

Module 2:Genesis and Mechanism of Formation of Engine Emissions

Lecture 13:Soot Formation Processes

Soot Formation Processes

The Lecture Contains:

- ☰ Soot Formation Stages
- ☰ Summary of Soot Formation Process
- ☰ NO_x -Particulate Emissions Trade Off

◀◀ Previous Next ▶▶

Module 2:Genesis and Mechanism of Formation of Engine Emissions

Lecture 13:Soot Formation Processes

Soot Formation Stages

Soot formation consists of four main stages viz,

- Inception and nucleation,
- Surface growth,
- Coagulation and Agglomeration, and
- Oxidation.

Soot Inception and Nucleation

Soot nucleation is a non-equilibrium process and is not yet fully understood. The nucleation process appears to consists of several processes viz.,

- Thermal cracking or pyrolysis of long chain fuel molecules in an environment of oxygen deficiency. During this process the large fuel molecules are broken into smaller molecules forming soot precursors.
- Condensation reactions and polymerization that result in larger molecules.
- The third process is dehydrogenation process that increases C/H ratio of fuel molecules enroute to soot formation.

The path to soot nucleation and formation also depends on temperature as below;

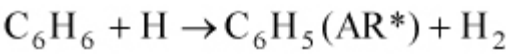
- At $T < 1800$ K, condensation reactions of aromatics and pyrolysis of other highly unsaturated hydrocarbons are likely to form soot.
- At intermediate temperatures, $2800 > T > 1800$ K, the thermal cracking leading to fragmentation of fuel molecules to smaller unsaturated hydrocarbon molecules followed by polymerization dominates soot nucleation. Acetylene, poly acetylenes and poly unsaturated hydrocarbon radicals are formed due to fragmentation reactions that lead to formation of soot.
- At still higher temperatures $T > 3000$ K the vapour phase condensation of molecules occurs to form soot nuclei.

The aromatic condensation route for soot nucleation is a more direct and faster route. The fragmentation to smaller molecules and polymerization to soot nuclei is a slower route.

Of all the products of fragmentation reactions and pyrolysis the acetylenes and poly aromatic hydrocarbons are considered the most likely precursors leading to soot formation. These gas-phase species on condensation reactions produce soot nuclei. Considering acetylene as an important soot precursor the formation of large ring structures, i.e., PAHs leading finally to soot formation has been proposed that involves the following three types of reactions known as Hydrogen-abstraction- C_2H_2 - addition (HACA) mechanism:

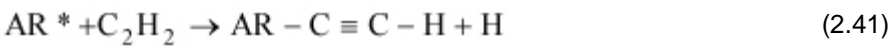
Reaction 1:

Hydrogen atom is removed from an aromatic molecule (AR) by a free hydrogen atom to form H_2 and aromatic radical (AR*);



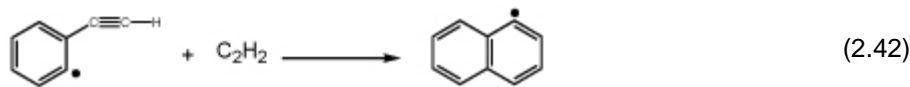
Reaction 2:

Addition of an acetylene to AR*;



Reaction 3:

Cyclization to form aromatic ring



Large PAH molecules are formed as this process repeats many times. The various PAHs formed polymerize to form a solid phase soot nuclei of 1 to 2 nm diameter. These soot nuclei on further surface growth produce soot particles.

Module 3:Genesis and Mechanism of Formation of Engine Emissions

Lecture 13:Soot Formation Processes

Surface Growth

A large number of soot nuclei are generated during soot inception stage. The soot nuclei grow in size as the gaseous products of fuel molecule fragmentation deposit on the surface of nuclei. The typical fuel has atomic H/C = 2 while soot has H/C in the range 0.1 to 0.2. Soot growth is caused more likely by the condensation of species with right H/C ratio on the nuclei surface with subsequent dehydrogenation. Gas-phase deposition of acetylene proposed in the HACA reactions is one of the mechanisms of surface growth. Here, in the Reactions 1 to 3 as above, the aromatic radical (AR*) is substituted by a carbon atom (C_s) on the edge of the soot surface and the process repeats itself.

Deposition of radicals of PAHs and small aliphatic hydrocarbons, which are present in high concentrations in sooting flames, may also result in surface growth of the soot particles.

Coagulation and Agglomeration

Collision of two spherical soot particles may form a larger spherical particle. This process occurs in the beginning when the particles are still small (<10nm) and are formed of a tarry liquid produced from pyrolysis of hydrocarbons. Once the particles have become larger and solidified, the particles resulting from collision resemble a cluster, like a bunch of grapes. Once the surface growth ceases, particles coalesce in the shape of chainlike structure and this process is termed as aggregation.

The rate of decrease of particle number density, N during coagulation is given by

$$-\frac{dN}{dt} = kN^2 \quad (2.43)$$

k is a rate constant that depends on pressure, temperature, gas density, particle size etc.

On integration the Eq. 2.43 yields,

$$\frac{N}{N_0} = \frac{1}{1 + (kN_0)t} \quad (2.44)$$

where N_0 is the initial number of particles. N/N_0 is inversely proportional to time and the initial number of particles. Thus, the soot coagulation as a result of particle collision decreases as the number of particles reduces due to coagulation and agglomeration.


The number of soot particles due to coagulation and agglomeration decrease rapidly during early part of expansion process and agglomeration is almost complete at the end of expansion stroke in the engine.

The soot concentration is expressed by a term soot volume fraction, F_v . The soot volume fraction in units of soot volume per unit volume of gas, is given by

$$F_v = \frac{\pi}{6} Nd^3 \quad (2.45)$$

where d is diameter of the spherical soot particles or diameter of a sphere of volume equivalent to an aggregated particle and N is the number of particles in unit volume. Due to agglomeration, number of

soot particles decrease but the F_v remains unchanged. It changes with surface growth or soot oxidation.

 **Previous** **Next** 

Module 3:Genesis and Mechanism of Formation of Engine Emissions

Lecture 13:Soot Formation Processes

Soot Oxidation

Oxidation of soot takes place during each stage of soot formation i.e., during formation of precursors, nuclei, primary soot particles and aggregates. A large fraction of soot that forms early in the combustion process is oxidized within the cylinder. Reactions with O, O₂, OH, CO₂ and H₂O oxidize soot. But, O, O₂ and OH are the main oxidants. OH radical plays an important role in soot oxidation in fuel rich conditions that exist in diffusion combustion systems. The OH radical is present in significant concentrations in the reaction zone of diffusion flames and oxidizes soot in the flame region. In the post combustion gases, O₂ is present in abundance and is the main oxidant. Rate of oxidation is also influenced by the shape and size of the soot particles. As the particles grow in size they tend to agglomerate instead of coagulation, and form clusters or chains. The oxidation of chain structure by O₂ is much slower than by OH.

Most widely used soot oxidation model in engines is that by Nagle and Strickland-Constable (NS-C). The NS-C soot oxidation mechanism was obtained from studies on oxidation of graphite by oxygen at 1000 to 2000° C. The NS-C mechanism assumes presence of two types of oxidation sites on soot particle surface. Site A is a nascent surface not covered by surface oxides and is more reactive. The site B is covered with oxides and is less reactive. The sites A change to sites B depending upon temperature and reaction time. The surface area fraction, x occupied by the sites A is calculated based on a rate constant, k_D . The NS-C mechanism for soot oxidation is given by

$$\frac{w}{12} = \left(\frac{k_A p_{O_2}}{1 + k_C p_{O_2}} \right) x + k_B p_{O_2} (1 - x), \quad \text{g carbon}/(\text{cm}^2 \cdot \text{s}) \quad (2.46)$$

where;

$$x = [1 + k_D / (k_B p_{O_2})]^{-1}$$

$$k_A = 20 \exp(-15,100/T), \quad \text{g}/(\text{cm}^2 \cdot \text{s} \cdot \text{atm})$$

$$k_B = 4.46 \times 10^{-3} \exp(-7640/T), \quad \text{g}/(\text{cm}^2 \cdot \text{s} \cdot \text{atm})$$

$$k_C = 21.3 \exp(2060/T), \quad \text{atm}^{-1}$$

$$k_D = 1.51 \times 10^5 \exp(-48,800/T), \quad \text{g}/(\text{cm}^2 \cdot \text{s})$$

From the soot oxidation rate, w the rate at which radius of a spherical particle is reduced may be calculated as below,

$$\frac{dr}{dt} = \frac{-w}{\rho}, \text{ cm/s} \quad (2.47)$$

ρ , the density of soot may be taken equal to 1.8 g/cm³.

From this relation the time required to completely burn a spherical particle can be calculated. Using the NS-C mechanism as above, at 1500 K it would take about 30 ms to completely burn a particle of 30 nm

diameter.

Trends in Soot Oxidation Rates

Typical variation in soot oxidation rates in a diesel engine using NS-C model are shown in Fig. 2.24. The oxidation rate depends on temperature, pressure and mixing rate. The soot oxidation rate initially increases to a peak as the concentration of O₂ rises due to mixing with air. The oxidation rate subsequently decreases as the gas temperature falls and more than offsets the effect of increasing O₂ concentration in the soot pocket. The mass of soot burned in the late mixing pocket is much lower (only about 40%) than for the early mixing pocket. The high mass of soot burned in the early formed soot pocket is due to high oxidation rate resulting from high temperatures rather than the higher residence time.

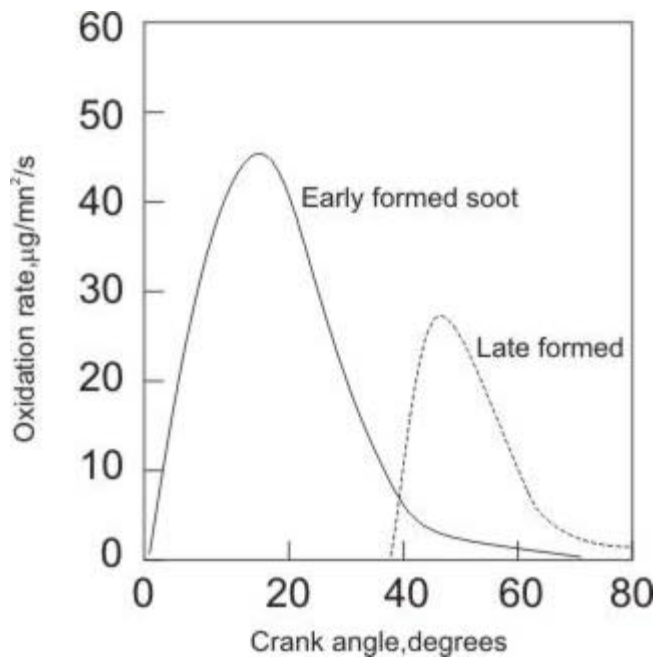


Figure 2.24.

Trends in soot oxidation rate in a diesel engine computed by NS-C model for an early (at tdc) and a late formed (40 °CA atdc) soot pocket, mixing rate with air was kept constant.

The net soot emissions depend upon the rates at which soot is produced and oxidized. Temperature plays an important role in net soot emissions. Temperature on one hand increases soot oxidation while on the other hand it increases fragmentation of fuel molecules that may lead to higher soot formation. The effects of several interacting factors thus govern the net soot emissions.

Module 3:Genesis and Mechanism of Formation of Engine Emissions

Lecture 13:Soot Formation Processes

Example 2.3

A diesel engine is operating at overall $f = 0.6$. Taking diesel fuel as $(CH_2)_n$ and the combustion gas temperature and pressure as 2200 K and 60 atm calculate the initial oxidation rate of soot particle using Eq. 2.46 and the reaction constants as given for the NS-C mechanism. Estimate the period during which a soot particle of 50 nm dia would get completely oxidized.

Solution

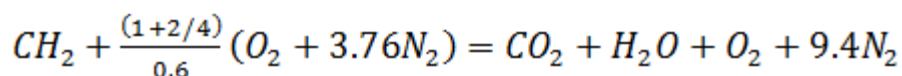
Combustion gas conditions are given as, $P = 60$ atm, $T = 2200$ K Eq. 2.46 gives the soot oxidation rate as

$$\frac{w}{12} = \left(\frac{k_A p_{O_2}}{1 + k_C p_{O_2}} \right) x + k_B p_{O_2} (1 - x) \quad g \text{ carbon}/(cm^2.s)$$

In the beginning of oxidation we may assume $x = 1$. Hence, the soot oxidation rate is,

$$\frac{w}{12} = \left(\frac{k_A p_{O_2}}{1 + k_C p_{O_2}} \right) g \text{ carbon}/(cm^2.s)$$

For p_{O_2} , combustion stoichiometry for this engine may be written as



Total number of moles of products $= 1 + 1 + 1 + 9.4 = 12.4$

Partial pressure of oxygen, $p_{O_2} = \frac{1}{12.4} \times 60 = 4.84, atm$

Reaction rate constants:

$$k_A = 20 \exp(-15,100/T) = 20 \exp(-15100/2200) = 0.021 \text{ g}/(cm^2.s.atm)$$

$$k_C = 21.3 \exp(2060/T) = 21.3 \exp(2060/2200) = 54.3 \text{ atm}^{-1}$$

The soot oxidation rate

$$w = 12 \left(\frac{0.021 \times 4.84}{1 + 54.3 \times 4.84} \right) = 4.62 \times 10^{-3} \text{ g}/cm^2.s$$

Rate of particle burning in terms of rate of change of its radius,

$$\frac{dr}{dt} = - \frac{w}{\rho}$$

Taking soot density $\rho = 1.8 \text{ g}/cm^3$

$$\frac{dr}{dt} = -\frac{4.62 \times 10^{-3}}{1.8} = -2.56 \times 10^{-3} \text{ cm/s}$$

For a particle of $dp = 50$ nm diameter time duration required to burn completely,

$$\Delta t = dp / 2 (dr/dt) = 50 \times 10^{-9} \times 100 / [2 \times (2.56 \times 10^{-3})] = 0.98 \times 10^{-3} \text{ s or } 0.98 \text{ ms}$$

At 2200 K and $p_{O_2} = 4.84$ bar, at 2000 rpm engine speed it would take about 12° CA to burn a 50 nm soot particle. *Ans.*

◀ Previous Next ▶

Summary of Soot Formation Process

Sequence of the different events taking place during soot formation process is summarized in Fig. 2.25.

- Pyrolysis of fuel molecules produces soot precursors.
- The precursors condense, polymerize and form soot nuclei which coagulate and also grow as a result of continuing condensation of precursor molecules. Thus, the nuclei grow to primary soot particles.
- Soot primary particles then, form chainlike structures.
- The soot particle surface growth finally ceases as the precursors are depleted or expansion in the cylinder cools the gases terminating formation of the precursors.

In the diesel engines, the flame temperature being high around 2800 K, entire soot formation and oxidation processes take place over a few milliseconds during engine combustion.

During expansion and exhaust strokes and in the exhaust system heavy hydrocarbons from unburned fuel and oil condense and are adsorbed on soot particles. Water, sulphates and other trace inorganic compounds such as ash formed by engine oil additives and fuel contaminants, wear particles etc. are also adsorbed on the particulate matter.

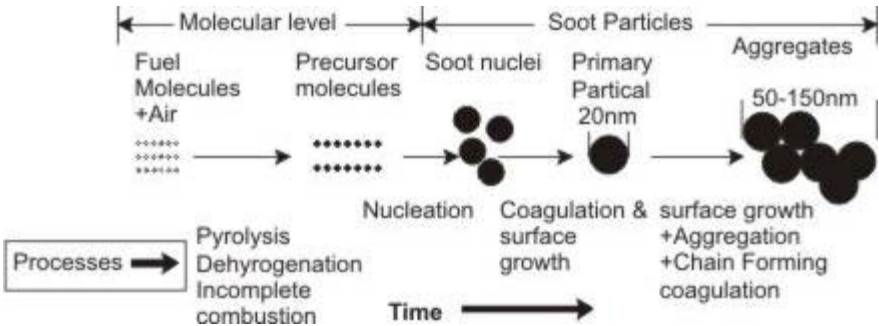


Figure 2.25

Sequence of events leading to soot formation in diesel engine combustion.

NO_x -Particulate Emissions Trade Off

Nitrogen oxides and particulates are the main pollutants emitted by the diesel engines although relatively small amounts of carbon monoxide and unburned hydrocarbons are also emitted. The combustion temperature as discussed earlier has a strong influence on the formation of both the nitrogen oxides as well as the soot. In the diesel engines, it is observed that when an engine design or operational parameter is adjusted to decrease combustion temperature to obtain reduction in nitrogen oxides emissions, soot and hence the particulate emissions increase. For example, when the injection timing is advanced it increases combustion temperatures. A higher injection advance thus, results in reduction of soot emissions but increase the NO_x. Lower soot emissions at higher combustion temperatures are attributed to higher soot oxidation rates. A typical effect of injection timing on soot and NO_x emissions is shown qualitatively in Fig.2.26. The selection of engine design parameters therefore, has to be optimized to obtain reduction in NO_x or PM without causing an excessive increase in the other. This process of adjustment of engine parameters is known as ‘NO_x-PM trade off’.

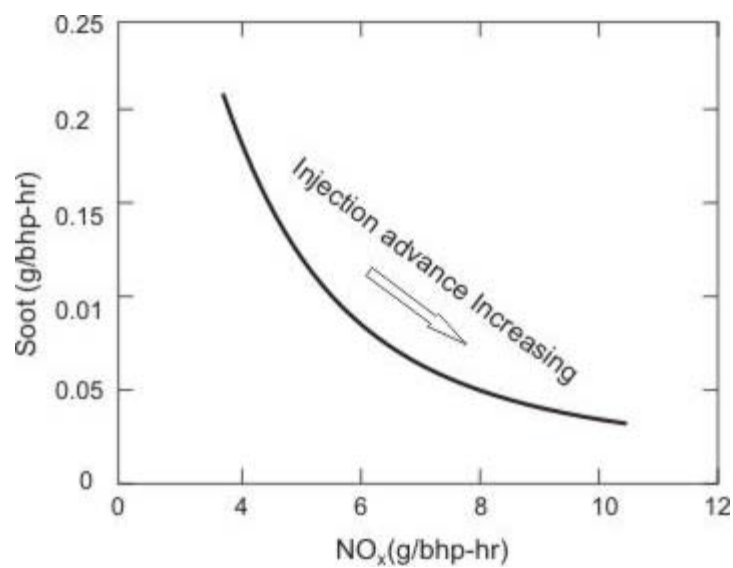


Figure 2.26

NO_x - PM emission trade off as demonstrated by the effect of injection timing on NO_x and PM emissions .

Module 3:Genesis and Mechanism of Formation of Engine Emissions

Questions

- 2.1 Show the effect of overall fuel-air equivalence ratio, ϕ on CO, HC and NO_x emissions for DI diesel engines on the same lines as the Fig 2.2.
- 2.2 Plot NO concentration versus ϕ for a CI and a SI engine on the same graph. Explain the differences between the trends for the two engines, if any.
- 2.3 Calculate average molar specific heat of combustion products of octane and air at $\phi = 1.0$. Compare it with that of air. Discuss why EGR is more effective than simply leaning of charge in reduction of NO formation. The average molar specific heats in 300- 2500K temperature range are; N₂ = 33.75, O₂ = 35.59, CO₂ = 55.37, H₂O = 44.94 kJ/kmol.K
- 2.4 Characteristic time, t_{NO} in seconds for NO to reach equilibrium value during combustion is given by
- $$t_{NO} = \frac{3.38 \times 10^{-16} T \exp(58,635 / T)}{P^{1/2}}$$

where T is in K, P in atm.

Calculate t_{NO} for the charge elements that burn early and achieve average temperature equal to 2800°K and pressure 30 atm. What would be t_{NO} for another charge element burning late in the cycle when combustion temperature and pressure are 2000 K and 18 atm? If the engine speed is 4000 rpm how many degrees crank angles are required to reach equilibrium value for NO in each case.

- 2.5 A single cylinder SI engine has 75 x75 mm bore x stroke and 8.5:1 CR, piston top land has 9 mm height and its diameter is 74.4 mm. Mixture conditions are 340 K and 100 kPa at the beginning of compression. Engine volumetric efficiency is 0.8 and mixture before entering the cylinder is at 300 K. The gas in the crevice can be assumed at wall temperature equal 400 K. If peak cylinder pressure is 40 bar. Calculate;
- the mass fraction of fresh mixture contained in piston-cylinder crevice at the point of peak pressure.
 - If one third of the crevice gas remains unburned what would be specific HC mass emissions (g of HC/kWh), the brake specific fuel consumption of the engine is 300 g/kWh.
- 2.6 In a diesel engine, HC emissions with nozzle sac volume of 0.2 mm³ and 1.4 mm³ were seen to be 125 ppm and 500 ppm HC emissions, respectively. Assuming variation in HC emissions with nozzle sac volume is linear, what is the contribution of fuel contained in nozzle orifice to HC emissions? If injector has five nozzle holes of length/diameter ratio (ln/dn) = 4, calculate the dia of nozzle holes.
- 2.7 Calculate critical fuel-air equivalence ratio above formation of soot may be expected theoretically when methane, benzene and typical diesel fuel (CH₂)_n are burned.