TECHNOLOGY PROGRESSES IN DIESEL EXHAUST PARTICLES CONTROL

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ABSTRACT

Implementation of straight and stringent legislation of the pollutant emissions from diesel-engine vehicles and exhaust after-treatment technologies requires the new technological development for diesel particulate matter (DPM) abatement. This article summarizes the current status of DPM control strategy. The main focus is put forward diesel particles composition, particulates formation mechanisms, the particle emissions standards, combustion control strategies and exhaust after-treatment systems for state-of-the-art DPF technologies. Also, the paper covers the DPF regeneration control methodologies. Furthermore, the progress of the highly optimized approaches, which involves the Catalyzed Diesel Particulate Filter (CDPF), the combined technologies of Diesel Oxidation Catalyst (DOC) and DPF and the combined technologies (Filters and SCR/NOx traps) are discussed.

INTRODUCTION

Besides NO_x, CO and unburned hydrocarbons (HC) from the exhaust diesel engine, particulate matter (PM) emission is actually regarded as a major environmental issue with serious impacts on health [1, 2]. To be viable solution, restrictive application of legislative standards on automotive diesel engines emissions must be accompanied with technological alternatives for a domestic use. Catalytic oxidation is one of the interesting solutions working well for CO and HC oxidation over a diesel oxidation catalyst (DOC) [3] based on noble metals (e.g. Pt, Pd), but the DOC system is not effective for the simultaneous reduction of NO_x and soot. Complex abatement strategies are then needed [4, 5]. For the NO_x abatement, the NH_3/urea selective catalytic reduction (SCR) and the NO_x trap, are promising NO_x control technology [6–9]. On the other hand, diesel particulate filters (DPF) are used to remove soot particles from the exhaust stream [10–12]. These filters usually consist of wall-flow monoliths, that is, honeycomb-like structures with 50% of the channels plugged at the gas filter inlet and the remaining channels plugged at the outlet. The soot particles are trapped from the gas stream in the porous walls of the filtering catalytic converter channels. The regeneration of used DPF filters is achieved using soot combustion; this operation which is necessary to avoid pressure drop in the exhaust can be conducted through several commercially available technologies [13]. Catalytic oxidation of the soot is one of the most favored solutions proposed for the regeneration of DPF. The use of a large number of catalytic materials has been documented in the last years [14, 15], including formulations with noble metals (mainly Pt), alkaline and alkaline earth metals or transition metals that can accomplish redox cycles (V, Mn, Co, Cu, Fe, etc.), and internal transition metals [16]. The challenges are mainly related to their low temperature activity and long-term thermal and chemical stability.

This article presents a review on the pollutant emissions from diesel engine vehicles and their control systems. In this context, the main pollutant emission (particulate matter PM) from diesel engines is principally addressed. This provides comprehensive information on techniques for meeting the particles emission standards including diesel particulate properties and their mechanisms of formation, the DPF and catalyzed-DPFs (CDPFs) trapping control strategies, the combined technologies of Diesel Oxidation Catalysts (DOCs) and DPF and the combined Filters and SCR/NO_x traps systems.

PROPERTIES OF DIESEL PARTICLES

General characteristics

The diesel PM is generally composed of the following four main fractions as depicted in figure 1. They are (1) elemental carbon (EC, solid), i.e. soot, (2) soluble organic fraction (SOF, solid or liquid substances finely distributed in gases) from fuel and engine lubricant oil, (3) sulfates (hydrated sulfuric acid, metal sulfates, and liquid, depending o the sulfur content of the fuel), which require the use of the ultra-low sulfur diesel (ULSD, US: ≤ 15 ppm; EU: ≤ 10 ppm), and (4) ash (inorganic materials), which requires low SAPS (sulfate ash, phosphorous, and sulfur) engine oils and other components (solid) mainly from engine corrosion and wear (Fe, cu, Cr and Al), lube oil with additive package (Ca, Zn, P, S,…) [17, 18]. It should be noted that the composition of PM vary widely depending on the engine design, the management strategies, the operating conditions and the fuel and oil used [18–20].

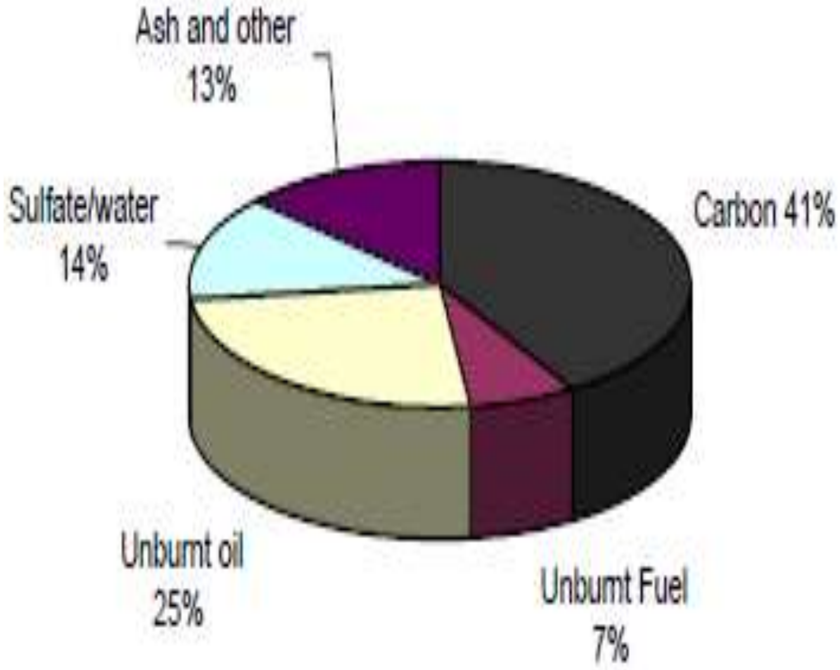

Figure 1: Average Composition of particulate matter (PM) for diesel engine [21, 22].

DPM size distribution

Figure 2 shows the physical relationship between diesel nucleation, accumulation and coarse modes for three weighted size distributions (number, surface area and mass [21, 23]. The curves have a lognormal, trimodal form and the concentration in any size range is proportional to the area under the corresponding curve in that range. The nucleation mode (3-30 nm) typically contains < 10% of the particle mass but > 90% of the particle number. Nucleation mode particles are usually composed of nearly all-volatile material. Most of the DPM mass is found in the accumulation mode (30-500 nm size particles) and is composed of carbonaceous agglomerates and adsorbed materials. The coarse mode consists of particles larger than 500 nm in diameter and contains 5-20% of the mass. The large particles are formed by reentrainment of DPM, which has been deposited on cylinder and exhaust system surfaces. All three modes are better defined by their formation mechanism than by rigid size boundaries.

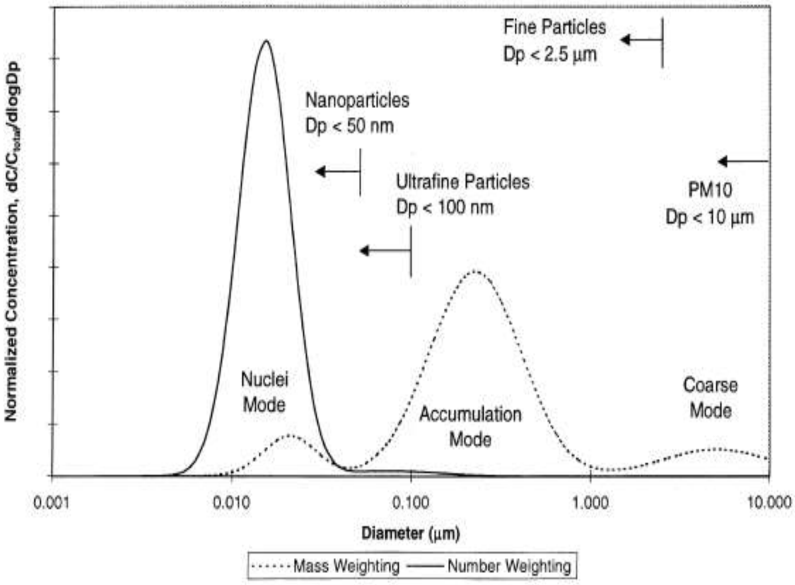

Figure 2: Typical mass and number weighted size distributions of diesel PM [21, 23].

PARTICLE FORMATION MECHANISM

Diesel Engine particulates, generated after combustion, consist in solid carbon particles commonly referred to as soot that result from cracking or agglomeration and upon which some volatile organic compounds are adsorbed. Diesel particle is defined as an ensemble of all substances other than water that are present in the exhaust gas in the solid (ash, carbon) or liquid phases. The carbon particles become coated with condensed and adsorbed organic compounds, including oxygenated hydrocarbons and unburned hydrocarbons. The condensed matter is comprised of inorganic compounds such as sulfur dioxide, nitrogen oxide and sulfuric acid [21, 24–26]. The process for Diesel particles formation takes place in two paths: training of primary particles and condensate, and agglomeration in cluster of particles. The formation of these particles is due to the strong heterogeneity of the flame in the combustion chamber.

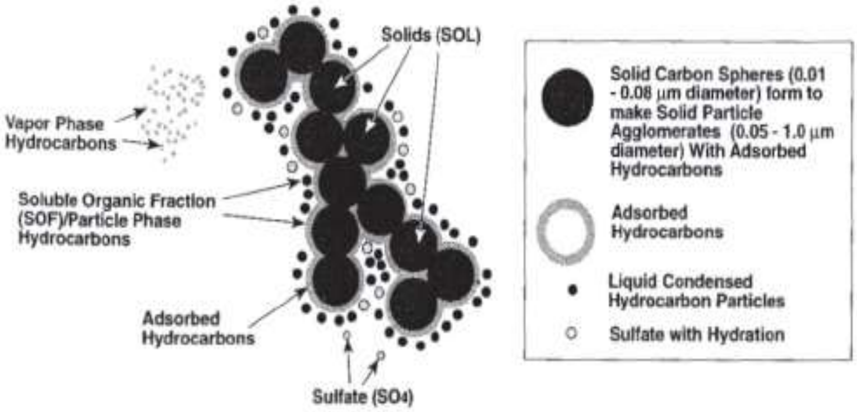

Figure 3: Morphology of the diesel aggregates with the elementary spherules and the SOF fraction adsorbed on the surface [27].

The mechanism of formation for the primary particles can be divided into 6 steps [28]:

1. During combustion, the fuel is reformed in aromatic compounds because of its depletion in hydrogen with the time;

2. These aromatic compounds react among themselves to form polymers of more cumbersome and poor hydrogen;
3. The compounds agglomerate in slips in which the hydrogen is absent;
4. The slips agglomerate to form crystalline graphite;
5. These micro-structures agglomerate to form a micro-particle;
6. The elementary spherules agglomerate in diesel particles.

Figure 4 shows the mechanism for the formation of diesel particles [28]:

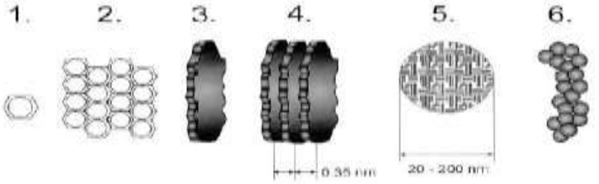

Figure 4: Steps for the formation of diesel particles [28, 29].

RECENT ADVANCES IN DIESEL PARTICULATE CONTROL

As mentioned above, the diesel particulate matter is composed of volatile material and carbonaceous agglomerates. The ratio of carbonaceous agglomerates to volatile precursor species changes when catalyzed after-treatment devices are used such as flow through oxidation catalysts or catalyzed filters [30, 31]. Oxidation catalysts are typically used to reduce carbon monoxide and volatile hydrocarbons while filters reduce particulate matter. Catalyzed filters may also reduce the hydrocarbon fraction, but the degree of reduction depends upon the type of catalyst. In addition, filters reduce the solid carbonaceous fraction in the exhaust.

Diesel particulate matter abatement technologies

Non catalyzed Diesel Particulate Filter

Diesel particulate filters (DPF) have been considered as a solution to the PM problem for the last twenty five years. Numerous DPF system concepts have been developed incorporating different filter media and geometric configurations. A list of the commercially available and prototype filter media includes the extruded ceramic materials (such as cordierite, aluminum titanate, silicon carbide, mullite etc.), and the metallic materials (such as sintered metal powders, non-woven fiber felts and metal foams) [32]. Some commercial (extruded ceramic) filter configurations, shown in Figure 5, were widely used: *cordierite* and *silicon carbide*. The first one is a synthetic ceramic developed for flow-through catalyst substrates and then adapted to filter; silicon carbide has been introduced as filter material, because of its better durability in high thermal stress applications, but, due to its weight and high cost, the market is still dominated by cordierite [33]. Other materials were studied, for example aluminum titanate whose properties are impressive compare to SiC materials: low thermal expansion and high strength; in fact no cracks in the filter material were observed even after a long run of severe regeneration cycles. Further, a tight control of pore size reduces the typical backpressure on filter with soot presence [34].

Figure 5: Example of commercial filter configurations

An estimated distribution of these materials on the global particulate filter market [35] can be seen in Table 1.

Table 1: Estimated Utilization of Filter Materials for Hot Gas and/or Exhaust Cleaning

Materiel	Extruded ceramics	Ceramic fibres	Sintered metals	All others
Utilization	70%	25%	4%	1%

Geometric DPF configurations include extruded honeycomb wall-flow monoliths, assembled parallel plate wall flow elements, cylindrical cartridges (based on fibrous structures), foam monolithic blocks and plates, and concentric tubular wall-flow elements. Some configuration examples of these are shown in Figure 6.

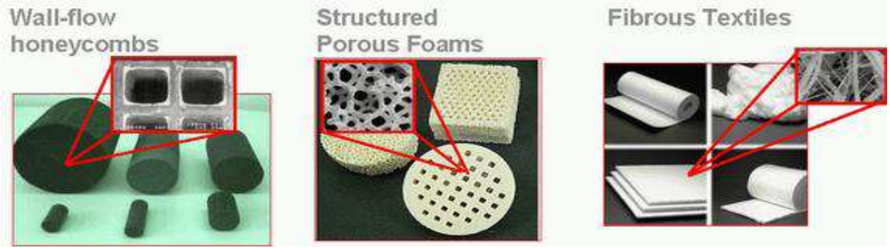

Figure 6: Different filter configurations

Much effort has been done on developing filters in Europe to satisfy the particulate standards (Euro IV). The typical filter, produced in 2001 by Peugeot Industries, was the ceramic wall-flow filter which is different when compared to the traditional automotive catalytic convertor. It consists of a honeycomb monolith structure made of porous material with alternate channels plugged at both ends so that exhaust gas is forced through the channel walls, trapping the PM in the process. Substantial improvements in PM emission reduction were made possible by the use of these systems [36]. An illustration of a DPF is shown in figure 7.

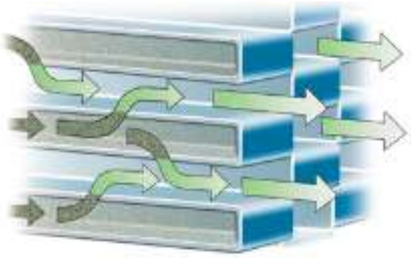

Figure 7: Typical design of a DPF used to reduce PM emissions in diesel engines

The main challenge in the use of the DPF is the need for periodically or continuously regenerating the filter by oxidizing the PM which has accumulated during the trapping process. Direct oxidation by O_2 is accomplished at temperatures of around 600°C where the carbonaceous soot oxidizes. However, the exhaust temperature of the Diesel engines under normal operation is in the range of 150°C to 200°C, therefore, efforts have been made to reduce the balance point temperature (BPT). The BPT is the temperature at which particulate accumulation is equal to particulate oxidation, wherein back-pressure is constant and the system is in balance. The main advantage of the use of DPFs which makes this technique very attractive, is the high surface area per unit volume which, combined with the high collection efficiency (up to 95% removal of PM by mass) if the pore opening is less than 40-80µm [37]. Durability of properly operated filter systems has been shown to be exceptional over as much as 600,000 km. It is shown that increasing the filter diameter/length ratio for any given filter volume will reduce pressure drop and also decrease peak temperatures in the filter during uncontrolled regeneration. The particulate collection mechanism is governed by:

- Depth filtration (particles with diameter size lower than the filter porosity are deposited inside the porous material);
- Cake filtration (particles are deposited on the channel as show in Figure 8).

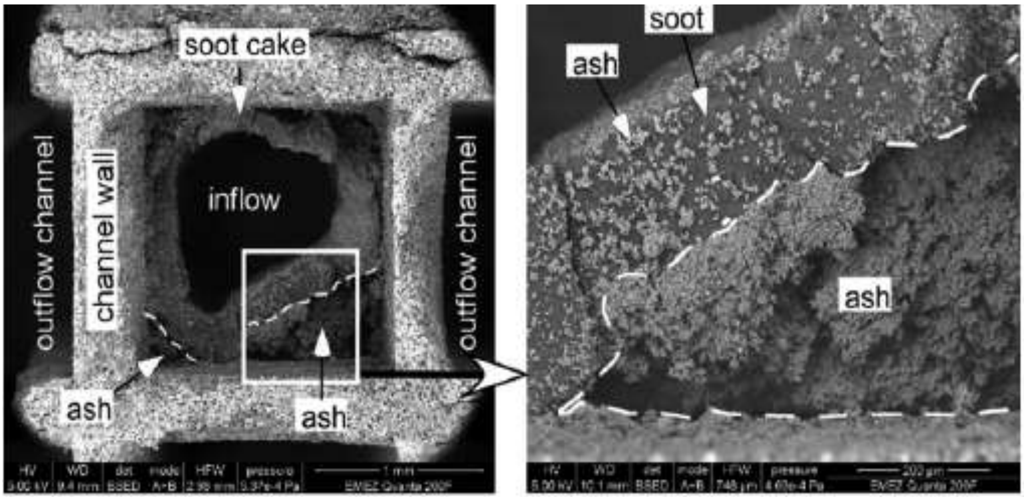

Figure 8: SEM-image of a DPF section showing the soot accumulation on a channel (left) and distinguishing the soot from the ash layer (middle and right) [37].

Obviously when filter collects the particulate matter from the exhaust gas an increase in filter backpressure is present. This provokes higher fuel consumption and reduces available torque [38]. Moreover the capacity of the filter is not infinite and it has to be regenerated. The regeneration process can be classified as *active* or *passive*. The active methods consist of burning off the collected particulate. Under the conditions met in Diesel exhaust systems regarding flow and oxygen concentration, the required reaction rates for complete regeneration are attained at temperatures above 550°C, which are reached at urban driving conditions. Thus several regeneration techniques have been suggested over the last 25 years, the most simple and effective based on catalysts: coated filter [39] or fuel doping [40]. The soot combustion temperature is lowered by doping fuel with catalytic additives, typically organometallic compounds: the organic part is oxidized in the engine combustion chamber, while the metallic part is well dispersed in soot. A lot of metals have been proposed: cerium [41] and iron [42] for their low cost and low toxicity. Also, copper [43] and molybdenum [44] have a higher activity but they have a negative influence on men health. Although the oxidation rate of soot is significantly increased, additional heating is necessary due to the exhaust gas temperatures under all operating conditions. PSA Peugeot-Citroen was the first car manufacturer that commercialized system with an active regeneration system represented in figure 9 [45].

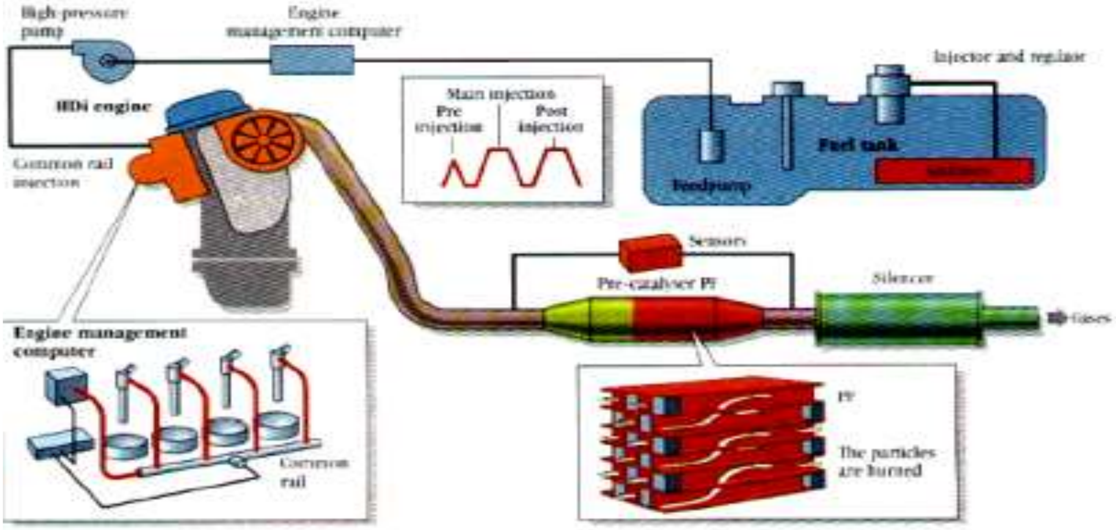

Figure 9: Schematic representation of an active regeneration system [45].

The system consists of a wall-flow SiC filter, an oxidation catalyst in front of the filter, a dosing filter for fuel additive and a number of sensors associated with a specific engine software which allows the regeneration process and guaranties system diagnosis. During the regeneration mode, occurring every 400-500 km, three injections are performed. These filters have to mainly face the ash accumulation which makes necessary to clean or to substitute the filter itself. Furthermore the additive tank has to be refilled periodically [37]. The alternatives to this kind of filters are the washcoated ones (Catalyzed Ceramic Traps), commercially introduced in 1985 on Mercedes cars sold in California [37]. The main component of the filter is the wall-flow monolith, whose walls are coated with an active catalyst: oxides of base metals, noble metals as well as a mixture of both.

Catalyzed Diesel Particulate Filter (CDPF)

Most catalyzed diesel particulate filters utilize monolithic wall-flow substrates coated with a catalyst. These catalytic systems, commonly referred to as after-treatment systems, use a solid catalyst in order to reduce the reactants of different reactions to various products. A typical converter design illustrated in figure 10 consists of monoliths coated with catalytic material. These monoliths have a number of parallel channels to facilitate the gas flow in the axial direction, and are made up of either ceramic or metal substrates. The substrates provide a high geometric surface area for gas contact. This substrate is coated with highly porous inorganic oxides such as γ-Al_2O_3, SiO_2 TiO_2 or ZrO_2, that can retain the noble metal. Noble metals such Pt, Pd, Rh etc. [46, 47], are then deposited on the washcoat (figure 10). Exhaust gas flowing through the catalytic converter diffuses to the catalyst surface where heterogeneous reaction takes place.

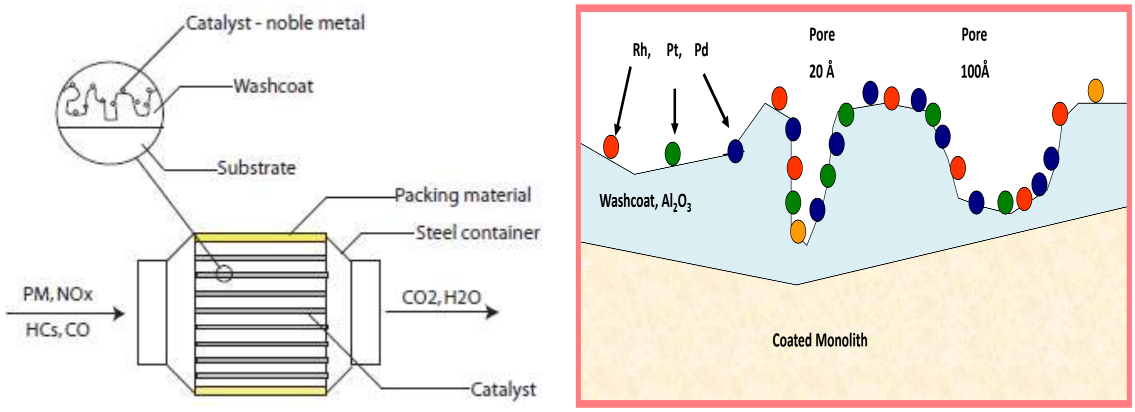

Figure 10: Structure of the monolithic catalytic converter.

The catalyst lowers the soot combustion temperature allowing the filter to self-regenerate during periods of high exhaust gas temperature. A number of diesel filters catalysts have been developed including both noble and base metals formulations [5, 14–16, 41, 48–50]. Catalyzed ceramic filters exhibit very good PM filtration efficiencies but are characterized by relatively high exhaust gas pressure drop. In the CDPF, a catalyst is applied onto the filters media to promote chemical reactions between components on the gas phase and the soot (carbon) collected in the filter (figure 11).

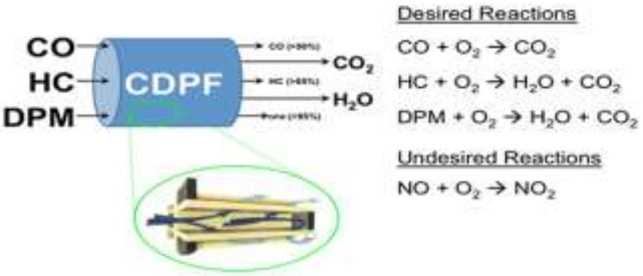

Figure 11: Catalyzed Diesel Particulate Filter (CDPF) and chemical reactions.

The main purpose of the catalyst is to facilitate regeneration of the filter by enabling the oxidation of diesel particulate matter under exhaust temperatures experienced under regular operation of the engine/vehicle, typically in the 300-400°C range. In the absence of the catalyst, particulates can be oxidized at appreciable rates only at temperatures around 550-560°C. Various catalyst systems used for diesel filters utilize noble metals, base metals as well as mixture of noble and base metals. Platinum is the most active and the most commonly used noble metal. CDPF can be divided in two categories: (1) platinum-based, and (2) base metal catalysts. These two groups exhibit certain differences in their emissions performance:

- Base metals tend to be less active in promoting filter regeneration, thus requiring higher regeneration temperatures and have low activity for the oxidation of CO and HC. On the positive side, they form little or no sulfate particulates and/or nitrogen dioxide emissions.
- Platinum (usually combined with promoters) is typically more active in supporting filter regeneration and for oxidizing CO and HC. The latter function is important in applications where gaseous emissions reductions are also required. The disadvantages of Pt include production of sulfate particulates and increased levels tailpipe NO_2.

The mechanisms of catalytic oxidation of soot are complex and not entirely understood. The mechanisms that play important role in the regeneration of CDPF can be classified as follows:

- Catalytic oxidation by oxygen – carbon: particles are oxidized by oxygen adsorbed on catalytic sites. This mechanism is limited to particles that physically contact catalytic sites (i.e., particles deposited directly on the catalyzed media).
- Oxidation by nitrogen dioxide NO_2 which can be generated by catalytic oxidation of NO is more effective in oxidizing carbon than oxygen. Nitrogen oxides may be also enhancing the regeneration due to synergistic effects with DPF catalysts.
- Thermal regeneration is the cleanest and most attractive method for regenerating DPF [48, 50]. During regeneration, the collected solid particulates are oxidized by O_2 and/or NO_2 to produce gaseous products, primarily CO_2. Both minimum temperature and adequate supply of O_2 and/or NO_2 must be present for the process to be performed. O_2 is found in excess in diesel exhaust and therefore does not constitute the problem in DPF regeneration. The temperature of the diesel exhaust gas is, however, insufficient to sustain the filter auto regeneration. This problem may be solved in either way: (1) decreasing the required soot oxidation temperature to a level reached during the regular engine operation; (2) increasing the PDF temperature to the point where the trapped soot starts oxidizing by auxiliary systems [48, 51]. The first approach is used in the passive filter systems and the second is used in the active filter systems.

More specifically, depending on the PDF system design and the engine operating conditions, such as the exhaust gas temperature, the oxidation of carbon in diesel soot can occur via reactions with the oxidizing agent O_2 (O_2 – based) or NO_2 (NO_2 – based):

O_2 is present in diesel exhaust at sufficient concentrations in practically all-operating conditions. However, relatively high temperatures (about 600°C), which are rarely experienced in the diesel engine operating conditions, are required to achieve appreciable regeneration rates with O_2. This can be achieved by means of in-cylinder post-injection, in exhaust fuel injection, flame burner, electric heater, and engine management. The O_2 based regeneration is mostly seen in the active PDF systems that do not utilize catalysts. The oxidation of diesel soot, represented here as carbon (C) by O_2, can be described by the following reactions:

$$C + O_2 \xrightarrow{\approx 600°C} CO_2 \ \Delta H_r = -393,51 \text{ kJ/mol} \qquad (1)$$

$$2C + O_2 \xrightarrow{\approx 600°C} 2CO \ \Delta H_r = -110,51 \text{ kJ/mol} \qquad (2)$$

$$HC\ (SOF) + O_2 \xrightarrow{\approx 450°C} H_2O + CO_2 \qquad (3)$$

Where C (carbon) represents the combustion portion of diesel PM. It should be noted that CO_2 is the preferred product, but increased CO emission may occur if O_2 is depleted in the reaction zone.

The NO_2 based regeneration is shown in reaction (5), NO_2 is a much stronger oxidizer than O_2, allowing PDF regeneration at lower temperatures, thus substantially reducing the temperature required for the regeneration and regeneration can be conducted at the temperatures as low as 260°C. The soot oxidation by NO_2 improves the fuel economy and the lower regeneration temperatures required [50, 52, 53]. However, the NO_2 concentrations must be increased via reaction (4), which is typically realized over DOC. The oxidation of soot by NO_2 is the dominant regeneration mechanism in most catalytic (passive and active) DPF systems.

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (4)$$
$$C + 2NO_2 \xrightarrow{\geq 260\text{-}300°C} CO_2 + NO \quad \Delta H_r = -279{,}41 \text{ kJ/mol} \qquad (5)$$
$$C + NO_2 \longrightarrow CO + NO \quad \Delta H_r = -53{,}47 \text{ kJ/mol} \qquad (6)$$

Combined technologies (DOC + DPF)

Oxidation catalysts are principally used to control CO and HC emissions. However, these catalysts also reduce the PM mass emissions since they can combust the organic volatile fraction (VOF) component of the PM. While oxidation catalysts convert the VOF component of the PM, the carbon component pass through them unconverted. Therefore, the PM conversion obtained by the oxidation catalyst depends strongly on the composition of the PM, with high levels of VOF enabling oxidation catalysts to provide high levels of PM conversion. An oxidation catalyst will typically provide around 20-40% PM conversion, which reflects the usual level of VOF in Diesel PM. The DOC catalyst is a non-filter based open monolith (flow-through) system resembling the conventional catalytic converters for gasoline and diesel engines with some significant variation of the catalyst composition so as to optimize the catalyst activity under lean conditions. The noble metals are impregnated into a highly porous alumina washcoat that is applied to the passageway walls. Most of the DOCs used in the international marked contain platinum (Pt) and palladium (Pd).

Combined technologies (Filters and SCR/NO_x traps)

Another technology for PM abatement has been studied in which filters are combined with SCR/NO_x traps systems. This combination consists of a wall-flow filter with an internal NO_x adsorbed catalyst coating. In their studies, Krijnsen and coll [54] have installed a DPF upstream of an SCR catalyst. The soot removal efficiencies reached 98% by mass and NO_x conversions ranging from 40 to 73%. Using Pt/Ce as fuel additives in their investigations, the authors have noted that the NO_2/NO_x ratio over the DPF does not increase with temperature. The conversion of NO to NO_2 was enhanced and NO_2 was used to oxidize the PM. Therefore, a decrease of NO_x conversion with decreasing DPF temperature was observed [55]. Another strategy combining a NO_2-based continuously regenerative trap particulate technology with a NH_3-based SCR NO_x removal technology leads to simultaneous conversions of 75 to 90% in NO_x and PM. The feed gas first passes a DOC system which converts unburned hydrocarbons HC and CO and oxidizes NO to NO_2 as described by reactions (1), (2) and (3).Then, NO_2 combust with PM in a particulate filter (CRT) following the reaction (4).

$$C_xH_{2x+2} + [(3x+1)/2]\, O_2 \rightarrow xCO_2 + (x+1)\, H_2O \qquad (1)$$
$$2CO + O_2 \rightarrow 2CO_2 \qquad (2)$$
$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$
$$NO_2 + 2C \rightarrow 2CO_2 + NO \qquad (4)$$

In a similar system, where a DPF was installed after a urea-SCR based technology [48], the use of a cerium fuel additive has been shown to facilitate filter regeneration. The process achieves 70% NO_x and 97% PM reduction on a heavy-duty engine reaching Euro V limits. For a successful vehicle application, the integration of NO_x and DPFs requires further investigation of the effect of filter regeneration (high temperatures) on the trap and the effect of fuel additives to reduce the balance point temperature (BPT) on NO_x emission.

EMISSION STANDARDS IMPLEMENTATION

Emission standards legislation

Emission control regulations have been introduced in all the industrialized countries in order to reduce the emissions from both gasoline and diesel engines. In particular diesel vehicles are increasing more their worldwide penetration, starting from European countries where Diesel motorization in 2008 reached gasoline one [29]. To comprehend this market change it is useful to analyze some differences between the two kinds of engine, summarized in Table 2:

Table 2: Diesel versus gazoline features [27].

	Diesel	Gasoline
Vehicle weight	More	Less
Noise and vibration	High	Low
Starting	Quite instant	Instant
Air/fuel ratio	> 14,7 (Lean condition)	14.7 (Stoichiometric)
Fuel consumption	Less	More
Compression ratio	15/24	9/12
Efficiency	35%	Less 30%
Turbocharging	Applied	Not used

However, diesel engines produce higher emissions of particulate matter (Figure 12) which have negative effects on environment.

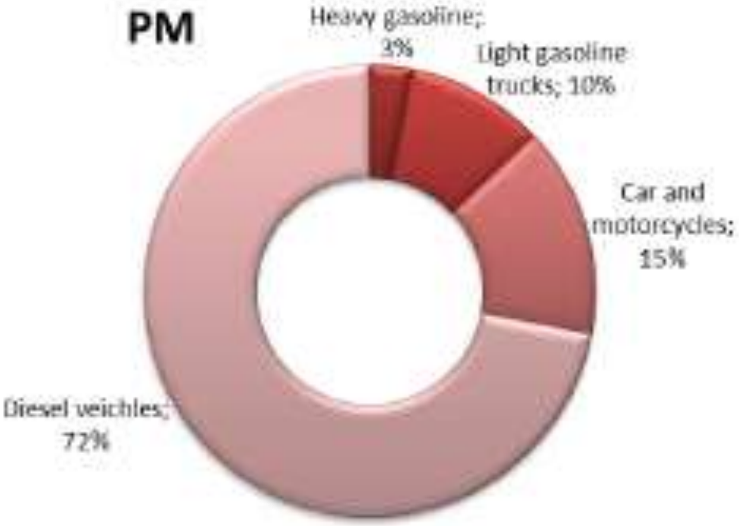

Figure 12: Diesel and gasoline PM emissions [22].

Over the world, emissions legislation has become increasingly stringent and this encourages new research projects. Several sets of standards have already been defined in the past years for different types of vehicles (table 3). European legislation concerns only some kinds of pollutants: CO, HC (Hydrocarbons), PM and NO_x. On the contrary CO_2 is not officially regulated, but EU and manufactures came to a voluntary agreement few years ago [33]. Furthermore, starting from Euro 3 stage, vehicles must be equipped with an On Board Diagnostic (OBD) system for emissions control [56]. Driver must be notified in case of a malfunction or deterioration of the emission system that would cause emissions to exceed mandatory thresholds.

Table 3: European standards emission for diesel particles (Journal de l'Union Européenne, 2007).

Standards emission		Euro 3 (2000/2001)	Euro 4 (2005/2006)	Euro 5a (2009/2011)	Euro 5b (2011/2014)	Euro 6b (2014/2016)
Diesel particles (g.km^{-1})	Gasoline	–	–	0,005	0,0045	0,0045
	Diesel	0,05	0,025	0,005	0,0045	0,0045

Soot particles, which contribute to the total mass of particulate matter emitted by the engine, are formed in the cylinder in the locally rich regions of the homogeneous combustion. The subsequent soot burn-up at the boundary of the diffusion flame sheath is favored by high temperatures. However, high temperatures also favor the generation of NO_x. Hence, decreasing the combustion temperature by exhaust gas recirculation as emission reduction technique in the cylinder for lower NO_x emissions results in an increase of PM. This dilemma is known as the NO_x-PM trade-off.

The technological development is obviously close to issued laws. Figure 13 shows the strategies adopted by automotive industry in order to respect the required standards for particulate matter.

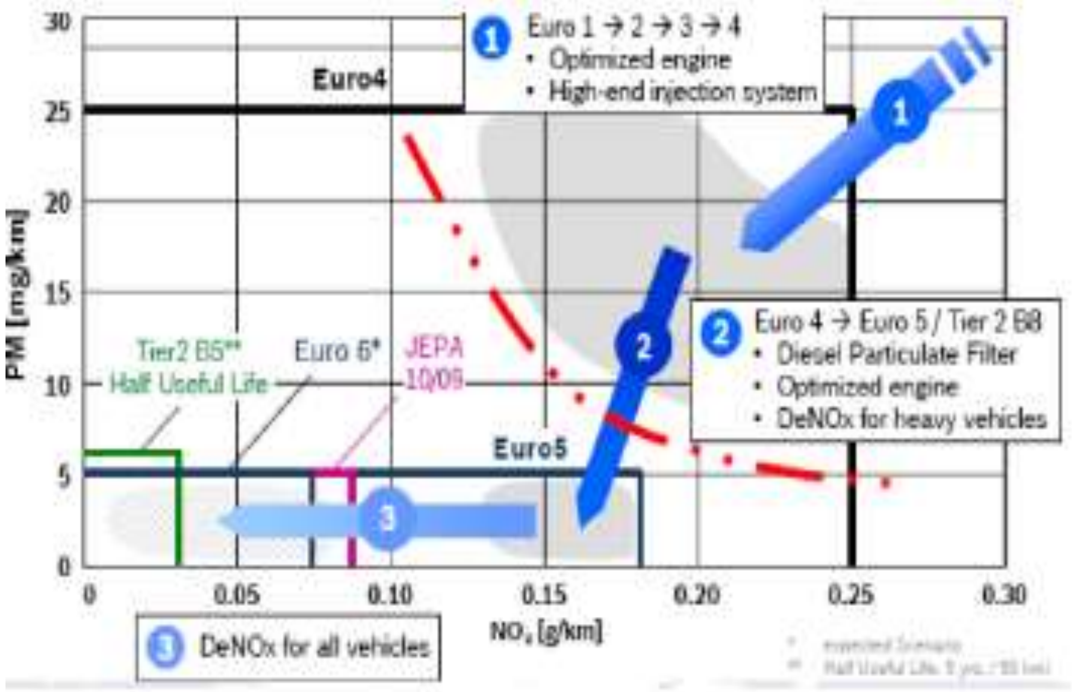

Figure 13: Measures to achieve emission levels for diesel equipped vehicles [57].

In order to abate particulate matter, the optimization of engine and the injection system as well as the use of an oxidation catalyst (DOC) were required (passage from Euro 1 to Euro 3). With Euro 3, NO_x limits were introduced for diesel engines. Then, issued standards for both the pollutants were respected with a further optimization of engine, injection system, combustion and fuel. Since Euro 4 has not ever been possible, there is a well-known trade-off between the two pollutants NO_x and PM for the engine out-emission. Over a period of time, the so-called *primary techniques* the trade-off curve moved to lower values of both NO_x and PM. This is not enough to join the limit emission of further legislation for both the pollutants, therefore *secondary techniques* are required. From Euro 4 to Euro 5, the DPF system for particulate matter abatement and a $deNO_x$ after-treatment technology as necessary on heavier vehicles were developed with an always more complex abatement technology (Figure 14). Eventually, only applying $deNO_x$ system Euro 6, US and Japanese NO_x limits will be respected.

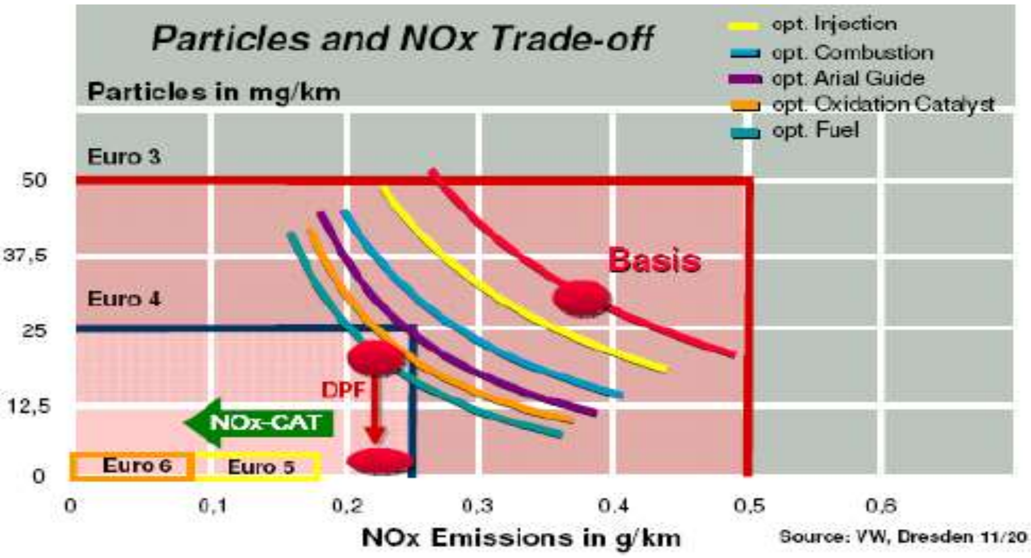

Figure 14: Trade-off curve [58].

Effect of International legislation: Advantages and deficiencies
In order to mitigate the adverse effects for the quality of the air associated with the constant increase of the automobile traffic, the introduction of stricter rules on emissions has become inescapable [56]. This pushes all the automotive industrial partners to innovate as shown in figure 15 which illustrates the establishment of post-processing systems (Tree Way Catalysts, TWC) of exhaust gas on light-duty and heavy-duty vehicles with gasoline engines since 1993 and PDF for diesel engines since 2000. The precursor to the State of California, European legislators, Japanese and United States impose since forty years, standards of more restrictive on emissions of pollutants. Scheduled until around 2016, these various regulations agree on the need to drastically reduce the emissions of diesel particles, although the procedures for the approval of new engines are not harmonized. From collaboration between the European Commission, the Association of European Automobile Manufacturers (ACEA) and the oil industry (Europa), the European Planning today for vehicles with a diesel engine has been established between 1994 and 1996 Providing the Euro II standards to Euro IV (see Table 3).

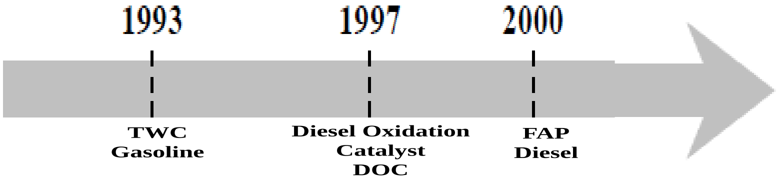

Figure 15: Post-processing systems of exhaust gas over the last twenty years (FAP: Diesel Particulate Filter).

European regulations are not the strictest ones: Japan and USA have traditionally harsher environment policies. There has been much talk in recent years about the need to harmonize global emissions standards. In Particular, the car industry has always been keen on this topic; in fact a car that just has to pass one emissions test could then be sold everywhere: Asia, Europe and USA [56]. Indeed some of the USA federal states (California, New York, Massachusetts, Maine and Vermont) have adopted more stringent standards.

In response to studies highlighting health and environmental effects of concern of the various pollutants emitted by internal combustion engines, the standards established have suffered a drastic hardening in fifteen year. As regards the limitation of emissions of particles diesel, the quantification of emissions remains subject to some controversy. Indeed, the current legislation provides only a global control of the mass of the particles emitted. Health studies tend to show that the particles of small sizes are the most harmful, although they represent only a small fraction of the total mass emitted. Therefore, it is not excluded that the future standards will take into account the control of particles number on the basis of their corresponding size.

CONCLUDING REMARKS AND FUTURE GUIDELINES

Technology development combined with a change in the standards for Diesel exhaust emissions is the realistic solution to mitigate the DPM concentration from automotive diesel engines. As described in this technical review, instruments are available, but our knowledge of fine particles using specific physico-chemical tools and performance of these instruments in practical conditions (ambient air, lower temperatures etc.) should be improved before to envisage their use in the application of new standards. More attention should be paid to the use of systems based on Diesel Oxidation Catalysts (DOC). The DOC systems can be seen as a key technology for diesel engines where the high oxygen content of the exhaust gases prevents the use of three-way catalysts. DOC converts CO and HC but also decrease the mass of diesel particulate oxidizer some hydrocarbons which are adsorbed by the carbon particles. An intimate correlation may be found between intrinsic characteristics of theses catalytic materials and the exhaust undesired products concentrations. This is what we are planning to report in a future review with a special emphasis on the capability of current technologies tuning towards new standards performances for Diesel automotive engines.

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