Application of a semi-detailed soot modeling approach for conventional and low temperature diesel combustion – Part II: Model Sensitivity

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Abstract

In Part-II of the current study, a detailed sensitivity analysis was performed on the soot model that was described in Part-I. The performance of the soot model, which was implemented in the 3-D CFD code KIVA-CHEMKIN, was evaluated by conducting a sensitivity analysis of the soot sub-model formation and oxidation rates and soot precursor chemistry. In terms of soot precursor chemistry, a detailed poly-aromatic hydrocarbon (PAH) chemistry mechanism from the literature was reduced in two stages: 1) using the directed related graph with error propagation (DRGEP) method and 2) using sensitivity analysis, and integrated into primary reference fuel (PRF) chemistry mechanism for simulating different diesel combustion cases. It was seen that the model-predicted soot mass was more sensitive to the acetylene and propargyl chemistry (C_2 - C_3 chemistry) as compared to the aromatic and PAH chemistry. In terms of the soot sub-models, the rates of soot surface growth through acetylene and OH-induced soot oxidation sub-models were modified to understand their effects on the predicted net in-cylinder soot mass, since the net soot mass is understood to be predominantly affected by these sub-models. The pre-exponential rate of the acetylene assisted surface growth rate had to be reduced by a factor of 2.5 (at baseline OH-induced oxidation rate) in order to match the exhaust soot mass of conventional diesel and premixed charge compression ignition (PCCI) experiments at various levels of EGR in a Caterpillar single cylinder oil test heavy-duty diesel engine. Similar results were also obtained when the OH-induced oxidation rate was increased (at baseline soot surface growth rate). It was found that the same sub-model constants were sufficient to yield good exhaust soot mass predictions with respect to the engine experiments operated under varied combustion modes, including single injection

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conventional diesel combustion at different levels of EGR and multiple injection PCCI experiments at no EGR and high EGR conditions.

Keywords

Soot model; Polycyclic aromatic hydrocarbon (PAH) chemistry; Low temperature combustion; Combustion chemistry; Sensitivity analysis; IC engines

1. Introduction

Modeling soot formation and oxidation for diesel engines has been a long standing challenge. Soot models developed over the past several decades range from simplistic phenomenological to complicated kinetic models. The detailed review of soot models by Kennedy [1] classifies the models as purely empirical correlations, semi-empirical correlations and detailed soot models. Purely empirical correlations are only curve-fits based on experimental data, while semi-empirical models solve rate equations with experimentally obtained model constants. Detailed soot models aim to solve rate equations for soot formation and oxidation and the associated precursor chemistry. Also, the degree of complexity of the semi-empirical and detailed soot models varies in the literature. Also, the choice of precursors for soot formation varies across the literature and type of models. The simplest assumption is to consider the fuel vapor as the precursor since precursors such as C_2H_2 and PAHs are generally found in fuel vapor rich regions. The Hiroyasu model [2] used the fuel concentration as the precursor for soot formation. However, with the use of detailed or reduced chemistry mechanisms, C_2H_2 has been widely used as the soot model precursor species, for example, by Leung et al. [3]. In the Leung et al. model, C_2H_2 was considered for both inception and surface growth of soot in laminar non-premixed flames. For relatively detailed models with reduced or detailed chemistry, generally an aromatic or PAH species is considered for the inception step and accordingly, mechanisms for ring formation are incorporated. There is still a lot of debate about whether the first aromatic ring formation (benzene and phenyl) occurs through the odd carbon (C_3) or even carbon (C_4) pathway. Miller and Melius [4] proposed that the first ring formation will be dominated by propargyl (C_3H_3) addition, as compared to originally proposed reactions (Westmoreland et al. [5]) of C_2H_2 with $n-C_4H_3$ and $n-C_4H_5$ that lead to cyclization (e.g., phenyl, benzene, fulvene etc.), as given below:

More recently Miller, Westmoreland and others have found out that the C_3 pathway is seen to dominate in premixed C_3H_4 isomer (allene/propyne) flames (Hansen et al. [6]), while both the C_3 and C_4 pathways equally contribute in 1-3 Butadiene (C_4H_6) premixed rich flames (Hansen et al. [7]). Hence the subsequent PAH formation chemistry is exposed to higher uncertainties due to uncertainties in the first ring formation itself. A detailed review of the mechanisms of first ring formation is also given by Richter and Howard [8].

It is generally well accepted in the literature that C_2H_2 leads to predominant soot mass addition in the post-inception phase by surface growth processes. The pioneering work of Harris and Weiner [9] proposed that the dominant contributor to surface growth was C_2H_2 in premixed flames, but later on Weiner and Harris [10] performed line-of-sight absorption measurements at a suite of laser wavelengths (488-1100 nm) on a laminar premixed $\text{C}_2\text{H}_4/\text{O}_2/\text{Ar}$ flat flame and found out that there may be a possibility of surface growth through PAHs. They observed that, subsequent to the post-inception region, the surface growth profiles follow closely the higher PAH concentrations, which consequently reduce after the growth regime.

Benish et al. [11] proposed that the contribution of C_2H_2 to surface-growth is marginal, while the PAHs contribute around 95% of the growth in C_2H_4 -air flames. The authors measured PAH profiles in the Harris and Weiner flames and argued that PAHs contributed significantly to surface growth since the collision efficiencies of PAH-soot interaction are 5000 times more than those of soot- C_2H_2 . However, this was later contradicted through a brief communication by Kazakov and Frenklach [12], who concluded that it was purely the data reduction technique that was responsible for significant over-prediction of PAH-soot surface growth rates. In fact, Kazakov and Frenklach [12] applied the Hydrogen Abstraction Carbon Addition (HACA) model, which neglects PAH induced soot growth, and obtained similar results as Benish et al. One of the inconsistencies pointed-out by Kazakov and Frenklach in the work of Benish et al. was the assumption of identical collision efficiencies between C_2H_2 -soot and C_2H_2 -PAH. However, Kazakov and Frenklach pointed-out that the C_2H_2 -PAH collision efficiency will be relatively much smaller due to reaction

reversibility. It has to be mentioned that Frenklach and Wang [13] were one of the earlier proponents of PAH-assisted surface growth and later went on to challenge the validity of this theory.

Based on the above discussion, it is seen that there are numerous uncertainties in the soot formation process involving aromatic and PAH chemistry and the soot surface growth process involving both C_2H_2 and PAH and their relative contributions. In the current study the soot mass prediction sensitivity to the PAH chemistry mechanism, including the C_4 pathway of aromatic formation, was tested along with the sensitivity to the soot surface growth model with C_2H_2 as the surface growth species. The relative contributions to soot mass by different soot surface growth species (C_2H_2 and C_6H_6) were already established in Part-I. In addition, the soot mass sensitivity to the OH-induced soot oxidation sub-model was also tested.

2. Model framework and implementation

2.1 Sensitivity to PAH chemistry mechanisms

In the current study, two reduced PAH chemistry mechanisms were tested for studying the sensitivity of soot model predictions to aromatic and PAH chemistry. The first PAH chemistry mechanism is the PAH-1 mechanism that was used in the Part-I of the paper, comprising 21 species and 52 reactions.

The second PAH chemistry mechanism that was used in the current study was reduced based on the work of Appel et al. [14]. Since PAH-1 considers benzene formation only through propargyl radicals and since the size of the reduced PAH-1 mechanism is small, it may lack essential pathways of higher PAH formation (e.g., C_4 pathway of A_1 formation). In order to assess the sensitivity of these pathways and in general, to evaluate the sensitivity of the soot model to the PAH mechanism, a second approach was taken to reduce a fairly detailed PAH chemistry mechanism. The Appel-Bockhorn-Frenklach (ABF) mechanism (Appel et al. [14]), comprising 101 species and 1037 reactions, was found suitable for PAH predictions up to A_4 in C_2H_6 , C_2H_4 , and C_2H_2 laminar premixed flames and was therefore used for the reduction. The reduction was done in two-stages as follows:

2.1.1. First stage reduction:

The directed relation graph with error propagation (DRGEP) technique was used for first-stage reduction of the chemistry mechanism (Lu and Law [15], Pepiot-Desjardins and Pitsch [16], and Shi et al. [17]). This method requires a set of search initiating species (e.g., fuel, CO etc.) for driving the mechanism reduction, and species are eliminated if their contribution to the initial species is less than a user-specified error tolerance. The searching can be done using tree algorithms. In the present case, the breadth-first search algorithm was used [17]. Since the ABF mechanism was devised for CH_4 , C_2H_2 , and C_2H_4 combustion and not for diesel combustion, the DRGEP method was used for C_2H_4 combustion at $\Phi = 2$ for a single cell constant volume reactor calculation using SENKIN (Lutz et al. [18]). C_2H_4 and A_4 were taken as the search initiating species. The first-step reduction yielded a chemistry mechanism comprising 63 species and 565 reactions. Although the mechanism was obtained for $\Phi = 2$ it was also tested at other conditions e.g. $\Phi = 4$, initial temperature of 1100 K and initial pressure of 75 atm. and $\Phi = 4$, initial temperature of 1200 K and initial pressure of 50 atm. for validating satisfactory PAH predictions.

2.1.2 Second stage reduction:

For the second stage reduction, a sensitivity analysis of the first stage reduction species, mainly aromatics and PAH, was done to eliminate the less dominant ones. For each species that was eliminated, the time evolution profiles of C_2H_2 and A_4 were compared with the detailed mechanism predictions. The analysis was done for C_2H_4 combustion at a condition of $\Phi = 4$, initial temperature of 1200 K and an initial pressure of 50 atm. The final chemistry mechanism was composed of 46 species and 378 reactions. Finally, only the reactions and species pertaining to C_2H_2 , aromatics and PAH (21 species and 184 reactions) were taken from the mechanism (i.e., the soot precursor chemistry) and combined with the PRF fuel chemistry (Mech-2 mechanism in Part-I). The alternative C_4 pathway of A_1 formation is also included in this reduced mechanism. Similar to the approach in the first stage, the reduced mechanism obtained from second stage was also tested at the remaining two in-cylinder conditions.

2.2 Sensitivity to soot sub-models

In order to assess the sensitivity of the soot model, the rates of critical sub-models were modified to understand the dependence of the predicted net exhaust soot on the sub-models. The soot mass addition process is predominantly driven by the surface growth process (Lindstedt [19]), and the oxidation in the flame zone is governed by the availability of OH radicals. Vishwanathan and Reitz [20] performed an order of magnitude analysis on two OH induced oxidation models, one developed by Neoh et al. [21] and the other by Fenimore and Jones [22] and found that the former model has a three orders of magnitude higher oxidation rate than the latter model. Similar observation with the Neoh et al. model was also recently found by Pang et al. [23]. As in Part-I, a modified version of the Fenimore and Jones model was used in the current work.

The soot surface growth step from Part-I is shown below:

$$\begin{aligned} \text{C(s)} + \text{C}_2\text{H}_2 &\xrightarrow{\text{R}_2} 3\text{C(s)} + \text{H}_2, \text{R}_2 = k_2 \cdot [\text{C}_2\text{H}_2], \\ k_2 &= 9.0 \cdot 10^4 \cdot \exp\left(-\frac{12100}{T}\right) \cdot \sqrt{S} \{\text{s}^{-1}\}, S = \pi d_p^2 \cdot N \{\text{cm}^{-1}\}, d_p = \left(\frac{6Y_{\text{C(s)}}\rho}{\pi\rho_{\text{C(s)}}N}\right)^{\frac{1}{3}} \{\text{cm}\} \end{aligned} \quad (1)$$

The tuned surface growth model was obtained by reducing the pre-exponential factor (k_2) in Equation (1) by a factor of 2.5.

The baseline OH induced oxidation model in Part I is given as:

For the tuned OH induced oxidation model, the Fenimore and Jones model without any modifications was used as below:

In Equation (3), P_{OH} is the partial pressure of OH radical. Equation (3) when applied to atmospheric conditions becomes:

Equation (4) was multiplied by a factor of 12 to yield Equation (2) and was also used in Part-I of the paper. This was done to obtain a better overall match with the experimental data (Vishwanathan [24]). There is significant uncertainty in the reaction rates of the OH oxidation models. As seen in Vishwanathan and Reitz [20], order of magnitude analysis for an in-cylinder computational cell at 50 bar and 1900 K yielded values of $6 \cdot 10^4 \cdot [\text{OH}] \cdot \text{S}$ and $500 \cdot [\text{OH}] \cdot \text{S}$ for Neoh et al. and the Fenimore and Jones model, respectively. It should also be pointed that many soot models in the literature do not take into account soot oxidation through OH radical. Hence the sensitivity analysis with respect to soot oxidation by OH radical was performed.

3. Results and Discussion

3.1 Sensitivity to PAH chemistry mechanisms

As discussed in the previous section, to evaluate the sensitivity of the soot model predictions to the soot precursor concentrations, A_4 and C_2H_2 , the detailed chemistry ABF mechanism (Appel et al. [14]) was reduced in two stages using DRGEP and sensitivity analysis. The DRGEP method was used for C_2H_4 combustion at $\Phi = 2$ for a single cell constant volume reactor calculation using SENKIN. Additionally, the sensitivity analysis was done for C_2H_4 combustion at a condition of $\Phi = 4$, initial temperature of 1200 K and an initial pressure of 50 atm. Figure 1(a) shows the impact on peak C_2H_2 and A_4 concentrations when each of the species was eliminated at the above conditions. Due to the relatively small effects, none of the species from Figure 1 were retained in the final mechanism.

Figure 1(b) shows the resulting SENKIN predicted concentration profiles of C_2H_2 and A_4 using the detailed and the reduced chemistry mechanisms (from both reduction stages) at $\Phi = 4$, initial temperature = 1200 K, and initial pressure = 50 atm. It is seen from the figure that the reduced mechanism performs well as compared to the detailed mechanism, albeit predicting slightly higher peak A_4 . The resulting C_2 - C_3 , aromatic and PAH species and reactions from the second stage reduction were either added or replaced (if they were already present) in the Mech-2 PRF mechanism yielding the Mech-2 + PAH-2 mechanism.

Figure 2(a) shows the soot mass predictions for the constant volume chamber cases with the baseline and Mech-2 + PAH-2 chemistry mechanisms. As seen from Figure 2(a), there is a large amount of sensitivity seen in the total amount of soot predicted in the n-heptane combustion when the entire PAH

chemistry along-with updated C₂-C₃ chemistry is used. Hence some of the soot mass prediction differences should also be attributed to C₂-C₃ chemistry along with PAH chemistry differences. For example, some sensitivity in the soot mass was attributed to the C₃H₃ oxidation reaction, which was different by a factor of two between the mechanisms, as seen in Table 1. This is because the first ring formation is dominated by C₃H₃ addition. A higher pre-exponential factor for the C₃H₃ oxidation reaction would lead to its higher reaction rate, which will compete with the first ring benzene formation reaction: $C_3H_3 + C_3H_3 = C_6H_6$. Hence benzene formation may be suppressed.

To understand the contributions of the C₂-C₃ chemistry to the total soot mass, another sensitivity study was undertaken in which the relevant C₂-C₃ reaction rates were kept the same as the baseline mechanism rates and only the aromatic and PAH chemistry were updated. Table 1 shows ten relevant C₂-C₃ reactions that fall under this category of analysis and are considered extremely crucial for soot mass predictions.

Figure 2(b) shows the comparisons between the baseline and Mech-2 + PAH-2 chemistry but now with the baseline C₂-C₃ rates of Table 1. When the baseline mechanism C₂-C₃ rates of Table 1 were retained, the total soot mass results were nearly the same when compared to the baseline cases, although there is some difference at high density or high pressure conditions, as seen in Figure 2(b). Hence it can be concluded from the above studies that the major contribution to soot mass sensitivity comes from C₂-C₃ chemistry, rather than PAH chemistry as the acetylene surface growth process contributes principally for soot formation. Thus, future soot model improvements and reaction updates should be aimed at the C₂H₂/C₃H₃ chemistry, rather than the PAH chemistry for the present model framework.

3.2 Sensitivity to soot sub-models

The soot model predictions in KIVA-CHEMKIN [25] were compared with engine-out smoke measurements for the Caterpillar 3401E single cylinder diesel engine. The model performance with the Mech-2 + PAH-1 mechanism was tested for an EGR sweep (Hardy [26]) with all other conditions remaining the same. Table 2 shows the details of the engine operating conditions. Figure 3(a) shows in-cylinder pressure and heat release rate profiles for the 20% EGR case and Figure 3(b) compares the model-predicted EVO soot and experimental engine-out soot as a function of EGR. The model-predicted heat release rate is

the chemical energy release rate and is higher than the apparent energy release rate from experiment, which accounts for heat- transfer. In general, the model predicted match of the pressure trace with respect to the experiment was considered to be satisfactory. The model tends to show increasing soot with increasing EGR similar to the experiments, which is expected at intermediate EGR levels. However, the model predicted values are much higher than the experimentally obtained soot levels. It should also be noted that the soot model predictions are also sensitive to the spray model predictions and subsequent vapor distributions.

In order to assess the sensitivity of the soot model, the rates of critical sub-models were modified to understand the dependence of the predicted net exhaust soot on the sub-models. As the soot mass addition process is predominantly driven by the surface growth process, and the oxidation in the flame zone is predominantly governed by the availability of OH radicals, both these sub-models were tuned to assess the sensitivity on the final results. Table 3 shows the sub-models that were tailored individually to gauge their respective effects on the net soot predictions. Figure 4(a) shows the performance of the soot model under the influence of the different sub-models. It is seen that with tuned surface-growth or tuned OH induced oxidation, the model predictions match well with the experiments. In fact, all the models show an increase in exhaust soot with increasing EGR at intermediate levels. In order to further assess this trend, simulations were also run at higher EGR conditions with the tuned surface growth rate, as shown in Figure 4(b). It is seen that the exhaust soot increases and reaches a plateau between 40-55 % EGR, then reduces, and is insignificant at 65% EGR. Thus, the model predicts the trends of increase in soot with initial increase in EGR and then subsequent sharp decrease in soot at high EGR, where the engine operates in a low temperature combustion (LTC) mode. Figure 5 shows the associated in-cylinder soot histories at different EGR levels. It is seen that the peak in-cylinder soot occurs at 30% EGR; however, soot oxidation is faster than the 40% EGR case giving lower EVO soot. Thus, the EVO soot peaks with respect to EGR do not necessarily correlate with the in-cylinder soot peaks. With subsequent increase in EGR, the in-cylinder soot formation and soot oxidation progressively reduce. At 65% EGR, the soot formation process is nearly averted yielding significantly lower EVO soot. The observed trends agree with current understanding of conventional diesel and LTC soot formation mechanisms.

In order to test the sensitivity of the tuned soot surface-growth model at other conditions, it was also applied to two other parametric sweeps for the engine as shown in Table 4. The model predictions were

tested for 0% EGR, 11 bar IMEP PCCI conditions with variable pilot SOI timings and for 0% EGR, 9 bar IMEP single injection conventional diesel combustion conditions (Tess et al. [27]) at variable SOI timings.

Figure 6(a) and Figure 6(b) show the EVO predicted soot for the conditions in Table 4. It is seen that for both PCCI and conventional diesel combustion, the model is able to predict the trends well. For the pilot SOI = -65 CAD ATDC, the early injection was believed to result in wall impingement and the resulting higher EVO soot from the experiments is thought to be due to wall-film burning. However, no such wall films were seen in the model. For the conventional diesel combustion case, the model is able to reproduce the trend of increasing soot at retarded SOI. This is due to the fact that the soot oxidation process is phased well into the expansion stroke, resulting in lower in-cylinder temperatures and higher net EVO soot. This is seen from Figure 7, which shows the in-cylinder history of soot, while applying the tuned surface-growth model.

More importantly, the tuned surface growth model is able to predict the disparity in sooting scales, which is roughly an order of magnitude different between the 9 bar IMEP conventional diesel and 11 bar IMEP PCCI combustion at 0% EGR. Figures 8(a) and 8(b) show the EVO distributions of soot particle size distribution, d_p vs. particle number and d_p vs. soot mass for the conventional diesel combustion case. For SOI = 0 CAD ATDC, (Figure 8(a)) the particle number peak is around 23 nm while the soot mass peak is around 26 nm. However, for the SOI = 5 CAD ATDC case (Figure 8(b)), the number of particles populating the 10 to 20 nm size is the highest while the peak soot mass is seen around 75 nm. The larger size particles persist due to slower oxidation, as seen from Figure 7. The particle size at SOI = 5 CAD ATDC case may be over-predicted as the soot mass was also over-predicted by the model as compared to the experimentally observed soot mass, which may be an artifact resulting from a model predicted slower-oxidation rate.

Figures 9(a), 9(b), 10(a), and 10(b) show the distributions of soot particle size for PCCI conditions with 0%, 20%, 30% and 40% EGR, respectively, using the tuned surface growth model. For the PCCI conditions, with increase in EGR, the peak particle number is always seen to occur close to 10 to 20 nm size particles, while the soot mass peaks transition from 10 to 15 nm size particles at 0% EGR to 25 to 35 nm size particles at 40% EGR. Similar to conventional diesel combustion, the slower oxidation at the 30% and 40% EGR conditions, as seen in Figure 5, leads to a higher soot particle size population. Thus, an increase in EGR increases the dominant size associated with the maximum soot mass. This trend was also seen in the

constant volume chamber simulations at high simulated EGR or lower in-cylinder O_2 (Part-I of the paper). Also, the dominant size associated with the maximum soot mass under high-sooting PCCI conditions (40% EGR at 11 bar IMEP) is smaller than for high-sooting conventional diesel combustion (SOI = 5 CAD ATDC, 0% EGR at 9 bar IMEP), while the soot size associated with the maximum number of particles is approximately the same between both conditions. In general, both conventional diesel and PCCI conditions yielded fairly unimodal soot particle size distributions.

It is very interesting to find that the same set of model constants were applicable for an engine operated under conventional and advanced combustion modes with and without EGR. Also, the model was able to capture the sooting tendencies that differed by nearly an order of magnitude. Hence it is proposed that the surface-growth model pre-exponential factor can be tuned within a factor of 2.5 and be used for different engines with advanced combustion strategies.

Figure 11(a) shows the history of characteristic soot particle diameter (number averaged diameter), which was obtained as

$$d_{\text{char}} = \left(\frac{6 \cdot M_s}{\pi \cdot \rho_{C(s)} \cdot N_s} \right)^{1/3} \{ \text{cm} \} \quad (5)$$

where M_s is the total soot mass and N_s is the total number of particles, at a crank angle. Again, it is seen that the characteristic diameter increases with increasing EGR for the Caterpillar engine PCCI cases. However, it is interesting to see that the characteristic diameter evolution during the soot formation period is nearly the same for all EGR cases. For the lower EGR cases, soot oxidation is prevalent, and the net EVO characteristic diameters are lower. For conventional diesel combustion, the characteristic soot particle diameter during the soot formation phase for the SOI = 0 CAD ATDC case is higher than those of SOI = 5 CAD ATDC, possibly due to higher formation rate and higher in-cylinder peak values. However again due to enhanced oxidation, the SOI = 0 CAD ATDC case yields lower EVO characteristic diameter.

For the GM light-duty diesel engine PCCI case (studied in Part-I), the SOI = -8 case always showed higher characteristic diameters as compared to the SOI = -2 CAD ATDC case throughout the formation and oxidation phases, possibly due to high soot mass existing throughout the cycle. Similar model trends of increasing EVO soot diameter distributions and characteristic diameters were observed by Boulanger et al.

[28] for single injection diesel combustion in a Caterpillar 3406 heavy-duty diesel engine at 0% and 8% EGR conditions, as shown in Figure 11(b). The characteristic diameter evolution between the 0% and 8% EGR cases is similar to that seen in the present study for the 0% and 20% EGR conditions with the characteristic diameters reaching the same peak values and then varying during the expansion stroke with higher EVO soot diameters obtained for higher EGR. This in-cylinder peak and subsequent reduction in the soot diameter was not seen for EGR rates greater than 30% in the present study, presumably due to slower soot oxidation rates.

Figure 12(a) shows the total in-cylinder number of soot particles for the Caterpillar PCCI engine. It is seen that the in-cylinder peak number of particles increases from 0 to 20% EGR and then decreases at higher EGR values, however the number of particles at EVO always increases with increased EGR. For the conventional combustion case (9 bar IMEP), the in-cylinder peaks are higher than for the PCCI conditions (11 bar IMEP), but the EVO numbers are of the same order of magnitude as those for PCCI combustion. The light-duty GM engine PCCI shows about a two-orders of magnitude lower in-cylinder peak number of particles and about one order of magnitude lower EVO number of particles, which leads to the inference that the heavy duty engine's PCCI combustion at a lower load of 9 bar IMEP may be characterized by a lower number of particles at EVO as compared to 9 bar light-duty conventional diesel combustion. The plots were obtained with the tuned surface-growth model for the heavy-duty engine and the baseline soot model for the light-duty engine, as the respective models predicted well the respective experimental soot mass trends.

Figure 12 (b) shows the in-cylinder evolution of total number of particles from the study of Boulanger et al. [28] for 0% and 8% EGR single injection combustion for qualitative comparison. The evolution trend of the total number of particles is very different between the models as the Boulanger et al. model shows a steady-state evolution with no reduction in the total number of particles. This may be due to differences in the competition between the inception and coagulation rates between the two models. In the Boulanger model, the inception is considered through 'pseudo-radicals' produced by unburned hydrocarbons (primarily C_2H_2 in the flame zone), while pyrene is used as the inception species in the present model. The number density destruction in both models occurs only through soot coagulation. However, both models predict an increase in the number of particles with increasing EGR at EVO.

4. Summary and conclusions

In this study a detailed sensitivity analysis was conducted on a previously developed soot model, as described in Part-I, for conventional diesel and low temperature diesel combustion. In order to assess the sensitivity of soot mass predictions on chemistry mechanisms, two different PAH chemistry mechanisms were used. The first reduced PAH chemistry mechanism was obtained from the literature and a second reduced PAH chemistry mechanism was developed from the detailed ABF chemistry mechanism using the directed related graph with error propagation (DRGEP) method and species sensitivity analysis. The analysis revealed that the soot mass predictions were relatively more sensitive to the lower carbon chemistry (C_2 - C_3) rather than the PAH chemistry itself. This is due to the fact that the major soot mass addition process is from acetylene surface growth and hence the total soot mass sensitivity is more directly related to the acetylene chemistry. Ten key reactions were identified that were crucial in affecting the total soot mass.

In terms of soot sub-models, the soot surface-growth model through acetylene and OH-induced soot oxidation models were identified as the key soot mass formation and consumption steps, respectively. The baseline model over-predicted EVO soot mass for a Caterpillar heavy-duty diesel engine, while the tuned surface-growth and tuned OH oxidation models proved to be more accurate for soot mass predictions. The improved models also predicted well the soot mass for other combustion strategies at different loads such as PCCI with different levels of EGR, PCCI with a pilot-start-of-injection timing swing at 0% EGR, and conventional diesel combustion with main-start-of-injection swing at 0% EGR. Thus, the same set of model constants were found to be applicable for an engine operated under varied advanced combustion modes. The tuned surface growth model was proposed for calibrating the soot model for an engine, where the soot surface-growth pre-exponential factor was tuned by a factor of 2.5, which is well within its uncertainty.

The trends of in-cylinder characteristic soot particle diameter were compared with available modeling studies in the literature and similar trends for in-cylinder soot particle diameter evolution were seen with the literature. For 0% EGR and lower rates of EGR, the characteristic in-cylinder soot particle diameter reaches a peak value and then reduces due to oxidation in the expansion stroke. However, at higher EGR rates this observation is not seen due to reduced oxidation rates. The same observations hold for

conventional diesel combustion at 0% EGR with retarded main-start-of-injection timings, where the available residence time for soot oxidation is lower than for advanced main start of injection cases.

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Figure 1: a) Results of sensitivity analysis on peak C_2H_2 and A_4 concentrations at $T = 1200$ K, $P = 50$ atm and $\Phi = 4$ and b) C_2H_2 and A_4 mole fractions as predicted by the detailed, first-stage and second-stage reduced mechanisms for C_2H_4 combustion at $\Phi = 4$, initial temperature = 1200 K and initial pressure = 50 atm.

Figure 2: a) Comparison of net soot predictions with the baseline and the Mech-2 + PAH-2 mechanisms and b) Comparison of net soot predictions with the baseline mechanism and the Mech-2 + PAH-2 mechanism with baseline $\text{C}_2\text{-C}_3$ rates from Table 1.

Figure 3: a) Model predicted pressure and heat release rate as compared to experiments for 20% EGR case and b) Baseline model predicted EVO soot as compared to CAT PCCI experiments.

Figure 4: a) EVO soot predicted by the various sub-models as compared to CAT PCCI experiments and b) Model predicted EVO soot as a function of in-cylinder EGR with tuned surface-growth model.

Figure 5: Model predicted in-cylinder soot histories as a function of in-cylinder EGR with tuned surface growth model.

Figure 6: (a) Model predicted EVO soot as compared to the CAT PCCI experiments at different pilot SOI and b) EVO predicted soot mass as compared to the CAT conventional diesel combustion as a function of SOI sweep.

Figure 7: In-cylinder soot histories at variable SOI for conventional diesel combustion using the tuned surface-growth model.

Figure 8: Histograms of d_p vs. number of particles and d_p vs. soot mass at EVO CAD ATDC = 130 for a) SOI = 0 CAD ATDC conventional diesel combustion and b) SOI = 5 CAD ATDC conventional diesel combustion.

Figure 9: Histograms of d_p vs. number of particles and d_p vs. soot mass at EVO CAD ATDC = 130 for a) 0% EGR PCCI condition and b) 20% EGR PCCI condition.

Figure 10: Histograms of d_p vs. number of particles and d_p vs. soot mass at EVO CAD ATDC = 130 for a) 30% EGR PCCI condition and b) 40% EGR PCCI condition.

Figure 11: Characteristic soot diameter for the metal engines as a function of crank angle for a) current study and b) reproduced from Boulanger et al. [28].

Figure 12: Total number of particles for the metal engines as a function of crank angle for a) current study and b) reproduced from the Boulanger et al. [28].

Table1: Salient C₂-C₃ reactions influential for soot formation

Reaction	Arrhenius parameters (PAH-2)	Arrhenius parameters (Baseline mechanism)
$\text{C}_3\text{H}_3 + \text{OH} \leftrightarrow \text{C}_2\text{H}_3 + \text{HCO}$	4E+13, 0, 0	2E+13, 0, 0
$\text{C}_2\text{H}_2 + \text{O} \leftrightarrow \text{C}_2\text{H}+\text{OH}$	4.6E+19, -1.4, 28950	4.6E+19, -1.4, 28950 Rev: 3E+15, -0.6, -1782
$\text{C}_2\text{H}_2 + \text{OH} \leftrightarrow \text{C}_2\text{H}+\text{H}_2\text{O}$	3.4E+07, 2, 14000	3.4E+07, 2, 14000 Rev: 4670, 3.1, 685
$2\text{CH}_2 \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2$	3.2E+13, 0, 0	1.2E+13, 0, 800
$\text{C}_2\text{H}_2 + \text{H}(+\text{M}) \leftrightarrow \text{C}_2\text{H}_3(+\text{M})$ $\text{C}_2\text{H}_2 + \text{H} + \text{M} \leftrightarrow \text{C}_2\text{H}_3+\text{M}$	$K_0 = 5.6\text{E}+12, 0, 2400$ $K_\infty = 3.8\text{E}+40, -7.3, 7220$ Troe: 0.75, 98.5, 1302, 4167	5.54E+12, 0, 2410
$\text{C}_2\text{H}_2 + \text{O} \leftrightarrow \text{CH}_2+\text{CO}$	1.0E+07, 2, 1900	6.96E+06, 2, 1900
$\text{C}_2\text{H}_2 + \text{OH} \leftrightarrow \text{CH}_2\text{CO} + \text{H}$	0.22E-03, 4.5, -1000	1.00E+11, 0.0, 12000
$\text{C}_2\text{H}_3 + \text{H} \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2$	3E+13, 0, 0	4E+13, 0, 0
$\text{C}_2\text{H}_3 + \text{OH} \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	5E12, 0, 0	3E+13, 0, 0
$\text{C}_2\text{H}_4 (+\text{M}) \leftrightarrow \text{H}_2 + \text{C}_2\text{H}_2(+\text{M})$	$K_0 = 8\text{E}+12, 0.44, 88770$ $K_\infty = 7\text{E}+50, -9.3, 99860$ Troe: 0.73, 180, 10350, 5417	$K_0 = 1.5\text{E}+15, 0, 55800$ $K_\infty = 1.5\text{e}+51, -9.3, 97800$ Troe: 0.73, 180, 10350, 5417

Units in mol, cm, s, K, cal

Table 2: Caterpillar heavy-duty diesel engine operating conditions

Engine	CAT 3401E SCOTE
% EGR	0, 3, 8, 15, 20, 24, 30
First SOI (CAD ATDC)	-56.5
Main SOI (CAD ATDC)	10.5
Intake press. (MPa)	0.22
Intake temp. (C)	31-33
Fuel in first pulse (mg)	55
Fuel in second pulse (mg)	78
First injection pressure (bar)	1500
Second injection pressure (bar)	1500
IMEP (bar)	11.13-11.45

Table 3: Baseline and modified rate constants for the surface growth and OH induced oxidation models.

Baseline surface growth	Tuned surface growth	Baseline OH induced oxidation	Tuned OH induced oxidation
$\dot{R}_2$	$\dot{R}_2/2.5$	Eq.(2)	Eq.(3)

Table 4: Conditions for PCCI and conventional diesel combustion at variable pilot and main SOI, respectively.

Regime	PCCI	Conventional
Pilot SOI (CAD ATDC)	-65, -60, -55, -50	-
Main SOI (CAD ATDC)	10.5	-10, -5, 0, 5
Intake press. (MPa)	0.220	0.172
Intake temperature (C)	31	36
Fuel in pilot/main pulses (mg)	55/78	-/118
Injection pressure	1500	755
IMEP (bar)	11	9