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Diesel sulfur content impacts on Euro VI soot-free vehicles: Considerations for emerging markets

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Summary

Euro VI diesel engines contribute significantly to vehicle emission reductions because they have advanced emission control aftertreatment systems for particulate matter (PM) and nitrogen oxides (NO_x). These systems are sensitive to the sulfur content in diesel fuel, and for this reason, most major vehicle markets have progressively limited fuel sulfur content to 10 parts per million (ppm), also known as ultralow-sulfur diesel. As emerging market nations adopt soot-free Euro VI emission standards for their new vehicles, they face a transition to ultralow-sulfur diesel, as well. But this fuel quality transition does not happen overnight. In some cases, Euro VI vehicles are fueled with higher sulfur content fuels during a nationwide transition, or due to regional fuel quality differences. Through a review of recent literature, this paper explores the impact of 50 ppm sulfur fuels on Euro VI technologies. We find that, while all emission control systems achieve maximum effectiveness around 10 ppm sulfur or less, some temporary exceedance of these levels can be tolerated without adverse effects. After short-term exposure to sulfur content at 50 ppm, adverse effects on emissions performance can be reversed with increases in exhaust gas temperatures. However, long-term exposure to 50 ppm sulfur introduces more serious challenges for real-world emissions compliance, including impaired diesel oxidation catalyst (DOC) operation that leads to thermal degradation of diesel particulate filter (DPF) and selective catalytic reduction (SCR) systems, and direct poisoning of catalyst sites on DPFs and zeolite-SCRs. Given this, governments wishing to achieve soot-free Euro VI real-world emission control performance should accelerate the fuel transition and limit nationwide diesel fuel sulfur content to 10 ppm.

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Background

The adoption of vehicle emission standards in the past few decades has driven major improvements in air quality in many parts of the developed world. Los Angeles, once infamous for its smog, has experienced a decrease in ozone concentrations greater than 50% below 1960 levels. Additionally, fine particulate matter ($PM_{2.5}$) concentrations are half the levels that they were in the early 1990s; this is thanks in large part to the California Air Resources Board and its Diesel Risk Reduction Plan.[1] Vehicle emission standards have also been given credit for the recent air quality improvements in Beijing.[2]

More stringent vehicle emission standards better protect the environment and human health. Figure 1 presents the emission limits for light-duty diesel passenger cars and for heavy-duty diesel vehicles in Europe. The European standards are the most widely followed vehicle emission program in the world.

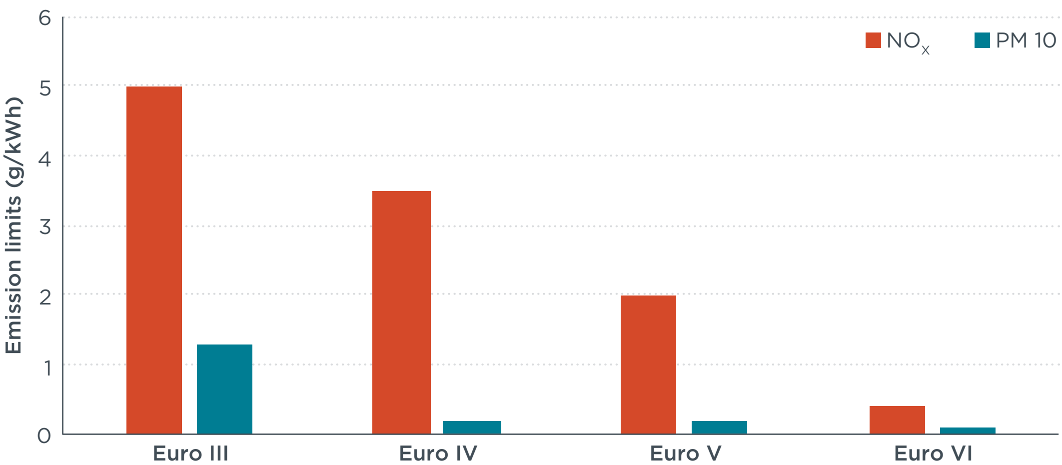

Figure 1. Vehicle emission limits evolution for heavy-duty diesel vehicles.

Every evolution of emissions standards leads to more advanced and efficient emission control technologies. Table 1 summarizes the progression of technologies that meet increasingly stringent emission standards for diesel light-duty vehicles (LDVs) and heavy-duty vehicles (HDVs) in Europe.[3] Current Euro VI and U.S. 2010 HDV emission standards can achieve an approximately 95% reduction in $PM_{2.5}$ and nitrogen oxides (NO_x) compared to the Euro II and U.S. 1994 standards.[4] Note, that emission control technologies that reduce pollutants during the combustion process are not listed here.

1 David D. Parrish et al., "Air Quality Improvement in Los Angeles—Perspectives for Developing Cities," *Frontiers of Environmental Science & Engineering* 10, no. 5 (October 2016): 11. https://doi.org/10.1007/s11783-016-0859-5.

2 "Beijing's Air Quality Improvements Are a Model for Other Cities," Climate & Clean Air Coalition Secretariat, March 9, 2019, https://www.ccacoalition.org/en/news/beijing%E2%80%99s-air-quality-improvements-are-model-other-cities.

3 Adapted from Francisco Posada, Anup Bandivadekar, and John German, *Estimated cost of emission reduction technologies for light-duty vehicles,* (ICCT: Washington, DC, 2012), https://theicct.org/sites/default/files/publications/ICCT_LDVcostsreport_2012.pdf and from Francisco Posada, Sarah Chambliss, and Kate Blumberg, *Costs of emission reduction technologies for heavy-duty diesel vehicles*, (ICCT: Washington, DC, 2016), https://theicct.org/sites/default/files/publications/ICCT_costs-emission-reduction-tech-HDV_20160229.pdf

4 There are important regulatory differences between the European and U.S. diesel emission standards, especially for heavy-duty vehicles. However, both are able to achieve the same extent of reduction of pollutants, and the technologies are similar in both jurisdictions. For more information on light-duty vehicle and heavy-duty vehicle emission standards and control technologies, refer to Posada et al., *Estimated cost of emission reduction technologies for light-duty vehicles* and Posada et al., *Costs of emission reduction technologies for heavy-duty diesel vehicles*

Table 1. Diesel emission control technology requirements to meet European regulations

Emission standard	Technology
Euro II and Euro III	• Emission is controlled via air and fuel mixing strategies. • No aftertreatment required
Euro IV	• NO_X control through vanadium-based, open-loop selective catalytic reduction (**SCR**) systems* or exhaust gas recirculation (**EGR**) • PM control through DOC in some vehicles, with most relying on in-cylinder control • The aftertreatment system is comprised of **DOC** + **SCR**
Euro V	• Same technology as Euro IV, also combinations of EGR and SCR • Small changes in NO_x limits are met with minimum hardware changes, mainly engine calibrations. • The aftertreatment system is composed of **DOC** + **SCR**
Euro VI	• NO_X control through zeolite-based, closed-loop SCR system or combinations of SCR and EGR • Ammonia slip catalysts (**ASC**) for ammonia control (ammonia is a byproduct of SCR reactions) • PM/particulate number control through DOC and DPF • The aftertreatment system is composed of **DOC** + **DPF** + **SCR** + **ASC**

*Some manufacturers have chosen to control NO_x in Euro IV and V heavy-duty vehicles through EGR.

Ultralow-sulfur diesel fuel, with less than 10 parts per million (ppm) sulfur, enables the DPF and SCR systems necessary to meet the very low emission limits of Euro VI standards. As Table 2 illustrates, targets for diesel sulfur content and European emission standards are set together. Each step toward lower emission limits has been matched and enabled by lower fuel sulfur content. For instance, 50 ppm sulfur diesel allows the DOCs necessary for PM and HC control and the vanadium-based SCR systems for NO_X controls to meet Euro IV emission limits.

Table 2. Regulatory step and corresponding maximum diesel sulfur level

Regulatory step	Application date in Europe (new models)	Corresponding maximum sulfur (S) level
Euro II	1996	S 500 ppm
Euro III	2000	S 350 ppm
Euro IV	2005	S 50 ppm
Euro V	2008	S 10 ppm
Euro VI	2013	S 10 ppm

More countries are decreasing the sulfur level in diesel fuel and simultaneously implementing stricter emission standards. Fuel quality improvements can sometimes outpace emission standards. For example, Euro IV low-sulfur diesel fuel was made available in most European countries when Euro III emission standards were still in place. At the same time, diesel with sulfur content at or above 50 ppm is still a barrier for soot-free, Euro VI-equivalent vehicle adoption in many countries, especially in South America, Africa, southeast Asia, and the Middle East. Figure 2 shows the diesel sulfur content and diesel HDV emission standards in countries and regions around the world in 2019.

Some countries and regions have more than one type of diesel available at retail gas stations. In countries like Peru, Mexico, Argentina, Chile, and South Africa, major cities and areas with chronic air quality challenges have access to more premium diesel that has lower sulfur content, but other parts of the country might only have diesel with higher levels of sulfur.

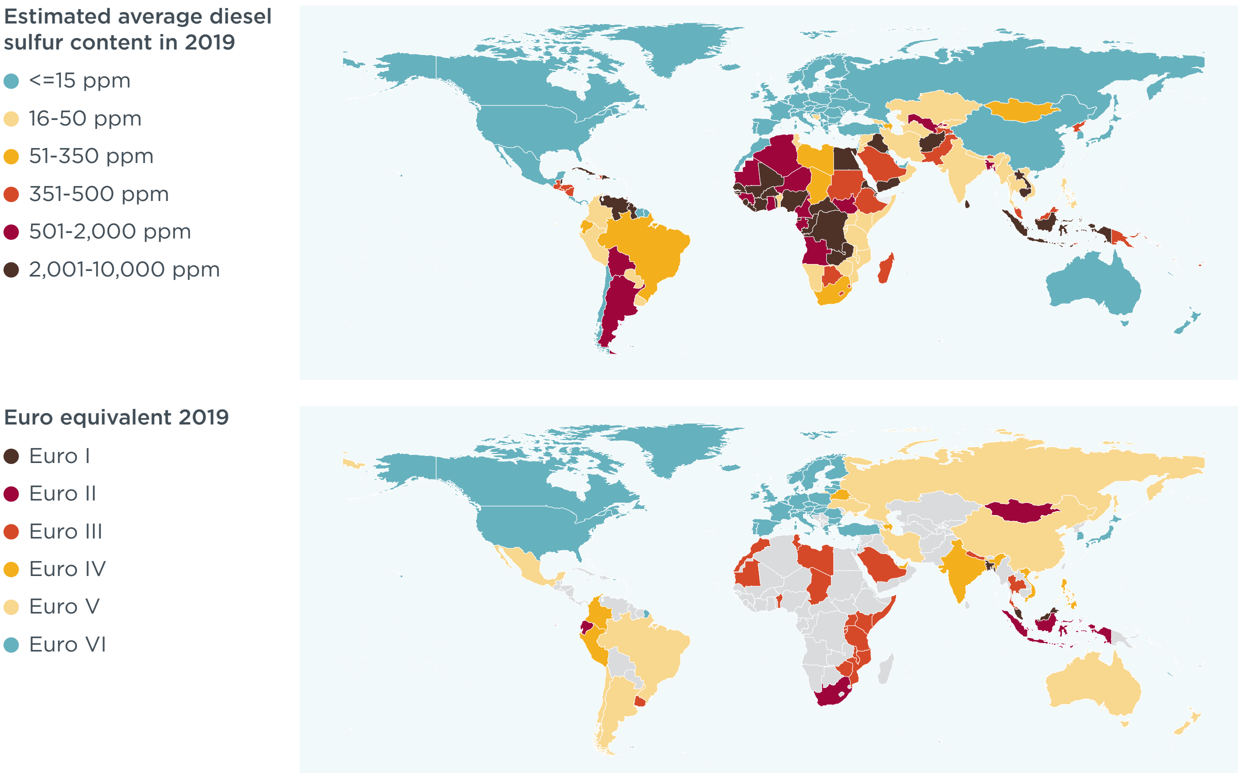

Figure 2. Diesel sulfur content (top) and HDV emission standards (bottom) worldwide in 2019. The United States and Canada follow the U.S. EPA diesel sulfur standards, which are equivalent, but not identical, to Euro VI standards. Source: Miller & Jin (2019).[5]

The automotive industry has historically recommended diesel below 50 ppm for standards that require SCR systems, such as Euro IV. DPF systems need to be matched with diesel sulfur content in a range below 10 ppm in Europe and 15 ppm in the United States. In countries where diesel fuel with different levels of sulfur are available at gas pumps, if misfuelling occurs, it poses a challenge for some emission control technologies. This is because some aftertreatment technologies are sensitive to fuel sulfur levels; they may experience pollutant conversion inefficiencies and, in some extreme cases, even catalyst poisoning.

The objective of this paper is to review the latest technical information on the impact of diesel sulfur content on emission control technology and the effect of permanent or temporary exposure to higher-than-recommended sulfur content. The research scope covers diesel vehicles and the emission control technologies that are needed to meet Euro VI emission standards. Gasoline vehicles and gasoline sulfur content are not covered.

Methodology

We performed an extensive literature search on the impacts of diesel sulfur content on diesel vehicle emission control components. The focus was on the impacts of criteria

5 Josh Miller and Lingzhi Jin, *Global progress towards soot-free diesel vehicles in 2019*, (ICCT: Washington, DC, 2019), https://theicct.org/publications/global-progress-toward-soot-free-diesel-vehicles-2019.

pollution on emission performance and deterioration of emission control system components. The main challenge for this analysis was that older technical SAE papers focus on technologies for matching fuel qualities, i.e., 50 ppm for Euro IV technologies and 10–15 ppm for Euro VI and EPA 2010 technologies. We found only one report, published in 1999, that systematically studied fuel quality variation impacts on emission control systems. Those older papers provide useful information about the physical and chemical fundamentals of sulfur content's impact on aftertreatment systems.

Several papers published in the last five years, however, are the source of new findings regarding sulfur's impacts on aftertreatment systems. These more recent documents are the result of research efforts in countries with dual sulfur offerings (national/regional), where the risk of fueling with higher sulfur diesel is high; the impact of this has largely not been addressed by prior research in developed markets. We focused on these recent publications as they provide insights into how manufacturers are addressing the risk to aftertreatment components posed by temporal exposure to fuel with higher sulfur content.

Review of emission control technologies

There are two categories of diesel emission control technologies: in-cylinder and aftertreatment systems. Each is a part of a complex diesel emissions control system. As in most systems, the design and function of each emission control component depends on the others. Their role in aftertreatment control and their design makes them more or less susceptible to fuel sulfur content, individually and as a result of cascading effects to other systems. This section provides an overview of key characteristics of each component and explains how these interact as a system.

In-cylinder emission control

As noted in Table 1, fuel injection systems and air handling technologies play a role in diesel engine-out emissions and fuel consumption. EGR is one of the most widely used technologies for in-cylinder NO_x control.

Fuel injection pressure, rate, and timing can control both NO_x and PM emissions. Fuel injection improvements involve the use of high-pressure fuel injection with variable fuel timing and metering. These changes help achieve a more complete combustion and reduce particulate formation and fuel consumption.

Air handling is focused on the use of variable geometry turbochargers to provide the right amount of air under specific engine operational conditions. Increasing the pressure of the air entering the chamber increases the air density and allows better combustion in the brief time available. Tuning these parameters minimizes production of both PM and NO_x.

An EGR system recirculates a portion of cooled exhaust gas back to the engine's cylinder, which reduces both peak combustion temperature and temperature-dependent NO_x formation. EGR is the most effective and commonly used technology for in-cylinder NO_x reduction in diesel engines. The EGR fraction, the share of recirculated exhaust gas in the total intake charge, is tailored to each engine operating condition and can vary from zero to 40% of the incoming air.

For most technologies involved in improving air and fuel mixing and for EGR systems, sulfur content at 50 ppm has not been a barrier for adoption. Advanced fuel injection technologies and turbocharging have been deployed in diesel engines since Euro 3/III standards were put in place in 2000, when 350 ppm was the sulfur limit.[6] Manufacturers, however, recommend EGR adoption at fuel sulfur levels at or below 50 ppm; this is to avoid durability and warranty issues that might arise if EGR cooling systems corrode pipes through the condensation of sulfur compounds.[7]

Aftertreatment

Limits on PM and NO_x emissions in the Euro VI standards are almost impossible to meet with in-cylinder emission reduction strategies alone, and thus aftertreatment control measures are required in these diesel engines. PM aftertreatment devices are DOCs and DPFs. The options for aftertreatment NO_x control are SCR with urea and lean NO_x traps (LNT). LNTs, although commercialized in some passenger cars in Europe, are being phased out of that segment and have never been commercialized in HDV diesel applications.[8] Therefore, they are not addressed here.

Diesel oxidation catalysts (DOC) use precious metals such as platinum and palladium to oxidize hydrocarbons (55%–90% efficiency), carbon monoxide (40%–70% efficiency), and up to 90% of the soluble organic fraction (SOF) of diesel PM.[9] During low-load driving cycles, the SOF fraction is high and the PM reduction can be significant; but in high temperature cycles, the SOF fraction in the PM is low and DOCs become less effective in controlling PM. DOCs also provide important support in achieving high NO_x conversion efficiencies in SCRs that are located downstream. The DOC oxidizes NO to NO_2. The higher fraction of NO_2 in turn leads to higher efficiency of SCRs at low temperatures and also makes continuous, passive DPF regeneration—in other words, the accumulated black carbon, or soot, burning—possible. This can only happen at relatively low temperatures when the NO_2-to-soot ratio is in the correct range.

Diesel particulate filters (DPF) capture the solid fraction of PM, including black carbon, from the vehicle exhaust. DPFs also provide effective control of CO and HC emissions, and reduce these emissions by 90% to 99% and 58% to 82%, respectively.[10] The DPF substrate is made of a highly porous ceramic material, either cordierite or silica carbide. The DPF traps particles while letting gases flow across its porous walls; they are also known as wall-flow DPFs. DPFs achieve PM reduction efficiencies greater than 95% and PN efficiencies above 99% due to their ability to accumulate the solid fraction of PM, including ultrafine particles.[11] The accumulation of PM solid fraction needs to be carefully monitored to avoid increasing exhaust backpressure, as that directly reduces engine performance.

The process of removing the accumulated PM from DPFs is called filter regeneration and it can be passive or active. Passive regeneration burns the deposited material using NO_2 that is formed from NO on the DOC upstream of the DPF or coated onto the filter itself.

6 Posada et al., *Estimated cost of emission reduction technologies for light-duty vehicles*

7 Ibid.

8 LNTs were used in some diesel LDVs certified to the early requirements of the Euro 6 program. The introduction of the Real Driving Emission (RDE) in-use testing requirements became a technical challenge that was solved by cost-effective SCR systems.

9 John J. Mooney, *Diesel engine emissions control requires low sulfur diesel fuel*, (SAE International: Warrenton, PA, 2000), https://doi.org/10.4271/2000-01-1434.

10 *Opening the door to cleaner vehicles in developing and transition countries: The role of lower sulphur fuels. Report of the Sulphur Working Group of the Partnership for Clean Fuels and Vehicles (PCFV)*, (United Nations Environment Programme: Nairobi, Kenya, 2008), https://www.unenvironment.org/resources/report/opening-door-cleaner-vehicles-developing-and-transition-countriesthe-role-lower.

11 W. Addy Majewski and Hannu Jääskeläinen, “Exhaust Particulate Matter,” *DieselNet*, August 2019, https://www.dieselnet.com/tech/dpm.php.

The NO_2 formation happens during normal engine operations and no external heat is necessary. On the other hand, active regeneration requires late fuel injections upstream of the DPF. In active regeneration, soot accumulated in the DPF is combusted with oxygen; this results in higher fuel consumption and there is a risk of having uncontrolled temperatures in the DPF.

Flow-through filters (FTF). Other types of diesel PM control for retrofit projects are offered by flow-through PM filters, which are often miscategorized as DPFs. FTFs, also commonly referred to as partial or open filters, do not capture or trap the solid fraction of PM in the same way porous wall-flow DPFs do. FTFs have PM reduction efficiencies of around 40%–60%. This is achieved by oxidizing the volatile and semi-volatile HCs deposited on the particle's surface. FTFs do not require maintenance and do not interact with engine functions, which makes them ideal for retrofitting.[12] They are no longer used in emission control systems of new vehicles.

Selective catalytic reduction (SCR) systems convert NO_x to water and nitrogen over a catalytic surface, and the catalytic reaction requires ammonia. Ammonia comes from the injection of a urea-water solution into the exhaust stream.[13] SCR systems can achieve high conversion efficiencies, as high as 98%, over a wide temperature range regardless of the engine-out NO_x.[14] SCR allows for higher engine efficiency and lower PM generation with high engine-out NO_x levels because SCR is able to treat the NO_x.

SCR systems are widely commercialized and, since 2005, they have been deployed in Euro IV vehicles fueled with up to 50 ppm sulfur diesel. Some SCR systems are designed with vanadium-based catalysts that are not very sensitive to sulfur; they tend to perform well at the mid-temperature range but lose NO_x conversion efficiency at both low and high temperatures. Exposure to high temperature exhaust for prolonged periods can also irreversibly deactivate the vanadium catalyst. For this reason, vanadium-SCR is used in aftertreatment systems that do not require DPFs—e.g., Euro IV and Euro V for HDVs—or in vehicles with passive DPF regeneration systems.[15]

In aftertreatment systems that require DPFs, an alternative to vanadium is a Cu-zeolite or Fe-zeolite catalyst. Because of their high thermal stability, these work well in systems with a wide temperature range and are especially well suited to withstand the high temperatures that result from active DPF regeneration.[16] Still, these catalysts are more sulfur sensitive and slightly more expensive.[17] Cu-SCR is used in active DPF regeneration systems that are applied in HDVs to meet Euro VI and EPA 2010 standards. Zeolite-based SCR has a further advantage of better performance at low NO_2-to-NO_x ratios, especially at low exhaust temperatures, and these are characteristic of driving and load conditions in many developing countries. Zeolite-SCR systems are applied in Euro VI vehicles in combination with passive DPF regeneration, and high efficiency can be achieved in a closed-loop, controlled setting with NO_x sensors before and after the SCR to better tailor urea injection management.

12 Ibid.

13 Urea for automotive applications is commercially known as aqueous urea solution (AUS 32) in India, AdBlue in Europe, and diesel exhaust fluid (DEF) in the United States.

14 Timothy V. Johnson, "Review of Diesel Emissions and Control," *SAE International Journal of Fuels and Lubricants* 3, no. 1 (2010): 16–29. https://doi.org/10.4271/2010-01-0301.

15 Sougato Chatterjee, Mojghan Naseri, and Jianquan Li, *Heavy duty diesel engine emission control to meet BS VI regulations*, (SAE International: Warrenton, PA, 2017), https://doi.org/10.4271/2017-26-0125.

16 Ibid.

17 W. Addy Majewski, "Selective Catalytic Reduction," *DieselNet*, May 2005, https://www.dieselnet.com/tech/cat_scr.php.

Effect of sulfur on emission control technologies

This next section summarizes the literature we reviewed about the impact of sulfur content on emission control performance and fuel consumption.

In most conditions, diesel sulfur content has little impact on engine-out HC, CO, and NO_x emissions. On the other hand, higher diesel sulfur does have an effect on engine-out PM emissions.[18] The sulfur in the fuel can be oxidized to sulfur dioxide (SO_2) and sulfur trioxide (SO_3) in the exhaust. SO_3 readily hydrolyzes to form sulfuric acid (H_2SO_4) with available and abundant water molecules in the exhaust gas mix. Sulfuric acid acts as a nucleation site for particle formation and growth once the exhaust gases have cooled down, and eventually increases the PM mass emissions from the engine. The sulfuric acid present in the engine-out exhaust may also condense into sulfuric acid in the EGR system during normal operations, because exhaust gas cooling is required for EGR to be effective at reducing NO_x emissions. [19] To minimize the risk of sulfuric acid corrosion of EGR, sulfur diesel content is preferred at less than 15 ppm.[20] However, there are a number of materials for the EGR cooling pipes that would be appropriate for vehicles designed to operate at higher ppm sulfur.

Depending on the types and configurations of various aftertreatment technologies, sulfur in diesel negatively affects them to varying degrees of severity and reversibility. Higher sulfur diesel negatively affects DOC performance by reducing the catalyst oxidation efficiency and by increasing engine-out PM emissions. The sulfur in fuel will be partially oxidized to SO_3 on the DOC catalytic coating, and this sticks to the catalyst sites and deactivates the catalytic performance. As a result, there will be reduced CO/HC-conversion during cold start conditions. In certain operating conditions, the sulfur stored in the DOC might be released again as SO_2 or SO_3, and sulfuric acid might be formed in the exhaust; this becomes a risk for visible white smoke emissions.[21]

Additionally, high sulfur diesel negatively affects the DOC because it amplifies the increase in PM emissions by the DOC in certain conditions.[22] The higher the sulfur content in the fuel, the more SO_2 present in the exhaust gas and the more sulfates generated in the DOC. In the Diesel Emission Control – Sulfur Effects (DECSE) Program, catalyst-out PM emissions were measured on an 11 liter (L), 1999MY Cummins ISM 370 diesel engine over the 4-mode Organisation Internationale des Constructeurs d'Automobiles (OICA) cycle, at OICA Mode 2 (peak torque) and on the heavy-duty FTP.[23] Results of the tests revealed that the magnitude of increase in sulfate PM is directly proportional to the amount of sulfur in the diesel fuel. This effect was most obvious in OICA Mode 2 (peak torque); compared to 3 ppm sulfur diesel, the catalyst-out PM emissions for 30 ppm sulfur diesel increased total PM by 50%, from less than 0.010 grams per brake horsepower-hour (g/bhp-hr) to 0.015 g/bhp-hr. For context, these PM

18 Albert M. Hochhauser, et al., *Impact of fuel sulfur on gasoline and diesel vehicle emissions*, (SAE International: Warrendale, PA, 2006), https://doi.org/10.4271/2006-01-3370.

19 Tom Darlington and Dennis Kahlbaum. *Nationwide emission benefits of a low sulfur diesel fuel*, (Air Improvement Resource Inc.: Novi, Michigan,1999), https://www.epa.gov/sites/production/files/2015-03/documents/10242001mstrs_diesel_sulfur_w97_0.pdf.

20 Hannu Jääskeläinen and Magdi K. Khair, "EGR Systems & Components," *DieselNet*, August 2019, https://www.dieselnet.com/tech/engine_egr_sys.php.

21 Andreas Wiartalla et al., *Future emission concepts versus fuel quality aspects – Challenges and technical concepts*, (SAE International: Warrendale, PA, 2011), https://doi.org/10.4271/2011-01-2097.

22 In DOC, the oxidation of SO_2 leads to the generation of sulfate particulates. Higher sulfate particulates may increase the total particulate emissions despite the decrease of the organic fraction.

23 U.S. Department of Energy et al., *Diesel Emission Control – Sulfur Effects (DECSE) Program phase I interim data report no. 1*, (National Renewable Energy Lab, Golden, CO, 1999), https://www.osti.gov/biblio/755348-diesel-emission-control-sulfur-effects-decse-program-phase-interim-data-report

emission values, even at 30 ppm sulfur content, are very close to PM emission limits of the EPA 2010 HDV emission standards, which are 0.010 g/bhp-hr.

Higher diesel sulfur content also affects the DPF's ability to reduce PM emissions. At elevated temperatures, catalysts present on DPF substrates may release sulfates produced from the oxidation of diesel sulfur. Gas-phase sulfates then undergo heteromolecular nucleation with water vapor to form more particulates as they are cooled downstream of the DPF, and this reintroduces sulfate particulate emissions.[24] In the aforementioned DECSE Program, tests were conducted on a 7.2L diesel engine equipped with electronic controls and two types of passive regeneration DPFs—a continuously regenerating DPF (CR-DPF) and a catalyzed DPF (cDPF).[25] Engine emissions were tested under OICA, at peak-torque and road-load duty cycles. The study found that fuel sulfur has significant effects on post-DPF total PM emissions. When used with 3 ppm sulfur fuel, both DPFs were effective in reducing tailpipe PM emissions 95% over the OICA cycle. When sulfur levels increased to 30 ppm, the PM reduction efficiencies dropped to 74% and 72% for the cDPF and CR-DPF, respectively. When tested with 150 ppm sulfur fuel, PM reductions were 0% and -3%, respectively.

As mentioned above, zeolite-based SCR performance is also sensitive to diesel sulfur content. Higher sulfur diesel can directly affect the ability of zeolite-based SCRs to convert NO_x. Sulfur oxides (SO_2 and SO_3) formed from the fuel combustion can poison a zeolite SCR catalyst during operation. In addition, SO_2 produced in the engine can be further oxidized to SO_3 across the DOC and DPF, and this can exacerbate poisoning of the SCR.[26] Using 50 ppm sulfur fuel, Chatterjee et al. (2017) ran multiple World Harmonized Transient Cycle (WHTC) tests on a 2007 8.9L Cummins ISL diesel engine fitted with DOC, cDPF, and SCR.[27] Results showed that the NO_x conversion activity of the Cu-SCR decreased after each WHTC cycle, while the NH_3 slip increased. Over 40 WHTC cycles, the NO_x conversion decreased from 88% to 80%. At low temperatures, which happen under light load, the SCR performance was affected the most.

High sulfur diesel interferes with DOC operation and leads to severe indirect impacts on the optimal operations of DPF and SCR that are needed for PM and NO_x control. The DOC plays an integral part in modern diesel aftertreatment systems by converting NO into NO_2 to support the passive regeneration process of the DPF and SCR. Sulfur decreases NO_2 formation in the DOC, which could lead to performance loss in downstream passively regenerating DPF systems that depend on upstream NO_2 to oxidize the soot. With higher sulfur content, NO_2 formation at the DOC can be reduced in the entire temperature range, with the most significant degradation occurring between 300°C and 450°C, the temperature range most relevant for passive DPF regeneration capability.[28]

Apart from sulfur's direct effect on reduced SCR performance, SCR efficiency is indirectly compromised by reduced NO_2 formation from the upstream DOC; this is due to the strong influence of the NO_2-to-NO_x ratio on SCR catalyst performance. With higher sulfur diesel, the reaction of ammonia with SO_3 to form $(NH_4)_2SO_4$ and NH_4HSO_4

24 Addy W. Majewski, "Diesel Particulate Filters." *DieselNet*, July 2019, https://www.dieselnet.com/tech/dpf.php.

25 U.S. Department of Energy et al., *Diesel Emission Control – Sulfur Effects (DECSE) Program phase I interim data report no. 4: Diesel particulate filters – final report*, (National Renewable Energy Lab, Golden, CO, 2000), https://www.osti.gov/biblio/755351-diesel-emission-control-sulfur-effects-decse-program-phase-interim-data-report-diesel-particulate-filters-final-report.

26 Chatterjee et al. *Heavy duty diesel engine emission control to meet BS VI regulations*

27 Ibid.

28 Wiartalla et al., *Future emission concepts*

also needs to be taken into account.[29] Both of these create significant risk of deposit formation in the exhaust line or on the SCR catalyst, and of fouling and deactivating the SCR catalyst.

Finally, the literature shows that higher diesel sulfur content does not increase HC or CO emissions. The DESCE Interim Report 4 concluded that changes in the HC and CO emission reduction efficiencies of DPFs with increasing levels of sulfur were not statistically significant. It also found no significant changes in the baseline gas phase emissions of HC and CO, or the baseline fuel consumption observed after increasing the fuel sulfur level. While indirect CO_2 penalties are expected as a result of additional desulfation cycles under higher sulfur content operation, none of the published literature reviewed quantified its magnitude.

Discussion

The literature detailed above shows that higher sulfur content is problematic for modern soot-free aftertreatment systems found on Euro VI or EPA 2010 HDVs in the following ways:

- Catalysts on DOC and DPF systems experience oxidation efficiency degradation..
- Zeolite-based SCR systems experience catalyst efficiency degradation with diesel that has more than 15 ppm sulfur.
- DPF regeneration is affected by higher sulfur because it decreases NO_2 formation in DOCs. This leads to performance loss in passive DPF systems that depend on upstream NO_2 from the DOC to oxidize the soot. Higher back pressure and more frequent active regeneration result in higher fuel consumption.
- SCRs convert less NO_x due to changes in NO_2-to-NO_x ratios, which are themselves a result of reduced NO_2 formation in DOCs exposed to higher sulfur content. Consequently, real-world emissions performance deteriorates.

These detrimental effects of sulfur are generally not permanent, and most performance can be restored with technology formulations and strategies. For example, experimental results demonstrate that a DOC-cDPF system is able to operate on higher sulfur fuel for short periods. In one example, a minivan with a 2.0L diesel engine first ran the New European Driving Cycle (NEDC) with less than 10 ppm sulfur diesel, then switched to 1,900 ppm sulfur diesel for approximately 800 km and had its emissions evaluated.[30] Subsequently, the minivan's tank was filled with less than 10 ppm sulfur fuel and the vehicle was conditioned and tested again over the NEDC. Results showed that the platinum-palladium (Pt/Pd) DOC's performance in removing CO was initially impaired by the higher sulfur, but was significantly restored after the vehicle switched back to low-sulfur diesel. In the same study, a fuel burner bench experiment that involved sulfur aging further demonstrated that the CO and HC oxidation performance with a Pt/Pd cDPF can be recovered. This is different from what was found in the DECSE study, suggesting that the impact is dependent on DPF catalyst and washcoat formulation. In addition, stable exotherm regeneration was shown to be achievable even after long-term exposure to high-sulfur fuel. Taken together, these results show that using suitably designed Pt/Pd catalysts, a DOC-cDPF system is able to operate on higher sulfur fuel to produce the

29 Chatterjee et al., *Heavy duty diesel engine emission control to meet BS VI regulations*

30 Alain Ristori et al., *A Diesel Passenger Car Euro V Compliant System for India*, (The Automotive Research Association of India, Kothrud, Pune, 2011), https://doi.org/10.4271/2011-26-0029.

same oxidation efficiencies of CO and HC, assuming the use is periodic and not long term, and that the catalyst and washcoat are formulated to support those events.

Similarly, for DOC, the loss of performance in CO and HC oxidation due to sulfur poisoning is observed but can be fairly easily restored, given the right catalyst formulation. In one study, the DOC inlet gas of a 4.5L turbocharged diesel Tier 3 John Deere engine without EGR was subject to highly accelerated sulfur poisoning of inlet gas at 40 ppm SO_2 at 270ºC for 60 minutes.[31] Different DOC platinum group metal (PGM) formulations were tested. Results showed that HC and CO conversion efficiency of Pt-zeolite DOC was almost unaffected by sulfur poisoning, while Pd-zeolite DOC did see a drop in both conversion efficiencies. However, after a 30-minute 350ºC desulfation step, the Pd-zeolite DOC recovered.

Another study demonstrated that the NO_2 conversion efficiency of SCR can be restored under the right conditions. In an experiment also using a 4.5L turbocharged diesel Tier 3 John Deere engine without EGR, following a 1 g/L of SCR volume system sulfur exposure, vanadium-SCR and Fe-zeolite SCR systems were able to recover to at least 90% conversion of NO_X after one or two high-temperature excursions on high-load engine cycles.[32]

The key to restoring the performance of diesel emission control systems here is desulfation, which is often done by raising the exhaust temperature. In emission control systems that consist of cDPF, DOC, and zeolite-based SCR, desulfation is achieved by engine post-injections during cDPF active regeneration. The post-injection is split into two stages. The first stage targets sulfur de-poisoning of the DOC and DPF substrate; this is because post-injection of fuel raises the exhaust temperature above the sulfur desorption temperature and results in sulfur removal from the DOC and DPF. The second stage is soot oxidation, which removes the soot loadings from the catalyst—the goal of active DPF regeneration. Chatterjee et al. (2017) explained that high temperature (575 °C) desulfation will be able to restore Cu-zeolite SCR performance when high sulfur – 50 ppm diesel is used.

However, it is important to note that thermal desulfation via post injection presents its own set of challenges and limitations. For one, it could be difficult to determine the appropriate timing. Post injection desulfation also increases fuel consumption and oil dilution. Thermal desulfation can also damage the catalyst and increase emissions. When desulfation happens at 250°C and above, SO_2 and SO_3 are desorbed from the catalyst surface. SO_3 is soluble in water and thus forms exhaust sulfuric acid; this leads to corrosion of the exhaust line and catalyst washcoat damage. When the gaseous H_2SO_4 condenses downstream of the exhaust line, it causes “white cloud” aerosol PM pollution.[33]

Another serious issue that should not be overlooked is the thermal and aging stability of emission treatment devices. This is particularly pertinent when considering post injection thermal desulfation, which exposes devices to thermal stress. Indian real-

31 Kenneth S. Price, Douglas Ummel, and Thomas Pauly, *A systematic evaluation of sulfur poisoning and desulfation behavior for HD diesel oxidation catalysts*, (SAE International, Warrenton, PA, 2018), https://doi.org/10.4271/2018-01-1262.

32 Douglas Lee Ummel and Kenneth Price. “Performance and Sulfur Effect Evaluation of Tier 4 DOC+SCR Systems for Vanadia, Iron, and Copper SCR,” *SAE International Journal of Engines* 7, no. 3 (2014): 1244–51. https://doi.org/10.4271/2014-01-1519.

33 Bandu Shamrao Zagade, Vijay Sharma, and Thomas Körfer, *Tuning and validation of DPF for India market*, (SAE International: Warrenton, PA, 2017), https://doi.org/10.4271/2017-26-0135. Also, Takahiro Hirano et al., Analysis of sulfur-related white smoke emissions from DPF system, (SAE International: Warrenton, PA, 2015), https://doi.org/10.4271/2015-01-2023.

world driving durability tests were conducted on passenger vehicles equipped with DOC and cDPF that are compliant with Euro 5 diesel emission standards, and the effects of Bharat stage IV (BS IV) diesel with 50 ppm sulfur and BS III diesel with 350 ppm sulfur were compared in both city and extra-urban duty cycles.[34] The results revealed that there was no DPF performance degradation or abnormal temperature behavior during regeneration when 50 ppm sulfur fuels were used. On the other hand, with 350 ppm sulfur fuel, the DPF had uncontrolled regeneration issues—very high regeneration temperatures in excess of 1,000°C that caused thermal crack of the DPF. Sulfur poisoning in the DOC was the cause for the uncontrolled regeneration and it led to unburned hydrocarbon slip. This unburned hydrocarbon slip was, in turn, responsible for elevating the temperatures during regeneration beyond the safety limits of the DPF catalyst.

Some studies found that the performance loss of zeolite SCR exposed to 50 ppm sulfur diesel is not permanent. One found that exposing the sulfated catalyst to 575°C appeared to completely restore the Cu-zeolite SCR performance.[35] In a separate study, researchers set up a diesel system simulator comprised of a DOC, a catalyzed soot filter (CSF), and a Cu-zeolite SCR, with SO_2 being fed in.[36] They found that Cu-zeolite SCR experienced reduction in NO_x conversion efficiencies from 98% to 60% after 1,300 hours of operation with a 35 ppm SO_2 in feed conditions. The system NO_x conversion performance was recovered after 500°C desulfation. Both studies confirmed that exposing Cu-zeolite SCR to high sulfur fuel will produce quick performance loss, but high temperature desulfation is able to restore performance.

Still, reversibility in aftertreatment systems other than the ones analyzed cannot be assumed from the studies discussed above. In Ummel and Price (2014), a Cu-zeolite SCR system with a 4:1 Pt/Pd DOC was not able to recover 90% of its NO_x conversion performance like the vanadium-SCR and Fe-zeolite SCR systems were able to do.[37] Studies that show reversibility of sulfur poisoning refer to the particular configuration(s) and formulation(s) of catalysts to explain why performance recovery is possible.

Conclusion

The literature we reviewed identifies risks to Euro VI emissions performance when diesel fuels containing sulfur content greater than 10 ppm are used. These risks involve immediate losses of pollutant conversion efficiency by sulfur poisoning and, in the long term, risks to systems durability. DOCs and DPFs with low Pt/Pd ratios are the most sensitive technologies to sulfur poisoning. Although vanadium-based SCR systems have been universally operated with 50 ppm sulfur diesel, the more advanced zeolite-based catalyst is sensitive to catalyst poisoning at that sulfur level.

The negative effects of short-term exposure to high sulfur content can be reversed via well-known protocols. Thermal desulfation via post-injections to increase exhaust gas temperatures is capable of restoring catalyst conversion efficiency to pre-exposure levels. In this scenario, a vehicle that has been fueled with 50 ppm could experience

34 Dhinesh Kumar et al., "On Road Durability and Performance Test of Diesel Particulate Filter with BS III and BS IV Fuel for Indian Market," *SAE International Journal of Engines* 9, no. 3 (2016): 1651–61. https://doi.org/10.4271/2016-01-0959.

35 Ibid.

36 Weiyong Tang, Xiwen Huang, and Sanath Kumar, "Sulfur Effect and Performance Recovery of a DOC+ CSF+ Cu-Zeolite SCR System," DEER Conference (2011). https://www.energy.gov/sites/prod/files/2014/03/f8/deer11_tang.pdf.

37 Ummel and Price, "Performance and Sulfur Effect Evaluation"

immediate catalyst degradation and could regain its conversion efficiency once fueled with 10 ppm diesel and after a defined number of desulfation cycles.

The main risk of using 50 ppm sulfur fuel comes from long-term exposure. There is a cascading effect that begins with impaired DOC operation and direct poisoning of catalyst sites in DPFs and zeolite-SCRs. Poisoning of catalyst sites in the DOC implies that hydrocarbons slip by the catalyst to severely increase exothermal events in the DPF; this, in turn, leads to thermal degradation of the DPF and the SCR located downstream. In this scenario, a vehicle that has an aftertreatment system that is not designed for 50 ppm operation—i.e., a post-Euro IV/4 vehicle—would be at high risk of DPF and SCR failure due to thermal degradation.

The world is moving toward tighter limits on diesel fuel sulfur content. As of 2019, 63 countries have retail diesel fuels averaging less than 15 ppm sulfur, which accounts for 70% of total global on-road diesel consumption. By 2025, 81% of on-road diesel fuel will contain no more than 15 ppm sulfur. But many countries with far higher fuel sulfur content have not committed the resources nor defined the policies necessary to match this global trend.[38] Among these are Indonesia, Thailand, Nigeria, and South Africa, all of which face significant air-quality challenges. These countries have committed to make 50 ppm sulfur fuels available, but have yet to take the final step toward ensuring 10 ppm sulfur fuels.

The evidence suggests that Euro VI diesel vehicles can temporarily tolerate fuels containing 50 ppm sulfur, but continuous operation is problematic. When it comes to fuel imports, governments have greater flexibility to shift to lower sulfur 10 ppm fuels and should leapfrog to this level. Countries that invest in 50 ppm sulfur domestic production should plan for 10 ppm sulfur production in the near future and adopt fuel quality standards that set this sulfur level as the ultimate target.

38 Miller and Jin, *Global progress towards soot-free diesel vehicles*

LIST OF ACRONYMS

ASC	ammonia slip catalyst
CO	carbon monoxide
CSF	catalyzed soot filter
DECSE	Diesel Emission Control – Sulfur Effects
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
DSS	diesel system simulator
EGR	exhaust gas recirculation
EPA	U.S. Environmental Protection Agency
HC	hydrocarbon
HDV	heavy-duty vehicles
HPFI	high pressure fuel injection
LDV	light-duty vehicle
LNT	lean NO_x trap
NEDC	New European Driving Cycle
NO_x	nitrogen oxides
OICA	Organisation Internationale des Constructeurs d'Automobiles
PM	particulate matter
ppm	parts per million
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SOF	soluble organic fraction
VGT	variable geometry turbochargers
WHTC	World Harmonized Transient Cycle

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