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NOx Reduction Systems: A Review

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ABSTRACT: With every new revision of government emission regulations, the limit on the tailpipe NOx is getting lower, forcing engine manufacturers to innovate in order to meet new targets. NOx emission reduction can be achieved through engine management strategies, however, there is a limit to the level of NOx reduction and, often, a penalty is associated with completely relying on engine strategies. Urea-SCR system, a type of diesel aftertreatment, provides a means of reduction of NOx downstream of the engine so as to provide the engine more flexibility to operate at higher efficiencies, which can be associated with high engine-out NOx emissions. In this review paper various NOx emission technologies are critically reviewed.

KEYWORDS: NOx, Diesel aftertreatment, Urea-SCR system, NOx emission technologies

I. INTRODUCTION

Diesel as a fuel is a power source to numerous industrial applications as it has higher energy density and is safer to handle because of its less volatile nature compared to gasoline. Diesel powered engines have attracted the automotive industry due to their better fuel economy and lower greenhouse gas (GHG) emissions compared to gasoline engines.

Complete combustion of diesel should produce only carbon dioxide (CO_2) and water (H_2O). However, several non-ideal processes occur along with the combustion, which are: incomplete combustion of fuel, undesirable reactions at high temperatures and pressures, combustion of engine lubricating oil, and combustion of non-hydrocarbon components of diesel fuel such as sulfur compounds and fuel additives. These processes lead to the formation of unburned hydrocarbons (UHC), carbon monoxides (CO), nitrogen oxides (NOx) and particulate matter (PM).

II. MECHANISM OF NO_X FORMATION

Nitrogen Oxides (NOx): NOx primarily consists of Nitric Oxide (NO) and Nitrogen Dioxide (NO2). These oxides of nitrogen are a result of the high temperatures and pressures in the diesel cylinder. The formation of NOx takes place in the close-to-stoichiometric regions of the flame front during combustion of the diesel spray. Peak cylinder temperatures are key factors in determining the content of NOx formation during the combustion cycle. High NOx concentrations are usually found in the tailpipe at high engine loads and, under some circumstances, are undesired by-products of operating at high thermal efficiency points (high Brake Mean Effective Pressure points) .

Nitrogen oxides are generally a combination of nitric oxide (NO) and nitrogen dioxide (NO2), with the former being the most abundant and constituting more than 70 – 90 % of the total NOx. High temperatures and pressures occurring in the cylinder during the combustion process as well as flame conditions, residence time and concentrations of key reacting species, all contribute to the formation of NOx in diesel engines. Obviously, the principal source for the formation of NOx is the oxidation of atmospheric nitrogen (N2). Additional sources of N2 can be due to inherent amounts in the fuel or additives to the fuel. The mechanism of formation of the main product in NOx i.e. NO, from molecular N2 is governed by the extended Zeldovich mechanism, which is illustrated below:

$$O + N_2 \leftrightarrow NO + N \quad (1.4)$$

$$N + O_2 \leftrightarrow NO + O \quad (1.5)$$

$$N + OH \leftrightarrow NO + H \quad (1.6)$$

Chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO2/NO ratios should be negligibly

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Small However in diesel engines, ratios as high as 30 % of the total oxides can be attributed to NO2 emissions. Due to this, a mechanism has been proposed which explains the NO2 formation process through reactions such as those shown below:

$NO + HO_2 \leftrightarrow NO_2 + OH$ (1.7)

Decay can also occur through the following reaction:
$NO_2 + O \leftrightarrow NO + O_2$ (1.8)

Reaction (1.8) shows the conversion of NO2 to NO occurring when the NO2 produced is not quenched by mixing with cooler fluid in the combustion chamber. It has been reported that this mechanism is accurate with the highest NO_2 formation;
occurring for engines operating at low engine load, hence lower peak combustion temperatures which allow for the quenching of the formed NO2, thus preventing its decomposition accordingly. Emissions of NOx contribute to the greenhouse effect and are ground-level ozone precursors; therefore their reduction from the exhaust of diesel vehicles is paramount from an environmental and physiological perspective. Adverse effects on health are dependent on the level of exposure. For example, NO itself is not an irritant but it reacts with haemoglobin (in blood) yielding meta-haemoglobin which at high levels can be lethal, while NO2 is an irritant gas and if breathed can cause severe damage to the lungs.

III. NOX EMISSION REDUCTION METHODOLOGIES ARE

3.1 EGR

EGR is a technique to reduce NOx at the source level in spark-ignition engines and compression-ignition engines. EGR can also be used to control autoignition in an HCCI engine. The trapped exhaust gas contains certain radicals that would be helpful to oxidize the intermediate products during combustion. Some quantity of exhaust gas that is trapped from the exhaust manifold is recycled to an engine cylinder through the engine's intake manifold, as shown in Figure 4.7. EGR can be classified into two categories: hot EGR and cold EGR. Hot EGR is directly recirculated to an engine. The trapped exhaust gas from the engine's exhaust manifold is cooled by an intercooler and then the gas is supplied to the engine, which is called cold EGR. Hot EGR contains primarily carbon dioxide, water vapor, and nitrogen with traces of oxygen (if a lean burn engine), carbon monoxide, hydrocarbon, and oxides of nitrogen. The composition of cold EGR is similar to hot EGR except for the presence of water vapor and other condensable matter. The trapped exhaust gas is mixed along with the inducted air during suction stroke and then enters into the engine's cylinder.

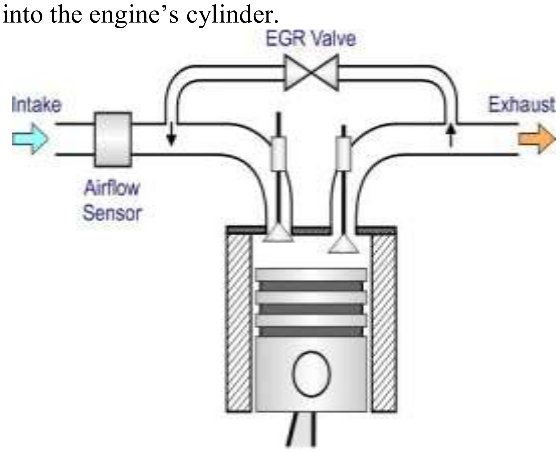

Fig 3.1 Exhaust Gas Recirculation

Source:**(https://www.openpr.com/news/1354663/global-exhaust-gas-recirculation-egr-valve-consumption-market-share-trends-business-strategy-and-forecast-to-2023.html)**

The EGR gas in an engine reduces oxides of nitrogen emission due to the following actions:
• Dilution of oxygen concentration due to recycled combustion products, which acts as a barrier between the nitrogen and oxygen
• Reduction of oxygen concentration as some of the oxygen/air is replaced by the circulated gas
• Decrease in in-cylinder temperature due to EGR acting as a heat sink mainly by CO2 and N2 (enriched), which increases specific heat of charge
• Less adiabatic flame temperature of the air-fuel mixture with EGR compared to the mixture without EGR

3.2SCR

SCR is an aftertreatment method used to control NOx emission in an engine exhaust system. A liquid reductant (e.g., ammonia, urea solution, cyanuric acid, ammonia-blended sodium carbonate, and xenon lamp based reduction) is injected into the catalyst coated exhaust system in which NO is converted to N2 and water. The SCR system consists of an SCR tank (for chemical solution), dosing injector, electronic control unit (ECU), and SCR catalyst. The reductant is injected into the hot exhaust gas trapped temporarily by the catalyst surface and the injector is controlled using the ECU. Equations 4.41 and 4.42 show the ammonia reaction with NO and NO2 and through these reactions, NO

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and NO2 are converted to nitrogen and water vapor. These reactions may proceed in temperatures from 800°C to 1200°C without a catalyst and 260°C to 500°C with a catalyst.

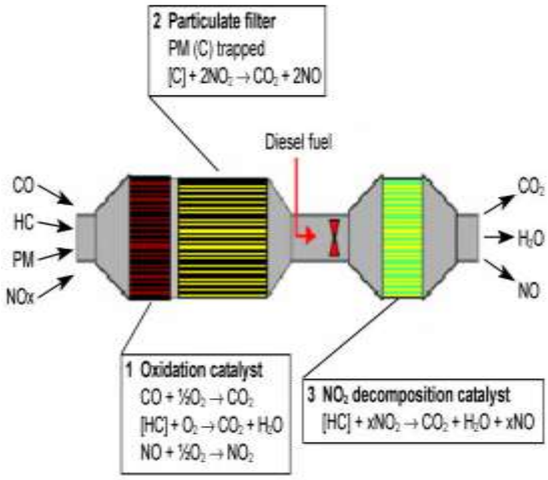

Fig3.2 Selective Catalytic Reduction
Source:(https://www.technology.matthey.com/wpcontent/uploads/articles/52/1/Johnson-52-1-jan08-f12.jpg)

NOx conversion efficiency depends on many parameters, including temperature of exhaust gas (Kuihua and Chunmei, 2007), residence time, degree of homogeneous mixing of reductant with exhaust gas (Røjel et al., 2000), NO and NO2 levels, and CO and O2 concentration.

Ammonia breaks down to NH2 by O and OH radicals and then NH2 is converted to nitrogen and water vapor.

3.3 Lean NOx Trap

A lean NOx trap (LNT) is an aftertreatment device used to reduce NOx emissions in a lean burn engine. NOx is stored in the LNT during the lean operation of an engine. When the air-fuel ratio becomes rich, the stored NOx is catalytically reduced by the reductants (CO, H2, and HC).

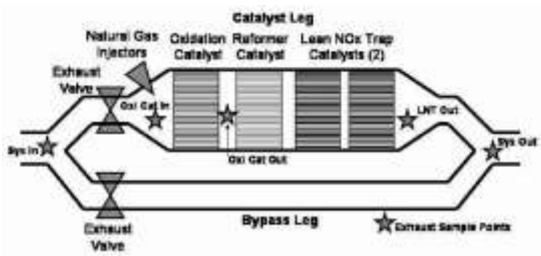

Fig: Lean NOx traps
Source:(https://www.researchgate.net/figure/Lean-NOx-trap-catalyst-system_fig1_238603924)

3.4Water Injection

The addition of water to the engine could decrease NOx emission significantly. Water is either injected into the intake manifold during a suction stroke or directly into the cylinder during combustion. NOx emission deceases with water mainly due to a reduction in combustion temperature as heat sink (due to high specific heat) and an increasing dilution effect. Besides NOx reduction, a water injection strategy provides increasing volumetric efficiency by creating a cooling effect and acting as a working fluid (mostly supercritical stage). Demineralized water is used for this purpose to avoid a corrosion problem in the engine components. Water can be emulsified with diesel, which is called a water-diesel emulsion or water-fuel emulsion. As water can't mix with diesel, it needs surfactant to make the emulsion. NO emission in a diesel engine with the emulsified fuel (diesel + water) at the rated load decreased from 752 to 463 ppm with a water-to-diesel ratio of 0.5:1 and it is reported that the optimum water-to-diesel ratio is from 0.4 to 0.5:1 (by mass) (Subramanian and Ramesh, 2001). Both methods (water injection and water emulsion) can reduce NOx emission at the source level, but the water emulsion method is more effective in terms of the quantum of NOx emission reduction because NO emission in a diesel engine is 398 and 477 ppm at 60% load with emulsion and injection, respectively.

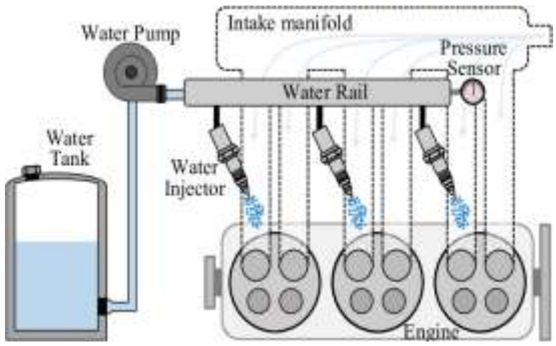

Fig: Water Injection [18]

3.5 Optimization of Injection Timing

NOx decreases with retarding injection timing as peak pressure and temperature are lower as they are shifted after TDC, which results in lower NOx formation. However, the opposite occurs as it increases with advanced injection timing. Similarly, spark timing retarding from maximum brake torque (MBT) timing, NOx emission is generally lower but is higher with advanced spark timing.

3.6 Fuel Options

More fuel based technological advances are occurring with the main purpose of compliance with newer more efficient exhaust treating devices which lead to lower engine out emissions. Varying different parameters such as the cetane number, fuel density, viscosity, lubricity and aromatics content can influence qualities like the ignitability of the fuel through to the combustion product emissions, e.g. NOx and PM

3.6.1ULSD Fuels

Ultra-low sulphur diesel (ULSD) fuel was introduced as a replacement for low sulphur diesel (LSD) and it has been in use for light duty vehicles from 2005 and 2007 in European and US models respectively (Fanick, 2008). It contains very low levels of sulphur (< 15 ppm) compared to LSD which has a higher content (< 500 ppm). The introduction of this fuel was in conjunction with emissions regulations being stipulated for diesel engines, making advanced after-treatment systems a necessary component in the emissions reduction strategy. Sulphur in the combustion fuel contributes to its natural lubricity, thus the lowering of fuel sulphur content yields a fuel with poor lubricity . However, additives are available that can improve the lubricity to commercially acceptable levels. Most after-treatment devices, such as diesel particulate filters (DPF), NOxadsorber catalysts (NAC) and SCR technologies are very sensitive to the amount of sulphur content in the diesel fuel, with greater emissions reduction efficiencies being observed for fuels with virtually no sulphur.

3.6.2 Bio-Diesel Fuels

Biodiesel is an alternative fuel consisting of alkyl monoesters of fatty acids from vegetable oils or animal fats (Monyem and Gerpen, 2001). These fuels are characterized by higher molecular weight and higher distillation temperatures compared to conventional diesel fuels e.g. ULSD. However, interest in biodiesel has increased over the years owing to pressures from governmental and environmental legislative bodies regarding the use of more sustainable and renewable fuel sources, which aid emissions reduction.

3.6.2 Fischer-Tropsch Fuels

The Fischer-Tropsch (FT) process converts a mixture of hydrogen and carbon monoxide derived from coal, methane or biomass to liquid fuels. The technologies are aptly named coal to liquids (CTL), gas to liquids (GTL) and biomass to liquids (BTL), respectively.

As with all FT process fuels, GTL is a virtually pure paraffinic hydrocarbon fuel with excellent combustion properties and burns with a smooth controlled flame (Shell Gas and Power, 2009). Furthermore, it is practically free of sulphur and aromatics, with a high cetane number (i.e. it has a short ignition delay) and as a result has emissions reductions associated with its use as a combustion fuel, which include; lower PM, NOx, un-burnt HC and CO (Dry, 1999; Larsen et al., 2007). These characteristics are favourable in lean after-treatment devices, as lower impurities in the engine exhaust gas generally lead to better NOx reduction efficiency over specific catalysts e.g. in HC-SCR and NOxadsorbers (Houel et al.,2007b; Theinnoi et al., 2008b; Johnson et al., 2001; Takeuchi and Matsumoto, 2004).

IV. CONCLUSION

Diesels engines produces, higher emissions of nitrogen oxides (NOx) and particulate matter (PM). The emissions levels which can be achieved depend on both the engine-out emissions and the performance of the emissions control system

Fuel quality,engine technology as well as advance emission control technologies are the main elements for achieving better performance and emission reduction in internal combustion engines to achieve exhaust emission levels by upcoming emission norms.

There are various technologies available to reduce the engine exhaust emissions especially NOx like EGR, SCR, Water injections, lean NOx traps advanced fuel options etc.

There are several additional complications in using urea-SCR like need for efficient ammonia release from the urea solution, and the related risks of deposits in the exhaust system due to by-products formation and accurate ammonia dosage.

There are certain limitations of EGR like Drop in volumetric efficiency and power with a higher percentage of EGR and volumetric efficiency of cooled EGR is better than hot EGR.

NOx conversion efficiency depends on many parameters, including temperature of exhaust gas, residence time, degree of homogeneous mixing of reductant with exhaust gas (Røjel et al., 2000), NO and NO2 levels, and CO and O2 concentration

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