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# Sensitivity study of engine soot forming using detailed soot modelling oriented in soot surface growth dynamic

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ABSTRACT

Development of detailed soot model independent of empirical expression is supposed to reasonably replicate the soot formation and oxidation dynamic kinetics over a wide range of diesel engine operations, thus facilitates exploring crucial factor of soot forming. Based on comprehending of varying mixture inhomogeneity on soot forming under engine operations, a new multi-step soot model oriented in surface growth dynamic had so far been updated in this study. By correlation analysis, the new soot model is able to display the influence of both temperature and mixture inhomogeneity on soot surface activity by revising the parameter of the fraction of active sites. Hence the dominant factor of soot forming is conducted by sensitivity study in aspect of three distinctive phases: fast soot inception, soot growth equilibrium and soot oxidation prevailing, under varying mixture inhomogeneity. The soot inception is more influenced by temperature under uniform mixture combustion, but the dominant factor is switched to mixture inhomogeneity in stratified mixture wherein the acetylene formation rate gets the maximum. Similarly, less oxygen helps soot abatement due to weaker chemistry reactive in soot surface growth caused by lower temperature in homogenous mixture. Nevertheless, stimulated soot surface growth by activated surface activity and vast precursor deposit under heterogeneous mixture conduces to soot forming. Simultaneously, impaired soot surface oxidation under nonuniform mixture accelerates the deteriorated engine-out soot in comparison with discharged soot in less homogenous mixture.



## 1. Introduction

The impact of engine-out emissions on human health and atmosphere pollution had been become prominent as the quantity of internal combustion engine increasing in world wide range. Fulfilment of more strict emission legislation stimulates research focusing on advanced control strategy of cleaning combustion engine, hence requiring more detailed mechanism feasible for modelling platform.

Soot forming stands for the most complex process in aspects of physical and chemical study. Modelling soot formation and oxidation for diesel engine has been a long standing challenge, and so far still been pressing concerned about. The classical two step soot model [1,2] was firstly and widely used as a pioneer in engine-out soot prediction, using empirical correlations in soot formation and oxidation individually. It has the advantage of simplicity and easy calibration via the use of tuning constants. Alternatively, the detailed soot model [3,4] dedicates in solving rate equations for soot formation and oxidation, usually associated with precursor chemistry. The detailed soot model is capable of representing major multi-step phenomenon during whole process of soot forming, including precursor formation, soot particle inception and coagulation, soot surface growth and oxidation. The model prediction of engine-out soot particle size and number density along with soot mass have been regarded as indicator of engine design to comply forthcoming particle number mandate [5,6].

Two key issues for soot formation were presented namely soot inception and soot surface growth. The rate of soot nucleation is determined by the speed of cyclization reaction of soot precursors [7], but the choice of precursor has always under debates, competing between acetylene and polycyclic aromatic hydrocarbon (PAH) and varies across research and models [8,9]. However, the fundamental studies guide in the selection of prominent soot precursor found in fuel rich combustion. It was suggested that nascent soot undergoing growth was drastically different from the mature soot which was PAH in nature with fractal aggregate of small primary particles [10]. And the discovery of aliphatic groups rather than aromatic groups at the early stage of soot forming in the incipient flame of rich ethylene combustion verified the vital existence of

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aliphatic species as soot precursor [10,11], thus ensuring the acetylene as prevailing species in soot inception. In addition, it is widely accepted that acetylene-assistant soot surface growth contributes principal mass loading in the post-inception phase [12,13], followed by hydrogen abstraction and acetylene addition as depicted in hydrogen abstraction carbon addition (HACA) soot surface growth mechanism proposed by Frenklach and Wang [13]. The latest study concluded that the model-predicted soot mass was more sensitive to the acetylene and propargyl ($C_2$–$C_3$ chemistry) as compared to the aromatic and PAH chemistry [14].

The scenario of soot dynamic analysis is dependent of reaction boundaries. Comprehending the synergetic effect of combustion factors makes it becoming essential theory to control soot scales. Combustion temperature should be the most direct factor relating to soot chemistry. It was found that excessively high temperature was adverse to precursor transforming into soot, and contrarily low temperature would impede soot nucleation rate [15]. Changing pressure, equivalence ratio and C/O ratio of reaction system [16–18] on sooting scales has never been attributed to one factor alone, but there was always a temperature-window wherein the soot scale get maximum [19,20]. Meanwhile, the alkane chain length and aromatic components in various types of surrogate fuel also did affect sooting tendency [21], which deserve much attention in guide choice of real surrogate fuel.

Advanced engine combustion modes are organized around pollutants mitigation and thermal efficiency improvement. Two pathways of diminishing engine soot are put forward as enhancing mixing and prolonging chemical reaction time scales. The new retrofit of injection system corresponds to exploiting maximum potential mixing energy, as double-hole injector for squish spray and bowl spray [22] and dual-pressure of split injection [23]. By means of exhaust gas recirculation (EGR) [24], and diesel/gasoline mixture [25] the chemical reaction time scales are profoundly affected by changing mixture heat value. Nevertheless, the motivation of exhaust particle reduction contributes the use of alternative fuel like biodiesel in engines [26].

From a modelling perspective, developing detailed soot model independent of empirical expression is driven by reasonably replication of the formation and oxidation kinetics over a wide range of engine operations, thus facilitates exploring crucial factor of soot forming. In the present study, based on comprehension of mixture inhomogeneity on soot forming under various engine operations, a new multi-step soot model oriented in surface growth dynamic was proposed, which is capable of representing the influence of both temperature and mixture inhomogeneity on soot surface activity. Furthermore, dominant factor of soot forming was conducted by sensitivity study in three distinctive stages: fast soot inception, soot growth equilibrium and soot oxidation prevailing, under varying mixture inhomogeneity.

## 2. Soot precursor chemistry

In this study, diesel was modelled with fuel properties of n-heptane, with existing SKLE n-heptane reduced chemical kinetic mechanism [27] which had been validated perfectly. Less concern about soot formation in previous study, hence adding soot precursor mechanism into n-heptane combustion is of great importance in predicting soot forming. Although there exist discrepancies of soot prediction as consequences of using different reaction mechanisms and attainable different predictions for the soot precursors, the role of the chemical mechanism in soot growth is to derive the concentration of four species, H, OH, $C_2H_2$ and the nucleating PAH, which are directly used by the soot model in soot inception, coagulation and soot surface growth and oxidation. However, sensitivity study revealed that the major contribution to soot mass sensitivity comes from $C_2$–$C_3$ chemistry, rather than PAH chemistry as the acetylene surface growth process contributes principally for soot formation [5]. Following this, in this study, reaction updates of $C_2$–$C_3$ chemistry in n-heptane mechanism will be taken into account in soot precursor inception.

Since acetylene was believed to be the primary growth species of soot precursor, sensitivity analysis by SENKIN code [28] was utilized to test the most important $C_2H_2$ related reactions in $C_2$–$C_3$ chemistry stem from Lawrence Livermore National Laboratory mechanism [29] under various engine combustion environment. Considering computational efficiency when coupled with computational fluid dynamics (CFD), six $C_2H_2$ participated reactions were yielded and added into SKLE mechanism as crucial delegation for soot precursor inception, as listed in Table 1. Two reversible reactions between acetylene ($C_2H_2$) <=> vinyl ($C_2H_3$) and acetylene ($C_2H_2$) <=> propane ($C_3H_4$) fall down under this category of analysis. As suggested by thermodynamic studies [30], oxidation of acetylene was conducted by oxygen in general, generating formyl radical (HCO) as final product no matter how complicated the chemical processes are. Eventually, the newly developed SKLE + $C_2H_2$ chemical mechanism involved 41 species and 68 reactions. It was primarily used to predict the $C_2H_2$ evolution in n-heptane/air premixed flame combustion at equivalence ratio of 1.9, analogical circumstance of soot formation in diesel fueling, where n-heptane was vaporized prior mixing with oxygen and nitrogen. It allows n-heptane flames stabilized on a flat-flame burner with the matrix made of a brass disc drilled with 0.5 mm diameter holes on a 4.0 cm diameter circular area. The predicted resultant acetylene agreed well with test data obtained by Bakali et al. [31], especially at initial and middle flame position where shaped major soot precursors, as shown in Fig. 1.

## 3. Soot surface growth sub-model oriented in mixture inhomogeneity

### 3.1. Study case set-up

In this study, the experimental study was conducted in the test bed of a modified single cylinder engine with intelligence control of fuel injection system and exhaust gas recirculation (EGR) system. AVL 415S smoke meter facilitates soot data acquisition. Measurements of engine out gases like $NO_x$, $CO_2$, CO, UHC are done by Horiba 7100 gas analyzer. More details of the test engine could be found in Ref. [32].

The boundaries condition for test and numerical simulations are shown in Table 2. This test matrix covers a range of operating conditions with variations in intake-oxygen content, load and injection patterns. All fuel injections were completed early before top dead center (TDC), conducting diesel engine Partially Premixed Combustion (PPC) mode. The test points were designed to probe alternative combustion strategies, not only to reduce emissions discharged from engine combustion chamber, but also from an efficiency standpoint.

**Table 1**
$C_2H_2$ related reactions in $C_2$–$C_3$ chemistry in SKLE mechanism.

| Reaction | $A$ | $n$ | $E$ |
|---|---|---|---|
| $C_2H_2 + H(+M) \Rightarrow C_2H_3(+M)$ | 3.11E+11 | 0.6 | 2588.9 |
| $C_2H_3(+M) \Rightarrow C_2H_2 + H(+M)$ | 2.03E+15 | −0.4 | 44460.1 |
| $C_3H_5 \Rightarrow C_2H_2 + CH_3$ | 9.60E+39 | −8.2 | 42030.1 |
| $C_2H_2 + CH_3 \Rightarrow C_3H_4 + H$ | 1.21E+17 | −1.2 | 16680.0 |
| $C_3H_4 + H \Rightarrow C_2H_2 + CH_3$ | 1.00E+14 | 0.0 | 4000.0 |
| $C_2H_2 + O_2 \Rightarrow HCO + HCO$ | 4.0E+12 | 0.0 | 28000 |

*Note:* The rate constants are listed in the form $k = AT^n\exp(-E/RT)$; $A$ units: mol cm s K; $E$ units: cal/mol.