Chapter

Diesel Exhaust Emissions and Mitigations

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Abstract

This chapter presents a concise treatment of diesel engine exhaust emissions and its mitigations. The working principle of the diesel engine is first given to establish the background and further to describe the influence of various parameters that affect the formation of engine exhaust emissions. The factors that influence exhaust emissions are linked to the engine design and the operating factors that promote good fuel-air mixing and combustion. These factors are air induction, fuel injection equipment, fuel injection schemes, in-cylinder gas exchange process and heat transfer. Thermochemistry essentially gives insight to the global reaction kinetics and how this is applied in practical engine combustion determinations in terms of equivalence ratios. Based on these, the fuel spray structure, atomization, penetration and the spray combustion model are described. The formation of exhaust emissions such as carbon monoxide, unburnt hydrocarbon and its intermediates, oxides of nitrogen and soot in diesel engines has been discussed. The techniques of their mitigation from the view of internal factors that deals with the optimization of engine design and it performance, as well as various exhaust after-treatment techniques used for NO_x and soot reduction have been briefly discussed.

Keywords: diesel engine, fuel-air mixing, combustion, exhaust emissions, mitigations

1. Introduction

The diesel engine is a type of internal combustion engine invented in 1892 by Rudolf Diesel. It is so named in recognition of his patent which described a highly efficient, slow burning, compression ignition engine, where liquid fuel sprays were ignited solely by the heat of compression as piston reciprocates inside a cylindrical barrel. Compared to contemporary engines of that time especially the rival gasoline engine, it has superior efficiency in converting energy stored in liquid fuel to mechanical power. This superiority in fuel economy which has remained till date, is because diesel engine admits and compresses air only, (and can indeed be made to admit more externally compressed air into the cylinder) which is compressed to very high pressures and temperatures, before fuel is introduced into the combustion chamber as highly atomized sprays. Fuel-air mixing is achieved through combined factors of air swirl introduced through purposeful designed flow path, high fuel injection pressures, fine fuel atomization, and high temperature rapid fuel evaporation [1]. The high temperatures of the compressed air, reaches the auto-ignition temperature of the air-fuel mixture which burns and releases chemical energy in the fuel. Therefore, the way diesel fuel burns in the engine and the ultimate exhaust emissions are related to the way it is introduced, mixed and ignited in the chamber. This is also dependent on the properties of diesel fuel and the geometric profiles of the chamber itself. These factors determine the index of air utilization in the combustion process and define the nature of exhaust emissions. Issues of diesel engine exhaust emissions have been of concern for diesel engine researchers and developers such that, although the principles remain the same; substantial improvements have been made to the original engine described by Rudolf. These have ensured better engine combustion and emissions; however stringent regulations on modern diesel engine exhausts, have further led to incorporation of after-treatment devices to attain compliant levels.

2. The working principles of diesel engine

The diesel engine converts chemical energy stored in the fuel into work at the output shaft. This involves two steps; first is conversion of fuel chemical energy into thermal energy through combustion, followed by consequent conversion of thermal energy into mechanical energy by expansion of burning fuel in high pressure air. In effect, the following events take place: air induction, air compression, air and fuel mixing, burning of air-fuel mixture, expansion of the burning gases and their exhaust. These events or processes occur in four piston strokes during two revolutions of crankshaft. This gives the popular four-stroke cycle of induction stroke, compression stroke, power stroke during gas expansion and exhaust stroke, **Figure 1**. These events can also be arranged in a technology of two stroke operation using different design possibilities. Details of these are available in many standard diesel engine text books like [1–4] and only short summaries of these events are given with reference to **Figure 1** as follows.

2.1 Intake stroke

The intake stroke is the period when piston moves down from the top dead center (TDC) to the bottom dead center (BDC). During this time, the intake valve is open while the exhaust valve is closed. In operation, the intake valve is timed to open shortly before the TDC and closes after the BDC. This enables

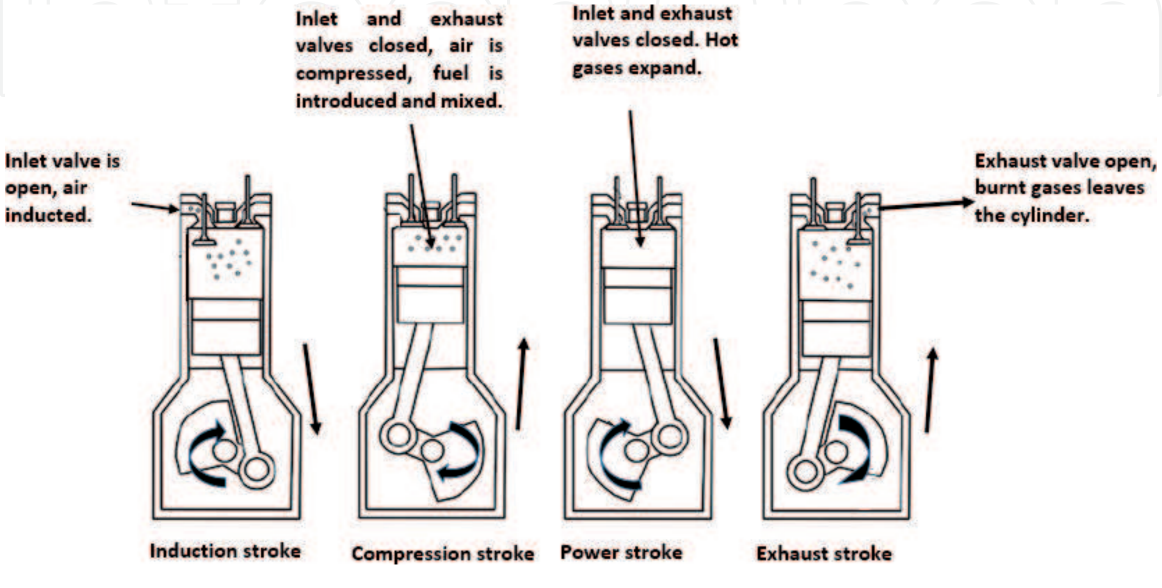

Figure 1.
The four-stroke cycle of typical diesel engine.

fresh mass of filtered air to be drawn into the cylinder. The higher density fresh charge displaces burnt gases, thus enhances scavenging of the cylinder of burnt gases from previous cycle.

2.2 Compression stroke

This is the period when the piston moves up from BDC to TDC, and compresses the air inside the cylinder to a small fraction of the total cylinder volume. During this time, the intake and exhaust valves are closed; and as the piston approaches the TDC, diesel fuel is injected into the hot compressed air at a temperature sufficiently high to ignite the fuel, which burns and releases high thermal energy.

2.3 Power or expansion stroke

The expansion of high temperature and pressure burning gases pushes the piston down from the TDC to BDC giving the useful power stroke. This is also called the work stroke because the high pressure gases act on top of the piston surface. Its impact on the connecting rod is transmitted to the crankshaft causing it to rotate and produce useful work on the shaft. During this process, both valves are theoretically closed between the centers but practically, the exhaust valve is timed to open some degrees before BDC to initiate pressure drop inside the cylinder by allowing burnt gases to escape.

2.4 Exhaust stroke

The upward movement of the piston again from BDC to TDC pushes out the burnt gases through the fully open exhaust valve. As the piston approaches the TDC, the intake valve also opens. This allows admission of fresh air into the cylinder, the density of which is greater than that of burnt gases, displace them and fill up the cylinder again. The pressure drop created by early opening of the exhaust valve also reduces the work done by the piston in pushing out the burnt gases. The cycle then continues.

3. Engine design factors that influence quality of exhaust emissions

At the core of diesel engine performance analysis is the efficiency of combustion and quality of exhaust emissions. These are related to the air utilization and fuel economy. Many factors affect engine combustion efficiency, which can individually and collectively affect the quality of exhaust emissions. Of interest in diesel engine emissions are the factors that promote generation of regulated variables which include soot, which along with other adsorbed particles like condensates of unburnt hydrocarbon (UHC) and its intermediates, is generally called particulate matter (PM); oxides of nitrogen (NO_x) and carbon monoxide (CO). Their emissions into the atmospheric environment have impact on human health and are therefore regulated in the concentrations they could be emitted from modern engines. The factors that influence their generation include fuel injection pressure, injection timing, ignition delay, fuel atomization, spray-configuration, technique of supplying air, either quiescent or swirl and level of turbulence. These are related to the way fuel is introduced, mixed and ignited in the chamber to achieve good air utilization in the combustion process. Another inherent factor is the very nature and properties of diesel fuel. Every factor simply helps to achieve the underlying chemical balance in combustion equation which can be technically challenging in the complicated engine environment. To obtain a chemically correct fuel-air combustion in diesel engine is complicated due to the presence of partly premixed fuel and air, and mainly due to unsteady-turbulent diffusion burning encountered in rapid vaporization of liquid fuel, with very short time for the fuel and air mixing. Diesel fuels contain different fractions of alkyl and aromatic components and the combustion mechanisms depend on the molecular structures of different species. These structures are based on the intra-molecular carbon bonds that may be single, double or triple bonds; and straight, branched or ringed chains. They determine the combustion characteristics associated with diesel fuels [5].

The consideration of these factors with the aim of improving exhaust gas emissions through better air utilization to achieve better combustion has led to optimal designs of key operating parameters [6].

3.1 Air induction

The air induction system consists of air filter, ducts, intake manifold, intake port and intake valves. The air charge induced into the cylinder is related to power output, quality of combustion and exhaust emission during a cycle. Cylinder displacement is fixed based on engine geometry; therefore naturally aspirated capacity is constrained. Design improvement to increase induction capacity is by compressing air to higher density prior to introduction into the cylinder. This is referred to as boosting or supercharging. Typical method of supercharging diesel engines is by allowing a portion of the escaping exhaust gases at high thermal and kinetic energy levels to flow and expand through turbine blades. The power imparted on the shaft is used to drive a centrifugal compressor, axially connected on the same turbine shaft to compress more air into the cylinder. This is known as turbocharging and the increased air charge in the cylinder boosts the power output from the fixed cylinder volume. Optimal design of turbochargers has increased power-to-weight ratio, improved engine efficiency, lowered exhaust emission and in general engine downsizing [1, 3, 4, 7].

3.2 Fuel injection equipment

Fuel injection equipment systems are used to supply finely atomized fuel sprays into the combustion chamber at precisely controlled time. Types of injection systems include pump-line-nozzle (P-L-N) systems, unit injector and common rail injection systems. These are general categories of injection systems, each having distinct designs. Common in the P-L-N system are in-line (**Figure 2**), the distributor or rotary pumps and the unit pump designs which are either mechanically or electronically controlled. The unit injectors are known to deliver very high pressure because of active mechanical intensifiers like plungers or large cams as in the pressure-time (PT) controlled systems. They are similarly controlled either mechanically or electronically. The common rail injection system (**Figure 3**) in conjunction with electronic control has been developed to overcome some of the draw backs in P-L-N and unit injection pumps. Essentially, it has overcome the dependency of fuel injection pressure and quantity on engine speed, enabled flexibility in matching the fuel injection timing, and smoothening fluctuations due to cycle-to-cycle variability. In all versions, filtered diesel fuel is first lifted from the tank to main gallery of a high pressure pump. The high pressure pump then delivers fuel to the injectors, (which are of different nozzles tip profiles) to spray fuel into the combustion chamber. Modern engine fuel injection systems are controlled by dedicated electronics giving rise to precise fuel spray at high pressures; and the fuel spray profiles are matched to optimized chamber to improve combustion and level

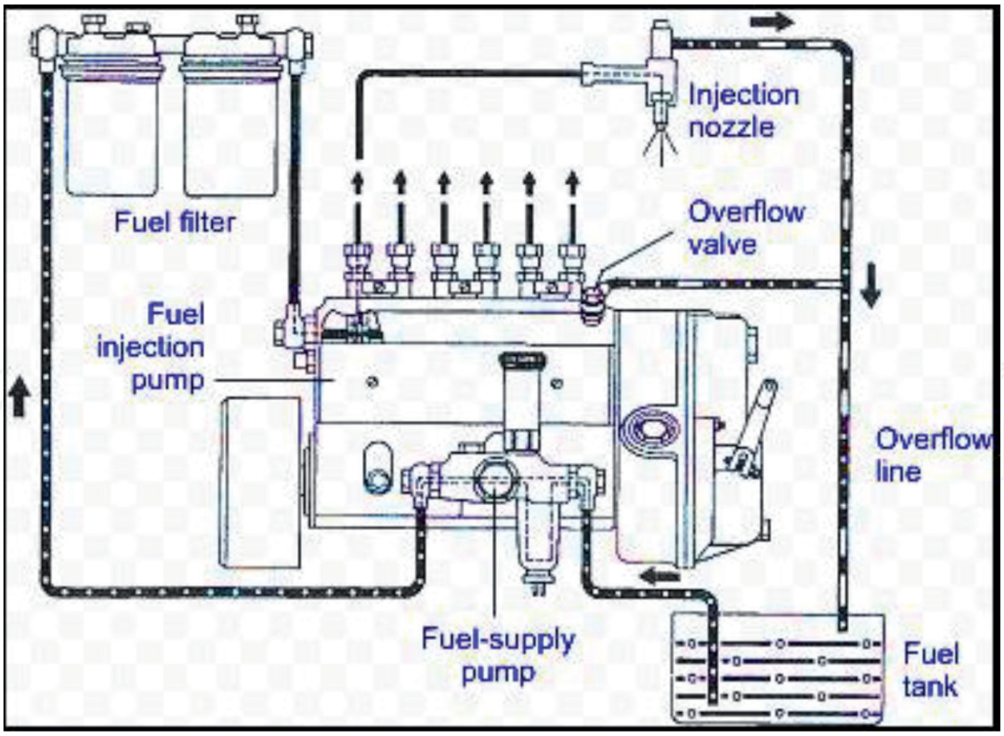

Figure 2.
Pump-line-nozzle system (adapted from DieselNet. Courtesy of Robert Bosch GmbH).

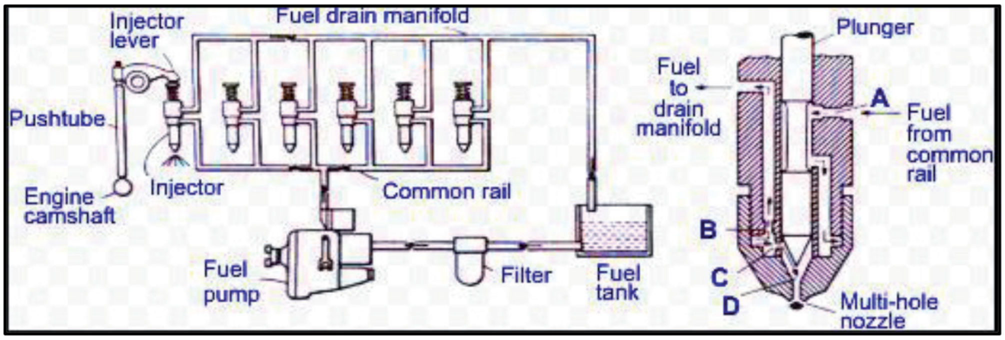

Figure 3.
Typical common rail lay-out of a typical Cummins PT fuel injection system (adapted from DieselNet. courtesy of Cummins Inc.).

exhaust emissions. Many manufacturers especially for heavy duty diesel engines have developed proprietary electronic fuel injection systems relevant to their total engine management system. Good discussions about different injection systems and their impact on exhaust emissions can be found on reference [3].

3.3 Diesel fuel injection

The scheme of injecting diesel fuel into the combustion chamber is multipurpose apart from mere delivery. The purposes are intricate functions that ensure efficient combustion and reduction of hazardous emissions. These include: timely control of fuel injection, control of right quantity of fuel delivered to meet engine duty or load and at high pressure to enhance good mixing with air. Good air-fuel mixture is an important parameter for efficient combustion through the injection of high pressure sprays that effectively entrains the compressed air in the combustion chamber. These functions are generally enhanced through different injection strategies. Studies have shown that splitting fuel injection into divided doses per combustion cycle reduces emissions [8–11]. This has enabled injection requirements to be met for different engine operating conditions since engines encounter varying demands, from low-speed, low-load; to medium and high-speed, high-load applications. Good fuel injection is synonymous with the choice of injection equipment which achieve the engine schedule of time, quantity and pressure. Injection pressures can range from 200 to 2000 bars or higher, with nozzle exit velocity of about 100–300 m/s. The in-cylinder air pressure is about 40–100 bars during the time of injection and about 15–25 kg/m^3 in density.

3.4 In-cylinder and gas exchange processes

The processes that occur inside the cylinder are usually described using the corresponding pressure—crank angle diagram. The sequence of valve actuations are numbered 1–4 in **Figure 4** for a four stroke naturally aspirated diesel engine.

A momentary period of valve overlap expressed in degrees of crank angle occurs between points 1 and 4 when both valves are open. This period is significant to the engine performance and emission characteristics because the volumetric efficiency, particularly in the absence of boosting depends on the in-cylinder filling during this period. As valve openings and closures are not instantaneous, the timing is designed to ensure that both are fully open when the benefit of maximum pressure difference will cause the working fluid to flow across them. In current designs, the poppet valves are located in overhead position in the cylinder head. The geometric profiles of intake manifold, intake port and the poppet valves are designed to enhance air breathing capacity of the engine and also to impact swirl and/or squish motion to the bulk flow into the cylinder. The air utilization during combustion process is dependent on how well it is premixed with fuel sprays prior to combustion or accessible during diffusion burning. Engine combustion chamber is designed to complement the effect of fuel spray profile while the air motion enhances mixing/burning process. The optimization of these engine elements are very significant to the level of exhaust emissions.

3.5 Heat transfer

The heat transfer considerations in the engine environment are complicated as all modes are involved within the combustion chamber. Preservation of the structural integrity and geometric profiles of the mating surfaces necessitates removal of heat generated during combustion, particularly from the hottest regions to avoid

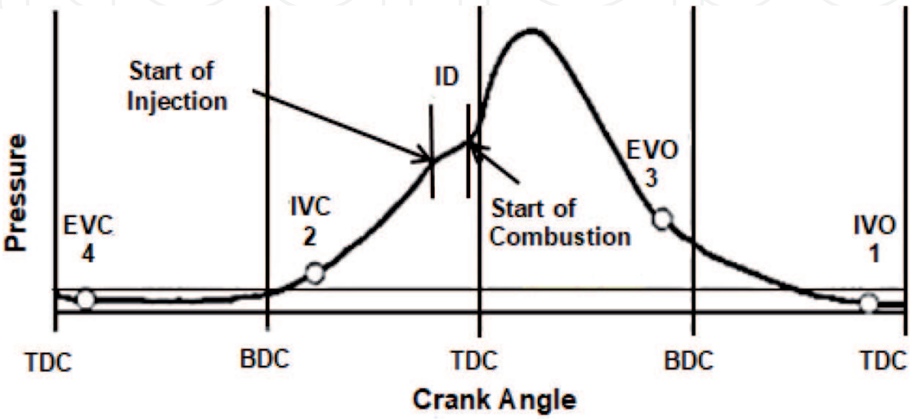

Figure 4.
In-cylinder pressure-crank angle diagram with sequence of valve actuations and processes in four stroke CI engine (IVO, intake valve open; IVC, intake valve closure; EVO, exhaust valve open; EVC, exhaust valve closure; TDC, top dead center; BDC, bottom dead center) [1, 3].

distortion of these surfaces. Engine heat transfer involves use of cooling water jackets around the regions with highest heat fluxes; the hot water is then pumped to the radiator where heat is lost to ambient environment by forced convection. Some low duty designs adopt the use of air cooling as it flows across an increased surface area created by fins around the cylinder head and walls. The engine efficiency, performance and emissions are greatly affected by heat transfer as such; it is optimized to retain enough heat required to maintain normal engine working temperature and the excess transferred to the cooling medium. This explains the inefficiency usually encountered during cold starting when the work transfer to the piston is reduced as high heat transfer occurs to the chamber walls and other working parts for quick warm up. Similarly, during this transient period, heat transfer affects the process of forming gaseous and particulate matter emissions both within the cylinder and exhaust line where post combustion reactions occur.

4. Thermo-chemistry

The stoichiometric air-fuel ratio $(A/F)_s$ is the chemically correct air-fuel proportion that will completely burn to yield only water, carbon dioxide, and nitrogen. It is dependent on the chemical composition of the fuel. Engine combustion makes use of atmospheric air which contains nitrogen; therefore a general expression for complete combustion of a molecule of hydrocarbon fuel C_aH_b with air is given as [1]:

$$C_a H_b + (a + b/4)(O_2 + 3.773N_2) = aCO_2 + (b/2)_2 O + 3.773(a + b/4) N_2 \quad (1)$$

Eq. (1) defines the stoichiometric ratio of fuel and air reaction that could be utilized for gravimetric analysis of complete fuel combustion in air. It depends on the fuel molecular structure. In engine combustion analysis, it is usual to also express $(A/F)_s$ as a reciprocal, meaning fuel-air ratio $(F/A)_s^{-1}$. Either way is useful in expressing engine operating condition because during engine testing, both air and fuel flow rates are measured to determine if the mixture is rich or lean. The degree to which fuel is rich or lean, is central to engine performance analysis especially with regards to emission considerations. The products of combustion emitted in either of the mixture situation differ significantly due to fuel chemical composition and structure. In this regard, a parameter: equivalence ratio (ϕ) that expresses the actual fuel/air ratio to the stoichiometric value is normally adopted for expressing the composition of mixture.

$$\phi = (F/A)_{actual} / (F/A)_s \quad (2)$$

Alternatively, the inverse of ϕ could be used as relative air/fuel ratio (λ), similarly defined as:

$$\lambda = \phi^{-1} = (A/F)_{\mathrm{actual}}\, (A/F)_s \quad (3)$$

Comparatively, mixture strengths are expressed as follows:
Fuel rich mixture: $\phi > 1$, $\lambda < 1$
Fuel lean mixture: $\phi < 1$, $\lambda > 1$
Stoichiometric mixture: $\phi = \lambda = 1$

From Eq. (1), exhaust emissions associated with engine combustion on stoichiometric condition are supposed to be carbon dioxide (CO_2), water vapor (H_2O) and nitrogen (N_2). However this is not practically possible as other emissions like carbon monoxide (CO), unburnt hydrocarbons (UHC), oxides of nitrogen (NO_x), oxides of sulfur (Sox) and soot are inevitably present. These emissions arise due to unsteady combustion, post combustion and engine cycle-to-cycle fluctuations. During combustion and about some degrees after the top dead center (TDC), the composition of combustion products corresponds to local equilibrium with respect to pressure, temperature and equivalence ratio. But as expansion stroke advances, recombination reactions of active species occur, and their compositions are changed. Due to fast changing cylinder condition during this period, recombination reaction is not able to maintain the species in chemical equilibrium. As the exhaust valve opens, exhaust flow process forces species compositions to freeze as they are expelled from the cylinder. By implication, even if the fuel-air mixture was lean, not all fuel species had opportunity to be fully oxidized. Also, it is not possible to equally match all the in-cylinder flow conditions in a multi-cylinder engine; therefore it is difficult to have the same exhaust composition from all cylinders. During testing, engines are calibrated to meet transient and stable operations of which fuel-air mixtures vary from rich to lean conditions, thereby giving various emission levels. Therefore evaluation of engine-out emissions is cumbersome and is best approached through experimental measurements [1].

5. Diesel spray structure, atomization and spray combustion

Prior to development of optical accessible engines with laser diagnostics, direct measurement of combustion events inside the engine cylinder was difficult; high speed movies were used to record the spread of fuel jets and flame propagations. Efforts were also made to calculate fuel injection rates from measurements of fuel injection parameters; and the associated heat release rates from engine pressure data in order to gain insights about the combustion process but, details could not be obtained about the true in-cylinder reactions. The development of laser diagnostics enabled in-situ measurements to be made as in-cylinder diesel-spray combustion reactions occur. It is through this approach that planar images have been recoded with good temporal and spatial resolutions, and generates data that offers better interpretations. The fuel spray trajectory, combustion and extinction is the conceptual basis for describing combustion in diesel engine. Currently, there are good insights into the complexity of fuel spray, lift-off length, air-fuel mixture formation, combustion and resultant emission formation through modelling and experiments. The conceptual model presented by Dec in 1997 based on laser sheet imaging [12] is the hallmark of several efforts made with his co-workers at Sandia National Laboratory and many other authors toward contributing to the current understanding. The laser sheet imaging diagnostics has revealed the true nature of in-cylinder processes like: entrainment of air as liquid fuel ejects from nozzle and mixes with hot swirling air to form combustible mixture, images of poly-aromatic hydrocarbons (PAHs), the auto-ignition event, soot formation which starts well from the upstream and central regions of the jet toward the head vortex, as well as the relative particle size distributions and concentrations of soot emission. Separate investigations made for fuel-air mixing, combustion and post-combustion reactions were used to establish the conceptual model (**Figure 5**) as a framework for describing spray combustion.

The original work of Dec used large bore diesel engine with nearly quiescent flow-field, and represented 'quasi-steady' free jet combustion without collision or wall impingement. Subsequent studies that gave information on fuel jet ignition and penetration, have dwelt on this model to elucidate the combustion phenomenon. Detailed information about these developments through modeling and experimental examinations can be checked in the following references: [13–21].

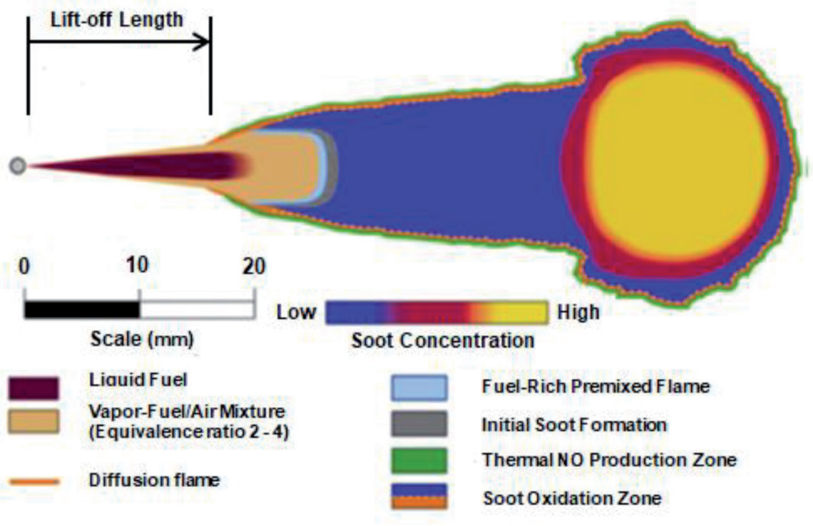

Figure 5.
Dec's conceptual model of quasi-steady spray combustion in conventional diesel engine [12].

5.1 Spray structure

The structure of spray evolving from the injector nozzle is related to the injection pressure, size of nozzle holes and their orientation in the combustion chamber. If flow through the nozzle is considered to be of a quasi-steady, incompressible nature in one dimension, the model for mass flow $\dot{m}_f$ rate of fuel injected is given as [1]:

$$\dot{m}_f = C_d A_n \sqrt{(2 p_f \, \Delta P)} \tag{4}$$

Where the C_d is the discharge coefficient, A_n is the nozzle flow area, p_f is fuel density, $\Delta P = (P_f - P_{cyl})$ the pressure drop across nozzle orifice, $\Delta\theta$ is the injection duration in crank angle degrees and N is the engine speed in RPM. If the pressure drop across the nozzle and nozzle open area are taken to be constant during the injection period, the mass of fuel injected is then

$$\dot{m}_f = C_d A_n \sqrt{(2 p_f \, \Delta P)} \, \frac{\Delta\theta}{360N} \tag{5}$$

This relation gives the dependency of overall fuel delivery characteristics of the injection system on injection parameters [2]. However in practice diesel injection is unsteady, the injection pressure as well as in-cylinder pressure vary during the injection period. Similarly, there are significant compressibility effects on the injection process at the very high unsteady pressures encountered in operation; but these are not considered here.

Information about the spray structure has been established though modeling and simulation as well as through laser diagnostics as in the references given. Volumes of publications that describe spray structure through simulations, used Reynolds Average Navier-Stokes (RANS) model and large eddy simulation (LES). The LES turbulence model capture large unsteady flow structures that are responsible for mixing. At a finite distance after nozzle exit called break-up length (L_{bu}), the jet flow becomes fully turbulent and the liquid fuel starts to breaks into small droplets as in **Figure 6**. This development creates a large surface area for air to be entrained into the spray, making it to increase in diameter even as it trust axially away from the nozzle tip. As the bulk of the spray penetrates into the cylinder, the early droplets that encounter hot dense air especially at the periphery, loses momentum to the air and the droplets behind the wake penetrate deeper into the

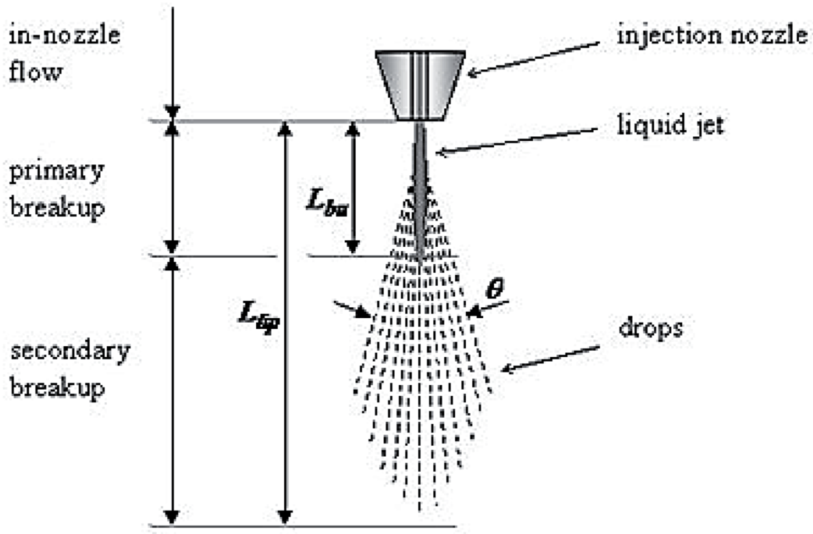

Figure 6.
Schematic of diesel spray structure (adapted from AdvancedEngineeringCenter@brighton.ac.uk).

combustion chamber. For large bore cylinders, the penetration is undisturbed and reaches full spray tip penetration length (L_{tip}); but for small bores cylinders, spray impinges on the chamber walls. This make the droplets to spread on the hot walls and experience quick evaporation and mixing with air.

5.2 Spray atomization

Diesel fuel is injected as conical-shaped spray jet into hot air at conditions that are higher than the critical temperatures and pressures of the fuel, and the increase in velocity of the jet leads to large scale instability. Studies have shown that the jet break-up depends on characteristic factors like the nozzle hole length to diameter ratio, its shape, smoothness, and the rate of injection pressure rise. The break-up mechanisms are classified into primary and secondary regimes depending on prevailing conditions [1, 22]. Primary break-up occurs when the liquid jet near the injector nozzle disintegrates into very small droplets due to interaction with in-cylinder gas. Generally this regime is used to classify break-up at the outer surface of the plane of nozzle exit due to very high jet velocity. The average droplet diameter are much smaller than the nozzle diameter. This initial break-up are considered to be initiated by many factors like turbulence and collapse of cavitating bubbles causing unsteadiness in the nozzle flow and full interaction with swirling air, effects of surface tension and aerodynamic forces, leading to break-off of some filaments or droplets. The continued influence of aerodynamic forces induce further break-up and reduction of the droplets sizes as flow penetrates into the surrounding air. This is called secondary break-up and together with progressively strong evaporative effects, droplet size diminishes in axial flow direction. At the droplet level, the break-up is assumed to be controlled by droplet Weber number (We), defined as the ratio of inertia forces to surface tension forces:

$$We = \rho_a D_d U_{rel}^2 / \sigma_f \tag{6}$$

where ρ_a—ambient air density, D_d—droplet diameter, U_{rel}—relative velocity between droplet and the ambient gases, σ_f—surface tension of fuel.

Weber number is typically in excess of 100 in modern diesel engines implying that stripping and catastrophic regimes are the important modes of droplet break-up regime (**Table 1**).

We	Break-up mode
We ≤ 12	Vibrational
12 < We ≤ 18	Bag
18 < We ≤ 45	Bag-and-stamen
45 < We ≤ 100	Chaotic
100 < We ≤ 350	Sheet stripping
350 < We ≤ 1000	Wave crest stripping
1000 < We ≤ 2670	Catastrophic

Adapted from [22, 44–46].

Table 1.
Secondary droplet break-up classification.

5.3 Spray penetration

Spray penetration is of great benefit for overall fuel-air mixing rates and degree of air utilization. Fuel atomization and evaporation enable fuel-air mixing in the immediate vicinity while substantial quantity of air may remain unutilized for combustion if not quickly reached by fuel species further inside the cylinder. Faster fuel spray penetration rate into the combustion chamber quickens the mixing rate. Many studies have been carried out to get good correlations both experimentally and by turbulent jet mixing theory to propose penetration models [23–25]. While it is good to achieve good penetration, in multi-spray nozzles in direct injection combustion engine, over-penetration leads to fuel impingement on the chamber walls which might be cool and lowers mixing rates thereby causing emissions of unburnt and intermediate hydrocarbon species.

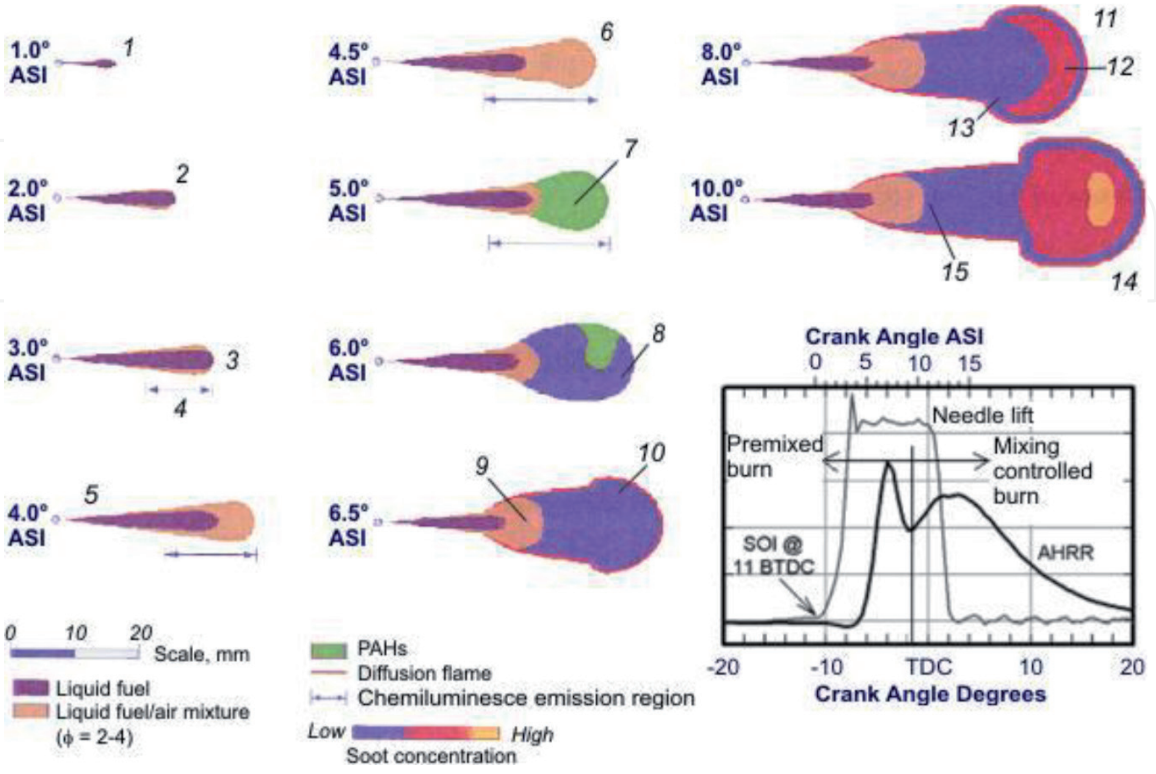

Figure 7.
Modified conceptual model [12, 19, 22].

5.4 Spray combustion

The original work of Dec used to establish the framework that described spray combustion used large bore diesel engine with near-quiescent flow-field, and represented 'quasi-steady' free jet combustion without collision or wall impingement. The temporal sequence of the conceptual model that have been modified to include some recent contributions [19] is described and adapted here as in **Figure** 7. The crank angle degree after the start of injection (*ASI*) is indicated on each image, is used to trace the history of spray combustion in the chamber.

5.4.1 Fuel jet and air entrainment (0.0–4.5° ASI)

Fuel sprays exiting the nozzles penetrate into the chamber and expand to near conical shapes. Based on the investigations in [26], the images were captured from nozzle exit at intervals of 0.5° of crank angle degrees. At 1.0°, liquid jet core (dark brown) moves a maximum of 23 mm downstream corresponding to 3.0° *ASI*. The fuel is all vaporized by the entrained air and this limits liquid core penetration. The gas-phase jet penetrates downstream and develops vortex-head due to further entrainment. Correlations for entrainment in [27] and direct fuel vapor measurement in [28] show that as entrainment increased downstream, there is inverse variation of equivalence ratio along the jet axis. Here the description of equivalence ratio is given as the ratio of local fuel-ambient charge mass ratio to the stoichiometric fuel-ambient mass ratio. The liquid fuel is heated and vaporized by the thermal energy of the entrained air, therefore at some distance downstream referred as liquid length, all liquid fuel are vaporized. The entrainment correlations have been used to determine this distance and also establish that it could be shortened if the ambient charge density is increased.

5.4.2 Auto-ignition (3.0–5.0° ASI)

The beginning of flame initiation is not definite; however Chemiluminescence imaging offers opportunity to examine auto-ignition in diesel combustion. The arrows under the vortex head in jets 3.0–5.0° *ASI*, indicate the Chemiluminescence region of the jet which may even appear earlier. At onset around 3.0–3.5° *ASI*, the vapor fuel-air mixture is thin and around 4.5° ASI, most of the Chemiluminescence emerge from the leading edge portion of the vapor fuel-air mixture and indicates fuel breakdown and formation of PAH in the region 4.5–5.0° *ASI*.

5.4.3 Pre-mixed combustion (4.0–6.5° ASI)

From the curve of heat release rate (insert), the rate starts to rise after 3.0° and the sharply from 4.0–5.0° ASI. During the same time, emergence of Chemiluminescence is followed by rapid fuel breakdown and formation of PAHs increasingly in the leading edge of the jet where an equivalence ratio is about 2–4.

The initial burning of this premixed rich mixture is indicated by sharp rise in the heat release rate followed by rapid PAH and soot formation between 5.0 and 6.0° ASI downstream of the jet. Upstream, there is more fuel break-down due to increase in temperature, as typified by jet at 6.0° ASI.

5.4.4 Early diffusion flame (5.5–6.5° ASI)

As the apparent heat release peaks during pre-mixed burn period, there is corresponding appearance of thin diffusion flame on the periphery of the vapor-fuel/air mixture. This is a consequence of fuel rich premixed combustion that burns comfortably in the presence of air. Quickly, the whole periphery of the jet downstream is covered by this thin diffusion flame burning at high temperature with consequent formation of nitrogen oxides. The flame is limited upstream to a point referred as 'Lift-off Length' from the nozzle tip which corresponds to the border region of the vapor-fuel/air mixture. Here the flame is lifted and due to increased local heating, the rate of fuel break-up increases as evidenced by a decrease in the liquid-fuel length by about 2–3 mm.

5.4.5 Last part of pre-mixed combustion (7.0–9.0° ASI)

As fuel-air mixing rate increases, PAH and soot formation are enhanced towards the end of pre-mixed combustion, and this extends length of the jet downstream. At about 8.0° ASI, the soot concentration is high and almost fills the jet cross-section bulging more towards the leading edge to form a head vortex. At the periphery of the jet, the thin sheet of turbulent diffusion flame produces larger soot particles that move inwards to mix with the inner smaller soot particles in the bulk volume of the jet, this is more active at the leading edge where there is more soot concentration. As the last portion of the premixed charge burns, smaller size soot particles are formed over the entire jet volume extending up to 27 mm from the tip of the injector but soot is entirely lifted off the nozzle tip for the reference low sooting fuel.

5.4.6 Mixing-controlled combustion (9.0° ASI to end of injection)

At about 9.0° *ASI*, the combustion has entirely become mixing-controlled and the appearance of the jet as used to hypothesize the conceptual model is fully established at about 10.0° *ASI*. At this point, the sizes of soot particles remain small from upstream edge where the last portions of the premixed burns, but the concentration increases downstream. The concentration is more at the center of vortex head which becomes very prominent with large soot particles as signified by color codes. This last image is ordinarily taken as a representative of the final jet development. It is typical of the observations made of the remaining mixing-controlled combustion of injected fuel.

5.4.7 The conceptual model

The typical conceptual model is used to explain full spray combustion during mixing-controlled phase towards the end of fuel injection, **Figure 8**. The model is a modification of the last stage in jet development captured about 10.0° ASI and to

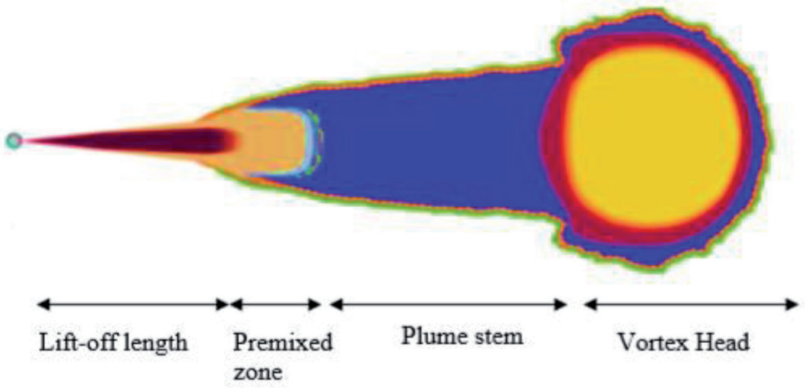

Figure 8.
Zones of Dec's conceptual model [29].

highlight the peripheral turbulent combustion. For the developed jet, the entrainment of turbulent air vaporize all liquid fuel after some distance from the nozzle tip leading to the formation of uniform fuel-air mixture. This is made up of fuel rich mixture and PAHs which afterwards, burn to generate small soot particles that fills and extends the jet length. The soot concentration and sizes increase downstream in a length referred to as 'plume stem' towards the leading edge and larger particles recirculate within the vortex. In the course of vortex recirculation, some soot particles reach peripheral flame front where they are further oxidized by OH radicals. Descriptively (using the same color codes as in **Figure 5**), the conceptual model could therefore be visualized as having four main zones: the lift-off length, the premixed zone, the plume stem and the vortex head [29]. The emissions and other contributions associated with combustion processes are still the subject of many further investigations.

6. The diesel engine exhaust emissions

Regulated exhaust emissions from the diesel engine include HC, CO, NO_x and PM. The conditions under which each of these is generated are interrelated in a complex web of factors; and much effort have focused on measures to improve the combustion process in order to counter their generation. These 'internal measures' target the highlighted emission factors like high injection pressures, injection rate shaping, combustion chamber designs, turbocharging and intercooling, transient control, spray-air interactions etc. Measures that target actual emissions in the exhaust system are considered as after-treatments. These measures deal with reduction or elimination of the emissions variables along the exhaust pipe prior to their release into the atmosphere.

6.1 The hydrocarbon (HC)

It is conventional in the domain of engine emission to refer the unburnt hydrocarbons (UHC) simply as 'hydrocarbons' (HC). The concentrations could range from 20 to 300 ppm; and for control purpose, distinction is often made of total hydrocarbons (THC) and non-methane hydrocarbons (NMHCs) by excluding methane gas from the total hydrocarbons. HC emissions contain several compounds, the variety and concentrations differ as the engine operating factors differ and vary. Small fractions of total unburnt hydrocarbons emerge as the originally sprayed fuel that survived oxidation during combustion, while higher proportions emerge as different intermediates due to pyrolysis and partial oxidation of fuel and lubricants. The diversity includes alkanes, alkene, alkynes and aromatic, meaning that HC emissions occur as single, double and triple bonds or in combinations; straight and branched chains or ringed chain structure as in aromatics. Aromatics with benzene basic ring structure are the building blocks for higher cyclic-structures of PAHs which can occur from fuel breakdowns and also from of incomplete combustion of fuel. The emission of hydrocarbons in diesel engines is significantly influenced by engine operating conditions of which, idling to light load modes are most culprits. The prevalent reasons include over-mixing of fuel with air which leads to over-leaning and therefore difficult to support combustion particularly at low temperatures; under-mixing which causes over-rich mixture and so difficult to ignite; and flame quenching at low temperature walls which causes partial burning. During ignition delay, the equivalence ratios attained by fuel-air mixture varies within a wide range. Some portions of the mixture are favorable to auto-ignition; some are locally too rich to burn while others are too lean to support combustion. For fuel injected when combustion has commenced, high temperature favors rapid oxidation of fuel-air charge towards complete combustion. However, there is over-rich portion of the mixture due to slow mixing of fuel and high quantity of intermediate products of pyrolysis due to high temperature and local starvation of air, fuel portions left in the nozzle sac, crevices volumes, as well as the effect of wall quenching as pointed. These lead to products of incomplete combustion and fuel in the exhaust. Many forms of intermediate products of incomplete combustion involve 'oxygenates' which are not pure hydrocarbons. Along with hydrocarbons, they constitute volatile components (VOCs) which condense as particulate matter as temperature drops on the exhaust line.

6.2 Carbon monoxide (CO)

During oxygen deficient combustion process, fuel is not fully oxidized; CO (which is an intermediate product on the fuel reaction-path), is produced along with HC as products of incomplete combustion. However combustion in most diesel engines are practically lean beyond stoichiometric, therefore CO emission is normally low except during transient operation and is easily oxidized to CO_2 upon release to the atmosphere.

6.3 Nitrogen oxides (NO_x)

The oxides of nitrogen relevant to diesel engine emission are nitrogen oxide (NO) and nitrogen dioxide (NO_2). Nitrous oxide (N_2O) is not a regulated emission; they are collectively referred to as oxides of nitrogen (NO_x) of which, NO is dominantly emitted during combustion and NO_2 is formed as a consequence of further oxidation. In the presence of ultra-violet light, NO_2 forms a photochemical smog with non-methane hydrocarbon. During combustion, the main oxidant is oxygen, a constituent of air drawn together with nitrogen, which is technically non-reacting to fuel. However at high temperatures, nitrogen reacts with oxygen; and the mechanism follow many pathways. As adapted from [30] the NO formation mechanisms are: the thermal or Zeldovich mechanism, the Fenimore or prompt mechanism, the N_2O-intermediate mechanism and the NNH mechanism. The thermal mechanism is dominant in high temperature combustion over wide equivalent ratios while Fenimore mechanism is predominant in combustion of rich fuel mixture. The N_2O-intermmediate is considered to play an important role in the production of NO in very lean, low temperature combustion and the NNH is a new introduction to NO formation mechanisms.

Thermal or Zeldovich mechanism consists of two chain reactions.

$$O + N_2 \leftrightarrow NO + N \tag{7}$$

$$N + O_2 \leftrightarrow NO + O \tag{8}$$

with an extended reaction.

$$N + OH \leftrightarrow NO + H \tag{9}$$

The forward ($_f$) and reverse ($_r$) reaction rate coefficients as in [31] are as follows:

$$k_{z1,f} = 1.8 \times 10^{11}\, exp\left[-38,370/T(K)\right] \;[=]\; m^3/kmol - s$$

$$k_{z1,r} = 3.8 \times 10^{10}\, exp\left[-425/T(K)\right] \;[=]\; m^3/kmol - s$$

$$k_{z2,f} = 1.8 \times 10^{7}\mathrm{T}\, exp\left[-4,680/\mathrm{T(K)}\right] \;[=]\; \mathrm{m^3/kmol - s}$$

$$k_{z2,r} = 3.8 \times 10^{6}\mathrm{T}\, exp\Big[- 20,820/\mathrm{T(K)} \;[=]\; \mathrm{m^3/kmol - s}$$

$$k_{z3,f} = 7.1 \times 10^{10}\, exp\left[-450/\mathrm{T(K)}\right] \;[=]\; \mathrm{m^3/kmol - s}$$

$$k_{z3,r} = 1.7 \times 10^{11}\, exp\left[-24,560/\mathrm{T(K)}\right] \;[=]\; \mathrm{m^3/kmol - s}$$

The reaction set are generally coupled to combustion chemistry through the O_2, O and OH species. However depending on the time scale, it is also possible that combustion is completed before NO formation becomes significant, then the two processes can be decoupled and the formation rate of NO is expressed as:

$$\frac{d[NO]}{dt} = 2k_{N,1f}[O]_{eq}[N_2]_{eq} \tag{10}$$

Thermal mechanism is highly dependent on temperature; as typified by equation (z1), the activation energy is very large (about 319,050 kJ/kmol), giving insignificant NO formation in reactions where temperatures are below 1800 K.

The NO formation by *Fenimore mechanism* is linked to the combustion chemistry of rapidly oxidizing flame zone of premixed hydrocarbon flames ahead of the NO formation through thermal mechanism. Fenimore [32] discovered this and gave it the appellation of *prompt NO*. The scheme is generally described as the reaction between hydrocarbon radicals and with molecular nitrogen leading to the formation of *amines or cyano-compounds*. These amines or cyano-compounds are then converted into intermediate compounds that yields NO. Starting from CH radicals in the formation process, the Fenimore mechanism can be expressed as:

$$\mathrm{CH + N_2 \leftrightarrow HCN + N} \tag{11}$$

$$\mathrm{C + N_2 \leftrightarrow CN + N} \tag{12}$$

For air-fuel mixture where equivalence ratios (Φ) are less than 1.2, hydrogen cyanide (HCN) forms NO through the following the sequence:

$$\mathrm{HCN + O \leftrightarrow NCO + H} \tag{13}$$

$$\mathrm{NCO + H \leftrightarrow NH + CO} \tag{14}$$

$$\mathrm{NH + H \leftrightarrow N + H_2} \tag{15}$$

$$\mathrm{N + OH \leftrightarrow NO + H} \tag{16}$$

When (Φ) are greater than 1.2, other reaction pathways open up with more complex chemistry. As stated [33], the NO formation will cease to be rapid instead, it is recycled to HCN. In addition, the Zeldovich reaction that couples to prompt mechanism further reduces the formed NO to elemental nitrogen as $\mathrm{N + NO \rightarrow N_2 + O}$.

The *N_2O-intermediate* mechanism is relevant in fuel-lean premixed combustion schemes where ($\Phi < 0.8$) and at low temperatures. Reaction steps for this mechanism are:

$$O + N_2 + M \leftrightarrow N_2O + M \tag{17}$$

$$H + N_2O \leftrightarrow NO + NH \tag{18}$$

$$O + N_2O \leftrightarrow NO + NO \tag{19}$$

In equations (17), 'M' represents a general third body; and by implication, the involvement of third bodies means that the mechanism is favored at elevated pressures. Similarly, equations (17) and (19) involve oxygen radical O, signifying that the mechanism favor oxygen rich conditions.

The NO formation by *NNH mechanism* is the most recently discovered reaction pathway and the steps involved are:

$$N_2 + H \rightarrow NNH \tag{20}$$

and

$$NNH + O \rightarrow NO + NH \tag{21}$$

This route to NO formation is linked to combustion of hydrogen, hydrocarbon fuels with high carbon-to-hydrogen ratios and certain fuels that contain nitrogen in their molecular structure (fuel nitrogen). The amount of fuel borne nitrogen is quite negligible with respect to diesel fuel and therefore insignificant.

Irrespective of the mechanism of formation, the NO in diesel engines is a by-product of combustion and not a compound in transit like CO. Although NO formation is possible through any mechanism, it can either be sustained or destroyed depending on the prevailing equilibrium direction. It is expedient that in mitigation strategy, more emphasis is laid on the formation through thermal or Zeldovich mechanism since high temperature formation is related to the time of post-flame reactions. This is the reason why the NO formation in diesel combustion are associated with the extended Zeldovich mechanism, favored at high (local) temperature equilibrium diffusion flames.

6.4 Particulate matter (PM)

The term particulate matter (PM) is used to describe any matter that could be trapped on a sample filter paper when the exhaust gases are cooled to 52°C or less. It includes all condensates formerly in vapor state from various substances like sulfates, nitrates, organics, as well as solid black carbon particles (soot) and ash. The sources and reasons for PM emissions are immense when the variety of species are considered; however the HC and the soot particles are of more interest. The multi-phase and the complex nature of PM are characterized by its chemical composition and its physical characteristics. Physically, the sizes at which PM occur bears greatest attribute to the way it is characterized. Three customary sizes used to describe PM are the nucleation mode, accumulation mode and coarse mode particles. The nucleation mode particles are the smallest particles that occur by nucleation of species from its vapor state. The sizes vary from the small nuclei at formation, to identifiable film drops; and they usually attach to aggregates of solid

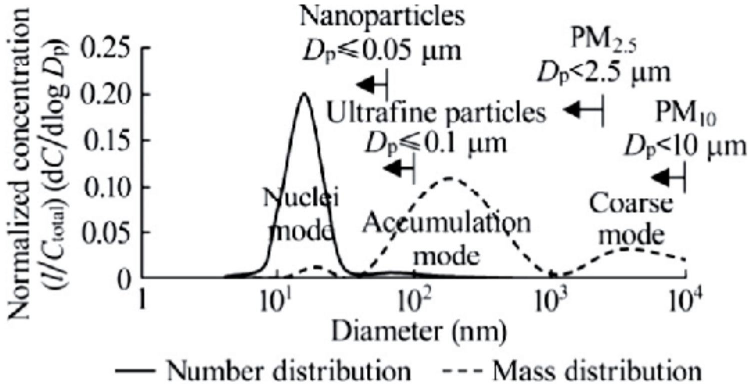

Figure 9.
Diesel engine exhaust PM size distributions expressed in number and mass metrics [34] as modified in [35].

particle if present. They are characterized by high number-concentrations, which are affected by heat, which cause vaporization and leads to drastic reduction in number concentration. The accumulation mode particles are usually aggregates of primary particles that form as solid carbonaceous core upon which condensates of volatile particles adhere. Coarse mode particles are larger, perceived as accretion of accumulation mode particles that were deposited at the walls and latter carried back to the aerosol bulk stream. These size distributions can be expressed either in number or mass metrics as shown in **Figure 9**. Chemically, the composition of PM are described as volatile or soluble; and the non-volatile or insoluble components (depending on method of separation). These are further classified according to their chemical speciation in assay as prescribed by various regulatory authorities that prescribe the acceptable test protocols and procedures.

Figure 10 gives conceptualization of composite fractions, typical of diesel PM emissions which include: sulfates, nitrates, organics carbonaceous and ash [1, 29, 34].

Sulfate ions SO_4^{2-} commonly emitted from diesel engine is water-soluble sulfuric acid, therefore assayed through solubility. Other possible sulfate particulates include metallic salt like calcium sulfate $CaSO_4$. The metal ion may originate from lubricant additives which actively react with sulfuric acid. They are less hydrophilic compared to sulfuric acid. Sulfate particulates have been drastically reduced in modern automotive engines as result of improvements in fuels technology leading to achievement of ultra-low sulfur diesels blended with synthetic lubricity additives.

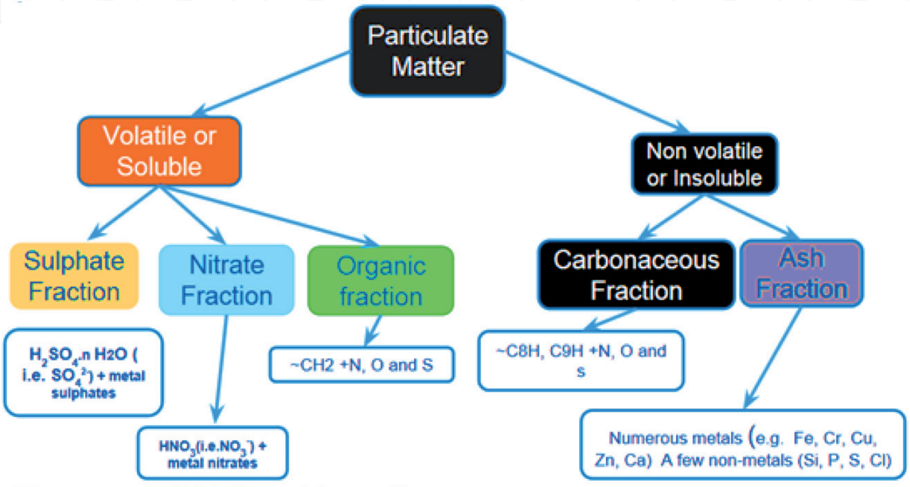

Figure 10.
Conceptualization of the composite fraction of particulate matter [6].

Nitrates are similarly water soluble and this also dictates the assaying technique. The major component formed by NO^{3-} ions is nitric acid (HNO_3) in the reaction perceived to be due to NO_2 and water.

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{22}$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + 2H_2O \tag{23}$$

Although the formation mechanism has not been well reported, the presence of HNO_3 in diesel exhaust is not in doubt. Nitrate particulates are more researched in atmospheric science where acid-ammonia reactions dominate.

Organic fractions assayed by heating or vacuum evaporation are referred to as volatile organic fraction (VOF); and if by dissolution in organic solvent, it is called soluble organic fraction (SOF). In either approach, the masses obtained are closely equal if proper adjustments are made for the non-organic compound in the case of heating. During heating process, evaporated fraction may include water-bound species, and are therefore called volatile organic components (VOC) to distinguish pure organic and from the presence of non-organic particles. The VOF is by far the most complex of the diesel PM because many organic compounds are present. Typical diesel emitted VOF are from unburnt or partially combusted hydrocarbons arising from fuels and lubricants emitted during low engine loads when the exhaust temperatures are low [6].

The *carbonaceous fractions* are also referred in many ways as elemental carbon (EC), soot, black carbon (BC) and graphite carbon. Diesel soot particles are generated mainly during diffusion regimes of the heterogeneous combustion in engines. It basically occur as primary particles in sizes of 20–50 nm which accretes to form identifiable aggregate structures, whose size depends on material availability and exhaust line temperature [29, 34, 36].

Ash fraction denotes the burnt or incombustible ashes that arise from metals. Substances such as oxides, sulfates and phosphates of metals used in lubricants additives are likely to be found as well as burnt material of the worn engine components.

6.4.1 PM formation process in the engine

The PM formation process in the engine is complex and majorly originate from fuel and lubricant. The spray combustion process presented earlier, is indeed the story of soot formation process. When fuel is only partially oxidized, it results in complex intermediates which constitute the volatile organic fractions in the exhaust stream and later condense as particles of organic compound along the exhaust line. The soot process in engine involves conversion of liquid fuel to vapor phase and then to solid particles which are oxidized back to gaseous products. The un-oxidized particles are emitted as the visible black soot. The identifiable steps in soot process could be outlined as pyrolysis, nucleation, coalescence, surface growth,

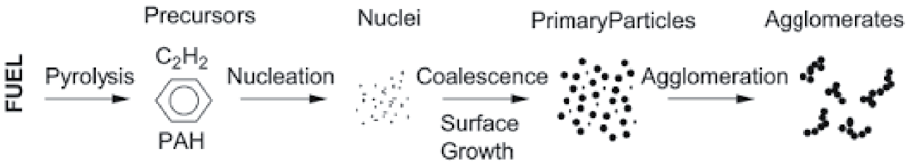

Figure 11.
Steps in soot formation process [37].

agglomeration and oxidation. The first five steps are outlined as in **Figure 11** but, any of these activities in the formation process could be terminated through oxidation.

The soot oxidation process does not necessarily follow in the sequence but recognized as the final step in the combustion process which could occur anytime and convert hydrocarbons to CO, CO_2 and H_2O. This means that the precursor feedstock, the nuclei, the primary and agglomerated particles could be consumed in the oxidation process into gaseous products at any stage. In effect, this highlights soot emission as an intermediate product due to incomplete combustion in the engine. Therefore reduction of soot emission through engine combustion process will involve prevention of its formation, promotion of its complete oxidation or both.

7. Mitigations of diesel engine emissions

Many strategies are used to eliminate or reduce the amount of diesel engine exhaust emissions released to the atmospheric environment. For long, a wholesome approach of integrating '*internal factors*' which aims to achieve better engine combustion and '*after-treatments*' which aims at reducing already borne pollutants in the exhaust stream are considered in application. These internal factors include improvements in combustion chamber design, air cooling and boosting; and fuel delivery systems. They are usually modified according to how each parameter is viewed to influence the generation of particular emission variable. Management of these factors can be challenging because some conditions that favor reduction of one variable may be opposed to the other as is typically the case of PM and NO_x reductions. The after-treatment technologies are also used in a way that, each or closely related emission variables are targeted for mitigation. These include the use of diesel oxidation catalysts to convert CO and HCs into CO_2 and water; diesel particulate filter (DPF) to trap soot; and suitable reductant like urea or ammonia to reduce NO to elemental nitrogen. Integration of these technologies for smooth engine operation is also a big challenge in modern engine technology. In operation, sensors and control loops are used to monitor and coordinate related issues for example, catalysts in the exhaust system operate within a reference temperature window and good thermal management is an issue; the need for additional air requirement to strike the right balance for exhaust-gas quality control or the need for right dosage of urea based on limiting trade-offs. Equipment manufacturers usually describe these peculiarities depending on their compromise path to achieve attainment of the prevailing regulatory emissions levels. Many texts approach the complexities of diesel after-treatments with specialized details [3, 29, 38]. For simplicity, the way some factors affect diesel exhaust emissions and how the mitigation strategies are pursued by targeting those factors are itemized as follows:

7.1 Mitigations by internal factors (air intake, engine-flow and injection related issues)

The importance of achieving stoichiometric air-fuel ratio has been highlighted to be necessary towards ensuring quality combustion. This is usually achieved through design and operating considerations for *intake port/injector profiles* and *orientations*, *swirl motion* in relation to *fuel injection timing and duration*.

For *naturally aspirated engines*, fixed cylinder volume means air charge per cycle is constant; and for a constant engine speed, the load is controlled through fuel injection. Increase in fuel injection in order to increase the load will affect the mixture composition in many ways. Some portion of fuel is injected during ignition delay period and greater quantity injected as large droplets towards the end of injection. These trigger wide range of equivalence ratios during the combustion phase. For the pre-mixed portion, some will attain stoichiometric proportion, some too lean and others may even be locally too rich to support combustion. The portion injected later will need high temperature to vaporize, fresh air or lean mixture to mix with, and which must be at a fast rate in order to undergo complete combustion. Different emission scenario are possible here depending on engine operating factors. For engine started from cold, rich mixture is inevitable, therefore, exhaust stream will be smoky due to initial richness; allowing the engine to idle for warm up and gradual load increase during the transient period before engine attain its operating temperature, this will lead to more emission of unburnt hydrocarbons and intermediates. Similarly, if combustion rate is not fast enough, lately sprayed fuel and some portion still undergoing pyrolysis will be caught up by fast cooling as expansion stroke progresses and this will lead to emissions of unburnt hydrocarbon and intermediates.

Some of these drawbacks are usually overcome with the *use of turbocharger* to increase the mass of air inducted into the cylinder. This permits proportional increase in fuel injection to suit required power output of the engine. As air velocity will be higher through the intake ports, whether as in swirl-supported or quiescent combustion system, air-fuel mixing is enhanced. This leads to better fuel oxidation and reduction in emission of HC, PM and CO; however, it is responsible for increase in NO formation.

The influence of *fuel injection* scheme on emissions and possible improvements that could be achieved through their modifications are also interesting. Increase in injection pressure can be used to improve entrainment rate which leads to improved combustion efficiency. This reduces emission of hydrocarbon and intermediates; while increasing combustion temperature. Higher temperature regime is a veritable platform for NO formation. On the other hand, injection timing has its own influence on these variables. Advance of injection timing promotes mixture formation which similarly enhances combustion and increase in temperature with attendant NO formation, retard in injection timing has a reverse effect as the premixed portion is reduced and ultimately NO formation is reduced.

One technique that has been used to reduce NO formation is *intake charge dilution*. This may be accomplished through methods like recirculation of exhaust gas, introduction of water spray or nitrogen. The mechanism behind these is that as diluents, they possess high specific heat capacity which make them sources of thermal sink. Since their presence reduce oxygen concentration of the fresh air charge, they will slow down the rate of combustion and thereby lower the peak pressures and temperatures that promote the formation of NO.

7.2 After-treatment mitigation technologies

As has been highlighted, three after-treatment technologies used in diesel engine exhaust emissions mitigations are use of *oxidation catalysts* that oxidizes CO, HCs (which includes PAHs) and SOF; catalyzed and non-catalyzed *diesel particulate filters* (DPF) to filter and regenerate soot and use of *NO_x reductants* like selective catalytic reduction (SCR) with ammonia, SCR with hydrocarbons (deNO_x or lean NO_x catalyst) and NO_x adsorber-catalyst system.

7.2.1 Diesel oxidation catalysts (DOCs)

These catalysts further oxidizes CO, HC, SOF and PAH into CO_2 and water as schematically represented in **Figure 12**.

The following chemistry are involved with the compounds:

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{24}$$

$$2CO + O_2 \rightarrow 2CO_2 \tag{25}$$

It is pertinent to note that DOC oxidizes all compounds with reducing character, and not all these are beneficial. The oxidation of sulfur dioxide to sulfur trioxide is an example; it is highly soluble in water and consequently it leads to formation of sulfuric acid which is emitted in the tail pipe.

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{26}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{27}$$

Similar incident occurs with the oxidation of NO to NO_2 which is more toxic than NO.

$$2NO + O_2 \rightarrow 2NO_2 \tag{28}$$

This was initially an undesirable development with the use of DOCs until it was discovered that NO_2 is a beneficial oxidizer in the catalytic regeneration of DPF where it donates one oxygen atom and reduces back to NO. Platinum, a highly acclaimed noble metal enables a high conversion efficiency of up to 90% to be achieved at a sufficiently high exhaust temperature. It is highly durable in operation and commercially available, DOCs can also remove diesel odor.

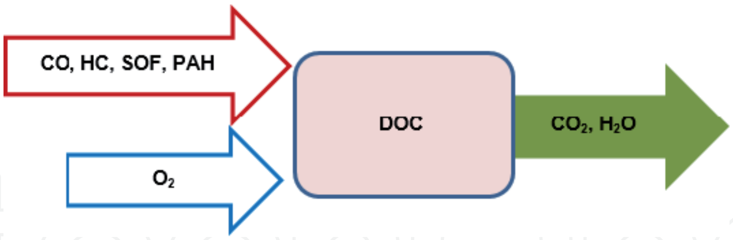

Figure 12.
Conversion chemistry with the use of DOC.

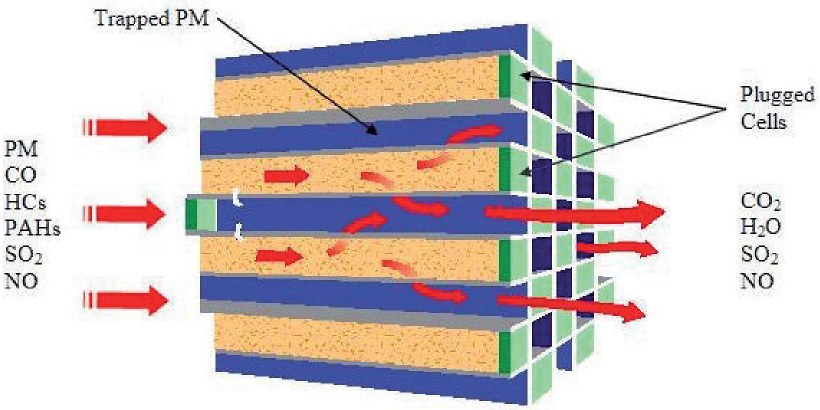

Figure 13.
Wall-flow diesel particulate filter.

7.2.2 Diesel particulate filter (DPF)

Diesel particulate filters are used to trap particles of micron and sub-micron sizes carried in the exhaust stream. In effect, condensed SOF, water, soot and ash are contained in the particulate soup. In application, the most commonly used is wall-flow DPF which has the cells alternately plug at each end, **Figure 13**. In this way, exhaust gas permeates through walls of the filter while the particles are trapped. The intricacies of PM depositions, measurements and removal are immense and beyond the scope of this piece, and the references already cited on 'after-treatments' can be further consulted. However, the key points to be noted are that PM filtration in the engine system has a technical problem of pressure drop across the filter when it is clogged with accumulated matter. The pressure drop across the DPF due to build-up of PM is critical for continuous safe engine operation. This is conventionally regarded as exhaust back pressure in a relaxed scientific sense.

The gas flow mechanics of the exhaust line is such that exhaust gas is driven by positive compression pressure of the engine, sufficiently high to overcome any obstruction along the exhaust flow line. In a strict sense therefore, the term 'back pressure' is more suitable to express the pressure drop across the entire exhaust line which is numerically equal to the exhaust pressure at the turbo (or exhaust manifold) outlet, not just the pressure drop across a component of the exhaust system [29, 39]. The factors that contribute to pressure drop across the filter can be classified into four perspectives: (a) the geometrical properties where the length, frontal area, wall thickness and channel dimensions are considered; (b) the substrate material properties whereby the porosity, permeability and pore size are considered; (c) the exhaust gas flow characteristics where the temperature, flow rate and viscosity are considered; and (d) the nature of PM membrane, where the particle size distribution, density and permeability are considered [38, 40]. These considerations are normally used to study pressure drop across DPF in both modelling and experimental efforts. With regards to engine operations, engine load and speed determines the exhaust flow rate. Increasing the load and speed increases the pressure upstream of the filter; this means that the quantity of soot accumulated by the filter depends on the usage of the engine. By implication, the pressure drop across the filter set at a pre-determined value has become a parameter to determine when to burn-off accumulated soot (to regenerate the filter). Many techniques are employed in regenerating DPF; these include the use of electric heaters, injection of fast burning fuel into the exhaust line upstream of the filter and use of microwave heating. Modern application adopt the use of catalyzed filters to lower the oxidation temperature of the trapped soot. This ensures continuous regeneration of DPF as the light-off temperature of the catalyst is reached. This is usually in the neighborhood of the exhaust line temperature. Further reading on filter loading and pressure drop across it can be seen in [6, 41–43].

7.2.3 NO_x reduction

Reduction of NO_x has been successful with reduction catalysts both for lean burn gasoline engines and diesel engines. The reduction chemistry of NO which is favored thermodynamically under the prevailing engine temperatures and pressure can be simply describe as follows:

$$2NO \rightarrow N_2 + O_2 \quad (29)$$

One of the best described catalysts is the copper exchange zeolite, Cu/ZSM5 and the decomposition is very sensitive to water and SO_2, and operates well at low

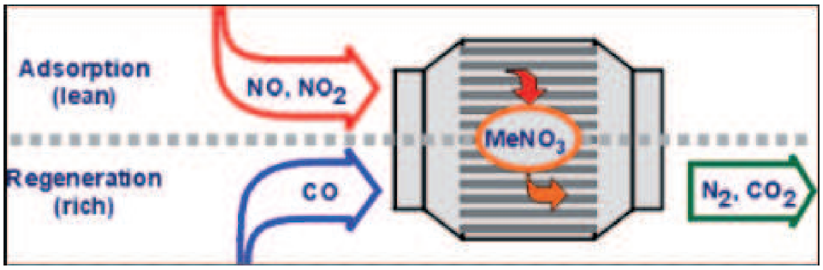

Figure 14.
Operations of NO_x adsorber. Adapted from [3].

space velocities. Ammonia and Urea offer good selective reduction in the presence of a catalyst over the competitively reaction process with oxygen. By far, this is the predominant technique in application. The chemistry can as well be simplified as:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (30)$$

SCR technique has a high NO_x conversion efficiency of about 90% and this has made it the choice for large diesel engine, co-generation plants and non-engine installations. However, it has a major disadvantage of high installation, space and operating cost. In addition, during operation, there is problem of ammonia slip which leads to equipment fouling with ammonia sulfate.

Lean NO_x or deNO$_x$ catalysts act by the replacement of ammonia with hydrocarbon. Platinum-based catalysts and base-metal catalyst like Cu/ZsM5 have proved successful but with the drawback of operating within a narrow temperature window and about 50% conversion efficiency in active systems and 10–20% in passive systems tested on regulatory test cycles.

NO_x adsorber catalysts have up to 80% reduction efficiency but depends on drive cycle through two stages of operation. The first stage is that of NO_x storage on the catalyst wash coat during lean operation also referred to as chemisorption stage. The second is regeneration of the trap through desorption and non-selective catalytic reduction of NO_x during periods of rich operation. These phases of operation are shown in **Figure 14** using upper and lower halves respectively; and a metal nitrate indicated as $MeNO_3$ used to store NO_x [3].

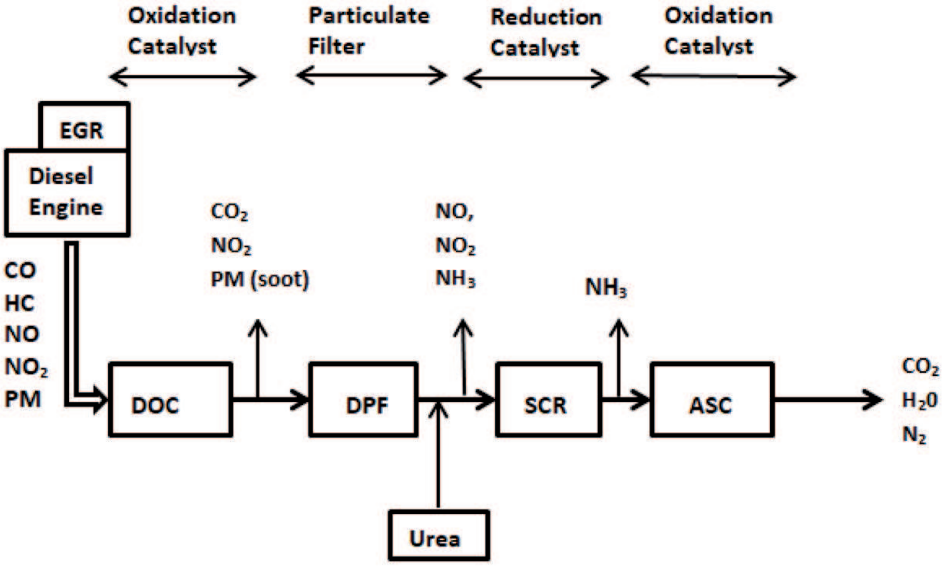

Figure 15.
Complete train of after-treatment technologies in the exhaust line.

8. Summary

Diesel emissions and mitigations are complex and can be discussed in diverse topics as highlighted in this piece. Understanding of the subject matter involves good grasp of the engine systems designs, and interplay of relevant integrated technologies. The operational perspectives also demand attention. This starts with the nature of diesel fuel itself, how it is delivered to the engine, mixed and burnt with oxygen of the air. The efficiency of the in-cylinder combustion is central to the quality of emission occurring at the tail pipe. Inevitably, combustion event varies from cycle to cycle according to engine load requirements. Therefore even the best designed engines are prone to emit some unwanted pollutants into the atmosphere. To combat this, after-treatment devices are now complementary to the overall engine technology.

The key after-treatment technologies have been briefly presented as independently considered techniques with respect to the variables they address. However this was for narrative convenience, as their inclusion extends the integration requirements of the engine. In a modern diesel engine especially for automotive applications, it is now customary that the exhaust train carry oxidation catalysts where CO, SOF and HCs are essentially oxidized to CO_2 and water. Further, NO is oxidized to NO_2 which in turn becomes an oxygen carrier for catalytic soot regeneration in the DPF and reduces back to NO. Then NO is reduced to elemental nitrogen through a SCR (**Figure 15**).

Nomenclature

A/F_S	stoichiometric air-fuel
A_n	nozzle flow area
ASI	after start of injection
BDC	bottom dead center
DPF	diesel particulate filter
HC	hydrocarbon
LES	large eddy simulation
N	engine speed
PAH	poly aromatic hydrocarbon
PM	particulate matter
RANS	Reynolds average Navier-stokes
SCR	selective catalytic reduction
TDC	top dead center
VOC	volatile organic component
VOF	volatile organic fraction
We	Weber number
Symbols	
CO	carbon monoxide
CO_2	carbon dioxide
H_2SO_4	sulfuric acid
HNO_3	nitric acid
NH_3	ammonia
NO	nitrogen oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
SO_2	sulfur dioxide
SO_3	sulfur trioxide

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