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The Lecture Contains:

- DIESEL EXHAUST GAS AFTERTREATMENT
- DIESEL OXIDATION CATALYSTS
- Design Features of DOC
- NO_X Storage-Reduction (NSR) Catalysts
- Selective Catalytic Reduction (SCR)
- NH_3/NO_X Ratio and Ammonia Slip
- SCR Catalyst System
- Comparison of NSR and SCR Catalyst Systems

DIESEL EXHAUST GAS AFTERTREATMENT

The combustion process and hence the exhaust gas composition and its thermodynamic state in diesel engines differ from SI engines. The main differences are;

- The overall air-fuel ratio in the diesel engines varies from about 19:1 to 75:1 resulting in large variations in the exhaust gas composition with excess oxygen always present in the exhaust gases.
- Due to heterogeneous combustion in diesel engines, a large concentration of particulate matter is present in the exhaust gases.
- The exhaust gas temperature varies usually from 150 to 350º C. The gas temperatures at the exit turbocharger are further lower compared to temperatures at the exhaust port due to expansion in the turbine

In the European heavy duty engine cycle the exhaust temperatures vary from 200 - 400º C although in the US transient cycle the gas temperatures may reach up to 600 C. On the other hand in the driving cycle for light duty vehicles the gas temperatures vary in the range of 150 350 C only. Until the year 2000, the diesel vehicle emission standards in the US and Europe were largely met by use of improved injection system, engine combustion improvements, EGR and turbocharging. The three-way catalytic converters are unable to function in diesel engines as a high amount of excess oxygen is always present in the exhaust gases. Hence, the nature of exhaust treatment in diesel engines is considerably different than for the stoichiometric SI engines. In the light duty diesel vehicle segment, diesel oxidation catalysts have found application for the Euro 2 and 3 vehicles. For the later standards such as Euro 4 and 5, advanced forms of exhaust aftertreatment like diesel particulate filters and lean de-NOx catalysts are being employed.

Exhaust aftertreatment in diesel engines may be grouped in two broad categories;

- Diesel catalytic exhaust aftertreatment and
- Diesel particulate filters (DPF)

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DIESEL OXIDATION CATALYSTS

The diesel oxidation catalyst is also termed as DOC. The DOC works in a similar fashion as the oxidation catalytic converter in the gasoline engines. However, the performance of DOC differs from oxidation catalysts in gasoline engines due to;

- Low exhaust gas temperatures
- Presence of particulate matter in the diesel exhaust and
- High fuel sulphur content compared to gasoline

Typically use of DOC depending on engine design and operating conditions results into;

- 30 –80% conversion of the gaseous HC
- 40 to 90 % reduction of CO
- Dry soot does not get oxidized. But, oxidation of 50 to 80% of soluble organic fraction and some PAH occurs that gives 30 to 50 % reduction in total PM emissions.
- Conversion of fuel sulphur to SO_3 and emission of sulphuric acid aerosol.

The fuel sulphur on combustion gets converted to sulphur dioxide in the combustion chamber. The SO_2 however, gets further oxidized to SO_3 on the catalyst which combines with water vapours to form sulphuric acid aerosols which is also termed as sulphate emissions. Part of SO_3 produced is stored on the catalyst. The reactions involving fuel sulphur proceed on the catalyst as below:

Oxidation of SO_2:

$$SO_2 + \tfrac{1}{2} O_2 \rightarrow SO_3 \qquad (6.3)$$

Sulphate storage:

$$SO_3 + MO \text{ (washcoat metal oxide)} \rightarrow MSO_4 \qquad (6.4)$$

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The particulate emission reduction by DOC is influenced by the exhaust gas temperature as shown on Fig. 6. 11. The optimum temperature range for the DOC operation is observed to be from about 200 to 350º C. At lower temperatures poor oxidation of SOF and PAH is obtained and at temperatures higher than 350º C a high conversion of SO_2 to sulphates results in an increase of mass of PM emissions.

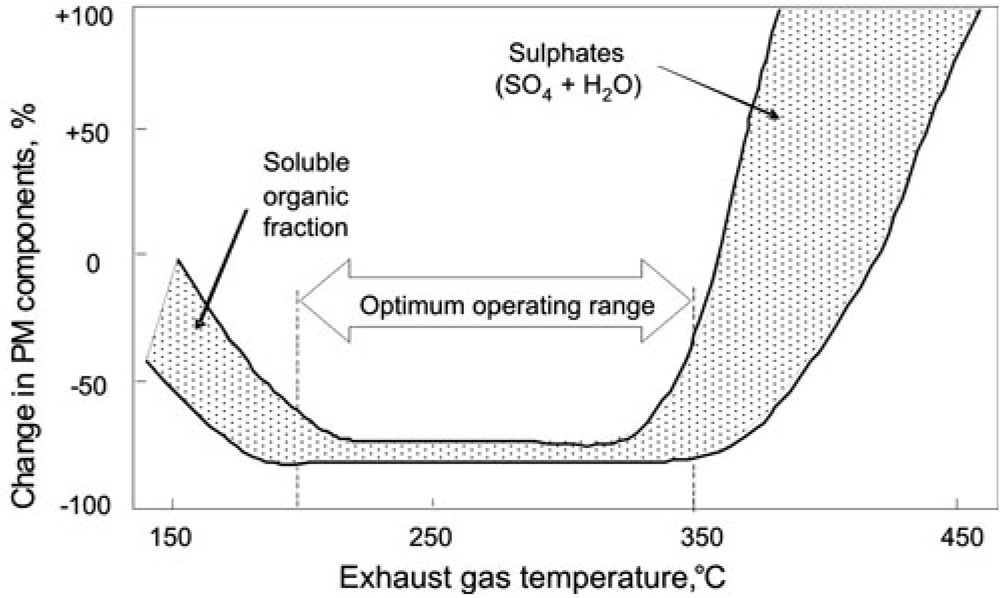

Figure 6.11	Effect of exhaust gas temperature on conversion of particulate mass by DOC.

The diesel fuels during early 1990s contained 0.2 to 0.3 % sulphur by mass Due to high fuel sulphur content the DOC design has to address to the following requirements;

- Minimize conversion of SO_2 to SO_3 at high exhaust gas temperatures
- Minimize formation and storage of the sulphate on the catalyst.
- Good conversion of SOF so that DOC reduces the mass of PM emissions in addition to conversion of HC and CO.

As sulphur in the diesel fuels has been reduced to around 0.03% the sulphate formation on DOC is not of serious concern. .

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Design Features of DOC

The catalyst volume is typically equal to the engine swept volume. A DOC although, may appear similar to the oxidation catalysts used for gasoline vehicles but the following differences in the design features are incorporated;

- Ceramic monoliths of a lower cell density having 200 to 400 cpsi are normally used to keep it free of clogging by soot.
- As alumina is more readily gets converted to $Al_2 (SO_4)_3$, different washcoat materials like titanium oxide, silicon dioxide, or mixtures of 50 % CeO_2 and 50% γ-Al_2O_3 are used.
- Mainly platinum is used in DOCs with metal loading varying from 0.5 to 2.0 g/l.
- The diesel oxidation catalyst is placed downstream of the turbocharger and experiences much lower temperatures (100-550º C) compared to the gasoline engine catalyst (300-1100º C). The thermal deactivation of DOC is not a major problem.
- Diesel engines burn more lubricating oil in the cylinder and the engine oils have a higher metal additive content than the gasoline engines. The pore structure of washcoat must be formed to tolerate larger amounts of these inorganic oxides

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DIESEL DE-NOX CATALYSTS

The diesel engine exhaust always has high amount of excess oxygen. Conversion of NO_x to N_2 requires a reducing atmosphere. In the diesel engines due to oxidizing atmosphere in the exhaust, a NO_xreduction catalyst different than the conventional 3-Way catalyst is required. For reducing NO_x in the oxygen rich atmosphere, the reducing agents also termed as 'reductants' are necessary. The reductants can be supplied either from the engine itself or added by external sources in the exhaust. Hydrocarbons or ammonia are the two most frequently used reductants. As discussed earlier, the main strategies employed for NO_x reduction in oxygen rich atmosphere are:

- NO_x Storage – Reduction (NSR) Catalysts
- Selective Catalytic Reduction (SCR)

Low temperature plasma/catalyst systems are also being developed for application to diesel engines.

NO_x Storage-Reduction (NSR) Catalysts

The NO_x storage-reduction catalyst system or 'NO_x Trap' was first developed for application to gasoline direct injection, lean-burn DISC spark ignited engines. It has been discussed in Module 5. In the diesel engines, diesel derived hydrocarbons are used as reductants. The principle of operation and basic features of Diesel NSR catalysts are the same as for the lean burn SI engines. The first step is to absorb NO_x (NO converted to NO_2 on the catalyst itself) on rare earth metal oxides and the second step is release of NO_x in presence of hydrocarbons for reduction to N_2.

For significant reduction in NO_x, typically 2 to 5:1 HC/NO_x molar ratios are required. Normally, engine out hydrocarbon emissions are quite low in the diesel engines. In the diesel NSR system, hydrocarbons are added to the exhaust gas by;

- post injection of fuel in the cylinder after the main fuel injection event
- adding secondary fuel into the exhaust system.

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About 2% of the main injection quantity is injected 90 to 200º CA after the main injection in the cylinder. The common rail injection system is well suited for providing post injection.

The best NO_x storage and conversion efficiency of NSR catalysts are obtained in a narrow temperature range of 200-350º C. Peak conversion efficiency may reach around 55 to 60% but overall conversion efficiency under driving cycle conditions is only around 35%. A number of catalyst modules to reduce space velocity and improve over all conversion have been employed in prototypes.

Sulphur Poisoning of NSR Catalysts

Sulphur on combustion forms sulphur dioxide, which gets oxidized to SO_3 over the catalyst and reacts with the rare earth oxides to form their sulphates such as barium oxide present in washcoat gets converted to barium sulphate. The mechanism of sulphur poisoning is similar to the mechanism of NO_x trapping by the catalyst. Hence, presence of sulphur in fuel reduces NO_x trapping efficiency. Even with 5 ppm sulphur in fuel the conversion efficiency has been seen to drop by half after about 25000 kms of operation.

To improve the catalyst resistance to sulphur poisoning new formulation of the adsorber material are being developed. The NSR catalysts so far are not being applied in diesel engines.

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Selective Catalytic Reduction (SCR)

The selective catalytic reduction of NO_x by ammonia has been applied now for several decades in the stationary systems like gas turbines, utility boilers, diesel engine power plants, and incinerators. Now, SCR is being used in heavy duty diesel vehicles quite widely in Europe to meet Euro 4 and later emission standards. On the road vehicles, urea is used as the carrier of ammonia. Hydrolysis of urea is carried out at first on a catalyst on board of the vehicle to produce ammonia and carbon dioxide. Ammonia then, reacts on the SCR catalyst with the NO_x and converts it to nitrogen. Vanadium and titanium oxide mixture (V_2O_5 + TiO_2 + WO_3) coated on a ceramic honeycomb substrate of 200- 400 cpsi is used as SCR catalyst. The basic chemical reactions in the urea-SCR process are as follows:

Hydrolysis of Urea:

$$(NH_2)_2\,CO + H_2O \rightarrow CO_2 + 2\,NH_3 \qquad (6.5)$$

NOx Reduction:

$$4NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (6.6)$$

$$6NO_2 + 8\,NH_3 \rightarrow 7N_2 + 12\,H_2O \qquad (6.7)$$

Urea concentrations of 30 to 40 % in water solution are stored on board as the temperature of crystallization is the lowest (-11º C) for 33% solution.

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NH_3/NO_x Ratio and Ammonia Slip

Based on the stoichiometric considerations, 90% conversion of NO_x requires the NH_3/NO_x molar ratio of about 0.9, assuming NO_2 constitutes 10% of NO_x. Concentration of NO_x in the exhaust gases varies depending upon engine operating conditions. Hence, for a vehicle continuously variable injection rate of urea is required. If more urea than stoichiometric requirements is injected, unreacted ammonia is emitted in the exhaust which is called 'ammonia slip'. To minimize ammonia slip, a dynamic urea dosage system governed by engine operating conditions is to be employed. Even with the dynamic dosage system, ammonia slip occurs during transient operation.

Typical conversion efficiency at different NH_3/NO molar ratio and ammonia slip are shown on Fig 6.12. With increase in NH_3/NO molar ratio NO_x conversion efficiency increases and but the ammonia slip also increases. An oxidation catalyst is therefore, added to SCR system to prevent emissions of ammonia.

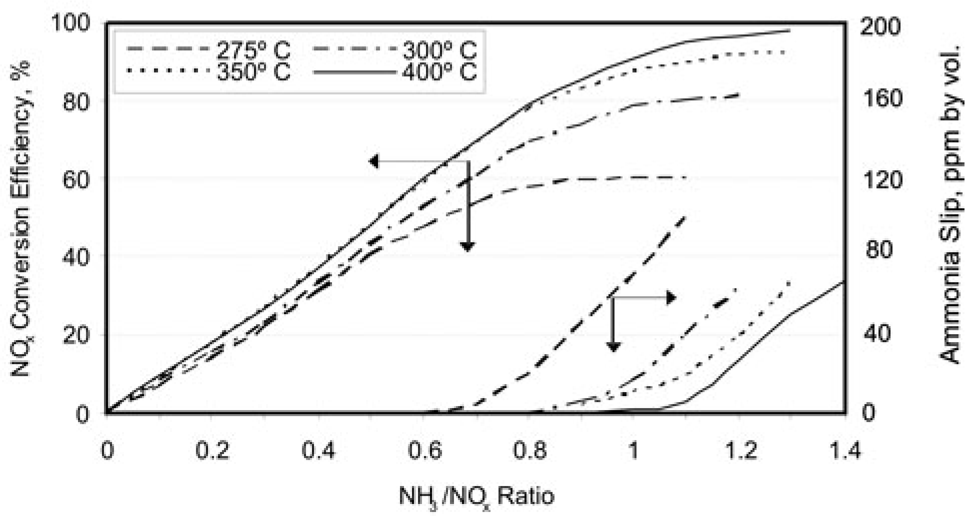

Figure 6.12	NO_x conversion and ammonia slip for a SCR catalyst as a function of NH_3/NO_x ratio.

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SCR Catalyst System

The basic SCR system using urea consists of three catalysts viz.,

- Hydrolysis catalyst
- SCR catalyst, and
- An oxidation catalyst to oxidize ammonia slip

NO_x conversion efficiency can however, be improved at low catalyst temperatures (< 300º C) when all the NO_x is converted to NO_2 before entering the SCR catalyst. An additional oxidation catalyst therefore, ahead of SCR catalyst is used in the modern SCR systems. A typical SCR system for heavy-duty vehicles is shown schematically in Fig. 6.13. NO_x conversions of more than 70 % have been obtained with SCR over the HD driving cycle. On road, over all reductions of close to 68 % have been obtained for heavy duty trucks. Urea consumption is about 5.5% of the fuel consumption. Urea requirements for several thousand kms of operation can be stored on board.

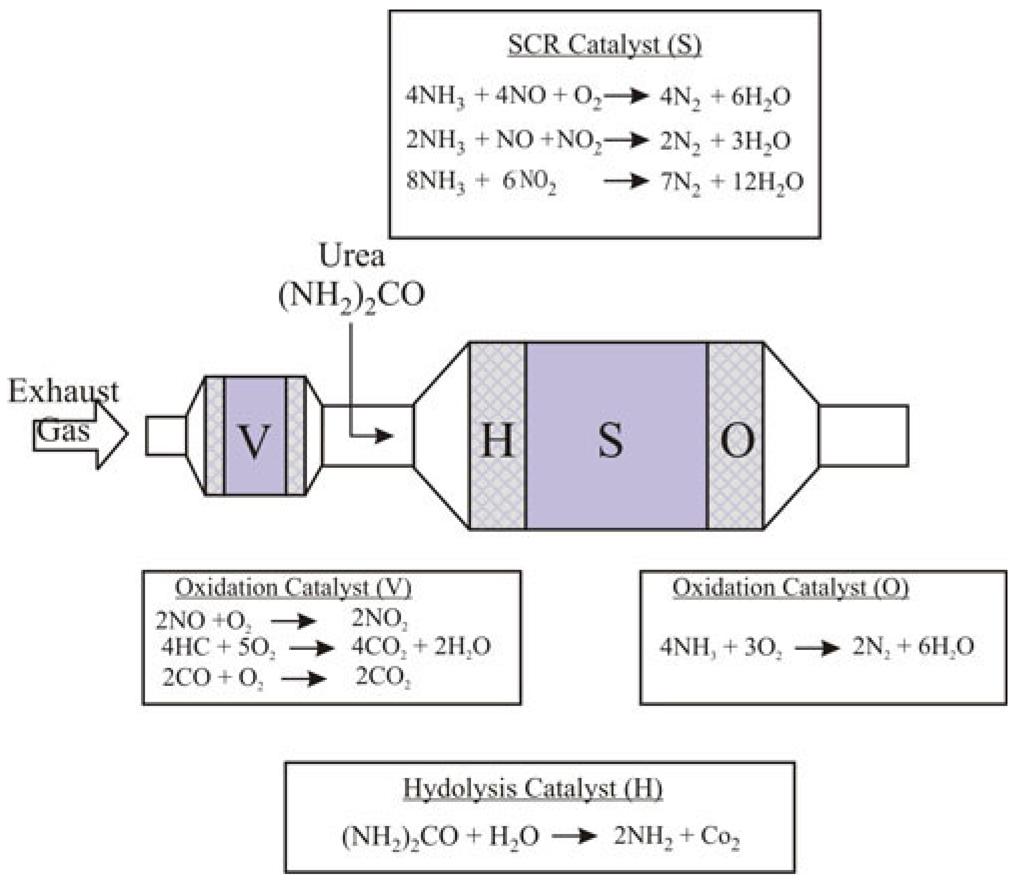

Figure 6.13	Schematic layout of SCR catalyst system using pre-oxidation catalyst.

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Comparison of NSR and SCR Catalyst Systems

Table 6.3
Comparison of SCR and NSR de-NO_x Technologies

Selective Catalytic Reduction (SCR)	NO_x Storage Reduction (NSR) Catalyst
Advantages: • High conversion rate up to 90% • Technology already developed and used in stationary applications	Advantages: • Using HC and CO exhaust emissions as reducing agents • Oxidation of SOF, HC, CO emissions possible due to the use of specially coated zeolite catalysts
Disadvantages: • Costly and large space requirements • Injections of another substance i.e., urea/ammonia as reductant • Dynamic dosage control of reducing agent needed • Extra oxidation catalyst for excess ammonia and SOF necessary • Additional urea distribution network required	Disadvantages: • Lower conversion rates (up to about 35% only) • Engine/Fuel system development for providing higher HC emissions needed in order to avoid additional HC injection before catalyst

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