

# CHAPTER 1

## INTRODUCTION

### 1.1 General

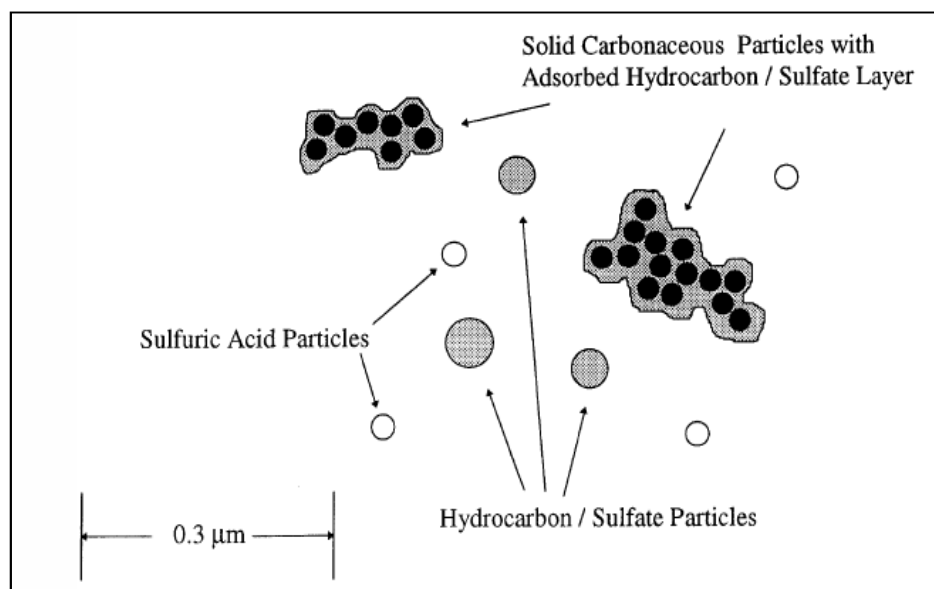
During the last decade, diesel engines have increased in popularity compared to gasoline engines around the globe, due to better fuel efficiency, lower operating cost, higher durability, and reliability, simultaneously associated with a favourable fuel tax situation in several countries [Banús et al. 2013]. They are widely used to transport goods, services and people. They are the power source behind commercial transport, being employed in trucks, buses, trains, and ships, as well as off-road industrial vehicles such as excavation machinery, and mining equipment [Badini et al. 1998]. They also play a vital role in power generation and are used for farming, construction, and industrial activities. However, a major environmental problem associated with diesel engines is the emission of particulate matter (PM)/soot from the exhaust, which consists mostly of carbonaceous soot and soluble organic fraction (SOF) of hydrocarbons [Abdullah et al. 2008]. Because of the carcinogenic properties of aromatic compounds, the photochemical hazardous products of hydrocarbons and presence of black carbon

associated with PM could induce serious health problems, adverse impact on environment and cause global warming and climate change [Lu et al. 2007].

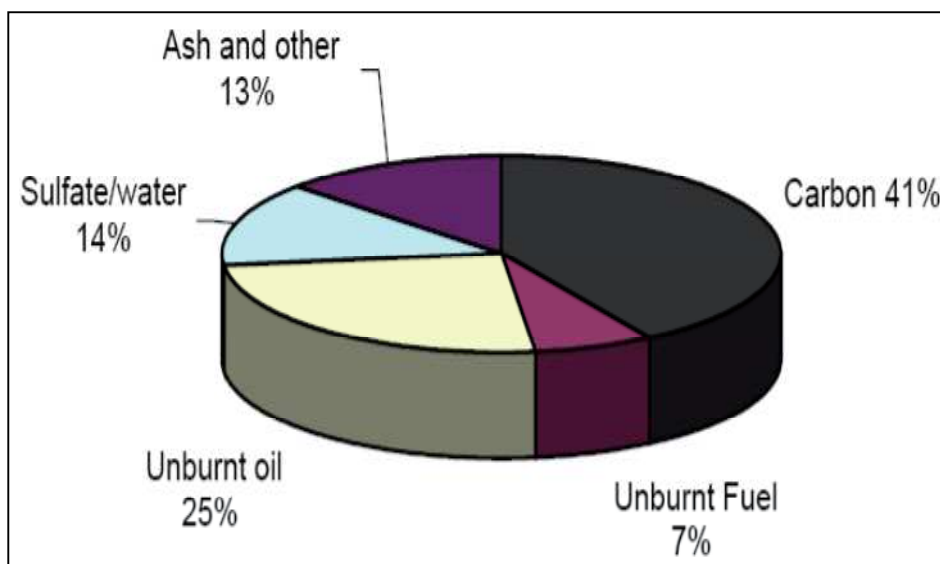
As the regulations on diesel engine emissions are becoming more stringent, engine modification and exhaust treatment have become essential. Up till now, plenty of research has been carried out worldwide on the removal of soot. For soot abatement, diesel particulate filter (DPF) technique is widely employed to trap the PM with trapping efficiencies  $> 98\%$  [Walker 2004]. As the filters accumulate PM, it builds-up backpressure that has many negative effects such as decreased fuel economy and possible engine and/or filter failure [Stamatelos 1997]. To prevent these negative effects, the DPF have to be regenerated by oxidizing (i.e. burning) trapped PM. An attractive option to remove PM is passive regeneration of DPF. Passive regeneration involves the catalytic combustion of the trapped PM during the normal operation of the engine. Soot is burned out by the oxidation catalysts deposited onto the filter [Van Setten et al. 2001, Maricq 2007]. The catalysts should promote soot combustion at a rather low temperature, and display excellent activity and durability under practical working conditions of the engine exhaust [Fino et al. 2003, Pisarello et al. 2002]. Many types of catalysts have been investigated for the soot combustion such as platinum group metals (PGM), perovskite-type oxides, spinel type oxides, rare earth metal oxides, and mixed transient metal oxides. The major challenge lies in finding catalysts capable of soot oxidation at temperatures normally reached at diesel exhausts (150-450°C). Perovskite oxides appear as an important family of catalysts and show potential as effective soot oxidation catalyst for the DPF because of their low cost, high thermal stability, and tailoring flexibility [Mishra and Prasad 2014].

## 1.2 Diesel Soot

PM/Soot is highly carbonaceous material, formed due to the incomplete combustion of hydrocarbons. It is a complex mixture of organic compounds, lubricating oil and inorganic compounds such as ash (mineral oxides) and sulphur compounds. It exists almost entirely in the forms of clusters and chains of individual primary soot particles (spherules). Clusters may contain as many as 4000 individual spherules, making the cluster size mostly within the range of 60-100 nm [Heywood 1988, Sakamoto et al. 1997]. The number of spherules that a cluster contains as observed to vary with the total air/fuel ratio over a range from 22 to 100 in a diesel engine [Roessler et al. 1981]. Clusters produced at lower air/fuel ratios are more highly agglomerated, and vice-versa. The structure and composition of soot are illustrated schematically in Figures 1.1 and 1.2.



**Figure 1.1** Typical composition and structure of engine exhaust particles [Kittelson 1998]



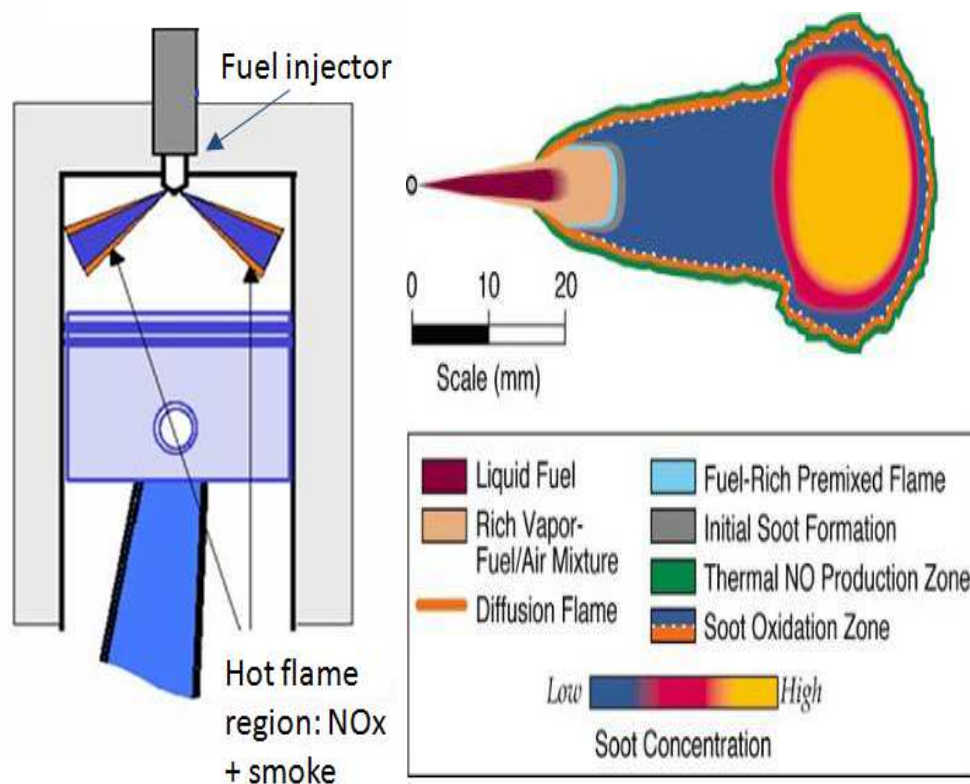
**Figure 1.2** Typical particle composition for a heavy-duty diesel engine tested in a heavy duty transient cycle. [Kittelson 1998]

### 1.2.1 Mechanism of Soot Formation in Diesel Engines

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 100% 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 and Kobayashi 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.

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 1.3 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.



**Figure 1.3** Schematic diagram of a steady burning jet on the basis of laser measurements

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 is focusing 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. 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;
- ii) The central region of the cylinder, where conditions are close to the stoichiometric ones;
- iii) The most separated region from the injector, where the fuel concentration is low [Banús et al. 2013].

If the generated turbulence is 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 soot, which constitutes the typical black smoke observed from diesel vehicles during high acceleration or when they are cold. In contrast, in the third

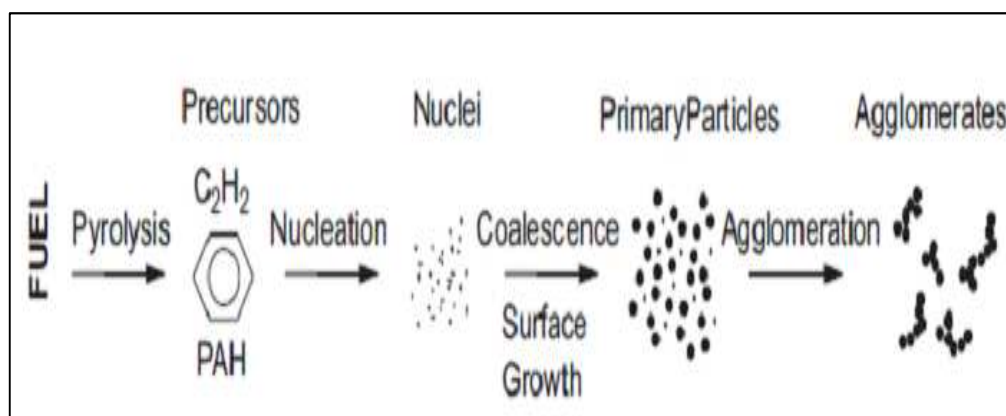
region, the oxygen excess and the very high temperature cause the appearance of important  $\text{NO}_x$  quantities. In the intermediate region, the diesel fuel/air ratio is close to the stoichiometric one so that the combustion is produced under near ideal conditions. Formation of PM involves four fundamental steps [Tree and Svensson 2007] as discussed below:

(i) **Pyrolysis:** High concentration of fuel at high temperatures provokes the fuel organic compounds to alter their molecular structure to form molecules like  $\text{C}_2\text{H}_2$ , 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.

(ii) **Nucleation:** The precursor molecules formed by pyrolysis arrange themselves to form nuclei of the PM primary particles.

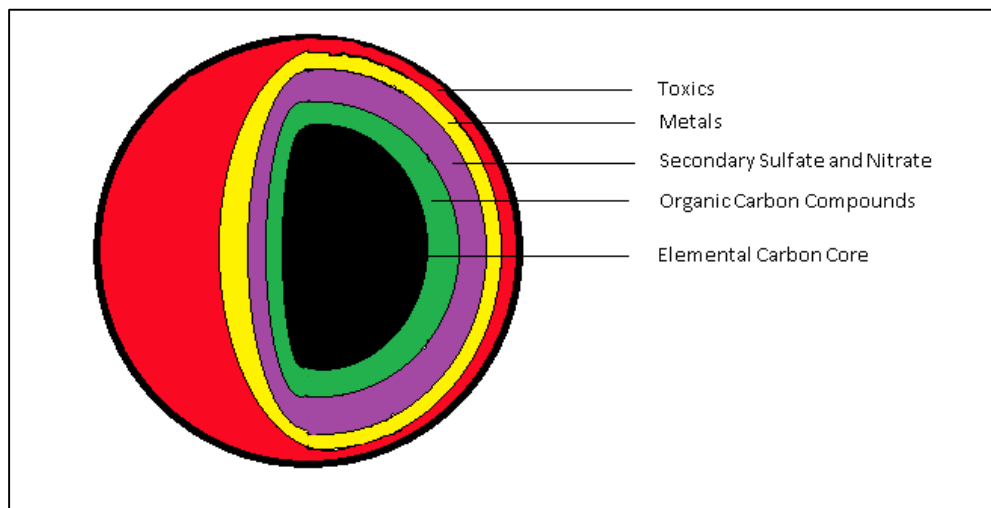
(iii) **Surface growing:** Nucleated soot particle adds mass to its surface to form the primary particles.

(iv) **Coalescence and 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. (Figure 1.4)



**Figure 1.4** Formation of PM [Tree and Svensson 2007]

PM is known to consist mostly of carbonaceous soot with minor components of SOF from unburned fuel, lubricating oil and inorganic compounds such as ash and sulphur compounds as shown in Figure 1.5.



**Figure 1.5** Typical structure of Soot

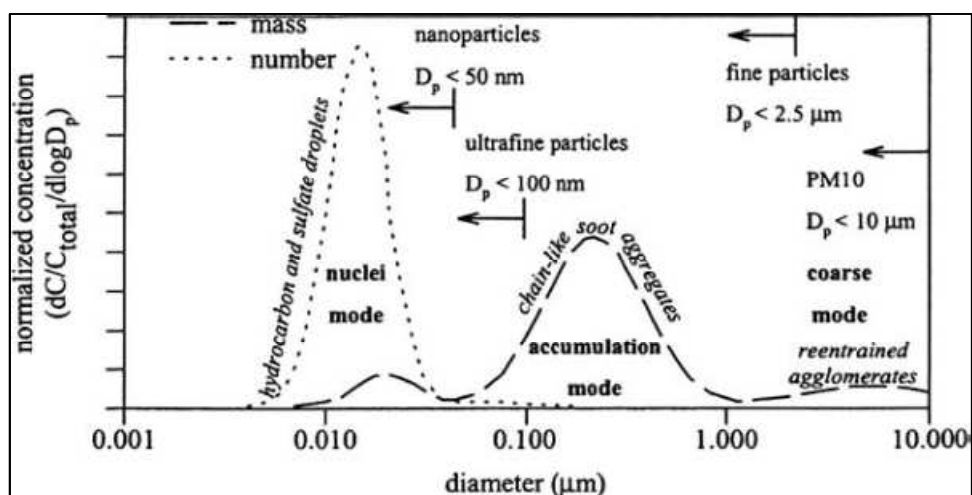
### 1.2.2 Classification of Diesel Soot

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. Soot particles can be categorized in the following four sizes:

- (1) Large particles  $>10\ \mu\text{m}$ ,
- (2) Coarse particles  $2.5\text{-}10\ \mu\text{m}$  (PM10),
- (3) Fine particles  $1.0\text{ - }2.5\ \mu\text{m}$  (PM2.5), and
- (4) Ultra-fine  $<1.0\ \mu\text{m}$  (PM1.0).



The size of the particles also determines the time they spend in the atmosphere. While sedimentation and precipitation removes PM<sub>10</sub> from the atmosphere within few hours of emission, PM<sub>2.5</sub> may remain there for days or even a few weeks. Consequently, these particles can be transported over long distances. The typical size distribution of diesel particles is shown in Figure 1.6.



**Figure 1.6** Schematic of mass and number based particle size distribution from diesel engines

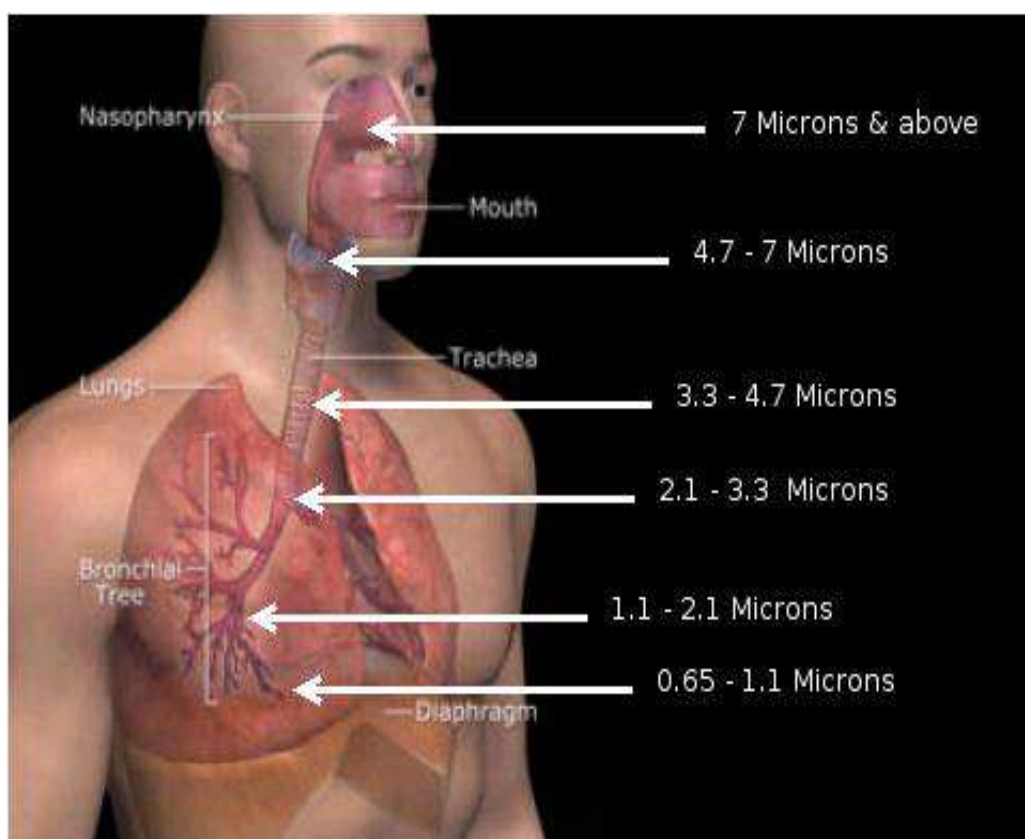
## 1.2.3 Effects of Diesel Soot

### 1.2.3.1 Effect of Soot on Human Health

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 PM, ozone and carbon monoxide formed from diesel

emissions on new-born children include birth defects, growth retardation and sudden infant death syndrome.

Figure 1.7 shows transport of soot particles with breath inside our body. Large particles, PM<sub>10</sub> 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<sub>2.5</sub>) 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].



**Figure 1.7** Transport of the PM with breath according to their size

### 1.2.3.2 Effect of Soot on Vegetation

Particulate deposition and effects on vegetation unavoidably include nitrate and sulphate and their associations in the form of acidic and acidifying deposition and Trace elements and heavy metals [Grantza et al. 2003]. Atmospheric diesel DPM impact agriculture productivity in a variety of ways:

- (1) Reduction of solar radiation in turn reducing photosynthesis,
- (2) Settling of soot particles on the plants can shield leaves from solar radiation hindering photosynthesis,
- (3) Soot deposition can increase acidity and cause plant damage, and
- (4) Reduction of rainfall by dimming induced by soot. It causes all type of injury in plants such as epinasty, necrosis, chlorosis, abscission, flower dropping etc as shown in figure. 1.8.



**Figure 1.8** Effect of soot on vegetation

### 1.2.3.3 Effect of Soot on Water and Soil Pollution

Atmospheric deposition of air pollutants released from diesel exhaust to ecosystems and their components, such as forests, water bodies, and soils, is another significant source of contamination [Arimoto 1989]. Water and soil are contaminated indirectly by dry and

wet deposition of diesel exhaust emitted to the atmosphere. 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 and 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 1989]. Enhanced levels of atmospherically deposited nitric and sulphuric acid (acid rain) adversely affect the health of ecological systems, such as agricultural crops, large water bodies, and forests. Arimoto [1989] concluded that deposition is the dominant source for a variety of chemical contaminants in the 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 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 PM. 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 and 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.

#### **1.2.3.4 Effect of Soot on Environment, Global Warming and Climate Change**

Atmospheric soot envelopes most part of the globe with a dense layer of brown clouds. A series of investigations [Ramanathan 2001] pointed out that soot in air pollution affects agriculture, water budget and climate at the local, the regional and the global level. Soot may cool or warm, depending on whether it is airborne or deposited. Atmospheric soot aerosols directly absorb solar radiation, which heats the atmosphere and cools the surface. Regionally (but not globally), as much as 50% of surface warming due to greenhouse gases may be masked by atmospheric brown cloud (ABCs) [Lahaye et al.1996]. The soot settling on glaciers or ice in arctic region absorbs solar heat directly contribute to melting of Himalayan glaciers [Kulkarni et al. 2005] and causing ice to melt. This can lead flooding, rise in water level of sea. Many low lying areas near coast will get submerged with water. The atmospheric solar heating by soot, next to carbon dioxide, is the major contributor to global warming [Roberts and Jones 2004]. The effect of global warming and climate change are now evident from observations of widespread melting of snow and rising of average sea level as well as record breaking localized rainfall, snowfall and drought affected areas around the globe. It is emphasized that the global environmental damage caused thermodynamically is more alarming to life on the earth than the risk of other problems. Such catastrophe examples indicate the risks will be larger in the future. Some localized effects of global warming and climate change are shown in figure 1.9.

Global dimming, a gradual reduction in the amount of global direct irradiance at the Earth's surface, has partially counteracted global warming from 1960. The main cause of this dimming is aerosols produced by volcanoes and pollutants. These aerosols exert a cooling effect by increasing the reflection of incoming sunlight.



**Figure 1.9** Localized effects of soot emission on environment

James Hansen and colleagues [2000] have proposed that the effects of the products of fossil fuel combustion- $\text{CO}_2$  and aerosols-have largely offset one another in recent decades, so that net warming has been driven mainly by non- $\text{CO}_2$  greenhouse gases. The influences of aerosols, including soot, are most pronounced in the tropics and sub-tropics, particularly in Asia, while the effects of greenhouse gases are dominant in the extra-tropics and southern hemisphere. Clouds modified by pollution have been shown to produce less drizzle, making the cloud brighter and more reflective to incoming sunlight, especially in the near-infrared part of the spectrum [Albrecht 1989].

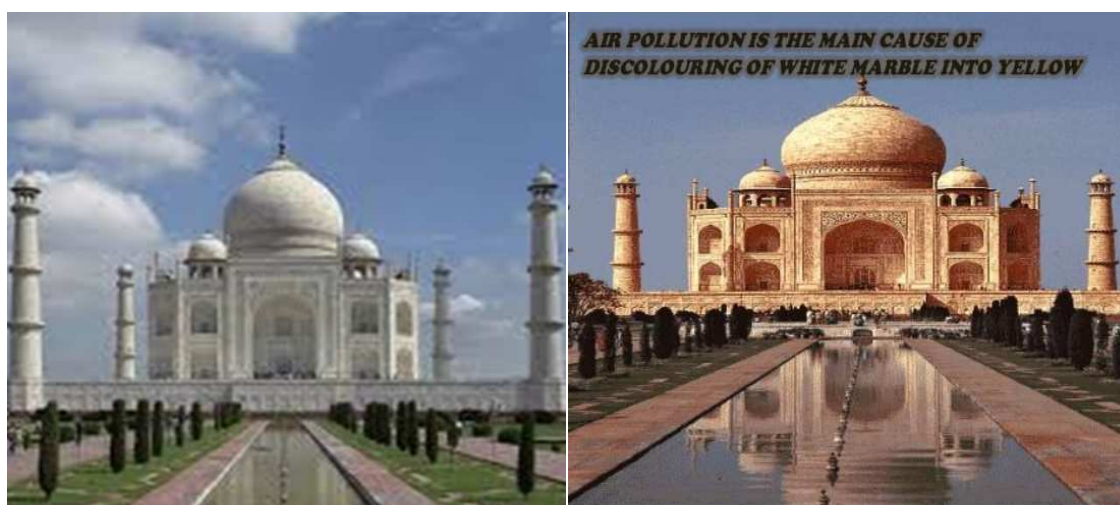
#### 1.2.3.5 Effect of Soot on Visibility

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  $\sim 12 Mm^{-1}$  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 ABC. Visibility reduction causes accidents on the roads.

### 1.2.3.6 Effect of Soot on Materials

The deposition of airborne soot on the surfaces of buildings, tunnels, highway bridges, and monuments of historical importance like Taj Mahal in India (figure 1.10) can cause damage and soiling, ventilation system blackening, thus reducing the useful life and aesthetic appeal of such structures. Diesel exhaust builds up in tunnels and underground garages where [El-Fadel and Hashisho 2000] it is difficult to remove. Soot promotes metal corrosion [Riederer 1974]. Many metals form a film that protects against corrosion however high concentrations of anthropogenic pollutants lessen the effectiveness of the protective film.



**Figure 1.10** Effect of soot emission on monuments

### 1.3 Diesel Engine Emissions and Legislations

A major environmental problem associated with diesel engines, especially diesel powered vehicles are the harmful emissions of primary pollutants PM, NO<sub>x</sub>, SO<sub>x</sub>, CO and Hydrocarbons [Kagawa 2002]. Diesel engines emit greater amounts of NO<sub>x</sub> and PM than equivalent petrol engines per unit of power output. Table 1.1 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.

**Table 1.1** Typical diesel exhaust composition [Jelles 1999]

Component	Concentration
CO	100-10000 ppm
HC (C1)	50-500 ppm,
NO <sub>x</sub>	30-1000 ppm
SO <sub>x</sub>	Proportional to fuel S content
DPM	20-200mg/m <sup>3</sup>
CO <sub>2</sub>	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, peroxyacetyl nitrate (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 1.2. 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 1.2** Euro emission standards for diesel vehicles

<b>(A) Diesel car [g/km]</b>					
<b>Standard</b>	<b>Year</b>	<b>HC + NO<sub>x</sub></b>	<b>NO<sub>x</sub></b>	<b>CO</b>	<b>PM</b>
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	0.50	0.005
EURO 6	2014	0.17	0.08	0.50	0.005

<b>(B) Light duty trucks [g/km]</b>						
<b>Class</b>	<b>Standard</b>	<b>Year</b>	<b>HC + NO<sub>x</sub></b>	<b>NO<sub>x</sub></b>	<b>CO</b>	<b>PM</b>
<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	0.50	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
>1760kg)	EURO 1	1994	1.70	-	6.90	0.25
	EURO 2	1998	1.2	-	1.5	0.17
	EURO 3	2001	0.86	0.78	0.95	0.10
	EURO 4	2006	0.46	0.39	0.74	0.06
	EURO 5	2010	0.350	0.28	0.74	0.005
	EURO 6	2015	0.215	0.125	0.74	0.005

<b>(C) Heavy duty diesel trucks [g/kwh]</b>						
<b>Standard</b>	<b>Year</b>	<b>HC</b>	<b>NO<sub>x</sub></b>	<b>CO</b>	<b>PM</b>	
EURO I	1992	1.1	8.0	4.5	0.61	
	(<85kw)					
EURO I	1992	1.1	8.0	4.5	0.36	
	(>85kw)					
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	
EUROVI	2013	0.13	0.4	1.5	0.01	

Indian government has also imposed various norms and setup Bharat Stage emission standard (BS) to regulate the output of air pollutants from internal combustion engine machineries, including motor vehicles. Table 1.3 shows the Bharat Stage emission standards for diesel vehicles. Since April 2010, Bharat stage III emission norms have been enforced across the country and Bharat Stage IV equivalent to EURO IV have been in place in 13 major cities at present. Thus, India is lagging behind developed countries where EURO IV has been implemented since September 2014.

**Table 1.3** Bharat Stage emission standards for diesel vehicles

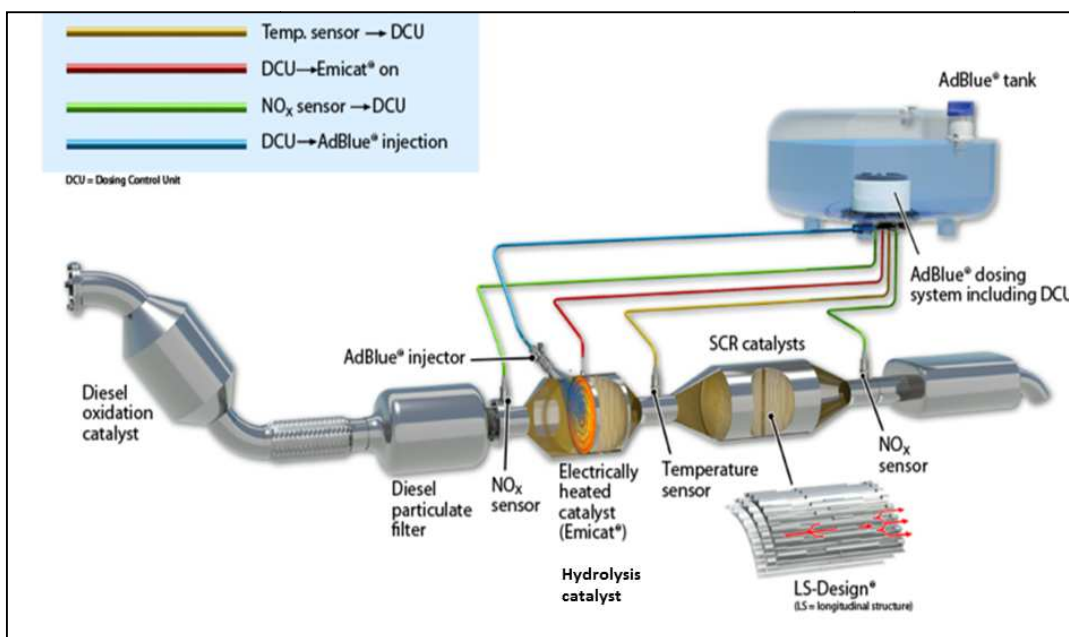
Standard	Reference	Date	Region
India 2000	Euro 1	2000	Nationwide
Bharat Stage II	Euro 2	2001	NCR*, Mumbai, Kolkata, Chennai
		April 2003	NCR*, 11 Cities†
		April 2005	Nationwide
Bharat Stage III	Euro 3	April 2005	NCR*, 11 Cities†
		April 2010	Nationwide
Bharat Stage IV	Euro 4	April 2010	NCR*, 13 Cities‡

\* 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.

The PM and NO<sub>x</sub> are the major pollutants emitted from the diesel engine. These pollutants are controlled from the exhaust by two entirely opposite technologies i.e. PM by catalytic oxidation in DPF whereas, NO<sub>x</sub> by selective catalytic reduction (SCR) as shown in figure 1.11. The present work is dedicated to abatement of PM by catalytic oxidation. NO<sub>x</sub> control is beyond the scope of the present study.



**Figure 1.11** Overall pollution control units in a typical diesel engine exhaust pipe

## 1.4 Diesel Soot Abatement Technologies

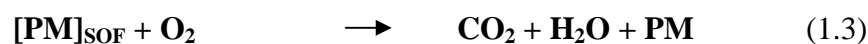
Nowadays the focus for the reduction of harmful diesel emissions is mainly on particulate matter (PM) and NO<sub>x</sub>. Hydrocarbons and carbon monoxide can be removed by use of wall flow oxidation catalysts. Furthermore, the SO<sub>x</sub> concentration of the exhaust gas is directly proportional to the sulphur content of the fuel and thus it could be removed with measures during the fuel distillation processes. According to EURO 6/IV norms the sulphur content of diesel in developed countries is 10 ppm, while in India diesel contains 50 ppm of sulphur at present. The most appropriate technology for the soot abatement is DPF as shown in figure 1.12. Controlling primary pollutants at the source of generation avoid formation of secondary pollutants in the atmosphere.



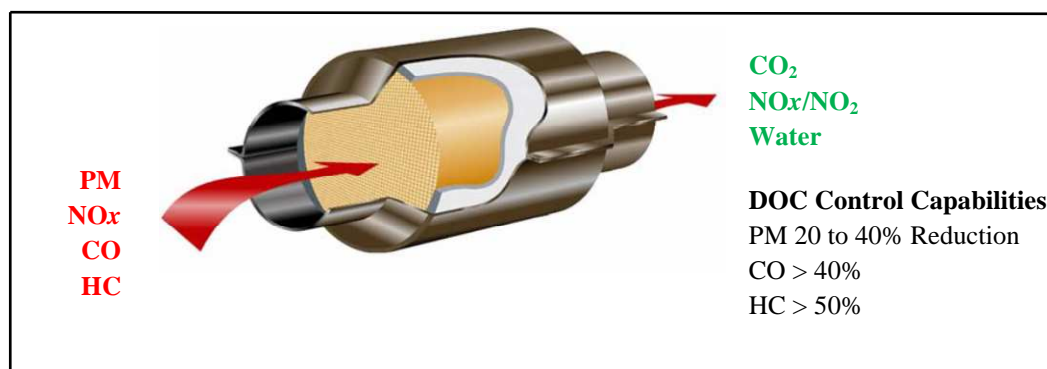
**Figure 1.12** Schematic diagram of DPF

#### 1.4.1 Diesel Oxidation Catalyst (DOC)

A diesel oxidation catalyst (DOC) is a flow through device that of a stainless steel canister containing a honeycomb structure called a substrate or catalyst support. The substrate has a large surface area that is coated with an active catalyst layer. This layer contains a small, well dispersed amount of precious metals such as platinum or palladium. As the exhaust gases traverse the catalyst, carbon monoxide, gaseous hydrocarbons and liquid hydrocarbon plus lubricating oil associated with particulates as SOF are oxidized as well as NO is converted to NO<sub>2</sub> being highly active than molecular oxygen of air, is needed for downstream oxidation of soot, thereby reducing harmful emissions equation (1.1 to 1.4).



About 30 per-cent of the total particulate matter (PM) mass of diesel exhaust is attributed to liquid hydrocarbons, or SOF [http://www.arb.ca.gov/regact/2010/res2010/res10isor.pdf]. Under certain operating conditions, DOCs have achieved SOF removal efficiencies of 80 to 90% [http://www.arb.ca.gov/diesel/documents/rrpapp9.PDF]. As a result, the reduction in overall PM emissions from DOC is often cited at 20 to 50% (table 1.4). Actual emission reductions may vary depending on operating conditions of the engine. The DOC can also be effective in generating sufficient exothermic heat over a catalyst which favors the regeneration of soot from a particulate filter as will be discussed in subsequent sections. Figure 1.13 systematically shows the functions of DOC.



**Figure 1.13** Diesel oxidation catalyst

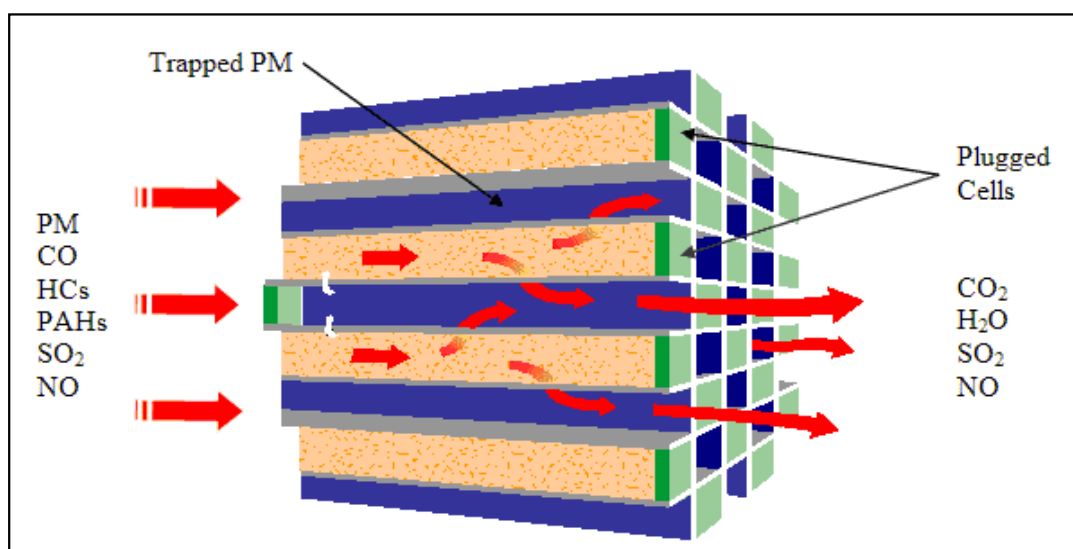
**Table 1.4** Typical Filtration Efficiency of Diesel oxidation catalysts [Source: DCL International Inc.]

Pollutants	Efficiency
NO <sub>x</sub>	Nil
CO	>90%
HC	80-90%
Aldehydes (odour causing)	70-90%
PM <sub>10</sub>	20-50%

\* Less than 50 ppm sulphur in diesel fuel is required for PM<sub>10</sub> conversion

### 1.4.2 Diesel Particulate Filter (DPF)

As the name implies, diesel particulate filters remove particulate matter in diesel exhaust by filtering exhaust from the engine. The diesel particulate filters are usually made of either cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) or silicon carbide (SiC) as shown in figure 1.14. The figure shows the PM trapping principle and main reactions of a catalyst-coated DPF. The device is generally positioned in the exhaust stream of a diesel vehicle. DPF system mechanically filters and collects the particulate matter from the exhaust gas. As the accumulated soot in the filter increases, the backpressure will progressively increase the fuel consumption and, in the end, stop the engine if the soot is not frequently or constantly removed by combustion reactions. To prevent these negative effects, the DPF have to be regenerated by oxidizing (i.e. burning) trapped PM. Thus, it is necessary to regenerate the trap by burning of soot. The main hurdle in the regeneration of DPF is soot kindling temperature ( $> 600\text{ }^\circ\text{C}$ ) which is not regularly achieved at vehicle exhaust conditions.



**Figure 1.14** Diesel particulate filter

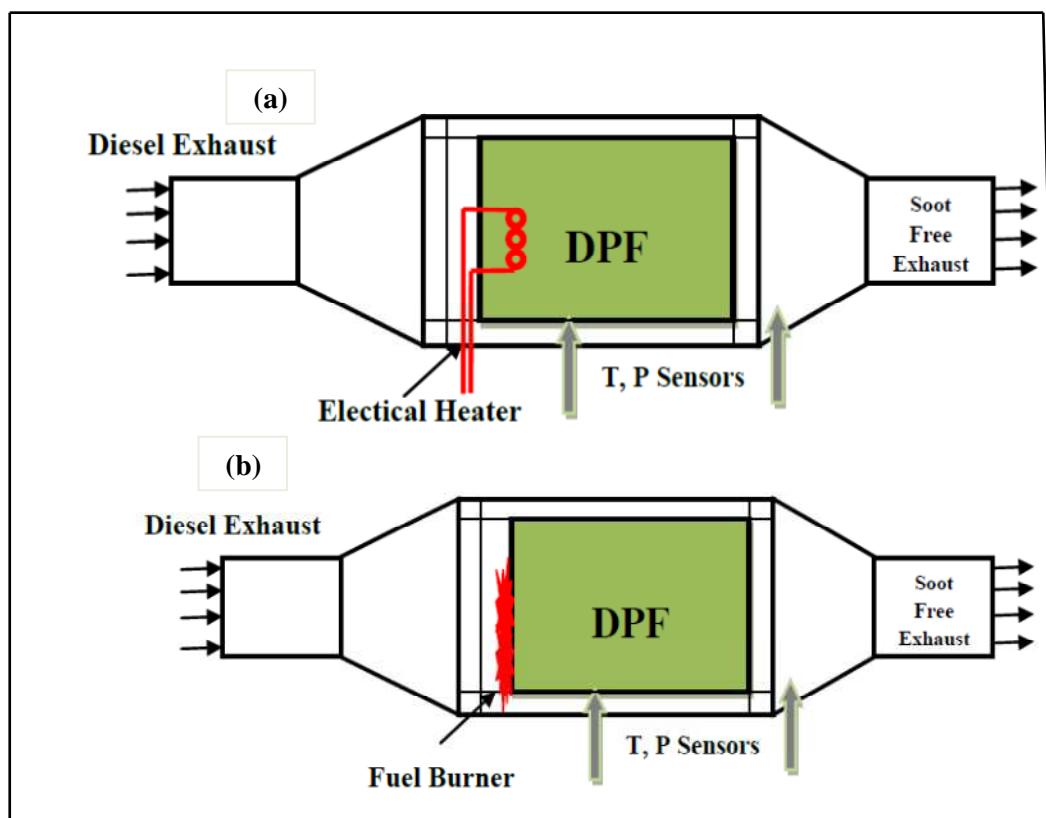
### 1.4.2.1 Regeneration of DPF

There are two basic approaches to burn the trapped PM [Farrauto & Voss, 1996, Neeft et al.1996]:

- 1) Periodic thermal combustion of the trapped soot by increasing temperature above  $600^{\circ}\text{C}$ , the process is known as *active regeneration*.
- 2) Continuous self-regeneration of trap, by lowering the combustion temperature of soot within the typical range of diesel exhaust using suitable catalyst deposited on the DPF, the process is known as *passive regeneration*.

#### (i) Active regeneration

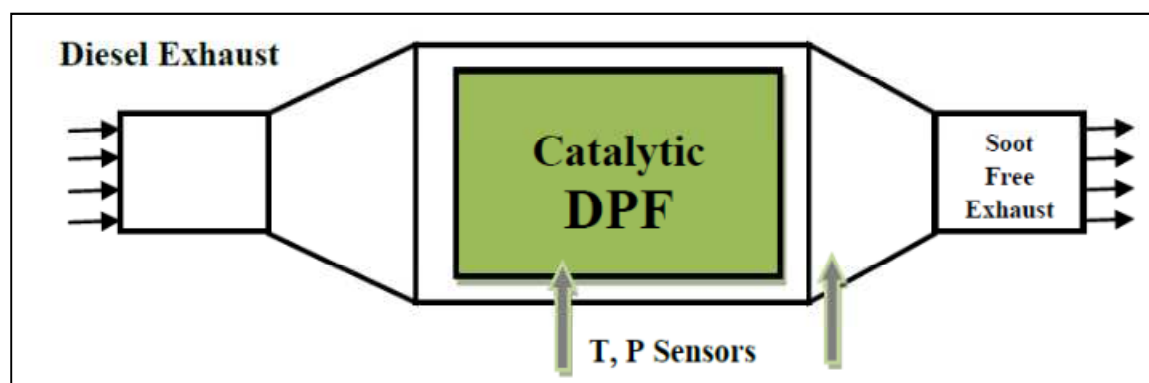
Thermal combustion or active regeneration is achieved either by applying flame or by electrical heating as shown in figure 1.15. Active regeneration is not favoured as it would increase the local temperature as high as  $1200^{\circ}\text{C}$  [Badani et al. 1996] and it may cause microcracks, which reduce filter durability [Ohno et al. 2000].



**Figure 1.15** Active Regeneration of DPF (a) electrical heater, (b) fuel burner

**(ii) Passive regeneration**

In passive regeneration of DPF, the soot is oxidized out of the filter by an ongoing catalytic reaction process that uses no additional fuel. Continuous self-regeneration of DPF occurs at the exhaust gas temperature, by catalytic combustion promoted by depositing suitable catalysts within the trap itself. The entire process is very simple, quiet, effective and fuel efficient. A passive regenerated system can reduce PM by 90%. The major challenge lies in finding catalysts capable of decreasing the soot combustion temperature from 600°C to the temperatures normally reached at diesel exhausts (150-450°C) [Fino et al. 2006]. 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. The objectives of the present work are in the same direction. Figure 1.16 pictorially shows passive regeneration systems.



**Figure 1.16** Passive regeneration of DPF

Some diesel particulate filters use a “passive” approach, and do not require an external or active control system to dispose of the accumulated soot. Passive filters are installed in place of the muffler. At the start of the engine at low temperature PM is collected on the filter. As the engine exhaust temperature increases, the collected material is burned



or oxidized by the exhaust gas, thus cleansing or “regenerating” the filter continuously. To ensure filter regeneration, various strategies (or combinations) are used. Regeneration methods include:

- Coating the filter substrate with PGM or free from PGM, thereby reducing the temperature needed for oxidation of the diesel particulate matter;
- Installing a catalyst (DOC) upstream of the filter increases the exhaust temperature which helps 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.

Plasma regeneration system is a more advanced 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 [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 NO<sub>2</sub> that facilitate the oxidation of soot particles at low temperatures.

**Table 1.5** Typical Filtration Efficiency of Diesel Particulate Filters (PM Mass) [Germany BMA 2001], [US non-coal mines MSHA 2001]

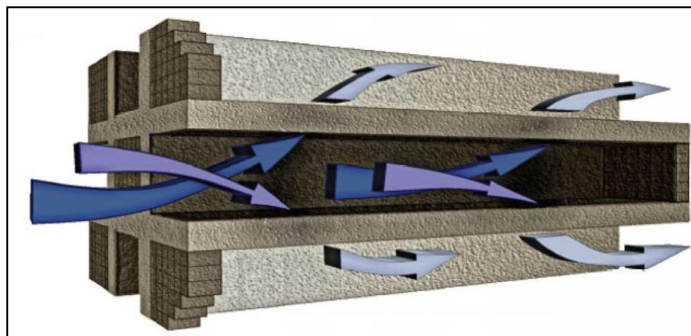
<b>Pollutants</b>	<b>Removal efficiency</b>
Elemental carbon	95 - 99.9%
Organic fraction (SOF)	50 - 90%
Sulphate particulates	No filtration
Total PM	70 - 95%

Table 1.5 describe the Typical Filtration Efficiency of Diesel Particulate Filters. There are varieties of diesel particulate filter technologies used as described below. Each is designed around similar requirements listed below:

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

### **1.4.3 Flow through Filter (FTF)**

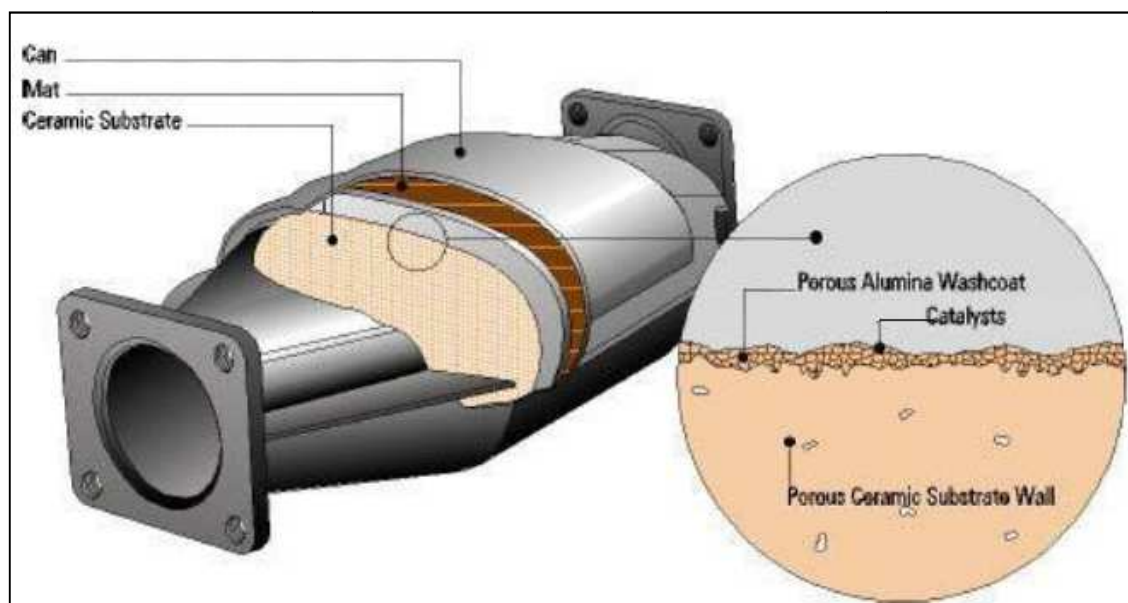
The FTFs are a relatively new technology for reducing diesel PM emissions. Wall flow filters are highly effective and can filter 99% of the particulate matter [Locker et al. 2004]. Unlike a DPF, in which only gases can pass through the filter components-the FTF does not physically "trap" and accumulate 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 unfavourable conditions (e.g. high PM emissions, low exhaust temperatures and emergency circumstances). The flow pattern of exhaust gases in wall flow monolith is shown in figure 1.17.



**Figure 1.17** Flow pattern in wall flow monolith

#### 1.4.4 Wash Coated Filter

The alumina Wash-Coated filters (Catalysed ceramic traps) were developed in the early 80's. Their first applications included diesel powered cars and, later, underground mining machinery shown in figure 1.18. Catalysed 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. Alumina wash coating increases the surface area of the porous walls of the monolith, which 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.



**Figure 1.18** Wash Coated Filter

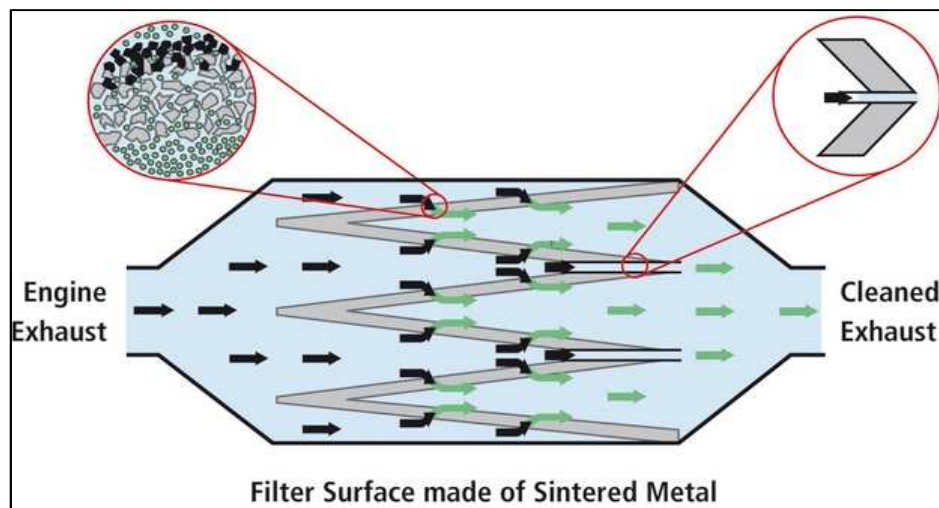
The main drawback of these systems is the poor contact between the catalytic coating and the soot particles. The distance is too high to enforce catalytic action. Only the particulates that are in direct contact with the catalytic coating are able to oxidize.

Another problem of catalysed filters is the generation of oxides by catalytic oxidation of the exhaust  $\text{SO}_2$  to  $\text{SO}_3$ , at high exhaust temperatures. The gaseous  $\text{SO}_3$  can penetrate the porous walls and freely leave the filter. Combining with water and reacting with other materials, it forms sulphate particulates that increase the total PM output especially in case of fuels with high sulphur 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  $\text{NO}_x$  reduction (DPNR). The Automotive Catalyst Division of Umicore (formerly Degussa/dmc<sup>2</sup>/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 catalysed DPF systems in large class vehicle models [<http://www.dieselnet.com/news/0311vw.html>].

#### **1.4.5 Partial-Flow Filters**

Partial-flow filters (Figure 1.19) 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  $\text{NO}_2$  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

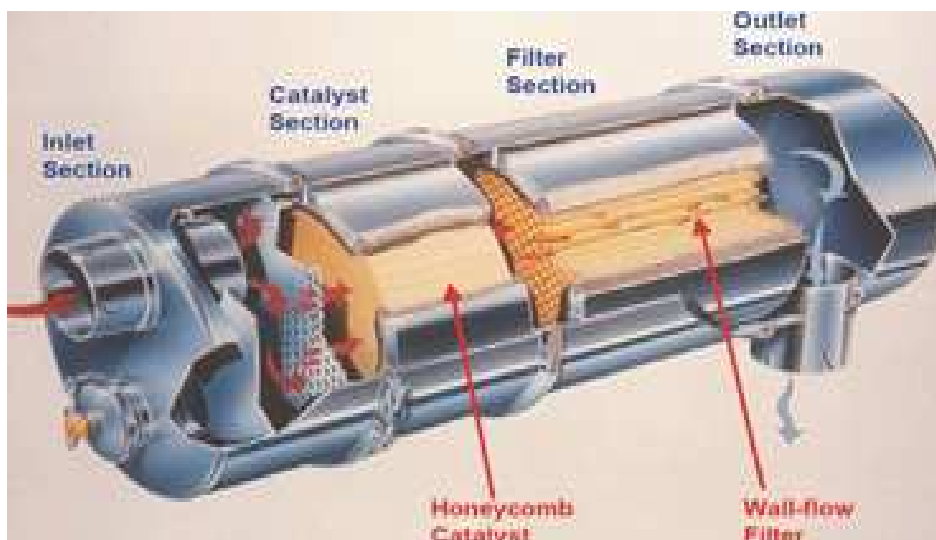
Flow Filters control capabilities are as follows: DPM 30-85% on gravimetric basis and approximately 90% on nano particles, HC and CO>50%.



**Figure 1.19** Partial flow diesel particulate filter

#### 1.4.6 Continuously Regenerating Trap (CRT)

The CRT particulate filter is emission control technology that uses a patented process that functions on the basis that soot will oxidize in the presence of  $\text{NO}_2$  at a lower temperature than with oxygen. In fact, this lower temperature is compatible with the typical exhaust temperature from diesel engines (150 to 400 °C). It is modularly engineered as a totally passive emission control system, which does not require the use of supplemental heat. As presented in Figure 1.20, the main parts of the CRT filter are a Platinum catalyst and a particulate filter.



**Figure 1.20** CRT filter system

The device is made up of two chambers where the oxidation step (DOC) is separate from the soot collection/combustion process. The DOC contains a substrate coated with highly active Pt oxidation catalyst which oxidizes a portion of the NO in the exhaust to  $\text{NO}_2$ , which is the key to the oxidation of soot collected by the CRT filter. In the second chamber, the exhaust flows through a DPF, where gaseous components pass through but soot is trapped on the walls of the filter. The trapped soot then is oxidised by the  $\text{NO}_2$  produced by the DOC. The DPF may be uncoated or it may be coated with Pt to further enhance the reaction of soot with  $\text{NO}_2$ .

### 1.5 Catalysts used in DPF

The catalysts used at present for soot oxidation are based on supported platinum group metals (PGM) [Uchisawa et al. 2003a, Uchisawa et al. 2003b, Hinot et al. 2007]. The noble metal catalysts are expensive and due to their scarcity to further price increase upon increasing demand. As an alternative to noble metals, oxides of transition metal, lanthanide group and alkaline earth metal are widely studied for soot oxidation [Shan et al. 2010, Jian et al. 2010, Shimizu et al. 2010, Mishra and Prasad 2014]. Neeft et al. [1996] arranged few single-component metal oxides for their relative activities in the

oxidation of carbonaceous material in following order: La > Mn > Sb > Bi > Ca > Cu > Ag > Ni > Cr > Zr > Ba > Zn. Various types of multi-component catalysts such as perovskite-type oxides [Teraoka et al. 2011, Peng et al. 2007], spinel type oxides [Shangguan et al. 1998, Fino et al. 2008, Zawadzki et al. 2011] rare earth metal oxides, hydrotalcite [Wang et al. 2012, Dai et al. 2012, Li et al. 2009] mixed transition metal oxides [Liu et al. 2005, Zhu et al. 2005, Tikhomirov et al. 2006] and other catalysts are reported in the literature for diesel soot combustion. The thermal stability of perovskite catalysts is very high in comparing to other types of catalysts including noble metals. The stability of the catalyst is highly desirable in comparison to the catalyst having very high initial activity but less stability. So, perovskite seems to be the potential candidate for this application, due to their thermal stability, tailoring capabilities to design the catalyst for soot oxidation and low-cost [Seiyama 1993]. Many papers related to soot oxidation over perovskite catalysts have been published but no review paper appears in the literature solely dedicated to soot oxidation.

## **1.6 Catalyst Design Parameters**

For catalyst design purposes it is first necessary to translate the catalyst performance parameters into a physical picture of catalyst structure. As one can see, different performance parameters give rise to different structural features and so a compromise is generally required [Kemball and Dowden 1981]. For example it is commonly found in industrial applications that initial catalyst activity may be sacrificed in favour of improved catalyst stability, since a lower activity and a prolonged operating catalyst life is in general preferable to a higher initial activity that decays rapidly. Therefore, first it should be discussed some of the relationships between the catalyst performance parameters and physical structure.

***(i) Activity***

In general activity arises from maximizing both the dispersion and availability of the active catalytic material. Ideally, from an activity viewpoint, the catalyst material should be highly dispersed throughout on the external as well as internal pore surfaces of the support. However, there is an inherent conflict as high concentrations of active material become progressively more difficult to disperse [Anderson et al. 1979].

***(ii) Stability***

By stability it is referred to the loss in activity with time [Kemball and Dowden 1981]. This is due to one or several of four main causes; fouling of the active surface with involatile reaction by-products, sintering or crystal growth of the active material, poisoning of the active surface by feed impurities, and blockage of the support pore structure.

***(iii) Selectivity***

Catalyst selectivity can change due either to physical or chemical reasons. For sequential reactions diffusivity and mass transport through the pore structure can lead to apparent loss in selectivity in the formation of intermediate products. Location of active ingredients and pore-size distributions are therefore again of importance. Changes in selectivity can also arise from changes in intrinsic chemical activity of the active component. Typically this can be affected by use of multi-component catalysts in which case, as it can be seen earlier for stability improvement, the location of the different components ideally should be the same. A specific example of this type of selectivity arises in the case of multifunctional catalysts in which a hydrogenation function is combined with an acid function. Since the latter is typically provided by the support and the former by the impregnated material, a uniform impregnation is required [Kemball and Dowden 1981].

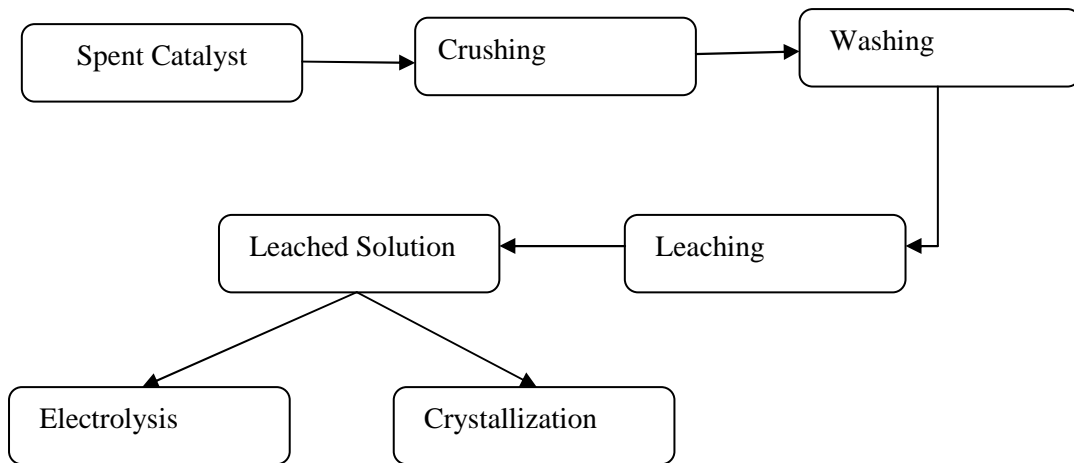


**(iv) Regenerability**

Regenerability refers to the reactivation of a catalyst, which typically will involve air combustion of carbonaceous deposits followed in some cases by a re-dispersion of the active components. From the catalyst design viewpoint this will generally imply enhanced thermal-hydrothermal stability of the support itself, combined with stability of the active components under the high temperature oxidizing environments required for the oxidation of the deactivating carbonaceous deposits. It is now generally recognized that many metals sinter more readily under oxidizing conditions and in extreme cases may even dissolve in the underlying support and become effectively removed from the reaction system. A further complication arises with multi-component catalysts in which the combination ratio is all important, since such combinations frequently are destroyed under oxidizing conditions [Argyle and Bartholomew 2015].

**(v) Reclaimability**

Reclamation stands for the recovery or restoration of useful substance from the spent catalyst. Emission control catalysts are precious metal catalysts (except for SCR catalyst). Depending upon the manufacturer and the catalyst type, these catalysts could contain one or more of the PGM: platinum, palladium, and rhodium. At the end of the catalyst's service life, these precious metals can be reclaimed and recovered. The service life is reached when the catalyst can no longer achieve the required performance, even after chemical washing and regeneration. Flow diagram of catalyst Reclamation is shown in figure 1.21.



**Figure 1.21** Flow diagram of catalyst Reclamation

## 1.7 Objectives of the Present Work

So far, the introductory discussions summarize that there is urgent requirement of a cost effective, active, selective and stable catalyst for the self-regenerative passive DPF. The work is motivated and performed with the following fundamental objectives:

- To scan the literature on the topic and write a review paper for publication.
- To develop a PGM free low cost and sturdy perovskite catalysts for oxidation of diesel soot.
- To optimize formulation of the catalysts and suitable calcination strategies.
- To compare the best screened PGM free perovskite catalyst with PGM catalyst.
- To study the effect of catalyst aging, catalyst reproducibility, catalyst - soot ratio and catalyst-soot contacts for diesel soot oxidation.
- To characterize the catalysts by low temperature N<sub>2</sub>-sorption, particle size analysis, X-ray diffraction, FTIR, XPS and SEM-EDX.
- To study the kinetics of catalytic oxidation of soot over the best screened perovskite catalyst.

## 1.8 Plan of Work

A brief outline of the research work carried out is summarized as follows:

- **Preparation of real diesel soot in the laboratory.**
- **Design and synthesis of following catalysts:**
  - LaCoO<sub>3</sub>, LaFeO<sub>3</sub>, LaNiO<sub>3</sub> and LaZnO<sub>y</sub> perovskite oxides catalysts.
  - Single (Sr-) substituted LaCoO<sub>3</sub> perovskite oxides catalysts.
  - Pd- substituted LaCoO<sub>3</sub> perovskite oxides catalysts.
  - Double Substituted (La by Sr and Co by (Cu, Fe, Ni)) in LaCoO<sub>3</sub> perovskite oxides.

➤ **Characterization of Diesel soot and catalyst samples:**

- Textural characterization including BET surface area, pore volume, pore size and pore size distribution.
- Spectral characterization by FTIR and XPS.
- X-Ray Diffraction analysis.
- Structural conformation of synthesized samples by SEM-EDX.

➤ **Catalytic performance evaluation for diesel soot oxidation**

Activity evaluation of all the catalyst samples for soot oxidation has been performed in a fixed bed tubular Reactor. The effluent gases were analysed by an online GC. Experiments were conducted under various operating parameters. Catalyst reproducibility, catalyst - soot ratio, catalyst-soot contacts and thermal stability of catalysts for diesel soot oxidation were also examined.

➤ **Kinetics study of diesel soot oxidation**

The kinetics of catalysed soot oxidation with air in laboratory has been studied under isothermal conditions in a specially designed semi-batch reactor over the best screened perovskite catalyst.