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Control of NO_x emissions in diesel powered light vehicles

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Abstract

The light duty diesel vehicle has undergone a dramatic improvement in customer acceptability and market penetration in Europe in recent years, largely because of significant improvements in engine design. The diesel engine is an inherently low emissions technology and until recently, it has not required secondary emission control technology such as catalytic converters. However in the near future more stringent legislation in the EC and USA poses some major challenges for the diesel passenger car which will be difficult to meet without secondary systems. The primary problem is control of NO_x under lean burn conditions but this must be considered in the context of the other requirements imposed on a modern diesel car. Useful lean NO_x control options must satisfy these other requirements as well as exhibiting lean NO_x performance. Without successful lean NO_x catalysts the diesel car will struggle to make further advances in the market.

Keywords: NO_x; Diesel; Emission control; Catalytic converter

1. Introduction

The control of NO_x emissions is essential for all vehicles in today's increasingly environmentally aware world but nowhere is this more apparent than in lean burn gasoline and diesel engines. Simply put, reducing NO_x under the net oxidising conditions of lean burn engines is difficult while oxidising hydrocarbons and CO under such conditions is much simpler. Lean burn gasoline vehicles are attracting increasing attention in Japan, and now the rest of the world, but it is with the diesel powered vehicle that the issues and options are most clear. This article attempts to review the emission control pressures on light diesel powerplants and the catalytic and non-catalytic options available to address the requirements.

Today, emissions control is increasingly a case of systems optimisation in which the emissions control strategy is integrated with the other systems requirements. It is important to understand these other requirements when considering lean NO_x emission control. In the case of the diesel engine, the development challenge has been to retain the inherent fuel economy advantages of the diesel over petrol engines while addressing its weaknesses, such as low specific power output and poor refinement. The success of these developments is vividly illustrated in the West European light vehicles market (where in 1994 diesels accounted for 23% of the car sales and 80% of light commercial vehicles) and the trend is for further market penetration. Other markets such as the USA and Japan have lagged behind Europe's enthusiasm for the new generation of diesels but the fuel economy of the diesel has meant that,

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worldwide, it dominates the heavy duty long distance truck market and it remains a powerful incentive to adopt diesels in the light vehicle markets.

The diesel's success in Europe has been based on turbocharging and aftercooling to improve specific power outputs (to @40 kW/l), reduced production costs, improvements in noise and refinement and a green image based on its low CO_2 emissions (low fuel consumption). This remains a powerful advantage for the diesel particularly in Europe where concern for global warming and energy efficiency is perhaps the highest. For example carbon taxation could strongly favour diesel powered cars while in many countries (but not the UK, Sweden and Ireland) there are price incentives making diesel fuel 20–30% cheaper than petrol.

In other respects too the diesel is a very 'green' powerplant. Hydrocarbon and CO emissions arise from the incomplete combustion of fuel and oil but the large excess of oxygen (@15%) ensures that these are naturally low in the diesel engine compared to the stoichiometric petrol engine. In passenger vehicles further improvements in emissions and diesel odours are simply achieved by fitting an oxidation catalyst to the exhaust. Despite this the outstanding challenge for the future of the diesel engine is emission control and in particular the linked problems of particulate, SO_x emissions, NO_x emissions and fuel economy.

NO_x is shorthand to describe the oxides of nitrogen formed during combustion, in fact the majority (about 90%) is NO, this oxidises in the exhaust stream and in the atmosphere to NO_2. The amount of NO formed during combustion depends primarily on the temperature in the combustion chamber, the residence time at very high temperature and the cylinder pressure.

SO_x emissions are due to oxidation of the sulphur compounds in the fuel. The sulphur oxides and especially SO_3 either combine with water vapour in the atmosphere to form sulphuric acid or combine with the metals from the additives, the lubricating oil or fuel ash to form sulphates. Fuel sulphur levels vary from 500 ppm up to 5% for a heavy residual fuel used in large stationary engines. Special blends are available with lower sulphur levels of 50–100 ppm and 500 ppm sulphur fuel is becoming more widely available compared to the 1500–2000 ppm levels of a few years ago. Simple oxidation catalysts in the exhaust stream must be carefully formulated to suppress the oxidation of SO_2 to SO_3 since sulphuric acid condensation onto the carbon particulates can be a major contribution to the mass of particulate emissions.

Particulate or smoke emissions are responsible for diesel's dirty image. They derive from incomplete combustion of the relatively involatile droplets of diesel fuel combined with the mineral ash from the fuel and lubricating oil and the sulphates mentioned earlier.

2. Legislative requirements

Given the importance of Europe for the diesel powered light vehicle the European limits are probably most relevant

For type approval purposes the limits over the combined EC 15 and extra urban driving cycle are currently:

Combined $HC+NO_x$	0.97	g/km
CO	2.72	g/km
Particulates	0.14	g/km

From January 1996 the requirement will become:

1. *Gasoline vehicles*

Combined $HC+NO_x$	0.50	g/km
CO	2.20	g/km
Particulates	–	g/km

2. *Diesels*

	Indirect injection	Direct injection	
Combined $HC+NO_x$	0.70	0.90	g/km
CO	1.00	1.00	g/km
Particulates	0.08	0.10	g/km

New measures (as yet undecided) will take effect from January 2000. German proposals for this Stage 3 legislation are:

Combined $HC+NO_x$	0.50 g/km
CO	0.50 g/km
Particulates	0.04 g/km

Limiting values for light commercial vehicles are dependant on the weight of the vehicle. For vehicles with a weight of more than 1700 kg the limits are currently:

Combined $HC+NO_x$	1.70 g/km
CO	6.90 g/km
Particulates	0.25 g/km

Interestingly from January 1997 all new vehicles must have CO_2 emissions measured although there are no limits yet specified.

The legislation in the USA is more complex but low emission vehicle (LEV) levels are likely to be commonplace by 2001.

CO	2.113 g/km
Hydrocarbons	0.047 g/km
NO_x	0.124 g/km

Japan's legislation is equivalent to current European levels and there are no plans for significant changes. Improved standards for diesel trucks will be introduced in 1995 but these will not require the use of autocatalysts.

Currently diesel cars can meet the existing standards in Europe without catalysts. From 1996 at least an oxidation catalyst will be required (although direct injection engines have until 1999 to comply) while Stage 3 and LEV standards will require some additional form of NO_x control. For large trucks there are several engine management related options to meet requirements; nevertheless a successful lean NO_x catalyst would have considerable advantages in terms of system complexity. In the more space and cost constrained light vehicles, however, a lean NO_x catalyst is vital if the diesel engine is to continue its progress. Given European manufacturers investment and expertise in advanced small diesels, this is of considerable importance to European industry as well as European consumers.

3. Emission control strategies

3.1. NO_x control using engine management options

All engine orientated NO_x control methods are at the expense of decreased fuel efficiency and increased particulate generation [1]. The primary aim is to reduce the peak temperature of combustion since NO_x is formed by the reaction of nitrogen and oxygen which requires very high temperatures. Several options are available including improved injector design and high injection pressures to provide good atomisation and good homogeneity, aftercooling on turbochargers and increasingly in future the use of exhaust gas recycle.

Most current diesels (95%) are indirect injection systems but due to fuel economy advantages of @10–15% the use of direct injection systems is likely to increase in future [2]. The hydrocarbon and particulate emissions from direct injection engines are, however, worse than indirect injection engines and mitigating these effects will require the use of high pressure fuel injection via common rail and electronically controlled variable timing injectors to optimise combustion over the load range. The trend to direct injection also favours the use of turbochargers as the naturally aspirated engine has a low specific power output. Aftercooling is also useful to increase power and reduce NO_x formation.

The recirculation of exhaust gas back into the combustion chamber is an effective means of NO_x control. Since the heat capacity of the CO_2 in the recirculated exhaust gas is some 20–25% higher than the O_2 and N_2, the energy released by the fuel combustion results in a lower temperature rise and a slower rate of combustion and hence a lower peak cycle temperature with consequent lower NO_x levels.

Table 1
The typical selectivity issues for a diesel exhaust after-treatment system can be summarized by the following conflicts

Desired reactions	Undesired reactions
$^{*}C_nH_m + (n+m/4)O_2 \rightarrow nCO2 + m/2\, H_2O$ (HC/VOF oxidation)	$^{*}SO_2 + 1/O_2 \rightarrow SO_3$
$^{*}CO + 1/2\, O_2 \rightarrow CO_2$	$^{*}SO_3 + MO \rightarrow MSO_4$ (sulphate storage)
$^{*}NO_x$ reduction	

3.2. *Particulate control using engine management options*

The particulate matter filtered out of the exhaust gas of a diesel engine consists of: carbon and hydrocarbons from the combustion of the fuel and lubricating oil, sulphate and bound water derived from the sulphur content of the fuel and fuel and lubricant ash.

Carbon is the largest component of particulate and arises from the incomplete burning of the interior of the fuel droplets. Particulate emissions can be reduced by using high air/fuel ratios, high pressure injection systems to give as small a fuel droplet size as possible (to give maximum surface area for combustion) and a combustion chamber optimised to give excellent fuel and air mixing prior to combustion.

Associated with the particulate is a volatile organic fraction (VOF) that desorbs slowly. This is derived from partly burnt hydrocarbons. The sulphate and ash components have been mentioned previously. Many of the NO_x engine control strategies increase particulate generation (e.g., lower peak temperatures) while methods of decreasing the particulates can increase NO_x (e.g., higher air fuel ratios)

3.3. *Catalyst options*

Catalysts are a vital tool in meeting future emission requirements when combined with the advances in diesel engine design described above. The use of oxidation catalysts is a valuable way of ensuring compliance with Stage 2 EC requirements and relaxes some of the constraints on the engine designer. They represent a powerful way of dealing with the volatile organic fraction and the odours associated with diesel cars. Lean NO_x catalysts will allow Stage 3 and LEV legislation to be met without sacrificing the traditional economic advantages of diesel cars and increasing costs by over-elaborate engine design measures.

The catalyst has a number of conflicting performance requirements [3]. A fundamental conflict is the requirement for high HC/CO/VOF conversion at low temperatures and low sulphate formation even at high temperatures. The reason for this is that the washcoat technologies typically used to control sulphate formation, also tend to partly deactivate the active sites for HC/CO/VOF oxidation. In addition, many of these washcoat technologies show poor thermal stability and very poor NO_x conversion.

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For the European passenger car application the scope of catalyst system design is further complicated by the fact that the certification cycle requires the catalyst to exhibit high activity at very low temperature (150–200°C), whereas the frequent full-load driving on the high-way and in mountainous areas requires high thermal stability and low activity for sulphate formation. These conflicting requirements call for a very selective catalyst, which indeed presents a major development challenge.

Due to the reasons mentioned above, the emission engineering targets can be divided into cycle-related (urban and extra-urban phases) and non-cycle-related ones, as shown below

Urban targets	Good low temperature activity for HC and CO High conversion of VOF Good NO_x performance
Extra-urban target	Low production of sulphates
Off-cycle targets	High thermal stability Low storage/release of sulphates

4. An example of modern catalyst development and performance

Meeting all these conflicting requirements is an essential condition for useful catalysts. The requirements derive from the gaps in engine design technology, fuel quality restrictions, environmental legislation and cost effectiveness.

In the following sections we discuss results on a currently available catalyst system and describe how they were obtained as an example of the full range of challenges in this field. It is important that data are obtained on realistic samples and under realistic conditions to ensure that the catalyst is subjected to the full range of challenges.

An example of the experimental procedures required is given by Smedler [3] but the essential features are:

(1) The use of full size monolith samples conditioned in a diesel exhaust stream at reasonable temperatures before collecting data. The space velocities are in the range 30 000–60 000/h.

(2) Diesel fuel is injected into the exhaust to provide a reductant for the NO_x. Fuel economy constraints limit the HC(based on propene)/NO_x ratio in the exhaust to 2:1.

(3) CVS Evaluation over the legislated driving cycles (eg ECER15 + EUDC) using a production vehicle and legislated sampling and analysis methods.

(4) Engine test bench evaluations and catalyst aging using production diesel engines with gaseous emissions analysis via infrared, chemiluminescence and FID and particulate analysis by thermogravimetric methods. Analysis is carried out at the engine and the tail pipe.

(5) Light off curves are obtained by running the engine at constant revolutions and increasing the brake torque to increase the temperature in steps. Typically 18 min is the time spent at each temperature.

(6) Sulphate storage on the catalyst and sulphate content of the particulate and VOF need to be determined.

5. Performance characteristics of standard diesel catalyst technology

5.1. Sulphate formation versus low temperature HC/VOF/CO activity

Particulate emissions are conventionally divided into the volatile organic fraction (VOF), carbon, ash and sulphates.

At the temperature prevailing at the catalyst location, the volatile organic fraction is predominantly present in the vapour phase. Therefore these high molecular weight organic species can be oxidized on the active sites in principally the same manner as the gaseous hydrocarbons.

Particulate carbon emission reduction by a flow-through oxidation catalyst has been observed and reported [4], but the exact mechanism of this reaction remains to be unambiguously demonstrated.

Ashes are built up of inorganic oxides from fuel and lubricant additives, and by metals resulting from engine wear. Ashes are unaffected by the catalyst, but may well contribute to deactivation [4,5].

The sulphate selectivity requirement of a diesel catalyst arises because SO_3 formed by SO_2 oxidation over the precious metal sites of the catalyst will appear as sulphate on the particulate collecting filter paper. The importance of this contribution is, for a given catalyst, governed by the engine load scenario (eg the average catalyst temperature) and the sulphur content of the fuel. Three different fuel sulphur levels are relevant: 1500 ppm (current German level), 500 ppm (certification level in Europe (1996), the USA (1994) and Japan (1996) and 25 ppm (typical for the current Swedish City Diesel).

On the 500 ppm sulphur level, a non-selective catalyst Pt/Al_2O_3 may be adequate for the ECER15 passenger car cycle with exhaust temperatures in the range 130–310°C, whereas for hotter applications, this sulphur level still requires a catalyst with considerable sulphate control since sulphates dominate the particulate emissions.

For Swedish City Diesel fuel (25 ppm sulphur), the sulphate contribution is almost insignificant over the entire temperature range. If such fuel were universally available efforts could be focused on maximum improvement of activity.

For the majority of near-term applications, however, the certification sulphur level will be 500 ppm. To avoid excessive sulphate emissions on that level, it is essential to properly address the SO_2 oxidation activity, as well as the sulphate storage capacity of the support system. Therefore, support materials with inherently low capacity for sulphate storage, as well as selective inhibitors of the SO_2 oxidation reaction are required.

5.2. *Sulphate performance versus durability*

Many of the inhibitors used to selectively deactivate the SO_2 oxidation activity can also have a negative influence on catalyst durability. The exact mechanism of their action varies from system to system, but acceleration of support sintering, pore blockage and formation of inactive surface compounds with the precious metal component, are three examples of high temperature deactivation effects that have frequently been observed. In addition, extended operation at low temperature (100–300°C), frequently results in partly reversible poisoning of the catalyst by fuel-derived sulphur, and by lubricant-derived zinc and phosphorous [4].

The practical result of these deactivation modes is that, following high temperature aging the light off temperature of the catalyst for CO reactions can be shifted from @200°C to nearly 400°C in bad cases simply due to the effect of the sulphate suppressing additive. Careful attention to the preparation chemistry can mitigate these effects substantially.

5.3. *Lean NO_x activity versus sulphate formation*

In comparison to a stoichiometric Otto engine with closed loop control and three-way catalyst, the diesel engine clearly has a disadvantage in terms of NO_x emissions.

The development of diesel catalysts with a good NO_x reduction activity is therefore one of the most intensive fields of automotive catalysis research and development today. A very large number of catalyst concepts have been screened and numerous papers have been published in recent years [5–11], some of them giving the encouraging impression that the problem is very close to its solution. Frequently these system (e.g., Cu/ZSM-5, Mordenite, Ga-Ferrite, Ga/ZSM-5, SnO or Ag/Al_2O_3) have peak conversion at high temperatures (400–600°C) when for the usual driving cycles low temperature performance is critical. It has also to be mentioned, that in our engine bench performance testing, we have not yet been able to reproduce the claimed laboratory performance of these systems.

Two systems that have drawn considerable attention are Pt/Al_2O_3 [12] and Cu/ZSM-5 [13,14]. These systems have been proven to give good performance at low and high exhaust temperature, respectively. In a recent Johnson Matthey study [12] some important aspects of the reaction mechanism on Pt/Al_2O_3 were discussed and the reader is referred to the other articles in this volume for further analysis. The mechanistic proposals for the Pt/Al_2O_3 and Cu/ZSM-5 systems are obviously fundamentally different in their approach and lead to a different temperature window in each case. In fact all known lean NO_x catalyst systems exhibit such a temperature window, wherein the catalyst is active for NO_x reduction. In general this behaviour can be explained by the respective rates of reaction of hydrocarbons with oxygen and NO_x. At temperatures below the window, both processes are negligibly slow and at temperatures above the window, virtually all the available hydrocarbons are consumed through direct oxidation to CO_2. The development challenge for a catalyst manufacturer is then to tailor the catalyst system in such a way that maximum activity within the temperature range of application is obtained. For current light duty vehicle requirements the development focus is on low temperature activity.

The performance of the simple Pt/Al_2O_3 is rather poor in this respect with peak conversions in the range of 30% at 220°C however proprietary developments in formulation have lead to catalysts capable of more than 40% conversion at about 190°C. While this is an encouraging improvement at this stage of development increased activity leads to unacceptably high sulphate formation when compared with a standard oxidation catalyst.

This conflict is similar to the conflict between sulphate formation and CO/HC/VOF conversion seen earlier. The requirement is therefore to develop a support system that simultaneously exhibits the properties of low sulphate storage, minimum deactivating effects of sulphate suppressing components and maximum promotion of platinum activity for CO and hydrocarbon oxidation and NO_x reduction.

For low sulphate emissions, the preferred support material is only weakly interacting with sulphur oxides, i.e., it does not adsorb SO_2 strongly and it does not react with SO_3 to form stable washcoat sulphates (sulphate storage). In a previous study by Johnson Matthey [15], a number of sulphate suppressing metal oxides were screened in model exhaust for their effect on the selectivity of supported platinum catalysts. The results of this study provide a comprehensive map over individual interactions between a single support component and a single base metal oxide additive, which gave valuable background information to the design of fully formulated catalysts. However to meet the requirements further developments have been made [3] resulting in commercially available catalysts capable of achieving fractional cycle emission reduction levels of nearly 90% for hydrocarbons, 95% for CO, 15% for NO_x, and 35% for particulates without exhaust line diesel injection. Sulphate production is such that sulphates contribute less than 10% of particulates at 400°C. Considering that the average HC/NO_x mole ratio was therefore 0.3, these NO_x reduction levels are clearly encouraging. With exhaust line diesel injection giving a HC/NO_x ratio of 2:1 NO_x conversions of better than 40% at 190°C are obtained. These conversion levels indicate that a non-turbocharged IDI vehicle that just meets the current legislation without a catalyst, has the potential of reaching emission levels far below the EC Stage 2 standards, by using these catalysts.

It is important to stress that the results shown by Smedler are on commercially available catalysts which meet the durability, poison resistance, aging resistance, production quality control and cost requirements of components in the modern motor industry.

As such these catalysts represent the first practical lean NO_x diesel catalysts available.

Despite these advances considerable effort is required to develop catalyst systems that while still meeting the constraints discussed above provide:

(1) Higher NO_x conversion levels.

(2)Extension of the operating winder to both lower and higher temperatures.

(3) Minimisation of the fuel injected into the exhaust stream.

The driving forces for these developments are the use of turbochargers which reduce exhaust temperatures significantly, NO_x control under severe loads and heavy duty applications requiring high temperature performance, fuel economy and of course the ever increasing concern over emissions and the legislation that follows.

6. Conclusions

(1) Legislation is driving lean NO_x catalyst development.

(2) The development of successful lean NO_x catalysts is vital to the future of the diesel car.

(3) Lean NO_x catalysts must satisfy the other vehicle requirements to be useful.

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