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REVIEW ARTICLE

Integrated catalytic systems for simultaneous NOx and PM reduction: a comprehensive evaluation of synergistic performance and combustion waste energy utilization

Dikra Bakhchin[1] · Rajesh Ravi[1] · Oumaima Douadi[1] · Mustapha Faqir[1] · Elhachmi Essadiqi[1]

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Abstract
The global transition towards sustainable automotive vehicles has driven the demand for energy-efficient internal combustion engines with advanced aftertreatment systems capable of reducing nitrogen oxides (NOx) and particulate matter (PM) emissions. This comprehensive review explores the latest advancements in aftertreatment technologies, focusing on the synergistic integration of in-cylinder combustion strategies, such as low-temperature combustion (LTC), with post-combustion purification systems. Selective catalytic reduction (SCR), lean NOx traps (LNT), and diesel particulate filters (DPF) are critically examined, highlighting novel catalyst formulations and system configurations that enhance low-temperature performance and durability. The review also investigates the potential of energy conversion and recovery techniques, including thermoelectric generators and organic Rankine cycles, to harness waste heat from the exhaust and improve overall system efficiency. By analyzing the complex interactions between engine operating parameters, combustion kinetics, and emission formation, this study provides valuable insights into the optimization of integrated LTC-aftertreatment systems. Furthermore, the review emphasizes the importance of considering real-world driving conditions and transient operation in the development and evaluation of these technologies. The findings presented in this article lay the foundation for future research efforts aimed at overcoming the limitations of current aftertreatment systems and achieving superior emission reduction performance in advanced combustion engines, ultimately contributing to the development of sustainable and efficient automotive technologies.

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Highlights

- This article reviews recent innovations in effective aftertreatment systems for the purification of diesel engine emissions, especially nitrogen oxides and particulate matter.
- This review depicts various methodologies, including selective catalytic reduction (NH3-SCR) to reduce NOx emissions and diesel particulate filters to minimize soot and particulate matter.
- This article evaluates various novel materials and methodologies, including LNT-SCR, to reduce NOx emissions and diesel particulate trapping and oxidation to minimize ash, soot, and PM.
- This review proposes a novel combined catalytic system with high efficiency to significantly enhance the overall thermal and catalytic efficiency of aftertreatment systems.
- This article explores the electrification of emissions aftertreatment modules, the use of thermoelectric oxides for boosting catalyst performance at start-up, and the cooling of exhaust for energy extraction and conversion purposes as potential engineering solutions for emission reduction.

Extended author information available on the last page of the article

Keywords GHG alleviation · LTC · ICE thermal management · NOx and PM mitigation · NH_3-SCR · Heterogenous catalysis technologies · Combined catalytic systems

Introduction

The global transition towards sustainable automotive vehicles has created a widespread demand for energy-efficient internal combustion engines with lower emissions (Huang et al. 2023b). Specifically, advanced aftertreatment systems, combined with in-cylinder innovations such as low-temperature combustion (LTC), can dramatically reduce particulate matter and nitrogen oxide (NOx) emissions, which are byproducts of the combustion process (Douadi et al. 2022; Kim et al. 2023). The development and optimization of these technologies are crucial for meeting increasingly stringent emission regulations while maintaining high engine performance and efficiency (Chun et al. 2023; Tamilvanan et al. 2023; Panahi et al. 2019). This comprehensive review aims to provide an in-depth overview of the latest research advancements in aftertreatment methodologies, including selective catalytic reduction (SCR), lean NOx traps (LNT), and diesel particulate filters (DPF) (Gao et al. 2019). The primary objective is to explore novel approaches for energy conversion and recovery that can enhance emission reduction capabilities and overall system efficiency. By examining the synergistic effects of pre-combustion and post-combustion purification technologies, this review seeks to identify strategies for effectively mitigating emissions while optimizing engine performance (Boretti 2020; Leach et al. 2020).

Nitrogen oxides (NOx) are primarily formed through three key mechanisms during combustion including thermal NOx, prompt NOx, and fuel NOx. Thermal NOx formation occurs at high temperatures (above 1800 K) via the Zeldovich mechanism, where molecular nitrogen (N_2) reacts with oxygen (O_2) to form nitrogen monoxide (NO). This reaction pathway involves intermediate species such as atomic nitrogen (N) and is highly temperature-dependent, becoming significant in high-temperature combustion environments. Prompt NOx formation takes place at lower temperatures near the flame front. This mechanism involves the reaction of atmospheric nitrogen with hydrocarbon radicals (CH) to form hydrogen cyanide (HCN), which further reacts to produce NO. Fuel NOx is relevant for fuels containing bound nitrogen, such as coal and heavy oils. This pathway includes the release of nitrogen from the fuel matrix and its subsequent oxidation to NO during combustion.

Thermal NOx formation: This occurs at high combustion temperatures, typically above 1800 K, where molecular nitrogen (N_2) reacts with oxygen (O_2) to form nitrogen monoxide (NO). The reaction follows the Zeldovich mechanism:

- $N_2 + O \rightarrow NO + N$
- $N + O_2 \rightarrow NO + O$
- $N + OH \rightarrow NO + H$

Prompt NOx formation: Also known as Fenimore NOx, this occurs at the flame front and involves the reaction of atmospheric nitrogen with hydrocarbon radicals (CH). This mechanism is significant at lower temperatures compared to thermal NOx:

- $N_2 + CH \rightarrow HCN + N$
- $HCN + OH \rightarrow CN + H_2O$
- $CN + O_2 \rightarrow CO + NO$

Particulate matter (PM) emissions, especially soot, form through a multi-stage process involving nucleation, surface growth, coagulation, oxidation, and aggregation. Nucleation initiates with the formation of small particles from gas-phase precursors like polycyclic aromatic hydrocarbons (PAHs). These nuclei then grow through surface growth, where additional hydrocarbons condense and react on the particle surface. Coagulation causes smaller particles to collide and combine into larger aggregates, reducing particle numbers but increasing their size. Oxidation processes, involving reactions with HO^- radicals, can partially reduce PM mass by breaking down some particles. Finally, aggregation results in the formation of larger particle clusters with a fractal-like structure. The characteristics and amount of PM can be influenced by combustion conditions, fuel composition, and the efficiency of after treatment systems such as diesel particulate filters (DPF). Both NOx and PM emissions are mitigated through strategies like low-temperature combustion (LTC), exhaust gas recirculation (EGR), and advanced after treatment technologies, which aim to balance and reduce these harmful byproducts while maintaining engine performance (Dahake et al. 2023).

Low-temperature combustion strategies, such as reactivity-controlled compression ignition (RCCI) and partially premixed compression ignition (PPCI), have emerged as promising techniques for overcoming the traditional NOx/soot trade-off inherent in diesel combustion (Venugopal et al. 2021; Suraj et al. 2022). These advanced combustion modes operate at lower temperatures, avoiding the formation of both NOx and soot, regardless of the local equivalence ratio (Jiang et al. 2020). LTC has the potential to significantly reduce engine-out emissions, thereby relaxing the demands on aftertreatment systems. However, the implementation of

LTC poses unique challenges for aftertreatment systems, particularly SCR, in low-temperature and cold-start conditions (Marzouk 2023; Zhang et al. 2021). SCR catalysts, which rely on the injection of a reducing agent (typically ammonia derived from urea) to convert NOx into nitrogen and water, face limitations in terms of catalytic activity, and ammonia slip at low exhaust temperatures (Huang et al. 2023a). This issue is especially pronounced during cold starts when a significant portion of NOx is emitted. The light-off temperature required for efficient NOx reduction is often too high for real engine operating conditions, leading to unabated NOx emissions (Zheng et al. 2023). Additionally, side reactions can lead to the formation of nitrous oxide (N_2O), a potent greenhouse gas with a global warming potential 298 times higher than carbon dioxide. These challenges necessitate the development of advanced SCR catalysts with improved low-temperature activity, sulfur tolerance, and thermal stability (Wardana and Lim 2023). Lean NOx traps, which store NOx under lean conditions and reduce it to nitrogen under rich conditions, also face challenges in terms of storage capacity, regeneration efficiency, and durability. The integration of LNT and SCR systems has shown promise in enhancing NOx reduction performance, but further research is needed to optimize these hybrid configurations for LTC applications (Senthil and Vijay 2023).

Diesel particulate filters, designed to capture and oxidize soot particles, must cope with the different particulate matter characteristics resulting from LTC (Sun et al. 2020). The lower exhaust temperatures associated with LTC can hinder passive regeneration, necessitating the development of advanced regeneration strategies and catalytic coatings to maintain DPF efficiency and durability (Wong et al. 2023) This review critically examines the current state of aftertreatment technologies and their integration with LTC strategies. It explores novel catalyst formulations, such as zeolite-based materials, perovskites, and mixed metal oxides, which have shown promise in enhancing low-temperature performance and durability. The review also investigates the potential of energy conversion and recovery techniques, such as thermoelectric generators and organic Rankine cycles, to harness waste heat from the exhaust and improve the overall efficiency of the aftertreatment system. Furthermore, this review delves into the complex interactions between engine operating parameters, combustion kinetics, and emission formation in LTC engines. By understanding the trade-offs between combustion efficiency, engine performance, and emissions, researchers can develop targeted strategies for optimizing both in-cylinder and aftertreatment processes. Advanced modeling techniques, such as computational thermal studies and kinetic simulations, are mediated as powerful tools for guiding the design and optimization of integrated LTC-aftertreatment systems. The review also highlights the importance of considering real-world driving conditions and transient operation in the development and evaluation of aftertreatment systems for LTC engines. Figure 1 shows a schematic diagram of a typical LTC diesel engine setup. Cold starts, low-load operation, and frequent transients pose significant challenges for emission control, requiring adaptive and robust control strategies. The integration of advanced sensors, diagnostics, and control algorithms

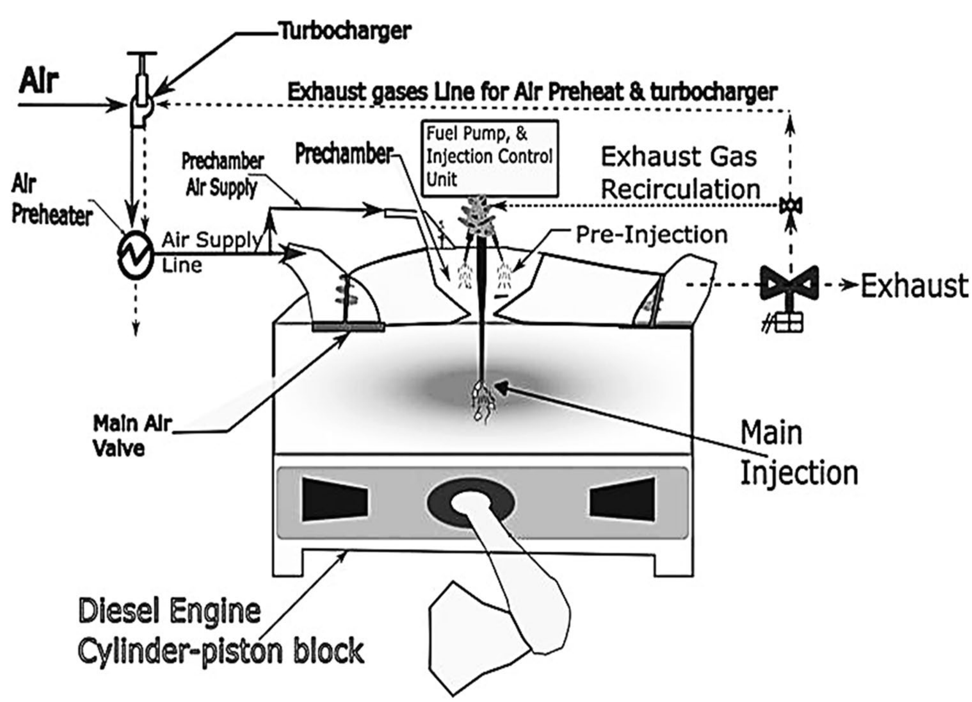

Fig. 1 Schematic diagram of a typical LTC diesel engine setup (Latha et al. 2019)

is explored as a means to ensure optimal performance and compliance with emission regulations under diverse operating conditions.

By providing a comprehensive analysis of the advancements and challenges in aftertreatment systems for LTC engines, this review aims to contribute to the development of sustainable and efficient automotive technologies. The insights gained from this study can guide future research efforts towards overcoming the limitations of current aftertreatment technologies in low-temperature conditions and achieving superior emission reduction performance in advanced combustion engines (Bakhchin et al. 2023; Manjunath et al. 2023). The comprehensive nature of this review, covering the latest advancements in aftertreatment technologies, their integration with LTC strategies, and the consideration of real-world driving conditions, makes it a valuable resource for researchers, engineers, and legislators working towards the development of clean and efficient automotive technologies. By providing a critical analysis of the state-of-the-art and identifying promising research avenues, this review aims to accelerate the progress towards sustainable transportation solutions that meet the growing demand for energy-efficient and cleaner vehicles.

NOx and PM emission trade-offs

Trade-offs between NOx and PM emissions in low-temperature combustion

Diesel engines have high fuel efficiency and energy density, but face challenges with soot and NOx emissions due to combustion conditions (Zhang et al. 2023a). Local equivalence ratio and combustion temperature affect NOx and soot emissions. Standard diesel combustion at high temperatures generates NOx and soot, but lower temperatures can prevent their formation (Riyadi et al. 2023; Panda et al. 2022). Low-temperature premixed combustion PCCI research aims to address the NOx/soot trade-off by achieving more homogeneous air-fuel mixtures (Teoh et al. 2022). Advanced strategies like RCCI and PCCI target lower local equivalence ratios and temperatures to reduce NOx and soot (as shown in Fig. 2).

Thus, LTC can effectively reduce NOx and soot formation through careful control of fuel reactivity and injection timing. However, implementing LTC comes with challenges such as increased HC and CO emissions, combustion instability, and a limited operating range (Gürbüz 2020).

Strategies for simultaneous reduction of NOx and PM

In order to utilize LTC for reducing NOx and PM emissions, a comprehensive approach involving in-cylinder and aftertreatment strategies is needed. In-cylinder methods optimize combustion, while aftertreatment systems address remaining pollutants. EGR is a promising in-cylinder strategy that lowers combustion temperature and suppresses NOx formation. Careful optimization of EGR rate is crucial to balance NOx and soot reduction. Manipulating fuel injection parameters can also help control heat release and reduce NOx and soot formation. Post-injections can aid in soot oxidation and reducing PM emissions. Fuel formulation, such as biodiesel, alcohols, and natural gas, can affect NOx and soot trade-off. The impact on NOx emissions varies with different fuel properties and engine conditions. Advanced fuel blends are being researched to optimize NOx and soot reduction (Lu et al. 2023). Table 1 summarize recent technique for simultaneous NOx, PM reduction.

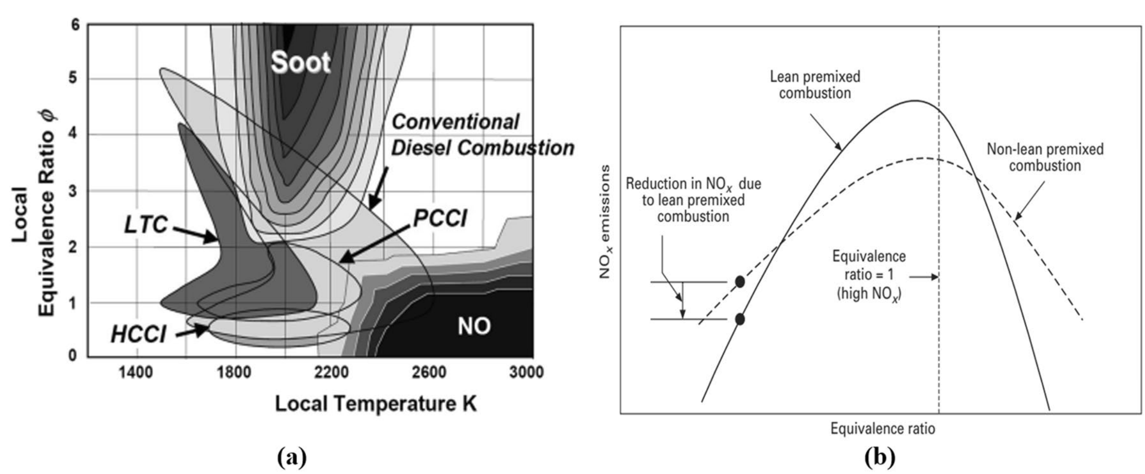

Fig. 2 **a** Optimized local equivalence ratio of low-temperature PCCI and HCCI for low emissions (Li et al. 2023). **b** The effect of lean premixed combustion on NOx attenuation. (Mohd Nurazzi et al. 2021)

Table 1 Summary of current technique for similtaneous removal of NOx,PM

Technique	Properties	Advantages	Disadvantages
LTC strategies	Lower combustion temperatures. More homogeneous air-fuel mixtures	Significant reduction in NOx and soot emissions	Increased HC and CO emissions Combustion instability Limited operating range
RCCI (reactivity-controlled compression ignition)	Combines two fuels with different reactivities Controlled auto-ignition	Flexibility in fuel types Potential for high efficiency and low emissions	Complex fuel system. Re quires precise control of fuel ratios and timing
PPCI (partially premixed compression ignition)	Premixing of fuel and air before compression Operates at lower temperatures	Reduced NOx and soot formation	Challenges with cold start and low-load conditions, Increased HC and CO emissions
SCR (selective catalytic reduction)	Uses a reducing agent (usually ammonia) to convert NOx to nitrogen and water	High NOx conversion efficiency	Efficiency drops at low temperatures (<200), ammonia slip, requires precise control of reducing agent dosing
LNT(lean NOx trap)	Stores NOx during lean operation and reduces it to nitrogen during rich operation	No need for external reducing agent (such ammonia, Adblue refueling).	Sensitive to sulfur poisoning Requires precise lean-rich cycling control
DPF(diesel particulate filter)	Captures and oxidizes soot particles	Effective in reducing particulate emissions	Increased backpressure. Requires regeneration to avoid clogging
Combined LNT-SCR systems	LNT stores NOx and generates ammonia SCR uses generated ammonia for further NOx reduction	Maximizes NOx conversion efficiency over a wide temperature range	Complex system requiring optimization of catalyst formulation, sizing, and regeneration strategy
Advanced catalysts (e.g., Cu-zeolites, Fe-zeolites)	High surface area and thermal stability. Enhanced low-temperature activity	Improved low-temperature NOx conversion	At a developmental stage. Long-term durability needs assessment. Not commercialized yet.
Fuel formulation (e.g., biodiesel, alcohols, natural gas)	Different chemical properties affecting combustion and emissions	Potential to optimize NOx and soot trade-off. Renewable fuel sources	Variation in impact on NOx emissions depending on fuel properties and engine conditions

Despite effective in-cylinder strategies, aftertreatment systems are still necessary for meeting emission regulations. SCR is commonly used for NOx reduction in diesel engines. SCR performance depends on exhaust temperature, with optimal efficiency in a narrow range (Velmurugan et al. 2024). Low-temperature SCR catalysts are being developed to achieve high NOx conversion at temperatures below 200°C. Zeolite-based catalysts, like Cu-zeolites and Fe-zeolites, show promise due to high surface area, thermal stability, and ammonia storage at low temperatures (Laguna et al. 2021). Novel catalyst support materials such as ceria-zirconia and titanium dioxide are explored to enhance low-temperature activity and sulfur resistance (Li et al. 2022). Lean NOx traps (LNTs) store NOx under lean conditions and reduce it under rich conditions. LNTs oxidize NOx to NO_2 and store it as nitrates, releasing and reducing it under rich conditions. Figure 3 depicts the exhaust gas conversion process through oxidation catalysts. LNTs do not need an external reducing agent but are sensitive to sulfur poisoning and require precise lean-rich cycling control (Naik and Dharmadhikari 2023). The combination of LNT and SCR systems, known as LNT-SCR or NSR-SCR, is a promising solution for efficient NOx reduction in LTC engines. LNT functions as a NOx storage device and ammonia generator, while downstream SCR catalyst uses the generated ammonia for further NOx reduction (Bhagat et al. 2023). This synergistic approach maximizes NOx conversion efficiency over a wide temperature range. Optimizing the LNT-SCR system, including catalyst formulation, sizing, and regeneration strategy, is crucial for performance and fuel penalty minimization (Jung and Kim 2020).

DPFs are commonly used for PM reduction by trapping soot particles. Soot accumulation in DPFs requires periodic regeneration, often involving high-temperature oxidation. Low-temperature combustion poses challenges for DPF regeneration due to decreased exhaust temperatures (Khdary et al. 2022). Catalyzed DPFs (CDPFs) are developed to enhance soot oxidation at lower temperatures. Incorporating catalytic materials onto DPFs can improve soot ignition and regeneration efficiency. Fuel-borne catalysts are explored to enhance soot oxidation kinetics in DPFs. Active regeneration strategies increase exhaust temperature but may impact fuel consumption. SCR-on-DPF integration is a cost-effective solution for NOx and PM reduction (Ahmad et al. 2022). Optimization of catalyst coating and regeneration strategies is crucial for SCR-on-DPF systems. Waste heat recovery technologies can enhance LTC engine efficiency and aftertreatment systems. LTC engine exhaust gas contains thermal energy that can be converted into useful work. Figure 4 illustrates ICE thermal energy conversion through a cooling system using WHR. TEGs convert temperature gradient into electrical energy using the Seebeck effect. ORC systems use exhaust heat to generate mechanical or electrical power via a turbine (Zhang et al. 2023b). The combination of ORC with LTC engines enhances thermal efficiency and boosts power for aftertreatment. Turbocompounding uses an extra turbine in the exhaust to recover energy from high-pressure gases. The turbine's mechanical energy can aid the engine or power a generator. Turbocompounding enhances LTC engine fuel efficiency and provides extra power for aftertreatment. Integrating waste heat recovery with LTC engines and aftertreatment needs a comprehensive approach. Design optimization and control strategies are crucial for maximizing system efficiency. Coordination with engine and aftertreatment operation is key for optimal performance (Lisi et al. 2020; Woon et al. 2023).

The requirements of SCR technology development

Principles and types of SCR catalysts

Selective catalytic reduction (SCR) is a widely used technique for NOx reduction in diesel vehicles. Urea-SCR

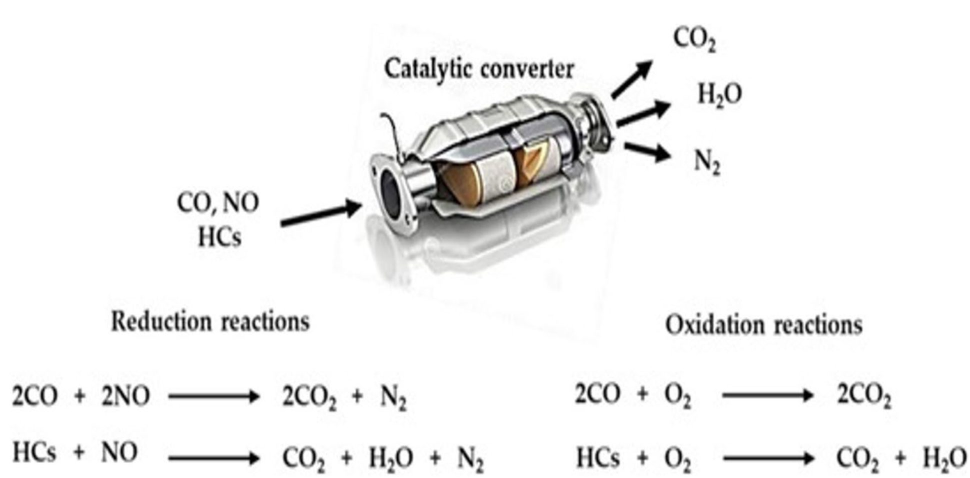

Fig. 3 Exhaust gas conversion process through oxidation catalysts (Bessagnet et al. 2021)

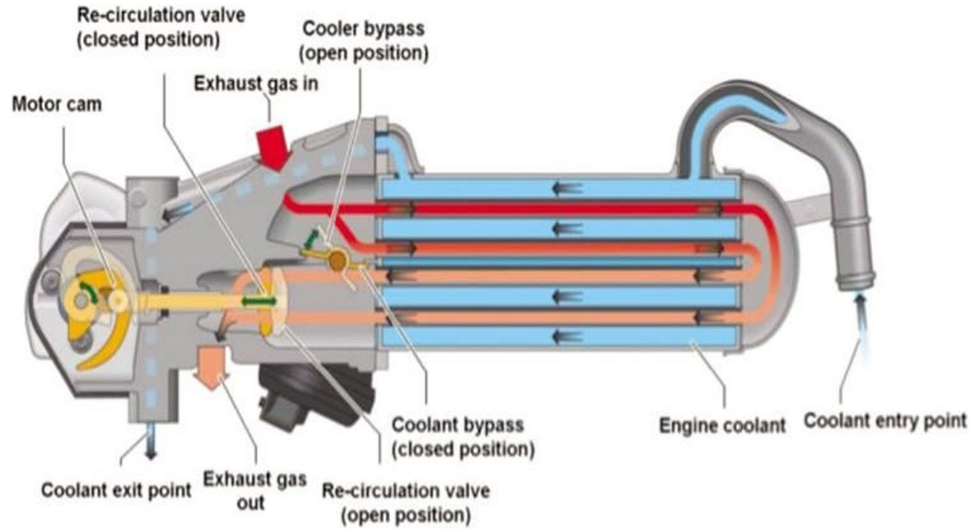

Fig. 4 Schematic of ICE thermal energy conversion through a cooling system using WHR (Shukla et al. 2023)

involves the injection of an aqueous urea solution, which decomposes to form NH_3 via thermal hydrolysis. The NH_3 then reacts with NOx over a catalyst to form nitrogen and water (He et al. 2024). However, SCR faces challenges such as NH_3 slip at low temperatures (<250°C) and limited catalytic activity during cold-start conditions. HC-SCR, using onboard diesel fuel as a reductant, emerged as an alternative approach to overcome these issues, but it suffers from high light-off temperatures (>300°C) and the formation of N_2O (Zhao et al. 2020; Martinović et al. 2021).

Various SCR catalysts like Cu-zeolite, Fe-zeolite, and V_2O_5-WO_3/TiO_2 have been studied. Cu-zeolite and Fe-zeolite catalysts are promising for similtaneous NOx and PM reduction, owing to high surface area, thermal stability, and NH_3 storage abilities. V_2O_5-WO_3/TiO_2 catalysts resist sulfur well but have lower NOx conversion efficiency than zeolite-based catalysts (Kim et al. 2020; Sittichompoo et al. 2022). NH_3-SCR is an efficient technology for NOx control, with V_2O_5-WO_3/TiO_2 being a widely used commercial SCR catalyst for high de-NOx efficiency at 300–400°C (Awad et al. 2022). A summary of commercially used catalyst for SCR are reviewed in the Table 2.

Advancements in catalytic materials and performance of LNT for SCR reaction

Lean NOx traps (LNTs), also known as NOx storage and reduction (NSR) catalysts, operate by storing NOx under lean conditions and reducing it to nitrogen under rich conditions (Muhammad Farhan et al. 2023).

LNTs have been combined with SCR catalysts to enhance NOx reduction efficiency over a wide temperature range. Recent advancements in LNT materials include the development of perovskite-based catalysts, such as $BaCoO_3$ and $SrCoO_3$, which exhibit high NO oxidation capacity

Table 2 The topmost used catalyst for SCR reaction and their properties

Vanadia catalysts V_2O_5-WO_3/TiO_2 Lian et al. (2020)	Preferred in areas with high-sulfur fuels, vanadia catalysts have greater resistance to sulfation but suffer from lower NOx conversion rates and stability issues at temperatures above ~500°C.
Copper–zeolite Mohan et al. (2020)	Cu-ZSM copper–zeolite, especially with small-pore zeolites like CHA chabazite, is favored for its high conversion rates and good hydrothermal stability. Efforts are focused on enhancing low-temperature conversion, durability, and sulfur tolerance. Thermal treatment can recover much of the catalyst's activity lost to sulfur poisoning. Fully restoring performance after sulfur exposure continues to be a major challenge. Sulfur exposure significantly degrades the performance of Cu–ZSM catalysts.
Fe–zeolite catalysts Fe-ZSM Zhang et al. (2022)	Iron–zeolite catalysts differ from copper variants by offering better performance at higher temperatures and reduced ammonia oxidation, making them preferable for applications requiring high sulfur resistance and lower desulfation temperatures.
Manganese-based catalysts MnXO Patil et al. (2016)	Manganese-based catalysts, such as Ce-Mn/TiO_2 and MnO_2/ZrO_2, are under investigation for their potential to enhance low-temperature activity and NOx conversion (>90% NOx conversion in the 140–260°C range) while also offering high-sulfur resistance and reducing N_2O formation.

(Alcantara et al. 2023; Yu et al. 2021). Platinum group metals (PGMs) like Pt, Rh, and Pd have also been incorporated into LNT catalysts to improve low-temperature performance and reduce N_2O formation, all of which is shown in Fig. 5.

Challenges and solutions for low-temperature SCR

The role of hydrogen in SCR has been extensively studied. It promotes the formation and decomposition of organo-NOx species at lower temperatures, increases the availability of hydrogen, and has an effectivness of 95% on thermal and prompt NOx removal (Zhang et al. 2023c; Appavu et al. 2019; Ravi and Pachamuthu 2018). One of the main challenges in SCR is the low catalytic activity at temperatures below 200°C, which is prevalent during cold-start conditions. To address this issue, researchers have focused on developing low-temperature SCR catalysts (Cao et al. 2020). Some solutions include the following:

(a) Zeolite-based catalysts (Cu-zeolite and Fe-zeolite) with high-surface area and thermal stability
(b) Novel catalyst support materials, such as ceria-zirconia and titanium dioxide, thermo electric promoters using TEPOC to enhance low-temperature activity and sulfur resistance
(c) The use of hydrogen and carbon dioxide to similtaneously improve low-temperature NOx reduction efficiency.

Integration of LNT with SCR systems

The combination of LNT and SCR systems, known as LNT-SCR or NSR-SCR, has emerged as a promising solution for efficient NOx reduction in diesel engines (Rahman et al. 2021). In this configuration, the LNT serves as a NOx storage device and an NH_3 generator, while the downstream SCR catalyst utilizes the generated NH3 for further NOx reduction. This synergistic approach takes advantage of the strengths of both technologies, enabling high NOx conversion efficiency over a wide temperature range. However, the optimization of the LNT-SCR system, including catalyst formulation, sizing, and regeneration strategy, is crucial for maximizing performance and minimizing fuel penalty (Kozina et al. 2020).

Advancements in LNT catalyst materials and performance

Recent advancements in LNT catalyst materials have focused on improving low-temperature performance, sulfur resistance, and thermal stability. Perovskite-based materials, such as $BaCoO_3$ and $SrCoO_3$, have shown high NO oxidation capacity and have been used as LNT catalysts. Platinum group metals (PGMs), including Pt, Rh, and Pd, have been incorporated into LNT catalysts to enhance low-temperature NOx storage and reduction (Rajesh et al. 2020; Castoldi 2020). Additionally, the optimization of catalyst support materials, such as $Al2O_3$, CeO_2, and ZrO_2, has been investigated to improve the dispersion and stability of active components (Ravi and Pachamuthu 2020). Figure 6 illustrates the SCR and LNT technologies in diesel engine.

The development of Pt/Rh-BaO bimetallic LNT catalysts has also shown promise in improving NOx storage and reduction efficiency under lean-burn conditions at low temperatures. The addition of Rh to the Pt/BaO system has been found to accelerate NOx release and increase NOx reduction efficiency. Furthermore, the optimization of the physicochemical properties of Pt in Pt-BaO/$Al2O_3$ LNT catalysts, such as surface area, oxygen storage capacity, and particle size, has been studied to better understand NOx sorption and storage kinetics (Rajesh et al. 2020; Kim et al. 2022).

The following equations illustrates the mechanism of reaction occuring in the all types NOx reduction process:

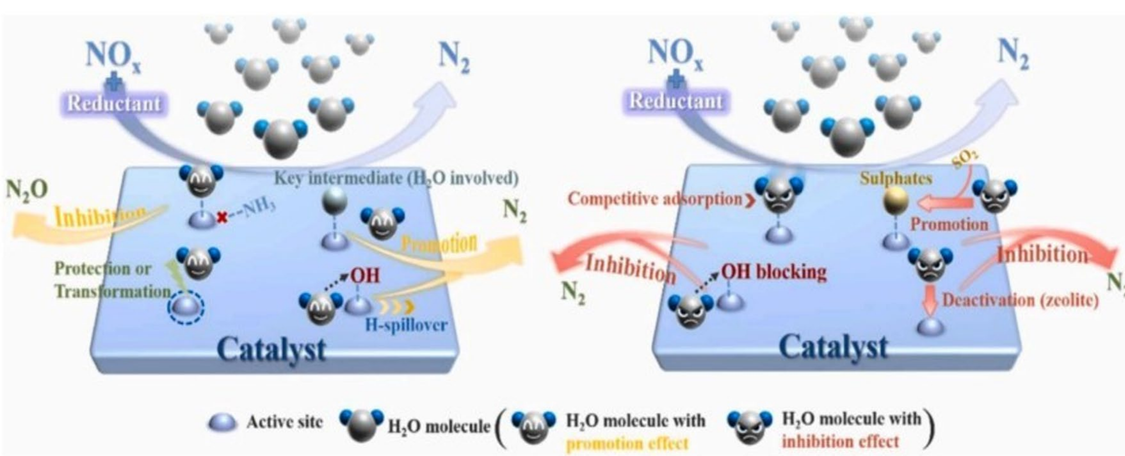

Fig. 5 The mechanism of NOx reduction in lean Nox trap catalyst during SCR reaction (Doppalapudi et al. 2023)

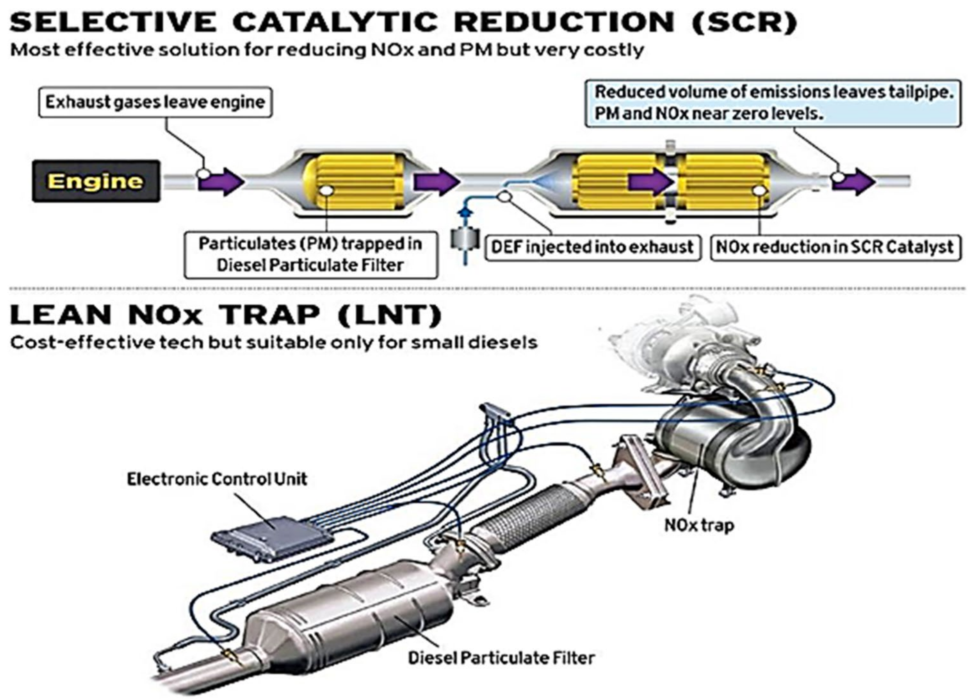

Fig. 6 Illustration of SCR and LNT advanced technologies in diesel engine (Sonawane and Agarwal 2021)

Urea thermal hydrolysis:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

Standard SCR reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Fast SCR reaction:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

NO oxidation (LNT):

$$NO + 0.5O_2 \rightarrow NO_2$$

NOx storage (LNT):

$$BaO + 2NO_2 + 0.5O_2 \rightarrow Ba(NO_3)_2$$

NOx reduction (LNT):

$$Ba(NO_3)_2 + 3H_2 \rightarrow BaO + 2NO + 3H2O\ Ba(NO_3)_2 + 3CO \rightarrow BaO + 2NO + 3CO_2$$

Advanced integrated thermal strategies and energy storage

Pyroelectric and thermoelectric materials potential usage in thermal energy recycling and promotion of sustainable LNT-SCR reactions

Coupling pyroelectric (PE) or else thermoelectric (TE) effects with electrochemical catalysis is a promising approach to convert thermal energy into chemical energy, particularly to utilize “waste heat” from natural and industrial sources (such diesel from plastic waste pyrolysis). PE catalysis has the advantage of utilizing temperature fluctuations, such as the differences in sunlight irradiation between day and night or temperature variations from atmospheric circulation and ocean currents. In contrast, TE catalysis is a relatively new direction that leverages constant temperature gradients to drive electrochemical redox reactions (Zhang et al. 2023d). Developing new PE material systems, such as two-dimensional (2D) materials, and tailoring the PE catalytic performance by modulating the microstructure and exposed crystal facets are important research directions. Advanced synthesis techniques can optimize PE catalysis activity through quantum confinement, epitaxial strains, and other strategies . Identifying PE materials with low Curie temperatures (Tc) is also a promising approach, as most natural temperature oscillations are relatively mild. Previous studies on PE catalysis have lacked quantitative analysis of energy input and thermo-to-chemical energy conversion efficiency. In the future, the PE effect can be coupled with other energy conversion mechanisms, such as photocatalysis or piezoelectric catalysis, to utilize diverse energy sources (Peng et al. 2024; Lion et al. 2020) .

The role of materials, manufacturing methods, and thermoelectric figure-of-merit (ZT) values on TE catalytic performance needs to be clarified. Identifying materials with both high TE performance and suitable redox potential is crucial, such as wide-bandgap semiconductors like TiO2, SrTiO3, and ZnO with appropriate doping. Quantum size effects can also enhance TE performance by increasing the

Seebeck coefficient (S) without sacrificing electrical conductivity (σ), while also reducing thermal conductivity (κ). Potential application scenarios for TE catalysts include utilizing the temperature difference between a reaction chamber and the ambient environment, converting exhaust gases from automobiles into non-toxic byproducts, and biomedical applications leveraging the small temperature difference between the human body and the surrounding environment (Saikia et al. 2023)

Despite recent progress, the fundamental mechanisms governing thermal-to-chemical energy conversion and the design of optimal TE catalytic materials are still in the early stages. Accurately evaluating the overall thermal-to-chemical energy conversion efficiency in nanostructured TE materials and overcoming the challenge of forming a steady, controllable temperature gradient at the nano-/microscale are critical areas for further research .

Finally, PE and TE catalytic materials and devices hold significant promise for advancing catalytic applications in energy, environmental, and biomedical technologies. By harnessing waste heat, this green catalytic technology can promote sustainable industrial production and environmental protection (Kurzydym et al. 2022; Fayyazbakhsh et al. 2022). Further research and development in this interdisciplinary field have the potential to revolutionize catalysis and contribute to a more advanced thermal management.

The integration of pyroelectric and thermoelectric materials into LNT-SCR systems can provide several benefits. First, the electrical energy generated by these materials can be used to heat the LNT catalyst during cold starts or low-temperature operation, improving its NOx storage capacity and NH_3 generation efficiency (Liang et al. 2021). Second, the electrical energy can be used to power the urea dosing system in the SCR catalyst, reducing the need for an external power source and improving the system's response time (Tan et al. 2023). Furthermore, the waste heat recovery achieved through pyroelectric and thermoelectric materials can help to maintain the optimal operating temperature of the LNT-SCR system, even under varying engine load conditions. This can lead to improved NOx and PM reduction efficiency, as well as increased catalyst durability and longevity (Ni et al. 2020).)

The efficiency of pyroelectric and thermoelectric materials in waste heat recovery is accordingly described by the following equations (Deng et al. 2021; Feng et al. 2023)

- The pyroelectric energy conversion:

  $$P = p \times A \times \mathrm{dT}/\mathrm{dt}$$

  where:

P generated electrical power (W)

A surface area of the pyroelectric material (m^2)

p pyroelectric coefficient ($C/m^2 \cdot K$)

dT/dt rate of temperature change (K/s)

- Thermoelectric energy conversion:

  $$V = \alpha \times \Delta T$$

  where:

V generated voltage (V)

α Seebeck coefficient (V/K)

ΔT temperature difference across the thermoelectric material (K)

The pyroelectric coefficient (p) and Seebeck coefficient (α) are intrinsic properties of the materials and depend on their composition and structure. Higher values of these coefficients indicate better performance in waste heat recovery (Koleva et al. 2023). To maximize the benefits of pyroelectric and thermoelectric materials in LNT-SCR systems, researchers are focusing on developing advanced materials with higher energy conversion efficiencies, improved thermal stability, and better compatibility with the harsh exhaust environment. Additionally, optimizing the system design and control strategies to effectively integrate these materials into the aftertreatment system is crucial for achieving the best performance and energy savings (Deng et al. 2019).

Low-grade waste-heat recovery is becoming important in power conversion and electricity generation due to significant energy losses. Traditional methods like heat pumps and thermoelectrics have not been very effective for this. Instead, other techniques like pyroelectrics, thermomagnetics, and thermogalvanics offer better options for recovering low-grade waste heat (Hur et al. 2023). Figure 7 depicts after-treatment thermal management through exhaust heat recirculation.

As a final point, solid-state thermal energy harvesting is gaining attention for its effectiveness in this area. Pyroelectric and thermomagnetic methods are particularly useful for environments with fluctuating temperatures. Thermogalvanic methods, similar to thermoelectrics, work well in steady temperature conditions. Therefore, pyroelectric and thermomagnetic techniques are promising for places with intermittent low-waste heat, such as exhaust from internal combustion engines (Cheng et al. 2023a).

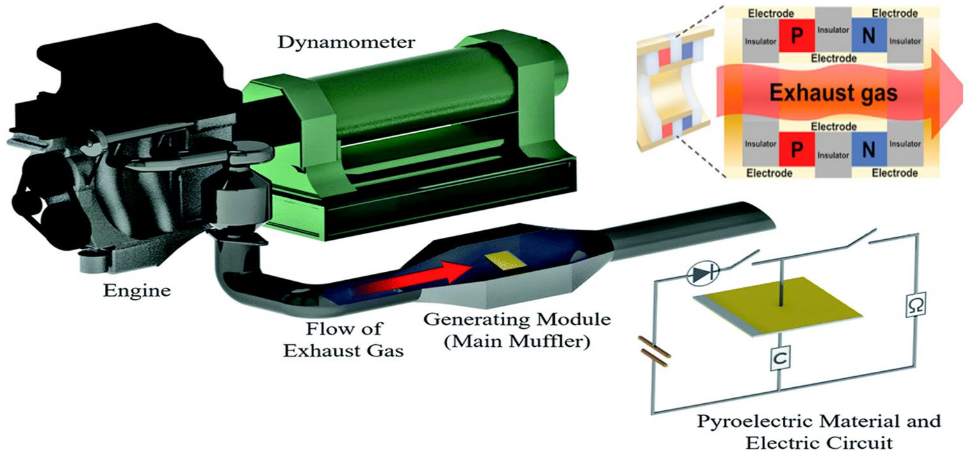

Fig. 7 Illustration of pyrolyse supplied thermal energy conversion process for thermal management through thermoelectric exhaust heat recirculation (Hur et al. 2023)

Combined catalytic systems for efficient thermal management

Synergies between LNT, SCR, and DPF technologies

Bakhchin et al. (2024) is the first group to introduce heat recovery from ICE to mitigate NO redox and UHC complete combustion using thermoelectric catalytic converters, overcomes cold start at low-temperature combustion technologies in automotive engineering. The combination of LNT, SCR, and DPF technologies has shown great potential for simultaneously reducing NOx and PM emissions in diesel engines. LNT catalysts store NOx under lean conditions and release it under rich conditions, along with NH_3 generation. The downstream SCR catalyst then utilizes the generated NH_3 for further NOx reduction. DPFs, on the other hand, physically trap soot particles and periodically regenerate through oxidation (Xue et al. 2022).

The synergies between these technologies can be exploited by integrating them into a single aftertreatment system design. For example, the LNT-SCR configuration allows for efficient NOx reduction over a wide temperature range, as the LNT provides NH_3 for the SCR reaction even at low temperatures (Pereda-Ayo and González-Velasco 2013). Additionally, the DPF can be coated with SCR or LNT catalysts (SCR-on-DPF or LNT-on-DPF) to achieve simultaneous PM and NOx reduction in a compact system, all of which is depicts in Fig. 8.

Novel combined catalytic system configurations

Several novel combined catalytic system configurations have been proposed to maximize the synergies between LNT, SCR, and DPF technologies, and Fig. 9 shows a thermally efficient new engineered after treatment combination (Mei et al. 2021). Some notable configurations include the following:

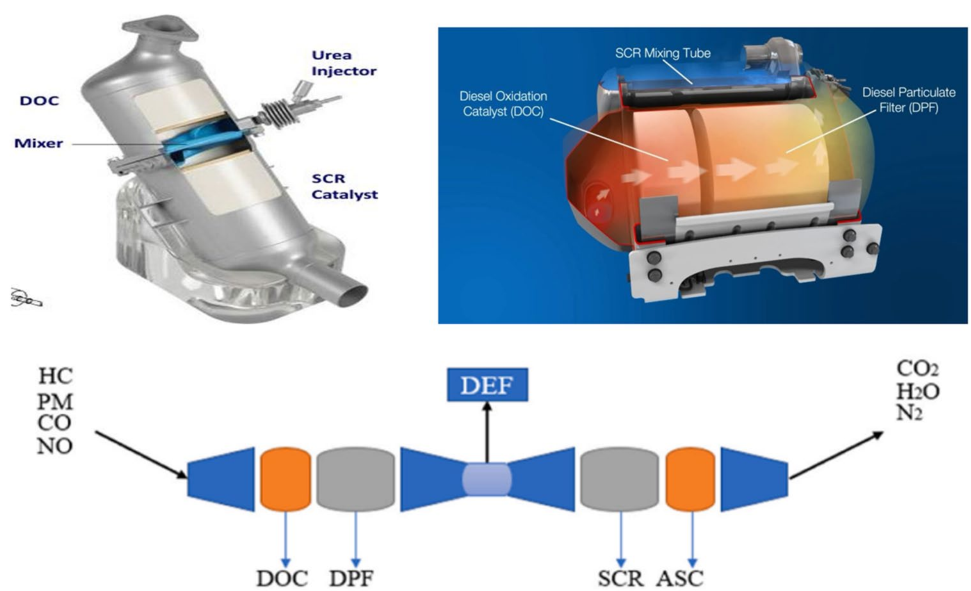

Fig. 8 Synergistic arrangement of modern after treatment systems (You et al. 2019)

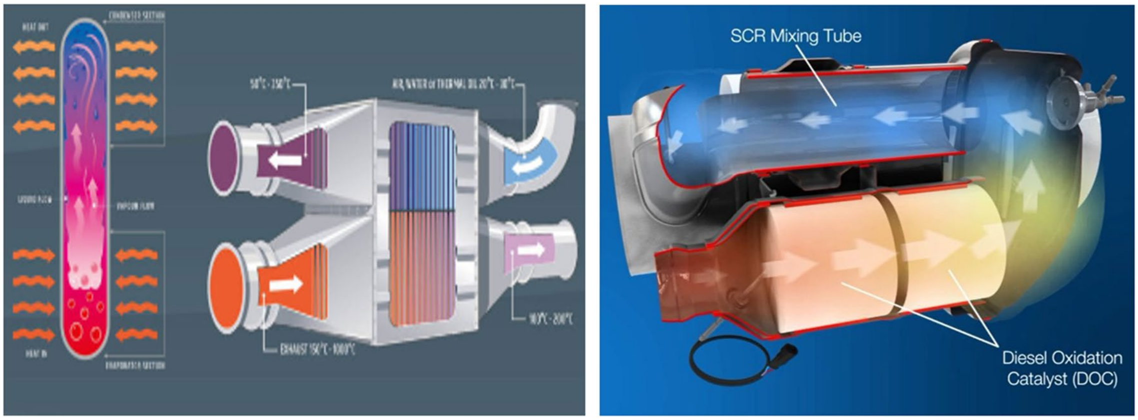

Fig. 9 Thermally efficient new engineered after treatment combination (Yakoumis 2021)

- LNT-SCR-DPF: In this configuration, the LNT is placed upstream of the SCR and DPF. The LNT stores NOx during lean operation and releases it as NH_3 during rich regeneration, which is then utilized by the SCR catalyst. The DPF downstream captures and oxidizes the PM.
- SCR-on-DPF: This configuration integrates the SCR catalyst onto the DPF substrate, allowing for simultaneous NOx and PM reduction in a single component. The compact design saves space and reduces system complexity.
- LNT-on-DPF with downstream SCR: This system combines an LNT-coated DPF with a downstream SCR catalyst. The LNT-on-DPF stores NOx and PM, while the downstream SCR further reduces the NOx using the NH3 generated during LNT regeneration.

Performance evaluation and optimization of combined systems

The performance of combined catalytic systems depends on various factors, such as catalyst formulation, system configuration, and operating conditions. Researchers have focused on optimizing these parameters to maximize NOx and PM reduction efficiency while minimizing fuel consumption and system complexity (Gui et al. 2022). One key aspect is the optimization of the catalyst formulation for each component. For example, the LNT catalyst should have high NOx storage capacity and NH_3 selectivity during regeneration, while the SCR catalyst should have high NOx conversion efficiency and low NH_3 slip. The DPF substrate and coating should be designed to minimize pressure drop and facilitate efficient soot oxidation (Choi et al. 2021).

Another important factor is the control of the regeneration strategy for the LNT and DPF components. The frequency and duration of the rich regeneration events should be optimized to maximize NOx and PM reduction while minimizing fuel consumption. This can be achieved through advanced control algorithms that take into account the real-time engine operating conditions and aftertreatment system state (Ahmad et al. 2022). The performance of combined catalytic systems can be evaluated using various metrics, such as NOx and PM conversion efficiency, NH_3 slip, fuel consumption, and system durability (Cheng et al. 2023b). Experimental studies and numerical simulations are used to assess the performance under different operating conditions and to identify potential areas for improvement (Palani et al. 2022).

Equations governing NOx storage and reduction:

(a) NOx storage in LNT (lean phase) $BaO + 2NO_2 + 0.5O_2 \rightarrow Ba(NO_3)_2$

(b) NOx release and NH_3 generation in LNT (rich phase) $Ba(NO_3)2 + 3H_2 \rightarrow BaO + 2NH_3 + 3H_2O$

SCR reactions:

Standard SCR $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

(c) Fast SCR $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

(d) Soot oxidation in DPF $C\ (soot) + O_2 \rightarrow CO_2$ $C\ (soot) + NO_2 \rightarrow CO_2 + NO$

In these equations (a,b), the LNT catalyst (e.g., BaO) stores NOx as nitrates ($Ba(NO_3)_2$) during lean operation and releases it as NH_3 during rich regeneration. The generated NH3 then participates in the standard and fast SCR reactions over the SCR catalyst, reducing NOx to N_2 (Manigandan et al. 2020). In the DPF, soot (C) is oxidized by O_2 and NO_2 to form CO_2, with NO_2 being more effective at lower temperatures compared to O_2.

Future perspectives and challenges

Emerging catalyst materials and technologies

The development of advanced catalyst materials and technologies is crucial for meeting the emission regulations and improving the efficiency of aftertreatment systems (Mourad et al. 2021). Some emerging catalyst materials include the following:

- Perovskite-based catalysts: Perovskite oxides, such as $LaCoO_3$ and $LaMnO_3$, have shown promise as alternatives to traditional platinum group metals (PGMs) in LNT and SCR catalysts. These materials exhibit high thermal stability, excellent redox properties, and good sulfur tolerance, making them attractive candidates for high-temperature applications.
- Ceria-based catalysts: Ceria (CeO_2) and its derivatives have gained attention as catalyst supports and promoters. Ceria-based materials can enhance the low-temperature activity and stability of LNT and SCR catalysts, as well as promote soot oxidation in DPFs.
- Metal-organic frameworks (MOFs): MOFs are highly porous materials with tunable chemical and physical properties. They have been explored as catalyst supports and adsorbents in aftertreatment systems, offering high surface area, controllable pore size, and good thermal stability. MOFs can be functionalized with active metal sites to achieve desired catalytic properties.

In terms of emerging technologies, the integration of non-thermal plasma (NTP) with catalytic aftertreatment systems has shown potential for improving low-temperature performance and reducing the dependence on precious metals (Norouzi et al. 2023). NTP can generate highly reactive species, such as oxidizing radicals and excited molecules, which can enhance the catalytic reactions at lower temperatures. The combination of NTP with LNT, SCR, or DPF catalysts can lead to improved NOx and PM reduction efficiency, as well as faster catalyst light-off during cold starts.

Trends in emission regulations and their impact on aftertreatment systems

The global trend in emission regulations is towards more stringent limits on NOx and PM emissions from diesel engines. For example, the Euro 7 standards, expected to come into effect in the mid-2020s, are likely to impose even lower NOx and PM limits than the current Euro 6 regulations. Similarly, the CARB has proposed the Heavy-Duty Low NOx Omnibus Regulation, which aims to reduce NOx emissions from heavy-duty trucks by up to 90% below current standards. These trends in emission regulations will have a significant impact on the design and development of aftertreatment systems (Lyu et al. 2023; Xiang et al. 2024). To meet the lower emission limits, aftertreatment systems will need to achieve higher NOx and PM conversion efficiencies, especially at low temperatures and under real-world driving conditions. This will require the development of advanced catalyst materials, improved system architectures, and more sophisticated control strategies (Zhang et al. 2024). Furthermore, the focus on real-world driving emissions (RDE) testing will necessitate the optimization of aftertreatment systems for a wider range of operating conditions, including low-load and low-temperature operation. This will require a better understanding of the complex interactions between engine, aftertreatment, and control systems, as well as the development of adaptive and predictive control algorithms (Vedagiri et al. 2020; Barbara et al. 2020).

Research directions and opportunities for further improvement

To address the challenges posed by the future emission regulations and the need for more efficient and cost-effective aftertreatment systems, several research directions and opportunities have been identified:

- Development of multi-functional catalyst materials: Researchers are exploring the development of catalyst materials that can perform multiple functions, such as simultaneous NOx and PM reduction, or combined LNT and SCR functionality. These multi-functional materials can help to simplify the aftertreatment system architecture, reduce precious metal loading, and improve overall system efficiency.
- Advanced catalyst characterization techniques: The use of advanced materials and techniques for emission storage and conversion. These techniques can help to guide the rational design and optimization of novel catalyst formulations.
- Predictive modeling and simulation: The development of predictive models and simulation tools can assist in the

design and optimization of aftertreatment systems, reducing the need for extensive experimental testing. These models can incorporate detailed kinetic mechanisms, fluid dynamics, and heat transfer effects to predict the performance of catalytic reactors under various operating conditions. Machine learning algorithms can also be employed to identify optimal catalyst formulations and operating strategies.

- Integration with advanced combustion technologies: The integration of advanced combustion technologies, such as low-temperature combustion (LTC) and reactivity-controlled compression ignition (RCCI), with optimized aftertreatment systems can lead to significant reductions in both NOx and PM emissions. The development of integrated engine-aftertreatment control strategies can help to maximize the benefits of these technologies and ensure compliance with future emission regulations.

By addressing these research directions and opportunities, the scientific community and automotive industry can work towards the development of more efficient, cost-effective, and environmentally sustainable aftertreatment systems for diesel engines. The successful implementation of these technologies will play a crucial role in meeting the challenges posed by the future emission regulations and contribute to the overall reduction of the environmental impact of transportation.

Conclusion

The development of efficient and sustainable aftertreatment systems for diesel engines is crucial in the global transition towards energy-efficient and environmentally friendly vehicles. This comprehensive review has explored the latest advancements in aftertreatment methodologies, focusing on the synergistic effects of in-cylinder combustion strategies and post-combustion purification technologies to effectively mitigate nitrogen oxides (NOx) and particulate matter (PM) emissions. Low-temperature combustion (LTC) strategies, such as reactivity-controlled compression ignition (RCCI) and partially premixed compression ignition (PPCI), have emerged as promising techniques for overcoming the traditional NOx/soot trade-off inherent in diesel combustion. By achieving a more homogeneous air-fuel mixture and operating at lower temperatures, LTC has the potential to significantly reduce engine-out emissions. However, the implementation of LTC poses unique challenges for aftertreatment systems, particularly in low-temperature and cold-start conditions.

SCR catalysts, LNT, and DPF have been extensively investigated to address the limitations of LTC aftertreatment. Novel catalyst formulations, such as zeolite-based materials, perovskites, and mixed metal oxides, have shown promise in enhancing low-temperature performance and durability. The integration of LNT and SCR systems (LNT-SCR) has demonstrated superior NOx reduction efficiency over a wide temperature range, while SCR-on-DPF and LNT-on-DPF configurations offer compact solutions for simultaneous PM and NOx reduction. This review has also explored the potential of energy conversion and recovery techniques, such as thermoelectric generators and organic Rankine cycles, to harness waste heat from the exhaust and improve the overall efficiency of the after-treatment system. The complex interactions between engine operating parameters, combustion kinetics, and emission formation in LTC engines have been highlighted, emphasizing the importance of a comprehensive approach to optimize in-cylinder and after-treatment processes. The insights gained from this study can guide future research efforts towards overcoming the limitations of current after-treatment technologies in low-temperature conditions and achieving superior emission reduction performance in advanced combustion engines. By providing a critical analysis of the state-of-the-art and identifying promising research avenues, this review contributes to the development of sustainable and efficient automotive technologies that meet the growing demand for energy-efficient and environmentally friendly vehicles. As the global community continues to strive for cleaner transportation solutions, the synergistic integration of advanced combustion strategies and innovative aftertreatment systems, will be crucial in achieving the ambitious emission reduction targets set by regulatory bodies worldwide. The use of waste heat recovery to reduce energy consumption and both types of NOx formations leveraging combustion and pyrolysis exergy to attenuate the generated emissions during combustion process.

Nomenclature and abbreviations *LTC*: Low-temperature combustion; *ICE*: Internal combustion engines; *SCR*: Selective catalytic reduction; *PGM*: Platinum group material; *DOC*: Diesel oxidation catalyst; *DPF*: Diesel particulate filter; *LD* & *HD*: Light duty & heavy duty; *ATS*: After treatment systems; *NSC*: NOx storage catalyst; *OSM*: Oxygen storage material; *PM*: Particulate matter; *NOx*: Nitrogen oxides (NO, NO_2); *LNT*: Lean NOx traps; *RCCI*: Reactivity-controlled compression ignition; *PCCI*: Partially premixed compression ignition; *NH3*: Ammonia; N_2O: Nitrous oxide; *HC*: Hydrocarbons; *CO*: Carbon monoxide; *EGR*: Exhaust gas recirculation; *TEG*: Thermoelectric generator; *ORC*: Organic rankine cycle; *XAS*: X-ray absorption spectroscopy; *ETEM*: Environmental transmission electron microscopy; *RDE*: Real-world driving emissions; *MOF*: Metal-organic framework; *NTP*: Non-thermal plasma; *CARB*: California Air Resources Board; *DMB*: Diesel/methanol/n-butanol; *PCCI*: Premixed charge compression ignition; *HCCI*: Homogeneous charge compression ignition; *PEMS*: Portable emissions measurement system; *SEMS*: Smart emissions measurement system; *SDPF*: SCR-coated diesel particulate filter; *WHR*: Waste heat recovery; *CRDI*: Common rail direct injection; *TEPOC*: Thermoelectric power generator and oxidation catalyst

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Author contribution All the authors contributed to the study conception and design. Dikra Bakhchin, Oumaima Douadi, and Rajesh Ravi performed the material preparation, data collection, and analysis. Faqir Mustapha and Elhachmi Essadiqi provided supervision and accommodations in the LERMA laboratory. Dikra Bakhchin wrote the first draft of the manuscript, and all the authors commented on previous versions of the manuscript. All the authors have read and approved the final manuscript.

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Data availability The data presented in this paper is available in the cited relevant references.

Declarations

Competing interests The authors declare the following financial interests/personal relationships, which may be considered potential competing interests: Dikra Bakhchin reports that the National Center for Scientific and Technical Research provided financial support.

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Authors and Affiliations

Dikra Bakhchin[1] · Rajesh Ravi[1] · Oumaima Douadi[1] · Mustapha Faqir[1] · Elhachmi Essadiqi[1]

✉ Rajesh Ravi
rajesh.ravi@uir.ac.ma

[1] School of Aerospace and Automotive Engineering, LERMA Laboratory, International University of Rabat, 11000 Rabat, Morocco