A Comprehensive Review on NOx & DPM Diesel Engine missions and Its Control Techniques

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Abstract

Diesel engine as a power source is widely used in automobile and industrial applications. Although this enormous use boomed the economic development, but it also caused serious environmental hazards. Diesel engine uses combustion phenomenon that gives birth to SO_X, NO_X, soot particles and other dangerous compounds. Diesel engine emissions highly contribute to the atmospheric pollution and other environmental effects. So, their treatment is considered as serious concern and has great significance in evaluation of feasible control techniques. Diesel engine emission encompasses many compounds but NO_x and Diesel particulate matters (DPM) are major emission due to human health and other environmental issues. NOx and DPM can cause serious health concerns especially for respiratory tract of living being. Therefore, efforts are made to summarize NOx and DPM formation process and its control techniques in diesel engine. Both Pre-combustion and Post-combustion techniques till to date are discussed and are compared. Various types of fuel additives are also discussed as a control technique for DPM emissions. This comprehensive study has created a junction to list out the numerous techniques evaluated by the various researchers.

Keywords

Exhaust Emission, Particulate matter, NOx Emission, Emission control techniques, Air pollution.

مراجعة شاملة لانبعاثات محركات الديزل NOx و DPM وتقنيات التحكم فيها

يستخدم محرك الديزل كمصدر للطاقة على نطاق واسع في السيارات والتطبيقات الصناعية. على الرغم من أنّ هذا الاستخدام الهائل ازدهرت به التنمية الاقتصادية، لكنه تسبب أيضا في مخاطر بيئية خطيرة. يستخدم محرك الديزل ظاهرة الاحتراق التي تولد SOX ، NOX وجزيئات أكاسيد النيتروجين، وغيرها من المركبات الخطيرة. تتسبّب انبعاثات محركات الديزل بدرجة كبيرة في تلوث الغلاف الجوي والتأثيرات البيئية الأخرى. كذلك، تعتبر معالجتها مصدر قلق بالغ ولها أهمية كبيرة في تقييم تقنيات التحكم الممكنة.

على الرغم من أن انبعاثات محركات الديزل تضم العديد من المركبات، إلا أن انبعاث أكاسيد النيتروجين NOX وجزيئات الديزل (DPM) تعد من الانبعاثات الرئيسية التي تشكل خطرا على صحة الإنسان والمشكلات البيئية الأخرى. أكاسيد النيتروجين NOX و DPM يمكن أن تسبب مشكلات صحية خطيرة وخاصة بالنسبة للجهاز التنفسي للكائنات الحية. نتيجة لذلك، تبذل الجهود لتلخيص عملية تشكيل أكاسيد النيتروجين NOX و *DPM* وتقنيات التحكم في محرك الديزل. تناقش لحدّ الآن كل من تقنيات ما قبل الاحتراق وما بعد الاحتراق وتتمّ مقارنتها. وتناقش أيضا أنواع مختلفة من إضافات الوقود كطريقة للتحكم في انبعاثات DPM . هذه الدراسة المعمّقة ولّدت تقاطعًا لسرد التقنيات العديدة التي قام بتقييمها مختلف الباحثين.

1. Introduction

Ever increasing energy demand and stringent regulation to control environmental pollutants like the emission of particulates, SO_X and NO_X are pressurizing the researchers to find energy viable and environmental friendly engine emission control technologies [1]. Various techniques were applied to make IC engines such as Diesel engines energy efficient.

In olden times smoke out of the chimney was considered the sign of prosperity of nation and then time changed and stringent laws was imposed to bring pollutants especially SO_X, NO_X, Lead (Pb) emission and particulate emissions from engines to acceptable concentration in order to avoid their effects on human health, property, and aesthetics of the environment [2].

In perfect combustion with clean diesel, combustion exhaust stream should have only CO_2 and H_2O. All carbon in the fuel is oxidized to CO_2 and hydrogen to H_2O. However, in actual conditions, fuel is not pure hydrocarbon and contains some amount of traces of nitrogen, sulfur and other chemicals constituent as impurities. Therefore, in real combustion process different compounds are there in the engine's exhaust in form of solid particles as well some gases. If the air fuel ratio is rich in nature the combustion stream would have CO, soot, black carbon smoke and unburned HC, and the other case when the mixture is lean then combustion process generates NOx at high temperature conditions as shown by figure 1. Among all exhaust emissions from diesel engine at different range of air fuel ratios, major concerns is associated with NOx, CO, HC, Smoke (Particles and soot)[3][4].

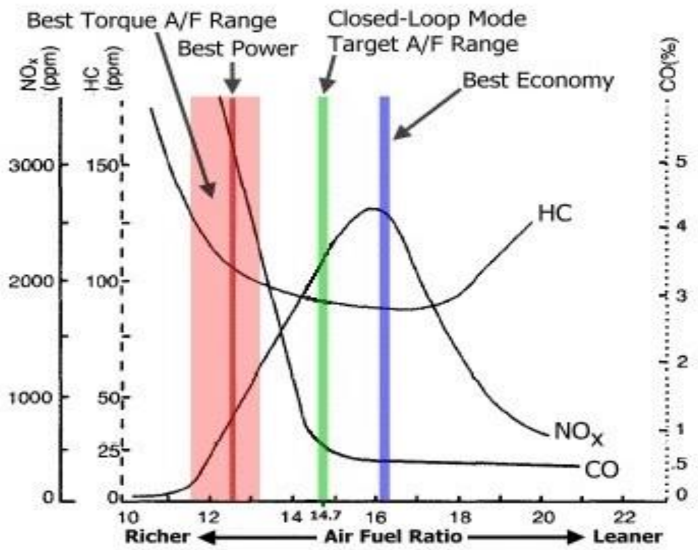

Figure 1. Diesel engine Emission against wide range of operating Air fuel ratios[5]

From Figure 1 it seems that however at all operating fuel mixture range diesel engine exhaust gas is composed of several dissimilar gases like NO, N2, CO2, H2O and O2. But among them, some are proved to be harmless, but some are considered as harmful and treated as major pollutants. The most dangerous among these, are NOx and particulate emissions and have different acute health problems[6], [7]. Therefore, it is obligatory to lessen these emissions [8].

In general all control techniques can be classified under the umbrella of two main categories for Diesel engine combustion engines[9] and its schematic is represented in Figure 2.

1. Pre-combustion control techniques 2. Post-combustion control techniques

Pre-combustion control techniques are also known as prevention techniques. These are methods which prevent creation of harmful pollutants inside combustion chamber during the combustion process before they started to generate. While post-combustion control techniques are those method which control the harmful pollutants before there emission or discharge into the ambient air or atmosphere. This kind of techniques deals with the after treatment of emissions once they have been formed [9].

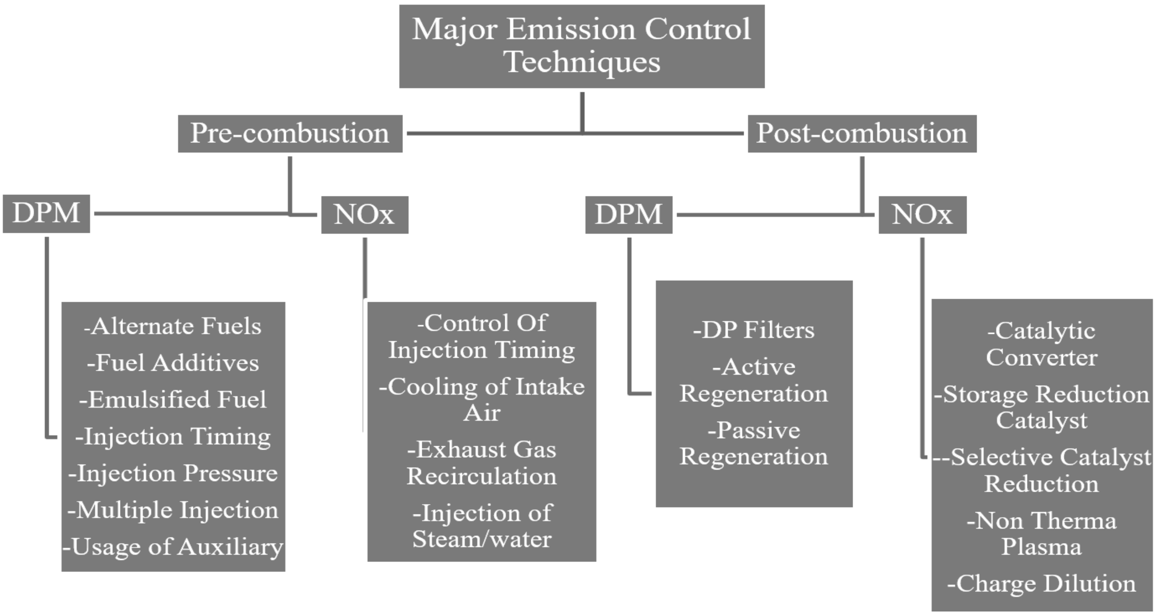

Figure 2. Detailed control emission techniques of NOx & DPM [10].

In this comprehensive review efforts are made to summarize all possible techniques reported to date to control the mentioned major emission. Pre-combustion and post-combustion techniques are separately discussed, and a comparison is made on the work of different researchers. CO_2 emission is not regulated, and study has been made to specifically discuss carbon dioxide emission in relation with NOx and DPM [11].

2. Diesel Particulate Emission and its control techniques

2.1 Particulate Matters and Human Health Concerns

Various studies have been made to explore the effects of DPM on human health. Even models are developed in laboratory experiments by using animal mouse. It has found that DPM especially short size (below 20 nm) is very dangerous for human respiratory system. They have ability to penetrate not only in lungs but also in alveoli of respiratory system. Some finer particles can even penetrate in human blood stream [10], [12]. Studies [11], [12]have shown the effect of fine particulates on lungs and human respiratory system and concluded that they may cause severe lungs injures and other severe diseases. Long exposure to DPM may leads to lungs cancer. These situation may be alarming for industrial labor working in the environment where they are more likely to be exposed to high concentration of particulates [10], [15], [16]. P. S Glimour et al. stipulated that DPM might lead in the production of free radicals. These radicals may lead to ill function of lungs [18]. Many researchers also reported that exposure to DPM may leads to cough, nausea, guinea pig, bladder cancer and bronchus problems [13], [19].

Moreover, DPM may cause lungs tumor, asthma, skin allergy and allergy. Some finer particles may even have a tendency to penetrate deep into brain and neuron cells. In this way they may cause malfunction of central nervous system. Health hazardous which are briefly summarized in this section forced the researchers to study the composition of DPM, its formation processes and techniques to control these fine particles.

2.2 Composition of DPM

There are various ways to define DPM composition and it be simplify with two major components of DPM namely:

1). Organic Portion 2) Inorganic Portion.

Organic portion may further be classified as soluble portion and insoluble portion (Fig. 3). Soluble DPM may be extracted from the mixture of burned gases by using different organic solvents. In general DPM are sum of unburned hydrocarbons, with liquid and other solid constituents. [20], [21].

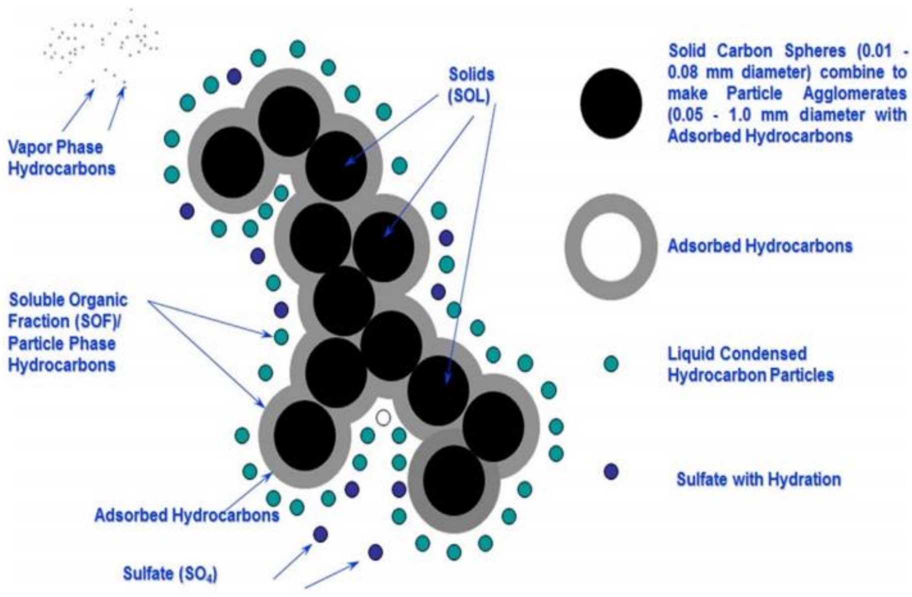

Figure 3. Composition of DPM [10]

2.3 Soot Formation

Soot formation from liquid organic fuel is detailed described by many researchers as Mohankumar et al. [10] [22]. In a condensed form it can summarize in following six steps in Figure 4 [22].

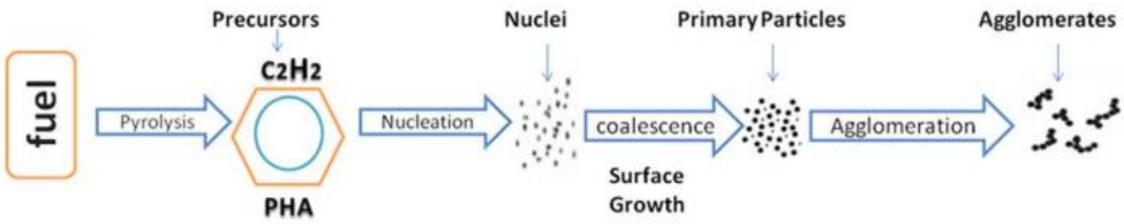

Figure 4. Mechanism Steps of Soot Formation [10].

Table 1. Summary of process forming particulates.

i) Pyrolysis	**ii) Nucleation**	**iii) Growth**	**iv) Conglomer -ation**	**v) Oxidizing environment**
-An endothermic process that leads to a change in molecular structure of the compounds at high temperature & in the absence of oxygen contents. -Soot composition & quantity depends on following two factors 1) Temperature 2) Oxygen concentration	-It is Formation of nuclei from gaseous phase in combustion chamber (Fig.3) [10]. -Process takes place at higher temperature (around 1300K). -Initially nuclei are small but later they may combine to form bigger ones.	-Growth occurs when hydrocarbon & other matters stick to the surface of nuclei generated earlier by nucleation. -Growth occurs more for small size particle This is due to reason that small particles have reactive radical concentration.	- Small particles combine to form large particles as result of coalesce. -Particle size increases & their quantity decreases. Sometime these particles may combine in fashion resulting in the formation of chain [22]	Oxygen rich environment suppresses the formation of soot to a much larger extent. This is the reason why premixed type of flame has relatively much less quantity of soot produced during combustion. The formation with flame is given in Figure 5

Premixed flames have higher concentration of oxygen in the mixture as compare diffusion flame. This process is responsible for the production of building blocks of suit [23].

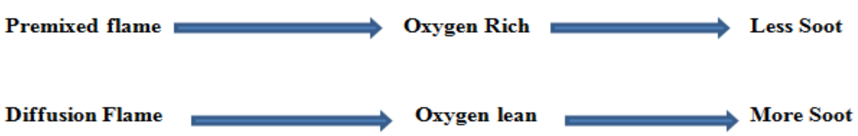

Figure 5. Soot Formation with respect to flame nature

2.4 Fuel Chemistry and Soot Formation

Fuel chemistry plays a major role in determining the quantity and composition of soot. If supplies excess amount of soluble fraction than soot mass may increase. Fuel structure i.e. bonds type and their strength is also major factors. Chemistry of fuel and its effect on soot was studied by many researchers [24], [25]. Table 1 below summarizes relation of soot formation with composition of fuel.

Table 2. Effects of Soot formation of fuel chemistry

Element in the fuel	Effects on the soot formation
Carbon	carbon has direct relation with soot formation. More carbon in the fuel means more soot production.
Oxygen	Oxygen in the fuel has inverse relation with the soot formation. This mean if there is less oxygen in the fuel than less soot will be formed. The best examples are premixed and diffusion flames.
Hydrogen	It also has inverse relation. Fuel with less hydrogen produces more soot.
Sulfur	It has no relation with soot formation but it may increase the mass of soot.

3. Diesel Particulate Matters Control Techniques

Complete Spectrum of DPM techniques is shown in Figure 6 as studied by researchers.

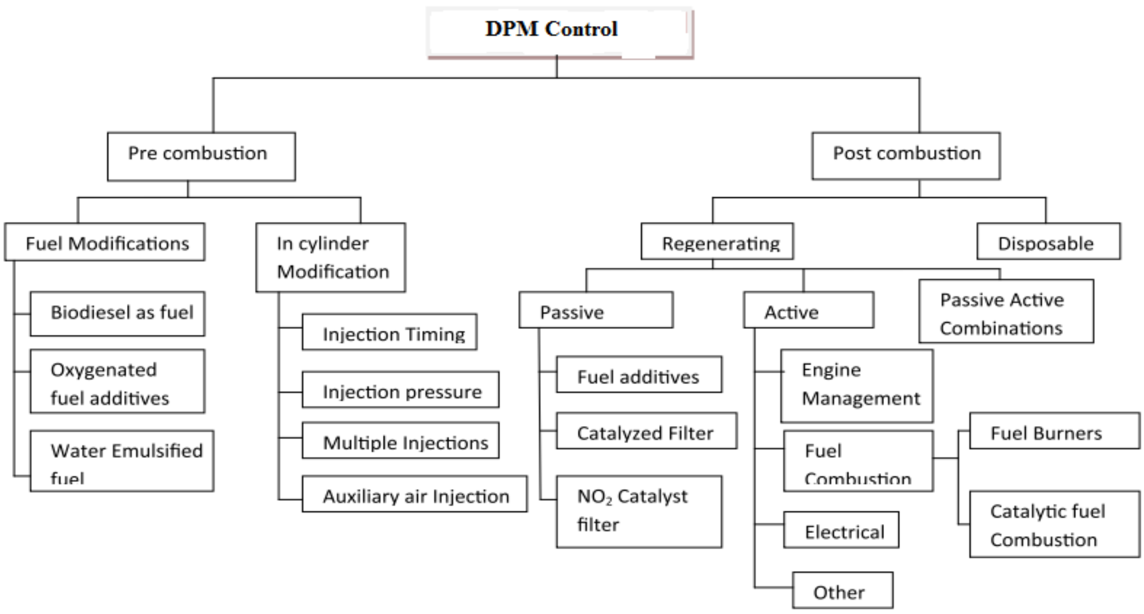

Figure 6. Complete spectrum of Techniques of DPM Emission [10].

3.1 Pre-Combustion Strategies

3.1.1 Alternate Fuels

Biodiesel fuels derived from animal fats and vegetable oils were found to be very effective for the reduction of DPM by many researchers. diesel engine operated with biodiesel instead of diesel reduces particulate emission to a considerable extent but unregulated emission may increase [28]. Same conclusion was also reported by many other researchers [29]–[31].

3.1.2 Fuel Additives

Various additives like methanol, ethanol, butanol, and ethyl ether are can be used as additives to the diesel engine fuel. These compounds can provide oxygen during chemical reaction. As discussed earlier oxygen rich combustion reduce soot formation by improving cetane number and overall quality of combustion [32]–[34].

3.1.3 Emulsified Fuels

Water emulsified fuels are made by dispersing primary fluid through immiscible secondary fluid. Water has relatively lower boiling point due to which it explodes earlier resulting in longer ignition delay and combustion duration. Process also provide more time for air fuel mixing. All these activities facilitate the reduction of particulate matters in the exhaust of diesel engine. M. Nadeem et al. & many researchers concluded that emulsified fuels reduces DPM and other diesel engine emission with a negligible compromise in the efficiency [35]–[37].

3.1.4 Effects of Injection Timing

Injection time can be used to somehow control DPM emission. Injection time has direct ignition delay. Ignition delay increases with increase in injection time. Increased ignition delay provides an opportunity to air and fuel to pre-mix thoroughly. This through mixing facilitates efficient combustion process resulting in reduction of DPM. Sayin and Canacki [38] investigated the effect of ignition time for different load condition on the emissions of hydrocarbons and came up with the same results.

3.1.5 Effects of Injection Pressure

Injection pressure is another parameter that can help to minimize DPM emissions. Subject was widely investigated by many researchers and same conclusion was drawn. DPM emission shows a rapid decrease with increase in injection pressure. Same conclusion was also reported by Peng Ye, and André L. Boehman [39].

There are three major reasons behind the reduction DPM with increasing injection pressure:

1. Enhancement in injection pressure forces fine atomization of fuel droplets.
2. Fuel droplet size gets reduced.
3. Enhanced pressure causes through mixing pre mixing of air and fuel.

Mohankumar et al. [10] also reported reduction in hole size of nozzle as parameter for reduction in DPM.

3.1.6 Auxiliary Injection Technique

DPM emission can be reduced by injecting air exactly after the end of injection. This can create turbulence and more refine mixing of air and fuel. Therefore, more through mixing results in proper combustion process that may lead to reduction in DPM.

But this technique has a few side effects. First, enhanced heat transfer reduces efficiency of engine. Therefore, it will cost a compromise on efficiency of engine. It may also lead to increase in manufacturing and designing cost as an auxiliary system is required to pump air in to the combustion chamber.

3.1.7 Multiple Injection Technique

Multiple-injection is a technique in which multiple injection strategy is used in a single cycle of combustion. It is effective for both NO_x and DPM control. Its effective was increased by using electronic gadgets to monitor time and injection pressure. Injection can be divided in three segments: Pilot injection, Post injection & Main injection [40][41].

4. Post Combustion Techniques

4.1 Diesel Particulate Filters (DPF)

A lot of work has been reported on this topic since 1980. DPF is widely used technology to control DPM from diesel engine. There are many types of DPF are under investigation depending upon porous media like ceramic fiber and ceramic monoliths, alumina coated mesh, and honey comb mesh are widely studied mediums. Geometry of mesh cells is another widely studied dimension in the public literature. It may be squared, honey comb shape, hexagonal, octagonal or any other shape. K. Tsuneyoshi and K. Yamamoto [42] for example studied hexagonal and square cell geometry and concluded that hexagonal geometry is far more efficient than conventional geometry. Studies have reported that they can be 99% efficient depending upon suitable selection of different parameters for the filter. [43]

On the other side, many factors have been found that badly affected the efficiency of DPF. For example, K. Yamamoto et al. studied the effect of soot deposition on the efficiency of DPF with different porosity and length. They reported increase in back pressure with increasing concentration of soot formation [44]. Ceramic wall-based filters are another type of filter widely investigated in the public literature. They use alternate cells that are plugged at one end and the other end is open. Exhaust flows downstream through one cell and enters the other cell that ultimately leads it out in the atmosphere as shown in Figure.7

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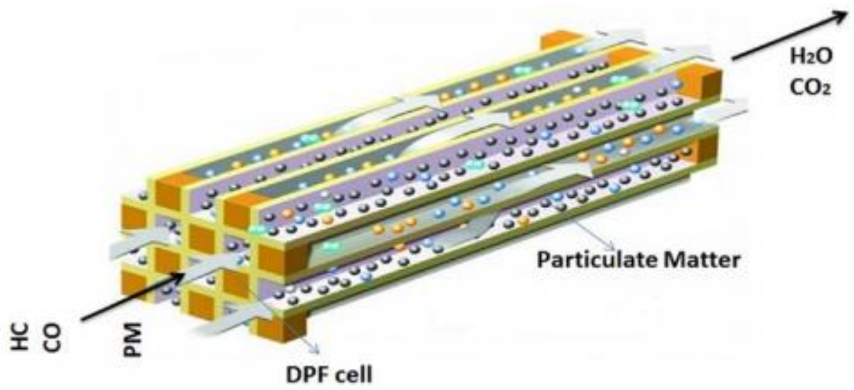

Figure7. Exhaust of diesel Engine flowing through Particulate Filter [10].

4.2 Regeneration

It is not tough to filter exhaust using a fine micro-structured mesh. Exhaust leaves soot particles when it is forced to pass through these micro paths. But these particles may lead to the blockage of these channels. Blockage of these channels reduces the filter efficiency of DPF. Most challenging job is to get these soot particles out of the refine mesh. Regeneration is a technique in which soot particles trapped in the mesh of DPF are oxidized to CO_2 at high temperature and pressure without melting and damaging the mesh itself. There are many categories of regeneration of briefly explained below Figure 8 and their detail is in Table 3.

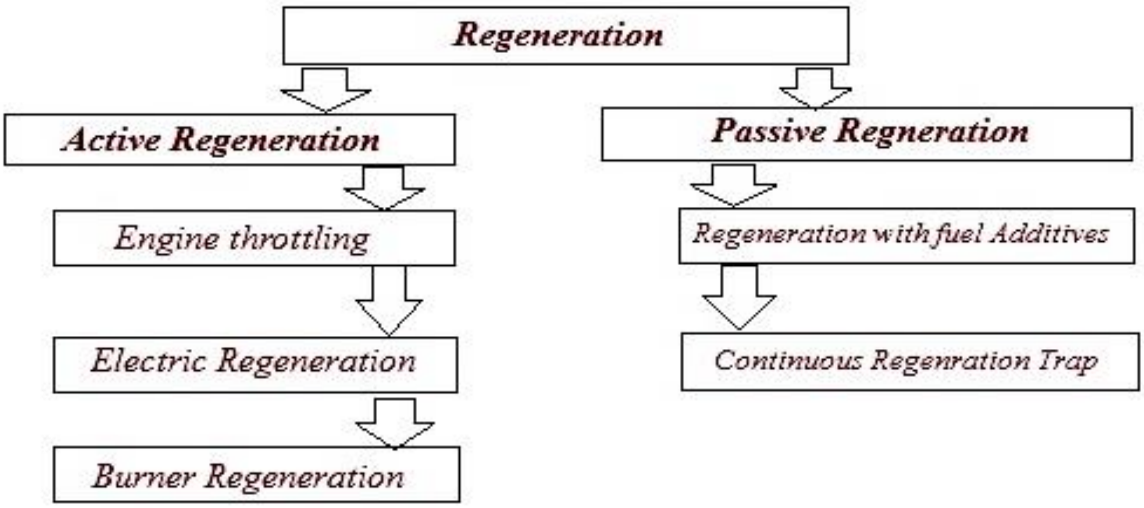

Figure 8. Sub classification of Regeneration [10].

Table 3. Sub Categories of Regeneration technique in Diesel Engine

<table>
<tr><th>Active Regeneration</th><th>Passive Regeneration</th></tr>
<tr>
<td>-Uses sensor technology to oxidize the soot particles
-Exhaust temperature is raised above 500K upon receiving the signal from sensor.
- Soot particles are ignited and oxidized at high temperature
03 means of temperature increment.
<table>
<tr><td>Engine Throttling
-Fuel air ratio is increased while throttling
Advantage
Exhaust temperature is enhanced
Drawback
-Fuel consumption is increased abruptly
-Reduction in air & more fuels lead to CO emissions</td>
<td>Burner Regeneration
uses a burner in front of the filter
Advantage
DP blocks the filter leads to increase backpressure sense by sensor
ECU on the burner at oxidation occurs at 6500 C and all soot removed
Drawback
Malfunctioning of sensor leads to damage of DPF</td>
<td>Electric Regeneration
Same as burner Reg. but uses electrical resistance to heat
Advantage
Less cleaning and easy to maintain the system</td></tr>
</table></td>
<td>-Catalyst to put on surface of filter
-specially designed catalytic oxidation device to enhance soot particle oxidation process
-Economic and easy maintenance
<table>
<tr><td>Regeneration by Fuel Additives
Fuel radicals as Fe, Zn, Cu, and Pb can be used as fuel additives to accelerate
Advantage
-Reduces the oxygen temperature of soot. Hence, oxidation occur now at lower temperature.
-This is very cheap method for regeneration</td>
<td>Continuous Regenerating Trap
Catalyst is employed on the surface of substrate
Advantage
Particulate matter removal due to oxidation at surface</td></tr>
</table></td>
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5. Emission of Nitrogen Oxides

Generally, NOx represents a family of seven compounds. Nitrogen (N_2) is a diatomic molecule & chemically inert gas. Our atmospheric air consists around 79% Nitrogen. At elevated temperatures (approx. around 1500°C and above this temperature) this Nitrogen (N_2) disassociate into its atomic state (N). This atomic Nitrogen (N) is highly reactive in nature and has ionization levels from +1 to +5 valence states. That's why nitrogen can exist in several different oxides like N_2O, NO, N_2O_2, N_2O_3, NO_2, N_2O_5 and N_2O_4 [45].

Environmental protection agency (EPA) regulates critically nitrogen dioxide (NO_2) among its family of compounds. The reason is that it is the most dominant form of NOx in the troposphere region that is resulted from stationary/automobile or by anthropogenic/human activities in urban areas of lower atmosphere [45]. Figure 9 shows the causes of NOx generated by activities. Most of NOx emitted from different sources is found as NO & this, later on, is oxidized in the atmosphere to NO_2 within very short interval of time. It is found that around 10 - 20% of total emission from diesel engines is emitted as NO_2, which is proved approx. five times more toxic and dangerous than NO regarding health. Both NO & NO_2 are collectively termed as NOx. The other oxides of nitrogen occur in minor quantities and rapidly react to NO and NO_2 in Diesel engine's combustion. EPA has recognized dedicated standards for human and welfare health called as "National Ambient Air Quality Standards (NAAQS)" for NO_2. These standards outline that level of air quality which is mandatory to maintain, with an adequate factor of safety, to care for public health (called as primary standard) and public welfare (termed as secondary standard). For restriction of NOx emission the primary and secondary standard both defined limit for NO_2 as 0.053 parts per million (ppm) (100 micrograms per cubic annual arithmetic mean concentration[46].

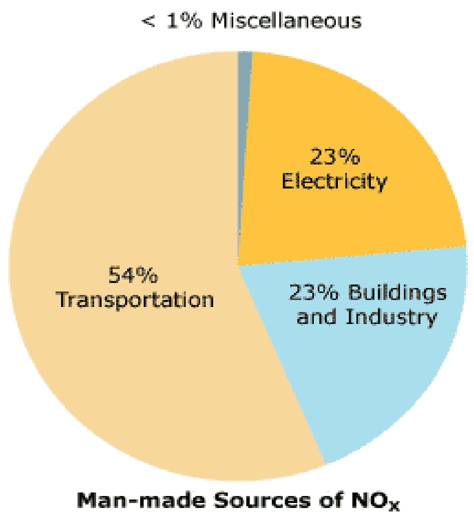

Figure 9. Typical Major sources of NOx Emission [47].

5.1. Sources of Nitrogen Oxides Formation

NOx can be formed inside the combustion chamber by three mechanisms.[48]

5.1.2 Thermal NOx

NOx emission from diesel engine exhaust is mainly considered by formation from Thermal effect. Thermal NOx is generated during combustion when nitrogen reacts with abundant oxygen at elevated temperature (usually at 1500°C or above). It is formed in exhaust gases behind the flame front. The chemical thermodynamics favor the formation of NOx generation at high temperature simply by the dissociation of molecular nitrogen and molecular oxygen. The strong covalent triple bond in N_2 molecule require high temperature to break into its atomic form or its radical N_2. NOx formation is highly depending upon the temperature so its trend formation against various temperature is shown in figure 10.

The chemical Equations can be understood by the Zeldovich mechanisms [49]

$$N_2 + O \leftrightarrow NO + N \quad (1)$$

$$N + O_2 \leftrightarrow NO + O \quad (2)$$

$$N + OH \leftrightarrow NO + OH \quad (3)$$

$$\text{Global reaction } N_2 + O_2 \longrightarrow NO + O \quad (4)$$

5.2. Prompt NOx

Prompt NOx forms from molecular nitrogen of atmospheric air when combine with fuel in rich mixture. This nitrogen then oxidizes along with the fuel and becomes NOx during combustion. It is called prompt NO because it forms quickly as the combustion reaction and it cannot be limited from its generation. Sources of Prompt NOx are the number of radicals that formed during fuel fragmentation in HC flames e.g. CH, CH_2, and C_2H.[49]

5.3. Fuel NOx

Fuel NOx is formed only when there is nitrogen itself in the fuel as a constituent. Fuels containing Nitrogen when burn (e.g., coal) creates fuel NOx that result from oxidation of the already-ionized nitrogen contained in the fuel. Gas fuels have relatively low amount of nitrogen and thus produced low fuel NO. During combustion, from 10-15% of this nitrogen will react with hydrocarbon radical's CH or CH3 and will form hydrogen cyanide HCN which will then lead to NO. Therefore, all of nitrogen which is basically the organic nitrogen does not transform to NO. If the mixture contains more fuel i.e. is fuel rich, then environment of combustion chamber becomes reducing one and this tends to push the fuel nitrogen form either N_2 or NH_3. But if the system is lean i.e. excess oxygen so there is oxidizing environment then more NO is formed. Unlike thermal NOx fuel NO is not very temperature sensitive. In diesel engine mostly hydrocarbon fuel is used so that fuel NOx is not considered as the formation criteria for NOx inside diesel Engine[49]. Variation of all this three NOx with combustion temperature inside Diesel Engine is shown in Figure 10 and Table 4 highlights the key differences between all NOx.

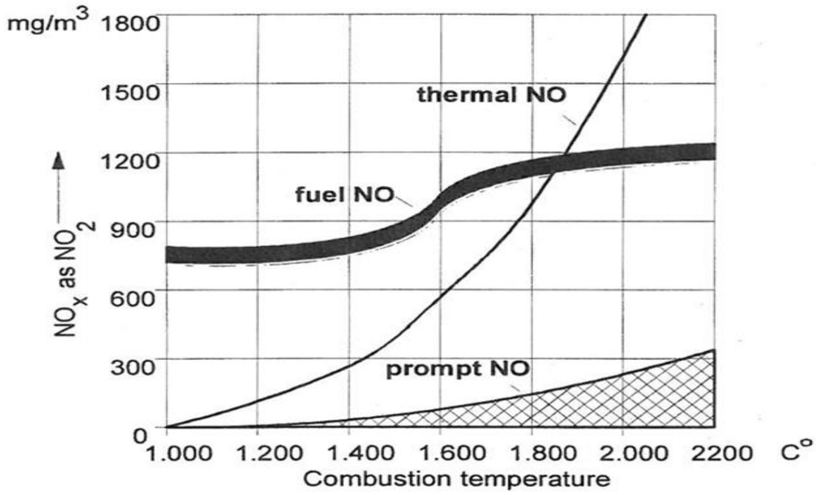

Figure 10. NOx forming inside a typical Diesel Engine against temperature in combustion zone [47].

Table 4. Main difference between three types of NOx [50].

Formation mechanism	Description
THERMAL NOx	Involves the oxidation of the atmospheric nitrogen contained in the duel oxidant mixture during the high temperature combustion of fossil fuels
PROMPT NOx	No formed at a rate faster than that from thermal NO due to high speed reactions that occur at flame from reactions of fuel derived radicals (typically CN- groups) with N2. This process is commonly referred as the “fenimore prompt NO” mechanism
FUEL NOX	Involves the conversion of originally bound nitrogen compounds contained within the fuel (primary coal and heavy oil)

6. Control Techniques of Nitrogen Oxides Emissions

6.1 Pre combustion/Active Control Techniques of NOx Emission

6.1.1 Injection Timing Control

Injection Timing of fuel greatly effects the formation of NOx inside the combustion chamber. Figure 11 represent NOx variation over injection timing. By reducing the timing at which fuel injector injects, peak cylinder pressure can be minimized, which in turn helps to reduce peak cylinder temperature also. As NOx is temperature dependent So ultimately NOx reduces.[9]

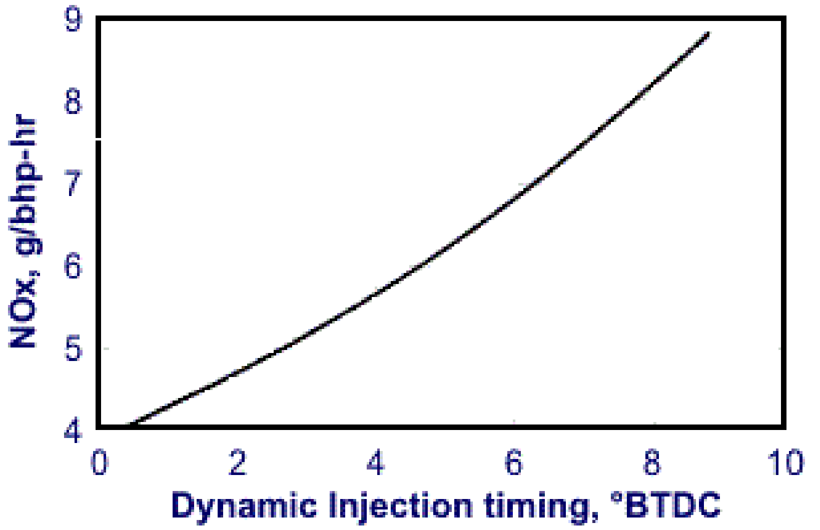

Figure 11. Trend of NOx inside a typical Diesel Engine with injection Timing[9]

6.1.2 Cooling the Intake Air

Unlike injection timing strategy, cooling of air in intake manifold has lower effect. Heat capacity of air increases as its temperature inside the intake manifold decreases by cooling, resulting overall reduction in peak cylinder temperature as well as lower peak temperature. This make impact the formation of NOx and enable the less production of NOx s. Figures 11 show the effect of intake manifold temperature on NOx emission[9].

6.1.3 Exhaust Gas Recirculation

Exhaust gas recirculation, also termed as EGR is one of the prominent techniques that have been employed in diesel engines for reduction of NOx emissions. NOx formation mainly depends upon the temperature of combustion reaction. EGR's Working principle favors those conditions which lessen the formation of NOx emission i.e. reduction of peak temperature during combustion reaction by diluting the concentration of oxygen in the combustion charge, increasing the thermal capacity of combustion mixture and dissociation of water molecules in recirculated exhaust by endothermically. [51]

Therefore it is Recirculating the small percentage of exhaust gas makes the combustion mixture lean and hence controls the temperature of combustion chamber[52].

6.1.4 Injection of Steam or Water:

Injection of water or steam in the air flow intake of diesel engine is effective techniques to lower the temperature of combustion zone. This can reduce temperature upto 1400 °F thus it lessens the NOx generation. This method found to reduce NOx emission upto 40ppm. But at the same time limitation of this method is that it causes the concentration of CO and unburned hydrocarbon at exhaust stream is increased[3][53].

The injection of water into the intake of air can be done through following methods

- Water fumigation along with intake air
- Dedicated injectors for direct injection of water into the combustion chamber mixture
- Premixing of fuel and water before the injection inside the combustion chamber[54]

It is observed that water injection in any form from above methods such as mixture of water and diesel called diesel emulsion, fumigation or direct injection in to cylinder, diminishes the established flame temperature and lessen thermal NOx formation. However the application of these methods causes the HC and CO emissions and SFC increment and this depend upon the method of water injection used with load and speed variations of engine[3].

6.2. Post Combustion/ Passive Control Techniques

6.2.1. Catalytic Converter

Catalytic converter is one of the foremost and longstanding techniques used in both commercial as well in automobile diesel engine to reduce the NOx, CO and other emission before emitting it into atmosphere. Physically it is a metal box whose size depends upon the application of engine. Two connecting pipes are there, one is called input pipe connected to the main hot exhaust manifold and other is connected to the stack or exhaust to emit final into atmosphere. It consists of dense honeycomb structure made of ceramic material with proper coating of catalyst. The honeycomb structure allows gases to pass through greater area so that reaction at the surface takes place efficiently[55].

The exhaust gases from the engine passes over the catalyst, chemical reaction happens on its surface, breaking the pollutant gases and transforming them into other gases that are harmless and can be discharge to atmosphere. One limitation with this kind of simple technique is to avoid the usage of lead containing fuel because lead in conventional fuel deteriorates the catalyst drastically and catalyst fail to take pollutant gases[56]. The chemical reactions inside the converter is shown in table 4.

A simple catalyst converter consists of two kind of catalyst

- Catalyst one serves the purpose of reduction of Nitrogen oxide pollutants. By reduction process, oxygen is removed from NOx and release Nitrogen in atmosphere which is harmless as ambient air contains 79% nitrogen.
- The other catalyst works exactly the same, but the chemical reaction is opposite to that of the reduction i.e. it works on oxidation process. CO is oxidized to CO_2 by providing the oxygen. In similar fashion unburned Hydrocarbon is converted to carbon dioxide and water and released to atmosphere.

Three different chemical reactions are going one for reduction of nitrogen and other two are oxidation of oxygen and unburned hydrocarbon. This specific type is called three-way catalyst converters. Figure 12 show three-way catalytic converter for NOx reduction.

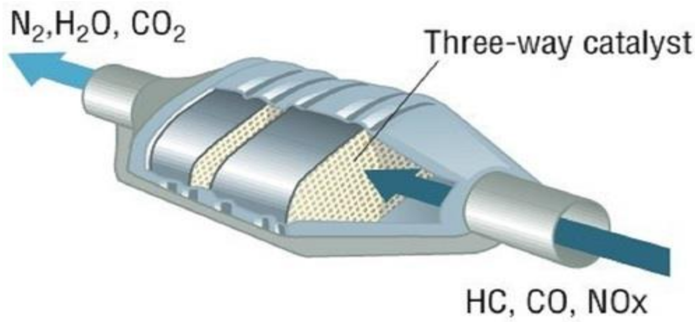

Figure 12. Three-way catalytic converter [47].

Table 5. Chemical reactions inside three-way catalytic converter for removal of NOx

Reduction of NOx to N_2	Oxidation of CO to CO_2	oxidation of unburned Hydrocarbon
$2CO + 2NO \rightarrow 2CO + N_2$ $HC + NO \rightarrow CO2 + H_2O + N_2$. $2 H_2 + 2 NO \rightarrow 2 H_2O + N_2$	$2 CO + O_2 \rightarrow 2 CO_2$	$HC + O_2 \rightarrow H_2O + CO_2$ [56]

6.2.2. NOx Storage-Reduction Catalysts (NSR)

Most of the diesel engine operates on lean mixture with excess amount of oxygen in its combustion chamber. This condition is not ideal for the catalytic converter because it require both oxidizing and reducing environment. Therefor for large industrial application a different kind of catalyst converter is required that must provide only reducing environment for reduction of NOx and in this regard NOx storage reduction catalyst is suitable for large diesel engine The NOx reduction process completed in two stages: 1- NOx stored when the engine is running on high air fuel ratio 2- Release along with lessening of NOx during engine operation when operating conditions are rich.

In this system, a catalyst which is usually platinum, used on metal oxide (Al_2O_3, SiO_2, TiO_2) with doped of BaO on it. Platinum assist the reduction of NO into NO_2 which then gets absorbed in the support as nitrate[9]. Figure 13a represent the simple pictorial view of mechanism of NSR while reduction and storage.

If fuel air mixture is rich in nature, these nitrates get release from the same support and converted to N2 in the presence of hydrocarbons, that serves to provide a reducing environment. This transformation is quite tough at either very low load engine or at very high load operations due to inadequate HC emission and catalyst remains inactive. There is a limit of exhaust temperature at which NOx conversion efficient has its maximum value. it is solely depending upon HC/NOx ratio. Higher will be the HC/NOx ratio, higher will be the value of temperature at which maximum NOx conversion occurs. Figure 13b shows the effect of HC/NOx ratio on the value of optimum temperature for maximum NOx conversion[57]. There is also limitation of this system like catalytic converter. Here that fuel should be used which have low sulfur content because NSR becomes deactivated as sulfur content passes over it [9].

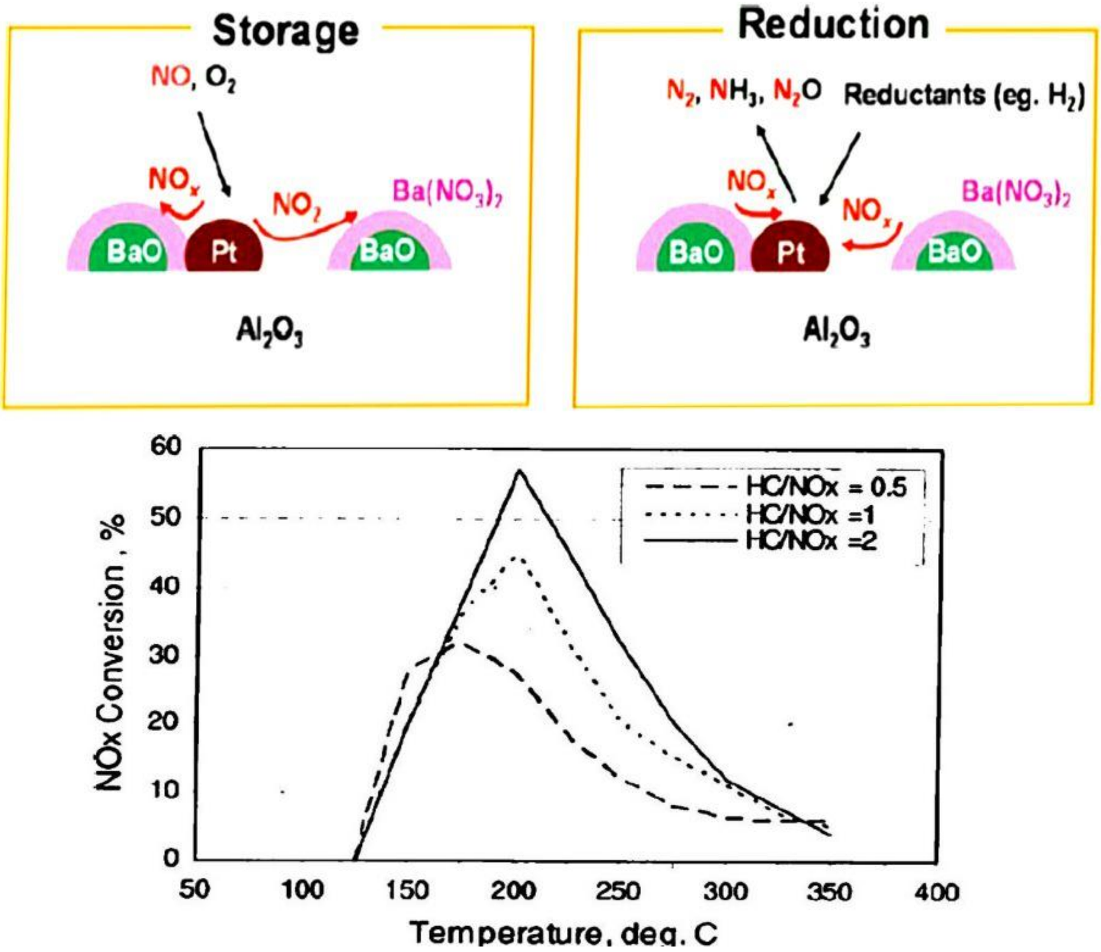

Figure 13. a) Storage of NOx & reduction during engine operation [47], b) NOx conversion Efficiency at combustion temperature at various ratios of Hydrocarbon [9]

6.2.3. Selective Catalyst Reduction

This technique utilizes ammonia for producing the reduction environment of NOx. Urea is the source of ammonia in this method with 30-40% concentration in water.

Figure 14 represents arrangement of SCR system. SCR system is ceramic honeycomb substrate with catalytic coating of mixture of vanadium, tungsten, and titanium oxide. There are 03 sections in this reduction technique: hydrolysis catalyst section, SCR catalyst section, and oxidation catalyst section. Urea is injected at upside of SCR system and per concentration of NOx. Urea breaks in the first step i.e. hydrolysis and produce ammonia. Ammonia comes into SCR catalyst and reduces NOx into harmless gas N_2 [9],[58].

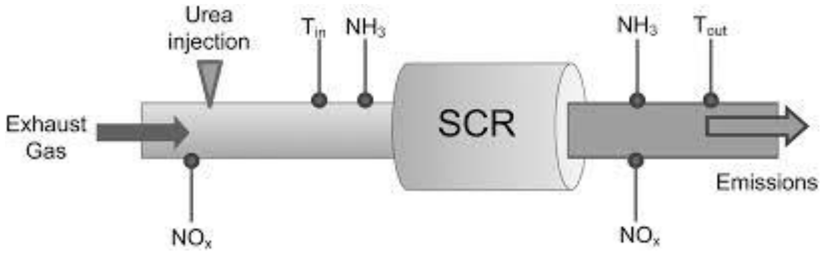

Figure 14. Selective Catalyst Reduction [47].

6.2.4. Non-Thermal Plasma

It is technique that control NOx after it has been produced in combustion engine. Non thermal Plasma is basically the ionized gas not produced from the heat but produced by the four techniques Dielectric Barrier Discharge (DBD), Corona Discharge (CD), Electron Beam Generated Plasma (EBGP) and Microwave Plasma (MP). It simply ionizes the reducing agents that injected the in-flue gases that react with NOx and reduced them. It is beneficial because it does not increase the flue gases temperature because it is non-thermal[59][60].

6.2.5. Charge Dilution Method

Diluting the intake mixture of diesel engine proved successful in reduction of NOx in diesel engine. Diluting the charge reduces the flame temperature which reduced the NOx generation. Gases such as N_2, CO_2, or inert gases if circulated with mixture charge are found successful in NOx reduction at wide range of operating conditions in diesel engines Figure 15a depicts the effect of different gases in dilution of intake charge and its temperature. CO_2 has found as one of the effective diluents in NOx reductions. Around with 6% CO_2 admission NOx emission reduce approximately by 50%. However, with the application of this technique, smoke emission found to be higher around 60% and CO emission also increased approximately by 8.5 times in comparison without the charge diluted. In addition to this, engine efficiency parameters alike torque, power, BMEP and SFC have deteriorated approximately 5.9%, 5.5%, 6%, 3.3% respectively form the value which obtained when there is no charge dilution[3].

Figure 15. Trade of between DPM and NOx in reduction techniques

7. Discussion Section

Two broad categories are there for emission control of NOx and DPM. Pre combustion techniques mostly focused on parametric control of intake charge such as air and fuel for controlled combustion in chamber. While post combustion techniques generally employed catalyst and other methods for promoting the chemical reaction that inhibit the pollutants level into atmosphere. Among three mechanism of NOx formation, thermal NOx is the dominant one in diesel engine and major source of harmful radical in environment. High temperature in Diesel engine (because of greater compression ratio) is the main cause of NOx formation during combustion while on the other hand DPM emission mostly occur due to rich mixture in combustion zone. The thorough review of control techniques depicts that these two emissions i.e. NOx and DPM are at the two-extreme end in term of controlling method. The employment of any technique for controlling one emission leads to some higher percentage of other emission due to parametric control of temperature and combustion zone mixture. Hence there is a general trade off exist between these two emissions and can be seen by general graph of figure 15b. Reduction in one emission produces a greater percentage of another pollutant in exhaust on practical ground applications, selection of any technique merely depends upon its feasibility and type of diesel engine for which it is to be employed.

8. Conclusion

Diesel Engines have been widely used from the earliest 21^{st} century as power source in marine, automobile and in industrial applications. With their usage, different emissions resulting from exhaust of diesel engine had become the source of environmental pollutions and severe threat for global environmental regulations. Most of the emission are result from impurities present in the intake fuel and chemical reactions taking place at high temperature inside the chamber. Among all emissions of diesel engine NOx and DPM are found acute ones from prepositive of human health and environmental policies. With technological advancement and time lots of research work has been performed to reduces these two emissions either before the combustion zone or after the combustion keeping the engine efficiency at optimum. Hence in this paper a comprehensive review is made on NOx and DPM emission covering their formation and types along with emphasizing on pre and post combustion reduction techniques. Employment of each method and their Resulting effect is described in detail with their advantages and limitations. With these techniques there is an inverse relation of PM and NOx emission. If one technique reduces NOx then PM found to be increase and vice versa. There is a tradeoff between NOx and PM emission. Selection of each technique depend upon the its application and feasibility.

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