Development of a Soot Module for Simulating Soot Emission from Diesel Engines using a Three Dimensional KIVA code

Environment and Energy Research Division Aerattukkara V. Kumar, Hajime Ishii and Yuichi Goto

1. Introduction

Particulate emission represents one of the most deleterious pollutants generated during diesel combustion. The United States Environmental Protection Agency (EPA) has prepared tough new standards on ambient fine particles, particles smaller than 2.5 µm. The new EPA standards are based on studies that show an association between adverse health effects and the concentration of fine particles in atmosphere [1]. These concerns have been amplified by observations that modern engines those emit low particle mass concentrations actually emit larger may number concentrations than older designs [2]. It has also been demonstrated that diesel engine with after treatment devices such as particulate traps may result in very high number concentrations under certain engine operating conditions [3].

Stringent standards on particulate emission along with specific emphasis on size of emitted particulates have resulted in increased interest in fundamental understanding of the mechanisms of soot particulate formation and oxidation in internal combustion engines. Lee, Goto and Odaka [4], have observed that the number of particles slipping through diesel particulate filter (DPF) in different operating cycles were maximum at 62 nm. A phenomenological numerical model which can predict the particle size distribution of the soot emitted will be very useful in explaining the above observed results and will also be of use develop better particulate to control techniques.

In this study a mathematical model based on the kinetics of the formation of particles of carbon black is formulated and implemented to a three dimensional KIVA [5], a computer programme for chemically reactive flows with sprays used for simulating internal combustion engines.

2. Soot Model

The basic soot model is derived from Surovikin [6]. The analytical description of the process assumes that the formation and growth of the nuclei of particles of carbon and the formation and growth of radical nuclei are different stages partially superimposed on one another and taking place by different mechanisms. The whole process from the moment when the hydrocarbon (HC) reaches the reaction temperature to the separation of particles of carbon black consists of three stages (shown in Figure 1) (1) the formation of radical nuclei, (2) the growth of the radical nuclei and their conversion to nuclei with a physical surface, on reaching a critical diameter and (3) the growth of the nuclei and their transformation into particles of carbon.



Figure 1. Basic soot model

The first two stages of the process have a chemical nature and are due to (1) the formation and growth of radical nuclei as a result of thermal decomposition of the molecules of the initial hydrocarbon with the splitting off of hydrogen and simultaneous rupture of the aromatic ring (i.e. C-H and C-C bond breaking) and (2) the branching of nucleus formation through the reaction of the radical nuclei with molecules of the hydrocarbon. Both these stages take place

from the beginning of the process to the complete consumption of the hydrocarbon. The third stage of the process consists of the interaction of the molecules of the hydrocarbon and of the radical nuclei with the extremely active surface of the growing nuclei of the carbon particles. This takes place through a mechanism different from the mechanism of the growth of the radical nuclei. This stage begins as soon as the first radical nucleus reaches a critical diameter (D_{rncr}) i.e. at the end of the induction period.

In the 1^{st} and 2^{nd} stages of the process, i.e. during the induction period, the accumulation of a number of radical nuclei (n) and their growth takes place. After the 1st radical nucleus has reached the critical diameter due to the appearance of a physical surface, the process of the appearance and growth of the particle nuclei (m) develops. At the end of the induction period, the process of the appearance and growth of radical nuclei, destruction of the radical nuclei and the appearance of new particle nuclei, all takes place simultaneously. The competition of the processes of the growth of the radical nuclei and the growth of the particle nuclei is due to the difference in values of the activation energies of growth. The destruction of the radical nuclei is accelerated through the appearance of the rapidly growing surface of the particle nuclei. The kinetic characteristics of different stages of the processes are shown in figure 2 and their formulations are discussed in the following sections.



Figure 2. Kinetics of soot formation

2.1. Rate of Formation of Radical Nuclei

It consists of four members (1) rate of continuous formation of new radical nuclei (V_0) , (2) branching of radical nuclei to the nucleus forming process (F), (3) destruction of radical nuclei by their mutual collision $(-G_0n^2)$ and (4) destruction of radical nuclei by their collision with the surface of the growing particle nuclei (- K)

$$\frac{dn}{dt} = V_0 + Fn - G_0 n^2 - K \quad (1)$$

 V_0 is the monomolecular decomposition rate E_1

given by,
$$V_0 = N10^{13} e^{-\overline{RT}}$$

where N is the concentration of hydrocarbon molecules at time 't' and 10^{13} is the preexponential factor of the rate of monomolecular reactions [7]. The activation energy of the nucleus formation E₁ is equal to the cleavage energy of a C-H or C-C bond. F reflects the branching of the nucleus forming process. Based on experimental results this coefficient has been found to be about 2.0 x 10^4 [6]. The coefficient G₀ represents factor for the collision of radical nuclei with one another.

$$G_0 = \pi D_{r-n}^2 \left(\frac{8RT}{\pi M_1^*}\right)^{\frac{1}{2}}$$

where D_{r-n} is the diameter of the growing radical nucleus at time 't', R is the gas constant, T is the temperature and M_1^* is the reduced molecular weight of the colliding radical nuclei.

$$M_{1}^{*} = \frac{M_{A1}M_{B1}}{M_{A1} + M_{B1}},$$
$$M_{A1} = M_{B1} = \frac{1}{2} \left(12\frac{V}{v} + M_{HC} \right)$$

where V is the volume of a radical nucleus $(\frac{\pi}{6} D_{r-n}^3)$; v is the volume of one carbon atom $v = \frac{12}{\rho_{r-n}N_A}$; M_{HC} is the molecular weight of the initial hydrocarbon; N_A is the Avogadro's number and ρ_{r-n} is the density of

radical nucleus. K is the rate of interaction of the radical nuclei with the surface of the growing particle nuclei,

$$K = Z_s S_{nuc}$$

where Z_s is number of collisions of the radical nuclei with the surface of the particle nuclei in unit volume per unit time

$$Z_s = n \sqrt{\frac{RT}{2\pi M_{A1}}} e^{-\frac{E_4}{RT}}$$

 S_{nuc} is the area of the surface of the particle radicals in unit volume of the reaction gas at time 't'

$$S_{nuc} = \pi \left(\frac{D_{r-n,cr} + D_{nuc}}{2}\right)^2 m$$

where $\left(\frac{D_{r-n,cr} + D_{nuc}}{2}\right)$ is the mean diameter

of the group of growing particle radicals

having dimensions from $D_{r-n,cr}$ to D_{nuc} at time 't'. E₄ is the activation energy of the reaction of the radical nuclei with the surface of the growing particulate nuclei.

2.2. Rate of Growth of Radical Nuclei

$$\frac{d(D_{r-n})}{dt} = \sqrt[3]{\frac{6}{\pi\rho_{r-n}}} \frac{1}{3} G^{-\frac{2}{3}} \frac{dG}{dt}$$
(2)

where G is the weight of the radical nucleus

and
$$D_{r-n} = \sqrt[3]{\frac{6}{\pi \rho_{r-n}}}$$
 is the diameter of a

radical nucleus. The weight of a radical nucleus at time 't' under the conditions that at each active collision with a molecule of hydrocarbon, the radical nucleus increases by the weight of the carbon part of the colliding molecule, can be represented as

$$G = \int_{0}^{t} m_c n_c Z^a dt$$

where m_c is the mass of a carbon atom, n_c is the number of carbon atoms in the hydrocarbon molecule and Z^a is the number of active collisions of the radical nucleus with the hydrocarbon molecule in unit time $Z_{per}^{a} = Z_{per}^{-\frac{E_2}{RT}}$

 $Z^a = Ze^{-\frac{E_2}{RT}}$, where Z is the total number of collisions of radical nuclei with hydrocarbon molecules in unit time.

$$Z = \pi \left(r_{A} + \frac{D_{r-n}}{2} \right)^{2} \left(\frac{8RT}{\pi M_{2}^{*}} \right)^{\frac{1}{2}} N$$

where r_A is the effective radius of the hydrocarbon molecule and M_2^* is the reduced molecular weight of the colliding radical nuclei.

$$M_{2}^{*} = \frac{M_{A1}M_{HC}}{M_{A1} + M_{HC}}$$

 E_2 is the activation energy of the growth of radical nuclei.

The rate of increase in weight of the radical dG -a

nucleus is
$$\frac{dG}{dt} = m_c n_c Z^a$$

2.3. Rate of Consumption of Hydrocarbon

In general form, the rate of the consumption of hydrocarbon (N) consists of the loss of hydrocarbon molecules as a result of active collisions with the surface of the radical nuclei and the particle nuclei.

$$\frac{dN}{dt} = Z_{r-n}S_{r-n} + Z_{nuc}S_{nuc} \quad (3)$$

where $Z_{r-n} = Z_s^m e^{-\frac{E_2}{RT}}$ is the number of active collisions of hydrocarbon molecules with the surface of the radical nuclei, considering it as a plane wall, in unit volume per unit time, S_{r-n} being the area of the surface of the radical nuclei in unit volume of reaction gas at time 't' and $Z_{nuc} = Z_s^m e^{-\frac{E_3}{RT}}$ is the number of active collisions of hydrocarbon molecules with the surface of the particle nuclei, considering it as a plane wall, in unit volume per unit time, distribute the surface of the particle nuclei, considering it as a plane wall, in unit volume per unit time, Z_s^m being the number of collisions of the molecules in unit volume with

unit surface per unit time. E_3 is the activation energy of the growth of particle nuclei. From molecular kinetic theory,

$$Z_s^m = \left(\frac{RT}{2\pi M_{HC}}\right)^{\frac{1}{2}} N$$

The surface of the radical seeds

$$S_{r-n} = \pi \left(r_A + \frac{D_{r-n}}{2} \right)^2 n$$

2.4. Oxidation of Soot Particle

The eventual emission of soot from a combustion device is usually much less than the amount actually generated within. The difference arises because of the combustion of soot particles in oxygen containing regions beyond the soot formation zone. The semiempirical formula of Nagle and Strickland-Constable [8], based on the concept that there are two types of site on the carbon surface available for O₂ attack, has been implemented in this model. For the more reactive type A sites, the rate is controlled by the fraction of sites not covered by surface oxides and is therefore of mixed order, between 0 and 1 in partial pressure of oxygen ($P_{O_{\gamma}}$). Type B sites are less reactive (desorption is rapid) and react with a rate first order in the oxygen concentration. Steady state analysis of this mechanism yields a surface mass oxidation rate (w),

$$\frac{W}{12} = \left(\frac{k_A P_{O_2}}{1 + k_z P_{O_2}}\right) x + k_B P_{O_2} (1 - x) \quad \text{g cm}^{-2} \text{ s}^{-1}$$

where k_A , k_B , k_Z , k_T are empirical rate parameters [8] and x is the fraction of surface occupied by type A sites and is given by

$$x = \left(1 + \frac{k_T}{k_B P_{O_2}}\right)^{-1}$$

Millikan [9] found evidence that OH inhibits sooting by consuming soot precursors and incipient particles. Fenimore and Jones [10] found that about 10% of collisions of OH radicals with soot molecules are effective in removing a carbon atom and the same has been included in the present soot model.

2.5. Rate of Growth of Particle Nuclei

Increase in volume of a seed can be expressed as

$$\frac{dV_{nuc}}{dt} = \left(-\frac{dN}{dt}\right)\frac{V^c}{m} \qquad (4)$$

where V^c is the volume of the carbon part of the hydrocarbon molecule

$$V^{c} = \frac{m_{c}n_{c}}{\rho_{nuc}}$$
$$V_{nuc} = \frac{\pi}{6} \left(\frac{D_{r-n,cr} + D_{nuc}}{2}\right)$$

On differentiating, we have

$$\frac{dV_{nuc}}{dt} = \frac{\pi}{2} \left(\frac{D_{r-n,cr} + D_{nuc}}{2}\right)^2 \frac{d\left(\frac{D_{r-n,cr} + D_{nuc}}{2}\right)}{dt}$$
(5)

Let the time of reaching the critical diameter by the first radical nucleus be t_{cr} . From this moment the other radical nuclei formed in the induction period, as they grow, also reach the critical diameter and are converted into particle nuclei. In the interval of time from t =0 to $t = t_{cr}$, the system is described by the three differential equations (1), (2) and (3) with three unknowns N, n and D_{r-n} . From the moment t_{cr} , a fourth unknown magnitude m (concentration of particle nuclei) appears in the system. In this case an additional condition is necessary to solve the above system of equations.

In the zone of the induction period an increase in the concentration of radical nuclei (RN) n and their growth takes place. The dimensions of radical nuclei depend on the time for which they remain in the zone of the induction period on the fully justified assumption that all the radical nuclei grow at the same rate. Thus at moment $t_{\rm cr}$ the first formed radical nucleus reaches the critical diameter $D_{\rm r-n,cr}$ and is converted into a growing particle nucleus (PN). As the particle nucleus grows the radical nuclei formed after the first also starts reaching the critical diameter.

Consequently, the kinetic curve m(t) repeats the n(t) curve at the beginning of the

induction period. Since some of the radical nuclei, having diameters close to the critical diameter and having been formed at the beginning of the induction period are destroyed on the surface of the particles, there will be deviation of m(t) based on the coefficient K. Let the approximate dependence of m(t) on n(t) be denoted as n'(t) (Fictitious Nuclei, FN). Kinetics of soot formation is shown in Figure 2.

If the rate of growth of a radical-nucleus remained constant and equal to V_{ind} , the curve of m(t) at t > t_{cr}, with the displacement of the initial point for reckoning time to the point t_{cr} will be described by the relation n'(t) (similar to equation 1):

$$\frac{dn'}{dt} = V_0 + Fn' - G_0 n'^2 - K \tag{6}$$

However, the rate of growth of the radical nuclei (say 'V'), in the zone of formation and growth of particle nuclei, differs from its growth rate in the zone of induction (V_{ind}), in view of the fact that because of the intensive consumption of hydrocarbon molecules in the growth of the nucleus, their (hydrocarbons) concentration falls to zero and at the same time the rate of growth of the radical nuclei falls to zero, if it has not reached the critical diameter.



Figure 2a. Relation of different growth rates

The radial growth of the radical nuclei in the zone of the induction period takes place by an amount δ in time $\Delta t = \delta/V_{ind}$ and in the zone of formation of radical nuclei and growth of particle nuclei, radial growth of an amount δ will be in time $\Delta t' = \delta/V$. Since V is less than V_{ind} , time taken for a small increment of δ will be always higher in the formation zone than the induction zone i.e. $\Delta t' > \Delta t$,

$$\Delta t' = \Delta t^* V_{ind} / V \tag{7}$$

The number of radical nuclei $\Delta n'$ formed in interval of time Δt in the zone of the induction period, reaching the critical diameter on radial

growth by a magnitude δ in time $\Delta t'$ will be only Δm . Thus at time 't' (from Figure 2a)

$$\frac{dm}{dt} = \tan \alpha' = \frac{\Delta m}{\Delta t} = \frac{\Delta n'}{\Delta t'} \qquad (8)$$
$$\frac{dn'}{dt} = \tan \alpha = \frac{\Delta n'}{\Delta t} \qquad (9)$$
$$\frac{dm}{dt} = \frac{dn'}{dt} \left(\frac{V}{V_{ind}}\right) \qquad (10)$$

The values D_{nuc} , N, n, m and n' are determined by solving the system of differential equations (1), (2), (3), (5), (6) and (10).

2.6. Soot Particle Size Distribution

After the induction period the first particle will grow and will keep on growing till the fuel is available. There will be loss in the size depending on the number of collisions and oxidation. At t_{max} (i.e. when the fuel is over), size will be maximum and there will be m particles of largest size. Just after induction of this first particle, another particle (a size smaller) starts growing and will follow the same path of the bigger particle (same radial growth, assumption). That means if the curve of the growth of the largest particle is traced back, the time just before the t_{max} shows the final growth of a smaller size particle (next lower size, i.e. particles which attained d_{rncr} size later) and the corresponding m; its number. Hence, particle size distribution can be derived from D_{nuc} vs time and particle number vs time variation.

3. Results and Discussions

The model tested for physical behaviour of different growth species has been implemented to the full three dimensional KIVA code, version KIVA3V. The model is capable of predicting the total in-cylinder soot concentration and particle size distribution. The soot model was simulated for a single cylinder DI diesel HINO engine (model YA18-R44) and the results were compared. The activations energies of the soot model were tuned to predict the total soot emission ratio (soot(g)/fuel(kg)) of 0.8 as that of the above engine for a medium load condition. The optimum activation energies of E_1 , E_2 , E_3 and E₄ reproducing the total soot emission ratio with n-tetradecane $(C_{14}H_{30})$ as fuel were found to be 150, 50, 20 and 0 kcal/mole. Figure 3 shows the rate of fuel injected and the history of vaporisation of fuel, inside the cylinder. Figure 4, shows the history of pressure variation inside the engine cylinder as modelled and that observed in the experiment. It can be seen that model simulated pressure variations are quite similar to the observed variations, indicating the engine combustion simulation capability of the KIVA code. The pressure values simulated are however slightly higher near the end of the injection compared to the observed pressure variations.



Figure 3. Rate of fuel injection and vaporisation



Figure 4. Modelled and observed pressure variation

History of in-cylinder total soot formation predicted by the model is shown in figure 5. It can be seen that the soot formation follows the fuel vaporisation with a slight lag indicating the soot induction period in case of a real engine.



Figure 5. History of in-cylinder soot formation

The mass and number size distribution of soot particles inside the cylinder as predicted by the model is shown in figure 6. The number size distribution shows a decreasing trend with increasing diameter range, as is usually observed. The maximum number concentration is observed in the size range 0 - 10 nm (lowest range). Mass size distribution

shows a bimodal distribution with a high peak in the 50 - 60 nm range and a low peak in the 110 - 120 nm range. Literature reported average soot particle diameters in engines are in the range of 20 - 50 nm [11,12].

The phenomenological soot model developed in this study predicted temporal soot variation and the size distribution that are consistent with experimental observation. The model performance is quite encouraging and further experiments are being planned to measure the soot and the particle size distribution, which can be used in model tuning and for comparing model performance.

References

- 1. Air quality criteria for particulate matter, EPA, Vol. 1, 1996.
- Bagley, S.T., Baumgard, K.J., Gratz, L/D., Johnson, J.H. and Leddy, D.G. Characterisation of fuel and aftertreatment device effects on diesel emissions, Health Effect Institute, Research report Number 76, September 1996.
- Mayer, A., Egli, H., Burtscher, H., Czerwinski, J. and Gehrig, H. Particle size distribution downstream traps of different design, SAE paper 950373, 1975.
- 4. Lee, J, Goto, Y. and Odaka, M. Measurement of the diesel exhaust particle reduction effect and particle size distribution in a transient cycle mode with an installed diesel particulate filter (DPF), SAE 2002-01-1005

- Amsden, A.A. KIVA3V : A block structured KIVA program for engines with vertical or canted valves. LA-13313-MS, UC-1412, July 1997. Los Alamos, National Laboratory, Los Alamos, New Mexico 87545.
- 6. Surovikin, V.F. Analytical description of the processes of nucleus-formation and growth of particles of carbon black in the thermal decomposition of aromatic hydrocarbons in the gas phase, *Solid Fuel Chemistry*, 10 (1), 92 101, 1976.
- 7. Semenov, N.N. Some problems of chemical kinetics and reactivity (in Russian), *Izd-vo SSSR*, 1958.
- Nagle, J. and Strickland-Constable, R.F. Oxidation of carbon between 1000-2000°C, Proceedings of the fifth conference on Carbon, pp. 154 - 164, Pergamon Press, London (1962).
- Millikan, R.C. and Foss, W.I. Non equilibrium effects in soot deposition, *Combustion and Flame*, 6, 210 – 211, 1962.
- Fenimore, C.P. and Jones, G.W. Oxidation of soot by hydroxyl radicals, Journal of Physical Chemistry, 71, 593 – 597, 1967.
- 11.Haynes Haynes, B.S. and Wagner, H.GG. Soot formation. Progress in Energy and Combustion Science, 7, 229 - 273, 1981.
- 12. Abdul-Khalek, I.S., Kittleson and D.B., Brear, F. Diesel trap performance – Particle size measurements and trends, SAE 982599.



Figure 6. Mass and number concentration of soot particles