CATALYTIC REDUCTION TECHNIQUES FOR POST-COMBUSTION DIESEL EXHAUST EMISSIONS

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ABSTRACT

Stiff exhaust emission regulations set for limiting the air pollution caused by motor vehicles have oriented the producers and researchers to investigate new techniques to reduce exhaust emissions. The main pollutants caused by diesel engines are particle matters (PM), nitrogen oxides (NO_x), hydrocarbons (HC), and carbon monoxides (CO). Among the preventive actions to keep the emissions caused by motor vehicles at a certain level are enhancing the fuel quality, preventing the pollutant formation in the engine, and developing the post-combustion emission control systems. There are many different technologies used for reducing the amount of pollutants in diesel engine exhausts. In this study, the main techniques applied for reducing these pollutants catalytically.

Key words: *Diesel engine, exhaust emissions, catalysts, catalytic reduction.*

1. Introduction

The transport sector is a major source of atmospheric pollutants (1). 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 agrowing 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 Europa 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 enviromental effects (2). The most important exhaust gases that are produced as a result of combustion in diesel engines and considered as aair pollutants are particulate matter (PM), nitrogen oxides (NO_x), hydrocarbons (HC), and carbon monoxide (CO) (3). Diesel-powered vehicles, because of their high thermal efficiency, emit less CO and unburned hydrocarbons than gasoline-fueled vehicles, but the emission of soot particulates and NOx are still high (4). Attention has mainly been paid on improvements in engine design (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 , or more simply by a better tuning of the combustion process , or modification of fuel formulation or use of alternative non-fossil fuel such as natural gas, alcohols or esters and, finally, the use of filtering or non-filtering aftertreatment devices (5). Since the reduction of both soot and NOx emissions to the regulated level cannot be accomplished by engine modifications alone, after-treatment techniques for the simultaneous reduction of their emissions from diesel exhaust should be developed (4). Euro emissions regulations are given in Figure 1. In this study, post-combustion catalytic techniques to reduce diesel engine exhaust emissions are being examined.

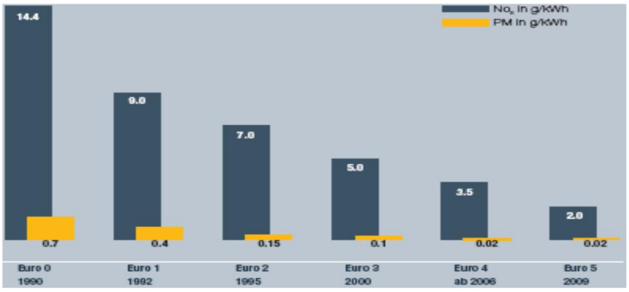

Fig. 1 Euro emissions regulations (6).

2. Diesel Catalysts

A catalyst is a substance that, even in small amounts, accelerates chemical reactions and may be recovered essentially unaltered. Some catalysts show selectivity as well as rate enhancement. In the presence of same source materials, a juducious choice of catalyst can accelerate only a selected chemical reaction where others are possible (7).Heterogeneous catalysts supported on high surface area porous oxides are used in emission control applications. The overall catalytic conversion in a heterogeneous catalyst is composed of several sub-processes which involve chemical reaction, bulk mass transfer and pore diffusion. Even though catalysts are not used in the reaction, they undergo gradual deterioration due to thermal deactivation and poisoning. The first diesel catalysts, introduced in 1970ĝs for under ground mining applications, were simple oxidation catalysts designed for conversion of CO and HC. These catalysts gradually evolved into the modern diesel oxidation catalysts, optimized for PM emission reduction. Future requirements for NO_x emission reduction from diesel engines call for new catalyst technologies, such as SCR, lean NO_x catalyst, and NO_x adsorber systems (8)

3.Diesel Oxidation Catalysts (DOC)

Diesel oxidation catalysts convert carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide (CO_2) and water and decrease the mass of diesel particulate emissions but have little effect on nitrogen oxides (NOx). An oxidation catalyst will remove the soluble organic fraction (SOF) of diesel particulate by up to 90%. (1) Destruction of SOF is important because this portion of the particulate contains numerous chemicals of concern to health experts. Diesel oxidation catalysts can thus reduce total particulate emissions by 25 to 50%, depending on the constituents that make up the total particulate. They also reduce diesel smoke and eliminate the pungent diesel exhaust odour as well as making significant reductions in CO and HC. However the number of particles is unchanged and issues associated with the effects of ultra-fine particulates are unresolved. DOC technology has been successfully used on all diesel cars sold in Europe since 1996 but only some, but not many, heavy-duty vehicles are series-production catalyst equipped. DOCs are also be used in conjunction with NOx adsorbers, DeNOx catalysts, DPFs or selective catalytic reduction (SCR) to increase NO_2 levels or to ñclean-upò any by-pass of injected reductant used for NOx reduction (hydrocarbons or ammonia).

4.Catalysts and Trap systems for NOx reduction with Diesel Engines

DeNOx catalysts and NOx traps bring the prospect of substantially reduced emissions of oxides of nitrogen (NOx). NOx conversion rates depend on exhaust temperature and availability of reducing agents. There are four systems under evaluation and development by industry:

1.Passive DeNOx Catalysts using reducing agents available in the exhaust stream

2. Active DeNOx Catalysts using added hydrocarbons as reducing agents

3. NOx Traps or Adsorbers used in conjunction with added hydrocarbons as reducing agents and a catalyst

4. Selective Catalytic Reduction using a selective reductant, such as ammonia from urea.

Each of these systems offers different possibilities in the level of NOx control possible and the complexity of the system. Fuel parameters such as sulphur content can affect catalyst performance.

4.1. DeNOx (or Lean NOx) Catalysts

Advanced structural properties in the catalytic coating of DeNOx catalysts are used to create a rich ñmicroclimateò where hydrocarbons from the exhaust can reduce the nitrogen oxides to nitrogen, while the overall exhaust remains lean. Further developments focus on increasing the operating temperature range and conversion efficiency.

4.2. NOx Adsorbers (or Lean NOx Traps)

NOx traps or adsorbers are a more promising development as results show that NOx adsorber systems are less constrained by operational temperatures than DeNOx catalysts. NOx traps adsorb and store NOx under lean conditions. A typical approach is to speed up the conversion of nitric oxide (NO) to nitrogen dioxide (NO_2) using an oxidation catalyst mounted close to the engine so that NO_2 can be rapidly stored as nitrate. The function of the NOx storage element can be fulfilled by materials that are able to form sufficiently stable nitrates within the temperature range determined by lean operating points of a direct injection gasoline engine. When this storage media nears capacity it must be regenerated. This is accomplished in a NOx regeneration step when the stored NOx is released by creating a rich atmosphere, for example, with the injection of a small amount of fuel and quickly reduced to N_2 by reaction with CO on a catalyst incorporated into this unique single catalyst layer.(10). NOx trapping mechanisms under lean operating conditions are given in Figure 2.

Developments and optimisation of NOx adsorber systems are currently underway for diesel and gasoline engines. These technologies have demonstrated NOx conversion efficiencies ranging from 50 to in excess of 90% depending on the operating temperatures and system responsiveness, as well as fuel sulphur content (9).

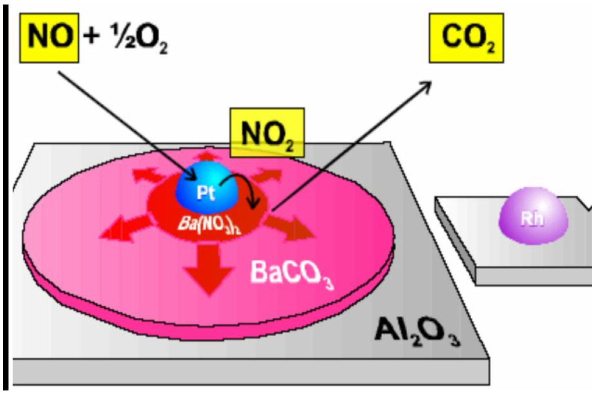

Fig. 2 NOx trapping mechanisms under lean operating conditions.(10).

4.3. Selective Catalytic Reduction (SCR)

SCR technology has been used successfully for more than two decades to reduce nitrogen oxide emissions from coal, oil and gas fired power stations, marine vessels and stationary diesel engines. SCR technology permits the NOx reduction reaction to take place in an oxidising atmosphere. It is called ñselectiveò because the catalytic reduction of NOx with ammonia (NH_3) as a reductant occurs preferentially to the oxidation of NH_3 with oxygen. Several types of catalyst are used and the temperature of the exhaust environment determines the choice. For mobile source applications the preferred reductant source is aqueous urea, which rapidly hydrolyses to produce ammonia in the exhaust stream (9).

Urea solution is a mixture of 32.5% urea and 67.5% water. When urea is injected into the exhaust stream, it decomposes to create ammonia. The SCR process requires precise control of urea injection rates. An insufficient injection amount will result in unacceptably low NOx reduction. An injection rate that is too high will result in the release of undesirable ammonia from the system. An advantage of SCR catalysts over lean NOx catalyst and NOx absorber systems is they can operate over a large temperature window. SCR systems can operate from 200-600ºC. Current SCR systems can achieve greater than 90% NOx reduction in steady state conditions. A disadvantage of SCR systems is that they require a sophisticated control system. Diesel engines in mobile applications operate in highly transient conditions. The control system must constantly adjust the amount of urea injected to match the changing operating conditions. Also, SCR catalysts have the ability to store ammonia. Ammonia is stored at low temperatures and released at high temperatures. To achieve peak NOx conversion rates without ammonia slip, the control system must also be able to predict the storage characteristics of the catalyst. Disadvantages of SCR systems also include poisoning of the SCR catalyst due to sulfur, phosphorous or other chemicals which can collect on the active material of the catalyst resulting in deactivation. These chemicals originate from the lubrication oil and fuel used in the engine. Also, thermal deactivation of the SCR catalyst can occur if exposed to high exhaust temperatures. The primary disadvantage of SCR systems is that urea must be constantly replenished to allow for NOx reduction(11).

SCR for heavy-duty vehicles reduces NOx emissions by circa 80%, HC emissions by circa 90% and PM emissions by circa 40% in the EU test cycles. The combination of SCR with a pre-oxidation catalyst, a hydrolysis catalyst and an oxidation catalyst enables higher NOx reduction under low load and temperature conditions (9).It was first commercially available in 2005 for European and Japanese HD applications. European SCR catalysts are based on vanadia, whereas those in Japan are zeolite-based (12).

5. Diesel Particulate Filteri (DPF)

A diesel particulate filter is positioned in the exhaust and designed to collect solid and liquid particulate matter (PM) emissions while allowing the exhaust gases to pass through the system. A number of filter materials are used, including ceramic monoliths, woven silica fibre coils, ceramic foam, wire mesh and sintered or shaped metals. Since the wall flow filter would readily become plugged with particulate material in a short time, it is necessary to ñregenerateò the filtration properties of the filter by regularly burning off the collected PM (9).

Based on the principle of regeneration, filter systems are classified into passive and active (8). In the active process external measures are implemented to heat the filter to the temperature necessary burning off the soot. In the passive process, the soot is burnt off by a catalytic reaction. For this purpose, catalytically active iron and cerium containing additives in the diesel fuel reduce the flammability of the soot particles to normal exhaust-gas temperatures. Other future passive regeneration options include catalytic coated filters or the Continuous Regeneration Trap(CRT) process (13).

5.1. Catalysed Diesel Particulate Filters

Catalysed DPF (CPDF) consists of a ceramic filter coated with a catalytic wash coat. The catalyst wash coat generally contains platinum (Pt) as the precious metal. The catalytic coating reduces the combustion temperature of the soot. The soot combustion temperature is not reduced to a level as low as with FBC. Due to precious metal requirement for CDPF, there is an associated cost increase. Unlike FBC, CDPF is maintenance free as the ash stored in the filter only comes from the lube oil and is at much lower quantities then the ash stored from a FBC(14).

The catalyst can be coated on the filterôs surface. This way the filter both acts as a means of collecting the soot particles and a substrate for catalyst. The reaction takes place on the filterôs surface, and the catalyst ï soot contact attained is a little worse than that of the fuel borne catalysts. However, by this way the problem of catalyst consumption is prevented and extra cost of using a separate system for blending and storage of catalyst is avoided (15).

Alternatively, catalyst coated SiC particulate filters reduce the ash deposition significantly. Catalysed systems are offered at the moment from Daimler-Chrysler, BMW, VW, Opel and Fiat. With catalysed particulate filters, only the lubricant oil ash will be deposited on the filter, which leads to significant benefits with regard to back pressure over the service life for the emission control system (16).

Catalyst-based DPFs are very successful in retrofit applications of older heavy-duty diesel (HDD) vehicles and buses in various regions over the world. Real world durability of these systems is proven every day in major cities in Europe and the US. With any catalyst/DPF combination including platinum group metals the use of diesel fuel with sulphur lower than 10 ppm is necessary to keep the formation of sulphate particulates within future legislated limits (9).Beside the DPF, where the exhaust gas is flowing through a porous medium, recently open systems have been developed. These systems are often called particulate catalysts or PM-cat. Figure 3 shows the principle of such a PM-cat.

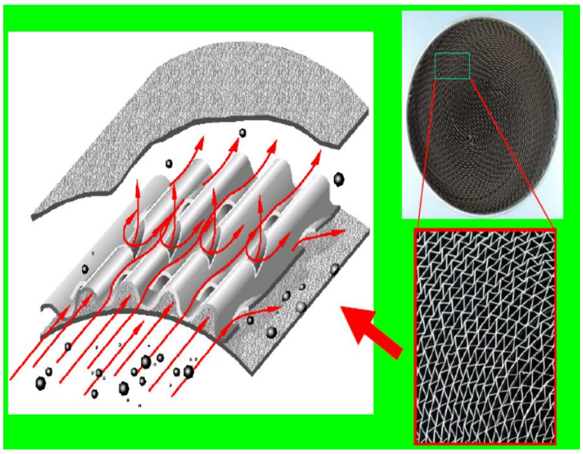

Fig.3 Schematic picture of a particulate catalyst filter (18).

Due to the special shaping of the catalyst, the exhaust gas is flowing into a storage medium where particles are deposited. If the storage medium is full , the exhaust is flowing through the open channels of the catalyst without further separation of the particles. As soon as the PM-cat reaches regeneration temperatures again, the particles are burnt and the PM-cat can work at the original efficiency levels again. The risk of damages to the engine or to the PM-cat is obviously much smaller than for a DPF without closed loop control. PM-cats have efficiencies in the range of approximately 50% (17).

5.2. Fuel Borne Catalyst

Fuel borne catalysts (FBC) are added to the fuel. Trough the combustion process the FBC is intimately mixed with the PM trapped in the fitler. The FBC reduces the combustion temperature of the soot. FBC adds ash to the filter, which eventually reduces the filter capacity for PM storage. Current FBC applications require servicing to remove ash from the filter. However, future applications will be service free. This is due to low FBC treat rates and novel fitler design. (14).The use of nanoparticle fuel borne catalysts to reduce Diesel engine soot emissions is given Figure 4.

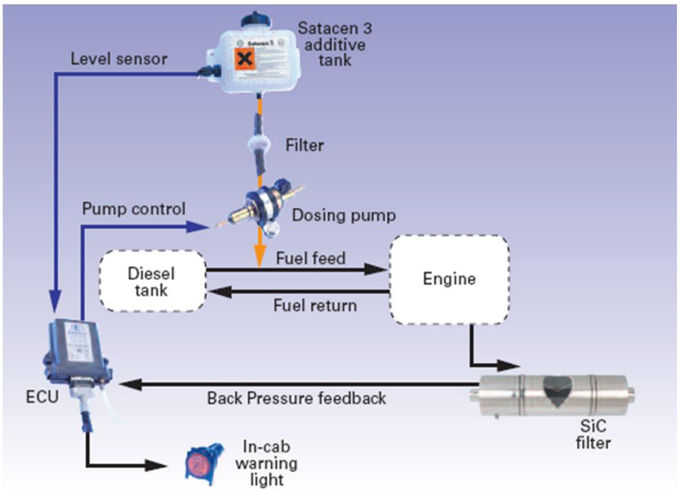

Fig. 4 The use of nanoparticle fuel borne catalysts to reduce Diesel engine soot emissions (19)

5.3 The continuously-regenerating-trap (CRT) system

The CRT system is a patented Johnson Matthey technology. The system consist of a wall-flow trap with an up-stream flow-trough diesel oxidation catalytic monolith called pre-oxidiser. 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 it is ability to promote a continous trap regeneration provided its operating temperature is kept in the range 200-450^{o}C (5).

6. Plasma Assisted Catalysts

Plasma is a gas consisting of positive and negative charges that has a tendency to remain overall electrically neutral over large length scales. It is composed of free electrons, ions, radicals atoms, and molecules in various states of excication. Plasma is divided to thermal or ñhotò plasma and non-thermal or ñcoldò plasma (20). Recently, plasma-assisted catalytic reduction of NOx under lean conditions has been extensively studied (21). The scheme for combined plasma and catalytic treatment is shown in Figure 5. The nanosecond corona discharge, dielectric barrier discharge and surface discharges are produced directly in gas.The formation of active particles is generated by electron impact with main components.The conversion NO initiated by discharges in different gas composition has been modeled and studied.The hydrocarbons lower the electrical energy cost for oxidation of NO to NO_2: In plasma selective catalytic reduction system the surface reactions are considered.Carbon monoxide and aldehydes are produced in plasma.Plasma catalyses systems operate by oxidation of NO to NO_2 in the plasma followed by reduction of NO_2 by reaction with NH_3 or with partially oxidized hydrocarbons during passage over the catalyst. Nonthermal plasma reactor can effect the oxidation of PM in diesel exhaust at low temperature (22).

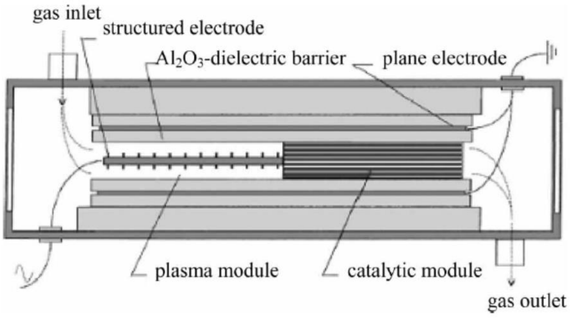

Figure 6: Reactor for combined plasma and catalytic treatment (21).

Conclusion

Catalytic reduction techniques studied here have both advantages and disadvantages. Some of these techniques are commercialized, some are still under investigation. In order to meet the new regulations, multiple techniques are applied in combination.

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