

Chapter 1

INTRODUCTION

This chapter briefly discusses the significance of diesel fueled engine for transportation sector. It also discusses the emissions and control of NO_x and soot from diesel vehicles.

1.1 General

During the last decade, diesel engines have increased in popularity compared to gasoline engines around the globe, due to better fuel efficiency, lower operating cost, higher durability, and reliability. In addition to these aforementioned benefits, diesel engines are simultaneously associated with a favorable fuel tax situation in several countries [Banús *et al.*, 2013]. A fuel tax is an excise tax imposed on the sale of fuel. Its cost is less in India for diesel than petrol. Thus, diesel is cheaper than petrol. The economy of a nation is very dependent on transportation. In this regard diesel engines are widely used to transport goods, services and people. Apart from transportation, they are used in several other fields such as agriculture, construction, mining, defense etc. Diesel engines are the power source for trucks, buses, trains, ships, as well as off-road industrial vehicles, such as excavation machinery [Badini *et al.*, 1998]. The diesel engine is an internal combustion engine, in which ignition of the fuel, which is injected into the combustion chamber, is caused by the elevated temperature of the air in the cylinder due to mechanical compression (adiabatic compression). Diesel engines work by compressing the air inside the cylinder. This increases the temperature to such a high degree that atomised diesel fuel that is injected into the combustion chamber ignites spontaneously. Figure 1.1 shows the ignition process in the diesel engine.

Diesel engines are the main type plant of vehicles used in heavy duty applications. This includes buses, large trucks, off-highway construction, and mining equipment. Furthermore, diesel engines are winning an increasing share of the light duty vehicle market worldwide [Hammerle *et al.*, 1994]. In Europe, for example, 100% of heavy duty, ca. 60% of light duty commercial vehicles and ca. 20% of passenger cars are diesel powered. According to a study conducted by Petroleum Planning and Analysis Cell, in India, the transport sector is a major consumer of diesel, accounting for 70% of the total Diesel sales (PPAC, 2014). Diesel fuel is important to the U.S. economy. In 2016, diesel fuel accounted for about 21% of the petroleum fuels consumed by the U.S. transportation sector and diesel-powered cars accounted for about 3% of total auto sales, which is considerably lower than 50% in Europe [Lussenhop *et al.*, 2015].

However, a major environmental problem associated with the diesel engines is the emissions of main primary pollutants such as particulate matter (PM) and nitrogen oxides (NO_x). The PM and NO_x from the diesel exhaust are major problems to health, adversely affect to environment, cause global warming and climate change [Lu *et al.*, 2012]. These primary pollutants react with other pollutants and moisture in the presence of sunlight forming more dangerous secondary pollutants, notably acid rain, smog, ozone (O₃), peroxy acetyl nitrate (PAN), polycyclic aromatic hydrocarbons (PAH), hydrogen peroxide (H₂O₂), and aldehydes which may also increase the greenhouse effect.

Due to adverse impacts of diesel emissions, the various governments (US, Japan, Europe, and India) have imposed specific and severe limits on vehicular NO_x and soot emissions. As the legislation limitation goes more stringent, there is a growing interest in developing the process that enables the reduction of such emissions. Therefore, to

control the emissions various separate technologies have been investigated such as DOC and DPF for PM, EGR, SCR, catalytic decomposition, and NSR for NO_x. These technologies are very cumbersome. On the other hand simultaneous catalytic control of soot and NO_x is attractive because of its compactness. Therefore, the present work aims to develop an efficient catalytic system for simultaneous abatement of diesel soot and NO_x emissions.

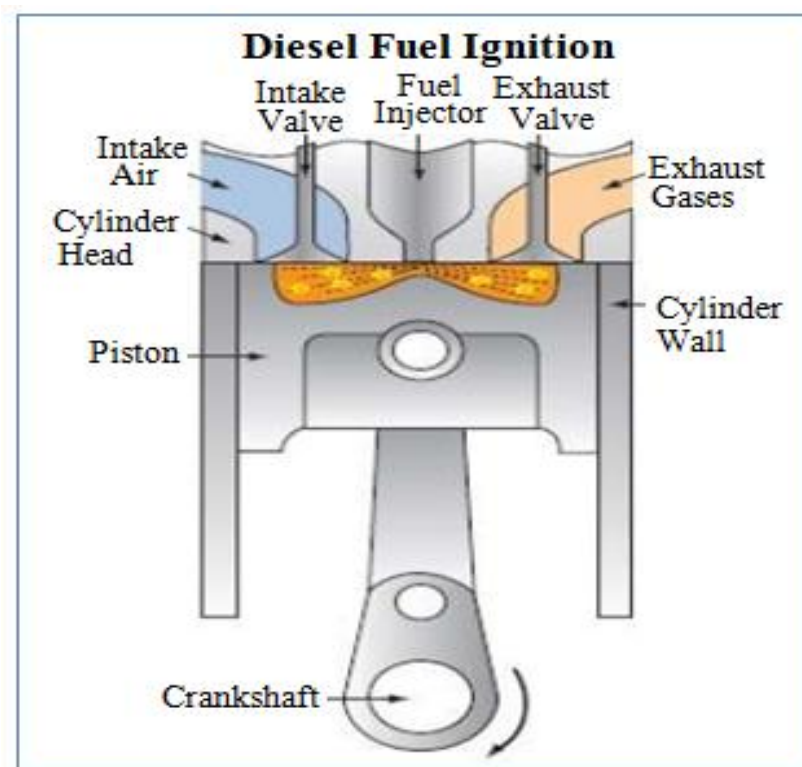


Figure 1.1 Diesel Fuel Ignition Process

1.2 Diesel Soot and NO_x Formation, Their Effects and Control Technologies

1.2.1 Particulate Matter/ Soot

Diesel engines have inherently high thermal efficiencies, resulting from their high compression ratios and fuel lean operation [Farrauto and Voss, 1996]. A high compression ratio produces high temperature facilitating auto-ignition of the fuel whereas high air/fuel (A/F) ratio allows for the complete combustion of the fuel. However, the A/F mixture is not homogeneous and always consists of fuel-rich and lean

regions. The heterogeneity in the composition of the fuel and air mixture in the combustion chamber of a diesel engine produces a great number of problems related to contaminant emissions [Banus *et al.*, 2013]. Diesel exhaust contains low concentration of carbon monoxide (CO) and unburned hydrocarbons (HC) but emissions of PM and NO_x are high. Therefore, level of PM and NO_x emissions need to be controlled. Since the reduction of both NO, and particulate emissions to the admitted level cannot be accomplished by engine modifications alone, after-treatment processes for the simultaneous reduction of their emissions from diesel exhaust should be developed [Castoldi *et al.*, 2015, López *et al.*, 2016, and Mescia *et al.*, 2008].

Diesel engine exhaust emissions are a mixture of gases, vapor, liquid aerosols and substances made up of particles. It consists of the products of combustion including particulate matter (soot), nitrogen, water, carbon monoxide, oxide of nitrogen, oxide of sulfur, and polycyclic aromatic hydrocarbons (PAH). Typical diesel exhaust composition is as shown in Table 1.1 [Prasad and Bella, 2010]. Out of these, the emissions of oxides of nitrogen (NO_x) and particulate matter (PM) are of major concern [Kagawa *et al.*, 2002].

Soot is the name given to carbonaceous agglomerates that are produced during the combustion of hydrocarbon fuels. Whilst regarded as not well defined [Svensson *et al.*, 2005], it is suggested that it is a solid insoluble substance composed of roughly eight to ten carbon atoms and a single hydrogen atom C₈H to C₁₀H [Melton *et al.*, 1984]. A representative particle molecular composition was produced [Idicheria *et al.*, 2005] in which 88.3% comprised carbon, 1.2% metals, with the remainder consisting of Oxygen (4.9%), Nitrogen (0.5%), Hydrogen (2.6%) and Sulfur (2.5%).

Table 1.1: Typical exhaust gas composition

Exhaust Pollutants	Four-stroke spark ignited gasoline engine	Four-stroke spark ignited lean-burn gasoline engine	Diesel engine
			Concentration
NO _x	100-4000 ppm	800-2300 ppm	30-1000 ppm
PM (soot)	Low	Low	20-200 mg/m ³
HC	Low	Low	50-500 ppm
SO _x	15- 60 ppm	10-50 ppm	10- 100 ppm
CO	0.1-6.0%	0.5-0.9%	100-1000 ppm
CO ₂	10-18%	10-15%	2-12 vol%

Some major characteristics of diesel soot are as follows:

- Soot is a carbonaceous particulate matter and is produced during combustion of the rich fuel - air mixtures [Srivastava *et al.*, 2008, Sakai *et al.*, 2017].
- Appearance of black smoke emissions in the exhaust indicates high concentration of soot in the exhaust gases [Reşitoğlu *et al.*, 2015].
- Soot is mostly produced in the diffusion combustion systems, but overly rich premixed combustion also produces soot [Zbarcea *et al.*, 2016, Dhal *et al.*, 2017]
- As the spark ignition engines generally operate close to stoichiometric air-fuel ratio, soot emissions from these engines are insignificant. With the use of unleaded gasoline, lead particulates from the SI engines have been eliminated [Flagan *et al.*, 1988, Zhao *et al.*, 1999].

Here, we will discuss particulate emissions only from the diesel engines as these are of major health concern and are more difficult to control. Soot emissions have been associated with respiratory problems and are thought to be carcinogenic in nature. The particle size is important as the particles smaller than 2.5µm can reach lungs along with the inhaled air and cause health problems. The particles smaller than 2.5µm constitute

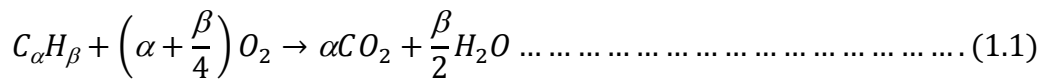
more than 90 percent mass of the total particulate matter in the diesel exhaust. The fuel composition also is an important factor in soot production and emissions. For diffusion combustion soot forming tendency is generally in the following order [McAuliffe *et al.*, 1966, Briker *et al.*, 2001].

Increasing Soot Formation

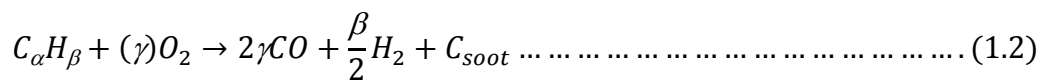


Alcohol < Paraffin < Olefins < Acetylene < Aromatics

Theoretically perfect combustion occurs when a stoichiometric mixture of oxidant and fuel are presented to the combustion region [Flagan *et al.*, 1988]. Such a reaction can be described by the reaction path Equation 1.1:



Carbon dioxide and water are produced, in addition to the desired release of energy. However, when a localized region has an excess of fuel relative to oxidant, incomplete combustion occurs in which some proportion may be left unburned or partially burnt but where the reaction pathway in which CO is produced, is dominant (Equation 1.2). For the unburned or partially burnt fuel, a pyrolytic reduction to more simple molecules may also occur, yielding an excess of carbon atoms that unless consumed by a subsequent reaction, and contribute to the formation of soot precursors. Other hydrocarbons or available molecules can be absorbed or condensed onto the resulting carbon solid [Haynes *et al.*, 1981 and DeLaurey *et al.*, 2015].



Typically, particulate matter is regarded as the insoluble constituent soot and other particles such as unburned and partially burnt hydrocarbons.

1.2.2 PM/Soot Formation

As mentioned above, air/fuel mixture inside the combustion chamber remains heterogeneous. At the moment of the fuel injection, three regions can be distinguished in the cylinder.

- i) A region close to the injector, where the concentration of diesel fuel is relatively high [Talibi *et al.*, 2014]
- ii) The central region of the cylinder, where condition are closed to the stoichiometric ones [Sun and Zhu, 2014]
- iii) The most separated region from the injector, where the fuel concentration is low [Banus *et al.*, 2013].

If the generated turbulence was not enough in the first region, in the proximities of fuel drops there would not be sufficient oxygen to complete the fuel combustion. This leads to the formation of particular matter (PM), which constitutes the typical black smoke observed from diesel vehicles during high acceleration or when they are cold. In contrast, in the third region, the oxygen excess and the very high temperature cause the appearance of important NO_x quantities. In the intermediate region, the diesel fuel/air ratio is close to the stoichiometric one so that the combustion is produced under near ideal conditions. Formation of PM involves four fundamental steps [Tree and Svensson, 2007].

The broadly accepted soot formation model consists of five processes: pyrolysis, nucleation, surface growth, coalescence and agglomeration (Figure 1.2). These processes occur approximately sequentially at a given location, triggered by temperature and pressure conditions as well as the population of the substances produced by the preceding process. However, at different locations at the same point in

time, different regions may be undergoing different processes, this is something of significance when considering the possibility for transportation of substance between adjacent regions and therefore between different processes [Saggese *et al.*, 2015, Atiku *et al.*, 2017].

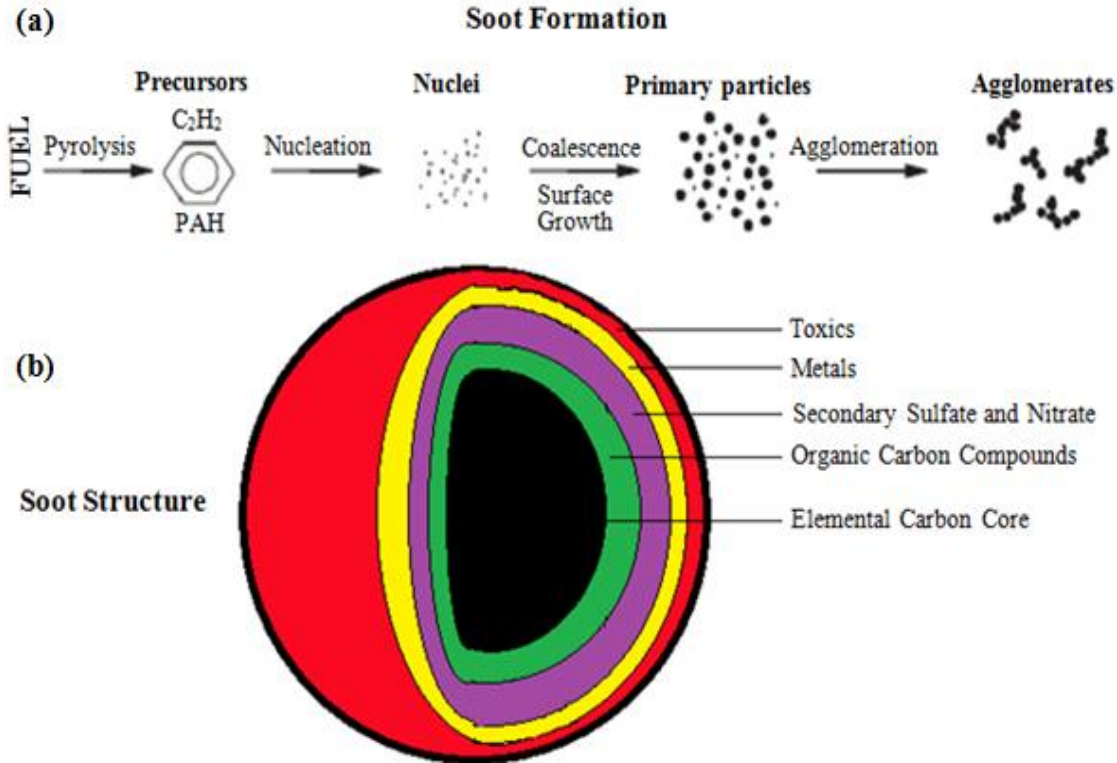


Figure 1.2 (a) Formation of particulate matter and (b) Structure of soot [Tree and Svensson, 2007]

The destructive process of oxidation occurs simultaneous to some of those of formation. The competition between these rival processes defines the soot population at each moment in time. As the local ambient temperature decreases, such as after a combustion event, a threshold is exceeded, below which all formation and destruction processes cease; the soot population ceases to change.

1.2.2.1 Pyrolysis

High concentrations of fuel at high temperatures provoke the fuel organic compounds to alter their molecular structure in order to form molecules like C_2H_2 ,

benzene and polycyclic aromatic hydrocarbons (PAHs) without significant oxidation of the fuel. However, some oxygen may be present in the structure of the formed species. The molecules thus formed are called PM precursors [Wilson *et al.*, 2013].

Pyrolysis of fuel is the thermo-chemical decomposition whereby unburnt liquid fuel is broken down into more simple molecules such as aliphatic hydrocarbons – alkanes, alkenes, and alkynes. Despite the likely presence of oxidant, pyrolysis is primarily caused by high temperatures, and is endothermic in nature. Accordingly, the rate of pyrolysis is highly dependent upon the temperature [Smith *et al.*, 1981]. It is considered that fuel pyrolysis is the most important factor of sooting tendency in non-premixed laminar diffusion flame structures [Ladommatos *et al.*, 1996]. The rate of pyrolysis is also dependent upon local fuel concentration. The molecules produced by the pyrolysis of pure fuel are described as soot precursors and typically consist of polycyclic aromatic hydrocarbons (PAH), unsaturated hydrocarbons, acetylene and polyacetylenes. It is reported that typical pyrolysis products in a non-premixed laminar diffusion flame structure are C_2H_2 , C_2H_4 , CH_4 , C_3H_6 as well as Benzene, C_6H_6 [Haynes *et al.*, 1981]. Polycyclic aromatic hydrocarbons are typically formed from monocyclic hydrocarbons by one of two rivaling mechanisms: hydrogen-abstraction-acetylene-addition (HACA) [Wang *et al.*, 1997] in schemes where acetylene concentration is at least equal to that of benzene (Figure 1.3), or direct ring-ring condensation (Figure 1.4) where aromatics concentration is sufficiently high [Wang *et al.*, 1997]. Other kinetic formation pathways are proposed [D'anna *et al.*, 2000] as producing Naphthalene, through radical addition (Figure 1.5), Phenanthrene through radical combination (Figure 1.6), and cyclization of bi-phenyl by acetylene addition (Figure 1.7).

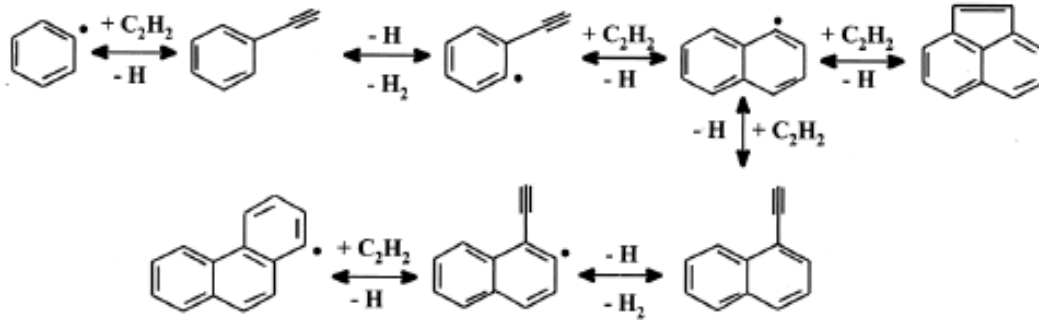


Figure 1.3 HACA mechanism of polycyclic aromatic hydrocarbon formation [adapted from Wang and Frenklach, 1997]

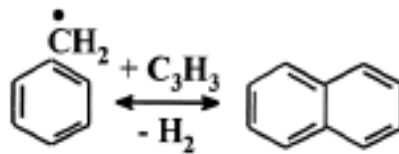


Figure 1.4 Direct ring-ring condensate of naphthalene from benzyl and propargyl [Colket *et al.*, 1994]

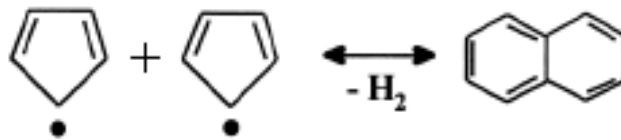


Figure 1.5 Formation of naphthalene from combination of cyclopentadienyl radicals oxidized benzene [Castaldi *et al.*, 1996]

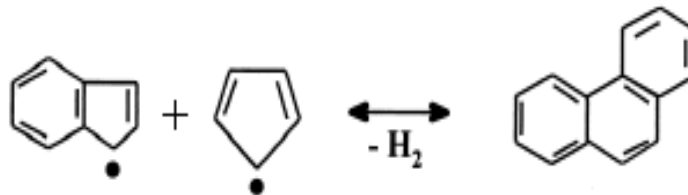


Figure 1.6 Phenanthrene formation by combination of cyclopentadienyl and indenyl (oxidized naphthalene) [Castaldi *et al.*, 1996]

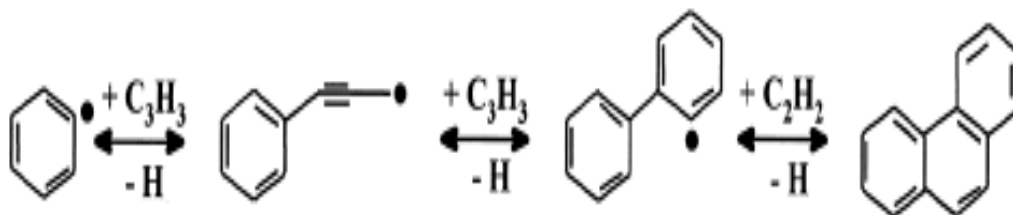


Figure 1.7 Phenanthrene formation by cyclization by acetylene addition, following sequential addition of propargyl radicals to phenyl [Danna *et al.*, 2000]

In premixed flame structures where an abundance of oxidative species such as the hydroxyl radical OH occurs, the pyrolysis and oxidation compete in their creation and destruction of soot precursors. In non-premixed flame structures, typical of direct injection diesel engines, minimal oxidative species are locally present and so almost no oxidation of precursors occurs. Both oxidation and pyrolysis processes rates increase with temperature. However, the rate of oxidation increases more quickly, a consequence of which is that premixed flames decrease in soot production by mass more quickly than non-premixed flames as temperature increases [Sakai *et al.*, 2017].

Pyrolysis occurs through a free radical mechanism so the diffusion of radicals (H, HO, O, O₂) into fuel rich zones in diffusion flames increases the rate of pyrolysis [Smith 1981, Glassman 1996]. Radicals are also produced due to pyrolysis, which may contribute to the rival process of oxidation.

1.2.2.2 Nucleation

The precursor molecules formed by pyrolysis arrange themselves to form nuclei of the PM primary particles. The initial formation of the smallest incipient particles (in the order of 1 nm diameter) from gas-phase reactants occurs through nucleation [Betrancourt *et al.*, 2017]. Nucleation is an irreversible process that occurs near the primary reaction zone, characterized as a region within which the highest temperatures as well as radical and ion concentrations occur for both premixed and diffusion flames [Bartok *et al.*, 1991]. Particle inception occurs when local temperature is approximately 1300 to 1600K, whereby small aliphatic hydrocarbons undergoing radical addition form soot precursors as well as polycyclic aromatic hydrocarbons (PAH). Also, a process of radical addition of small, probably aliphatic, hydrocarbons to larger aromatic molecules may occur [Melton *et al.*, 1984]. Nucleation, of itself does not directly contribute significantly to the total mass of soot. It is however, highly significant regarding the

overall production of soot in that it provides sites for the surface growth mechanism to subsequently occur [Frenklach et al., 1996].

1.2.2.3 Surface growth

Nucleated soot particles add mass to their surface to form the primary particles. Whilst no clear division between the end of nucleation and the beginning of surface growth is apparent, they are distinctly separate mechanisms [Khalizov *et al.*, 2009]. Surface growth is principally a process of mass increase of the soot nuclei and occurs when the hot surface accepts principally gas phase acetylene. As soot particles are transported away from the primary reaction zone to cooler and therefore less reactive regions, surface growth is still observed, even where hydrocarbon concentration is less than the soot inception limit [Haynes *et al.*, 1981]. Surface growth is the dominant mechanism with regard to increase of soot particle size and mass and accordingly has a significant effect upon the final soot mass and volume fraction. It has been noted that smaller young particles exhibit higher growth rates than older, similarly sized particles due to a higher number of available radical sites [Bartok *et al.*, 1991].

Acetylene and other aromatic species more effectively promote surface growth than species aliphatic species. It has been demonstrated that the rate of surface growth is higher for larger molecules [Haynes *et al.*, 1981]. Due to this preferential addition of larger molecules, the hydrogen to carbon ratio of the soot particle decreases throughout the surface growth process. This is an indication that the polyacetylenes added have a very high molecular weight or that dehydrogenation takes place concurrently. As the soot particles grow, they lose their affinity for polyacetylenes [Smith *et al.*, 1981].

1.2.2.4 Coalescence

Coalescence, also referred to as coagulation, is the process by which the soot particles that have previously undergone surface growth, and join together to form larger spherule-like particles in the order of 30 to 70 nm diameter [Tree *et al.*, 2007, Park *et al.*, 2003]. Overall particle mass is conserved and therefore soot volume fraction remains unchanged. The soot particles count is therefore reduced by coalescence.

1.2.2.5 Agglomeration

Primary particles combine to produce agglomerates, bigger in size than primary ones. During this process, a wide range of particles of varying size are formed [Kiselev *et al.*, 2010]. Agglomeration is a process by which particles become attached to other particles. The possibility exists for infinite variation of agglomerated particle structure, though typically chain like structures occur with some clumping. When considering a soot population, the number of particles becomes reduced as they agglomerate into the larger, fractal like geometry particles. Since agglomeration constitutes a rearrangement of material, no change of mass or soot volume fraction occurs. The resultant size, and the amount of particles agglomerated together is dependent upon the duration of the agglomeration process, which in turn is dependent upon the residence time within the flame structure [Xu *et al.*, 2001].

The agglomerated soot structures formed can be characterized by the mass fractal concept, using the fractal dimension, D_{fr} [Koylu *et al.*, 1995, Koylu *et al.*, 1997, and Growney *et al.*, 2015]. Figure 1.8 supports the validity of Equation 1.3, the relationship between the number of primary particles N_p , and the non-dimensional ratio of radius of gyration, R_g , to mean particle diameter, d_p :

$$N_p = K_{fr} \left(\frac{2R_g}{d_p} \right)^{D_{fr}} \dots \dots \dots (1.3)$$

N_p = number of primary particles per unit volume [m^{-3}]

K_{fr} = fractal prefactor

R_g = radius of gyration [m], equivalent to half of the projected maximum diameter of the aggregate (L)

d_p = mean primary particle diameter [m]

D_{fr} = fractal dimension

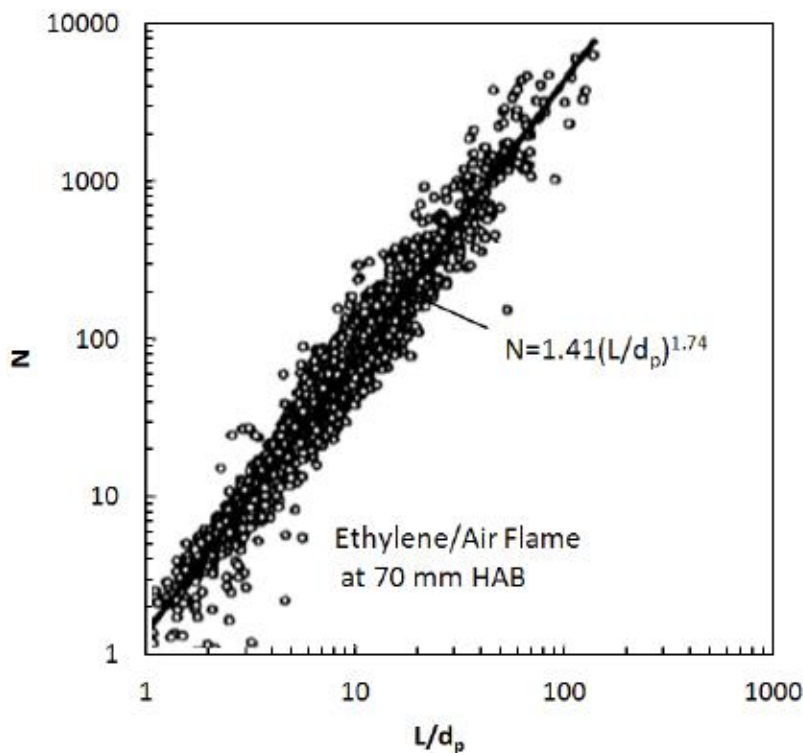


Figure 1.8 Number of particles per aggregate as a function of non-dimensional length parameter L/d_p [Koylu et al., 1997]

1.2.3 Mechanism of diesel soot formation

Diesel engines produce soot as a result of incomplete fuel combustion. Ideally, complete combustion in a cylinder would only produce carbon dioxide and water, but no engine is perfectly efficient. The diesel combustion process is very complex due to its unsteady, heterogeneous and turbulent nature. This complexity makes a fundamental

understanding of the location, the timing and the mechanisms of pollutants formation a real challenge. Among many reviews of diesel combustion and pollutant formation reported in the literature, the work done by [Kamimoto *et al.*, 1991] is especially succinct. In that study, only the essential features of diesel combustion related to soot formation are summarized. Liquid fuel is injected just before the end of compression into hot air, where it starts evaporating and mixing. After a short ignition delay, premixed fuel-air auto-ignites and rapid heat release occurs. As more fuel is injected, combustion is then controlled by the rate of diffusion of the air into the flame [Pischinger *et al.*, 1994].

According to the original diesel combustion description, all fuel injected right after the premix burn would be exclusively consumed in the diffusion flame. It was generally assumed that soot was exclusively formed in the fuel-rich side of the diffusion flame; where high temperatures prevailed and parent fuel molecule decomposition was possible. The initial premixed burn was not considered as a source of soot particles because it was thought to be stoichiometric. A much better insight into the processes involved in diesel combustion was gained by Dec *et al.*, 1995 via optical studies. Figure 1.9 shows a schematic diagram of quasi-steady burning jet in a diesel engine based on the findings from the in-cylinder laser measurements. Soot formation is observed in the central region of the jet just downstream the liquid fuel spray.

Conceptual Models of Soot Formation

Two conceptual models of soot formation in spray combustion have been suggested [Chen *et al.*, 2014]:

- One model suggests that the soot is formed in a narrow zone of rich mixture at the spray boundaries close to the diffusion combustion region.

- Another conceptual model based on laser imaging studies of diesel spray combustion in a supercharged engine at Sandia Laboratories has been proposed. Figure 1.9 shows schematically a diesel spray jet. It is seen in these studies that the liquid jet is relatively short and the fuel ahead of liquid jet is in vapor phase. It was seen that the soot appeared for the first time just downstream of liquid jet in the rich premixed combustion region. The concentration of soot increases and particle size grows as soot flows downstream towards the spray boundary. The highest soot concentration and largest particle size are in the region forming head or leading edge of the jet. The model suggests that the formation of soot precursors and consequently generation of soot particles takes place in the rich premixed flame where fuel-air equivalence ratio is in the range 2 to 4. The soot particles grow in size as they pass through the spray towards the spray leading edge. The soot finally gets oxidized in the diffusion flame at the spray boundaries by OH radical rather than the molecular oxygen, O_2 [Tao *et al.*, 2009].

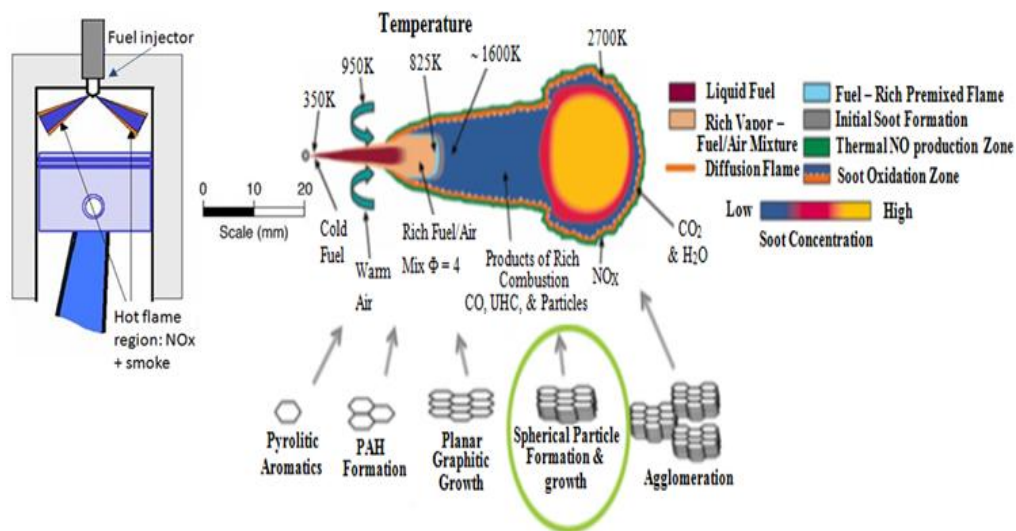


Figure 1.9 Conceptual model of DI combustion process soot and NO_x formation

There are two major characteristics of this diesel combustion conceptual model that are worth noting:

- The fuel goes through a two-stage oxidation process even after the diffusion flame establishes. The first is at the fuel-rich premixed zone just downstream the liquid spray and the second at the diffusion flame in the periphery of the plume.
- Soot is formed in the fuel-rich premixed zone where fuel-air equivalence ratio was measured to range from 2 to 4. Soot then grows in the centre of the plume due to surface growth before part of it being oxidized in the diffusion flame.

It is evident that understanding soot formation in diesel engines involves studying the kinetics of the fuel-rich premixed zone just downstream the liquid spray. Therefore, this study focuses on using experimental and computational tools, in order to gain some insight into the soot formation fundamentals under conditions similar to the diesel engines operation.

1.2.4 Diesel PM components

Diesel particulate matter has two main components such as dry soot or solid carbonaceous material and soluble organic fraction (SOF).

- ***Dry soot or solid carbonaceous material***

Dry soot is mainly the carbonaceous fraction of the particulate and its typical chemical formulae are C_8H , C_9H and $C_{10}H$. About 5 to 10 % by mass oxygen and 0.5% nitrogen are also present. The typical empirical formula of dry soot would be $CH_{0.11}O_{0.065}N_{0.005}$. Dry soot results from several processes like pyrolysis, dehydrogenation and condensation of fuel molecules.

- ***Soluble organic fraction (SOF)***

Soot is mostly consisted of carbonaceous soot and soluble organic fraction (SOF) of hydrocarbons [Abdullah *et al.*, 2008]. The soluble organic fraction originates from the fuel and oil hydrocarbons, and hence has H/C ratio ~ 2 . However, depending upon engine operating conditions, it may vary from 1.25 to 2.0. The hydrocarbons C_{17} to C_{40} are present in the particulate SOF phase, with C_{23} - C_{24} being close to the mean. Typically, SOF has an empirical formula $CH_{1.65}O_{0.1}N_{0.007}$. The soluble organic fraction is adsorbed on the solid soot core. The SOF also consists of partial oxidation products and poly aromatic hydrocarbons besides hydrocarbons originating from fuel and the lubricating oil. The mass content of SOF varies significantly depending upon engine design and operating conditions, but mostly it is in the range from 20 to 45 percent.

In addition to SOF, sulphates originating from fuel sulphur, nitrogen dioxide, and water are also absorbed on the particle core formed by soot. Other inorganic compounds of iron, silicon (fuel contamination), phosphorous, calcium, zinc (source is oil) etc. are also present in traces in the particulates.

1.2.5 Typical Composition of Diesel PM

The content of different constituents of diesel particulate matter can be significantly different for different engine designs. These also vary with the emission control technology employed and the fuel quality particularly the sulfur content. Fuel sulfur content has been drastically reduced as the emission standards are becoming more stringent. The typical particulate composition for a Euro 3 turbocharged, after-cooled diesel engines considerable reduction in carbon (dry soot) content, fuel and oil derived SOF and sulfates have taken place since early 1990s when PM emission standards were enforced for the first time and became further stringent during the

following years. SOF content depends on engine design, operating conditions, lubricating oil consumption, and fuel quality. As regards sulfates, with the current low sulfur fuels (sulfur content down to 50 to 350 ppm by mass compared to 0.5 % prior to 1990), sulfate content would be less than 2 percent of total PM mass. Diesel particles as well as particles from other combustion sources are a complex mixture of elemental carbon (EC), a variety of hydrocarbons (HC), sulfur compounds, and other species. Particles differ in size, composition, solubility and therefore also in their toxic properties. The Figure 1.10 shows the composition of particles from heavy-duty diesel engines. Many of these species are volatile depending on temperature and other conditions the volatile fraction i.e. (i) remain in the gas phase, (ii) condense on existing solid particles, (iv) nucleate and form new particles.

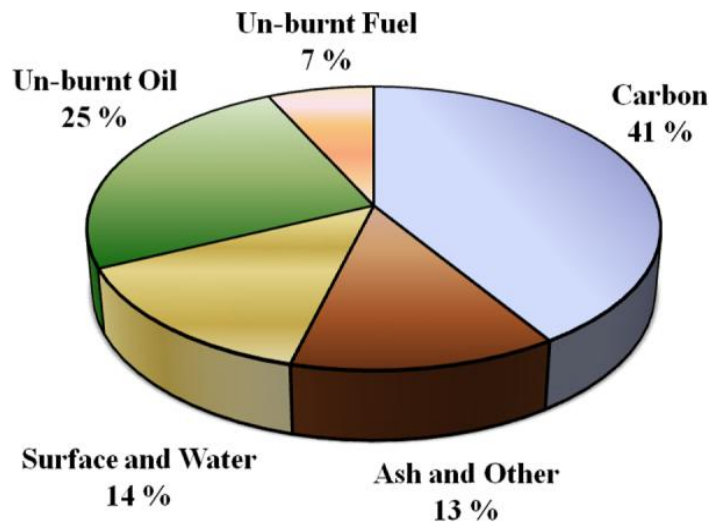


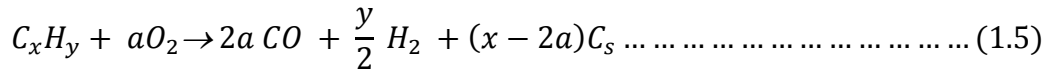
Figure 1.10 Composition of diesel PM (Soot) [Kittelson *et al.*, 1998]

As the diesel particulate matter (PM) mainly consists of soot and the adsorbed unburned hydrocarbons (SOF) on soot core, the PM content has been related to exhaust soot content and HC concentration as presented in Equation 1.4:

$$PM = 1.024 Soot + 0.277 HC \dots \dots \dots (1.4)$$

Soot Formation Stoichiometry

From equilibrium considerations soot will appear when oxygen is not sufficient to oxidize carbon even to carbon monoxide, i.e., C/O atomic ratio in the mixture is greater than unity. Using the following stoichiometric reaction for a hydrocarbon (C_xH_y) as shown in Equation 1.5:



When x is greater than 2a i.e. C/O is greater than unity, solid carbon, C_s or soot is produced during combustion.

The fuel-air equivalence ratio for the above reaction is:

$$\phi = 2 \left(1 + \frac{y}{4x} \right) \left(\frac{C}{O} \right) \dots \dots \dots (1.6)$$

For practical diesel fuels H/C ratio (y/x) is ~2. Hence, for the critical C/O = 1, the fuel-air equivalence ratio, φ= 3 (Equation 1.6). However, in practical systems the soot has been observed to form at C/O ratio of 0.5 to 0.8 indicating that soot formation is a kinetically controlled process. It may be noted that for methane (CH₄), the theoretical critical φ is equal to 4. The critical C/O ratio for soot formation increases with increase in temperature. Pressure has a strong influence, higher pressures yielding higher soot formation at the same value off. In other words, increase in pressure results in lowering of critical value of f at which soot is formed [Bockhorn *et al.*, 2000 and Stagni *et al.*, 2018].

- **Composition and Structure of Diesel Particulates**

PM is known to consist mostly of carbonaceous soot with minor components of soluble organic fraction (SOF) from unburned fuel, lubricating oil and inorganic

compounds such as ash and sulphur compounds. US Environmental Protection Agency (USEPA) defines the particulate matter as any substance other than water that is collected by filtration of the diluted exhaust gases at or below 325 K (125 F). Composition of particulate matter collected on a filter and various components adsorbed on the surface of spherical soot particles are shown as shown in Figure 1.11 [Bagi *et al.*, 2016, Ferraro *et al.*, 2018]. It represents diesel PM formed during combustion of atomised fuel droplets. The resulting carbon cores agglomerate and adsorb species from the gas phase.

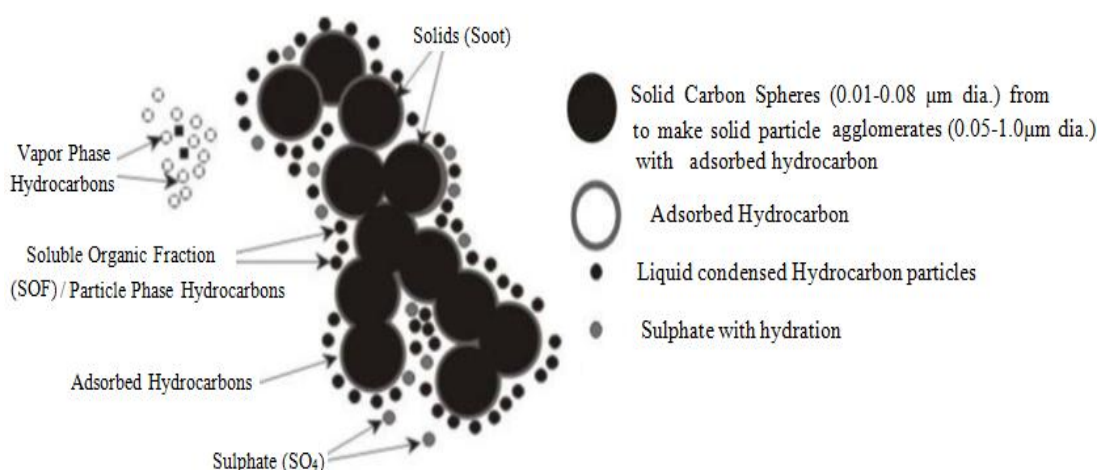


Figure 1.11 Illustrates the nature of diesel PM [Twiggs and Phillips, 2009]

1.2.6 Classification of Diesel Soot

Primary particles are directly emitted into the atmosphere through diesel exhaust. Secondary particles are formed usually by chemical reactions of gaseous pollutants, such as sulphur oxides and nitrogen oxides, interacting with other compounds in the air to form fine particles. These tiny bits of soot can travel hundreds of miles downwind of the original pollution sources.

On the basis of particle size PM are broadly classified into four categories: (1) Large particles $>10 \mu\text{m}$, (2) Coarse particles 2.5-10 μm (DPM_{10}), (3) Fine particles 1.0-2.5 μm ($\text{DPM}_{2.5}$), and (4) Ultra-fine $<1.0 \mu\text{m}$. ($\text{DPM}_{1.0}$) [Stratakis *et al.*, 2004].

However, the PM particles range from large number of small particles to small number of bigger particles [McClellan, 1989]. The typical contribution of varying size particles to particle number and particle mass is shown in Figure 1.12 [Mayer *et al.*, 1995].

It has been reported that small diameter particles are more harmful for human health as these particles are easily respirable and penetrate deep through the lungs and even enter the blood stream (Zhu *et al.*, 2007).

The size of the particles also determines the time they spend in the atmosphere. While sedimentation and precipitation removes PM₁₀ from the atmosphere within few hours of emission, PM_{2.5} may remain there for days or even a few weeks. Consequently, these particles can be transported over long distances.

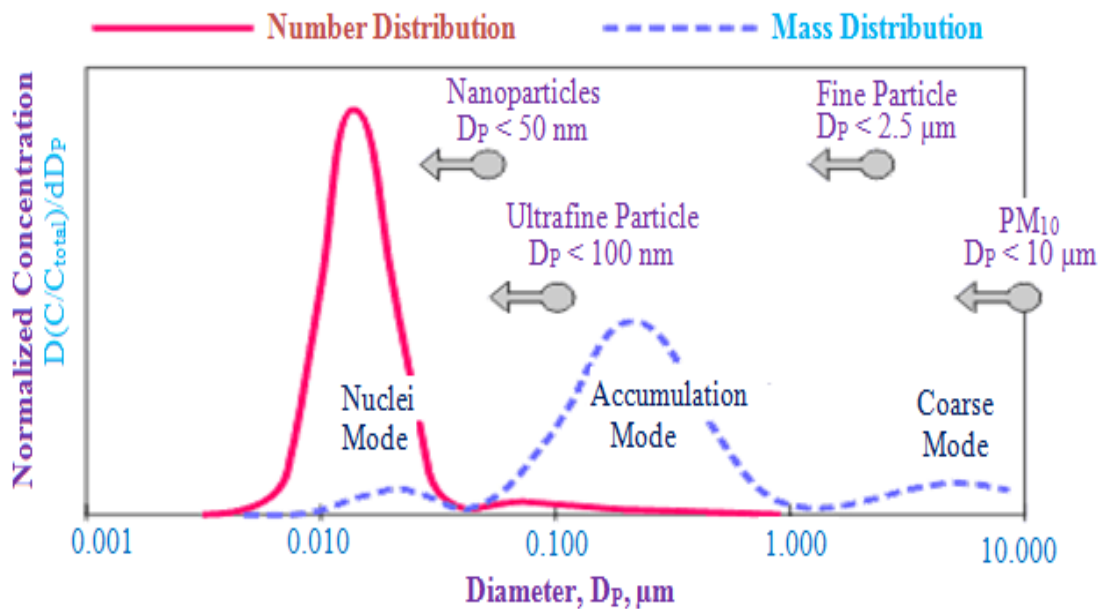


Figure 1.12 Mass and number based particle size distributions from diesel exhaust [Mayer *et al.*, 1995]

1.2.7 Morphology of PM

Throughout the formation processes, soot or its precursors assume structures that are difficult to define to a completely satisfactory extent. Agglomeration of primary particles into clusters of ~10⁵ carbon atoms occurs. Agglomerated soot particles can be

composed of up to 4000 spherule-like particles and may form structures that are from 10 to 1000 nm long as shown in Figure 1.13 and Figure 1.14 [Liu *et al.*, 2004 and Wentzel *et al.* 2003].

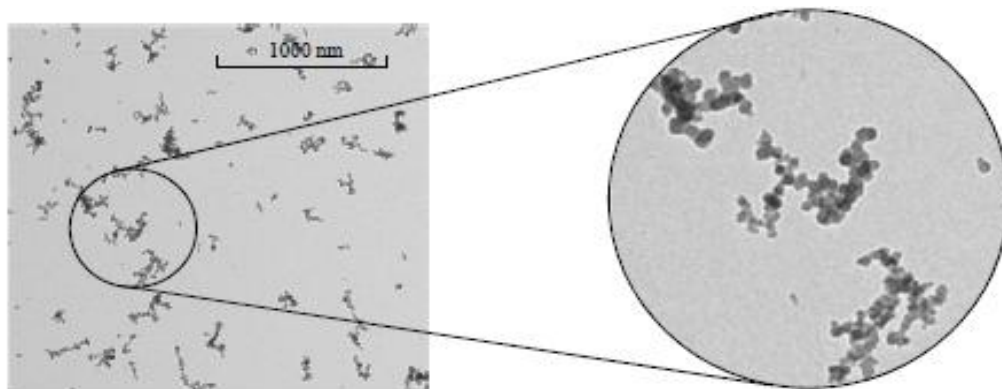


Figure 1.13 TEM images of soot agglomerates imaged using transmission electron microscopy [adapted from Snelling, Liu *et al.*, 2004]

Whilst the particle diameter range may span between 10 and 80 nm, the majority are between 15 to 30 nm in size [Amann *et al.*, 1981]. A tailpipe sampling probe and laser elastic scattering based size measurement technique has yielded a size range of 30 to 70 nm [Bruce *et al.*, 1991]. In-cylinder laser elastic scattering experiments in diesel engines have resulted in 30-50 nm (Tree *et al.*, 1994) and 40-65 nm [Pinson *et al.*, 1994] range of particle sizes. The agglomerated soot particles that are formed by the end of the combustion process have been determined to be in the order of 0.1 to 2 μm in size [Ladommatos *et al.* 1994, Vander Wal *et al.* 1999, and Desantes *et al.*, 2005].

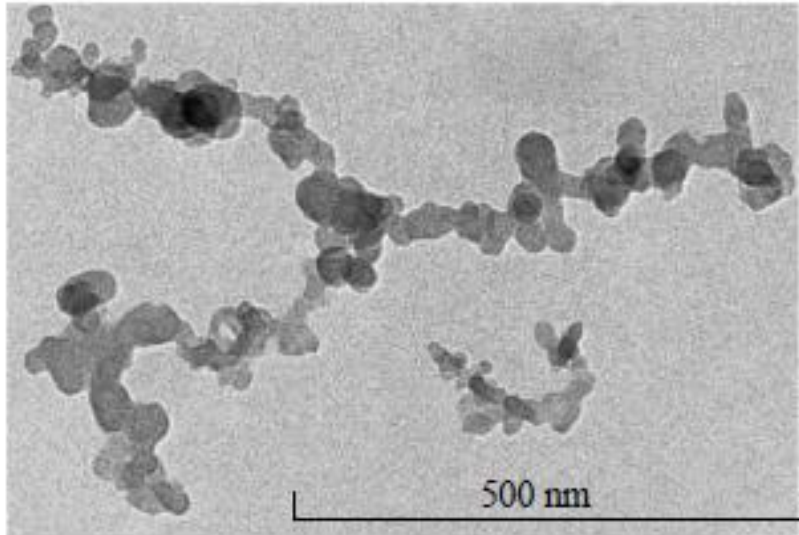


Figure 1.14 TEM image of chain like agglomerates of diesel soot [adapted from Wentzel *et al.*, 2003]

Figure 1.15 shows the graphitic (turbostratic) structure within a soot spherule. It has widely been likened to an ‘onion’ structure in that it is composed of thousands of unordered shells or layers of smaller crystallite structures.

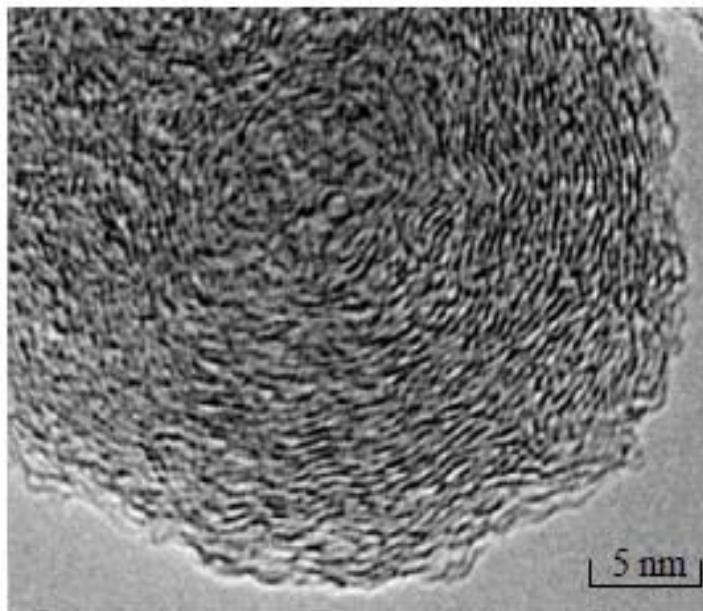


Figure 1.15 Soot spherule composed of nanocrystalline graphitic carbon and portraying an onion shell type structure [Russo, 2015]

Crystallite structures are themselves composed of between two and five platelets that are hexagonally face centered plane arrays of carbon atoms illustrated in Figure 1.16. Though physically and chemically distinct from soot [Watson *et al.*, 2001], and

particularly soot produced through diesel combustion [Clague *et al.*, 1999], carbon black has typically been used as an experimental analogue. For carbon black, platelet separation is typically between 0.35 and 0.36 nm.

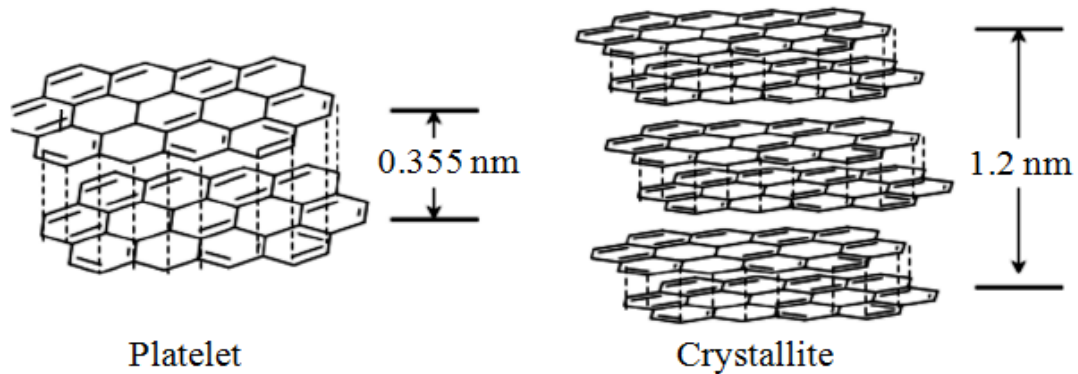


Figure 1.16 Substructure schematic of carbon particles [Vander Wal *et al.*, 1999]

1.2.8 Harmful Effects of Soot

1.2.8.1 On water and soil pollution

Nutrient enrichment problems (eutrophication) occur in bodies of water when the availability of either nitrates or phosphates becomes too large [Hook *et al.*, 1994]. An alteration in the ratios of nitrogen to phosphorus, silicon, iron, and other nutrients impairs the water quality. These alterations induce change in phytoplankton and lead to production of noxious and toxic brown or red algal blooms. They also stimulate growth of other plants in the water bed and disrupt the chemical balance of nutrients in water bodies, especially in coastal estuaries, neutening biodiversity through excessive nitrogen input. The algal blooms and plant growth causes the death of other plants in the water, which depletes the oxygen content of the water when the plants die, sink, and decay. Such eutrophication can make the bottom strata of water uninhabitable for both marine animals (such as fish and shellfish) and aquatic plants such as sea grass beds. For many species of fish and shellfish, these sea-grass beds are essential nurseries and places to escape from predators.

Atmospheric deposition of air pollutants released from diesel exhaust to ecosystems and their components, such as forests, water bodies, and soil is another significant source of contamination [Arimoto *et al.*, 1989]. Water and soil are contaminated indirectly by dry and wet deposition of diesel exhaust emitted to the atmosphere. Wet deposition is rain, sleet, snow, or fog that has become more acidic than normal. Dry deposition is another form of acid deposition, and this is when gases and dust particles become acidic. Wet deposition dominates the transfer of airborne contaminants to the Earth's surface, but dry deposition may be important in arid areas where ambient concentrations are high and rainfall is limited. In urban areas, sedimentation of large particles is more important than wet deposition, dry gaseous, and small particle deposition [Schroder *et al.*, 1997]. Environmental effects of atmospheric deposition have been studied for a long time, but the mechanism is poorly understood [Arimoto *et al.*, 1989]. Enhanced levels of atmospherically deposited nitric and sulfuric acid (acid rain) adversely affect the health of ecological systems, such as agricultural crops, large water bodies, and forests. Arimoto *et al.*, [1990] concluded that deposition is the dominant source for a variety of chemical contaminants in the Great Lakes.

Atmospheric deposition provides most of the dissolved inorganic and total nitrogen in the nutrient load of the lakes and is responsible for water nitrification and forest damage [Davis *et al.*, 2000]. Atmospheric wet deposition to a high-elevation forest at Whiteface Mountain, NY, was 12 times more efficient at transferring nitrogen to the forest canopy than was dry deposition [Miller *et al.*, 1993]. Heavy metals, PAHs, and dioxins common to diesel exhaust can be transported long distances as gases or DPM. They are often resistant to degradation and are found in relatively high concentrations in many rural and remote areas. Simcik *et al.* [1996] and Wik & Renberg [1991] reported higher atmospheric loading of PAHs in lake sediments in Michigan and

Sweden, respectively. Schroder *et al.*, [1997] reported that wet deposition accounted for 85% of the total deposition of toxic materials in a terrestrial ecosystem. PAHs and dioxins have also been detected in German forest canopy.

1.2.8.2 On Vegetation

Diesel soot settled on the surface of plant leaves obstructs the solar radiation and hinders the process of photosynthesis. It also increases the acidity and causes plant damage [Prasad *et al.*, 2010]. This could lead to development of deep necrotic spots on foliar organs including leaves, flowers, and branches. The pictorial views of effects are shown in Figure 1.17.



Figure 1.17 Effect of soot on vegetation

1.8.2.3 On Visibility

Visibility degradation (or haze) is caused by both primary and secondary particles emissions. It is measured as the light extinction coefficient, which is the natural logarithm of the fractional reduction of light transmission per unit distance, usually expressed as Mm^{-1} (inverse mega-meters) [Pitchford and Malm, 1994]. Light extinction consists of scattering and absorption by gases and particles [Watson and

Chow, 1994]. Clean air scatters light with $\sim 12 \text{ Mm}^{-1}$ at sea level, and NO_2 is the only gaseous pollutant that appreciably absorbs light. Particle light scattering depends on the particle size distribution, which can shift as hygroscopic chemical species absorb water with increasing humidity [Ansari and Pandis, 2000]. Light absorption is mostly due to visibility reduction causes accidents on the roads [Anwar *et al.*, 2017]. The global impacts of soot are described in Figure 1.18. (a) Great Smog of 1952, was a severe air pollution event that affected the British capital of London, enveloped under a toxic mix of dense fog and sooty black smoke for four days [Steve Tracton, 2012], (b) soot from factories creates acid rain that destroyed Europe Black Triangle [Transboundary Pollution in Europe, 2016], (c) soot is now as the second worst greenhouse gas after CO_2 , it warms the atmosphere by absorbing incoming and scattered heat from the sun [The guardian, environment, 2013], and (d) soot emission warming at the Earth's surface, lead to cooling in the upper atmosphere. This cooling promotes formation of more clouds that destroy ozone layer [John Bluck, NASA ARC, 2001].

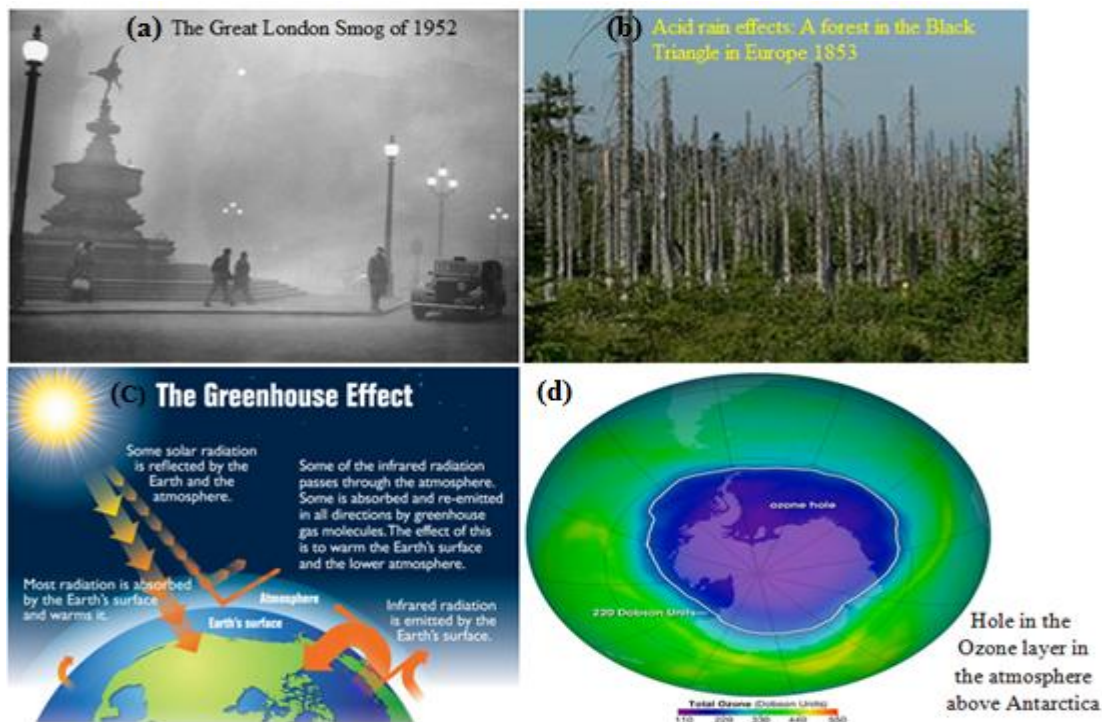


Figure 1.18 Effects of soot on Environment

Fine particles of soot and the ones formed in the atmosphere by the conversion of NO_x emission scatter light and create hazy conditions which decrease visibility and contribute to regional haze [Husar *et al.*, 2000]. The impact of diesel particulate matter on visibility ranges from continental regional haze to the small-scale impacts that occur from an individual vehicle's exhaust plume. Diesel engines could contribute from 10% to 75% of visibility degradation in urban areas, depending on surrounding source characteristics [Eldering *et al.*, 1996]. Visibility reduction causes accidents on the roads and leads to mortality. Visibility impairment also causes loss of scenic vistas as shown in Figure 1.19, air pollutants including diesel soot serious impact on atmospheric visibility in Delhi due to the rapidly expanding industrial and vehicular developments [Goyal *et al.*, 2014]



Figure 1.19 Effect particulate matters in the air (PM_{2.5}) in Delhi

Visibility degradation (or haze) is caused by both primary and secondary particles emissions. It is measured as the light extinction coefficient, which is the natural logarithm of the fractional reduction of light transmission per unit distance, usually expressed as Mm^{-1} (inverse mega-meters) [Pitchford and Malm, 1994]. Light extinction consists of scattering and absorption by gases and particles [Watson and Chow, 1994]. Clean air scatters light with $\sim 12 \text{ Mm}^{-1}$ at sea level, and NO₂ is the only

gaseous pollutant that appreciably absorbs light. Particle light scattering depends on the particle size distribution, which can shift as hygroscopic chemical species absorb water with increasing humidity [Ansari and Pandis, 2000]. Light absorption is mostly due to ABC visibility reduction causes accidents on the roads.

1.8.2.4 On Materials

Soot and acid particles deposition damage materials and cultural resources. Significantly large number of properties of aesthetic and historical importance including building, bridges, tunnels, monuments and statues are in danger due to the corrosion caused by the depositions. Structures made of limestone and marble are more sensitive to acid deposition. Acid particles and deposition increase the rate of weathering for these materials, eventually resulting in aesthetic and/or structural damage. The pictorial view (Figure 1.20) of our monument (Agra Taj Mahal) is affected due to the soot [Bergin MH *et al.*, 2015].

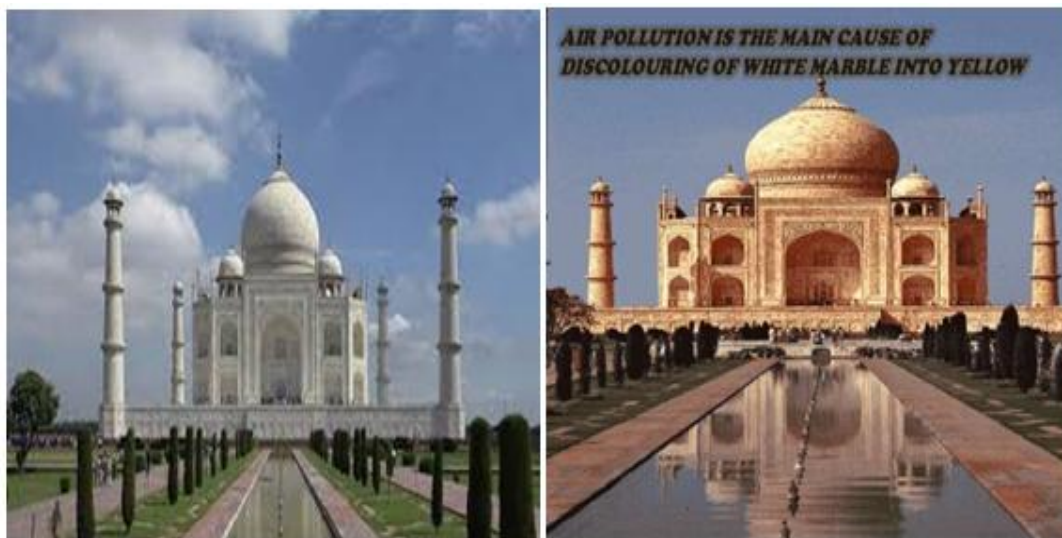


Figure 1.20 Effect of soot emission on monuments

1.2.8.5 On Health

Emissions from diesel vehicles have been reported to be significantly more harmful than those from petrol vehicles. Diesel combustion exhaust is a source of

atmospheric soot and fine particles, which is a component of the air pollution implicated in human cancer, heart and lung damage, and mental functioning. Moreover, diesel exhaust contains contaminants listed as carcinogenic (Group 1) for humans by the World Health Organization (WHO). As we breathe, the small particles of diesel exhaust are drawn into the lungs. The microscopic particles in diesel exhaust are less than one-fifth the thickness of a human hair and are small enough to penetrate deep into the human lungs, where they contribute to a range of health problems [Cassee *et al.*, 2012 and Steiner *et al.*, 2016].

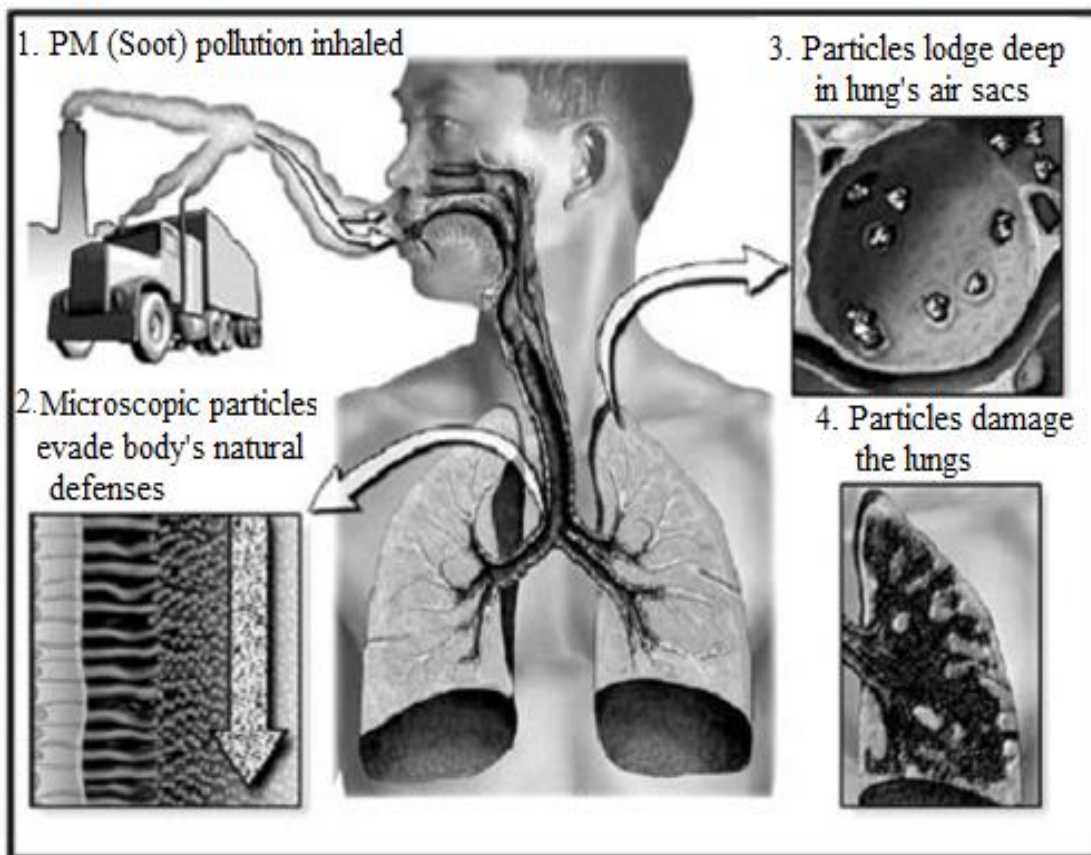


Figure 1.21 Different effects of soot on health

Exposures have been linked with acute short-term symptoms such as headache, dizziness, light-headedness, nausea, coughing, phlegm, difficult or labored breathing, tightness of chest, and irritation of the eyes and nose and throat [Armor *et al.*, 2005]. Long-term exposures can lead to chronic, more serious health problems such as

cardiovascular disease, cardiopulmonary disease, lung cancer, and worsening of symptoms in people with asthma [Boyano *et al.*, 2009]. In fact, long-term exposure to diesel increases the risk of exhaust particles poses the highest cancer risk of any toxic air contaminant evaluated by CEPA (California Environmental Protection Agency). It has estimated that about 70 percent of the cancer risk that the average Californian faces from breathing toxic air pollutants stems from diesel exhaust particles by California Air Resources Board (CARB). It has also been reported that children are especially affected by soot exposure by significant reduction in lung growth as the soot particles disrupts the cellular growth. Soot also has potential hazardous effects on newborn children including birth defects, growth retardation and sudden infant death. Soot particles can also induce inheritable mutations [Krewski *et al.*, 2002, and Somers *et al.*, 2004].

Figure 1.21 shows transport of soot particles with breath inside our body. Large particles, PM_{10} deposit from the air into the nose, throat, and lungs, causing coughing and irritating the throat, and are ejected from the body through sneezing, coughing, and nose blowing. Coarse particles ($2.5-10\mu m$) inhaled into the windpipe and settle there, causing more irritation and more coughing. Fine and ultra-fine soot particles ($< 2.5\mu m$, $PM_{2.5}$) the most successful at invading the body, being small enough and inhaled into the deepest parts of the lungs where it is able to enter the bloodstream and even reach the brain, [Zhu *et al.*, 2007] can accumulate in lungs over time, obstructing oxygen transfer to the blood and causing many health problems [Oberdorster *et al.*, 2004].

1.2.9 Approaches for Diesel Soot Reduction

To control the diesel emissions various technologies have been introduced from time to time in the past decades. The major technologies that have been employed to control PM are as follows:

- a) Diesel oxidation catalysts (DOC)

- b) Diesel Particulate Filter (DPF)
 - i. Continuously Regenerating Trap (CRT)
 - ii. TU Delft Filter

1.2.9.1 Diesel oxidation catalysts (DOC)

Diesel oxidation catalysts (DOC) have been used for controlling the diesel emissions since the early 70's. DOCs can reduce more than 90% of the CO and HC emissions coming from the combustion chamber by oxidizing them into CO₂ and H₂O [Cooper and Roth, 1991]. These are generally based on flow through monolith structure coated with oxidizing catalyst such as Pt or Pd [Howitt and Montierth, 1981].

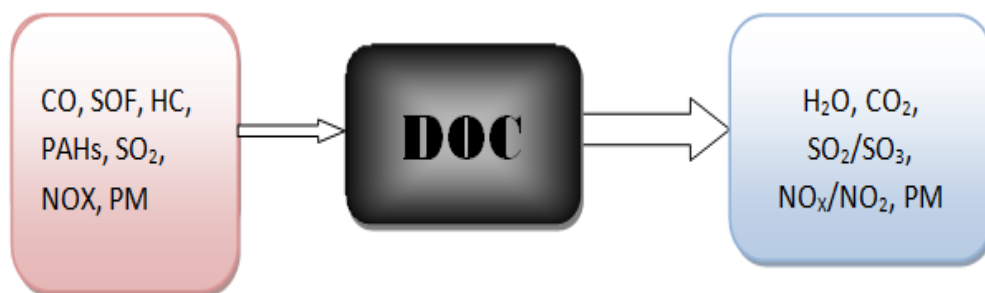


Figure 1.22 Function of a DOC Catalyst

The working principle of a typical DOC is depicted in Figure 1. 22, which is fitted with engine exhaust system. DOC efficiently removes CO, HC, and some particulate mass, which are absorbed hydrocarbons on the soot but it has some limitations also. It does not alters the amount of PM and NOx and requires low sulfur fuel. The sulfur content of the fuel has considerable effect on the activity of the oxidation catalyst [Huang *et al.*, 2004]. The catalyst oxidizes SO₂ into SO₃ which further combines with water to form sulfates and add to the particulate matter. DOCs are found to perform better with fuels having sulfur content up to 500ppm. One other route is fuel borne catalyst which involves mixing of the catalyst directly in the fuel and

is not supported on the filter. Fuel-borne catalysts (FBC) are colloidal dispersion of base metal oxides or organic compounds containing precious or base metal ions such as platinum, cerium or iron which are added to the diesel fuel prior, to the combustion process [Vincent *et al.*, 2003]. The quantity of catalyst added is small, generally in parts per million. FBC are either directly in the fuel tank or mixed with the fuel onboard the vehicle prior to injecting the catalyst-fuel mixture into the cylinder. In the combustion process, the organic fraction of the additive is combusted leaving the inorganic metal or Oxide catalyst finely distributed within the soot particles and other combustion products [Hosoya *et al.*, 1996, Vaaraslahti *et al.*, 2006].

The homogeneous distribution of the catalyst in the fuel prior to combustion results in a fine, intimate distribution of catalysts particles within the soot. The direct contact between catalyst particles and soot particles reduces the temperature required for ignition of trapped particulate matter that is collected together on” the filter media. When used with high efficiency wall-flow filters, the catalyst remains in the filter media and adds to the inorganic ash that accumulates within the filter and must be periodically, removed as part of a regularly scheduled filter maintenance program [Rohart, 2008]. For the better control of PM the concept of DPF (diesel particulate filter) came into picture which was capable of removing soot form the exhaust.

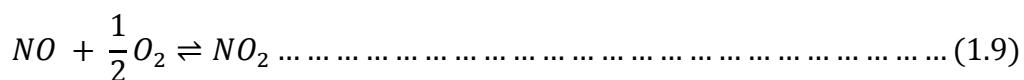
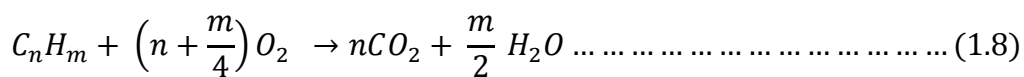
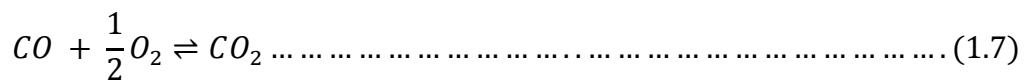


Table 1.2 Functionality of catalyst systems used for diesel oxidation catalysts and diesel Filters

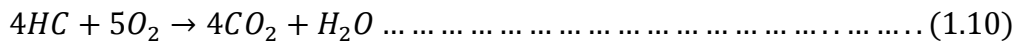
Functionality	Catalytic Components	Comments
Oxidation of gasses and SOF	Noble Metals (e.g. Pt, Pt/Pd)	<ul style="list-style-type: none"> • High Pt loading at typical diesel exhaust temperatures to promote CO and HC oxidation • Production of sulphate particulates • Increased levels of NO₂
Cracking and/or oxidation of SOF	Base Metals (e.g. Ceria)	<ul style="list-style-type: none"> • Often include low loaded Pt • Can be used for PM emission control • Low activity for the oxidation of CO and HC • Produce little sulphate particulates and/or NO₂
Washcoat Storage of HC's	Zeolite	<ul style="list-style-type: none"> • Used for HC trapping • Added to DOC washcoat for cold start improvement
Lean NOx Activity	Platinum	<ul style="list-style-type: none"> • Limiting low-temperature range • Not commercially available
NO ₂ Emission Control at Low Temperatures	Novel Base Metal-Palladium Coatings	<ul style="list-style-type: none"> • Ability to react NO₂ with soot or carbon monoxide under a temperature window of 180-330°C • Limited NO₂ formation above 330°C • Soot combustion with HC/CO conversion properties comparable to Pt-based coatings

In general, the catalytic oxidation mechanism consists of oxygen being bonded to the catalytic sites; reactants of CO and HC diffuse and react with the surface oxygen forming reaction products of CO₂ and H₂O as shown in Equation 1.7 and 1.8. Additionally, oxidation of NO to NO₂ as shown in Equation 1.9 is another reaction which occurs over the DOC. Interest in NO₂ has been attributed to facilitating passive

DPF regenerations as well as enhances the performance of some SCR catalysts. The functionality of catalyst systems used for diesel oxidation catalysts (DOCs) and diesel particulate Filters are shown in Table. 1.2.

In order to respect the PM and HC/CO limit emissions imposed by EURO IV the introduction of DOC was critical. It is a flow-through device that consists of a stainless steel canister containing a honeycomb-like structure or substrate. The substrate has a large surface area coated with a catalyst layer containing a small, well dispersed amount of precious metals such as platinum or palladium.

The DOC is also called 2-way oxidation catalyst because, as the exhaust gases pass through the catalyst, CO and unburned compounds are oxidized according to the following reactions (Equation 1.10):



Diesel oxidation catalyst removes up to 90% of carbon monoxide and hydrocarbons. It can also reduce diesel particulate matter by up to 30%, though typically it is in the region of 8-10%. Actually the used catalysts lead to the oxidation of NO to NO₂, which is more dangerous for human health but which is very useful to improve the performances of downstream devices:

- DPF regeneration (CRT-Continuously Regeneration Trap);
- NH₃ - SCR nitrogen oxides reduction at low temperature

1.2.9.2 Diesel Particulate Filter (DPF)

DPF was introduced in 1980 and was commercially fitted in the passenger cars for the first time in 2000 by PSA Peugeot Citron [Suzuki *et al.*, 2004]. It is one of the most effective and widely used technologies to reduce the PM emissions, DPF are

capable of reducing up to more than 90% of PM [Russell and Epling, 2011]. A typical high efficiency DPF is based on a porous wall, square cell, and honeycomb design with every alternate channel plugged on each end as shown in Figure 1.23. The filter material can be either ceramic or sintered metallic fibers. Exhaust laden with soot, air enters the filter and is forced to pass through the porous walls by the blocked ends. During their passage through the walls, soot gets deposited on the walls and clean gases leave the filter. However, a back pressure is developed on the filter as the operation proceeds and the filter gets blocked by the deposition of soot as shown in Figure 1.24 (b). Increase of the back pressure decreases the efficiency of the engine and consumes more fuel.

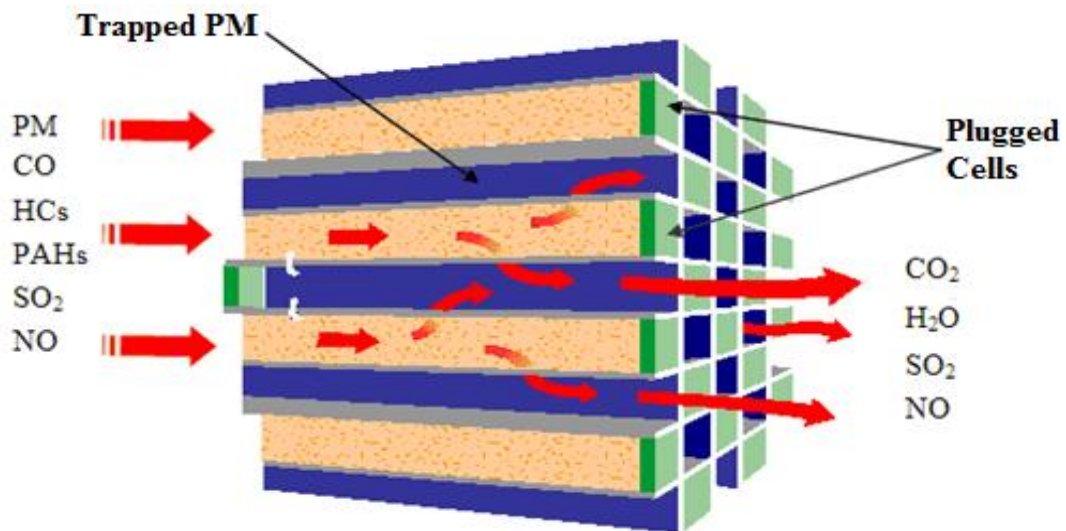


Figure 1.23 Functioning of typical DPF

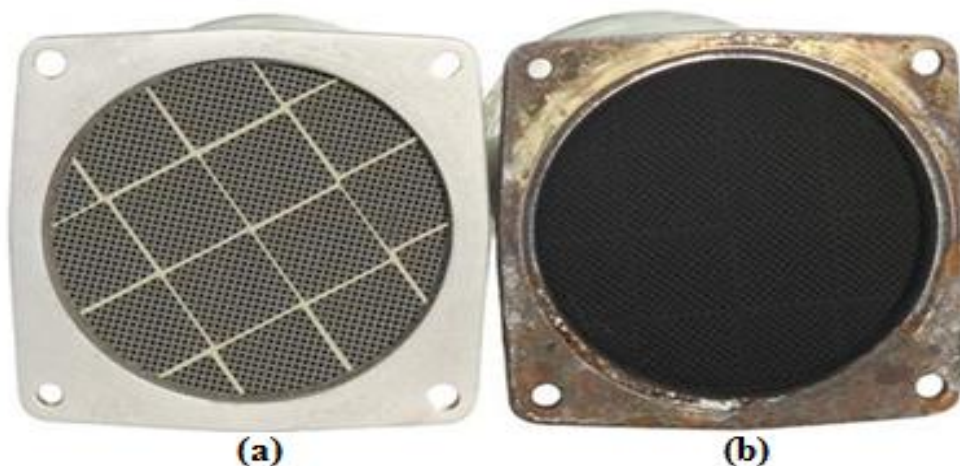


Figure 1.24 (a) Clean DPF and (b) Soot laden DPF

Therefore, to ensure the efficient functioning of the filter its regeneration is required. The regeneration is achieved by burning of the trapped soot which in turn requires high temperature ($>650^{\circ}\text{C}$) [Farrauto and Voss, 1996]. Since, the temperature of the exhaust is very less, as compared to that required for soot oxidation, so soot is oxidized by two methods i.e. active method and passive method. The active method is not continuous but applied periodically when backpressure is exceeded by certain limit. During regeneration of DPF by active method, serious stability problems for the filter materials entails, since temperatures as high as melting point of the filter can be locally reached when the soot is burned suddenly as shown in Figure 1.25. Active regeneration is not favoured as it would increase the local temperature as high as 1200°C [Badani *et al.*, 1996] and it may cause microcracks, which reduce filter durability [Ohno *et al.*, 2000]. In addition, thermal regeneration consumes large amounts of energy.



Figure 1.25 DPF damage due to high temperature

In passive method highly active catalyst is coated over filter to burn the soot at lower exhaust temperature window ($150\text{-}450^{\circ}\text{C}$) to regenerate the filter continuously [Fino *et al.*, 2006]. Being continuous burning of soot, in passive method there is no chance of increase of backpressure. The main challenge of passive DPF is the development of highly active, selective, stable, and regenerative catalyst.

Precious or base metal based catalyst is applied on the surface of the walls which reduce the oxidation temperature to the exhaust temperature window. Most of the catalysts used in the international markets are noble metal based (Pt, Pd), which are expensive and due to a low abundance vulnerable to further price increases upon increasing demand. Therefore, the searches for catalysts free of or low in noble metals are of global importance. Catalyst-based passive regeneration also relies on an upstream oxidation catalyst to facilitate oxidation of nitric oxide (NO) to nitrogen dioxide (NO₂). Nitrogen dioxide is a much stronger oxidizer than oxygen allowing filter regeneration at lower temperatures. The nitrogen dioxide oxidizes the collected particulate thus substantially reducing temperature required to regenerate the filter. In passive process, the continuous regeneration of DPF systems is provided by CRT technique (continuously regenerating trap).

To ensure filter regeneration, various strategies (or combinations) are used. Regeneration methods include:

- Coating the filter substrate with PGM or PGM free, thereby reducing the temperature needed for oxidation of the diesel particulate matter;
- Installing a catalyst (DOC) upstream of the filter, again lowering the exhaust temperature needed to burn off the particulates;
- Using fuel-borne catalysts to reduce the burn-off temperature of the collected particulates. This system uses air to burn the carbon in the filter. An additive is dosed into the fuel and passes through the engine to be deposited on the filter. This additive reduces the temperature at which the carbon will react with the air.

This is a more advanced regeneration system capable to reduce diesel particulate matter attaining low oxidation temperatures. The oxidation behaviour of soot in air that have been ionised by an electric arc (thermal plasma) at temperatures in the range from

200 to 450°C was investigated by Levendis and Larsen [1999]. It was found that the oxidation rate might increase more than 100%. This is attributed to some reactive species generated in plasma, such as O and OH radicals or NO₂ that facilitate the oxidation of soot particles at low temperatures.

There are varieties of diesel particulate filter technologies used as described below. The typical filtration efficiency of diesel particulate filter is mentioned in Table 1.3.

- Fine filtration
- Minimum pressure drop
- Low cost
- Mass production suitability
- Product durability

Table 1.3 Typical filtration efficiency of diesel particulate filters (PM Mass) [Germany BMA 2001], [US non-coal mines MSHA 2001].

Pollutants	Removal efficiency
Elemental carbon	95 - 99.9%
Organic fraction (SOF)	50 - 90%
Sulphate particulates	No filtration
Total PM	70 - 95%

Flow through filter (FTF)

The FTFs are a relatively new technology for reducing diesel PM emissions. Wall flow filters are highly effective and can filter 99% of the particulate matter [Locker *et al.*, 2004]. Unlike a DPF, in which only gases can pass through the filter components-the FTF does not physically "trap" and accumulate PM [Sahoo *et al.*, 2009]. Instead, exhaust flows through a medium (such as wire mesh) that has a high

density of interrupted flow channels, thus giving rise to turbulent flow conditions. The filtration efficiency of an FTF is lower than that of a DPF, but the FTF is much less likely to clog under unfavorable conditions (e.g. high PM emissions, low exhaust temperatures and emergency circumstances). Monolithic diesel filters consist of many small parallel channels, typically of square cross-section, running axially through the part, the flow pattern of exhaust gases as shown in Figure 1.26.

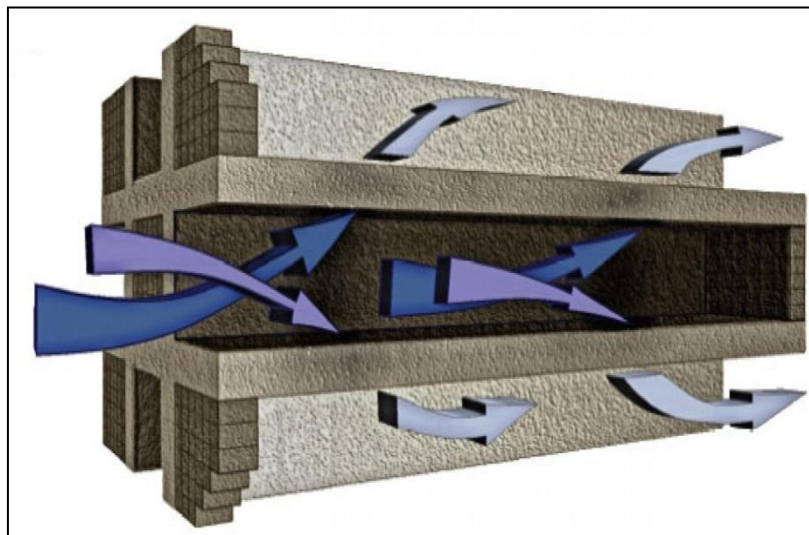


Figure 1.26 Flow pattern in wall flow monolith

Wash coated filter

The alumina Wash-Coated filters (Catalyzed ceramic traps) were developed in the early 80's. Their first applications included diesel powered cars and, later, underground mining machinery. Catalyzed filters were commercially introduced for Mercedes cars sold in California in 1985. The main component of the filter is the ceramic (cordierite, SiC) wall-flow monolith. The porous walls of the wash-coated monolith are impregnated with an active catalyst. Many materials active in soot oxidation catalysts have been studied over the last 20 years as coating of a particulate filter. Mainly oxides of base metals (Ba, Ca, Ce, Co, Cr, Cu, Fe, La, Mn, V) and noble metals (Pd, Pt) as well as mixtures of base and noble metals.

The main drawback of these systems is the poor contact between the catalytic coating and the soot particles. The distance is too high to enforce catalytic action. Only the particulates that are in direct contact with the catalytic coating are able to oxidize. Another problem of catalyzed filters is the generation of oxides by catalytic oxidation of the exhaust SO_2 to SO_3 , at high exhaust temperatures. The gaseous SO_3 can penetrate the porous walls and freely leave the filter. Combining with water and reacting with other materials, it forms sulfate particulates that increase the total PM output especially in case of fuels with high sulfur content. Toyota introduced for the first time a wash-coated filter system (redesigned Avensis, beginning of 2004 in the United Kingdom and Germany), with the diesel particulate NO_x reduction (DPNR). The Automotive Catalyst Division of Umicore (formerly Degussa/dmc²/OMG), has also developed a new catalyst technology for wash coated diesel particulate filters [Gieshoff *et al.*, 2001]. These systems will initially be used in Daimler Chrysler's C-Class and E-class models with 4-cylinder diesel engines, to comply with the 2005 EU IV legislation. The active regeneration strategy for catalytically activated diesel particulate filters, developed jointly with Daimler Chrysler, makes it possible to guarantee filter regeneration without extra additives. Recently, VW/Audi has also announced the introduction of catalyzed DPF systems in large class vehicle models.

Partial-flow filters

Partial-flow filters (Figure 1.27) are available in various materials from fibre-based to metallic. The metallic partial flow filter uses a special perforated metal foil substrate with a metal 'fleece' layer so that the exhaust gas flow is diverted into adjacent channels and the particles are temporarily retained in the fleece before being burnt by a continuous reaction with NO_2 generated by an oxidation catalyst located upstream in the exhaust. The advantages (Babu *et al.*, 2009) of partial-flow filters are: no back pressure

builds up as this is an open system, no external electronic control unit is required, fuel penalty is nil, and regeneration is passive, continuous and maintenance free. Partial Flow Filters control capabilities are as follows: DPM 30-85% on gravimetric basis and approximately 90% on nano particles, HC and CO >50%.

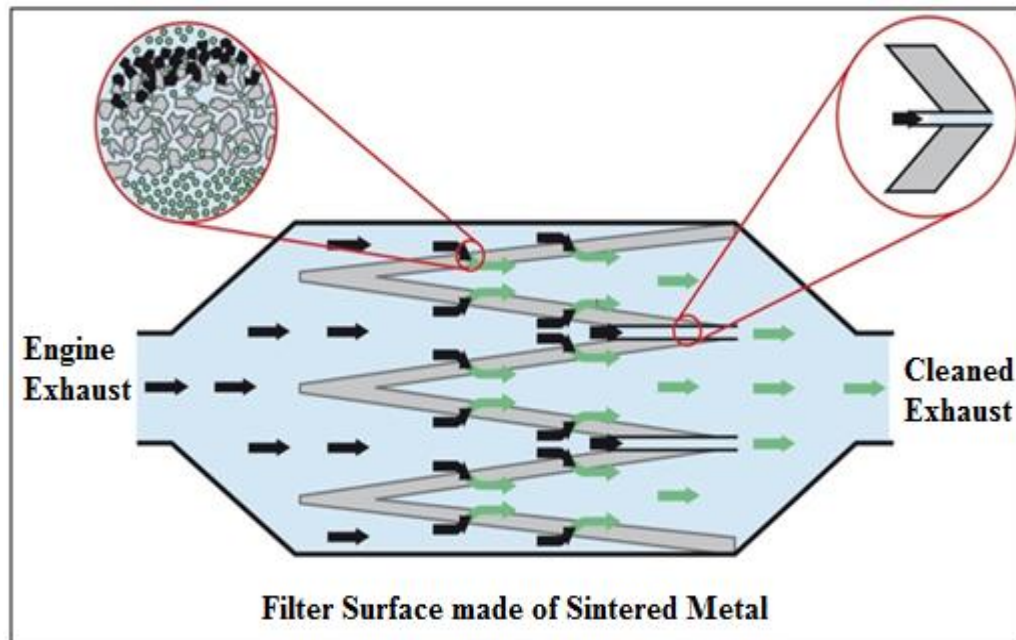


Figure 1.27 Partial flow diesel particulate filters

A combined DOC and a catalyst-coated DPF (diesel exhaust gas treatment equipment) is used to remove particulate matter, hydrocarbons (HC), and carbon monoxide (CO). It is also able to decompose particulate matter directly without using NO_2 as shown in Figure 1.28.

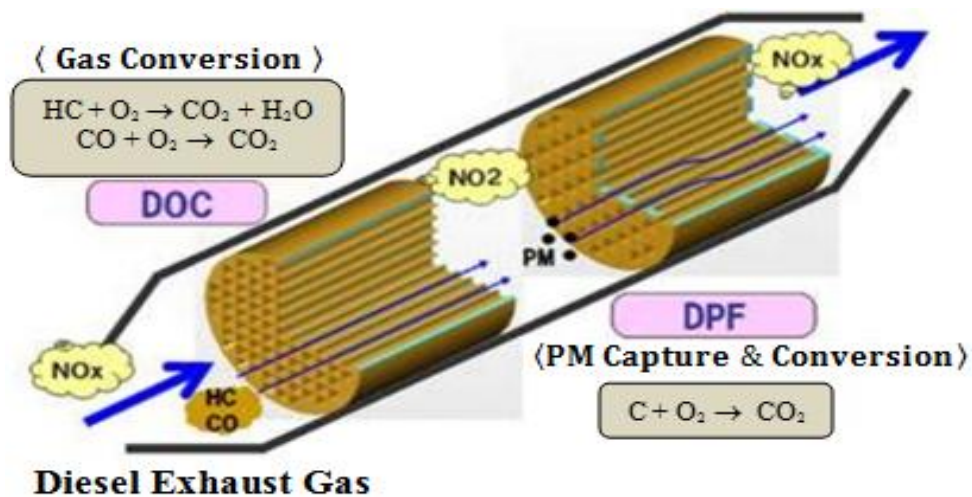


Figure 1.28 Structure of diesel exhaust gas treatment equipment

1.2.9.3 Continuously Regenerating Trap (CRT)

The concept of CRT was developed by researchers from Johnson Matthey. The filter system is composed of two devices an oxidation catalyst (upstream) and a ceramic wall-flow diesel filter (downstream) as a schematic configuration of the CRT is shown in Figure 1.29. Oxidation catalyst generates NO_2 necessary for filter regeneration from NO present in diesel exhaust and NO_2 oxidizes soot which is being trapped in the filter (Figure 1.30). It is aimed that the third generation CRT filter is able to reduce HC and PM by over 90% and CO by over 70%, but is not efficient to reduce NO_x emissions while NO_2 slip occurs [Setiabudi *et. al.*, 2003 and Fino *et al.*, 2006].

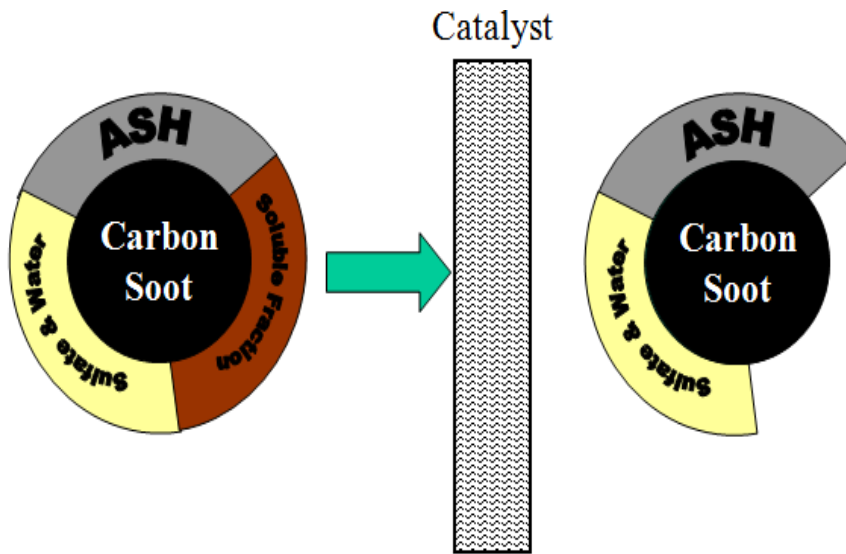


Figure 1.29 Particulate matter reductions by CRT filter

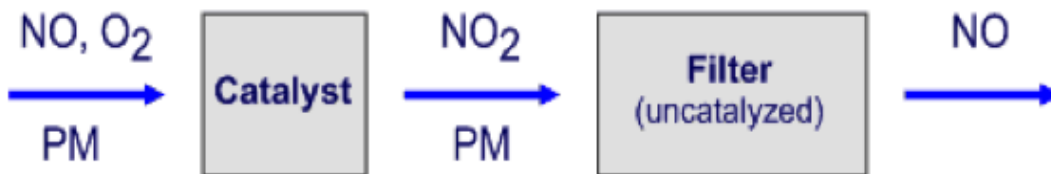


Figure 1.30 Configuration and principle of operation of CRT filter

1.2.9.4 Mechanism for catalytic oxidation of soot

There are two explanations given for catalytic combustion of soot particle. First one, less accepted, is electron transfer mechanism, which suggests a redistribution of the pi electrons in the carbon matrix. Second one, which is widely accepted, is oxygen transfer mechanism where the catalyst is considered as a renewable activated oxygen donor. Catalysts are capable of delivering active oxygen species to the reacting carbon particulate which help in lowering activation energy for soot oxidation. Oxygen chemisorbed on the catalyst surface is the active oxygen center for soot oxidation. Higher the capacity of catalyst to deliver active oxygen species the superior is the activity of catalyst toward carbon oxidation.

Transient thermal analysis studies (oxygen TPD plots) were quite helpful in understanding the behavior of the catalysts toward soot oxidation. Lower the temperature at which oxygen species are desorbed the higher the soot combustion activity. From this standpoint, Fino *et al.*, 2006 compared the activity order of spinel catalysts toward soot combustion as $\text{CoCr}_2\text{O}_4 > \text{MnCr}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$. Comparing with the TPD plots of CoCr_2O_4 and MnCr_2O_4 catalysts, Fino *et al.*, 2006 suggested that the temperature at which the oxygen species can be released is even more important than the amount of such oxygen species [Fino *et al.*, 2006].

Physical contact between soot and catalyst is also an important parameter for soot oxidation. Without physical contact the catalyst could still act as a renewable activated oxygen donor. But activated oxygen radicals recombine themselves too rapidly in the gas phase before reaching carbon. For supported catalysts, it was proposed that activated oxygen could migrate on the support to the carbon. This is called the spillover effect theory [Neri *et al.*, 1997]. Otherwise the catalyst could also catalyze other oxidation reaction of the gas phase. It could accelerate the transformation

of NO to NO₂, which can oxidize the carbon. Also, it can oxidize the CO from the thermal carbon oxidation to CO₂, releasing some heat that can accelerate the carbon combustion. In affirmation with this fact, Fino *et al.*, 2006 compares the results of the runs performed under loose or tight contact conditions and found that there is 60 to 80°C temperature difference for soot combustion, a higher value for loose contact [Fino *et al.*, 2006].

1.3.1 Nitrogen Oxide (NO_x)

Nitrogen oxides are the other primary pollutants emitted from diesel engines. The NO_x are consisted 90% nitric oxide (NO), 4.5% nitrogen dioxide (NO₂) and 0.5% nitrous oxide (N₂O). The N₂O is the greenhouse gas 300 times worse than CO₂ due to its radioactive effect and breakdown of ozone layer [Daniel *et al.*, 2012]. It is possible that NO_x emissions cause an increase in secondary pollutants formation and global warming [Sindhu *et al.*, 2017]. The harmful effects of primary and secondary pollutants are listed in Table 1.4.

1.3.2 NO_x Formation

NO_x is formed when the nitrogen reacts with the oxygen at high temperature at the far end in the engine combustion chamber; it mainly contains NO nitrogen monoxide (~95%) and NO₂ nitrogen dioxide (~5%). The formation of NO₂ however has been found to be variable depending upon the condition of operation. Lean operating conditions leads to the complex formation process and makes it difficult to control of nitrogen oxide emissions [Pope *et al.*, 2002). The formation rate is highly dependent on the temperature in the combustion chamber. NO_x concentration increases exponentially with increase in temperature.

The NO_x generation during combustion processes can take place through following three different reaction paths, which have unique characteristics [Gomez-

García *et al.*, 2005]. There are basically three recognized mechanism on NO_x formation – Thermal, Fuel and Prompt.

1.3.2.1 Thermal NO_x

The reaction between atmospheric nitrogen and oxygen at high temperatures produces NO_x. The typical mechanism of this reaction was established by Zeldovich in 1946 [Fritz *et al.*, 1997]. The proposed mechanism involves a chain reaction of O* and N* activated atoms, NO being the final product. The conversion of NO to nitrogen dioxide (NO₂) occurs at low temperatures when exhaust gases are vented to the atmosphere. The mechanism is given as:

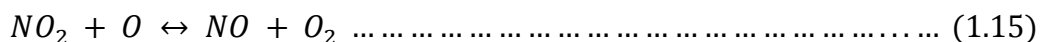
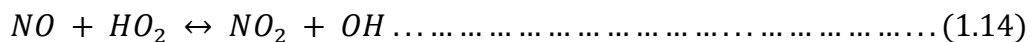
• **NO: Extended Zeldovich mechanism**



The first step is rate limiting, and due to its high activation energy (314 KJ/mol) it requires high temperatures to proceed. Equations (1.11 - 1.13) are only significant under reducing conditions

- Very temperature sensitive: favored at high temperature
- Diffusion flame: locally high temperature
- More severe than SI case because of higher CR

• **NO₂:** High temperature equilibrium favors NO, but NO₂ is formed due to quenching of the formation of NO by mixing with the excess air (Equation 1.14 and 1.15).



- Gets 10-20% of NO₂ in NO_x

By kinetic analysis it is possible to derive an overall expression for the rate of thermal NO_x formation (Bowman, 1975) (Equation 1.16),

$$\frac{d[NO_x]}{dt} = \frac{6.0 \times 10^{16}}{T^{0.5}} \bullet \exp \left\{ \frac{-69090}{T} \right\} \bullet [N_2] \bullet [O_2]^{0.5} \dots \dots \dots (1.16)$$

Where T = absolute temperature (K)

[N₂], [O₂] = concentration of nitrogen, oxygen (mol/cm³)

$\frac{d[NO_x]}{dt}$ = rate of NO_x formation (mol/cm³/s)

In practice, the control/minimization of thermal NO_x is accomplished primarily by measures, which reduce temperature, but dilution of the available oxygen is also beneficial.

1.3.2.2 Fuel NO_x

Fuel NO_x arises from the reaction of the organically bound nitrogen in the fuel with oxygen. The process is complex (reaction schemes typically consider of the order of 50 intermediate species and several hundred separate reversible reactions, and there is still considerable uncertainty as to the true value of the various rate constants, etc.), but can be simply expressed as follows:

- i) Volatile fuel nitrogen is evolved mainly as HCN (and NH₃) during the processes.
- ii) The HCN reacts with various free radical species (O, OH) to form intermediates such as CN, NCO, HNCO and ultimately with reaction with H to produce NH, NH₂,
- iii) Fuel NO_x can be most effectively minimized by burning the fuel by staged combustion, which implies delayed mixing between the fuel gas and air.

Fuel-bound nitrogen (FBN) is the source of NO_x emissions from combustion of nitrogen-bearing fuels such as heavy oils. FBN is converted to fixed nitrogen

compounds such as HCN and NH₃ in the reducing region of the engine (high fuel/air ratio zone). Subsequently, the latter compounds are oxidized to NO_x in the low fuel/air ratio region.

1.3.2.3 Prompt NO_x

Prompt NO_x is formed by the reaction of hydrocarbon radicals with atmospheric nitrogen to produce HCN and hence NO_x via a complex series of gas phase reactions. The contribution of the prompt NO_x to the total emission in pulverized coal combustion is small (about 5%). Measures, which are effective in minimizing thermal and fuel NO_x, are also effective in minimizing prompt NO_x [Sindhu *et al.*, 2017].

In the fuel-rich region, atmospheric nitrogen can react with different hydrocarbon fragments (C, CH, and CH₂), producing nitrogen containing intermediate species (NH, HCN, H₂CN, CN) as shown Equation 1.17, 1.18, 1.19, 1.20, and 1.21. These fragments further react with O₂ in the low fuel/air according to the Fennimore mechanism as shown in Figure 1.31.

- Conversion of N₂ (Rate limiting step)



- Conversion to NO



- conversion to NO via radical/radical reactions

The relative amounts of the three types of NO_x produced depend on factors like type of fuel, temperature of chamber, fuel to air ratio, and the combustion technology employed.

NO_x plays a crucial role in the formation of ozone and secondary aerosol and is involved in the chemical transformation of other atmospheric species (e.g., CO, CH₄, VOCs) through feedback on HO_x (OH + HO₂). Consequently, NO_x can have broader effects on human health, atmospheric composition, acid deposition, air/water quality, visibility, and radioactive forcing. The NO_x and soot emitted from diesel engines causes pollution problems affecting the atmosphere like acid rain, smog, global warming and human health causing respiratory problems, lung cancer, birth defects and mutagenic problems [Galvez *et al.*, 2011].

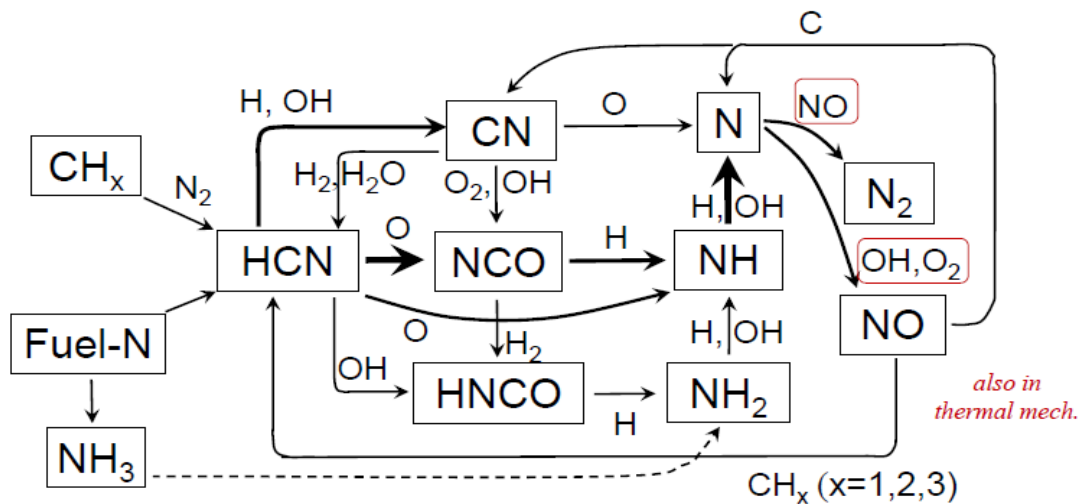


Figure 1.31 Graphical representations of general prompt NO_x mechanism and reactions of rich mixtures/fuels [Bowman, 24th Combustion Symposium]

1.3.3 Effects of NO_x

1.3.3.1 On Human Health by NO_x

In recent years, studies have converged to reveal the importance of NO to the living organisms [Snyder *et al.*, 1992, Anenberg *et al.*, 2017] while the NO emitted

freely from a car engine presents a real hazard of toxicity. In the presence of air, NO is oxidized to NO* and the reaction is known to accelerate in the presence of sunlight and hydrocarbons. This oxide is poisonous for the respiratory system, provoking both lung infection and respiratory allergies since it is able to diffuse through the alveolar cells and capillary vessels of the through the alveolar cells and capillary vessels of the lungs and damage their structure through their propensity towards oxidation [Oberdorster *et al.*, 2004]. Epidemiological studies have revealed that concentrations of nitrogen oxides having hazardous effects for people in good health are above 0.05 ppm for an exposure of over 24h [Bosch *et al.*, 1988]; however, this concentration is often exceeded in towns with dense traffic during peak hours or during the summer. Human and animal are exposed to nitrogen oxide (NO_x) via inhalation. It impacts on lung as a prime target organ, and variety of acute and chronic toxicological effects depending on varying degrees of severity, level of exposure, and concentration as shown in Figure 1.32.

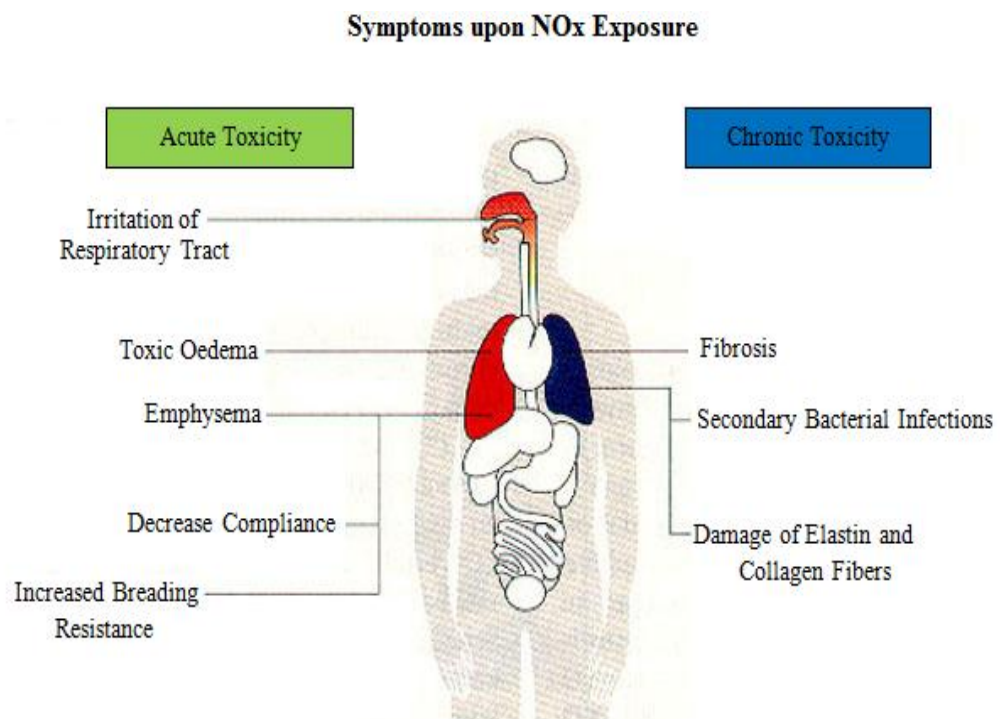


Figure 1.32 Adverse effects of NO_x

Many toxicological and epidemiological studies indicate that exposure of diesel exhaust have been linked with acute short term/long term problems such as irritation of the eyes, nose, and throat, vomiting, light-headedness, headache, heartburn, numbness, bronchitis, chronic respiratory, cardiovascular, cardiopulmonary and allergic diseases such as shortness of breath and painful breathing, cancer, and premature death. Some investigations indicate that particles can induce inheritable mutations [Pope *et al.*, 2002]. Potential health impacts of DPM, ozone and carbon monoxide formed from diesel emissions on new-born children include birth defects, growth retardation and sudden infant death syndrome.

Table 1.4 Lists the primary and secondary pollutants and their harmful effects

Pollutants	Description	Sources	Health Effects	Welfare Effects
Hydrocarbons (HC)	Organic compound consisting entirely of hydrogen and carbon	Fuel molecules in the engine do not burn or burn only partially	Irritates the eyes, damages the lungs, and aggravates respiratory problems	Ground-level ozone
Particulate Matter (Soot)	Impure carbon; Very small particles of soot, dust, or other matter.	Diesel engines, power plants, industries, incomplete combustion of hydrocarbons; windblown dust, wood stoves.	Eye irritation, asthma, bronchitis, lung damage, cancer, heavy metal poisoning, cardiovascular effects.	Visibility impairment, atmospheric deposition, aesthetic damage.
Sulfur Dioxide (SO ₂)	Colorless gas that dissolves in water vapor to form acid, and interact with other gases and particles in the air.	Coal-fired power plants, petroleum refineries, manufacture of sulfuric acid and smelting of ores containing sulfur.	Eye irritation, wheezing, chest tightness, shortness of breath, lung damage.	Contribute to the formation of acid rain, visibility impairment, plant and water damage, aesthetic damage.
Carbon Monoxide (Co)	Colorless, odorless gas	Motor vehicle exhaust, indoor sources include kerosene or wood burning stoves.	Headaches, reduced mental alertness, heart attack, cardiovascular diseases, impaired fetal development, death.	Contribute to the formation of smog.

Nitrogen Oxides (NO _x)	Reddish brown, highly reactive gas.	Motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels.	Susceptibility to respiratory infections, irritation of the lung and respiratory symptoms (e.g., cough, chest pain, difficulty breathing).	Contribute to the formation of smog, acid rain, water quality deterioration, global warming, and visibility impairment.
Ozone (O ₃)	Secondary gaseous pollutant, it is formed in the troposphere.	Vehicle exhaust and certain other fumes. Formed from other air pollutants in the presence of sunlight.	Eye and throat irritation, coughing, respiratory tract problems, asthma, lung damage.	Plant and ecosystem damage.
Peroxy acetyl nitrate (PAN)	Secondary pollutant present in photochemical smog, an oxidant that is more stable than ozone	Thermally unstable and decomposes into peroxyethanoyl radicals and NO ₂	Powerful respiratory and eye irritants present in photochemical smog.	Carrier for oxides of nitrogen (NO _x), causes ozone formation in the global troposphere
Polycyclic aromatic hydrocarbons (PAH)	PAHs emissions of diesel engine fueled with diesel, biodiesel (B100) and its blend (B20)	Exposure to diesel exhaust	Chronic or long-term effects, includes decreased immune function, cataracts, kidney and liver damage (e.g. jaundice), breathing problems, asthma-like symptoms, and lung function abnormalities	Carcinogenic and mutagenic effects and are potent immunosuppressants.
Lead (Pb)	Metallic element	Metal refineries, lead smelters, battery manufacturers, iron and steel producers.	Anemia, high blood pressure, brain and kidney damage, neurological disorders, cancer, lowered IQ.	Affects animals and plants, affects aquatic ecosystems.

1.3.3.2 Global Warming

NO_x and soot both positively contribute to enhance the problem of global warming. Soot has been reported to contribute majorly to global warming next to carbon dioxide [Collins *et al.*, 2010]. It absorbs solar radiation while it is suspended in the atmosphere. Also, soot deposition on the surface of snow and ice bodies melts them by absorbing sunlight. NO_x, like other greenhouse gases, also has the tendency to absorb long wavelength infra-red radiations and thus holds heat. NO₂ reacts in the

presence of air and ultraviolet light (UV) in sunlight to form ozone and nitric oxide (NO). The NO then reacts with free radicals in the atmosphere, which are also created by the UV acting on volatile organic compounds (VOC). Higher temperatures, strong sunlight and a stable air mass are ideal for formation of ground-level ozone. Ozone, if present, in sufficient amount, permeates to the lung cells, rendering them more susceptible to toxins and microorganisms.

Due to global warming, several other problems are encountered like harm to public health, more frequent, longer and severe heat waves, increment in electricity demand, smog formation and increase in forest fires, rise in sea levels [Neeft *et al.*, 1997]. During hot summer days, frequent air conditioner use leads to increased demand for electric power production and an associated increase in smog-forming pollutants, such as nitrogen oxide (NO_x) emissions. Hot and dry weather associated with global warming is an ideal condition for large wildfires. Wildfire smoke, a mixture of fine particles including soot and ash, poses significant health risks ranging from irritation to the eyes, nose and throat to aggravation of existing heart and lung disease, such as congestive heart failure, chronic obstructive pulmonary disease, emphysema and asthma.

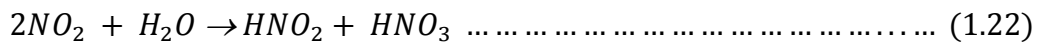
Excess tourist, vehicular movements, destruction of forest, increasing aerosol and soot (PM_{2.5}) concentration that causes unprecedented changes in the climatic condition such as for glacier outburst flood in Kedarnath region of Uttarakhand (16- 17 June 2013) (Figure 1.33 a), Drought fears in Vidarbha (March, 2016) (Figure 1.33 b), high rainfall unexpected area like Jammu Kashmir (September 2014) (Figure 1.33 c), slowing Arctic ice melt (Figure 1.33 d) [Shukla *et al.*, 2016].



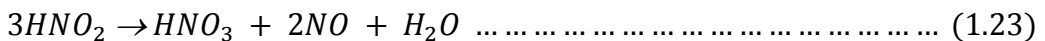
Figure 1.33 Localized effect of soot on environment

1.3.3.3 Acid rain and dry deposition

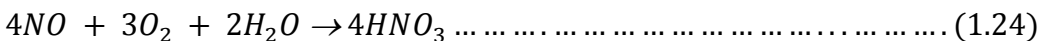
NO_x when captured by moisture in the atmosphere form acids [Arimoto, 19891, as per the following chemical reactions Equation 1.22:



Nitrous acid then decomposes as follows in Equation 1.23:



Further, NO oxidizes to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid (Equation 1.24):



Acid deposition occurs from airborne acidic or acidifying compounds, primarily nitrates that can be transported over long distances before returning to earth. This

occurs through rain or snow ret deposition), fog or cloud water (cloud deposition), or transfer of gases or particles (dry deposition). The acid deposition can damage vegetation and cause lakes and streams to acidify. These acid precipitations perturb ate the aquatic ecosystems and causes the biological death of lakes and rivers. Acid rain upsets chemical balance of aquatic wildlife, killing fishes. Acidification (low pH) and the chemical changes that result, including higher aluminum levels, take it difficult for some fish and other aquatic species to survive, grow, and reproduce.

Acid rain can harm forest ecosystems by directly damaging plant tissues by soil idification and depletion of soil nutrients and hampering the growth of the plants. One of the best examples of direct damage involves the leaching of nutrients from the needles of red spruce, Much reduces the ability of the trees to tolerate cold winter temperatures and has contributed to decline of red spruce forests throughout the mountains of the eastern U.S. [Eyring *et al.*, 2007]. Acid deposition and particles speeds up weathering of monuments, buildings, and other tone and metal structures which are inherent part of cultural heritage.

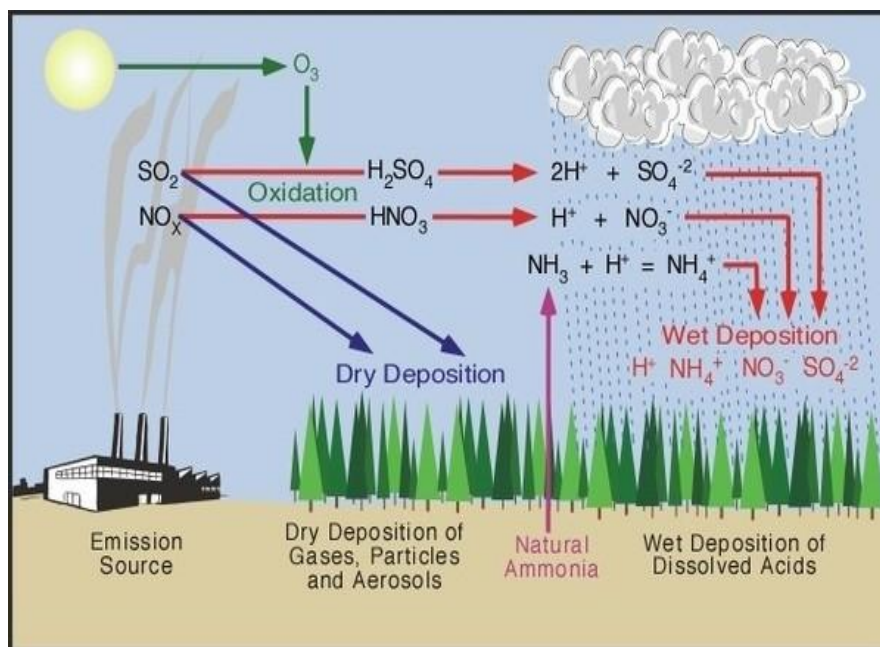


Figure 1.34 Acid rain and dry deposition

In other cases, acid rain can combine with hydrocarbons and other atmospheric constituents in presence of sunlight forming toxic secondary pollutants such as ozone, peroxy- acetyl nitrate (PAN), smog, etc. as pictorially shown in Figure 1.34. Wet deposition is rain, sleet, snow, or fog that has become more acidic than normal. Dry deposition is another form of acid deposition, and this is when gases and dust particles become acidic.

1.3.3.4 Emission and Legislations

PM is often called “smoke” because it’s the soot that comes out of the exhaust pipe appearing as smoke. It’s essentially an incomplete combustion of diesel fuel. Table 1.5 shows the detail concentration of all the components emitted from diesel exhaust however it varies depending on engine design, operating conditions (idling/ accelerating/ cruising/ decelerating), fuel composition and age of the engines [Fiebig *et al.*, 2014, Dhal *et al.*, 2016, 2017].

Table 1.5 Typical diesel exhausts composition [Jelles, 1999]

Component	Concentration
CO	100-10000 ppm
HC (C1)	50-500 ppm,
NO _x	30-1000 ppm
Sox	Proportional to fuel S content
DPM	20-200mg/m ³
CO ₂	2-12 vol%
Ammonia	2.0 mg/mile
Cyanides	1.0 mg/mile
Benzene	6.0 mg/mile
Toluene	2.0 mg/mile
PAH	0.3 mg/mile

Primary pollutants react with hydrocarbons and other atmospheric constituents in presence of sunlight forming toxic secondary pollutants such as ozone, PAN, smog,

etc. Due to harmful effects of primary and secondary pollutants the international legislation from the early 80's has acknowledged the problem and posed limits on these emissions. The standards have the detail limits to diesel engine emissions as shown in Table 1.6. It reflects that in developed countries lowering of the PM emissions of the order of 80%, with progressive Euro standard from 1992 to 2014 for light duty vehicles (LDV) as Euro 1 - 6 and heavy duty vehicles (HDV) as Euro I - VI. While in developing countries including India, BS IV equivalent to EURO IV norms is operative even today.

Table 1.6 Euro emission standards for diesel vehicles

(A) Diesel car [g/km]						
Standard	Year	HC + NO_x	NO_x	CO	PM	
EURO 1	1992	0.97	-	2.72	0.14	
EURO 2	1996	0.70	-	1.00	0.10	
EURO 3	2000	0.56	0.50	0.64	0.05	
EURO 4	2005	0.30	0.25	0.50	0.025	
EURO 5	2009	0.23	0.18	0.05	0.005	
EURO 6	2014	0.17	0.08	0.50	0.005	
(B) Light duty trucks [g/km]						
Class	Standard	Year	HC + NO_x	NO_x	CO	PM
<1305kg)	EURO 1	1994	0.97	-	2.72	0.14
	EURO 2	1998	0.7	-	1.0	0.08
	EURO 3	2000	0.56	0.50	0.64	0.05
	EURO 4	2005	0.30	0.25	0.50	0.025
	EURO 5	2009	0.23	0.18	0.50	0.005
	EURO 6	2014	0.17	0.08	0.05	0.005
(1305-1760kg)	EURO 3	2001	0.72	0.65	0.80	0.07
	EURO 4	2006	0.39	0.33	0.63	0.04
	EURO 5	2010	0.295	0.235	0.63	0.005
	EURO 6	2015	0.195	0.105	0.63	0.005
	EURO 1	1994	1.70	-	6.90	0.25

(>1760kg)	EURO 2	1998	1.2	-		0.17
	EURO 3	2001	0.86	0.78	1.5	0.10
	EURO 4	2006	0.46	0.39	0.95	0.06
	EURO 5	2010	0.350	0.28		0.005
	EURO 6	2015	0.215	0.125	0.74	0.005
(C) Heavy duty diesel trucks [g/kwh]						
Standard		Year	HC	NO_x	CO	PM
EURO I		1992 (<85kw)	1.1	8.0	4.5	0.61
		1992 (>85kw)	1.1	8.0	4.5	0.36
EURO II		1996	1.1	7.0	4.0	0.25
		1998	1.1	7.0	4.0	0.15
EURO III		2000	0.66	5.0	2.1	0.10
EURO IV		2005	0.46	3.5	1.5	0.02
EURO V		2008	0.46	2.0	1.5	0.02
EURO VI		2013	0.13	0.4	1.5	0.01

Indian government has also imposed various norms and setup Bharat Stage (BS) emission standard parallel to Euro norms to regulate the output of air pollutants from IC engine machineries, including motor vehicles. Table 1.7 shows that the BS emission standards for diesel vehicles are lagging behind Euro norms. The Indian emission standard jumped from BS IV to BS VI bypassing BS V. The BS VI emission standard was implemented in April, 2018. Whereas, the Euro VI norms were implemented in September, 2014.

Table 1.7 Bharat stage emission standards for diesel vehicles

Standard	Reference	Date	Region
India 2000	Euro 1	2000	Nationwide
Bharat Stage II	Euro 2	2001	NCR*, Mumbai, Kolkata, Chennai
		April 2003	NCR*, 11 Cities†
		April 2005	Nationwide

Bharat Stage III	Euro 3	April 2005	NCR*, 11 Cities†
		April 2010	Nationwide
Bharat Stage IV	Euro 4	April 2010	NCR*, 13 Cities‡

* National Capital Region (Delhi)

† Mumbai, Kolkata, Chennai, Bangalore, Hyderabad, Secunderabad, Ahmedabad, Pune, Surat, Kanpur and Agra

‡ Above cities plus Solapur and Lucknow. The program was later expanded with the aim of including 50 additional cities by March 2015.

- **Diesel emission regulations**

The ill-effect posed by the vehicular emissions has made the emission regulating legislation stricter over the years [Tables 1.8-1.12, Refs. www.dieselnet.com and www.delphi.com). The increased environmental concern reduced the standard emission levels of PM and NO_x for Euro 5 to Euro 6 for light duty vehicles from 5 to 4.5 mg/km and 180 to 8 mg/km respectively. For heavy duty vehicles the reduction in emissions of PM and NO_x from Euro V to Euro VI were 30 to 16 mg/kWh and 600 mg/kWh to 2000 mg/kWh respectively. Thus, Euro 5/V had mainly focused on reduction of soot emissions. However, Euro 6/VI primarily alerted on the reduction of NO_x emissions, which was implemented in September 2014.

Table 1.8 Emission limits for diesel light vehicles and heavy vehicle

Vehicle	LDV(mg/Km)			HDV(mg/kWh)		
	Euro 4 (2005)	Euro 5 (2011)	Euro 6 (2014)	Euro IV (2005)	Euro V (2009)	Euro VI (2014)
Soot	25	5.0	4.5	30	30	10
NO _x	250	180	80	3500	2000	4000

- India Environmental Standards of Vehicular Exhaust

Table 1.9 Emission norms in India for passenger cars

Norms	1991	1996	1998	BS-2000	BS-II	BS-III	BS-IV
HC+ NOx (g/km)	2.0 (Only HC)	3.00- 4.36	1.50-2.18	0.97	0.5	0.35 (combined)	0.18 (combined)

Table 1.10 Emission norms for 3 wheelers

Norms	1991	1996	BS-2000	BS-II	BS-III
HC+ NOx (g/km)	8-12 (only HC)	3.6	2.0	1.5	1.0

Table 1.11 Emission norms in India for heavy diesel vehicles

Norms	1991	1996	BS-2000	BS-II	BS-III	BS-IV
HC (g/kmhr)	3.5	2.4	1.1	1.1	1.6	0.96
NOx (g/kmhr)	18	14.4	8.0	7.0	5.0	3.5
PM (g/kwhr)	–	–	0.36	0.15	0.10	0.02

Table 1.12 Implementation schedules of EU emission standards in India

Norms	Euro	Year	NOx g/km	HC + NOx (g/Km)	Soot (g/Km)	Light duty diesel (mg/km) (1- 6)		Heavy duty diesel (mg/kWh) (I-VI)	
						NOx	Soot (DPM)	NOx	Soot (DPM)
1991	-	-	-	2.0 (Only HC)	-	-	-	-	-
1996	-	-	-	3.00 - 4.36	-	-	-	-	-
1998	-	-	-	1.50 – 2.18	-	-	-	-	-
India 2000	Euro 1	2000	0.50	0.97	-	-	140-250	800	360
BS II	Euro 2	2001	0.50	0.5	-	-	80-170	700	150
BS III	Euro 3	2005	0.25	0.35	-	500-780	50-100	500	100
BS IV	Euro 4	2010	0.180	0.18	-	250-330	25-40	350	20
BS V	Euro 5	2011	0.180	0.16	0.005*	180-235	5	180 mg/km	5 mg/Km
BS VI	Euro 6	2014	0.080	0.170	0.005*	80	4.5	80 mg/km	4.5 mg/km

*Introduction of a limit that did not exist for the Euro 4 standard

1.3.3.5 Overview of Diesel Emissions and Current Situation

The challenge for CI diesel engines lies primarily on the control of the three pollutant phases (solid, liquid, and gaseous) emitted from the exhaust, which is much more complicated than the control of gas phase emissions from spark-ignition (SI) gasoline engines. In a diesel engine, the resulting exhaust gas contains a large amount of O₂, thus three-way catalysts (TWC), which rely primarily on a the stoichiometric mixture of fuel and air, cannot be employed as a balance of pollutants is required in the exhaust in order to carry out both oxidation and reduction reactions [York *et al.*, 2010]. The emissions from a diesel engine are composed of gaseous pollutants and PM. The particulates are an amalgamation of soot and other liquid or solid phase materials that are collected once exhaust gasses are passed through a filter medium below 52°C (EPA) or 47°C (EC) and are responsible for the black smoke associated with diesel powered vehicles. Soot (referred to as the insoluble dry fraction), mostly clusters of solid carbon particles are formed from the unburned fuel, nucleating from the vapor to solid phases in the fuel-rich regions during combustion [Ganesan, 2008]. Depending on the local conditions, the hydrocarbons may then condense on or be adsorbed by the soot forming soluble liquid or solid phase materials. The liquid HC (i.e. the heavier component of the HC emission) present in the PM is a combination of unburned diesel fuel and evaporated lubricating oil which appear as soluble (SOF, soluble organic fraction) or volatile organic compounds (VOF, volatile organic fractions) in the exhaust which tend to adsorb onto the dry carbon particles [Tree and Svensson, 2007, Kennedy, 1997].

The main constituents which make up the gaseous phase are the HC (i.e. the lighter component of the HC emission), CO, oxides of nitrogen (NO, NO₂; etc) and sulphur dioxide (SO₂) [Farrauto and Voss, 1996, Vaaraslahti *et al.*, 2006]. SO₂ emissions from internal combustion engines are solely a result of fuel-bound sulphur

and are readily reduced by limiting sulphur in the fuel. HC's are divided into nonreactive and reactive categories, based upon their role in photochemical smog formation. The simplest such breakdown is categorising HC's as methane (CH₄) and non-methane hydrocarbons (NMHC's) since all HC's except for CH₄ will react given sufficient time. Actual emissions vary greatly on engine design, fuels combusted, and combustion and post-combustion controls involved. Few of the factors affecting air pollutant emissions include ignition and valve timing, fuel types and additives combusted, the lubricants employed in the engine, and exhaust gas treatments employed. Although the diesel engine is an appealing solution for CO₂ reduction, there remains a challenge to control simultaneously NO_x and PM emissions to a level essential by prevailing regulations [Kitano *et al.*, 2005, Abu-Jrai *et al.*, 2006]. Unfortunately, if the diesel combustion systems are not well controlled, it can produce higher levels of PM and/or NO_x. PM, which is composed of soot and sulphate bound with water and unburned oil and fuel, can have associated health issues. NO_x, which is formed by oxidation of atmospheric and/or fuel contained nitrogen at high temperatures in the power cylinder, is capable of producing smog and acid rain, therefore polluting waterways and crops [McGeehan *et al.*, 2005].

Since PM and NO_x emissions from current diesel technologies are close to the limits permitted by regulations and both limits will become more strict in the near future, these two emissions will be critical factors in the development of new diesel engines. An upgrade knowledge of the potential to reduce these types of emissions could help engine manufacturers adapt their engines to the use of bio-fuels and to optimise them. This can be done by readjusting the compromise between efficiency, costs, and emissions within the regulation limits (Lapuerta *et al.*, 2008a). However as engines are currently calibrated to be as effective as possible while complying with the

emission standards, there still stands a trade-off between the emissions potential and efficiency. Among other solutions to reduce both NO_x and PM such as REGR, SCR catalysts, and DPF's, alternative fuels like bio-fuels and designed fuels such as Fischer-Tropsch (F-T) diesel fuels appear to be the feasible short term solution [Abu-Jrai *et al.*, 2006]. There are two strands to the European Legislation which promote the use of biofuels, namely article 7bis of the Fuels Quality Directive and the Renewable Energy Directive [Teraoka Y., 2000]. The European directive 2009/EC was adopted to revise the Fuel Quality Directive 98/70/EC. Apart from establishing the target aiming to fulfil 10% of its transport fuel needs from renewable sources, it introduces a requirement for fuel suppliers to lower the greenhouse gas (GHG) intensity of energy supplied for road transport in article 7bis (EC 2009a). The European Union (EU) Renewable Energy Directive sets out a path targeting 15% of energy from renewable sources by 2020 (RES 2009). With ongoing improvements aimed at enhancing performance and reducing noise and emissions, the diesel engine has become an increasingly attractive choice for passenger car applications. Over the past years, stringent emission legislations have been imposed to regulate emissions such as NO_x, smoke, and PM emitted from automotive diesel engines worldwide.

1.3.4 Approaches for Reduction of NO_x in Diesel Engine

The limits of NO_x emissions set by legislations cannot be accomplished by either engine modifications, fuel pre-treatments, and more simply by a better tuning of the combustion process [Fino *et al.*, 2008, Musthafa *et al.*, 2016]; a convenient way of treating off-gases require the development of a secondary or clean-up technology, it measures include both wet and dry methods [Chithambaramasari *et al.*, 2011]. So far the wet methods are limited to small waste stream cleanup and are not suitable for NO_x removal from large volumes of flue gases [Ming *et al.*, 2005] and also for vehicular

exhaust. The dry methods consist of catalytic and non-catalytic types. Catalytic systems are the most efficient techniques for NO_x control. Bosch and Janssen have reviewed details of the various methods developed before 1988. Up-to-date following secondary emissions control technologies have been proposed and being adopted as an end-of-the pipe treatment technologies.

Reducing NO_x is more complicated than DPM in a diesel engine. Thus, it is a significant challenge for the scientific community to improve the efficiency of NO_x removal (DeNO_x) technologies in the transport sector. This task is getting even more important due to the tightening NO_x emission limits throughout the world. Various technologies developed to control the emission of NO_x are as follows:

- i) Exhaust gas recirculation (EGR)
- ii) Selective catalytic reduction (SCR)
- iii) Nonselective catalytic reduction (NSCR)
- iv) NO_x adsorber catalyst (NAC) / NO_x storage and reduction (NSR) / Lean NO_x traps (LNT)
- v) Catalytic decomposition of NO_x

1.3.4.1 Exhaust gas recirculation (EGR)

Exhaust gas recirculation has been used to reduce NO_x emissions in light duty diesel engines [Kreso, 1998; Sasaki, 1997; Mikulic, 1993]. EGR is effective to reduce NO_x because it lowers the flame temperature [Pierpont, 1995] and the oxygen concentration of the working fluid in the combustion chamber, as the formation of NO_x is highly temperature dependent [Levendis *et al.*, 1994]. However, as NO_x reduces, PM, CO and unburned hydrocarbons increases, resulting from the lowered oxygen concentration. EGR works by re-circulating 5-10% of the cooled exhaust gases back to

the engine air inlet in order to lower the combustion temperature (several hundred degrees), and thus lower NO_x emissions.

EGR works by recirculating a portion of the engine's exhaust gas back to the combustion chamber recirculated exhaust gas consists of inert gas (CO₂ and H₂O), which dilutes the incoming air reducing a possible oxygen excess and lowering the adiabatic flame, and peak combustion temperature, responsible for the formation of thermal NO. In modern diesel engines, the EGR gas is cooled by a heat exchanger which allows the introduction of a great mass of recirculated gas (Figure 1.35).

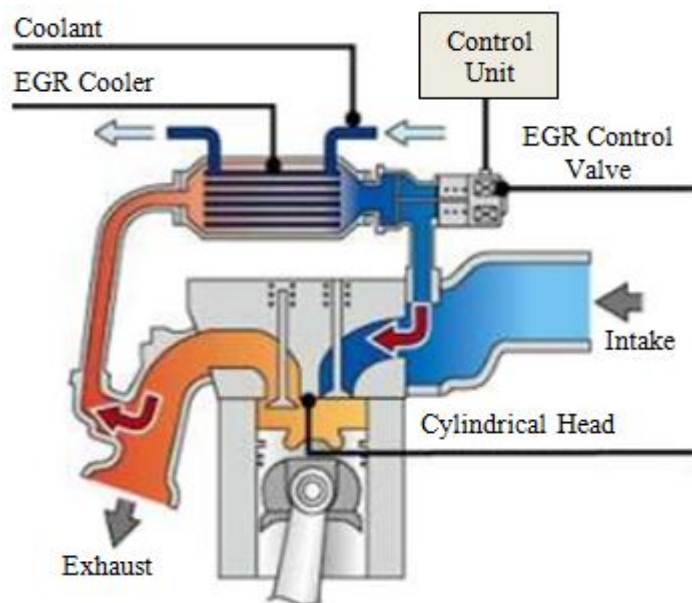


Figure 1.35 Exhaust Gas Recirculation

Exhaust consists of CO₂, N₂ and water vapors mainly. When a part of this exhaust gas is recirculated to the cylinder, it acts as diluents to the combusting mixture. This also reduces the O₂ concentration in the combustion chamber. The specific heat of the EGR is much higher than fresh air; hence EGR increases the heat capacity (specific heat) of the intake charge, thus decreasing the temperature rise for the same heat release in the combustion chamber [Agrawal *et al.*, 2004]. EGR ratio is defined as (Equation 1.25),

$$\% EGR = \left[\frac{\text{volume of EGR}}{\text{total intake charge into the cylinder}} \right] \times 100 \dots \dots \dots (1.25)$$

Another way to define the EGR ratio is by the use of CO₂ concentration (Equation 1.26) [Baert *et al.*, 1999],

$$EGR \text{ ratio} = \frac{[CO_2 \text{ intake} - CO_2 \text{ ambient}]}{[CO_2 \text{ exhaust} - CO_2 \text{ ambient}]} \dots \dots \dots (1.26)$$

Three popular explanations for the effect of EGR on NO_x reduction are increased ignition delay, increased heat capacity and dilution of the intake charge with inert gases. The ignition delay hypothesis asserts that because EGR causes an increase in ignition delay, it has the same effect as retarding the injection timing. The heat capacity hypothesis states that the addition of the inert exhaust gas into the intake increases the heat capacity (specific heat) of the non-reacting matter present during the combustion. The increased heat capacity has the effect of lowering the peak combustion temperature. According to the dilution theory, the effect of EGR on NO_x is caused by increasing amounts of inert gases in the mixture, which reduces the adiabatic flame temperature [Pierpont *et al.*, 1995]. Figure 1.36 shows the reduction in NO_x emission due to EGR at different loads [Mehta *et al.*, 1994].

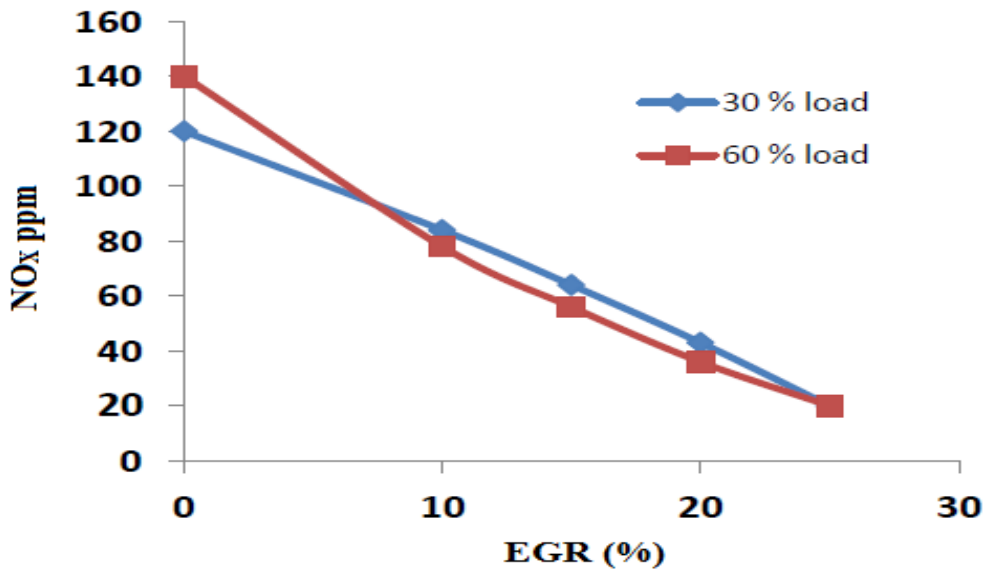
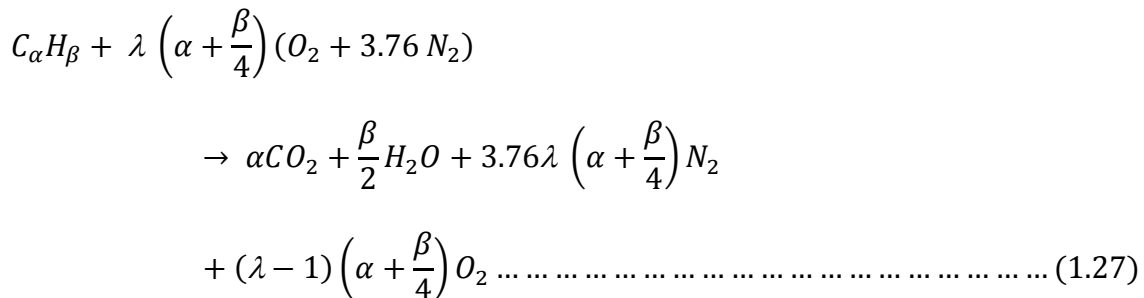


Figure 1.36 Effect of EGR on NOx emissions at different loads [Mehta *et al.*, 1994]

EGR system has already been used to mass produced diesel engines, in which EGR is used at the low and medium load of engine operating condition, resulting in effective NOx reduction. EGR systems can be either a high or a low-pressure system. Low-pressure systems can be retrofitted since they require no engine modifications. EGR can reduce NOx by about 40 -50%. But at high loads, it is difficult to employ EGR due to deterioration in diffusion combustion and this may result in an excessive increase in smoke and particulate emissions.

The complete combustion equation without EGR when Lambda (λ) > 1 (Equation 1.27)



The complete combustion equation with EGR (Equation 1.28)

$$\begin{aligned}
 C_\alpha H_\beta + a(O_2 + 3.76 N_2) + \left(\frac{\alpha \times EGR}{1 - EGR}\right) CO_2 + \left(\frac{\frac{\beta}{2} EGR}{1 - EGR}\right) H_2O + 3.76 \times a \\
 \times \left(\frac{EGR}{1 - EGR}\right) N_2 + \frac{\left[a - \left(\alpha + \frac{\beta}{4}\right)\right] EGR}{1 - EGR} O_2 \rightarrow \left(\frac{a}{1 - EGR}\right) CO_2 \\
 + \left(\frac{\frac{\beta}{2} EGR}{1 - EGR}\right) H_2O + \left(\frac{a \times 3.76}{1 - EGR}\right) N_2 \\
 + \left[\frac{a - \left(\alpha + \frac{\beta}{4}\right)}{1 - EGR}\right] O_2 \dots \dots \dots (1.28)
 \end{aligned}$$

Where $EGR = \frac{N_{CO_2 \text{ intake}}}{N_{CO_2 \text{ exhaust}}}$ $a = \lambda \times \left(\alpha + \frac{\beta}{4}\right)$

The mass fraction of the CO₂ from exhaust (Equation 1.29):

Mass Concentration of CO₂

$$= \frac{\left(\frac{\alpha \times EGR}{1 - EGR}\right) \times 44}{\left(\frac{\alpha \times EGR}{1 - EGR}\right) \times 44 + \left(\frac{\frac{\beta}{2} EGR}{1 - EGR}\right) \times 18 + 3.76 \times a \left(\frac{EGR}{1 - EGR}\right) \times 28 + \frac{\left[a - \left(\alpha + \frac{\beta}{4}\right)\right] EGR}{1 - EGR} \times 32} \dots \dots \dots (1.29)$$

where $a = \left(\alpha + \frac{\beta}{4}\right)$

Amount of O₂ (mole) consumed each step size (0.1 Crank Angle):

$$N_{rac_{O_2}} = n_{fuel} \times \left(\lambda + \frac{\beta}{4}\right)$$

Where: n_{fuel} is the amount of fuel consumed each step size (0.1 Crank Angle);

Amount of CO₂, H₂O produced each step size (0.1 Crank Angle): (Equations 1.30-1.35)

$$N_{rac_{CO_2}} = n_{fuel} \times \left(\frac{a}{1 - EGR} - \frac{\alpha \times EGR}{1 - EGR}\right) \dots \dots \dots (1.30)$$

$$N_{rac_{H_2O}} = n_{fuel} \times \left(\frac{\frac{\beta}{2}}{1 - EGR} - \frac{\frac{\beta}{2} EGR}{1 - EGR}\right) \dots \dots \dots (1.31)$$

$$n_{O_2(i)} = n_{O_2(i-1)} + n_{rac_{O_2}} \dots \dots \dots (1.32)$$

$$n_{CO_2(i)} = n_{CO_2(i-1)} + n_{rac_{CO_2}} \dots \dots \dots (1.33)$$

$$n_{H_2O(i)} = n_{H_2O(i-1)} + n_{rac_{H_2O}} \dots \dots \dots (1.34)$$

$$n_{total(i)} = n_{O_2(i)} + n_{CO_2(i)} + n_{H_2O(i)} + n_{N_2(i)} \dots \dots \dots (1.35)$$

The mole fraction of O₂, N₂, CO₂, and H₂O are as follows: (Equations 1.36 – 1.39)

$$O_{2molefrac(i)} = \frac{n_{O_2(i)}}{n_{total(i)}} \dots \dots \dots (1.36)$$

$$N_{2molefrac(i)} = \frac{n_{N_2(i)}}{n_{total(i)}} \dots \dots \dots (1.37)$$

$$CO_{2molefrac(i)} = \frac{n_{CO_2(i)}}{n_{total(i)}} \dots \dots \dots (1.38)$$

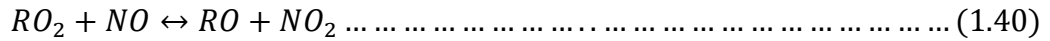
$$H_2O_{molefrac(i)} = \frac{n_{H_2O(i)}}{n_{total(i)}} \dots \dots \dots (1.39)$$

Diesel engines operate with an excess of air and they benefit from EGR rate as high as 50% in controlling NO_x emissions, but an increase in particulate matter production is present due to the reduction of the specific heat ratio of the combustion gases in the power stroke. Even if the combination of good mixing and high EGR helps to reduce soot and NO_x, a particulate matter abatement technology is required, typically DPF.

Effects of EGR

The combustion temperature with EGR decreased, reducing the total engine-out NO_x and increasing the NO₂ concentration (i.e. primarily the NO₂/NO_x ratio). The latter is associated with the production of the HO₂ radical which is suggested to be the most effective agent for promoting NO oxidation [Hargeaves *et al.*, 1981]. Several studies [Hori *et al.*, 2002, Hargeaves *et al.*, 1981, Hori, 1988] have suggested that the oxidation of NO to NO₂ is dependent on temperature and HC presence. At low

temperatures, the formation of HO₂ and RO₂ peroxy radicals are essential for promoting NO oxidation as shown previously in Equation 1.40 and through the following reaction:

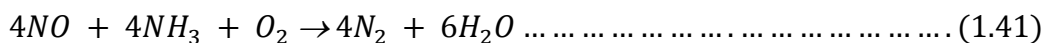


Using EGR under the engine condition considered in this study, the indicated specific fuel consumption (ISFC) and the indicated engine thermal efficiency (IETE) are not substantially affected. Some increase in fuel consumption and reduction in thermal efficiency was seen as expected with the addition of EGR.

1.3.4.2 Selective Catalytic Reduction (SCR)

Selective catalytic reduction (SCR) is the most widely used NO_x control technology for stationary diesel engines. It is called “selective” because the catalytic reduction of NO_x with ammonia (NH₃) as a reductant occurs preferentially to the oxidation of NH₃ with oxygen. The process involves mixing the exhaust air with reductant such as ammonia or urea. These homogenous mixtures pass over the catalyst bed to react at the air stream temperature [Mehring *et al.*, 2012]. The catalyst promotes a reaction between NH₃, NO_x and the rich oxygen in the exhaust stream to form nitrogen and water. Initially, SCR was designed with Pt catalyst but the catalyst can be used only at temperatures less than 250°C, because of its poor selectivity for NO_x reduction at higher temperatures. Presently, base metal and zeolite catalysts are employed in the place of Pt. With compression ignition engines, zeolite catalysts achieve a reduction efficiency of more than 90%, while base-metal catalysts can achieve a 80% to 90% reduction, the reaction as shown in Equation 1.41 and 1.42.

The reaction scheme is given as



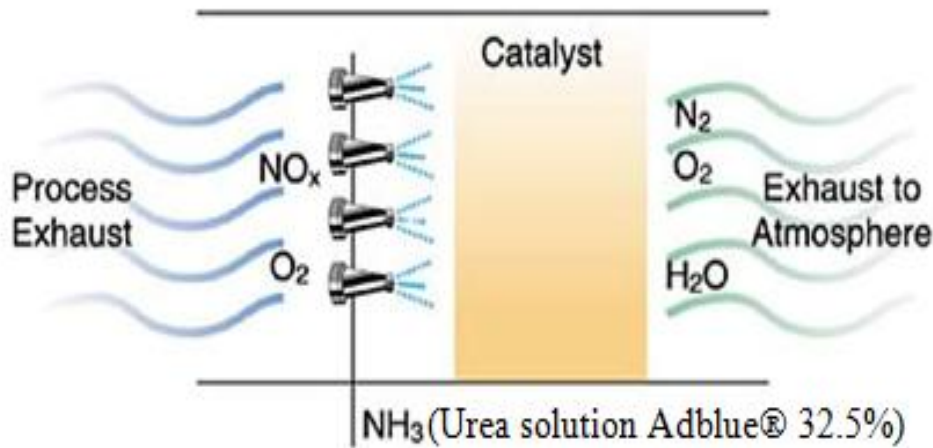
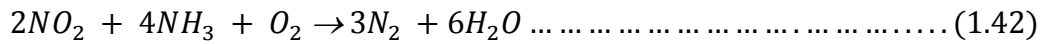
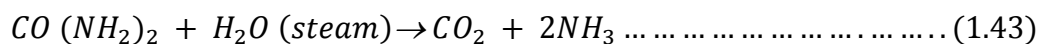


Figure 1.37 NO_x control by SCR [Gruenwald *et al.*, 2007]

The reagent injection systems need to be designed to make sure the complete mixing of reagent with the flue gas as an aid to the conversion process. However, this technology has a high initial cost. The disadvantage of this technology is that catalytic reduction with ammonia requires the special handling, storage and a special metering system to keep away from NH_3 slippage. When excess residual ammonia (ammonia slip) discharges to the atmosphere, it is environmentally harmful. Thus, to avoid the use of ammonia, its precursors like urea are used. Adblue® a high purity solution of 32.5% urea in water is most commonly used for vehicles [Gruenwald *et al.*, 2007]. Unlike NH_3 does not require any special handling precautions. It is kept in a separate tank and is sprayed into the exhaust system where it hydrolyses into ammonia ahead of the SCR catalyst as shown in reaction below (Equation 1.43).



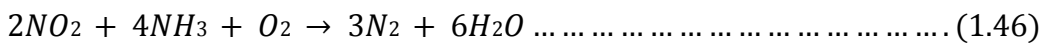
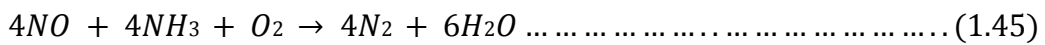
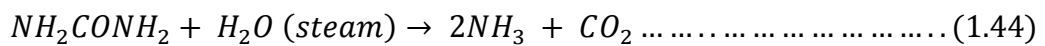
Other reductants like HC, oxygenated HC, and H_2 have also been employed for SCR technology. Recently, it has been reported that the coexistence of hydrogen and hydrocarbons in the reactants over catalysts highly promoted the SCR reaction, Hydrogen is widely considered as an ideal co-feeder gas in active mode (i.e. injected

HCs). Satokawa *et al.*, 2014 reported that when hydrogen and hydrocarbons are present in the SCR reactants, low temperature activity was significantly improved and the maximum NO_x reduction rate was highly increased as well [Satokawa, 2003].

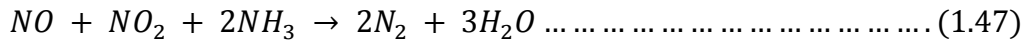
One of the first articles describing an SCR system applied in a vehicle was published by Held *et al.*, 1990, who suggested using urea as the reducing agent, from which ammonia could be released under hydrothermal conditions. In 2005 urea-SCR was introduced for commercial heavy-duty vehicles in Europe, and more recently also for passenger cars [Brink *et al.*, 2002]. Several automotive companies, such as Daimler Chrysler, Iveco, Volvo and Renault [Stratakis *et al.*, 2004; Prasad & Bella, 2010; Prasad & Bella, 2011], commercialized this technology for the abatement of NO_x emissions from heavy duty diesel vehicles.

Ammonia/urea-SCR

In ammonia/urea-SCR, a gaseous reductant, typically anhydrous ammonia, aqueous ammonia or aqueous solution of 32.5% urea Ad Blue, is injected to a stream of flue or exhaust gas and is adsorbed onto a catalyst (Figure 1.37). CO₂ is a reaction product when urea is used as the reductant. Ammonia commonly comes from the in-exhaust dissociation of urea [Johnson, 2009]. Ammonia/urea sets off chemical reaction in presence of a SCR catalyst that converts NO_x into nitrogen and water (Equations 1.44-1.46).



SCR with NH₃ is a widely commercialized technology for NO_x removal from stationary sources [Rahai, 2008]. Koebel *et al.*, 2004 reported a very fast SCR reaction at low temperature, if the NO in the NO_x gas is partially oxidized to NO₂ to a mixture of NO and NO₂ in a 1:1 ratio following reaction dominates (Equation 1.47).



Under the right conditions of equi-molar NO/NO₂ ratio, and above 200°C, this reaction proceeds approximately ten times as fast as reaction. Thus, under equi-molar NO/NO₂ ratio the process is known as “fast SCR”. However, the temperature and reactant ratio control are very important as the reaction proceeds in an alternative pathway in Equation 1.48, if the temperature falls below 180°C and or the NO₂ dominates the NO_x gas mixture as shown in Figure 1.38.

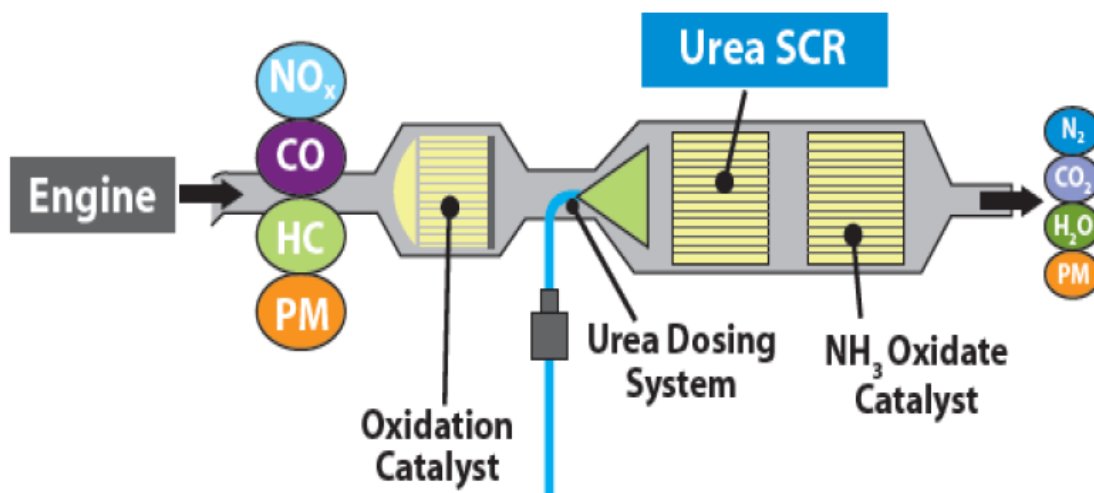
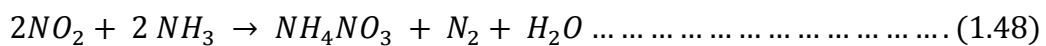


Figure 1.38 Selective catalytic reductions of NO_x

This reaction is undesirable as it can potentially render the catalyst unusable by depositing solid ammonium nitrate on the catalyst surface. This technology has a high initial cost. In addition, catalysts have a finite life in flue gas and some ammonia “slips

through” without being reacted. For stationary power generators, the storage of large quantities of toxic NH₃ is less of an issue compared to mobile applications. Therefore, NH₃ is not the desired source of reductant for mobile applications. To overcome the difficulties associated with ammonia, urea was used as alternative reducing agent because it is safer and can hydrolyzed to generate ammonia.

One of the first articles describing an SCR system applied in a vehicle was published by Held *et al.*, 1990, who suggested using urea as the reducing agent, from which ammonia could be released under hydrothermal conditions. SCR with urea as reducing agent is presently considered the most promising technique for the removal of NO_x from the exhaust of heavy-duty diesel vehicles, e.g. trucks [Koebel *et al.*, 2000]. Very high conversions of NO_x may be obtained and the reducing agent is consumed very selectively for the reduction of NO_x. In automotive applications, urea is preferred to ammonia as reducing agent for toxicological and safety reasons [Maurer *et al.*, 1999].

HC-SCR

In the HC-SCR technology, NO_x is reduced through catalytic reactions with hydrocarbons present in the diesel exhaust under rich condition or injected upstream in case of lean-burn state. The reaction pathways depend on the hydrocarbon used but the following describes the total reaction in the system (Equation 1.49).



Additional quantities of hydrocarbons, such as diesel fuel, are often injected upstream of the catalyst to achieve higher NO_x reductions. The commercial use of the technology-also known as the “lean NO_x catalyst” has been very limited due to low NO_x reductions and high fuel economy penalties in systems with HC injection. More

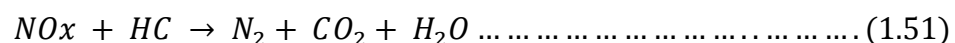
active and durable lean NO_x catalysts would be necessary for a wider commercial deployment of HC-SCR.

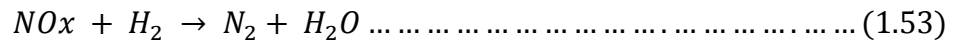
H₂-SCR

Hydrogen has been reported to be very active towards catalytic reduction of NO into N₂, and it could potentially be used to reduce NO_x emissions [Kobylinski & Taylor, 1974; Huang *et al.*, 1998]. It has been found that the addition of hydrogen to the up-stream of exhaust in presence of Ag/Al₂O₃ catalyst resulted in a remarkable improvement in the level of NO_x reduction [Burch *et al.*, 2002] in the range of temperature over which NO_x could be selectively reduced [Satokawa *et al.*, 2000]. Several workers have investigated H₂-SCR using different catalyst like precious metals [Satokawa *et al.*, 2003; Shibata *et al.*, 2004; Shibata *et al.*, 2003 and 2004; Shibata *et al.*, 2003; Richter *et al.*, 2004], base metal oxides [Roth & Doerr, 1961; Baker & Doerr, 1964; Baker & Doerr, 1965; Klimisch & Barnes, 1972], perovskite-related oxides [Costa *et al.*, 2001; Costa & Efstathiou, 2004; Costa & Efstathiou, 2004]. Savva, and Costa have critically reviewed H₂-SCR over noble metals catalysts up to 2011 for reduction of NO with H₂ in strongly oxidizing conditions.

1.3.4.3 Non-selective Catalytic Reduction (NSCR)

In non-selective catalytic reduction, CO, NO_x and hydrocarbons are converted into CO₂ and N₂ via a catalyst. This technique does not need additional reagents to be injected because the unburned HCs and CO are used as a reductant. Though, gases must not possess more than 0.5% oxygen. NO_x removal takes place in two sequential phases, with the following reactions (Equations 1.50 - 1.53):





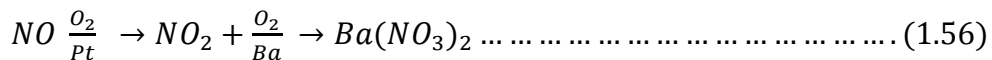
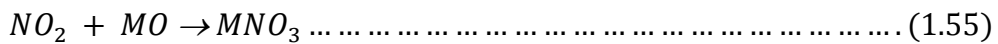
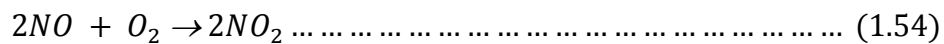
NSCR has been used to control NO_x emissions from rich-burn engines for over 15 years. The systems have demonstrated the ability to achieve 90-98 % and NO_x emissions of 25 ppmv can be realized (ECMA, 2012). Over 3000 rich burn IC engines have been equipped with NSCR technology in the U.S. alone [Basu, 2007]. The catalysts used are normally based on platinum. As may be observed from the reactions above, it requires the presence of the reactants in stoichiometric amounts to remove all of them simultaneously so that none of these compounds remain in flue gas as residuals. But the requirement can be fulfilled by feeding air and the fuel in ratios within a very narrow range, which is maintained by an automatic feedback control loop based upon residual oxygen concentration in the final exhaust [Basu, 2007]. NO_x conversion efficiency drops dramatically when the engine is run in the lean regime, while HC and CO conversion efficiency also declines somewhat [Basu, 2007]. The use of NSCR could possibly result in higher CO levels due to the engine's need for a rich mix, to ensure that CO is available to the catalyst for the removal of NO_x. If the CO level is too high after the catalyst, it may be necessary to later employ an oxidation catalyst to oxidize the CO into CO₂.

1.3.4.4 NO_x adsorber catalyst (NAC)/NO_x storage and reduction (NSR) / Lean NO_x Traps (LNT)

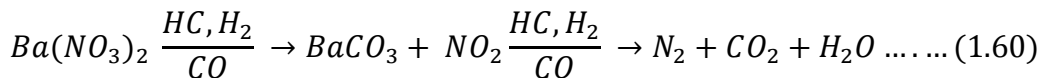
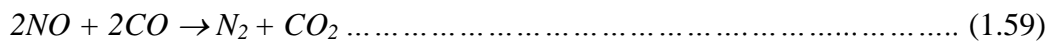
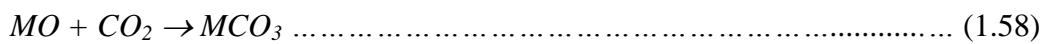
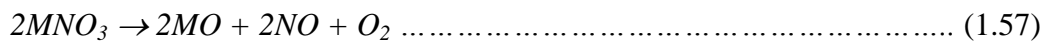
Primary application of the NO_x storage and reduction catalyst is the elimination of NO_x emissions from diesel and lean-burn gasoline engines, where direct NO_x reduction is hindered due to an excess of oxygen in the exhaust gas. The principle of NSRC operation is based on periodical alternation between the lean and the rich phase.

NO_x can be removed from a lean gas stream by chemisorption onto a catalyst, hence the term NO_x adsorber catalyst (NAC). NAC, NO_x storage reduction (NSR) and Lean NO_x traps (LNT) are synonymous terms. NO_x storage and reduction (NSR) technology was first proposed by Toyota in mid 1990's and is promising technology for NO_x control [Takahashi *et al.*, 1996]. It is a two-step technique for NO_x reduction in which NO_x is stored during the lean exhaust condition (Equations 1.54-1.56) and is reduced to N₂ during the fuel rich condition (Equations 1.57-1.60). During the first step NO is oxidized to NO₂ over some precious metal catalysts (Pt, Pd, Rh) NO₂ thus produced combines with NO_x storage compounds to form nitrates [Gill *et al.*, 2004; Liu & Woo., 2006]. The NO_x storage compounds are generally alkali or alkaline earth metal oxides (BaO, K₂O) over high surface area support (γ -alumina) [Taylor, 2007].

i. Lean phase



ii. Rich phase



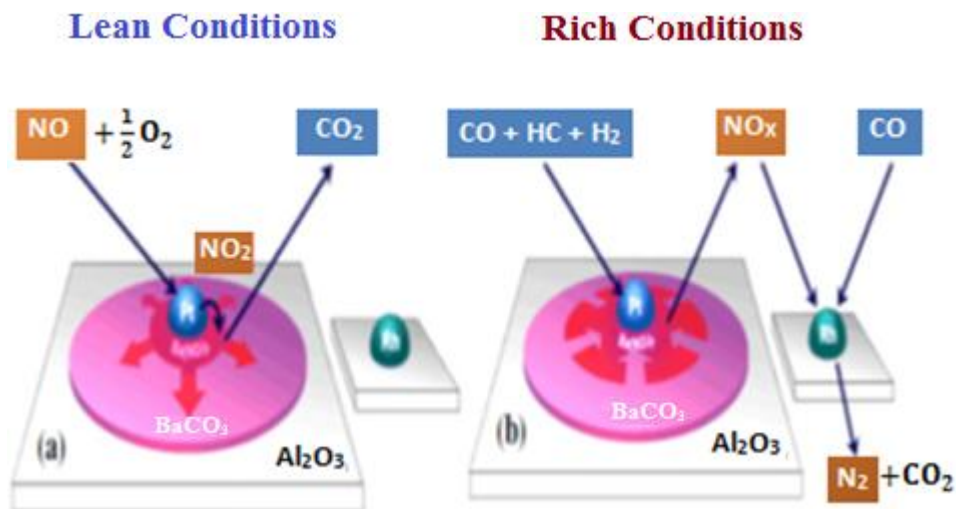
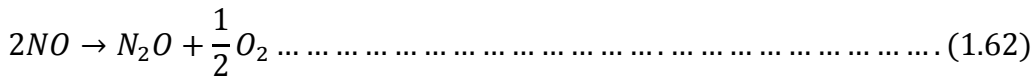


Figure 1.39 (a) Reaction steps for lean and (b) rich NO_x conversion respectively

During the rich phase, the stored nitrate species decompose again to produce NO which is further reduced by H₂, HC or CO present over the precious metal catalyst as shown in Figure 1.39. However, the basic NO_x storage compounds have a tendency to combine with the sulphur present in the fuel resulting in formation of sulfates and reduction of NO_x storage capacity of the catalyst. Thus LNT technology requires low sulfur fuels. NSR catalysts also faces problem of thermal deteriorations.

1.3.4.5 Catalytic Decomposition of NO_x

The decomposition of NO would represent the most attractive solution in emission control because the reaction does not require adding any reactant to NO exhaust gas and could potentially lead to the formation of only N₂ and O₂. Additional reductants such as hydrocarbons, CO, H₂ or ammonia can lead to the production of secondary pollutants like oxygenated hydrocarbons, CO, N₂O or ammonia or, even, as was often reported in the past, cyanate and isocyanate compounds (Equations 1.61-1.62). In the direct NO decomposition reaction, the exhaust containing NO is passed over a heterogeneously catalytic surface, where the NO bond is split, and N atoms recombine to N₂ while the O atoms recombine to O₂ which shown in Figure 1.40.



The direct NO decomposition reaction is thermodynamically favored at low temperatures below 900°C, but it has proven difficult to find a catalyst that is both active and oxidation resistant. Therefore, a catalyst is necessary to lower the activation energy thus facilitates the reaction. The most promising decomposition catalysts are transition metal-exchanged zeolites and perovskites [Sindhu *et al.*, 2017, Imanaka *et al.*, 2012, Piumetti *et al.*, 2015].

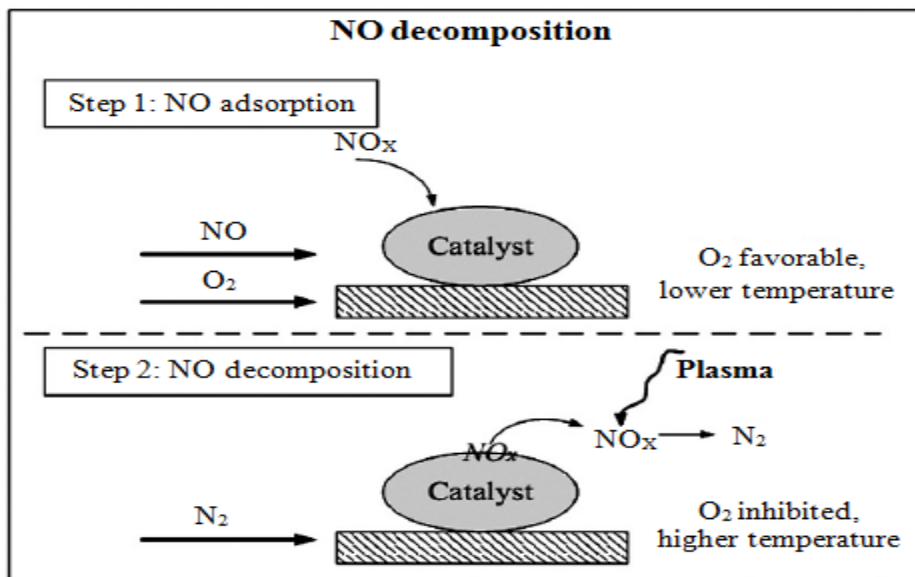


Figure 1.40 Mechanism of decoupled deNO_x process: direct NO decomposition

Catalytic activities for direct NO decomposition of nitric acid is both of practical and theoretical interest. Direct NO decomposition could be the best way to remove NO in the presence of dioxygen as it allows for the elimination of secondary pollutants. The techniques involves kinetically controlled reduction of NO, based in part on increased residence time at high temperatures and in part on the presence of chemical species that reduce the NO to N₂. Effective catalysts are decomposed of NO into N₂ and O₂.

The linear relationship perhaps indicates the decomposition of NO, is a First-order kinetics reaction, retarded by adsorbed oxygen (Equation 1.63). The rate equation to describe such behavior could be written as follows.

$$r = -\frac{dP_{NO}}{d\theta} = k \left(\frac{P_{NO}}{P_{O_2}} \right) \dots \dots \dots (1.63)$$

Another form of the rate of equation was presented as Equation 1.64.

$$r = -\frac{dP_{NO}}{d\theta} = k \left(\frac{P_{NO}}{1 + k'P_{O_2}} \right) \dots \dots \dots (1.64)$$

Bachman, however, from his studies in the temperature range of 1900 to 2500 °F, proposed that the reaction was second order with respect to nitric oxide but was also retarded by oxygen as shown in Equation 1.65:

$$r = -\frac{dP_{NO}}{d\theta} = k \left[\frac{(P_{NO})^2}{P_{O_2}} \right] \dots \dots \dots (1.65)$$

In the later work, the Armour Research foundation screened a large number of catalysts to determine their effectiveness in decomposing nitric oxide which was present in nitrogen at a concentration 0.2% by volume. The conditions of this test simulated those which are found in automobile exhaust manifolds. Several experiments were being conducted to determine the magnitude of wall effects on the decomposition reaction and to select a suitable catalyst for use in intensive kinetic studies of the reaction.