



## Diesel engine emission and after treatment-a review

Hussain.J<sup>1</sup>, Palaniradja.K<sup>2</sup>, Alagumurthi.N<sup>2</sup>, Manimaaran.R<sup>1</sup><sup>1</sup>Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry, India,.<sup>2</sup>Faculty of Mechanical Engineering, Pondicherry Engineering College, Pondicherry, India.

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### ABSTRACT

Implementation of straight and stringent legislation of Nox emission requires the new technological development for Nox abatement from exhaust gases. This paper summarizes the current status of Nox abatement strategy. The main focus is put forward on Nox control methods applied in combustion of diesel fuel in CI Engines furthermore the various methods of Nox abatement techniques emphasized.

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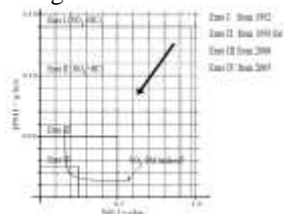
### Keywords

EGR, Emission,  
Pollution,  
Combustion,  
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### Introduction

The diesel engine's reputation as a noisy, smoky, and sluggish power plant (the reasons for this have been explained in Chapter 1) has changed due to modern diesel engine technology which allows one to combine the inherent low fuel consumption with excellent driving performance and low emission characteristics [LSG99]. After carbon dioxide (CO<sub>2</sub>) was identified as a greenhouse gas contributing to global warming, diesel engines have emerged as an alternative to gasoline engines due to their low fuel consumption and hence low CO<sub>2</sub> emission. While carbon monoxide (CO) emissions are negligible in CI engines due to lean operation and emissions of unburnt hydrocarbons (uHC) can be handled with oxidation catalysts, the emissions of oxides of nitrogen (NO<sub>x</sub>) and particulate matter (PM) are of particular concern and therefore the topic of this chapter. With respect to after treatment solutions, the focus will be on NO<sub>x</sub> traps because their regeneration requires tight control over the air path and constitutes the main motivation for this dissertation. The formation of NO<sub>x</sub> as well as PM is closely linked to the combustion process (cf. Section 2.1) which depends on engine design variables such as combustion chamber and fuel injector design, pressure and timing of the injection (modern injection system such as common rail also allow multiple injections), swirl ratio, valve timing, compression ratio, etc. In general, these variables can only be optimized for the reduction of one of these two main pollutants due to the so-called NO<sub>x</sub>-PM trade-off described in Section 2.1 (although there are exceptions, e. g. two-stage combustion can break the trade-off by forming a fuel rich mixture at the initial combustion stage to prevent NO<sub>x</sub> formation and inducing strong turbulence in the combustion chamber at the later stage of the combustion to oxidize the particulates [CA96]). Typically, the other pollutant is controlled by after treatment. Alternatively, NO<sub>x</sub> and PM after treatment solutions can be integrated which allows the combustion system and engine calibration to be optimized with respect to performance/efficiency. This chapter gives an overview of currently available after treatment techniques.

Concerning in-cylinder emission reduction techniques, only exhaust gas recirculation (EGR) and fuel composition (especially water emulsions) will be discussed. Engine design changes are a whole other area to address emissions and performance, but they are beyond the scope of this review. Legislation is the driving force for the reduction of diesel engine emissions as already mentioned in Chapter 1. Figure 2.1 depicts the current and future emission standards for light-duty diesel engines in the European Union. The depicted NO<sub>x</sub>-PM trade-off curve for a 1590 kg vehicle with a 2.0 liter high-speed DI diesel engine indicates that advanced after treatment is not necessary to satisfy Euro IV regulations (at least in this weight class) [Joh00]. However, marketing reasons require further reduction of both NO<sub>x</sub> and PM in Europe, while the proposed emission standards in the US are already tighter. Since a direct comparison between European and US standards is not fair due to completely different emission drive cycles, Figure 2.1 only shows the European regulations.



**Figure 2.1: Evolution of emission standards in the European Union and typical NO<sub>x</sub>-PM trade-off curve for a light-duty vehicle [Joh00]**

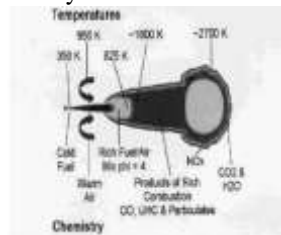
After describing the formation of NO<sub>x</sub> and PM during the diesel combustion process in the next section, this chapter will give an overview of diesel emission reduction strategies. Exhaust gas recirculation (EGR) is not only a well established means to reduce NO<sub>x</sub> emissions; it also plays a key role in the regeneration strategy for NO<sub>x</sub> traps. Therefore, its different effects on NO<sub>x</sub> emissions are discussed in Section 2.2. The emphasis of this chapter is on NO<sub>x</sub> traps in Section 2.3.

In addition to their operating principle, the status quo of regeneration and desulphation techniques which are a crucial factor in the potential success of NOx traps will be presented. Section 2.4 gives an overview of alternative solutions for NOx reduction such as DeNOx catalysts, selective catalytic reduction (SCR), and non-thermal plasma technology, while Section 2.5 elaborates on the nature of diesel particulates and their elimination in the diesel exhaust by particulate filters. The chapter finishes with a discussion of integrated NOx and PM solutions in Section 2.6 and conclusions in Section 2.7. It is worth warning the reader that this topic is still a very active research area and it is not clear yet which after treatment solutions will prevail. Therefore, this review describes the most promising methodologies up to date.

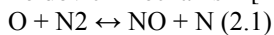
### Emission constituents

#### Formation of Nitrogen Oxides (NOx) and Particulate Matter (PM)

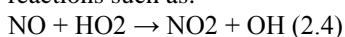
The diesel engine combustion begins around 5° after start of injection (ASI) in a locally rich premixed zone as described in Section 1.1.1 and depicted in Figure 1.1. The products from this early reaction are small, partially burnt fragments of hydrocarbons which are generally believed to lead to the formation of polycyclic aromatic hydrocarbons (PAH) that constitute the building blocks for particulates in flames [FDH+99]. When the air entrained during the premixed burn is entirely consumed, the temperature reached by this partial oxidation is about 1600 K and the reaction products (CO, CO<sub>2</sub>, fuel fragments and water vapour) will subsequently receive heat from the hot diffusion flame to form an environment favorable for the formation and agglomeration of soot particles. The fuel fragments and soot particles are subsequently transported through the interior of the plume toward the boundary of the diffusion flame sheath where they are oxidized in a thin reaction layer at temperatures around 2,700 K. Experiments show that these particulates are completely consumed by the hot diffusion flame sheath so that diesel soot emissions appear to be the result of quenching this final phase of oxidation. The temperature profile of the quasi-steady flame is shown in Fig. 2.2.



The major part of NO from the diesel combustion is formed by the oxidation of atmospheric nitrogen via the extended Zeldovich mechanism [Hey88]:



This formation of NO is highly temperature dependent due to large activation energies for the forward reaction (2.1) and the reverse reactions in (2.2) and (2.3). It is initiated at temperatures greater than 1900 K and the NO stays around during cooling since the reverse reaction is very slow. Fuel nitrogen is also a source of NO via a different and yet to be fully explained mechanism, however, its contribution is less significant in diesel engine combustion than the formation of NO via the Zeldovich mechanism. The produced NO can then be converted to NO<sub>2</sub> by reactions such as:



However, this NO<sub>2</sub> is converted back to NO via  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$  (2.5)

In the preceding discussion of the diesel combustion process, high temperatures in a region where oxygen is available along with nitrogen characterize the diffusion flame sheath rendering this area the ideal region for the formation of NOx. According to [FDH+99], two-thirds of the total Nox emissions are formed in the diffusion flame while one-third is formed in the hot post-combustion gas regions. Chemical equilibrium considerations indicate that at typical flame temperatures, the NO<sub>2</sub>/NO ratio should be negligibly small which is true for SI engines. However, in CI engines, NO<sub>2</sub> can contribute 10 to 30% of the total NOx emissions because the back reaction from NO<sub>2</sub> formed in the flame to NO (2.5) is quenched by mixing with cooler regions especially at light load [Hey88].

#### NOx-PM trade-off

Soot particles, which heavily contribute to the total mass of particulate matter emitted by the engine, are formed in the cylinder in the locally rich regions of the inhomogeneous 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 NOx. Hence, decreasing the combustion temperature (e. g. by exhaust gas recirculation as explained in Section 2.2) for lower NOx emissions results in an increase of PM. This dilemma is known as the NOx-PM trade-off.

#### Exhaust Gas Recirculation (EGR)

The recirculation of exhaust gas through an EGR valve into the intake manifold where it dilutes the incoming fresh air (thereby replacing oxygen with carbon dioxide and water vapour in the charge) is a well established and efficient means of reducing in-cylinder Nox emissions. EGR is also a feature of the engine under investigation as depicted in Figure 1.2. However, the reduction of NOx occurs at the expense of (initially slightly) lower thermal efficiency and higher PM emissions (following the NOx-PM trade-off). In order to understand the principles behind the combustion process with a diluted charge, Ladommatos et al. separated five possible effects of EGR (here presented in the order of significance for CI engines) on the in-cylinder NOx production:

##### Dilution Effect

The replacement of in-cylinder oxygen with exhaust gas reduces the availability of oxygen during the combustion, which lowers the temperature of the whole combustion process in the premixed burn as well as in the diffusion flame, where most of the NOx is created according to the combustion model from Section 2.1. This is due to the effect that the combustion still occurs in a region where the ratio of fuel and oxygen is around stoichiometric but now with exhaust gas acting as a diluents. The NOx emissions decrease significantly with reduced oxygen availability and its consequent reduction of the peak flame temperature. The latter has actually the dominant effect on the NO formation through the extended Zeldovich mechanism in (2.1) - (2.3). Note that the dilution effect is the most influential one in the NOx reduction by exhaust gas recirculation. While the dilution of the inlet charge has only a minor effect on the thermal efficiency of the engine, particulate emissions increase significantly with decreasing inlet charge oxygen. ([LAZ+96],[LAZ+97b])

##### Inlet Charge Temperature Effect

The recirculation of exhaust gas raises the temperature of the inlet charge and consequently leads to a higher flame temperature resulting in higher NOx emissions (although less

significantly than the dilution effect). It is observed that an increase in inlet charge temperature results in substantially higher emissions of PM (especially soot). This could be due to an increased rate of fuel pyrolysis in the premixed burn. The thermal efficiency of the combustion decreases slightly with rising inlet charge temperature which can be attributed to higher heat losses. In order to minimize the inlet charge temperature effect, the recycled exhaust gas needs to be cooled. ([LAZ+96],[LAZ+97b])

#### Ignition Delay Effect.

While the increase of the inlet charge temperature shortens the ignition delay, the lower oxygen availability increases it such that the net effect of EGR is an increase of the ignition delay. This increase potentially affects the combustion by increasing the fuel fraction burnt during the premixed burn and by shifting the auto-ignition towards the combustion chamber wall, however, the lower oxygen availability due to the dilution effect actually reduces the peak rate of premixed burning. This reduced burning rate and the delay of the combustion towards the expansion stroke reduces peak temperatures and pressures and the time the combustion gases spend at these conditions. Thereby, NO<sub>x</sub> emissions are reduced (although significantly less than the dilution effect) at the expense of PM emissions and thermal efficiency. Obviously, the ignition delay effect can be compensated for by adjusting the injection timing. ([LAZ+96],[LAZ+98])

#### Chemical Effect.

This effect describes the phenomenon that the dissociation of burnt gases at high temperatures can result in the reaction of NO with the resultant hydrocarbon free radicals (so-called denoxing). However, it is suggested that other mechanism might also play a role. While approximately 10% of the total NO<sub>x</sub> reduction can be attributed to the chemical effect of carbon dioxide, the chemical effect of water vapour was negligible (the dissociation of water is highly endothermic so that it occurs only at higher temperatures than the dissociation of carbon dioxide). ([LAZ+96b],[LAZ+97],[LAZ+97b])

#### Thermal Effect.

Due to the higher average specific heat capacity of the reacted exhaust gas components as compared to the specific heat capacity of oxygen that is replaced in the charge the combustion temperature is lowered. Traditionally, this was thought to be the reason for the NO<sub>x</sub> reducing effect of EGR. However, in diesel engines where the exhaust gases replace atmospheric air, the change in the heat capacity of the charge is minor. Thus, the thermal effect is considered insignificant here. Note that this is different from conventional SI engines, where the recycled exhaust gases are added to a virtually unchanged fuel/air mass (i. e. the manifold pressure is higher with an EGR flow). Hence, the thermal capacity of the cylinder charge is increased due to the increase in both mass and specific heat capacity which renders the thermal effect the most significant one in SI engines. ([LAZ+96b],[LAZ+97],[LAZ+97b])

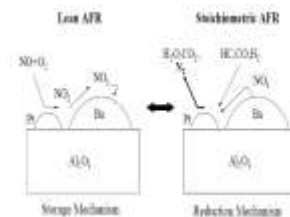
#### NO<sub>x</sub> Traps (Absorbers')

The raw emissions levels of NO<sub>x</sub> for lean-burn engines and stoichiometrically operated engines are actually quite similar. However, in SI engines running stoichiometric, NO<sub>x</sub> can effectively react with uHC and CO to nitrogen gas using a three way catalyst while preferring to react with excess oxygen in lean environments. Different solutions have been developed over the years [Joh00, Joh01]: NO<sub>x</sub> Traps (NO<sub>x</sub> Absorbers) which are described in this section and DeNO<sub>x</sub> Catalysts, Non-thermal plasma treatment as well as Selective Catalytic Reduction which

are described in Section 2.4. While these are all after treatment solutions, exhaust gas recirculation is an important way of reducing NO<sub>x</sub> emissions by changing the combustion characteristics as described in detail in Section 2.2. The NO<sub>x</sub> trap technology had first been introduced for direct injection gasoline engines and was then adapted to diesel applications which run at lower exhaust gas temperatures due to the high air mass flows in lean operation and high thermal efficiency of the diesel combustion. Hence the temperature window of NO<sub>x</sub> traps for diesel applications has to be lowered as depicted in Figure 2.4. Diesel NO<sub>x</sub> traps can already achieve over 80% efficiency at steady-state, but have problems with sulphur poisoning (desulphation of the trap requires high temperatures which expedite thermal aging), and also with the fuel penalty due to regeneration in a rich environment.

#### Operating Principle

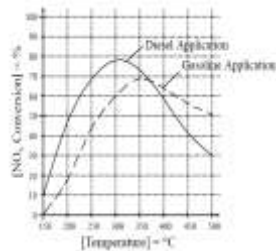
The operating principle, which is depicted in Figure 2.3, was discovered while investigating the selective reduction of NO<sub>x</sub> by uHC (cf. Section 2.4.1) and is described in Toyota's milestone paper in 1995 [MMK+95]: The trap temporarily stores NO<sub>x</sub> as a nitrate on alkaline earth compounds under lean conditions. In periodic rich conditions, called regeneration, which last for a few seconds after of the order of 100 seconds of lean operation, the nitrate dissociates and the NO<sub>x</sub> is reduced as in a three way catalyst. The reduction occurs in a rich environment as opposed to DeNO<sub>x</sub> catalysts; hence, the mechanism is advantageous for less generation of nitrous oxide (N<sub>2</sub>O, a potent greenhouse gas, cf. Section 2.4.1). Note that the regeneration, i. e. running a diesel engine rich, is a major challenge and is only possible with state-of-the-art diesel injection systems such as common rail to avoid excessive black smoke.



**Figure 2.3: Operating principle of NO<sub>x</sub> traps.**

In NO<sub>x</sub> storage catalysts, both oxidation steps occur in the same device (NO to NO<sub>2</sub> on a noble metal substrate, e. g. platinum, and NO<sub>2</sub> to nitrates in a second step). The trap only works in a temperature window (typically 250 to 500°C, cf. Figure 2.4); the lower limit is determined by the oxidation of NO to NO<sub>2</sub> (slow at low temperatures at the noble metal surface), the upper limit is determined of the thermal stability of the nitrates (they become unstable). Due to the use of high

EGR rates at low loads, the low activity at 100 to 250°C comes along with relatively low NO<sub>x</sub> flow emissions. The increase of activity at higher temperatures is accompanied by higher NO<sub>x</sub> concentration and space velocity. In [GBB+00], different absorber materials exhibit quite different temperature windows and one trap achieved 85% NO<sub>x</sub> efficiency on the NMVEG (New Motor Vehicle Exhaust Gas) cycle while three other traps only achieved around 45% (however, they all display similar behavior towards regeneration efficiency; especially interesting is the lack in the low temperature region regenerability, important under typical urban driving conditions, which is ascribed to a slow NO<sub>x</sub> reduction at that temperature compared to the nitrate decomposition rate).



**Figure 2.4: Typical NOx trap temperature window for a diesel (solid) and lean gasoline (dashed) application obtained from model gas tests [KBH+01].**

In addition to the temperature, other operating parameters influencing NOx adsorption efficiency are the trap regeneration frequency, the space velocity, and the NOx feed-gas concentration. With respect to the trap formulation, it has been shown in [MMK+95] that increased storage component basicity increases the NOx storage potential. However, it deteriorates the activity of the three-way catalytic reduction. Hence, a trade-off has to be found. In the same paper, it is observed that greater particle size of the noble metal reduces its activity. In a NOx trap this behavior is particularly distinctive for NOx conversion as the storage amount of the absorber increases when noble metal is in the proximity which is less likely if the metal particle size increases. In [BBM+96] the effect of a closed-coupled oxidation catalyst (for faster light-off in lean gasoline applications) upstream of a NOx trap is investigated. The minimum regeneration duration had to be increased from 300 ms to 700 ms due to the oxygen storage and hence oxidations of the reductants for the NOx trap. It is observed that the light-off temperature for lean NOx conversion is reduced.

This is explained by the oxidation of uHC and CO in the oxidation catalyst under lean conditions which reduces their partial pressure and therefore lowers the competition for the platinum sites on the trap leading to improve NO oxidation. The authors do not mention the NO oxidation in the oxidation catalyst though. Moreover, it is observed that the close-coupled catalyst improves the sulphur tolerance of the system significantly which is attributed to a largely reversible sulphur storage mechanism on the close-coupled catalyst. While the formulation of NOx traps has already been thoroughly investigated, the work is now shifting towards reducing the impact of NOx trap regeneration/desulphation on vehicle drivability especially during transients.

#### Trap Regeneration by Rich Combustion

In order to avoid the breakthrough of CO and uHC emissions and a higher than necessary fuel penalty, the dosage of the rich spikes has to comply with the amount of NOx adsorbed in the trap. Hence, a precise observation of the trap state has to be implemented. Moreover, the rich excursion needs to be imperceptible to the driver. An enriched exhaust gas composition can be achieved either via

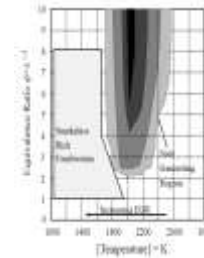
##### Engine modifications:

- 1.) Reduction of fresh air (intake air throttle, high EGR rate), which is rather slow,
- 2.) Increase of fuel mass (very early or late injection timing, changing the injection characteristic),
- 3.) Post injection or via

##### Exhaust system modifications:

Injection of reducing agents in front of the trap. Due to the inhomogeneous mixture formation in a diesel engine, rich operation leads to locally enriched zones, which usually results in a significant increase in black smoke emissions. However, an optimized calibration of all engine operating parameters can

reduce the increase of black smoke to an acceptable level. In [LSG99], uHC concentrations up to 7,500 ppm and CO concentrations as high as 4% are reported to be achieved in steady-state, which is sufficiently high for NOx absorber regeneration, without exceeding a smoke number of 2.8 Bosch. Moreover, a test cycle is shown to be successful where every 50 s of lean operation, a rich spike for 2 s would occur. Typically, during the rich spikes, sharp NOx desorption peaks occur. This happens when the nitrates dissociate in a rich environment but not enough reduction capability is available to reduce all of the released NOx. As described in Section 2.2, decreasing the AFR by increasing the EGR rate results in higher smoke emissions. However, Akihama et al. recently discovered that this holds true only up to a critical point [ATI+01]. Further increasing the EGR level then leads to a sharp decrease of smoke emissions even in rich conditions. In fact, total smoke is high, but it is largely an unburnt fuel cloud, rather than black (carbonaceous) soot. This phenomenon can be explained by the  $\phi$ -T-map, where  $\phi = \lambda - 1$  is the local fuel to air equivalence ratio. Figure 2.5 shows the local temperature and equivalence ratio region where soot is generated indicating that soot formation is suppressed at temperatures below 1,700 K even if rich combustion occurs. Hence, smokeless rich combustion is achieved by reducing the temperature by very high EGR rates such that the soot formation region is avoided. No improvement of the mixture formation is required. The lower temperature freezes the reactions from PAH (polycyclic aromatic hydrocarbons, cf. Section 2.1) to soot particles. Thus, while the soot emissions are reduced, the PAH emissions which account for the soluble organic fraction (SOF, cf. Section 2.5) of the PM emissions increase. However, the latter can be oxidized by a catalyst. Due to the large amount of EGR (about 55 %) the rich operation is limited to low load. It has the advantage of increasing the exhaust gas temperature under these conditions to values similar to gasoline engines, thus allowing improved catalytic removal of uHC and CO.



**Figure 2.5: Soot generating region on the  $\phi$ -T-map [ATI+01].**

#### Effects of Sulphur and Desulphation Strategies

The sulphur content of diesel fuel is typically higher than in gasoline, and the sulphur content of the respective mineral oil depends greatly on the location of the oil fields. Typical diesel fuel in Europe has a sulphur content of 370 ppm (the legal limit is 500 ppm since 1996), but 10 ppm diesel fuel is nowadays also available in many markets. Recently, the Environmental Protection Agency (EPA) in the US proposed a 15 ppm limit on sulphur content starting in June 2006. However, current research indicates that even with such low sulphur contents desulphation strategies for NOx traps are required. The effects of sulphur in diesel fuel can be summarized as follows [KAD+99]:

1. Emissions: Formation of sulphur dioxide SO<sub>2</sub> during combustion with by-products SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (involved in causing *acid rain*); formation of sulphates and adsorption on soot particulates.
2. Corrosion and wear: Increasing wear of engine parts through the corrosion by internally formed acid under cold start

conditions; corrosion in the exhaust system through sulphuric acid and condensate accumulation.

3. Formation of sulphates due to oxidation of sulphur in the catalyst and therefore increasing PM (in particular at high exhaust gas temperatures, which supports the finding in [SMB00], where PM number increased at high speed). In the NO<sub>x</sub> trap, the oxidation of SO<sub>2</sub> to SO<sub>3</sub> is in direct competition to the oxidation of NO to

NO<sub>2</sub>. The formation and accumulation of sulphates in the storage catalytic converter also occurs in a similar way to the nitrate process. Hence, the trap becomes poisoned by sulphates. Unfortunately, the sulphates are thermodynamically more stable than the nitrates, which means that the reaction conditions for sulphate regeneration are much more extreme (even under rich exhaust gas conditions; temperatures higher than 650°C and for a longer period are required). In 1999, DaimlerChrysler investigated the effect of the fuel sulphur level on the performance of a NO<sub>x</sub> storage catalyst [KAD+99]. Their experiments show that using standard diesel fuel with a sulphur content of 370 ppm, the efficiency of the NO<sub>x</sub> trap is significantly reduced within a few operating hours. However, with 10 ppm diesel fuel, over 50% NO<sub>x</sub> reduction efficiency can be achieved on the New European Drive Cycle (NEDC). Note that for a sulphur fuel concentration of less than 50 ppm, the oil contribution has to be taken into account such that desulphation strategies are required for NO<sub>x</sub> traps even with <5 ppm sulphur content fuel [GBB+00]. In this paper, Guyon et al. also show in their experiments that the NO<sub>x</sub> conversion efficiency drops from 95 to 55% after 4,250 km without desulphation using 50 ppm fuel. Moreover, desulphation ( $\lambda=0.83$ , T=680°C for 10 minutes) does not allow one to recover the initial efficiency: After five desulphations corresponding to 12,000 km, 30% of the initial NO<sub>x</sub> storage capacity had irreversibly been lost. It is worth mentioning that results of this type are dependent on details of the NO<sub>x</sub> trap formulation —constant improvements are being made, but the basic challenges as evidenced by the results being quoted seem universal. A particularly thorough investigation of desulphation strategies has been conducted by Klein et al. from dmc2 and AVL [KBH+01]. The authors show that desulphation in a vehicle is practical. In order to demonstrate this, a diesel NO<sub>x</sub> storage catalyst has been developed which has a significantly higher NO<sub>x</sub> conversion rate between 150 and 250°C as compared to NO<sub>x</sub> traps for lean-burn gasoline engines which have typically higher exhaust gas temperatures (cf. Figure 2.4). The conversion rate at different temperatures is investigated using a model gas at different temperatures but fixed space velocity (which does not represent typical engine installations) and averaging over 28 lean-rich cycles. For sulphation of this trap, a diesel engine is run at a fixed operating point for 120 s lean and

5 s rich ( $\lambda=0.90$ ) using 330 ppm sulphate content in the fuel. A fresh catalyst reaches an average Nox conversion of 85% which reduces to 63% after ten desulphations. However, one has to consider that the lean-rich cycle time has been optimized for a fresh catalyst and could be adapted to the state of the catalyst for better performance. This would hence require one to observe the catalyst state in the vehicle. The desulphation temperature is also examined: It turns out that for a practicable desulphation (low sulphate content in the trap after desulphation) temperatures higher than 600°C are necessary which, however, permanently reduces the NO<sub>x</sub> conversion rate at low temperatures. In tests with sulphur-free fuel, it is shown that the main reason for the reduced NO<sub>x</sub> conversion is the thermal aging of the trap due to

the high temperature desulphations and not sulphate poisoning. Further investigations show that for an efficient desulphation, rich spikes of  $\lambda < 0.9$  and length >10 s enable a sufficient desulphation within a few rich-lean-cycles. As explained before, the desulphation process requires temperatures in the exhaust of 500 to 700°C (as compared to gasoline applications with trap formulations that allow desulphation at 500°C, temperatures around 450°C required for DPF regeneration, and a temperature of 250°C for continuous NO<sub>x</sub> reduction in the NO<sub>x</sub> trap). In [KBH+01], a temperature rise from 150 to 250°C (at 1300 rpm, 1 bar BMEP steady-state) is achieved using engine parameter variations (multiple injection, injected fuel mass, injection timing, rail pressure, intake air throttling, and EGR rate), the rise up to 650°C is then achieved using post injection which generates uHC for an exothermal reaction in the oxidation catalyst (11,000 ppm uHC in feed-gas, double fuel consumption, soot and NO<sub>x</sub> emission less than in standard calibration, nanoparticles not mentioned). The alternative of externally heating the exhaust gas has not been examined. The main problem with the described desulphation strategies is the permanent deterioration of the NO<sub>x</sub> efficiency due to thermal aging. Moreover, spikes of bad smelling sulphur emissions (H<sub>2</sub>S) can occur during desulphation. An alternative solution is to place a sulphur trap in front of the Nox trap as investigated by Strehlau et al. in [SLL+96] for a lean-burn gasoline engine. The SO<sub>x</sub> trap adsorbs the sulphur oxides under lean conditions in order to keep them away from the NO<sub>x</sub> trap.

During the rich spikes for regeneration of the NO<sub>x</sub> trap, the sulphur trap releases the sulphate mainly as SO<sub>2</sub> which is then not oxidized to SO<sub>3</sub> in the Nox trap (due to the rich environment) and hence not stored as sulphates. This is shown to work in general, but it will mostly delay the sulphur poisoning, thus extending the NO<sub>x</sub> absorber lifetime, rather than preventing the poisoning completely.

### Alternative DeNO<sub>x</sub> Solutions

#### DeNO<sub>x</sub> Catalysts

DeNO<sub>x</sub> catalysts consist of precious metal or zeolites and they use unburnt hydrocarbons (as opposed to ammonia which leads to the SCR reaction, cf. Section 2.4.2) to reduce NO<sub>x</sub> in a lean environment. For example, copper ion exchanged ZSM-5 is known to decompose NO into N<sub>2</sub> and O<sub>2</sub>. The exhaust uHC is increased by in-cylinder injection modifications or direct injection of uHC into the exhaust gas. DeNO<sub>x</sub> catalysts achieve in general up to 35% efficiency, but have up to 6% fuel penalty due to the need of hydrocarbon reductant. Higher efficiencies (up to an impressive 70 %) have been shown using diesel fuel reductant on engine exhaust, resulting in a fuel penalty of 4% but with a catalyst volume of four times the engine swept volume. The major problem is the tight temperature window in which the catalyst works efficiently. For gasoline applications typical zeolite catalysts (high efficiency at higher temperatures than desirable in diesel engines) exhibit, moreover, poor thermal stability due to the H<sub>2</sub>O present in the exhaust gas. Yet another problem is that NO<sub>x</sub> conversion in an excess oxygen atmosphere using a catalyst of a noble metal family produces significant quantities of nitrous oxide (N<sub>2</sub>O), a potent greenhouse gas (which can be avoided by using NO<sub>x</sub> traps where the conversion occurs near stoichiometric [MMK+95]).

#### Selective Catalytic Reduction (SCR)

In an SCR system, the NO<sub>x</sub> present in the exhaust gas is mixed with ammonia as a reductant and catalyzed to nitrogen and water. The ammonia reductant needed for the selective catalytic reduction is typically obtained from on-board urea. The

urea is injected into the exhaust gas. A typical SCR system consists of three different catalysts in series after the urea injection point [GSS+00]:

- 1.) Hydrolysis catalyst which converts the urea with water selectively to ammonia (NH<sub>3</sub>) and carbon dioxide,
- 2.) SCR catalyst (e. g. V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>), where the ammonia reacts with NO<sub>x</sub> to form nitrogen and water, and
- 3.) Oxidation catalyst to avoid ammonia slip during transient operation.

Over 90% efficiency is possible with SCR systems. Problems are a possible ammonia slip, the compactness of the system, and the requirement for an urea distribution network; an advantage compared to traps is the less complex engine management requirement (however, a dosage system for the urea is required). Recently, the advantages of first oxidizing NO using an oxidation cat to NO<sub>2</sub> have been discovered [GSS+00] for a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst. The higher NO<sub>2</sub>/NO<sub>x</sub> ratio results in better low-temperature efficiencies of the SCR (typically 30 to 40 %). However, at NO<sub>2</sub> fractions larger than 50 %, the higher stoichiometry needed to convert NO<sub>2</sub> (1.33 compared to 1.0 for NO), and the slower reaction of NO<sub>2</sub> with NH<sub>3</sub> which results in NH<sub>3</sub> slip limit the maximum conversion without secondary emissions. It has also been found in the same study that V<sub>2</sub>O<sub>5</sub> (vanadium oxide) containing catalysts are irreversibly deactivated at temperatures above 700°C. In a follow-up study, the same authors demonstrate the NO<sub>x</sub> reduction potential of ion exchanged synthetic zeolites and their favorable aging properties (only slight NO<sub>x</sub> conversion reduction after aging at 800°C) [GPS+01]. It is also shown that the crucial component to achieve high NO<sub>x</sub> conversion is NO<sub>2</sub>; hence, a pre-oxidation catalyst is required. There is some concern that high-efficiency SCR systems generate sulphate PM, therefore ultralow sulphur fuel is needed (although the SCR is not as sensitive to sulphates as a NO<sub>x</sub> trap). SCR is effective in removing uHC and some of the PM (probably SOF, cf. Section 2.5). Since an SCR system does not directly interact with the engine control unit, the technique is suitable for retrofitting. Urea injection strategies are being reported. The first SCR system in a vehicle application was reported in 1995. The current research focuses on the development of solid reductant technology which would allow extending the refilling interval to service intervals. While the SCR technology has been proven successful in stationary applications like engine driven power stations for decades, the first studies on automotive applications emerged around 1995. Havenith et al. [HVG+95] investigate an SCR system with urea injection and a downstream oxidation catalyst in steady-state and transient operation. The steady-state efficiency decreases from above 90% at low load to about 65% at high load due to reagent oxidation. Note that below 25% load, urea injection is withheld due to low oxidation catalyst temperatures (≈300°C) where ammonia slip might occur. Note also that the sulphate emission increases due to the oxidation cat and that the N<sub>2</sub>O emission is ten times higher than normally expected without NO<sub>x</sub> after treatment (ammonia undergoes partial oxidation to N<sub>2</sub>O and possibly more complete oxidation to NO and NO<sub>2</sub> over an oxidation catalyst). In transient cycles, the system is found to be effective in NO<sub>x</sub> reduction although peaks in NO<sub>x</sub> emission occur after load steps, which is supposed to be caused by buffering effects.

#### SCR versus Traps

NO<sub>x</sub> absorbers' with desulphation might draw 1 to 2% more 'effective' fuel penalty (considering urea), but the user will have to deal with an added reagent on board. It is therefore

likely that Europe will commercialize SCR on a large scale and the US NO<sub>x</sub> traps. Certainly, NO<sub>x</sub> sensors will become important and are already appearing on lean-burn cars in Europe.

#### Non-thermal Plasma Technology

The operating principle of the non-thermal plasma technology is as follows: A high local electrical field is applied to generate micro discharges in the exhaust gas which directly produce highly energetic electrons. Due to the short duration of the micro discharges (<100 ns) the electrons and the bulk gas do not thermally equilibrate and, hence, the temperature of the bulk exhaust gas remains essentially constant [LSG99]. The plasma generated electrons dissociate oxygen which reacts with unburnt hydrocarbons to form a variety of partial oxidation products. Moreover, NO is oxidized to NO<sub>2</sub>. When uHC is present in the plasma the oxygen radicals react preferentially with the unburnt hydrocarbons instead of with SO<sub>2</sub> thus there is only a small conversion to sulphates as opposed to an oxidation catalyst [Hoa01]. The gas phase plasma alone does not remove NO<sub>x</sub> from the exhaust, hence, a combination of plasma and catalyst is needed. In [Hoa01] it is observed that a NaY catalyst achieves 58% No<sub>x</sub> conversion at 180°C, a Cu-ZSM5 simply converted the NO<sub>2</sub> back to NO. Therefore, the plasma catalyst NO<sub>x</sub> reduction obeys a different reaction mechanism at lower temperature than the thermal catalysis. The advantage of the non-thermal plasma technology is a wider temperature range for No<sub>x</sub> conversion (150 to 500°C) than non-plasma catalysts and reduced sulphur sensitivity (urea SCR and zeolitic DeNO<sub>x</sub> do not extend to such low temperature, precious metal DeNO<sub>x</sub> does not extend to such high temperature and NO<sub>x</sub> traps are more fuel sensitive). Moreover, in [Hoa01], high particulate removal has been demonstrated although not yet simultaneously with NO<sub>x</sub> reduction in a single system. Non-thermal plasma technology achieves 60 to 70% NO<sub>x</sub> reduction efficiency, but the fuel penalty is around 6% due to the cost of electric power and addition of unburnt hydrocarbons for best conversion efficiency. However, note that these techniques are still in their early development stages.

#### Particulate Matter

##### Nature of Diesel Particulates

Most of the particle *number* emitted by engines is in the nanoparticles range,  $D < 50$  nm, while most of the *mass* is in the accumulation mode,  $50 \text{ nm} < D < 1000 \text{ nm}$  [Kit98]. *Nanoparticles*: Typical type is uHC/Sulphate, but may also contain solid carbon and metal compounds; they form by nucleation during dilution and cooling; they also appear in SI engines; there may actually be more in some state-of-the-art diesel engines (the better combustion produces less accumulation mode particles on which small particles can absorb; this was observed on an engine with high values of the soluble organic fraction SOF). *Accumulation Mode Particles*: Mainly carbonaceous soot agglomerates directly from the combustion; 10 to 100 times more than in SI engines. Typical particle composition for a HDD engine on a transient cycle (in percent by mass):

- 41% Carbon (Soot)
- 14% Sulphate and Water
- 13% Ash (from metal compounds in fuel and lube) and other
- 32% Soluble Organic Fraction (SOF), consisting of 25% unburnt oil and 7% unburnt fuel with high boiling point; the low boiling point unburnt components become uHC emissions SOF values can range between 10% and 90% and are highest at light engine loads when exhaust temperatures are low. The sulphuric

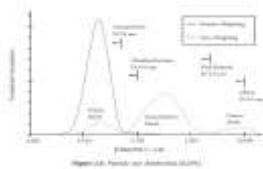
acid/sulphate concentration is roughly proportional to the fuel sulphur content. As the exhaust gas is cooled and diluted, nucleation, condensation, and adsorption transform volatile materials to solid and liquid particulate matter.

The particle size distribution (Figure 2.6) shows three peaks corresponding to the following modes:

- Nuclei Mode: 5 to 50 nm diameter range, contains 1 to 20% of particle mass and 90% of particle number
- Accumulation Mode: 100 to 1000 nm diameter range, contains most of the mass

- Coarse Mode: 1 to 10  $\mu\text{m}$ , contains 5 to 20% of particle mass consisting of accumulation mode particles that have been deposited on cylinder and exhaust system surfaces and later re entrained. Current emission standards are the result of many studies that have shown a link between fine particle (with a diameter of less than 2.5 micrometers) air pollution and adverse health effects (e. g. [PTN+95]). These standards are based on mass and do not address particle size. However, many recent studies indicate that at similar mass concentrations nanometer size particles are more dangerous than micron size particles (e. g. [DLM98]). Due to their extremely small size, nanoparticles (i. e. with a diameter of less than 50 nanometers) can penetrate deeper into the lung and are more difficult to remove from the lung tissue. This is associated with respiratory inflammation and acute pulmonary toxicity for people with a preexisting condition. Moreover, the large surface area provided by nanoparticles in contact with the lung provides the opportunity for surface chemistry of the particles to have a profound effect. The problem for legislation is that the mass is conserved, but not the number. This phenomenon is due to nucleation and coagulation during dilution and sampling, making it difficult to design a standard. Note that particulates also affect engine performance and wear, e. g. when they are recycled to the engine via EGR. A review of particulate research is given in [Joh01]. Some of the remarks are:

- The particle size distribution of solid soot particles generated in the cylinder varies little with fuel. Soot mass is generated about 10 to 20°ATDC, with sizes up to 110 nm; as the piston drops, these particles oxidize and decrease in number about two orders of magnitude and in size to about 70 nm.
- Nucleation and growth phenomena are strongly dependent on concentration (exhaust dilution ratio), time, and temperature and, even soot concentration.



### Particulate Filters

Diesel Particulate Filters (DPF) has been considered as a solution to the PM problem for twenty years. Although not really necessary in Europe to satisfy Euro IV, much effort is being done on developing filters in Europe, lead by Peugeot's introduction of a DPF in serial production in 2001. A typical filter is the ceramic wall-flow filter, where the exhaust gas is forced to flow through the walls of the monolith which removes PM very efficiently. To avoid clogging up of the filter, the PM has to be oxidized, either periodically or continuously. Direct oxidation by O<sub>2</sub> is accomplished at temperatures of around 550°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 are being 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 BPT depends on flow rate, particulate composition, NO<sub>x</sub> content, sulphur levels, soot loading rate, and perhaps many other engine/fuel parameters. The idea is to bring the BPT down to ease regeneration —see next section. Filters are most effective at removing solid accumulation mode particles (letting through mainly SOF and sulphates which are almost completely gaseous at typical filter temperatures), while catalysts remove mainly organic compounds that will contribute to SOF and nuclei mode [Kit98]. According to [Joh01], however, numerous studies have demonstrated that filters take out more than 90% nanoparticles, but it might be that gaseous nanoparticle precursors are not removed and sulphate nanoparticles might actually increase. There are actually conditions, where filters increase the number of nanoparticles, since they take away the soot under hot conditions, while letting escape gaseous aerosol precursors which condense downstream in larger numbers than if carbon soot was available. Three things have to be done to eliminate nanoparticles:

- 1.) Carbon soot needs to be taken out by filters or change in combustion processes (e. g. HCCI),
- 2.) Sulphates have to be eliminated as much as possible by reducing sulphur content in fuel lube or by preventing oxidation of SO<sub>2</sub> (e. g. in catalysts),
- 3.) Eliminating hydrocarbon precursors with oxidation catalysts (which in turn produce sulphates) or combustion optimization (HCCI results in high uHC). Moreover, the fuel quality also plays an important role: high natural Cetane number and low polyaromatic compounds reduce the number of carbon particulate precursors. Indeed, by optimization of the combustion process from IDI to DI, especially common rail, a 60% reduction of particulate mass could be achieved. This is due to high fuel injection pressures over the whole operating range by common rail technology, optimized combustion chamber design, and elaborated liner machining to reduce oil consumption. However, diesel engines still produce a higher amount of PM mass than SI engines. DPFs are very effective (up to 95% removal of PM by mass) if the pore opening is less than 40 to 80  $\mu\text{m}$ . 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.

### Regeneration Strategies

As mentioned above, reducing the balance point temperature is a crucial factor to enable regeneration at lower temperatures. This can be done by reducing the sulphur content, coating a catalyst such as platinum onto the wall-flow filter, introducing an oxidation catalyst before the filter (so-called CRT in which the catalyst oxidizes NO<sub>x</sub> to NO<sub>2</sub> which is a strong oxidizing agent for soot at 250°C, but at the same time, it forms sulphate particulates [MAB95]), using non-thermal plasma to replace the oxidation catalyst (the plasma converts NO to NO<sub>2</sub> without significant conversion of SO<sub>2</sub>), or using fuel-borne catalysts (e. g. iron or cerium additives which strengthen radical-carbon bonds which play an important role in soot oxidation) [Joh01]. So far, the diesel exhaust temperatures can be too low to regenerate the filters under all driving conditions; hence, active regeneration techniques are still needed. The Peugeot system [SMB00] uses a cerium-based fuel borne catalyst (which reduces the required regeneration temperature from 550°C to

450°C and in addition increases the soot combustion rate), a diesel oxidation catalyst in front of the filter, back pressure monitoring to trigger regeneration (in addition, the amount of residues from the additive and lube oil ashes are calculated at every moment, as well as there is a soot mass estimation based on engine parameter maps; pressure drop measurement is however necessary after partial regeneration), and engine controls (multiple injection management: shortened main injection, introduction of a post injection to burn the maximum amount of fuel as late in the expansion stroke as possible without by-product formation such as CO, uHC, and soot) to increase exhaust temperature to 450°C but keeping the torque constant, aided by a tuned post injection (and exothermal reaction in catalyst) if necessary. The paper does not mention any change in the EGR control; however, the VGT has to be adjusted due to increased exhaust gas enthalpy during regeneration. Optimal regeneration frequency (trade-off between increased back pressure fuel penalty and penalty due to post injection) was established as 400 km. The filter needs to be cleaned and the additive to be refilled every 80,000 km. The fuel penalty is 5% for city driving conditions (fewer elsewhere) and the maximum torque is reduced by 2% due to increased back pressure. It is noted that at speeds higher than 100 kph, the PM number emission becomes larger than without catalyst and filter. This is due to sulphate formation on the oxidation catalyst. Hence, fuel sulphur content less than 50 ppm is required. Other regeneration strategies include direct electrical heaters or fuel burners, non-thermal plasma, and microwave regeneration techniques. None of these appear to be serious contenders at the time of writing.

#### **Integrated DeNOx and PM solutions Filters and SCR/NOx Traps**

Filters combined with SCR seem to have been investigated more than filters combined with traps, and already are giving promising results. A different approach used a combination NOx trap/filter consisting of a wall-flow filter with an internal NOx adsorbed catalyst coating. In [KBM+01], a DPF is installed upstream of an SCR catalyst. They report soot removal efficiencies of 98% by mass and NOx conversions ranging from 40 to 73 %. A BPT of 315°C at 55% rated power is achieved using Pt/Ce fuel additives. In their investigations, the NO<sub>2</sub>/NOx ratio over the DPF does not increase with temperature, (NO is catalytically converted to NO<sub>2</sub> first but then used to oxidize soot), therefore a decrease of NOx conversion with decreasing DPF temperature (which decreases the NOx inlet temperature) is observed. In [CCH+00], a system combining a NO<sub>2</sub> based continuously regenerative trap particulate removal technology with a urea-based Selective Catalytic Reduction (SCR) NOx removal technology which shows beneficial synergistic effects and leads to simultaneous conversions of 75 to 90% in NOx and PM. The feed-gas first passes an oxidation catalyst which converts uHC and CO and in addition oxidizes NO to NO<sub>2</sub>. The NO<sub>2</sub> subsequently combusts with PM in a particulate filter (CRT). If some of this NO<sub>2</sub> reaches the following SCR catalyst, it will lead to an improvement in the low temperature NOx conversion of the SCR system (it is shown that a combined CRT + SCR system results in less NOx than the SCR alone). In a similar system, Khair et al. [KLF00] put a DPF after an SCR system (hence, avoiding ammonia slip) and use a cerium fuel additive to facilitate filter regeneration. They achieve 70% NOx and 97% PM reduction on a heavy-duty engine achieving the Euro V limits already. For a successful vehicle application, the integration of NOx traps and DPFs requires further investigation

of the effect of filter regeneration (high temperatures) on the trap and of the effect of fuel additives to reduce BPT on NOx emission.

#### **Fuel Enhancement**

Water emulsified fuel is one of the few primary techniques that can reduce PM and NOx emissions simultaneously [LPS01]: The break of the correlation between NOx reduction and PM increase (NOx-PM trade-off) is possible because the presence of water not only physically changes the way the combustion occurs but also the chemical kinetics of the combustion process. The physical changes (the reduction of the peak combustion temperature in the presence of water) lead to lower NOx emissions of up to 19 %, while the chemical changes (different relative quantities of fuel, oxygen, and inert during the rich premixed-burn stage of diesel combustion, where water acts as a temporary source of oxygen) lead to reduced PM mass of up to 83% independent of the temperature change. The combination of water emulsified fuel in combination with a diesel oxidation catalyst is shown to reduce PM nearing the level typically offered by a DPF. The big advantage of water emulsified fuels is that this technology can easily be retrofitted to existing vehicles, therefore speeding up the process of improving the air quality. However, the maximum water content in diesel fuel is limited due to a decrease in ignition performance. Moreover, the water has to be prevented from having contact with metal surfaces in order to avoid corrosion. A new commercially available fuel called PuriNox® achieving this by using an additive which surrounds the water droplets has been certified by the California Air Resources Board (CARB) in 2001, therefore qualifying for governmental funding. CARB ascribed the new fuel a 14% reduction in NOx and 63% reduction in PM mass emissions. The costs per kilometer are slightly higher compared to conventional fuel, therefore tax concessions are needed (and some have already been granted) to encourage the widespread use of this water emulsified fuel. Note that a break of the NOx-PM trade-off can also be achieved by other oxygenated agents. In particular, diethylene glycol dimethyl ether which has a high oxygen content (35.8 mass percent) and high ignitability has been found to simultaneously improve smoke, PM, NOx, uHC, and noise emissions as well as thermal efficiency [MON+98].

#### **Conclusions**

From this survey, it is apparent that no consensus has yet been found on what technology will be used for diesel after treatment. It seems clear, however, that the systems will be complex, and require very refined engine control to achieve their optimal performance and longevity.

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