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Modeling of soot characteristics of diesel engines – A review.

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ABSTRACT

The heterogeneity of air-fuel mixture and the very nature of diesel fuel promote the soot formation in diesel fueled engines. Soot is formed due to the burning of carbonaceous fuels under local reducing conditions. However, the so formed soot is subsequently oxidized which is of great significance for pollution control in internal combustion engines. Currently, the stringent emission norms forced researchers to explore new techniques and fuel modifications, etc., to abate an emission from the engines. The formation and its oxidation of soot are one of the complex processes in diesel engines which necessitated in developing the mathematical model to predict the soot formation mechanisms so as to guide modern engine developers. The phenomenological models used for predicting the soot formation and its oxidation ranges from a simple two-step soot model to a detailed nine-step soot model. While the two-step soot model utilizes the fundamental mechanism of soot formation and its oxidation, the nine-step soot model extends its physics on capturing most of the soot formation process like pyrolysis, surface growth, and coagulation. Hence, the various soot models that are used to predict the engine soot emission are discussed in this work. This review article will be useful for researchers to understand the development of various soot models are used to predict the soot characteristics of the diesel engines and to appropriately select the soot models needed for the study.

Keywords: soot, emission control, modeling, two-step model.

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INTRODUCTION

According to environmental protection agency's (EPA) standards, very strict rules obligatory on particulate emissions from diesel combustion. Hence, interest in getting a fundamental understanding of the soot particle establishment and oxidation in compression ignition engines is exaggerated [1]. Diesel fueled engines are popular in terms of energy efficiency for on-road applications however at the value of oxides of nitrogen and soot emissions [2]. In recent year's attention are paid to mitigate the soot particles formed during diesel fuel combustion. As so much because the environmental and health aspects are concerned, these soot particles are harmful carcinogenic particulate matters (PM). This particulate matter has an adverse impact on respiratory organ sickness and causes carcinoma, lung cancer, asthma attack and increase the chance for a fatality rate [3]. Hence, soot emission from diesel engines attracts much attention from the scientific community as they found that soot furthermore plays an important role in global warming and greenhouse gas emissions [4]. To reduce engine-out soot emissions and investigate progressed in engine operating modes, it's vital that accurate and realistic soot models be employed in diesel engine simulations to predict soot formation process[5]. Studies reveal that the fuel composition influence the soot formation emissions in combustion of diesel fuel and mathematical modeling have shown that oxygen within the fuel could be helpful for suppressing formation of soot precursors in rich fuel regimes, and it direct towards reduction of soot [6]. Hence, this paper presents a review on the development of soot models that are being used for predicting the soot characteristics of the diesel engines.

SOOT MODELING

Soot could be a complex solid substance and it comprises of carbon and hydrogen and it is produced from unburned fuel and nucleated from the gaseous phase to a solid phase in fuel rich regimes at raised temperatures [7]. Fuel composition deals with the amount of carbon, hydrogen, sulfur, and oxygen in the fuel and those compositions have influenced the possibility of producing soot in compression ignition engines [8]. The development of liquid phase hydrocarbon to solid soot particles and once again back to volatilized phase products consists of the succeeding processes: Pyrolysis, nucleation, coalition, surface growth, accumulation, oxidation [9]. Precursors are formed during pyrolysis. After pyrolysis, nucleation of species happens to form a large aromatic molecule during which origin of soot mainly begins from the species, then the nucleation process is trailed by soot surface growth throughout that mass of a particle is superimposed close to nucleate soot particle throughout this method; the hot surface of soot particles accepts the vaporized organic compound that seemed to be acetylene. This causes an increase in soot mass and its duration of surface growth and therefore it's the massive influence on total soot mass or soot volume fraction [8]. After, surface growth soot particles strike with each other contributed to coagulation and thus particle size increase considerably like a spherical shaped particle. Agglomerates area unit composed of terribly smaller particles, in turn; it causes a group of smaller carbonic spherules having diameters of 10 to 50 nm. Finally, oxidization of soot happens at any instant throughout the formation of soot from beginning pyrolysis to agglomeration process at two stages: Chemical absorption of O_2 to the surface and desorption of O_2 with the fuel component from the surface [8]. A schematic of soot establishment process is shown in figure 1.

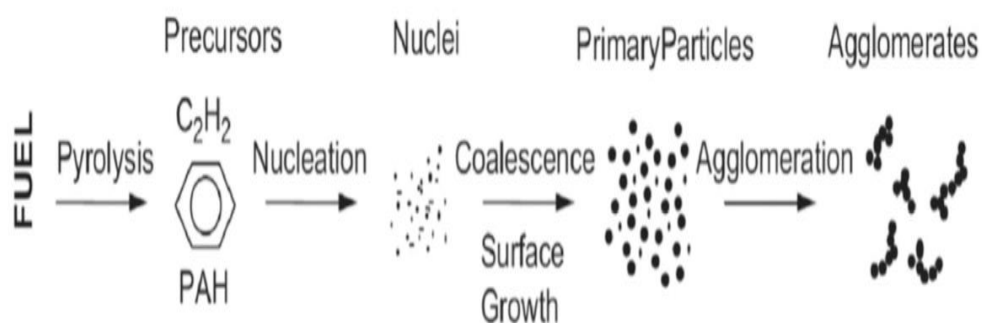


Figure 1: Schematic representation of a soot formation process [8].

As hydrocarbons pyrolyze, in turn, they produce smaller hydrocarbons, specifically acetylene. The essential step in the production of soot is the formation of the first aromatic species from this aliphatic

hydrocarbon. Primarily three models are utilized to anticipate engine soot emissions; two-step empirical soot model, an eight-step phenomenological soot model, and complex chemistry coupled phenomenological soot models. These three models have diverse ways to deal with soot formation. The prediction of soot is one of the challenging problems in theoretical and applied combustion and it has a chemical process which is very complicated and not fully understood. Soot modeling has become increasingly important as legislation allows only less soot to be emitted from diesel engines [10]. One of the essential purposes of phenomenological modeling is to predict the emissions to a reasonable degree of accuracy with lesser computing time and storage resources compared to the (Computational Fluid Dynamics) CFD package. For nitric oxide (NO) prediction, the extended Zeldovich mechanism has remained an exact alternative altogether phenomenological model. However, diesel engine soot modeling evolved from a very simple proposal of Khan and co-workers put forward in the early 1970s. They proposed an overall rate equation in terms of equivalence ratio (ϕ) and thermodynamic conditions [11-12].

As the soot mass is that the forecast of the distinction between its formation and chemical reaction, the more exact soot predictions put into effect expansive throughout of its formation and oxidation rates. The soot formation could be a complex process and requires a precursor during this regard; the three-step model of Tesner et al. (1971) remains a milestone and has formed an elemental principle of predicting the soot formation within multi-zone models [13]. This review paper provides a vital insight on soot modeling of diesel engines.

Two-step models

Two-step models were created using empirical and semi-empirical relations. Soot molecule breakup happens once OH concentration will increase, which breakup of soot molecule is owing to the very fact internal burning by O_2 [9]. The density of sites depends on the chemical environment and therefore the utilization of two-step model predicts the particle origination and soot particle structure [14]. The very basic soot model is based on Hiroyasu's soot formation and chemical reaction mechanisms [15]. In addition to the present, the impact of the OH radical in soot oxidation is critical throughout late combustion stages. The model used is shown below as referred from [15].

1) Soot formation

$$\frac{dm_{sf}}{dt} = A_{fe} m_{fv} p^{0.5} \exp\left(\frac{-E_f}{RT}\right) \quad (1)$$

Where dm_{sf}/dt is that the rate of change of soot formation, A_{fe} is empirical constant, m_{sf} is that the soot formation rate, m_{fv} is that the mass of fuel vaporized, p is pressure in bars, R is net reaction rate and E_f is an activation energy of soot formation 12500 kcal/kmol.

2) Soot oxidation by O_2

$$\frac{dm_{so}}{dt} = A_c m_s \frac{p_{O_2}}{p} p^{1.8} \exp\left(\frac{-E_{sc}}{RT}\right) \quad (2)$$

Where dm_{so}/dt is the rate of change of soot oxidation, E_{sc} - 1.4 E^{04} kcal/kmol.

3) Soot oxidation by OH

$$\left(\frac{dm_{so}}{dt}\right)_{OH} = \eta \frac{6MW_c}{\rho_s d_s} \left(\frac{RT}{2\pi MW_{OH}}\right)^{\frac{1}{2}} [OH] m_s \quad (3)$$

$$\eta_T = 0.43405 - 2.175 \times 10^{-4} T; \eta = \max(\eta_T, 0)$$

Where Mw_c is the molecular weight of carbon, d_s is the soot particle diameter.

4) The overall rate of change of soot mass is given by

$$\left(\frac{dm_s}{dt}\right) = \left(\frac{dm_{sf}}{dt}\right) - \left(\frac{dm_{so}}{dt}\right)_{O_2} - \left(\frac{dm_{so}}{dt}\right)_{OH} \quad (4)$$

Where a_{fe} is an empirical constant, m_{fv} is that the mass of fuel vaporized, p is a pressure in bars, ρ_s is the density of soot, R is the net reaction rate and E_f , and E_{sc} the activation energy of soot formation and oxidation respectively, and Mw_c is the molecular weight of carbon, d_s is that the soot particle diameter.

Despite the fact that forecast from Hiroyasu's model [15] is sufficient to match with experimental measurements, it requires higher turbulence ($k-\epsilon$) model for accurate turbulence and needs a lot of chemical reactions to increase the performance of the associate emission model of the fundamental soot model of Hiroyasu and NSC requires some upgraded numerical calculation program and lower run times [16]. It is additionally found that the shape and size appropriation of soot strictly rely on motor load and particle size gets increased once load on engine raised [17].

Enhancement in two-step soot model

The modeling approach by the moment method used here is taken from Hong et al., mentioned below [7]:

$$n(v, t) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left[-\frac{\ln^2 \left(\frac{v}{v_g} \right)}{2 \ln^2 \sigma} \right] \quad (5)$$

Where n is that the soot particle number density of volume v , v_g is average particle volume distribution.

The transient feature of the soot moments is found out via

$$\frac{\partial M_0}{\partial t} = I_0 - C_0 \quad (6)$$

$$\frac{\partial M_1}{\partial t} = I_1 + G_1 \quad (7)$$

$$\frac{\partial M_2}{\partial t} = I_2 + G_2 + C_2 \quad (8)$$

Where I_k is the rate of nucleation, G_k is that the growth of particle and oxidization rates, C_k is the coagulation rate for $K=0, 1, 2$.

The mean diameter d_m of the essential soot particles is given by

$$\frac{\pi d_m^3}{6} = \frac{m C_{soot}}{\rho_{soot}} \quad (9)$$

The rate of nucleation in the moment method $I_k = A_c v_1^k \dot{\omega}_{nucleation} N_0$ (10)

Where A_c is a correction factor, v_1 is that the specific volume of the soot primary particle and N_0 is Avogadro's number.

The rate of soot nucleation expression considered here is suggested by Leung et al.,

$$\dot{\omega}_{nucleation} = 10,000 \exp \left[\frac{-21000}{T} \right] \times [C_2 H_2] \text{ mol/cm}^3 \quad (11)$$

This model had shown some improvement in the soot prediction.

Multi-Step Soot model

Recently, soot formation models are proposed considering the multi-process single step to multi-process, multi-step schemes involving considerations of physical processes like radical antecedent formation, particle origination, particle development, a formation of acetylene, coagulation of particle, etc., with their single or multi-step rate kinetics. The other vital stage of soot modeling included the chemical reaction of soot particles and antecedents. The oxidization model of Nagle and Strickland-Constable [18] has been prominently

used for soot oxidation. In a multi-process soot model proposed by Fusco et al. [19], extremely essential steps requiring contemplations are incorporated. This sort of model is observed to be effective within the multiple-injection study [15] as compared to a simple two-step soot model, whereas eight global reaction steps are the beginning of a molecule, coagulation of molecule, surface development, and surface oxidation, as well as intermediate formation and oxidation [20]. The schematic of eight stage soot model is shown in Figure 2. The detailed soot model equations are provided in Table 1.

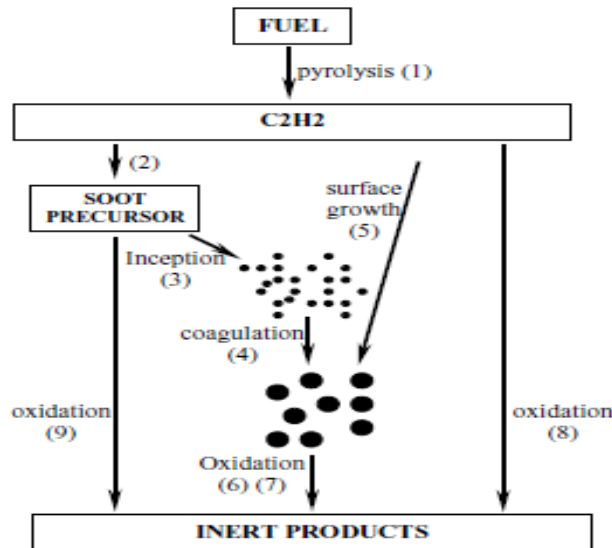


Figure 2: Schematic of an eight-step soot model [20]

Table 1: Soot model equations

Process	Rate Equation	A_i	E_i (J/kmol)	Eq.
Radical precursor formation $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_1 = \frac{m}{2} A_1 \exp\left(\frac{-E_1}{R_u T_{SP}}\right) [\text{fuel}]$	$0.7 \times 10^{12} \text{ s}^{-1}$	5.02×10^8	(12)
Origin of particle $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_2 = A_2 \exp\left(\frac{-E_2}{R_u T_{SP}}\right) [R]$	$1 \times 10^{10} \text{ s}^{-1}$	2.09×10^8	(13)
Particle growth $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_3 = A_3 \exp\left(\frac{-E_3}{R_u T_{SP}}\right) [C_2H_2] A_s^{0.5}$	$4.2 \times 10^3 \text{ m}^{0.5} \text{ s}^{-1}$	5.02×10^7	(14)
C_2H_2 formation $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_4 = \frac{m}{2} A_4 \exp\left(\frac{-E_4}{R_u T_{SP}}\right) [\text{fuel}]$	$2 \times 10^8 \text{ s}^{-1}$	2.05×10^8	(15)
Particle coagulation $\text{m}^{-3}\text{s}^{-1}$	$R_5 = K_{\text{coag}} T^{0.5} SVF^{0.167} PND^{1.833}$ $K_{\text{coag}} = 1.05 \times 10^{-12} \text{ m}^{2.5} \text{ K}^{-0.5} \text{ s}^{-1}$	-	-	(16)
Radical oxidation $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_6 = A_6 \exp\left(\frac{-E_6}{R_u T_{SP}}\right) [R][O_2]$	$1 \times 10^9 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$	1.68×10^8	(17)
C_2H_2 oxidation $k\text{-mol m}^{-3}\text{s}^{-1}$	$R_7 = A_7 \exp\left(\frac{-E_7}{R_u T_{SP}}\right) [C_2H_2][O_2]$	$6 \times 10^{10} \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$	2.09×10^8	(18)
Soot Oxidation	Adopted form NSC model			

The eighth step of soot oxidation model of Nagle and Strickland-Constable [18] given in the Table 2 is widely adopted. Nagle and Strickland-Constable (NSC) soot oxidation model considers the oxidation of pyrographite at a temperature and pressure conditions, which are closer to the operating temperature and pressure ranges of diesel engines. In this oxidation model, two types of active sites are proposed viz. a more

reactive type 'A' site and a less reactive 'B' considering changes in surface oxidation characteristics with temperature and partial pressure of oxygen. Thus, the soot chemical reaction equation is given as:

$$R_8 = \left[\left(\frac{K_A \cdot P_{O_2}}{1 + K_z \cdot P_{O_2}} \right) x_A + K_B \cdot P_{O_2} \cdot (1 - x_A) \right] S_A \quad (19)$$

Where K_A and K_z are rate constants, P_{O_2} is the partial pressure of oxygen, S_A is that the surface area of the soot, x_A is the fraction occupied by type 'A' sites on the soot surface and given by the thermal rearrangements of type 'A' and 'B' sites as:

$$x_A = \frac{P_{O_2}}{P_{O_2} + \frac{K_T}{K_B}} \quad (20)$$

Where k_t and K_B are rate constants. The values of all rate constants are given in Table 2. The surface area of the soot is calculated by assuming the soot diameter (d_s) to be 25 nm and particle number density (refer eq.14) as:

$$S_A = \pi \cdot d_{soot}^2 \cdot PND \quad (21)$$

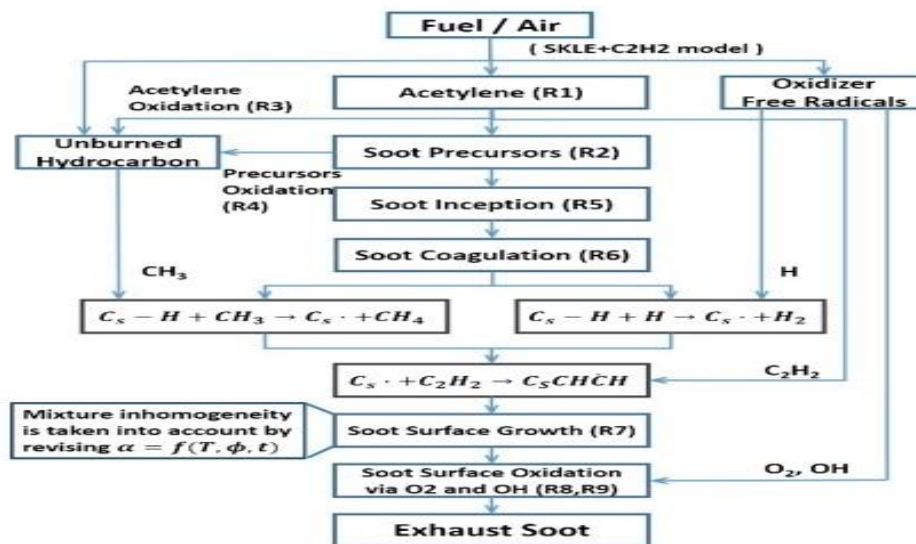


Figure 3: Schematic of new multistep HACA model [23]

Table 2: Coefficients of NSC soot oxidation model

Subscript i	K_i	Pre-exponential constants (C_i)	Activation energies E_i (J kmol ⁻¹)
A	$C_A \cdot \exp\left(\frac{-E_A}{R_u \cdot T_{sp}}\right)$	$1974 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	126×10^6
B	$C_B \cdot \exp\left(\frac{-E_B}{R_u \cdot T_{sp}}\right)$	$0.4402 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	63.6×10^6

T	$C_T \cdot \exp\left(\frac{-E_T}{R_u \cdot T_{sp}}\right)$	$1.15 \times 10^6 \text{ kmol m}^{-2} \text{ s}^{-1}$	406×10^6
Z	$C_Z \cdot \exp\left(\frac{E_Z}{R_u \cdot T_{sp}}\right)$	$210.2 \times 10^{-6} \text{ Pa}^{-1}$	17.2×10^6

The Oxidation by OH radical is considered in addition to the above eight equations, thus forms a nine-step model. The nine-step model is capable of predicting soot emission for shows for low Exhaust gas recirculation (EGR) cases than for high EGR cases. Physics and chemistry of soot formation, oxidation is fundamentally reproducible with a nine-step model when compared with a two-step Hiroyasu's soot model [21]. The volume fraction of soot decreases at a far larger rate in biodiesel combustion owing to the raised oxidation of soot and its precursors compared to diesel combustion. The soot correlates closely with a concentration of C_2H_2 and C_3H_3 , each being best-known soot precursors, likewise because of the concentration of acetylene C_2H_4 , an important species among C_2H_2 formation [22]. The schematic of a nine-step soot model is shown in Figure 3 [23].

CONCLUSIONS

In this paper, the various soot models that are adopted for predicting the soot characteristics of diesel engines are reviewed. The multi-step model can be used as a tool to analyze the diesel engines operating characteristics. The multi-step model offers a better prediction of soot yield than simple two-step model. The deficiency of the adopted two-step empirical soot model in modeling could be improved by the multi-step soot model. Hence, soot characteristics of the recent advancement combustion technique like split injection and EGR could be predicted better by an eight/nine-step soot models. It is also reported that the multi-step soot models are robust than two-step model in terms of accuracy and reliability.

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