

Review

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*Review*

# After-Treatment Technologies for Emissions of Low-Carbon Fuel Internal Combustion Engines: Current Status and Prospects

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**Abstract:** In response to increasingly stringent emission regulations, low-carbon fuels have received significant attention as sustainable energy sources for internal combustion engines. This study investigates four representative low-carbon fuels—natural gas, methanol, hydrogen, and ammonia—by systematically summarizing their combustion characteristics and emission profiles, along with a review of existing after-treatment technologies tailored to each fuel type. For natural gas engines, unburned hydrocarbon (UHC) produced during low-temperature combustion exhibit poor oxidation reactivity, necessitating integration of oxidation strategies such as diesel oxidation catalyst (DOC), particulate oxidation catalyst (POC), ozone-assisted oxidation, and zoned catalyst coatings to improve purification efficiency. Methanol combustion under low-temperature conditions tends to produce formaldehyde and other UHCs. Due to the lack of dedicated after-treatment systems, pollutant control currently relies on general-purpose catalysts such as DOC, Three-way catalyst (TWC), and POC. Although hydrogen combustion is carbon-free, its high combustion temperature often leads to elevated NO<sub>x</sub> emissions, requiring a combination of optimized hydrogen supply strategies and selective catalytic reduction (SCR)-based denitrification systems. Similarly, while ammonia offers carbon-free combustion and benefits from easier storage and transportation, its practical application is hindered by several challenges including low ignitability, high toxicity, and notably NO<sub>x</sub> emissions compared to conventional fuels. Current exhaust treatment for ammonia-fueled engines primarily depends on SCR, SCR-coated diesel particulate filters (SDPF). Emerging NO<sub>x</sub> purification technologies such as integrated NO<sub>x</sub> reduction via hydrogen or ammonia fuel utilization still face challenges of stability and narrow effective temperature.

**Keywords:** low-carbon fuels; internal combustion engines; unburned hydrocarbons; nitrogen oxides; emissions after-treatment

## 1. Introduction

With the accelerating pace of urban industrialization, countries around the world are confronted with the major issue of global climate change and environmental warming. Reducing greenhouse gas emissions as much as possible has become an essential part of ecological and environmental construction worldwide. Internal combustion engines, as the core power units for transportation, engineering machinery, and marine vessels, consume approximately 70% of the world's petroleum resources, making them the primary sector of oil consumption and a significant source of greenhouse gas (GHG) emissions. To address the challenge of reducing greenhouse gas (GHG) emissions from internal combustion engines, the utilization of low-carbon alternative fuels—such as natural gas, methanol, ammonia, and hydrogen—has emerged as a pivotal research focus in ICE technology. These fuels offer significant potential to decarbonize transportation and industrial sectors while maintaining engine performance. However, these alternative fuels still face critical challenges, particularly in pollutants include nitrogen oxides (NO<sub>x</sub>), particulate matter (PM), hydrocarbons (HC), and carbon monoxide (CO) [1–4]. Among the various application fields of internal combustion

engines, road vehicles face the most stringent exhaust pollutant standards globally. To better regulate vehicle pollutant emissions, countries around the world have progressively implemented stricter emission standards [8,9], as shown in Figure 1. Since California introduced the first emission regulations in 1966, and up to the present day with the Euro VII emission standards, the limits on harmful emissions have become increasingly stringent, approaching "zero emissions." Non-road mobile machinery and marine engines currently operate under comparatively lenient emission standards. However, this regulatory gap is narrowing as international bodies (IMO Tier III for ships) and regional policies (EU Stage V for off-road equipment) progressively adopt cleaner fuel specifications and aftertreatment technologies. Therefore, in response to these tightening emission regulations and to better protect the atmospheric environment, it is essential to use low-carbon fuels, develop new low-emission engines, and employ after-treatment technologies to purify emission pollutants.

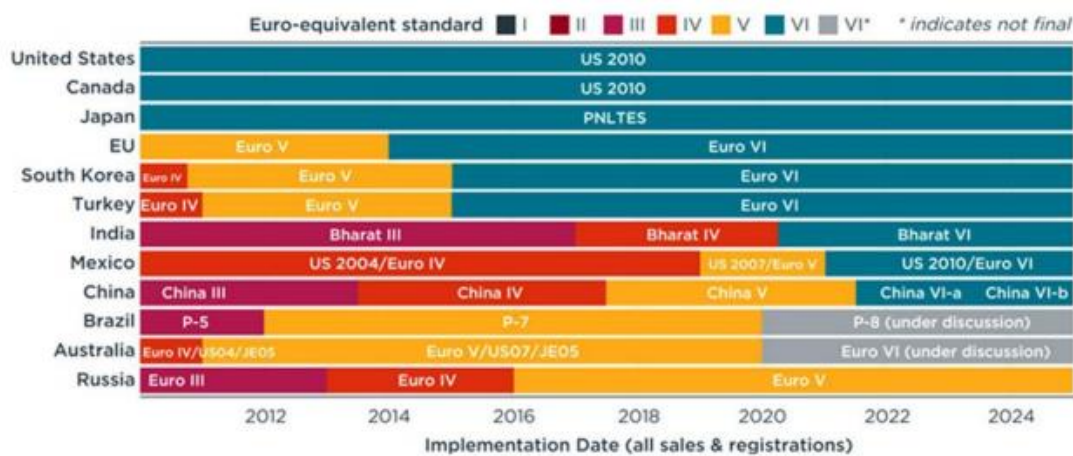


Figure 1. Emission regulations in various countries [8].

The energy structure of the internal combustion engine industry is gradually transitioning from high-carbon fossil fuels to carbon-neutral and low-carbon energy sources. Currently, commercially deployed low-carbon alternative fuels include biodiesel and natural gas. Emerging solutions such as renewable hydrogen, electronic methanol and ammonia (produced via catalytic synthesis of renewable hydrogen and CO<sub>2</sub>/N<sub>2</sub>) demonstrate life-cycle CO<sub>2</sub> reductions of 70-90%, though face scalability challenges due to energy-intensive production. Finding efficient combustion and low-pollution after-treatment technologies for low-carbon fuel engines is a key focus of current internal combustion engine combustion technology development.

## 2. Low-Carbon Fuels and Corresponding Emission After-Treatment Technologies

### 2.1. Natural Gas Fuels

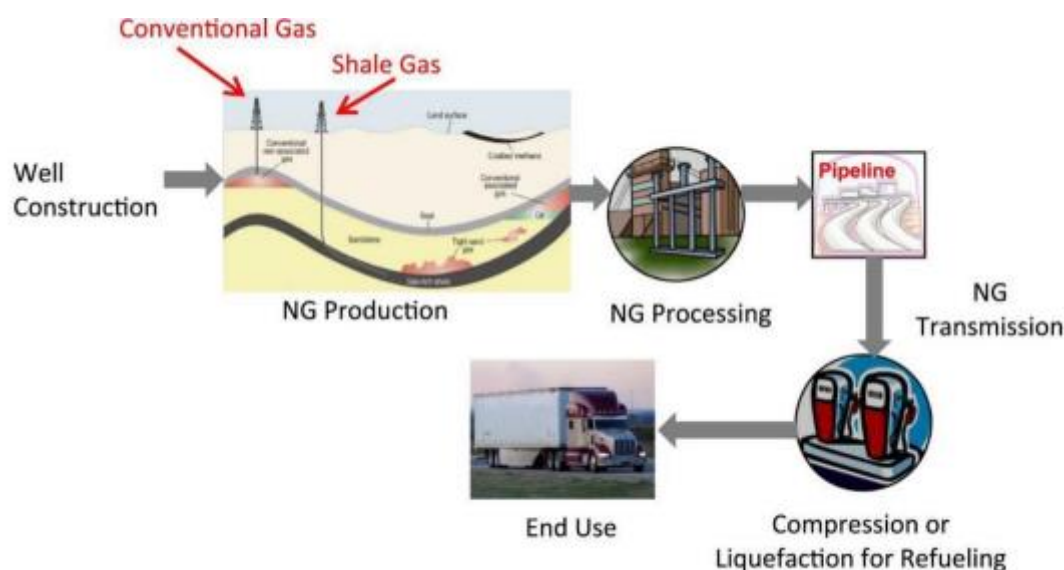
Natural gas, as the third-largest global energy source after coal and oil, plays a crucial role in the transition towards low-carbon energy. Its application in internal combustion engines is increasing, highlighting the growing importance of natural gas in this field [10]. Compared to other low-carbon fuels such as ammonia and hydrogen, natural gas offers several advantages.

#### 2.1.1. The Use of Natural Gas Fuels

Firstly, natural gas benefits from an established infrastructure for transportation, storage, and distribution, allowing it to be directly utilized through existing pipelines, whereas ammonia and hydrogen require new infrastructure. Additionally, natural gas has a higher energy density, while

hydrogen has a lower energy density and requires high-pressure storage or liquefaction. When burned, natural gas emits fewer CO<sub>2</sub> and NO<sub>x</sub>, whereas ammonia usage can lead to NO<sub>x</sub> emissions, and hydrogen production may be associated with higher carbon emissions. In terms of cost, natural gas is relatively inexpensive, and its price is stable, while hydrogen, particularly green hydrogen, has higher production costs. Overall, natural gas offers advantages in terms of infrastructure, cost, and technological adaptability, but both hydrogen and ammonia hold significant potential for future low-carbon energy transitions.

Natural gas can be divided into two main types: conventional natural gas and unconventional natural gas. Conventional natural gas is typically found alongside oil, while unconventional natural gas must be extracted from sources such as shale, tight sandstone, coal seams, deep aquifers, and deep-sea sediments. The extraction of unconventional natural gas is more challenging compared to conventional natural gas [11]. Although the sources of unconventional natural gas vary, its main components are generally consistent, including methane (CH<sub>4</sub>), ethane, propane, isobutene, n-butane, CO<sub>2</sub>, and N<sub>2</sub> [12]. As shown in Figure 2, the flow chart of natural gas extraction and application demonstrates that, compared to gasoline and diesel, natural gas produces the least pollutant emissions throughout its entire lifecycle, including extraction, production, storage, transportation, and use [13].



**Figure 2.** Natural gas extraction process[13].

Due to the concentration of fossil fuels in the Middle East, international oil prices are often influenced by regional security issues. In contrast, natural gas has more abundant reserves and is widely distributed across the world, making it easier to establish a stable supply chain. This not only helps reduce atmospheric pollution but also contributes to maintaining energy security. When natural gas is used as an alternative fuel for internal combustion engines, it has the following characteristics:

(1) Compared to diesel and gasoline, natural gas has a higher octane rating, better anti-knock performance, and lower chemical reactivity. These characteristics allow for an increase in the engine's compression ratio range, which in turn improves the engine's thermal efficiency, reduces fuel consumption, and significantly enhances fuel economy [14].

(2) Natural gas has a wide flammability limit, which facilitates the expansion of the lean burn limit. The laminar flame propagation speed is slower, which helps reduce NO<sub>x</sub> emissions [15,16].

(3) Natural gas has a higher calorific value compared to diesel and gasoline. Therefore, compared to gasoline and diesel engines of the same displacement, natural gas can significantly increase engine power [17].



(4) Natural gas is a colorless, odorless, non-toxic gas, primarily composed of methane ( $\text{CH}_4$ ). It has a lower carbon content than gasoline and diesel, and produces relatively lower  $\text{CO}_2$  emissions during combustion, making it a cleaner fuel [18,19].

In summary, natural gas can improve engine combustion efficiency while achieving cleaner combustion, making it an ideal alternative fuel for reducing  $\text{CO}_2$  emissions. Therefore, natural gas is considered a promising low-carbon fuel, and the promotion and application of natural gas engines are of significant importance. This provides a viable energy development path for reducing carbon emissions and maintaining a healthy atmospheric environment.

#### 2.1.2. After-Treatment System for Natural Gas Engines

Natural gas engines, recognized as a promising low-carbon fuel alternative, have played an important role in reducing energy consumption and emissions. However, like conventional gasoline and diesel engines, they still produce pollutants during operation, making it necessary to implement effective emission control strategies. Among these pollutants, Unburned hydrocarbon (UHC), with methane as the primary component, are particularly significant [20]. Since current emission standards do not clearly distinguish between methane and non-methane hydrocarbons, regulating UHC emissions remains difficult. Nonetheless, with increasingly stringent environmental regulations, enhancing the control of UHC emissions, especially methane, has become an urgent priority.

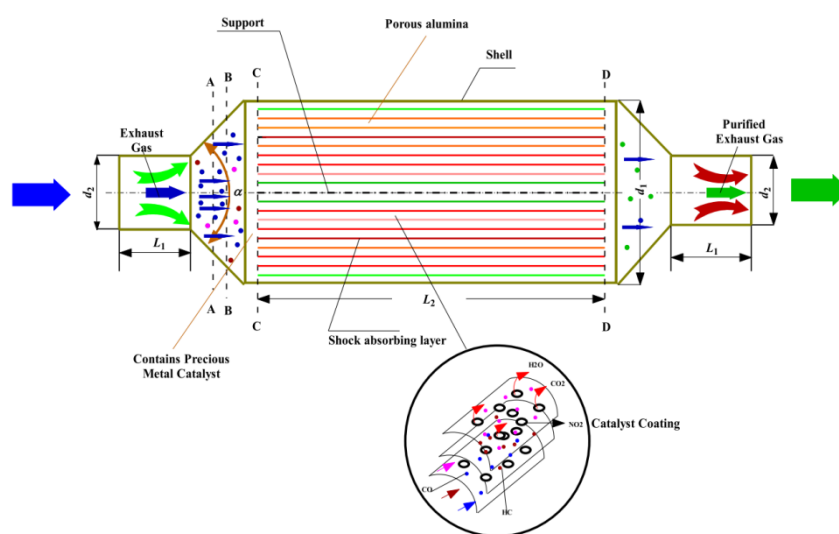
At present, the three-way catalyst (TWC) remains one of the primary technologies used to treat emissions from natural gas engines [18,19]. TWC can effectively remove non-methane hydrocarbons while simultaneously reducing carbon monoxide (CO) and  $\text{NO}_x$ , all within a relatively compact after-treatment system. However, methane, a colorless, odorless, and non-toxic but highly flammable gas, possesses a high hydrogen-to-carbon ratio and high calorific value, with combustion products consisting mainly of  $\text{CO}_2$  and water ( $\text{H}_2\text{O}$ ) [23,24]. Due to its stable molecular structure and high auto-ignition temperature, methane is difficult to oxidize at lower temperatures [25], which makes it challenging to achieve effective conversion using TWC alone.

Currently, further reductions in methane and other HC emissions can be achieved by optimizing the mixture formation process and adopting lean-burn combustion strategies in engine operation [26,27]. While enhancing the mixture formation process can help reduce UHC emissions to some extent, it may also lead to increased fuel consumption and higher  $\text{NO}_x$  emissions. To balance  $\text{NO}_x$  control and fuel economy, exhaust gas recirculation (EGR) technology is often employed to reduce thermal load by reintroducing a portion of the exhaust gas into the combustion chamber, thereby lowering the combustion temperature. However, when applied to dual-fuel engines such as diesel/natural gas systems, EGR may contribute to increased PM emissions. In addition, one of the main drawbacks of EGR is that it can significantly lower exhaust temperatures, which in turn further reduces the effectiveness of the TWC in oxidizing methane [25,28]. In contrast, lean-burn combustion offers the advantage of maintaining high thermal efficiency while reducing fuel consumption and significantly lowering the engine's raw  $\text{NO}_x$  emissions. However, due to the lower exhaust temperatures associated with lean-burn operation, additional catalytic systems are still required to effectively remove  $\text{NO}_x$ . In addition to methane and  $\text{NO}_x$ , natural gas engines also emit other pollutants, such as formaldehyde ( $\text{HCHO}$ ) and small amounts of PM [29]. Formaldehyde poses serious health risks due to its neurotoxicity and potential carcinogenicity, and therefore requires strict control under ultra-low emission standards [30].  $\text{HCHO}$  formation is primarily attributed to the incomplete oxidation of natural gas in low-temperature combustion zones. PM emissions may originate from unburned hydrocarbons or partial combustion of lubricating oil in direct contact with the flame. Nevertheless, compared with conventional diesel engines, natural gas engines generally produce lower levels of PM emissions [31].

In addition to optimizing combustion strategies and employing TWC, exhaust purification in natural gas engines also relies heavily on noble metal catalysts coated onto carrier materials. Commonly used active metals include platinum (Pt), palladium (Pd), and rhodium (Rh), which are typically supported on alumina or ceria-zirconia composite oxides. Under lean-burn conditions, Pt

and Pd generally exhibit better catalytic oxidation performance for methane compared to Rh [32]. However, noble metal catalysts often suffer from poor thermal stability and are susceptible to deactivation due to water vapor interference and sulfur poisoning during high-temperature operation. As a result, enhancing the stability and durability of these catalysts while maintaining high conversion efficiency has become a critical focus in current research on after-treatment technologies.

As previously discussed, the purification of methane relies on noble metal catalysts supported on substrate materials. Therefore, the after-treatment system of natural gas engines share the same structural framework used in conventional gasoline or diesel engines while implementing specific design modifications to enhance methane oxidation efficiency. For instance, placing a diesel oxidation catalyst (DOC) at the upstream section of the system can significantly enhance both methane conversion efficiency and catalyst durability [33]. The DOC typically adopts a flow-through structure and is installed at the forefront of the after-treatment system, as illustrated in Figure 3 [37]. Catalysts such as Pt and Pd are commonly used in DOC, which function primarily by lowering the activation energy of chemical reactions for exhaust pollutants, thereby enabling oxidation at relatively low temperatures. In addition, the DOC can contribute to the removal of acetaldehyde and certain exhaust odors [35], making it, alongside the TWC, one of the key components in current natural gas engine after-treatment systems. However, the DOC may also generate by-products such as ammonia( $\text{NH}_3$ ) and Nitrous Oxide( $\text{N}_2\text{O}$ ) during methane oxidation, which pose risks of secondary pollution [33]. Therefore, future efforts should focus on precise control of exhaust gas composition and the optimization of catalytic oxidation strategies in DOC to mitigate these issues.



**Figure 3.** Cross-sectional schematic diagram of DOC[34].

Kinnunen et al. [36] proposed a combined methane purification strategy based on the TWC configuration by placing the TWC upstream of the methane oxidation catalyst to form a synergistic system with the downstream catalyst. This setup provides a certain degree of sulfur storage capability under lean-burn conditions, thereby improving the sulfur tolerance of the after-treatment system and reducing the risk of sulfur poisoning to some extent. Moreover, under rich-burn conditions, the TWC can promote the formation of reductive gas species, which further enhances the purification performance of downstream catalysts. To efficiently remove methane while reducing cost, some studies have explored the use of ozone instead of oxygen for catalytic oxidation. Keenan et al. [37] conducted ozone-assisted oxidation experiments using an iron-based zeolite catalyst, and achieved a methane conversion rate of up to 60% at 220 °C. This approach demonstrated promising potential under low-temperature conditions, particularly for large-scale stationary engine systems. Yasumura et al [38] using a computational catalyst design approach, developed a proton-type  $\beta$ -zeolite catalyst containing silicon and aluminum, which significantly improved methane combustion efficiency in

the presence of ozone. This catalyst outperformed conventional Pd-based catalysts in the temperature range of 100–300 °C, and also exhibited good water and sulfur tolerance. However, under higher temperature conditions, traditional catalysts such as Pd still demonstrated superior catalytic activity. Although ozone has demonstrated promising performance in methane purification, the energy consumption involved in its generation and the potential formation of secondary pollutants such as NO<sub>x</sub> cannot be overlooked.

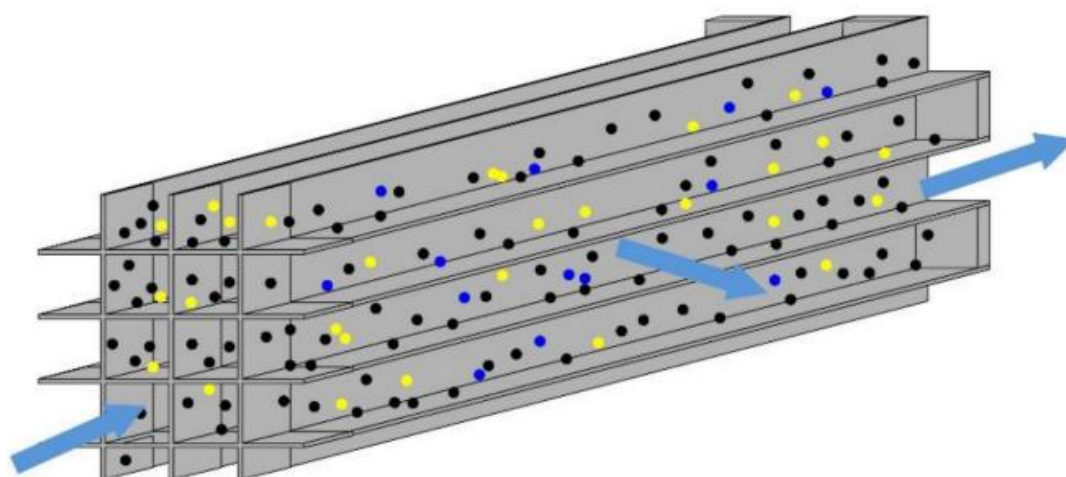
## 2.2. Methanol Fuel

### 2.2.1. The Use of Methanol Fuel

Methanol is widely used as a low-carbon and clean alternative fuel in engine applications. Besides NO<sub>x</sub>, methanol and formaldehyde are important components of UHC emitted from methanol engines. To reduce the emissions of such pollutants, technologies such as low-temperature combustion, water or ethanol injection, and combustion chamber optimization are commonly employed to improve overall engine performance and enhance combustion efficiency, thereby limiting pollutant formation [39]. Although these approaches have shown some effectiveness in reducing methanol-related emissions, they often come at the expense of engine power output. Consequently, under the limitations of current in-cylinder control strategies, additional exhaust after-treatment technologies are typically required to further reduce methanol and formaldehyde emissions. However, there are currently no dedicated after-treatment systems specifically designed for these two pollutants. Instead, pollutant control is generally achieved using devices such as the DOC, TWC, and particulate oxidation catalyst (POC), as previously discussed [40–42].

### 2.2.2. After-Treatment System for Methanol Engines

The purification of methanol and formaldehyde by the DOC primarily relies on the synergistic effect between the catalyst and oxygen under high-temperature conditions. As exhaust gases pass through the DOC, unburned methanol and formaldehyde react with oxygen and are converted into CO<sub>2</sub> and H<sub>2</sub>O. During this process, the catalyst facilitates the catalytic oxidation of these unburned components. As previously noted, TWC is not only effective in reducing emissions of HC, CO, and NO<sub>x</sub>, but also exhibits a certain capability in removing unburned methanol and formaldehyde [43,44]. The POC proposed by Ecocity Oy in 2004, it is a semi-flow-through filtration device designed for exhaust gas treatment [45]. Constructed from corrugated stainless-steel mesh and featuring a multi-layer folded design with non-blocking channels, the structure of the POC is illustrated in Figure 4. This device can effectively reduce HC compounds and CO produced from the combustion of natural gas or methanol, achieving a purification efficiency ranging from 40% to 70%.



**Figure 4.** Simplified schematic of the POC structure.

Compared with conventional exhaust purification devices, the POC features a simpler structure, lower operating costs, and can function independently without complex system integration. Recent studies have shown that placing the POC downstream of the DOC can further improve the removal efficiency of unburned methanol and formaldehyde [46].

### 2.3. *Hydrogen Fuel*

#### 2.3.1. The Use of Hydrogen Fuel

As a representative zero-carbon fuel, hydrogen produces only water vapor upon combustion, with negligible emissions of CO<sub>2</sub>, PM, or UHC, making it widely regarded as a key energy carrier for achieving zero-carbon emissions. Hydrogen possesses exceptionally low ignition energy, a wide flammability range, and a high flame propagation speed, which provides excellent combustion reactivity and rapid flame development in engines. These properties make hydrogen well-suited for lean-burn conditions and contribute to improved thermal efficiency. However, hydrogen combustion is still associated with certain emission risks and engineering challenges. Its high flame temperature may substantially promote NO<sub>x</sub> generation, especially during high-load operation with fuel-rich combustion conditions. Furthermore, hydrogen's low molecular weight and high diffusivity characteristics can lead to inhomogeneous mixture formation, resulting in localized fuel-rich zones. These zones may induce abnormal combustion phenomena such as knocking, pre-ignition, or backfire, thereby compromising engine operational stability and long-term durability. In summary, hydrogen itself is a clean fuel that does not directly produce pollutant emissions during combustion. The primary challenge lies in the formation of NO<sub>x</sub>, which occurs indirectly due to variations in combustion conditions. Therefore, the application of hydrogen in internal combustion engines requires not only the optimization of hydrogen supply and combustion control strategies but also the integration of efficient NO<sub>x</sub> after-treatment technologies to achieve low-emission and high-efficiency combustion, in line with increasingly stringent future emission regulations.

#### 2.3.2. After-Treatment System for Hydrogen Engines

SCR has become a well-established aftertreatment technology for engines, extensively employed to mitigate nitrogen oxide (NO<sub>x</sub>) emissions. Its primary working principle involves the injection of a urea-water solution through a dosing system, which is then thermally decomposed into ammonia (NH<sub>3</sub>) at high temperatures. The NH<sub>3</sub> subsequently reacts with NO<sub>x</sub> to produce harmless nitrogen (N<sub>2</sub>) and H<sub>2</sub>O [47]. With a NO<sub>x</sub> conversion efficiency exceeding 90%, SCR is currently one of the most effective technologies for controlling NO<sub>x</sub> emissions [48]. A schematic diagram of the SCR system is shown in Figure 5.



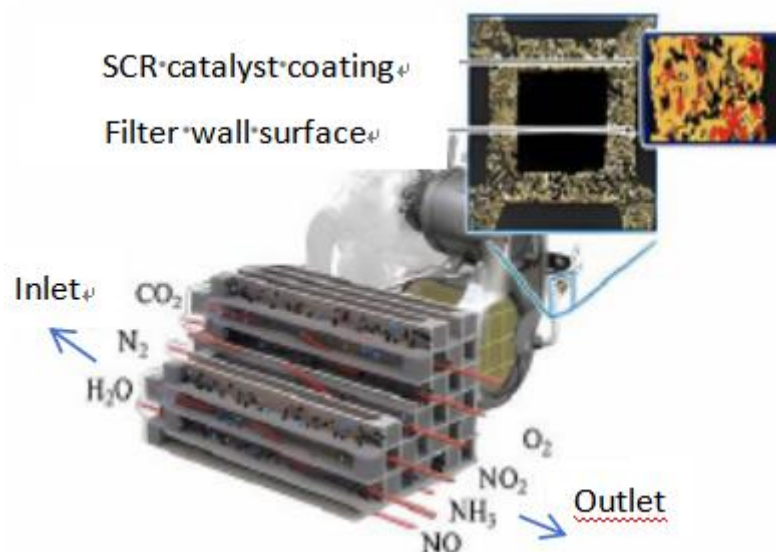


Figure 5. Schematic diagram of SCR structure.

During the operation of SCR systems, catalyst selection plays a crucial role in determining overall conversion efficiency [49]. Currently, the most commonly used catalysts are copper-based and iron-based zeolites. Copper-based zeolite catalysts offer high NO<sub>x</sub> conversion efficiency at low temperatures and exhibit good thermal stability. In contrast, iron-based zeolites demonstrate excellent catalytic performance at higher temperatures, with an effective activity window typically ranging from 458 to 598 °C [50,51].

At present, copper-based zeolites have been successfully applied to NO<sub>x</sub> conversion in diesel vehicles in both the European Union and the United States, due to their wide operating temperature window and favorable hydrothermal stability [52]. Chen et al [53] found that the auto-reduction of isolated copper sites in copper-based zeolites can enhance low-temperature NO<sub>x</sub> conversion efficiency in SCR. Shan et al. [54] observed that under fast SCR conditions, hydrothermal aging of copper-based zeolites leads to a reduced inhibitory effect of NO<sub>2</sub> on NO<sub>x</sub> conversion. Peng et al [55] investigated the influence of alkali metal potassium on the physicochemical properties of cerium–copper-based catalysts and reported that cerium modification improves SCR performance and mitigates catalyst deactivation caused by potassium poisoning. Xi and Lee et al [56,57] demonstrated that prolonged pre-sulfation aging reduces the extent of activity loss in SCR reactions and enhances sulfur resistance at low sulfur loading. They also found that the mobility of copper ions is a key factor determining catalytic activity and, ultimately, SCR conversion efficiency. Shen et al [58] reported that during steady-state active regeneration, the NO<sub>x</sub> conversion efficiency of copper-based SCR catalysts drops to approximately 80.3%.

In addition to copper-based zeolites, Liu et al [59] proposed that iron-based zeolites, due to their excellent high-temperature NO<sub>x</sub> conversion performance and low N<sub>2</sub>O selectivity, could serve as a promising complementary catalyst to copper-based systems. Jung et al [60], through investigation of N<sub>2</sub>O formation during the SCR process, found that N<sub>2</sub>O generation is closely related to the NO<sub>2</sub>/NO<sub>x</sub> ratio at the inlet, and that iron-based zeolites tend to form N<sub>2</sub>O more rapidly than their copper-based counterparts. Yu and Wang et al [61,62] explored the roles of iron sites and acidity in the SCR reaction and concluded that the catalytic activity of iron-based zeolites primarily depends on the type and concentration of active iron species. Qiao et al [63] studied the effect of CO<sub>2</sub> on the SCR performance of iron-based catalysts and found that CO<sub>2</sub> significantly inhibits catalytic activity at temperatures below 300 °C.

Although SCR technology offers significant advantages in NO<sub>x</sub> removal, its application in future hydrogen-fueled engines still faces challenges, particularly under low-temperature operation and cold-start conditions, which are difficult to avoid. Under such circumstances, the SCR system often

struggles to maintain effective denitrification efficiency due to insufficient reaction temperature. In addition, hydrogen-fueled engines tend to emit a certain amount of unburned H<sub>2</sub> during transient operation conditions [64]. Therefore, achieving efficient NO<sub>x</sub> removal under low-temperature conditions while simultaneously utilizing unburned H<sub>2</sub> has become a pressing issue. In response, hydrogen selective catalytic reduction (H<sub>2</sub>-SCR) technology has emerged. This approach uses H<sub>2</sub> as a reductant to convert NO<sub>x</sub> into harmless N<sub>2</sub> with the help of a catalyst. Notably, it can effectively reduce NO<sub>x</sub> even in high-oxygen environments and is less likely to produce secondary pollutants [65,66]. Recent studies have further demonstrated that, with the aid of specific catalysts, the H<sub>2</sub>-SCR process can achieve high NO<sub>x</sub> conversion efficiency even at temperatures below 200 °C [67].

## 2.4. Ammonia Fuel

### 2.4.1. The Use of Ammonia Fuel

Ammonia (NH<sub>3</sub>) has emerged as a promising zero-carbon alternative fuel, garnering significant research interest in recent years. Its synthesis from hydrogen and atmospheric nitrogen, coupled with existing large-scale production infrastructure, guarantees reliable supply chain continuity [68]. NH<sub>3</sub> is easy to liquefy, convenient to store, transport, and offers a higher volumetric energy density than liquid hydrogen. Moreover, its strong pungent odor provides a “self-alarming” characteristic that facilitates early detection and risk prevention in the event of a leak [69,70]. In addition, its high hydrogen content and compatibility with renewable energy sources make NH<sub>3</sub> one of the most promising candidates for future clean energy systems [71,72].

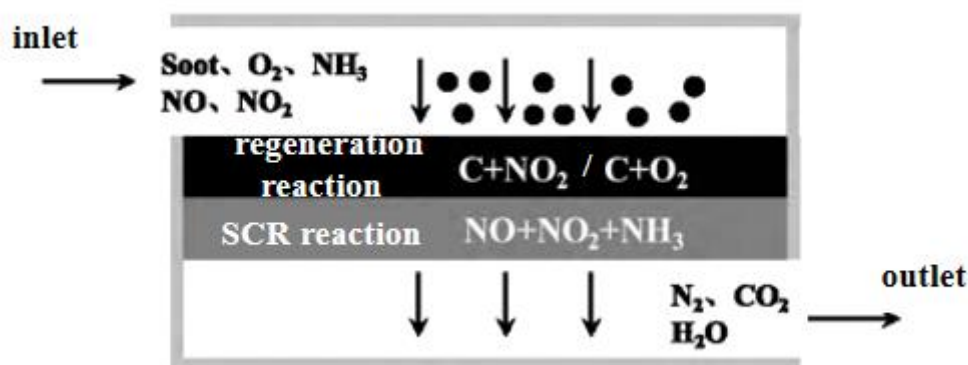
However, the practical application of NH<sub>3</sub> still faces dual challenges related to poor combustion characteristics and significant pollutant emissions. NH<sub>3</sub> exhibits a low laminar burning velocity, along with a high auto-ignition temperature and ignition energy requirement, which makes it difficult to ignite and results in slow flame propagation. These factors contribute to incomplete combustion, ultimately affecting energy efficiency and system stability [73]. More critically, NH<sub>3</sub> combustion leads to substantial NO<sub>x</sub> emissions, including both thermal NO<sub>x</sub> and fuel NO<sub>x</sub>, with emission levels significantly higher than those of conventional hydrocarbon fuels. Experimental studies have shown that the volume fraction of NO in ammonia flames can reach up to 2000 ppm, far exceeding the levels observed in methane and other hydrocarbon fuels [74,75]. Beyond NO<sub>x</sub>, the emission of residual/unburned NH<sub>3</sub> constitutes another critical environmental challenge. This compound exhibits dual hazards: direct toxicity and corrosivity endangering human respiratory systems, and material degradation risks for engine/exhaust components through chemical attacks on metal surfaces.[68].

### 2.4.2. After-Treatment System for Ammonia Engines

Similar to NO<sub>x</sub> control in hydrogen combustion, SCR has also become one of the primary after-treatment technologies for NH<sub>3</sub> engines due to its high denitrification efficiency [76]. Kurata et al [77] demonstrated effective NO<sub>x</sub> reduction using an SCR system combined with an ammonia–kerosene co-firing strategy. Further research indicated that integrating SCR with low-NO<sub>x</sub> combustion methods not only enhances purification efficiency but also allows for downsizing the SCR unit, thereby reducing its impact on the overall system layout—an advantage particularly relevant for high-power NH<sub>3</sub>-fueled gas turbines [78]. For the large-scale deployment and commercialization of NH<sub>3</sub> as a fuel, the denitrification after-treatment system must be considered a critical component, especially under operating conditions that demand both high power output and low emissions. Only through the coordinated optimization of combustion and after-treatment systems can NH<sub>3</sub> truly serve as a clean and viable substitute in the ongoing energy transition.

Although SCR is highly effective in reducing NO<sub>x</sub> emissions, the use of NH<sub>3</sub> as a fuel introduces the potential risk of ammonia slip. To address this issue, an ammonia slip catalyst (ASC) is typically incorporated into the system to suppress NH<sub>3</sub> release. Additionally, conventional SCR systems only achieve optimal NO<sub>x</sub> conversion efficiency at temperatures above 473 K, making it challenging to

control NO<sub>x</sub> emissions during low-temperature operation or cold-start conditions [73]. Ammonia-fueled engines exhibit notably poor combustion and emission characteristics under low-temperature and low-load conditions, so engines typically adopt a dual-fuel combustion strategy when utilizing NH<sub>3</sub> as fuel, where diesel serves as the ignition source to initiate ammonia combustion. In this case, PM emissions become unavoidable. Against this backdrop, SDPF technology has gained significant attention due to its strong potential for low-temperature NO<sub>x</sub> removal and effective PM capture. The core concept of SDPF technology lies in coating the SCR catalyst onto the porous filtration walls of the DPF. As exhaust gases enter through the inlet channel and pass through the filter walls, PM is trapped on the wall surfaces, while in the presence of NH<sub>3</sub>, the SCR catalyst facilitates the reduction of NO<sub>x</sub> in the exhaust to harmless N<sub>2</sub> [79]. A schematic diagram of the SDPF working principle is shown in Figure 6.



**Figure 6.** The schematic diagram of SDPF technology[75].

Tan et al [80] investigated the emission characteristics of SDPF under different catalyst coating loadings. The experiments showed that as the catalyst coating loading increased, both the NO<sub>x</sub> conversion efficiency and particulate matter filtration efficiency of the SDPF changed. However, excessively high coating loadings led to an increase in exhaust backpressure, which affected performance. When the coating loading was 90 g/L, the SDPF exhibited the best balance between NO<sub>x</sub> conversion and particulate matter filtration. Chen et al[81] investigated the impact of catalyst coating on the emission characteristics and performance of SDPF under different soot loadings. The study found that as the soot loading increased, both the pressure drop and inlet temperature of the SDPF gradually rose, while the NO<sub>x</sub> conversion efficiency significantly decreased. When the soot loading reached 9.97 g/L, the SDPF lost its ability to reduce NO<sub>x</sub> emissions. The study also showed that in nucleation-mode particle emissions, SDPF could reduce emissions by 2 to 3 orders of magnitude, while the reduction in accumulation-mode particle emissions was less significant. Furthermore, increasing the soot loading improved the particulate matter filtration efficiency of the SDPF, especially at low-speed conditions, where the filtration efficiency for both nucleation-mode and accumulation-mode particles was significantly enhanced. Tan et al [82] proposed a novel catalyst region coating strategy and compared the effects of different coating distributions on SDPF performance in their experiments. The study found that the SDPF with a localized coating still maintained good NO<sub>x</sub> conversion efficiency under most operating conditions, while significantly reducing exhaust backpressure at high speeds and heavy loads, which helps improve fuel economy. Although the localized coating strategy slightly reduced the filtration efficiency for nucleation-mode particles, it had almost no impact on the capture of accumulation-mode particles, demonstrating the potential of this strategy to balance emission control and backpressure optimization.

Kim et al [83] investigated the impact of different after-treatment systems (SCR, Lean NO<sub>x</sub> Trap(LNT) +SCR, and SDPF) on NO<sub>x</sub> emissions from Euro 6 compliant light-duty diesel vehicles. By analyzing diesel vehicles sold in South Korea since 2018, the study found that the LNT+SCR after-treatment system is applied to most vehicles meeting the Euro 6 standard. The NO<sub>x</sub> emission characteristics were tested under various driving modes, such as NEDC and WLTP. The study revealed that NO<sub>x</sub> emissions are closely related to the signals from the Engine Control Unit (ECU) and the Dosage Control Unit (DCU). Furthermore, control strategies such as urea injection quantity and timing have a significant impact on emissions, particularly during cold starts and high-load conditions. The study also showed that the SDPF system plays a key role in simultaneously reducing both PM and NO<sub>x</sub> emissions. Karamitros et al [84] studied the impact of model-based catalyst partition optimization on the performance of SDPF. The study simulated different coating partition strategies (uniform coating and regionally partitioned coating) to investigate the effects of coating quantity on SCR reactivity, pressure drop, and NO<sub>x</sub> conversion efficiency. The results showed that regionally partitioned coating significantly improved NO<sub>x</sub> conversion efficiency under different soot loads, particularly under soot-loaded conditions, where regionally partitioned coatings outperformed uniform coatings. The study also highlighted that regionally partitioned coatings help reduce the consumption of NO<sub>2</sub> in the contaminated front regions, thus enhancing passive regeneration rates and improving SCR reactivity. Marchitti et al [85] studied the interaction between soot combustion and NH<sub>3</sub>-SCR reactivity on copper-based zeolite catalyst coatings in SDPF. The study found that NO<sub>2</sub> significantly promotes soot combustion, accelerating its oxidation at low temperatures and notably reducing its ignition temperature. However, the presence of NH<sub>3</sub> inhibits the reaction between NO<sub>2</sub> and soot, leading to an increase in ignition temperature and slowing down soot combustion. Additionally, the study revealed that soot has a slight negative impact on SCR reactivity, particularly when there is excess NO<sub>x</sub>, which increases SCR reaction activity. Purfürst et al [86] studied the impact of soot on ammonia adsorption and denitration performance of SDPF catalysts. The experiment found that under soot loading, the NO conversion efficiency of the SDPF decreased, and NH<sub>3</sub> storage capacity was reduced. The diffusion barrier layer formed by soot within the porous walls of the filter restricted the transport of ammonia, leading to a decrease in NO conversion efficiency. By developing a one-dimensional micro-model of the filter wall, the study explained the effects of soot on ammonia adsorption and SCR reactivity, highlighting the significant impact of soot layer thickness on NO conversion and NH<sub>3</sub> storage. The model indicated that increasing soot loading directly affected the reaction rate and the diffusion of gas species, subsequently influencing both NO<sub>x</sub> conversion and ammonia storage.

Compared with conventional NO<sub>x</sub> treatment technologies such as SCR and SDPF, which rely on external reductants, electrochemical NO<sub>x</sub> decomposition has attracted increasing attention in recent years. This approach directly reduces NO<sub>x</sub> to harmless products using an externally applied electric current, thereby eliminating issues related to reductant storage, transportation, and potential secondary pollution caused by leakage. The operating principle involves applying an external voltage to an electrolytic cell, which polarizes the solid electrolyte and generates additional oxygen vacancies (OVS). At the three-phase boundary (TPB) on the cathode, NO is reduced to N<sub>2</sub>, while the resulting O<sup>2-</sup> ions migrate to the anode under appropriate temperature conditions, release electrons, and form O<sub>2</sub>[87]. Although this technology eliminates the need for external reductants and holds great potential for efficient NO<sub>x</sub> removal, its high energy consumption limits its application in ammonia-fueled engines. Therefore, this technology is more suitable for ammonia-fueled hybrid vehicles equipped with multiple power sources.

In addition, Direct Ammonia Injection for NO<sub>x</sub> Reduction is regarded as a novel and promising NO<sub>x</sub> control approach. This technology utilizes NH<sub>3</sub> directly as a reductant to react with NO<sub>x</sub>, converting it into harmless N<sub>2</sub> and H<sub>2</sub>O. It is particularly suitable for ammonia-fueled engines, as it leverages the ammonia already present in the fuel system, eliminating the need for additional reductant supply. Recent studies have proposed the application of this method in high-pressure direct injection (HPDI) ammonia/diesel dual-fuel combustion modes. By carefully managing the



timing of post-injection of ammonia, NO<sub>x</sub> formation can be effectively suppressed. However, excessive delay in post-injection may lead to a decrease in indicated thermal efficiency and significantly increase emissions of N<sub>2</sub>O and unburned NH<sub>3</sub>. Research indicates that maintaining the post-injection ammonia ratio within the range of 20% to 30% is generally optimal[88].

### 3. Conclusion

To better achieve the dual goals of energy transition and environmental protection, the promotion and application of low-carbon fuels in internal combustion engines has become a key research focus. This paper provides a systematic summary of the emission characteristics and corresponding after-treatment technologies of representative low-carbon fuels, including natural gas, methanol, hydrogen, and ammonia. The main conclusions are as follows:

- Natural gas as a fuel results in relatively low CO<sub>2</sub> and PM emissions, but tends to produce significant amounts of unburned hydrocarbons such as methane and formaldehyde. Due to the chemical stability and low reactivity of methane, traditional TWC are generally ineffective at converting these compounds at low temperatures. Therefore, current strategies rely on integrating DOC with methane oxidation catalysts, implementing zoned catalyst designs, or applying ozone-assisted oxidation to improve low-temperature methane conversion efficiency.
- Methanol combustion under low-temperature conditions tends to generate unburned methanol and formaldehyde, yet no dedicated after-treatment systems have been developed specifically for methanol-fueled engines. As a result, general-purpose devices such as DOC, TWC, and POC are commonly used for emission control. Among them, POC has gained attention for its simple structure, low cost, and high purification efficiency. Furthermore, the combining DOC and POC demonstrates significant potential for improving the removal efficiency of methanol-derived pollutants.
- Hydrogen combustion produces only water vapor, making it a zero-carbon fuel in terms of direct emissions. However, the high combustion temperature easily leads to the formation of thermal NO<sub>x</sub>. In addition, hydrogen's high diffusivity and low ignition energy can cause backfire and pre-ignition issues. To achieve ultra-low emissions, hydrogen-fueled engines require an integrated approach combining optimized hydrogen injection/combustion strategies with advanced NO<sub>x</sub> after-treatment technologies such as SCR, to ensure low emissions.
- Ammonia, as a carbon-neutral fuel, offers significant advantages including wide availability and ease of storage/transportation, positioning it as a promising low-carbon alternative. However, its practical application is hindered by inherent combustion challenges—notably low flame propagation speed and high minimum ignition energy—which often result in incomplete fuel oxidation and increased NO<sub>x</sub> emissions. Moreover, the toxic and corrosive nature of ammonia raises concerns over its unburned slip. SCR remains the dominant after-treatment technology for ammonia-fueled engines, and its combination with ASC and SDPF can significantly improve system stability and emission control. Electrochemical NO<sub>x</sub> decomposition, a novel reductant-free technology, also shows promise, though its high energy consumption currently limits its application to ammonia-based hybrid power systems.
- To enable the widespread application of low-carbon fuels in internal combustion engines, it is necessary to develop fuel-specific after-treatment routes that strike an optimal balance between emission reduction efficiency, thermal management, catalyst durability, and cost-effectiveness.

### 4. Prospects

With the tightening of global emission regulations and the ongoing pursuit of carbon neutrality, the research and application of low-carbon fuels in internal combustion engines are steadily advancing. However, the significant differences in physical and chemical properties and combustion characteristics among various fuels pose complex challenges for emission control technology development. Future research should focus more on developing fuel-adaptive after-treatment

systems, particularly those capable of maintaining high pollutant conversion efficiency under low-temperature conditions.

For pollutants such as methane and formaldehyde, future efforts should prioritize enhancing the hydrothermal stability and sulfur resistance of catalysts. In terms of hydrogen and ammonia fueled engine emissions, it is essential to develop more compact and integrated systems that combine combustion control with emission reduction, with a particular focus on NO<sub>x</sub> control technologies and the mitigation of ammonia slip. Existing mature engine emission control technologies remain valuable references, particularly the continued optimization of NO<sub>x</sub> reduction techniques such as SCR and SDPF, which will continue to be key areas of future research. The development of multifunctional catalytic materials, combined with advanced modeling and real-time optimization algorithms, represents a critical pathway toward achieving coordinated system-level control in emissions after-treatment processes. In addition, emerging technologies such as electrochemical NO<sub>x</sub> decomposition offer new pathways for reductant-free and energy-efficient pollutant removal.

Finally, emerging NO<sub>x</sub> purification technologies such as H<sub>2</sub>-SCR still face challenges including limited water resistance of catalysts and low reaction efficiency at lower temperatures. Future research should focus on developing catalytic materials with higher selectivity and enhanced stability, while integrating optimized thermal management strategies to improve practical applicability. In contrast, the direct utilization of NH<sub>3</sub> from ammonia fuel for NO<sub>x</sub> reduction enables synergistic integration between fuel combustion and emission control systems, eliminating the need for external reductants while streamlining overall system design. However, this approach also faces issues such as ammonia slip, difficulty in controlling injection precision, and a narrow effective temperature window. These challenges become more pronounced under variable operating conditions and high power output scenarios, imposing stricter demands on system safety and response performance.

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Abbreviations

The following abbreviations are used in this manuscript:

ICE	Internal combustion engine
UHC	Unburned hydrocarbon
DOC	Diesel oxidation catalyst
POC	Particulate oxidation catalyst
TWC	Three-way catalyst
SCR	Selective catalytic reduction
SPDF	SCR-coated diesel particulate filters
GHG	Greenhouse gas
NO <sub>x</sub>	Nitrogen oxides
PM	Particulate matter

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