Diesel emission control: Catalytic filters for particulate removal

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Abstract

The European diesel engine industry represents a vital sector across the Continent, with more than 2 million direct work positions and a turnover of over 400 billion Euro. Diesel engines provide large paybacks to society since they are extensively used to transport goods, services and people. In recent years increasing attention has been paid to the emissions from diesel engines which, like gasoline engine emissions, include carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx). Diesel engines also produce significant levels of particulate matter (PM), which consists mostly of carbonaceous soot and a soluble organic fraction (SOF) of hydrocarbons that have condensed on the soot.

Meeting the emission levels imposed for NOx and PM by legislation (Euro IV in 2005 and, in the 2008 perspective, Euro V) requires the development of a number of critical technologies to fulfill these very stringent emission limits (e.g. 0.005 g/km for PM). This review is focused on these innovative technologies with special reference to catalytic traps for diesel particulate removal.

Keywords: Diesel particulate; Soot combustion; Catalytic filter; Diesel emissions; Catalytic oxidation

1. Introduction

The high efficiency of diesel engines, their low-operating costs, high durability and reliability have provided them with a leadership role in the heavy-duty vehicle market. Recently, diesel engines also achieved a growing share of the light-duty vehicle market (60% of all commercial vans are equipped with these engines), especially in those areas where fuel costs are high. In Asia and Europe particularly, sales are expected to grow considerably over the next years. This trend of growth of the diesel market requires a careful evaluation of the related environmental effects. In this context, diesel particulate rises serious health concerns due to its carcinogenity[1], owing to the presence of polycyclic aromatic hydrocarbons (PAH) and nitro-PAH in its soluble organic fraction (SOF), as well as to a particulate size falling into the lung-damaging range (10–200 nm).

During the 1980s and the early 1990s there have been significant advancements in the development of technologies for the control of diesel particulate emissions. Attention has mainly been paid to improvements in engine design [2] (e.g., as high pressure fuel injection, small injection nozzle hole area, high swirl ratio, large volume ratio of the piston cavity, improvement of combustion chamber shape and high response turbo-charger), or fuel pre-treatments [3], or more simply by better tuning of the combustion process [4], or modification of fuel formulation or use of alternative non-fossil fuel such as natural gas, alcohols or esters [5] and, finally, the use of filtering or non-filtering after-treatment devices. In this last context, the non-filtering devices use honeycomb monolithic oxidation catalysts (also called diesel oxidation catalysts—DOCs) with the aim to reduce at least the soluble organic fraction of particulate. Conversely, the filtering systems consist of a trap capable of collecting the particulate matter (PM). Such filters can be ceramic wall-flow monoliths, ceramic or metallic yarns, or ceramic or metallic foams. All these devices operate mostly through inertial impaction, interception or diffusion mechanisms [6]. Wall-flow filters act as “cake filters”, while foams and fibre yarns act as deep bed filters.
Once the particulate is collected, it is necessary to burn it off. Diesel particulate spontaneously burns in air at about 600–625 °C. This temperature range is not regularly achieved in the typical diesel vehicle operations for sufficient periods of time to enable self-regeneration. If an excess of soot is collected on the filter, the exhaust gas temperature raises due to the increased back-pressure, and leads to a sudden burn off, which might occasionally cause the filter temperature to raise above the melting point of the filter itself [7].

The task of a “controlled” regeneration can be faced following two different approaches: either the exhaust gas and/or the filter is heated to the particulate ignition temperature, or the ignition temperature is lowered with the aid of substances which catalyse soot oxidation. A system incorporating both of these approaches has been developed by the Peugeot-Citroën Société d’Automobiles (PSA) group and been installed on more than 1 million vehicles produced since 2000 [8].

In the first case the exhaust gas temperature can be raised by the occasional post-injection of some fuel that gets burned in a specific honeycomb oxidation catalyst placed upstream of the trap [9] or using an external heating system. The filter can be heated by means of electrically driven devices, such as microwave heating [10], when using a conducting material for the filters [11], or by equipping the filter with heating wires [12]. Alternatively, the filter can be heated by a burner [13]: for this purpose, automatic dual filter systems have been developed, in which one clean filter is loaded by the exhaust gas and simultaneously the second filter is regenerated off-line by the burner [14] (Table 1).

Concerning the second approach (i.e. the use of catalysts), there are two different alternatives: the addition of the catalyst to the fuel in the form of organic derivatives of active metals and the deposition of a catalytic coating onto the filter surface.

EURO V regulations will force, from 2008 on, to adopt the latter solution. Most car manufacturers admit that time has come for combined use of catalysts and particulate traps. This paper reviews this technology development field.

### Table 1

| Measure                | Alternatives                                      |
|------------------------|---------------------------------------------------|
| Exhaust gas heating    | Fuel post injection + oxidation precatalyst        |
|                        | External heating devices                          |
| Filter trap heating    | Microwaves                                        |
|                        | Heating wires                                     |
| Catalytic soot oxidation | Dual filter heated via burner                   |
| Combined measures      | Metal organic compounds in fuel (additives)       |
|                        | Catalyst coated traps                             |
|                        | Combined heating and catalytic soot oxidation     |

Fig. 1 shows the three major trap types available in the market [15]. Wall-flow filters (Fig. 1a; materials: partially sintered SiC or cordierite (Mg2Al4Si5O18) grains; pore size: 10 μm) are very efficient (> 90%) since they are based on a shallow-bed filtration mechanism, whereas foam (Fig. 1b; materials: zirconia-toughened-alumina or—mullite, SiC; pore size: 100–400 μm) and fibre filters (Fig. 1c; materials: doped-alumina; fibre size: 10 μm) are somehow less efficient as a consequence of the deep filtration mechanism they enable. The traps, located in the under-floor exhaust line, get laden by particulate. This increases their pressure drop up to a level which entails such a fuel penalty that trap regeneration is required. This is accomplished by burning the trapped particulate off, an operation which can be assisted by the use of catalysts.

Fig. 2 shows commercial and R&D-level catalytic systems used in this context. Beyond non-trapping catalytic converters (i.e. DOCs), the use of fuel additives [16] has been employed commercially, as well as the production of NO2 by upstream catalytic oxidation on NO (NO2 is a much stronger particulate oxidizer than O2 [17]). Conversely, directly catalysed traps based on either deep- or shallow-bed filtration are currently being developed. A crucial issue in this context is the contact between catalyst and carbon which can be improved by the use of liquid-phase-generating catalysts (Fig. 2.1, tailored for deep-filtration systems [18–20]), of oxygen-spillover-promoting catalysts (Fig. 2.2 [21,22]) or of multifunctional catalysts enabling particulate direct- (via contact points) and indirect- (via NO2 formation) particulate oxidation (Fig. 2.3 [23]).

### 3. Commercial catalytic system

#### 3.1. Diesel oxidation catalysts

The first contribution to the reduction of particulate mass emission has been the use of the so-called DOCs [24], become mandatory for new diesel-engined cars in 1996 in
the US and in 1998 in Europe. These converters resemble the conventional catalytic converters for gasoline engines with some significant variation to the catalyst composition (in any case based on noble metals) so as to optimize the catalyst activity under lean conditions. Obviously, soot particles are not trapped by these systems but CO and hydrocarbons (including those of the SOF of the particulate) are burned out from $10^2\text{C}_n$ [25]. The particulate mass abatement efficiency in the flow-through DOC is however lower than 5% at gas hourly space velocities of 50,000–300,000 h$^{-1}$ [26]. Finally, some problems might arise due to the SO$_2$ oxidation activity of the catalyst that can lead at temperatures above 300 $^\circ\text{C}$ to significant formation of SO$_3$ (which dissolves in condensed water droplet to give H$_2$SO$_4$ after engine switch off) and even a possible increase of the total particulate mass [26].

3.2. The Peugeot-Citroën Société d’Automobiles system

The key components of the Peugeot-Citroën Société d’Automobiles (PSA) system (Fig. 3), are [8]:

- **SiC wall-flow monolith**: selected for its high filtration efficiency and superior physical properties (high-temperature and thermal-shock resistance).
- **Active regeneration strategy**: when trap regeneration is needed owing to the high-pressure drops detected by a proper sensor, fuel post-injection, enabled by multi-jet common-rail engines, provides unburned hydrocarbons to the pre-oxidiser, resulting in an increase of the exhaust gas temperature.
- **Pre-oxidiser**: a catalytic converter that burns out the post-injected hydrocarbons thereby enhancing further the flue gas temperature and igniting the trapped particulate.
- **Ce-fuel additive**: this fuel additive leads to formation of CeO$_2$ particles well embedded in the structure of diesel particulate and thus in very good contact with the soot, which lowers ignition temperatures by catalytic means with the benefit of post-injected fuel savings [27].

As above anticipated, this system is now running on more than 1,000,000 cars with apparently no major problems. However, it has some drawbacks:

- **CeO$_2$ deposits**: periodic cleaning or trap over-sizing is needed to cope with the cerium oxide that remains in the traps,
- **High investment costs**: they are entailed by the presence of many components (additives, additive-storage tank and dosing pump, pre-oxidiser, pressure and temperature sensors, control electronics, common-rail diesel system),
- **High operating costs**: post-injected fuel does not contribute to driving power and thus corresponds to a cost (fuel penalty). A trade-off with the fuel penalty caused by the increased trap pressure drop due to particulate loading leads to the determination of an optimal interval between subsequent regenerations of 300–400 km, which results in an overall fuel penalty of about 4%.

3.3. The continuously-regenerating-trap (CRT) system

Another patented and tested technology is the continuously regenerating-trap (CRT) system by Johnson Matthey based on the early discoveries by Cooper and Roth [24] concerning the role of NO$_2$ in diesel particulate combustion (Fig. 2); it consists of a wall-flow trap with an up-stream flow-through diesel oxidation catalytic monolith called pre-oxidiser (Fig. 4).
The pre-oxidiser converts about 90% of the HC and CO present in the exhaust gas and promotes the abatement of at least 3% of nitrogen oxides. The most interesting feature of the CRT system is its ability to promote a continuous trap regeneration provided its operating temperature is kept in the range 200–450°C [28]. Above 200°C the pre-oxidiser activity is sufficient to oxidize the HC and CO as well as to convert NO to NO₂ which can rapidly react with diesel particulate leading to its combustion to give CO₂ and NO. Above 450°C thermodynamics becomes unfavourable for NO₂ formation in the pre-oxidizer. Because of continuous regeneration, extreme temperature gradients within the trap are avoided which prolongs the trap life expectation. A satisfactory performance over 600,000 km has been reported by Hawker and coworkers [29]. The major drawback of the CRT system lies in the sensitivity of the pre-oxidiser to the presence of sulphur compounds which has hampered significant introduction in the market [29]. However, since 2005 low fuel sulphur levels (50 ppmw) have been mandatory in Europe and this may lead to massive introduction of this technology. Another weak point of the system is its dependency on the presence of NOₓ, as it is uncertain whether future diesel engines will produce high-enough NOₓ-to-soot ratios.

3.4. The Toyota Motors system

In the diesel particulate and NOₓ reduction (DPNR) Toyota Motors system [9,30,31] a layer of an “active oxygen” storage alkali metal oxide hosting Pt is deposited
over the diesel soot filtration device. The “active oxygen” is created by the conversion of gas-phase NO over the platinum into surface nitrate species. These surface nitrates are decomposed at the interface between soot and active oxygen layer producing very reactive adsorbed oxygen atom and NO. The NO can be reoxidized to surface nitrate, while the reactive adsorbed oxygen atoms can oxidize the soot at temperatures and 300°C and above. If the system cannot convert all the deposited soot the back pressure over the filter will increase and trigger the regeneration of the trapped soot due to a temperature rise in the filter. The increase in temperature is accomplished, once again by fuel post-injection.

The active storage material acts at the same time as a NO$_x$ trap. When the NO$_x$ trap has reached its maximal allowable buffer capacity for retaining NO$_x$ as nitrates, then the NO$_x$ trap needs to be regenerated. CO and HCs can then reduce these surface nitrates to N$_2$. These CO and HCs are generated by running the engine rich or by fuel addition into the exhaust stream at a temperature of around 450°C. The newly generated CO and HCs are converted into CO$_2$ by surface nitrates while the nitrates themselves convert mainly to N$_2$ and, to some extent, to NO. Fig. 5 illustrates the chemical processes of the Toyota system.

Total reduction of diesel exhaust emissions (CO, HCs, PM, and NO$_x$) is preferably achieved in a single filter system such as the DPNR system. However, this system may encounter several problems such as engine ash deposit, complexity of data logging, and the effectiveness of engine-out NO$_x$ concentration. It is reported that the fresh DPNR system reduces 80% of NO$_x$ and PM emissions and might meet the US tier 2 bin 5 or 6 emissions standards using low-sulfur diesel fuel. Fleet test should however, demonstrate the efficiency and robustness of this system [32].

### 3.5. R&D systems developed at Politecnico di Torino

Finally, some more innovative technologies still at the R&D stage at Politecnico di Torino and in many other Research Centres are described (Fig. 2). For instance, catalytic foam traps were developed in the framework of the activities of a just-ended EU project (CATATRAP) by depositing through tailored techniques Cs-V-based catalysts over the pore walls of zirconia-toughened alumina foams developed by Centro Ricerche FIAT and Saint Gobain. The catalysts employed in this context were of the mobile type either by liquid-phase formation (CsVO$_3$ + KCl [33]; Cs$_2$O · V$_2$O$_5$ [34]) or via oxygen spillover (Cs$_4$V$_2$O$_7$ [35]) so as to improve the contact conditions between catalyst and carbon. With catalytic foams EURO IV legislation limits were achieved in standard driving cycles, with no need of active regeneration means. However, the filtration efficiency of foams is too low (about 50%) to provide them with future perspectives. Conversely, wall-flow catalytic filters enabled efficiencies higher than 95% at the price of the need of active regeneration means like those employed by the PSA system. However, this catalyst cannot be employed with wall-flow filters as their pores are so fine that the liquid catalyst phase would be rapidly sucked into them plugging the trap. For this reason, mixed-oxide catalysts (e.g. LiCrO$_2$) were deposited on the walls of the inlet channels of wall-flow traps via an ad-hoc-developed technique, the in situ combustion synthesis [36–38] (Fig. 6). The foamy microstructure of nanosized catalyst particles (Fig. 6b) thereby obtained is particularly suitable to achieve...
intensive contact conditions between catalyst and soot, a prerequisite to achieve required combustion kinetics.

The development of the common-rail engines in last 1990s has deeply changed the perspectives in the diesel-exhaust treatment field, by enabling a momentary rise of the exhaust gas temperature for trap regeneration purposes, even if this implies a certain fuel penalty. On the grounds of good thermal and chemical stability, several perovskite, delafossite and spinel type oxide catalysts were prepared by solution combustion synthesis, characterized and tested as catalysts for both NO\textsubscript{x} and soot removal [39–41] or only particulate combustion [37,38,42–46].

Nanostructured spinel-type oxides catalysts \( AB_2O_4 \) (where \( A = \text{Co and Mn}, \) and \( B = \text{Cr and Fe} \)\), prepared by the solution combustion synthesis method, proved to be effective in the simultaneous abatement of soot and NO\textsubscript{x}. The activity order for soot combustion was found to be \( \text{CoCr}_2O_4 > \text{MnCr}_2O_4 > \text{CoFe}_2O_4 \), while the activity order for NO\textsubscript{x} reduction was found to be \( \text{CoFe}_2O_4 > \text{CoCr}_2O_4 > \text{MnCr}_2O_4 \) [39]. The best compromise between soot and nitrogen oxide abatement was therefore shown by CoCr\textsubscript{2}O\textsubscript{4} catalyst; it could promote soot combustion and appreciable NO\textsubscript{x} reduction below 400 °C (see Fig. 7), the maximum temperature reached in the exhaust line of a diesel engine. The activity of the chromite catalysts could be explained by their higher concentration of suprafacial, weakly chemisorbed oxygen, which contributes actively to soot combustion by spillover in the temperature range 300–500 °C.

As previously discussed in a review by Seyama [47] and in some papers by the Authors [42–46], the most recent catalysts developed at Politecnico di Torino can desorb two different types of oxygen species accompanied by related desorption peaks (Fig. 8): oxygen desorbed in the low-temperature range of 300–600 °C named either \( \varepsilon \) species or suprafacial species or weakly chemisorbed species, and oxygen desorbed at high-temperature (600–900 °C), named either \( \beta \) or intrafacial species, more bound to the perovskite structure and therefore less easily desorbed [42]. The main reason for the superior activity of them towards carbon oxidation should indeed lie in a radically higher specific surface concentration of active oxygen.

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**Fig. 7.** Concentration plots of the outlet gaseous species in a TPR run performed with the CoCr\textsubscript{2}O\textsubscript{4} catalyst under tight contact conditions (feed concentrations: \( O_2 = 10 \text{ vol\%}, \) \( NO = 1000 \text{ ppmv}, \) \( He = \text{balance}; \) catalyst—soot mass ratio = 9:1; \( W/F = 27.1 \text{ kg Nm}^{-3} \)) [41].

**Fig. 8.** Results of the temperature-programmed desorption tests on all selected perovskite catalysts; low-temperature oxygen species \( \varepsilon \); high temperature oxygen species \( \beta \) [44].
species compared to other catalytic materials developed in the late 1990s. The Li-substituted chromite catalysts (La_{0.8}Cr_{0.9}Li_{0.1}O_3, La_{0.8}Cr_{0.8}Li_{0.2}O_3) exhibit the highest activity as a consequence of their superior amount of weakly chemisorbed O\(^{−}\) species (\(\alpha\)-oxygen), that were pointed out as the key player in the soot oxidation state. In subsequent investigations the LiCrO\(_2\) catalyst was pointed out to be even more active than the above counterparts [37]. This catalyst was lined by in situ combustion synthesis over ceramic wall-flow monolith traps and tested according to a standard loading and regeneration cycle. Fig. 9 shows that the LiCrO\(_2\) catalyzed trap gave a more complete regeneration compared to a non-catalyzed trap and in ca. half the time.

In a parallel effort, catalytic materials characterized by the highest possible \(\alpha\)-oxygen type concentration were developed, with careful attention to their compatibility with the substrate material or the poisoning components present in the diesel exhaust gas (e.g. sulfur oxides). The durability tests performed on LiCrO\(_2\) delafossite catalyst powders under accelerated ageing conditions in the presence of some of the most critical compounds in diesel exhaust gases, showed a comparatively good behaviour, with limited loss of catalytic activity, as shown in Table 2 [37]. No serious deactivation was found after any of the ageing test protocols. The highest deactivation (limited, however, to an increase of about 30 °C of the \(T_p\) value) was noticed after high temperature hydrothermal ageing, which mostly affected the specific surface area of the catalyst and slightly reduced the selectivity to CO\(_2\) (\(\eta_{\text{CO}_2}\)).

Finally, an innovative multifunctional catalyst (La_{0.8}K_{0.1}Cr_{0.9}O_3 + 1 wt%Pt [48]), with a very low content of precious metal (widely used in this kind of catalysis), was developed for diesel soot combustion combining direct and indirect (NO–NO\(_2–\text{NO}\) cycle) oxidation mechanisms (Fig. 2.3). This catalyst was applied over a wall-flow SiC trap and tested according to a standard protocol on an engine bench. It was found that the presence of the catalyst not only accelerates soot combustion on occasional trap heating (regeneration phase) but also prolongs the trap-loading phase (soot accumulation during normal operation) due to the indirect oxidation mechanism. This should allow a more than 50% reduction in a post-injected fuel consumption.

4. Conclusions

The current scenario of catalytic traps for diesel particulate abatement has been briefly reviewed, enlightening the most promising commercial technologies available and the most interesting opportunities that might outperform in a few years the nowadays available systems.

The 2010 European law limits (EURO V) will almost certainly been met by wall-flow type traps using either fuel additives or NO\(_x\)-aided regeneration or catalysts deposited over the trap itself. In any case, the use of active means to occasionally rise the trap temperature would likely be required, accompanied by the related fuel penalty.

The next frontier for further progress in the field will be to find the technological means to reduce or even eliminate this fuel penalty. Both catalyst and trap development will be needed for this sake. Targets will be lower soot ignition temperature but also lower trap pressure drop, efficiency remaining excellent. Opportunites for innovation will provide many R&D challenges for this field in the future.

Table 2

| Ageing conditions | BET area (m\(^2\)/g) | \(T_p\) (°C) | \(\eta_{\text{CO}_2}\) (%) |
|-------------------|---------------------|--------------|------------------------|
| LiCrO\(_2\) (fresh) | 24                  | 387          | 99                     |
| 96 h 300 °C air   | 18                  | 387          | 98                     |
| 96 h 300 °C wet   | 18                  | 385          | 96                     |
| 96 h 300 °C air + SO\(_2\) | 18        | 392          | 98                     |
| 24 h 650 °C air   | 4                   | 389          | 98                     |
| 24 h 650 °C wet   | 4                   | 410          | 96                     |
| 24 h 650 °C air + SO\(_2\) | 17        | 395          | 98                     |

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