Catalisadores: Como Eles Podem Facilitar e Auxiliar a Adaptação dos Motores Diesel aos Novos Potenciais Limites do Proconve P8 estágio D e E?

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RESUMO

A possível evolução do Proconve P8 para os estágios D e E, alinhados ao Euro 6, estabelece requisitos mais rigorosos para os testes em condições reais de operação (RDE). Entre as mudanças, destacam-se a redução da carga útil dos veículos, menores níveis de potência e a introdução de ciclos de partida a frio. Essas alterações impõem desafios ao gerenciamento térmico do motor e ao desempenho dos sistemas de pós-tratamento, exigindo estratégias avançadas para um controle eficiente das emissões de NOx. Além disso, a fase E introduz limites para o número de partículas (PN) no ciclo RDE, ampliando os desafios técnicos. Para atender a esses requisitos, o sistema SCR (Calisador de Redução Seletiva) precisará de catalisadores com maior eficiência em baixas temperaturas. O uso de um catalisador de amônia (ASC) será essencial para minimizar emissões de NH_3 e permitir maior flexibilidade na dosagem de Arla 32. O DOC poderá demandar formulações otimizadas para potencializar NO2 e acelerar a conversão de NOx no SCR. Já o CSF (Filtro Catalítico) enfrentará limites mais rígidos para retenção de nanopartículas, exigindo maior eficiência de filtragem em condições de baixo acúmulo de fuligem. O desenvolvimento desses catalisadores poderá ser crucial para reduzir a complexidade da adaptação dos motores ao novos possíveis estágios do Proconve P8.

Catalysts: How Can They Facilitate and Support the Adaptation of Diesel Engines to the New Potential Proconve P8 Stage D and E Limits?

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ABSTRACT

The potential evolution of Proconve P8 to stages D and E, aligned with Euro 6, establishes stricter requirements for real driving emissions (RDE) testing. Key changes include reduced vehicle payload, lower power output, and the introduction of cold-start cycles. These modifications present significant challenges for engine thermal management and aftertreatment system performance, requiring advanced strategies to ensure effective NOx emissions control. Additionally, phase E introduces limits on particle number (PN) within the RDE cycle, further increasing technical challenges. To meet these requirements, the SCR system will need catalysts with higher conversion efficiency at low temperatures. The integration of an ammonia slip catalyst (ASC) will be essential to minimize NH_3 emissions, enabling greater flexibility in Diesel Exhaust Fluid (DEF) dosing while maintaining precise pollutant control. The oxidation catalyst (DOC) may require optimized formulations to enhance NO_2 generation and accelerate NOx conversion in the SCR system. Meanwhile, the Catalyzed Soot Filter (CSF) will be subject to stricter nanoparticle retention limits, demanding improved filtration efficiency under low soot accumulation conditions. The development of these catalysts could be crucial in simplifying engine adaptation, ensuring regulatory compliance, and facilitating the implementation of potential new Proconve P8 stages.

INTRODUCTION

In recent years, the tightening of emission standards for internal combustion engines has posed significant challenges to the automotive industry worldwide. Brazil, following the path of the European Union, has implemented the Proconve P8 legislation, aligned with Euro 6 stage C regulations, which requires diesel engines to comply with stricter limits on regulated pollutants.

A potential evolution of the Proconve P8 program toward even more stringent Euro 6 stages, "Stage D" and "Stage E", introduces critical changes in Real Driving Emissions (RDE) testing procedures – such as reduced vehicle payload, lower engine output, and the inclusion of cold-start cycles – while adding new requirements such as the introduction of particle number (PN) limits during in-service conformity (ISC) and off-cycle emission (OCE). These conditions are particularly challenging for diesel engines due to their lean combustion characteristics and the thermal inertia of aftertreatment systems, which require sufficient exhaust gas temperature to activate catalytic reactions efficiently.

Meeting these upcoming limits will require optimization of engine calibration and thermal management strategies, however significant advances in emission control technologies could facilitate and support the adaptation to new stages. Aftertreatment systems composed of Diesel Oxidation Catalysts (DOC), Diesel Particulate Filters (DPF), Selective Catalytic Reduction (SCR) units, and Ammonia Slip Catalysts (ASC) will need to perform more effectively under increasingly complex and restrictive operating conditions.

DOCs will need enhanced NO2 generation, resulting in an optimum NO2/NOx ratio, achieving fast SCR reactions. DPFs must achieve high fresh filtration efficiency for both PM mass and number, especially in the ultrafine particle size range. SCR systems must maintain high NOx conversion rates over a wider temperature window, and ASCs must reliably manage ammonia slip, particularly when urea dosing is increased to compensate for thermal limitations.

This paper presents a technical assessment of how these catalyst-based technologies can be developed and integrated to address the emission control challenges posed by the proposed Proconve P8 Stages D and E. Emphasis is placed on catalyst formulation, drawing from commercial and pre-commercial applications that demonstrate feasibility within the Brazilian market context.

DIESEL OXIDATION CATALYST

The Diesel Oxidation Catalyst (DOC) is a key component of diesel aftertreatment systems, primarily responsible for oxidizing carbon monoxide (CO), unburned hydrocarbons (HC), nitric oxide (NO), and soluble organic

fraction (SOF) of the total particulate matter (TPM). Beyond these primary oxidation functions, the DOC plays a strategic role in enhancing the performance of downstream catalysts by increasing the NO_2/NO_x ratio in the exhaust stream. This function is particularly relevant in systems equipped with Selective Catalytic Reduction (SCR) and Diesel Particulate Filter (DPF) technologies, where NO_2 promotes passive soot oxidation and enables faster NO_x conversion reactions.

The oxidation mechanisms within the DOC follow a three-step sequence: (i) adsorption of O_2 molecules onto the active catalytic surface—typically composed of noble metals such as platinum (Pt) and palladium (Pd); (ii) diffusion of gas-phase reactants, such as NO, CO, and HC, to the catalyst surface, where they undergo redox reactions with the adsorbed oxygen; and (iii) desorption and diffusion of the oxidation products (e.g., NO_2, CO_2) into the exhaust flow. Since diesel exhaust naturally contains low levels of NO_2, its controlled generation within the DOC is essential to activate key SCR reaction pathways, especially under low-temperature operating conditions.

The chemical environment created by the DOC directly influences the efficiency and selectivity of subsequent reactions in the SCR system. The primary reactions involved in ammonia-based SCR processes are outlined below (Majewski, Selective Catalytic Reduction, 2025):

1) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$

2) $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ "standard" SCR reaction

3) $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ "slow" SCR reaction

4) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

5) $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ "fast" SCR reaction

Among these, the fast SCR reaction (Eq. 5) is of particular interest because it proceeds more rapidly than the standard reaction (Eq. 2), allowing for enhanced NO_x conversion efficiency at lower exhaust temperatures. This makes the DOC's role in generating an optimal NO_2/NO_x ratio (ideally close to 0.5) even more critical, especially under transient and urban driving conditions.

However, the increase in NO_2 concentration must be carefully managed, as excessive levels (>0.5 NOx) may lead to the formation of undesirable byproducts. One of the main concerns is the production of nitrous oxide (N_2O) (Koebel et al., 2002). N_2O is a greenhouse gas with a global warming potential 265-298 times greater than that of CO_2 (Luo et al., 2017). The formation of N_2O can occur through the following reactions (Majewski, Selective Catalytic Reduction, 2025):

6) $8\ NO_2 + 6\ NH_3 \rightarrow 7\ N_2O + 9\ H_2O$

7) $4\ NO_2 + 4\ NH_3 + O_2 \rightarrow 4\ N_2O + 6\ H_2O$

In addition to gaseous byproducts, ammonium nitrate (NH_4NO_3) and ammonium nitrite (NH_4NO2) may also form when excess NO_2 reacts with ammonia in the presence of water, particularly at lower exhaust temperatures (Majewski, Selective Catalytic Reduction, 2025):

8) $2NH_3 + 2NO_2 + H_2O \rightarrow NH_4NO_3 + NH_4NO_2$

These species can condense and deposit within the pore structure of the SCR or downstream catalysts, leading to temporary deactivation. To mitigate this risk, control strategies must ensure that exhaust temperatures remain above 200 °C. However, since maintaining such temperatures is often challenging, particularly during cold-starts or low-load operation, ammonia dosing should be limited to sub-stoichiometric levels (< 1), thereby minimizing the formation of ammonium-based deposits.

The effectiveness of NO-to-NO_2 conversion within the DOC depends significantly on the type and distribution of noble metals. Platinum (Pt) demonstrates superior activity for NO oxidation and is therefore essential in applications where high NO_2 formation is desired. Palladium (Pd), on the other hand, is more efficient in oxidizing CO and HC but has limited ability to oxidize NO. For this reason, Pt-rich formulations are typically preferred when supporting fast SCR reactions is a design priority. Nevertheless, modern DOCs often adopt a Pt–Pd combination to balance catalytic performance, cost, and durability, with better stability at high temperatures.

In the context of increasingly stringent emission standards, such as those proposed in potential Proconve P8 stages D and E, the correct formulation of the DOC becomes even more critical. Optimizing the Pt/Pd ratio, along with ensuring appropriate metal dispersion and thermal stability, is essential to deliver consistent NO_2 generation across a wide range of engine conditions. It is important to note that part of the NO_2 produced by the DOC is consumed in the passive regeneration of the Diesel Particulate Filter (DPF). In this process, NO_2 reacts with the accumulated soot (C) to form CO_2, as described by the following reaction (Majewski, Catalytic Diesel Filters, 2024):

9) $C + 2NO_2 \rightarrow CO_2 + 2NO$

This reaction enables passive soot oxidation at moderate temperatures (250–300 °C), but it also reduces NO_2 availability for the SCR catalyst (Majewski, 2024). Since fast SCR operates most effectively between 200 and 280 °C, where soot oxidation is minimal, the associated NO_2 loss can be neglected, making it a less critical factor in DOC design for low-temperature applications.

An integrated calibration strategy is therefore essential to balance NOx conversion, soot management,

catalyst durability, and efficient use of precious metals under dynamic operating conditions.

CATALYZED SOOT FILTER (CSF)

The Catalyzed Soot Filter (CSF) is a wall-flow particulate filter coated with an oxidation catalyst. This configuration enhances passive regeneration by promoting soot oxidation at lower exhaust temperatures and helps reduce both the frequency and duration of active regeneration events, improving system efficiency and fuel economy.

The filtration of a wall-flow filter occurs through a combination of physical and chemical mechanisms, which can be categorized into six primary modes (Hinds, 1999):

1. Sieving: Particles larger than the pore size of the filter are physically retained, forming a surface layer or "filter cake", which subsequently enhances the capture of smaller particles, although this results in an increase in back pressure.

2. Gravitational Settling: Heavier particles are driven downward by gravity, causing them to settle within the filter structure.

3. Inertial Impaction: Due to their inertia, particles deviate from the gas streamlines and impact directly onto the filter walls.

4. Interception: Smaller particles, though capable of following the gas flow paths, come into contact with and adhere to the filter surfaces as they pass close to the walls.

5. Diffusion: Ultrafine particles undergo Brownian motion, a random movement caused by collisions with gas molecules, which increases the probability of contact with the filter surface, enhancing their capture through adhesion.

6. Electrostatic Attraction: Particle capture is further influenced by electrostatic interactions between the particle surface charge and the filter material.

Together, these mechanisms provide effective filtration over a wide particle size range, as illustrated in Figure 1. The combined efficiency curves of these mechanisms typically show a dip in filtration efficiency for particles between 0.1 and 1.0 µm, depending on flow conditions within the filter. The particle diameter with the lowest filtration efficiency is known as the MPPS (Maximum Penetration Particle Size).

The potential stage E of Proconve P8 establishes a particle number (PN) limit of 9.78×10^{11} solid particles during real driving emissions (RDE) testing, targeting particles with diameters above 23 nanometers (PN23), or 0.023 µm. As this threshold overlaps with the MPPS, it is crucial to optimize the filter design to close this efficiency gap, ensuring effective particle retention and regulatory compliance.

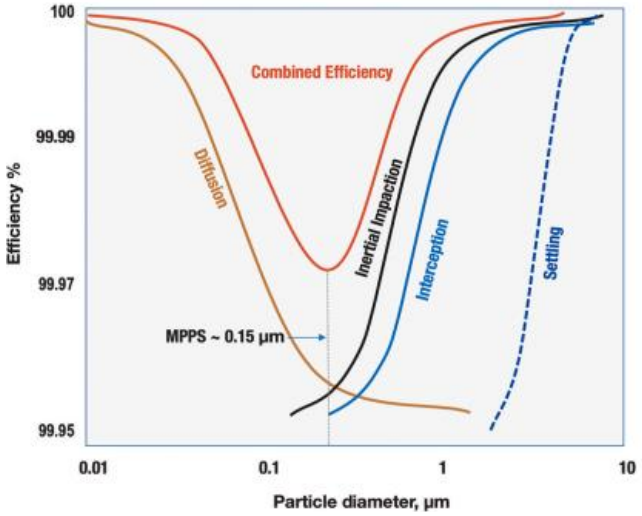


Figure 1. Particle filtration efficiency (%) as a function of mechanism and particle size (Yunchen et al., 2021).

While the oxidation catalyst coating on the CSF plays a critical role in enabling passive soot oxidation, it may adversely affect filtration efficiency, potentially worsening the filtration gap. The catalytic washcoat can partially obstruct or constrict the filter pores, reducing both porosity and open frontal area. According to the Bernoulli principle, for a constant volumetric flow rate, a reduction in flow area leads to an increase in gas velocity through the remaining open pores. This rise in superficial gas velocity reduces residence time within the filter walls, diminishing the effectiveness of diffusion-based capture mechanisms, particularly for ultrafine particles.

To address these limitations, several well-established strategies, already implemented in Europe, can be adopted to mitigate the filtration gap. One approach involves reducing the mean pore size (MPS) of the filter substrate, which enhances the capture of finer particles and potentially increases backpressure if the filter manufacturer does not offset this effect with increased porosity, which could compromise engine performance and fuel economy. Another strategy is the application of an artificial filter cake to the fresh substrate, thereby activating the sieving mechanism and improving initial filtration efficiency.

Both strategies, however, may be disproportionate to the actual needs introduced by the proposed Stage E of Proconve P8. Current CSFs are already capable of meeting Stage C requirements, which regulate particle number under laboratory-based test cycles. The main challenge posed by Stage E lies in its application to real driving emissions (RDE), where conditions are more variable, including engine out particle number emissions. In particular, filtration inefficiencies can arise in moments

immediately following active or prolonged passive regenerations, when the filter cake is thinner.

In this context, improving the oxidation catalyst coating itself, minimizing its impact on filtration performance, emerges as a more balanced and effective path for meeting the potential Stage E requirements. One promising advancement is the development of P8 Step E CSF coating technology, which aims to maintain filtration efficiency at the expense of a slight increase in back pressure. To evaluate this new coating, a PN10 Breakthrough test was developed as described in the next topic.

PN10 Breakthrough Test Procedure

To evaluate filtration performance under conditions representative of real-world operation, a PN10 Breakthrough test was developed and applied to a 13-liter diesel engine platform. The test protocol consists of four main phases. Initially, a pre-conditioning step is conducted to stabilize engine operation and ensure thermal equilibrium throughout the aftertreatment system. This is followed by a soot loading phase, in which the filter is loaded with 3.3 g/l of soot—an amount reflective of typical field usage—after which the corresponding pressure drop was recorded.

Next, a conditioning phase is carried out to promote uniform soot distribution within the filter, reducing variability and enhancing test reproducibility. The final phase involved operating the engine under steady-state full load at 1200 rpm for a continuous period of two hours. During this stage, particle number emissions downstream of the filter are continuously monitored, with a focus on PN10 (particles larger than 10 nanometers). The filtration performance is quantified using the 90th percentile breakthrough value, expressed in [giga particles (GP) per kWh], providing a reliable metric for comparison between the baseline CSF and the proposed P8 Step E CSF coating technology.

After 2 hours of regeneration, the pressure drop is compared with the maximum pressure drop of the soot loaded filter at the start of the full load sequence.

PN10 Breakthrough Results

The PN10 Breakthrough test results demonstrated a significant improvement in filtration efficiency with the newly developed coating. The new CSF technology emitted approximately 250 x 10^9particles/kWh, whereas the conventional CSF system reached around 900 x 10^9 particles/kWh under the same test conditions. This represents a reduction of more than 70% in ultrafine particle emissions, confirming the effectiveness of the improved coating in minimizing the filtration gap, particularly in scenarios with limited soot cake formation.

The new coating technology demonstrates improved distribution across the filter substrate, which helps minimize pore blockage and preserves a greater portion of the open flow area. As a result, the increase in superficial gas velocity is reduced, mitigating its adverse effects on diffusion-driven filtration mechanisms, particularly critical for capturing ultrafine particles, thus contributing to more stable and effective filtration performance.Another key

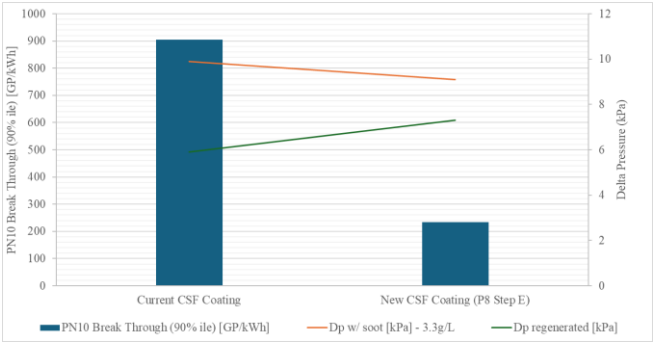


Figure 2. Filtration Efficiency and pressure drop comparison between current and new coating (Authors).

consideration for filter design is its impact on engine backpressure, which directly influences performance and fuel efficiency. The P8 Step E CSF coating technology exhibited a slightly higher pressure drop than the current CSF coating after soot removal. However, when tested under equivalent soot loading conditions (3.3g/L), the new technology demonstrated a lower pressure drop.

Improving the filtration gap through optimized oxidation catalyst coating appears to be the most effective strategy to support the transition toward a potential new Proconve P8 stages.

SELECTIVE CATALYTIC REDUCTION (SCR)

The Selective Catalytic Reduction (SCR) is predominantly used to reduce oxides of nitrogen (NOx) emissions in post-combustion diesel catalyst technologies.

A variety of catalyst formulations are employed in SCR systems, each offering specific chemical and thermal performance characteristics. Metal-based catalysts, such as those containing vanadium oxides, have historically been favored for their low cost and effective NOx conversion at temperature range (200-550ºC).

Vanadium-based SCR (V-SCR) catalysts have been continuously improved to enhance NOx conversion efficiency at low temperatures. High-performance formulations are already available to meet stringent emission standards, such as those proposed for Euro VII. However, a key limitation of V-SCR catalysts remains their relatively low hydrothermal stability. In particular, vanadium compounds can begin to sublimate at temperatures just below 600 °C, especially in the presence of water vapor (Moreau et al., 2015).

In contrast, zeolite-based catalysts have become a prevalent SCR system solution. This is especially relevant considering the compact design requirements and typical layout of the exhaust line, where the SCR catalyst is positioned downstream of the Diesel Oxidation Catalyst (DOC) and Catalyzed Soot Filter (CSF). Under such configurations, exhaust temperatures entering the SCR can exceed 600 °C during active regeneration events (Tong et al., 2018), reinforcing the need for catalysts that combine high thermal resilience with minimum catalyst volume demand.

Given the stricter emission targets anticipated in the upcoming Proconve P8 stages, especially under real driving emissions (RDE) requirements, zeolite-based catalysts stand out as viable option.

Zeolite-based catalysts, composed of microporous aluminosilicate frameworks, offer high NOx reduction efficiency over a broad temperature range (150ºC - 550ºC), excellent resistance to hydrothermal degradation, and greater durability under real-world operating conditions.

Zeolites are three-dimensional crystalline aluminosilicates with fixed microporous structures that enable selective molecular transport, making them highly efficient as shape-selective catalysts. Their framework consists of tetrahedrally coordinated silica and alumina units, and their pore geometry plays a critical role in determining NOx conversion efficiency by influencing the number and accessibility of active sites (Kumar et al., 2023).

Small-pore zeolites are particularly advantageous, as they exhibit higher selectivity for NOx reduction and are less susceptible to degradation such as by hydrocarbon fouling compared to large-pore counterparts, which can suffer from active site blockage (Cheng et al., 2022).

Pore or channel geometry can differ in structure and size because of different synthesis recipes. Zeolites with different channels are given their own names, e.g. Beta (BEA), Chabazite (CHA), MFI or zeolite Y (there are many more zeolites known). Chabazite can have different Al/Si ratios and different Cu content. But since the channel structure remains the same, it is still a chabazite.

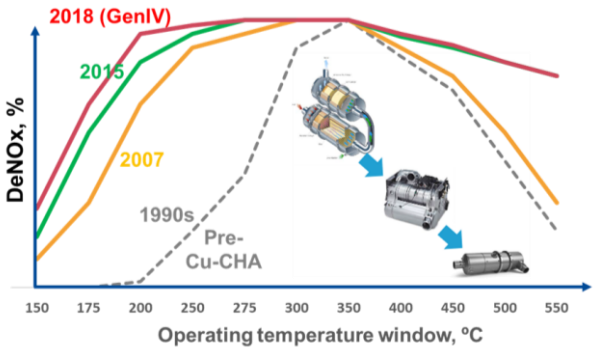
Figure 3 presents a comparative evaluation of successive generations of Cu-CHA SCR catalysts, highlighting the continuous improvements in NOx conversion efficiency over an expanded temperature range. Recent developments have focused on enhancing NOx reduction performance at low temperatures and reducing N_2O formation. These technological advancements are expected to be critical for compliance with the stringent emission limits of the upcoming Euro VII regulation. Additionally, they hold potential for application in future phases of the Proconve P8 program, supporting compliance while simplifying and reducing engine calibration efforts.

At low exhaust temperatures—such as during cold starts, urban driving, or low-load operation—engine strategies may require more aggressive urea dosing to maintain NOx conversion efficiency, particularly below 200 °C. Although urea injection can typically begin at around 180 °C, operating at this threshold introduces two main challenges.

The first is **ammonia slip**, which occurs when unreacted ammonia passes through the SCR system. At low temperatures, Cu-CHA-based SCR catalysts can effectively store ammonia; however, under Real Driving Emissions (RDE) conditions, transient events often cause abrupt increases in exhaust temperature. This can lead to the sudden release of stored ammonia, resulting in slip. The excess ammonia contributes to secondary emissions and complicates compliance with stringent emission regulations.

The second challenge is the **formation of solid deposits** due to incomplete urea decomposition. This issue is particularly associated with the formation of **HNCO (isocyanic acid)**, a reactive intermediate produced in the initial step of urea thermolysis. These deposits can affect system durability and performance.

To mitigate first effect, an **Ammonia Slip Catalyst (ASC)** placed downstream of the Cu-CHA (Gen IV) SCR is essential. The ASC converts excess ammonia into nitrogen and water, enhancing system robustness, reducing secondary emissions, and supporting regulatory compliance.



CONCLUSION

The potential implementation of Proconve P8 Stages D and E presents a new level of complexity in emissions regulation, primarily due to more stringent requirements under real driving conditions, cold-start operation, and particle number limits. In this scenario, catalysts play a pivotal role in enabling diesel engine platforms to achieve compliance without requiring extensive redesign of the base engine.

Optimized Diesel Oxidation Catalysts (DOCs) are essential for generating the right NO_2/NOx ratio to activate fast SCR reactions and ensure passive soot oxidation in the DPF, all while minimizing the formation of undesired byproducts such as N_2O or ammonium salts. Catalyzed Soot Filters (CSFs), especially those employing advanced coating techniques such as " P8 Step E CSF coating" can help close the filtration efficiency gap for ultrafine particles especially when the filter cake is thin, ensuring particle number compliance during transient tests. Meanwhile, zeolite-based SCR catalysts offer a robust solution for NOx control across a wide temperature range, maintaining high conversion efficiency and durability even under harsh thermal conditions. The inclusion of Ammonia Slip Catalysts (ASCs) becomes increasingly important as dosing strategies become more aggressive to compensate for low-temperature operation.

Altogether, the integration and calibration of these catalyst technologies are not just supportive, but essential, in facilitating the transition of diesel engines toward future Proconve P8 emission stages. Continuous development in catalyst formulation, coating techniques, and system-level integration will be critical to ensure technical feasibility, regulatory compliance, and sustained competitiveness of diesel-powered platforms in Brazil.

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