using equation 1

$$X_i=\frac{F_{i_{in}}-F_{i_{out}}}{F_{i_{in}}}\times 100 \tag{1}$$

where F_i denotes the concentration of “i” species, the subscripts “in” and “out” indicate the gas concentration at the reactor’s inlet and exit, respectively, X denotes conversion [34].

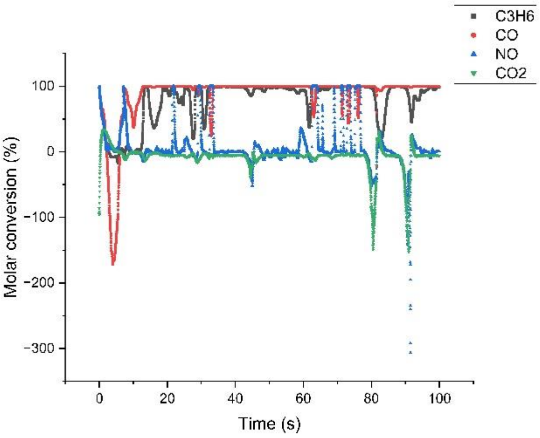

Figure 4. Molar conversion of C_3H_6, NO, CO, and CO_2 as a function of time

Molar conversions of C_3H_6, CO, NO are analyzed as functions of time, with conversion effectiveness determined by comparing the inlet mole fractions to outlet mole fractions or by directly calculating conversion efficiencies. Under the specified conditions, C_3H_6 and CO exhibit more effective conversion than NO. During the early stages of the simulation, conversion rates are low for all species. While the calculated molar conversion at t=0 is 100%, this outcome is solely a result of setting the initial reactor conditions to pure air, which dictates the initial exit flow composition.

At certain points, the calculated conversion rates for CO and NO become negative, a phenomenon arising from their potential formation on the catalyst surface as surface states evolve, effectively causing these species to be "produced." The relationship between inlet and exit gas temperatures over time indicates that the gas heats up relative to the inlet due to exothermic surface reactions. The catalyst becomes effective only after reaching a temperature above approximately 600 K, consistent with findings reported by Chatterjee et al.

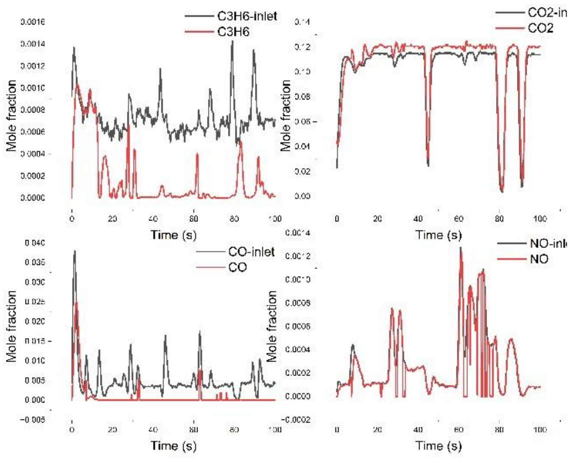

Figure 3. Mole fraction of C_3H_6, NO, CO, and CO_2 at the inlet and outlet of the catalytic converter as a function of time.

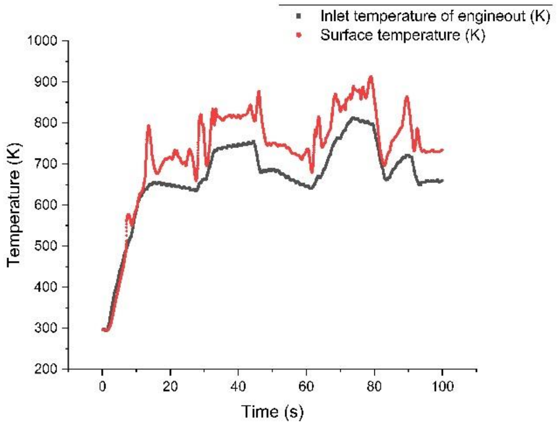

Figure 6. Temperature of engine-out exhaust gas and catalyst surface in K versus time

4 CONCLUSIONS

The findings reveal that optimal engine performance, in terms of indicated work output and reduced emissions, is achieved at 89% ammonia energy share (AES) under stoichiometric conditions ($\Phi = 1$), with a compression ratio of 16, engine speed of 1200 rpm, NH_3 injection at -22.45 crank angle for 7.05°, and n-heptane injection at -12.45 crank angle for 2°. This condition minimizes NO_x, CO_2, CO, and UHC emissions, while enhancing work output. However, N_2O emissions are significantly higher during cold starts in fuel-lean conditions and are also observed under stoichiometric conditions at lower AES levels. The potential for unburned NH_3 to reduce NOx to N_2 is most effective under slightly fuel-rich conditions ($\Phi \geq 1$), while H_2 and H_2O emissions, which act as indirect greenhouse gases, increase in the exhaust. The impact of these emissions on catalyst performance is critical for the development of efficient after-treatment strategies.

The analysis of molar conversions for C_3H_6, CO, and NO highlights differences in conversion effectiveness under the given conditions, with C_3H_6 and CO exhibiting higher conversion efficiencies compared to NO. Early in the simulation, low conversion rates are observed for all species, with an artificially high initial molar conversion due to the reactor's pure air starting conditions. Negative conversion rates for CO and NO at certain intervals reflect their formation on the catalyst surface as surface states evolve, demonstrating the dynamic interaction between surface and gas-phase chemistry. The rise in gas temperature, attributed to exothermic surface reactions, emphasizes the importance of thermal activation, as the catalyst becomes effective only after reaching approximately 600 K.

This study highlights the importance of integrating gas-phase and surface kinetic modelling to optimize NH_3 combustion in CI engines. The results provide valuable insights into achieving lower emissions and higher performance while addressing challenges associated with N_2O emissions and catalytic system efficiency, paving the way for the adoption of NH_3 as a viable low-carbon fuel.

5 ACRONYMS, ABBREVIATIONS

AES	Ammonia energy share
CA	Crank angle (º)
CI	Compression ignition
CR	Compression ratio
DF	Dual-fuel
DI	Direct injection
EGT	Exhaust gas temperature (K)
IDT	Ignition delay time
PSR	Perfectly stirred reactor
SOI	Start of injection
TDC	Top dead centre
UHC	Unburned hydrocarbon

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