Mechanisms of Formation of Soot and PM

The Lecture Contains:

- SOOT AND PARTICULATE EMISSIONS
- Composition and Structure of Diesel Particulates
- Typical Composition of Diesel Particulate Matter
- Soot Structure
- Diesel Smoke
- Soot Formation Stoichiometry
- Conceptual Models of Soot Formation

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SOOT AND PARTICULATE EMISSIONS

- Soot is a carbonaceous particulate matter and is produced during combustion of the rich fuel - air mixtures.
- Appearance of black smoke emissions in the exhaust indicates high concentration of soot in the exhaust gases.
- Soot is mostly produced in the diffusion combustion systems, but overly rich premixed combustion also produces soot.
- As the spark ignition engines generally operate close to stoichiometric air-fuel ratio, soot emissions from these engines are not significant. With the use of unleaded gasoline, lead particulates from the SI engines have been eliminated.

Here, we will discuss particulate emissions only from the diesel engines as these are of major health concern and are more difficult to control. Soot emissions have been associated with respiratory problems and are thought to be carcinogenic in nature. The particle size is important as the particles smaller than 2.5 µ can reach lungs along with the inhaled air and cause health problems. The particles smaller than 2.5 µ constitute more than 90 percent mass of the total particulate matter in the diesel exhaust.
The fuel composition also is an important factor in soot production and emissions. For diffusion combustion soot-forming tendency is generally in the following order;

Composition and Structure of Diesel Particulates

US Environmental Protection Agency (USEPA) defines the particulate matter as any substance other than water that is collected by filtration of the diluted exhaust gases at or below 325 K (125 F).
Composition of particulate matter collected on a filter is schematically shown on Fig. 2.20. Various components adsorbed on the surface of spherical soot particles are shown.

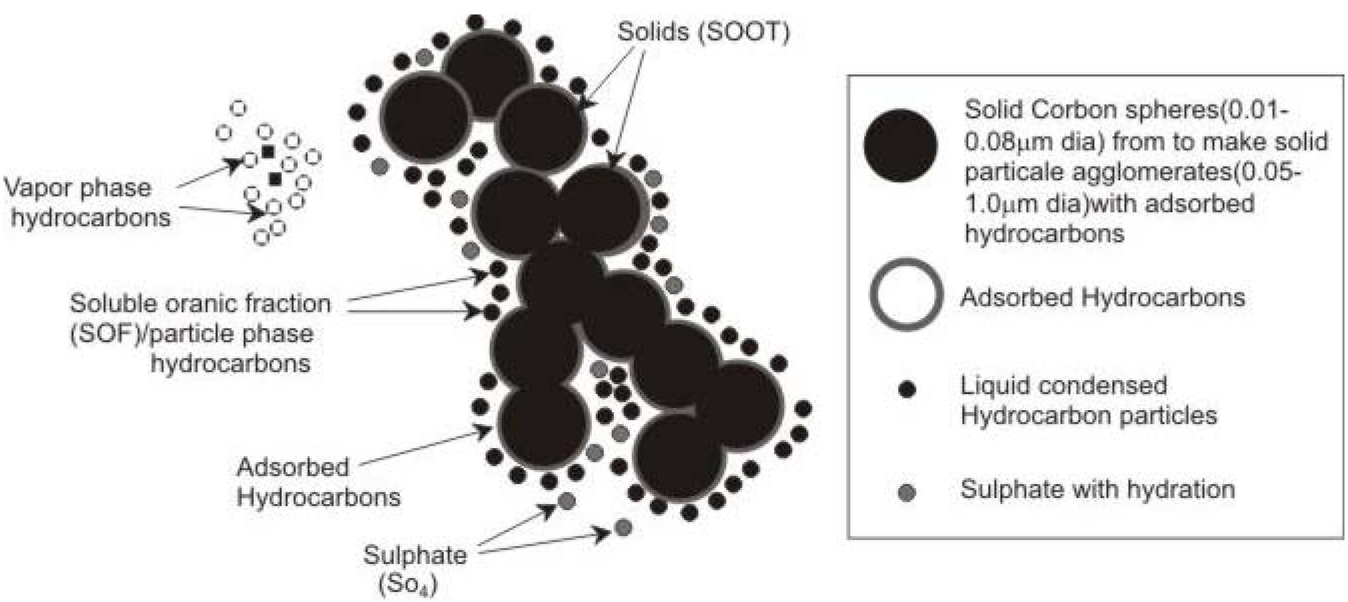

Figure 2.20	Schematic representation of diesel particulate matter collected from diluted exhaust on filter.

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Diesel particulate matter has two main components;

- Dry soot or solid carbon material

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

- Soluble organic fraction (SOF) that can be extracted by a solvent like dichloromethane.

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

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

Typical Composition of Diesel Particulate Matter

The content of different constituents of diesel particulate matter can be significantly different for different engine designs. These also vary with the emission control technology employed and the fuel quality particularly the sulphur content. Fuel sulphur content has been drastically reduced as the emission standards are becoming more stringent. The typical particulate composition for a Euro 3 turbocharged, after-cooled diesel engines is shown on Fig 2.21. Considerable reduction in carbon (dry soot) content, fuel and oil derived SOF and sulphates have taken place since early 1990s when PM emission standards were enforced for the first time and made further stringent during the following years. SOF content depends on engine design, operating conditions, lubricating oil consumption and fuel quality. As regards sulphates, with the current low sulphur fuels (sulphur content down to 50 to 350 ppm by mass compared to 0.5 % prior to 1990), sulphate content would be less than 2 percent of total PM mass.

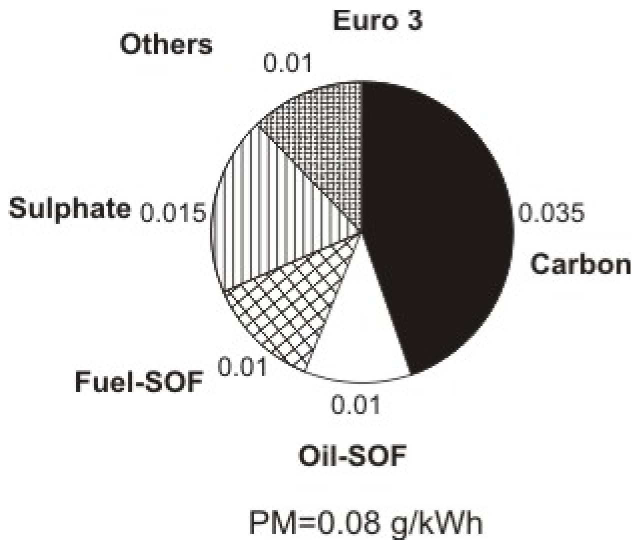

Figure 2.21	Typical diesels PM composition for a Euro 3 engine.

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Soot Structure

Electron micrographs of soot have been obtained in diffusion flames and in the engine combustion chamber. Soot is seen to be aggregates of primary spherical particles. The primary soot particles are mostly in the 15 to 30 nm size range. Typical electron micrograph of soot obtained from acetylene-air diffusion flame is shown in Fig. 2.22. Primary soot particles are seen as spheroids on the micrograph. Primary particles of about 30 nm size and branched chainlike soot aggregates are clearly observed in this micrograph at 80000 magnifications.

A single spherical soot particle contains 10^5 to 10^6 carbon atoms. Initially, the combustion-generated soot particles have one hydrogen atom to about 8 carbon atoms, $(C_8H)_n$ with a density of approx. 1800 kg/m^3.. The primary soot particles form aggregates in the combustion chamber of 100-200 nm in size containing generally 20 to over 100 primary particles. These aggregates may further agglomerate to particles as large as 1 µ. The aggregates usually resemble a cluster of spheres in branched or chain like structure.

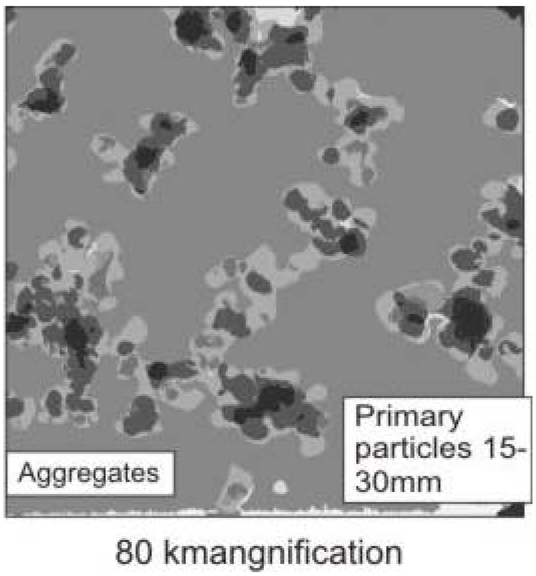

Figure 2.22	Transmission electron microscope (TEM) images of soot in acetylene-air diffusion flames. Micrograph at 80K magnification shows branched chainlike soot aggregates

Diesel Smoke

Visible black smoke emissions from diesel engine result on account of high concentration of soot in the exhaust gas. All the diesel engine design and operating variables that affect soot formation and oxidation also influence black smoke intensity. Initially, smoke emission standards for production diesel vehicles were in force to control black smoke.

- Smoke emissions increase with increase in engine load due to overall richer fuel-air ratios and hence, the rated engine power was specified based on the maximum permitted smoke density to curb black smoke emissions during engine operation. The rated power was also known as '*smoke limited power*'.
- Poor control of fuel injection rate during acceleration also increases smoke.
- Use of EGR reduces combustion temperatures and oxygen concentration in the burned gases. EGR also reduces oxidation of soot and hence overall effect of EGR is to increase smoke.
- Smoke emissions can be reduced by accelerating combustion. Higher combustion rates are obtained by increasing fuel air mixing through use of high swirl rates, by increasing injection rate and improving fuel atomization. Advancing injection timing increases combustion temperatures and allows more time for oxidation of soot thereby reducing smoke emissions.

Smoke is measured by measurement of light absorbed (opacity) in a defined specific length of column of exhaust gas. The smokemeters employing this principle are known as light extinction type of smokemeter such as Hartridge or AVL smokemeters. Smoke has also been measured by filtering a fixed volume of exhaust gases through a filter paper and the smoke stain thus formed is evaluated on a grayness scale by a light reflectance meter (Bosch smokemeter).
As the diesel particulate matter (PM) mainly consists of soot and the adsorbed unburned hydrocarbons (SOF) on soot core, the PM content has been related to exhaust soot content and HC concentration as below;

$$PM = 1.024\ Soot + 0.277\ HC \qquad (2.37)$$

Soot content and HC concentration are in mg/m^3. Soot content can be roughly estimated from smoke measurement from correlations developed by SAE (SAE Handbook), where soot content has been correlated with Bosch and Hartridge smoke units and opacity measured by full flow type smoke meters.

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Soot Formation Stoichiometry

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

$$C_xH_y + aO_2 \rightarrow 2aCO + \frac{y}{2}H_2 + (x-2a)C_s \qquad (2.38)$$

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

The fuel –air equivalence ratio for the above reaction is;

$$\varphi = 2\left(1+\frac{y}{4x}\right)\left(\frac{c}{o}\right) \qquad (2.39)$$

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

Conceptual Models of Soot Formation

Two conceptual models of soot formation in spray combustion have been suggested;

- One model suggests that the soot is formed in a narrow zone of rich mixture at the spray boundaries close to the diffusion combustion region.
- Another conceptual model based on laser imaging studies of diesel spray combustion in a supercharged engine at Sandia Laboratories has been proposed. Fig 2.23 shows schematically a diesel spray jet. It is seen in these studies that the liquid jet is relatively short and the fuel ahead of liquid jet is in vapour phase. It was seen that the soot appeard for the first time just downstream of liquid jet in the rich premixed combustion region. The concentration of soot increases and particle size grows as soot flows downstream towards the spray boundary. The highest soot concentration and largest particle size are in the region forming head or leading edge of the jet. The model suggests that the formation of soot precursors and consequently generation of soot particles takes place in the rich premixed flame where fuel-air equivalence ratio is in the range, =2 to 4. The soot particles grow in size as they pass through the spray towards the spray leading edge. The soot finally gets oxidized in the diffusion flame at the spray boundaries by OH radical rather than the molecular oxygen, O_2.

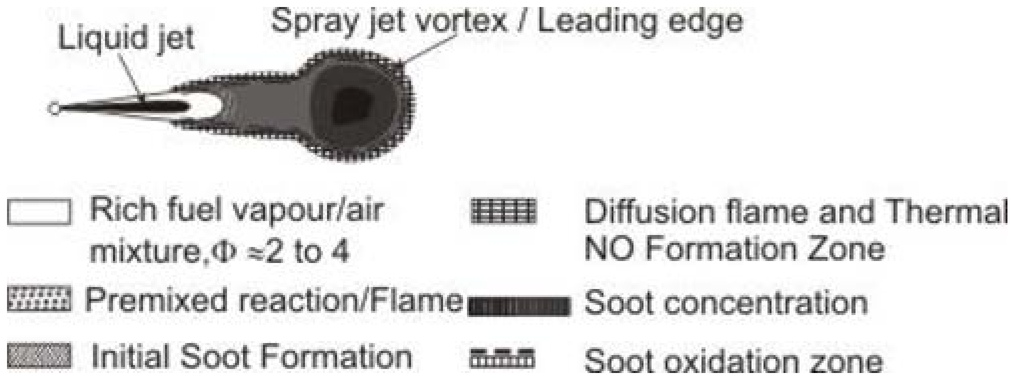

Figure2.23	Conceptual model of soot formation in diesel spray combustion

The Sandia model varies from the earlier models as it suggests that the formation of soot is the result of rich premixed combustion rather than the diffusion combustion phenomena. Further studies however, are required to confirm validity of this hypothesis for all diesel engine combustion conditions.