EMPIRICAL SOOT FORMATION AND OXIDATION MODEL

by

Karima BOUSSOUARA and Mahfoud KADJA

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Modelling internal combustion engines can be made following different approaches, depending on the type of problem to be simulated. A diesel combustion model has been developed and implemented in a full cycle simulation of a combustion, model accounts for transient fuel spray evolution, fuel-air mixing, ignition, combustion, and soot pollutant formation. The models of turbulent combustion of diffusion flame, apply to diffusion flames, which one meets in industry, typically in the diesel engines particulate emission represents one of the most deleterious pollutants generated during diesel combustion. 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. 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 to develop better particulate control techniques. A diesel engine chosen for simulation is a version of the Caterpillar 3406. We are interested in employing a standard finite-volume computational fluid dynamics code, KIVA3V-RELEASE2.

Key words: flame, turbulence, modelling, soot formation and oxidation

Introduction and aim of work

The general fact that the net soot formation rate is primarily affected by pressure, temperature, and equivalence ratio has been fairly well established. However, the details of the mechanism leading to soot formation are not known. Consequently, semi-empirical, two-rate equation models have been used to describe the soot dynamics. Soot is a solid black material that consists mostly of carbon and hydrogen in the core and with toxic components like metals, acids and organics absorbed on the surface area. Many studies have shown that human exposure to soot particles can lead to changes in heart. To avoid the formation of soot and soot precursors in combustion processes, complex pathways have to be examined. For this reason soot formation has been widely studied in the last decades but is nevertheless not fully understood [1]. The mathematical and numerical description of soot formation and oxidation in technical combustion systems has been studied for decades. It can be regarded as a complex challenge, since the formation and destruction of soot involves many physical and chemical processes that are still under discussion. Modelling approaches range from rough empirical models that employ simple correlations based on experimental data to predict global soot formation characteristics. In this study a mathematical model based carbon black is formulated and implemented to a three-dimensional KIVA3V-RELEASE2, a computer programme for chemically reactive flows with sprays used for simulating internal combustion engines. We wanted to create a relatively simple.

Soot model

The concentration of soot in the exhaust is governed by the formation and oxidation of soot during the engine cycle. The soot model is primarily based on that of Surovikin [2], while the oxidation of soot particles follows the procedure of Haynes and Wagner, with rate constants from Nagle *et al.* [3]. The eventual soot emission from a combustion device is usually much less than the amount actually generated within. This difference arises because of the combustion of soot particles in oxygen-containing regions beyond the soot-formation zone, and is an important process. The concentration of soot in the exhaust is governed by the formation and oxidation of soot during the engine cycle.

Formation of soot - Surovikin soot model

The whole process from the moment when the hydrocarbon reaches the reaction temperature to the separation of particles of carbon black consists of three stages. First is the formation of radical nuclei. Second is the growth of the radical nuclei and their conversion to nuclei with a physical surface, on reaching a critical diameter. Third is the growth of the nuclei and their transformation into particles of carbon [4]. First two stages of the process have a chemical nature and are due to the formation and growth of radical nuclei as a result of thermal decomposition of the molecules of the initial hydrocarbon (HC) with the splitting off of hydrogen and

also the branching of nucleus formation through the reaction of the radical nuclei with molecules of the HC. 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 stage begins as soon as the first radical nucleus reaches a critical diameter. This model is capable of predicting the total in-cylinder soot concentration and particle size distribution. The eventual soot emission from a combustion device is usually much less than the amount actually generated within. This difference arises because of the combustion of soot particles in oxygen-containing regions beyond the soot-formation zone, and is an important process. The whole process from the moment when the HC reaches the reaction temperature to the separation of particles of carbon black consists of three stages (shown in fig. 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. Phenomenological Surovikin soot model

Oxidation of soot

The oxidation process for the soot particles is based on the formula of Nagle and Strickland-Constable (NSC), which uses empirical rate parameters, and is based on the concept that there are two types of sites on the carbon surface available for O_2 attack. For the more reactive sites, the rate is controlled by the fraction of sites not-covered by surface oxides, whereas in the less reactive sites, the reaction rate has a first-order dependence on the oxygen concentration. In this model, carbon oxidation occurs by two mechanisms whose rates depend on the surface chemistry involving more reactive A species (sites) and less reactive B species (sites) [5]. The chemical reactions are:

$$A + O_2 \qquad A + 2CO \tag{1}$$

$$B + O_2 \qquad B + 2CO \tag{2}$$

The semi empirical formula of NSC is based on the concept that there are two types of sites on the carbon surface available for O_2 attack. For the more reactive type A sites the oxidation rate is controlled by the fraction of sites not covered by surface oxides.

Type B sites are less reactive and react at a rate which is first order in PO₂. The NSC soot oxidation rate is given by: $dm_{so} = M_C$

$$\frac{\mathrm{lm}_{\mathrm{so}}}{\mathrm{d}t} = \frac{M_{\mathrm{C}}}{\rho_{\mathrm{s}}d_{\mathrm{s}}} m_{\mathrm{s}} w \tag{4}$$

where $M_{\rm C}$ is the carbon molecular weight = 12, ρ – the soot density 2.0 g/cm³, $m_{\rm s}$ – the mass [g], w – the surface mass oxidation rate [gcm⁻²s⁻¹], and $d_{\rm s}$ – the particle diameter [cm]. The soot particle diameter is 2.248·10⁻⁸ m [5].

A thermal re-arrangement of A sites into B sites is also allowed with rate constant k_{t} .

A steady-state analysis of this mechanism gives a surface mass oxidation rate define by *w*, also, this term (w) in eq. (4) in $[gcm^{-2}s^{-1}]$ is the net reaction rate of reactions eqs. (1), (2), and (3) and is defined as:

$$w = \frac{K_{\rm A} P_{\rm ox}}{1 - K_{\rm Z} P_{\rm ox}} x - K_{\rm B} P_{\rm ox} (1 - x)$$
(5)

where: P_{ox} is the oxygen partial pressure [atm], and x – the fraction of surface occupied by type A sites [ani unit],

X

The proportion *x* is given by:

$$\frac{P_{\rm ox}}{P_{\rm ox} - \frac{K_{\rm T}}{K_{\rm R}}}$$
(6)

Empirical rate constants K_A , K_B , K_T , and K_Z in the oxidation of soot particles (NSC model) are given in tab. 1 [5].

Table 1. Rate constants for NSC soot oxidation model

Rate constant	Units
$K_{\rm A} = 20 \exp(-15100/T)$ $K_{\rm B} = 4.46 \cdot 10^{-3} \exp(-7640/T)$ $K_{\rm T} = 1.51 \cdot 10^{5} \exp(-48800/T)$ $K_{\rm Z} = 20 \exp(-15100/T)$	$\begin{array}{c} gcm^{-2}s \cdot atm^{-1} \\ gcm^{-2}s \cdot atm^{-1} \\ gcm^{-2} \cdot s^{-1} \\ atm^{-1} \end{array}$

Specification of engine diesel used

Measurements and modelling are undertaken on a representative, modern, con-

Bore [mm]

Stroke [mm]

Squish [mm]

Speed (rpm)

Conrod length [mm]

Compression ratio

trolled diesel engine commonly found in heavy-duty trucks (Caterpillar 3406), with four strokes, in-line, six cylinders, turbocharged, water-cooled, direct injection version (tab. 2) [6].

Grid generation

The combustion chamber employs a bowl shape are shown in fig. 2.

|--|

Figure 2. Bowl grid at crank –30 before top dead centre (bTDC)

Workig conditions

In this study, the operations condition of caterpillar 3406 diesel engine, are schematized in tabs. 2, 3, and 4, successively. This engine has 15:1 for compression ratio, and 100 mm/95.5 mm for bore and stroke. The injection of fuel (C_7H_{16}) started are 21 bTDC.

Table 3. Injector and intake conditions

Parameter	Value
Hole diameter [mm]	0.18
Hole length [mm]	1.1
Number of hole	1
Injection timing [deg. bTDC]	21
Inlet air temperature [K]	400
Inlet air pressure [MPa]	1.5

Table 4. Hydrodynamic properties of fuel

Property	N-heptane
Density [kgm ⁻³]	685
HHV [MJkg ⁻¹]	48.1
Max. adiabatic temperature [K]	2200
Autoignition point [K]	500

Table 2. Heavy duty diesel engine specification

100

95.5

9.55

169.2

15:1

1600

Governing equations

N-heptane mechanism

$$C_7H_{16} + 11(O_2 + 3.76N_2) = 7CO_2 + 8H_2O + 41.36N_2$$
 (7)

$$\frac{A}{F} \underset{\text{stoic}}{=} \frac{11\ 2\ 15.99940\ 11\ 3.76\ 2\ 14.00870}{10020557} \quad \frac{1510.7864}{10020557} \quad 15.076871 \tag{8}$$

$$aC_{7}H_{16} + bO_{2} + cN_{2} = 7aCO_{2} + 8bH_{2}O + 41.36cN_{2}$$
 (9)

Equivalence ratio
$$\frac{\frac{A}{F}}{\frac{A}{F}} = \frac{15.076871}{\frac{31.9988b}{100.20557a}}$$
(10)

Surovikin model equations

 $- 0 < t < t_{crit}$:

Before the first nucleus reaches the critical diameter and is converted into particle nuclei [4]

$$\frac{\mathrm{d}n}{\mathrm{d}t} = V_0 = F_{\mathrm{n}} = G_0 n^2 = K$$
 Rate of formation of radical nuclei (11)

$$\frac{\mathrm{d}(D_{\mathrm{r}-\mathrm{n}})}{\mathrm{d}t} \sqrt{\frac{6}{\pi\rho_{\mathrm{r}-\mathrm{n}}}} \frac{1}{3} \sqrt[3]{G^2} \frac{\mathrm{d}G}{\mathrm{d}t} \qquad \text{Rate of growth of radical nuclei}$$
(12)

$$\frac{\mathrm{d}N}{\mathrm{d}t} = Z_{\mathrm{r-n}} S_{\mathrm{r-n}} = Z_{\mathrm{nuc}} S_{\mathrm{nuc}} \qquad \text{Rate of consumption of hydrocarbon}$$
(13)

where N is the concentration of hydrocarbon molecules, n – the concentration of radical nuclei, and D_{r-n} – the diameter of radical.

$$-t > t_{crit}$$
:

After the first nucleus reaches the critical diameter and is converted into particle nuclei [6].

$$\frac{dn}{dt} V_0 F_n G_0 n^2 K \qquad \text{Rate of formation of radical nuclei}$$
(14)

$$\frac{\mathrm{d}(D_{\mathrm{r-n}})}{\mathrm{d}t} \sqrt{\frac{6}{\pi\rho_{\mathrm{r-n}}}} \frac{1}{3} \sqrt[3]{G^2} \frac{\mathrm{d}G}{\mathrm{d}t} \qquad \text{Rate of growth of radical nuclei}$$
(15)

$$\frac{\mathrm{d}N}{\mathrm{d}t} = Z_{\mathrm{r-n}} S_{\mathrm{r-n}} = Z_{\mathrm{nuc}} S_{\mathrm{nuc}} \qquad \text{Rate of consumption of hydrocarbon}$$
(16)

$$\frac{\mathrm{d}V_{\mathrm{nuc}}}{\mathrm{d}t} = \frac{\pi}{2} \frac{D_{\mathrm{r-n,cr}}}{2} D_{\mathrm{nuc}} = \frac{2}{2} \frac{\mathrm{d}}{\frac{D_{\mathrm{r-n,cr}}}{2}} \frac{D_{\mathrm{nuc}}}{\mathrm{d}t}$$
Rate of growth of particle nuclei (17)

$$\frac{\mathrm{d}n}{\mathrm{d}t} \quad V_0 \quad Fn \quad G_0(n)^2 \quad K \qquad \text{Dependence of } m(t) \text{ on } n(t) \tag{18}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} \quad \frac{\mathrm{d}n}{\mathrm{d}t} \frac{V}{V_{\mathrm{ind}}} \qquad \qquad \text{Rate of formation of particle nuclei} \qquad (19)$$

where *m* is the concentration of particle nuclei, n' – the dependence of m(t) on n(t), and D_{nuc} – the diameter of particle nuclei.

For the previous equations one can mention the definitions of the different variable as follows [6]: V_0 – rate of continuous formation of new radical nuclei, is the monomolecular decomposition rate, F – branching of radical nuclei to the nucleus forming process, $-G_0n^2$ – destruction of radical nuclei by their mutual collision, K – destruction of radical nuclei by their collision with the surface of the growing particle nuclei, $V_0 = 10^{13}Nexp(-E_1/RT)$ where N is the concentration of HC 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 E_1 is equal to the

cleavage energy of a C-H or C-C bond [8]. *F* reflects the branching of the nucleus forming process. Based on experimental results this coefficient has been found to be about $2.0 \cdot 10^4$ [6]. The coefficient G_0 represents factor for the collision of radical nuclei with one another:

$$G_0 = \pi D_r^2 \sqrt{\frac{8RT}{\pi M_1^*}}$$

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:

$$M_1^* = \frac{M_{A1}M_{B1}}{M_{A1}-M_{B1}}$$
$$M_{A1} = M_{B1} = \frac{1}{2} \cdot 12\frac{V}{v} = M_{HC}$$

where V is the volume of a radical nucleus $(\pi/6D_{r-n}^3)$, v - the volume of one carbon atom ($v = 12/\rho_{r-n}N_A$), M_{HC} – the molecular weight of the initial HC, N_A – the Avogadro's number, and ρ_{r-n} – 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 the number of collisions of the radical nuclei with the surface of the particle nuclei in unit volume per unit time:

$$Z_{\rm S} = n \sqrt{\frac{{\rm R}T}{2\pi M_{\rm A1}}} {\rm e}^{-\frac{E_4}{{\rm R}T}}$$

 S_{nuc} is the area of the surface of the particle radicals in unit volume of the reaction gas at time t, $S_{\text{nuc}} = \pi [(D_{\text{r-n,cr}} + D_{\text{nuc}})/2]^2$ m, where $(D_{\text{r-n,cr}} + D_{\text{nuc}})/2$ is the mean diameter of the group of growing particle radicals having dimensions from $D_{\text{r-n,cr}}$ to D_{nuc} at time t. E_4 is the activation energy of the reaction of the radical nuclei with the surface of the growing particulate nuclei.

G is the weight of the radical nucleus and $D_{r-n} = (6/\pi\rho_{r-n})^{1/3}$ 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 HC, the radical nucleus increases by the weight of the carbon part of the colliding molecule, can be represented as $G = {}_{0}^{t} m_{c} n_{c} Z^{a} dt$, where m_{c} is the mass of a carbon atom, n_{c} – the number of carbon atoms in the HC molecule, and Z^{a} – the number of active collisions of the radical nucleus with the HC molecule in unit time ($Z^{a} = Ze^{-E_{2}/RT}$), where *Z* is the total number of collisions of radical nuclei with hydrocarbon molecules in unit time, $Z = \pi (r_{A} + D_{r-n}/2)^{2} (8RT/\pi M^{*}_{2})^{1/2}N$, where r_{A} is the effective radius of the HC molecule and M_{2}^{*} – the reduced molecular weight of the colliding radical nuclei ($M_{2}^{*} = M_{A1}M_{HC}/M_{A1} + M_{HC}$). E_{2} is the activation energy of the growth of radical nuclei.

The rate of increase in weight of the radical nucleus is $dG/dt = m_c n_c Z^a$.

In general form, the rate of the consumption of HC (N) consists of the loss of HC molecules as a result of active collisions with the surface of the radical nuclei and the particle nuclei, where $Z_{r-n} = Z_s^m e^{-E_2/RT}$ is the number of active collisions of HC 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 $Z_{nuc} = Z_s^m e^{-E_3/RT}$ is the number of active collisions of HC molecules with 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, $Z_s^m = (RT/2\pi M_{\rm HC})^{1/2}N$. The surface of the radical seeds $S_{\rm r-n} = \pi (r_{\rm A} + D_{\rm r-n}/2)^2 n$.

Increase in volume of a seed can be expressed as $dV_{nuc}/dt = (-dN/dt)V^c/m$ where V_c is the volume of the carbon part of the HC molecule ($V_c = m_c n_c / \rho_{nuc}$), $V_{nuc} = (\pi/6)[(D_{r-n,cr} + D_{nuc})/2]$. On differentiating, we have:

$$\frac{\mathrm{d}V_{\mathrm{nuc}}}{\mathrm{d}t} = \frac{\pi}{2} \frac{D_{\mathrm{r-n,cr}}}{2} \frac{D_{\mathrm{nuc}}}{2} = \frac{2}{2} \frac{\mathrm{d}}{\frac{D_{\mathrm{r-n,cr}}}{2}} \frac{D_{\mathrm{nuc}}}{\mathrm{d}t}$$

Let the time of reaching the critical diameter by the first radical nucleus be t_{crit} . 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 $t = t_{crit}$, the system is described by the three differential eqs. (11), (12), and (13) with three unknowns N, n, and D_{r-n} . From the moment t_{crit} , 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 RN depend on the time for which they remain in the zone of the induction period on the fully justified assumption that all the RN grow at the same rate. Thus at moment t_{crit} the first formed RN reaches the critical diameter $D_{r-n,cr}$ and is converted into a growing particle nucleus (PN). As the PN grows the RN formed after the first also starts reaching the critical diameter.

The values D_{nuc} , N, n, m, and n' are determined by solving the system of differential eqs. (11)-(19).

For a speed of rotation of 1600 rpm and for $aTDC = -180^{\circ}$ (crank angle after-top-dead-center at time t = 0.0) [7], the relation between tine and rpm and aTDC: cRANK = $aTDC + (rpm/60) \cdot t \cdot 360$

 $Crank = -180 + (1600/60) \cdot t \cdot 360 = -180 + (26.666 \cdot 360) \cdot t = -180 + 9600 \cdot t \qquad t = (crank + 180)/9600, \text{ for TDC, } crank = 0 \qquad t = (0 + 180)/9600 = 0.01875.$

Therfore, for TDC the time is 0.01875 s.

The kinetic characteristics of different stages of the processes are shown in fig. 3 gives by Kumar *et al.* [4]. Results obtained with the Surovikin model.

Results obtained and discussions

In this study, our interest was to simulate numerically thermodynamic cycle of an diesel engine [9, 10]. The conditions used in this simulation are: speed of engine 1600 rpm, the spray mass injected in grams tspmas = 0.01 g of n-heptane, start of injection 21 bTDC (21 °CA bTDC), and the duration of injection pulse in crank angle degrees 12.

Figure 4 shows the history of modelled pressure variation inside the engine cylinder. The pressure values simulated are higher near the end of injection. This figure shows simulated cylinder pressure traces at the operating condition selected for model calibration. Note that peak pressure is 23.9 MPa at crank +6.19 crank angle degree (aTDC). Therefore, both the magnitude and timing of occurrence of the peak pressure are precisely predicted by the model. The observed cylinder pressure profiles reflect the effects of in-cylinder heat release, heat transfer to the cylinder surfaces, and work transfers. Figure 5 shows the rate of fuel (C_7H_{16}) inside the cylinder. As the amount of fuel (n-heptane) injected is 0.01 g, who is verifying by the plot schematized in fig. 5. The spray vaporized rapidly and disappeared before the start of main injection. However, due to the low local temperature and pressure, the visible combustion did not



Figure 3. Kinetics of soot formation according to [4]

appear. During the injection, the liquid jet penetrated almost linearly reaching the maximum length. the mass fraction of C_7H_{16} decrease and undergoes in value of injection, after the injection of first particles of fuel, the mixture with air start and combustion also start. Therefore, the concentration of fuel injected in cylinder (chamber of combustion) increase successively, it is depend with concentration of oxygen contain in air compressed. The mechanism air-fuel interaction and the spatial location of start of combustion were investigated following the progress of fuel injection, vaporization, autoignition, and combustion [11].

The plots schematised on the figs. 4 and 5 verified the phenomena physique of cycle thermodynamic and the rate obtained are in the domain of work.



Figure 4. Modelled pressure history



The quantities solved for predicted soot formation and oxidation are usually particle number concentration (no size distinction) [12].

The formation of soot according to Surovikin model follows three stages: (1) formation of RN

(2) growth of the RN and conversion to nuclei with a physical surface on reaching, and(3) growth of the nuclei and their transformation into particles of carbon

The accumulation of a number of RN and their growth takes place during the induction period in the 1^{st} and 2^{nd} stages of the process, fig. 6a. In the zone of the induction period, an increase in the concentration of RN *n* and their growth takes place. The dimensions of RN depend on the time for which they remain in the zone of the induction period on the fully justified as-

sumption that all the RN grow at the same rate. Thus at moment t_{crit} the first formed radical nucleus reaches the critical diameter $D_{r-n,cr}$ and is converted into a growing PN, fig. 6b.

After the 1st radical nucleus has reached the critical diameter due to the appearance of a physical surface, the surface, the process of the appearance and growth of the PN develops.

At the end of induction period, the process of the appearance and growth of RN, destruction of RN and the appearance of new PN, all take place simultaneously. The competition of the process of the growth of RN and the growth of RN is due to difference in values of the activation energies of growth. In fig. 6c one schematised the FN with time. The destruction of the RN is accelerated through the appearance of the rapidly growing surface of the PN. The kinetic characteristics of different stages of the process connect with fig. 6. Nucleation produces a large number of very small particles with insignificant soot loading. The bulk of solid phase is generated by surface growth, which involves the gas phase of HC intermediates on the surfaces of the particles that develop from the nuclei. The two processes may not be separated in time and agglomeration may begin at the onset of soot nucleation. These stages of particle generation and growth constitute the soot formation process.

In general form, the rate of the consumption of HC consists of the loss of HC molecules as a result of active collisions with the surface of the RN and the PN [13], fig. 6d. 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.



Figure 6. Surovikin soot formation

The results obtained, illustrate on fig. 6, compared by the results obtained by Kumar *et al.* [4], illustrate on fig. 3. One can notice that the curve present the evolution of number concentration of RN, PN, FN, and consumption of the HC are the same compared by the results obtained by Kumar *et al.* [4], but the only difference is values obtained according to conditions of simulation.

In general, the rate of heterogeneous reaction such as the oxidation of soot depends on the diffusion of reactants to and products from the surface as well as the kinetics of the reaction [14]. The soot oxidation process in the diesel cylinder is kinetically controlled. It has proved difficult to fellow the oxidation of soot in flames. The semi empirical formula of Nagle et al. [3], based on the concept that are two types of sites on the carbon surface available for O₂ attack. For more reactive type A sites, the oxidation rate is controlled by the fraction of sites not covered by surface oxides. Types B sites are less reactive, and react at a rate which is first order in P_{O_2} . A thermal rearrangement of A sites in to B sites is also allowed (with rate constant $K_{\rm T}$). In this study, the analysis of this mechanism (the semi empirical formula of NSC) gives a surface mass oxidation rate ω [gcm⁻²s⁻¹] according to eq. [5]. The empirical rate constants determined for this model are listed in tab. 1, according to this mechanism, the reaction is first order at low oxygen partial pressures, but approaches zero order at higher pressures. At a given oxygen pressure, the rate initially increases exponentially with temperature (equivalent activation energy is K_A/K_Z). Beyond a certain temperature the rate decrease as the thermal re-arrangement favors formation of less reactive B sites (section *Oxidation of soot*). Figure 7 shows the oxidation rate predicted by NSC model (section Oxidation of soot) as a function of temperature and oxygen partial pressure. The rate ω gives by eq. (5) used to estimate the amount of soot can be oxidized in specified diesel engine. In the overall soot formation process, shown schematically in fig.1, oxidation of soot at the precursor, nuclei, and particle stages can occur. The rate of consumption of the HC consists of the loss of HC molecules as the result of active collisions with the surface of the RN.

The history of in-cylinder total soot formation predicted by the model is shown in fig. 8. The results obtained compared by the results obtained by Kumar *et al.* [4].

One can notice that the curve present the evolution of soot in the cylinder is the same compared by the results obtained by Kumar *et al.*, but the only difference is values obtained according to conditions of simulation. Therefore, we can conclude that our results are just. 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 7. Soot oxidation rate according to NSC after injection of fuel

Figure 8. History of in-cylinder soot formation

The comparison with the results given in [4] allows us to conclude that the retard of injection is considered as a solution for minimise the rate of soot formed, therefore, the amelioration of engine efficiency.

Conclusions

The model tested for physical behaviour of different growth species has been implemented to the full three dimensional KIVA code, version KIVA3Vrelease2. The model is capable of predicting the total in-cylinder soot concentration. The soot model was simulated for caterpillar 3406 diesel engine and the results obtained compared with results of Kumar *et al.*

The phenomenological soot model developed in this work predicts temporal soot variation. The complete model also accounts for the creation and growth of soot particle nuclei, through the use of a fictitious soot-forming species, and particle destruction through particle-particle collisions. In conclude for this study the soot phenomenon is treated globally, incorporate the details of soothing process such as particle inception, surface growth, and particle oxidation. Rate expressions are developed for each processes, Economic in computation, the validity of the correlations is quite uncertain for situations that vary only slightly from the conditions where modelling parameters are calibrated, the Nagle and Strickland-Constable model is a model most accepted expression of the oxidation rate by O_2 .

The model used in this study for predicted the soot formation and oxidation process, we can conduct to control of soot formed kinetically and estimate the amount of soot than can be oxidized in a typical diesel engine.

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Authors' affiliations:

K. Boussouara (**corresponding author**) Laboratory of mechanic, University of Constantine, Algeria E-mail: balance_027@yahoo.fr

M. Kadja Laboratory of mechanic, University of Constantine, Algeria

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