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## Towards a detailed soot model for internal combustion engines

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#### Abstract

In this work, we present a detailed model for the formation of soot in internal combustion engines describing not only bulk quantities such as soot mass, number density, volume fraction, and surface area but also the morphology and chemical composition of soot aggregates. The new model is based on the Stochastic Reactor Model (SRM) engine code, which uses detailed chemistry and takes into account convective heat transfer and turbulent mixing, and the soot formation is accounted for by SWEEP, a population balance solver based on a Monte Carlo method. In order to couple the gas-phase to the particulate phase, a detailed chemical kinetic mechanism describing the combustion of Primary Reference Fuels (PRFs) is extended to include small Polycyclic Aromatic Hydrocarbons (PAHs) such as pyrene, which function as soot precursor species for particle inception in the soot model. Apart from providing averaged quantities as functions of crank angle like soot mass, volume fraction, aggregate diameter, and the number of primary particles per aggregate for example, the integrated model also gives detailed information such as aggregate and primary particle size distribution functions. In addition, specifics about aggregate structure and composition, including C/H ratio and PAH ring count distributions, and images similar to those produced with Transmission Electron Microscopes (TEMs), can be obtained. The new model is applied to simulate an n-heptane fuelled Homogeneous Charge Compression Ignition (HCCI) engine which is operated at an equivalence ratio of 1.93. In-cylinder pressure and heat release predictions show satisfactory agreement with measurements. Furthermore, simulated aggregate size distributions as well as their time evolution are found to qualitatively agree with those obtained experimentally through snatch sampling. It is also observed both in the experiment as well as in the simulation that aggregates in the trapped residual gases play a vital role in the soot formation process.

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## **1** Introduction

The formation of soot and other particulate matter in internal combustion engines is a common problem [1, 2]. While soot formation is usually associated with conventional Diesel, i.e. Compression Ignition Direct Injection (CIDI) engines [3], gasoline Spark Ignition (SI) engines are increasingly coming under scrutiny [2]. More generally, soot can also be shown to be relevant in engines with other (multiple) Direct Injection (DI) strategies such as partially premixed Diesel, partially stratified Homogeneous Charge Compression Ignition (HCCI) [4], and Direct Injection Spark Ignition (DISI) engines [5].

Given the importance of direct injection technology for mixture preparation and combustion control in modern engines, and the fact that stratified operation bears the possibility of locally fuel-rich mixtures, the formation of soot is an important factor in the design of cleaner engines. Such development is assisted by detailed understanding of the processes involved, to which modelling and simulation can contribute significantly.

The literature on soot modelling in engines has been largely restricted to Diesel engines and to strongly simplified soot models, such as most frequently empirical ones, e.g. [6, 7], or [8], but also models based on the method of moments, e.g. [9, 10]. The majority of methods has been incorporated into the Computational Fluid Dynamics (CFD) code KIVA.

Among the works using moment methods, in [11], a two-variable description (soot number density and volume fraction) has been implemented in KIVA coupled to detailed chemistry by means of Representative Interactive Flamelets (RIFs). Although using only two quantities is beneficial for computational expense, one drawback is for example that the important influence of aggregate morphology, which is usually complex, on surface area and collision diameter can only be captured through the use of empirical constants and assumptions on the fractal dimension.

In [9], a review of pre-2005 work on soot modelling in engines is given, showing that most models in the past have been based on simple, empirical expressions, many essentially variants of Hiroyasu's model [12, 13], and that the most complex ones have been based on the method of moments. In particular, a need for more detailed but still computationally affordable engine soot models is emphasized. In [9], a moment method, using a presumed shape of the size distribution, and the assumption of spherical particles, is integrated into KIVA. An 11-step surface growth and oxidation mechanism is used, with acetylene as inception species. This work has been continued in [10] with improved turbulence models. While this surface chemistry model is relatively detailed compared to earlier work, a significant remaining shortcoming is the fact that the chemical composition of the soot particles, which strongly affects their reactivity, is not accounted for. Instead, an assumption on the reactivity must be made which is then not altered throughout the simulation.

More recently, the focus has still remained on phenomenology and on using descriptions based on only a small number of quantities, although improvements have been made [14, 15, 16]. In [17], three empirical soot models of varying complexity implemented in KIVA are reviewed and compared.

The aim of the present work is to develop a computationally cheap engine simula-

tion code containing a highly detailed soot model which describes not only soot mass, number density, volume fraction, and surface area but also the morphology and chemical composition of soot aggregates.

As engine model we use the Stochastic Reactor Model (SRM) [18, 19, 20, 21, 22, 23, 24] which includes detailed chemical kinetics, and possesses sub-models for turbulent mixing and convective heat loss, thereby accounting for inhomogeneities, i.e. stratification in composition as well as temperature. The main strength of the SRM is its capability of qualitatively predicting emission trends of CO,  $CO_2$ ,  $NO_x$ , and unburnt hydrocarbons at reasonable computational cost of 1-2 hours per engine cycle. This enables convenient multi-cycle, sensitivity, and parameter studies.

For the simulation of soot formation we use SWEEP, a Monte Carlo based population balance solver [25] which includes a large amount of detail on structure and composition of soot particles. A number of algorithmic improvements and model extensions have been implemented previously, such as a Linear Process Deferment Algorithm (LPDA) [26], an Aromatic Site model for surface reactions [27, 28], and improved oxidation rates [29]. One of the most important features of SWEEP is its ability to accommodate up to thousands of internal coordinates, or in other words highly detailed particle descriptions covering aggregate structure and chemical composition – problems which would be intractable with moment or sectional methods.

In order to link the gas-phase to the particulate phase, we extend a detailed chemical kinetic mechanism for Primary Reference Fuels (PRFs, mixtures of n-heptane and iso-octane) used previously so that small aromatic species which function as soot precursors are covered. This new fuel model is validated independently using a set of fuel-rich premixed laminar flame experiments from the literature.

The integrated engine-soot model is applied to simulate an n-heptane fuelled Homogeneous Charge Compression Ignition (HCCI) engine operated at an equivalence ratio of 1.93. A key advantage of such a setup, with model development in mind, is that the complications relating to mixture preparation, in particular the notoriously difficult issue of spray modelling, do not need to be considered. An additional reason for choosing this study is, in contrast to many other studies in the literature, the availability of in-cylinder soot data obtained through snatch sampling.

The paper is structured as follows. In the next section, the numerical models and the extension of our chemical mechanism to include soot precursors are presented, and the incorporation of the soot model into the SRM framework is explained. Subsequently, we present results of numerical simulations in which the model is applied to simulate an HCCI engine run under fuel-rich conditions and compare our results to experimental measurements. Finally, we summarize our conclusions and outline how to extend the model to engine operating modes utilizing direct fuel injection.

### 2 Model description

In this section, we briefly summarize the main features of the engine model as well as the soot model, both of which have been described in detail elsewhere. Then, the extension of

the chemical mechanism is explained, and the steps taken to integrate all the model parts.

#### 2.1 Engine model

The Stochastic Reactor Model (SRM) engine code has been successfully employed in a number of earlier studies (not involving soot formation) such as port fuel injected HCCI combustion [20], single early direct injection HCCI [21], dual injection HCCI [19], multicycle transient simulation and control [22], and has been coupled to the Computational Fluid Dynamics (CFD) code KIVA [23].

The model was originally inspired by Probability Density Function (PDF) transport methods [30]. It employs detailed chemical kinetics and possesses sub-models for turbulent mixing and convective heat transfer. For the description of turbulent mixing we use the Euclidian Minimum Spanning Tree (EMST) model [31], in which fluid parcels to be mixed are chosen based on proximity in composition-enthalpy phase space.

Since it includes detailed chemistry, the SRM can qualitatively predict emission trends of CO,  $CO_2$ ,  $NO_x$ , and unburnt hydrocarbons at modest computational cost of 1-2 hours per engine cycle, making possible convenient multi-cycle, sensitivity, and parameter studies.

An important concept within the SRM is what in previous work has been termed 'stochastic particle'. However, in order to improve clarity, we refer to them here more explicitly as *SRM particles* since in this work four different types of 'particles' play a role. The number of SRM particles governs the precision of physical predictions. Asymptotically, any such prediction should be independent of the particle number, and we find that for many purposes  $10^2$  are sufficient.

#### 2.2 Soot model



Figure 1: Types of functional sites on the edge of a PAH molecule.

Our model for the formation of soot is given by a detailed set of population balance

equations. The solver, which is based on a Monte Carlo method [32, 33], is implemented in a library called SWEEP [25].

The soot model as it is used in this study, as far as the morphology of soot aggregates is concerned, tracks for each aggregate the surface area  $S_a$ , the number  $N_{PP}$  of primary particles and for each primary particle *j* its diameter  $d_j^{PP}$ . In addition to that, the chemical composition of soot is modelled as follows: for each aggregate, the number *C* of carbon atoms, the number *H* of hydrogen atoms, and the number  $N_{PAH}$  of PAH molecules are stored. As a further refinement, we use the Aromatic Site Counting Model [27], which tracks for each aggregate the number of occurrences of each type of functional site on a PAH. The site types considered here are free edge, armchair, zigzag, and bay sites, and five-membered rings (Fig. 1), with numbers  $N_{ed}$ ,  $N_{ac}$ ,  $N_{zz}$ ,  $N_{bay}$ , and  $N_{R5}$  respectively. More formally, each soot aggregate is fully described by a vector

$$E = (C, H, S_{a}, N_{ed}, N_{ac}, N_{zz}, N_{bay}, N_{R5}, N_{PAH}, N_{PP}, d_1^{PP}, \dots, d_{N_{PP}}^{PP}).$$

This statistical representation of PAHs and their functional sites is employed because tracking every single molecule is computationally prohibitive.

We note that the number of internal coordinates used to describe soot aggregates in our model can easily reach more than  $10^3$ , so that Monte Carlo methods are ideally suited for solving the corresponding population balance equations. Such high-dimensional problems are currently intractable with sectional or moment methods.

The modelled processes which soot aggregates undergo include the following: Inception, i.e. dimerization of pyrene molecules, condensation, i.e. addition of a pyrene molecule taken from the gas-phase to an existing particle, and surface growth are the three possible pathways in our model from the gas-phase to the particulate phase, i.e. when molecules are held together in a particle through physical forces rather than chemical bonds. In the particulate phase, coagulation and surface chemistry, including growth and oxidation reactions on the surface of particles are taken into account. Details of the surface chemistry are given in [28]. The rates of the surface reactions depend on the attacked functional site and also the neighboring ones. This information can be provided through statistical correlations obtained from Kinetic Monte Carlo (KMC) simulations [28]. For the computational speed-up of surface reactions the Linear Process Deferment Algorithm (LPDA) [26] is employed.

This detailed chemical description of soot aggregates allows for example to plot distributions of aggregate C/H ratio and (approximate) PAH ring count versus aggregate collision diameter.

The physical population of soot aggregates is represented numerically by an ensemble of stochastic soot particles, and, just as with the SRM, any physical prediction must be asymptotically independent of the number of stochastic particles.

#### 2.3 Chemical kinetic mechanism

Since the SRM simulates engine combustion employing detailed chemical kinetics, in order to include a soot model, the chemical mechanism needs to be extended to include



(a) Validation of benzene formation sub-mechanism against a fuel-rich n-heptane *flame* [34].



(b) Validation of naphthalene formation sub- (c) Validation of PAH formation up to coronene mechanism against a fuel-rich propylene against a fuel-rich naphthalene flame [36]. flame [35].

**Figure 2:** Validation of the extended detailed chemical mechanism against flame experiments. soot precursor species. The mechanism which served as starting point for this work is a detailed kinetic model for Primary Reference Fuels (PRFs), i.e. mixtures of n-heptane and iso-octane, used extensively in previous studies [19, 20, 21]. The chemical mechanism describing the kinetics, which also features  $NO_x$  chemistry, contains 157 species and 830 reactions.

These earlier simulation efforts were targeted at the prediction of quantities such as pressure, CO,  $NO_x$ , and unburnt hydrocarbon (HC) emissions in engines fuelled with PRFs. Here, the formation of soot precursors including Polycyclic Aromatic Hydrocarbons (PAHs) and other highly unsaturated hydrocarbon species is of particular interest. The modification and extension of the existing mechanism were built upon earlier flame studies of commercial liquid fuels [37, 38, 39, 40]. The new, extended chemical mechanism contains 208 species and 1002 reactions.

The validation (Fig. 2) of the extended mechanism was accomplished in four steps.

- 1. The fuel consumption rates and the evolution of intermediates were critically examined and substantially improved.
- 2. New reactions describing the formation of benzene were added to the mechanism. A fuel-rich n-heptane flame [34] was taken as the reference experimental data and the predicted results of selected species are shown in Fig. 2(a).
- 3. A new naphthalene formation sub-mechanism was added and was validated using the measured concentrations of a fuel-rich propylene flame [35]. The predicted concentrations of important soot precursors are compared with the measured values in Fig. 2(b).
- 4. The final step involved the extension of the PAH chemistry up to coronene and the measured profiles of a fuel-rich naphthalene flame [36] were compared as a validation reference with the simulated profiles in Fig. 2(c).

Additionally, by comparing to the original PRF mechanism in homogeneous constant volume calculations, we ensured that none of the alterations made significantly affect ignition delay over a range of pressures, temperatures, and equivalence ratios.

#### 2.4 Integrating the models

The main step of integrating the SWEEP population balance solver into the SRM code consists of associating a population balance with each of the SRM particles and solving them in every computational time step, i.e. solving the soot population balance is implemented as an additional operator splitting step. Another key ingredient is to link the gas-phase to the particulate phase by identifying one or more species in the new chemical mechanism as inception and condensation species. Basic validity tests of the software include stability with respect to the number of SRM particles, the number of stochastic soot particles, and the size of the time step.

In this work, we exclusively use pyrene, a PAH with four benzene rings, as inception and condensation species. This is a common assumption in the soot modelling literature, but less so in the engine community, where inception is more often based on acetylene (e.g. [9]). Our new mechanism, containing aromatic compounds of up to seven rings, allows investigating the influence of different inception pathways, which we defer, however, to a subsequent study.

It turns out that aggregates present in the trapped residual gases play an important role for operating conditions with non-negligible (internal or external) EGR rates, so it is necessary to create an adequate infrastructure for recirculating population balances. Since stochastic soot particles represent number *densities*, this requires in particular to ensure the ensemble normalizations are adjusted appropriately for any change in volume, or otherwise spurious re-sampling (doubling or contraction through uniform random deletion of stochastic particles) of the ensembles will occur.

### **3** Experimental setup and measurements

Bore	86 mm
Stroke	86 mm
Displaced volume	$499 \text{ cm}^3$
Compression ratio (CR)	12
EGR mass fraction	22%
Inlet valve opening (IVO)	2 CAD ATDC
Inlet valve closing (IVC)	228 CAD ATDC
Exhaust valve opening (EVO)	-225 CAD ATDC
Exhaust valve closing (EVC)	3 CAD ATDC
Speed	600 RPM
Inlet temperature	412 K
Fuel/air equivalence ratio $\Phi$	1.93
1	

**Table 1:** Engine specification and operating condition.

Experiments were carried out on an SI engine converted for single-cylinder HCCI operation. The main advantage of operating in HCCI mode for a fundamental study on soot formation in engines is that the complications arising from the direct injection process such as droplet evaporation and mixing do not need to be taken into account.

The engine was run port-injected, fuelled with pure n-heptane, at an equivalence ratio of  $\Phi = 1.93$ . The fraction of trapped residual gases (internal EGR rate) was relatively large at 22%, which, however, is useful in this particular study for charge dilution in order to keep the total heat release and hence peak in-cylinder pressures reasonably small. In addition to that, the engine was run throttled for the same reason. Main engine specifics and operating parameters are summarized in Table 1.

Particle-laden in-cylinder gases were extracted through snatch sampling, accumulated over a number of cycles in steady-state operation. The obtained aggregates were analyzed



Figure 3: Experimental setup of in-cylinder snatch sampling measurements.

through a Scanning Mobility Particle Sizer (SMPS) and a High-Resolution Transmission Electron Microscope (HR-TEM). A schematic of the experimental setup is given in Fig. 3.

## 4 Simulations, results, and discussion



Figure 4: Comparison of measurements with simulation.

As the first step of applying the model, physical model parameters not easily accessible to measurement need to be calibrated, such as most importantly the turbulent mixing time and the heat transfer constant. Some results of this tuning process are shown in Fig. 4 for in-cylinder pressure (Fig. 4(a)) and heat release rate (Fig. 4(b)), which show satisfactory agreement. As far as purely numerical parameters are concerned, we chose to set the number of SRM particles to 100, whereas the maximum number of stochastic soot particles in each SRM particle was set to 1024. The latter is required to be a power of two due to a binary-tree based algorithm. In initial tests we ensured that main physical predictions are at least stable with respect to perturbations in these numerical parameters. We found



 (a) Total number of soot aggregates in the cylinder (b) Average primary particle count per aggregate and their average diameter.
 (b) Average primary particle count per aggregate and average primary particle diameter.

Figure 5: Simulated average soot quantities as function of crank angle.

that the number of stochastic soot particles per SRM particle is sufficient for low statistical noise, due to the relative homogeneity of the considered fully premixed operating condition. We also found that while the dominant contribution to the CPU-time spent overall still stems from solving the chemical kinetic equations, solving the population balance can reach about the same computational cost.

Experimental results of this study, as well as findings in the literature [14], suggest that aggregates recirculated in exhaust gases play an important role, as described in more detail below, which we substantiated by preliminary simulations. For this reason, we decided to conduct all our simulations over ten consecutive cycles, starting with trapped residuals with typical gas-phase composition, but not containing any soot. All simulation results presented in the following are taken from the tenth cycle unless stated otherwise. When carrying out such studies, it becomes clear that low computational cost is highly desirable. Even under heavily sooting conditions with large numbers of primary particles per aggregate, one engine cycle consumes usually less than four hours of CPU-time.

Figure 5 shows a number of simulated average soot quantities as function of crank angle. In Fig. 5(a), the total number of soot aggregates in the cylinder and their average diameter is plotted. Ignition starts at about 9 CAD ATDC, which brings about rapid inception of a large number of small aggregates into an ensemble of large aggregates remaining from the previous cycle. Fig. 5(b) shows the average number of primary particles per aggregate and the average primary particle diameter. While averages can be useful, care should be taken when drawing conclusions from them, as the underlying distributions can possess a non-trivial shape.

In Fig. 6, the rates of all processes involving the particulate phase included in the model are shown as function of crank angle. Inception, condensation, and coagulation are shown in Fig. 6(a), growth via acetylene addition and free-edge desorption in Fig. 6(b), a number of five-membered ring addition, conversion, and desorption processes in Fig. 6(c), and oxidation via OH and O<sub>2</sub> in Fig. 6(d). Free-edge growth and desorption are the dominant processes, at least early in the formation phase. Note that, due to premixed fuel-rich conditions, oxidation by OH is much more significant than by O<sub>2</sub>.

Figure 7 shows an experimental as well as a simulated aggregate both sampled at about 16 CAD ATDC. In Fig. 7(a), an experimental HR-TEM image of a primary particle





Figure 6: Rates of the soot processes considered in the model as function of crank angle.

is shown together with some indicated internal length scales. A simulated aggregate is shown in a TEM-style projection in Fig. 7(b). The largest simulated primary particles are about the same size as the ones in Fig. 7(a), which are also among the largest experimentally. The size distribution of primary particles of the simulated aggregate is plotted in Fig. 7(c). We note that it deviates significantly from the log-normal shape which has been reported in the literature a number of times based on measurements in Diesel engines (see for example [41]).

Figure 8 shows experimental as well as simulated in-cylinder aggregate size distributions at various crank angles. An early part of the cycle, ranging from just after the start of ignition to about the time when peak temperature is reached, is shown in Figs. 8(a) (experiment) and 8(b) (simulation), whereas the subsequent, later part of the cycle is shown in Figs. 8(c) (experiment) and 8(d) (simulation). Both the shape of the distributions and the trends of their time evolution agree well qualitatively. In particular, we recognize the aggregates recirculated in trapped residual gases as a prominent feature.

Further size distributions are displayed in Fig. 9. Figure 9(a) shows the time evolution of the aggregate size distribution between 5 and 65 CAD ATDC. In a later stage of the cycle, as is well known, the distribution turns bimodal, since inception is present throughout and large aggregates act as 'vacuum cleaners', rapidly coagulating with the small ones. Again we note the presence of recirculated aggregates. In Fig. 9(b), aggregate size distributions at 10 CAD ATDC are plotted for ten consecutive cycles, where the first starts



(a) Experimental HR-TEM image of an aggregate sampled at about 16 CAD ATDC. Indicated are length scales of structures within a primary particle.



(b) TEM-style image of simulated aggregate (c) Primary particle size distribution of simulated aggre-(sampled at 15.6 CAD ATDC, 65 primaries, collision diameter 16.5 nm, C/H ratio 1.61).

**Figure 7:** *Experimental and simulated aggregates. The largest simulated primaries are roughly the same size as the largest experimental ones (chosen for 7(a)).* 



Figure 8: Experimental and simulated in-cylinder aggregate size distribution functions at various crank angles.



(a) Time evolution of the size distribution. Prominent (b) Size distribution at 10 CAD ATDC for ten feature: aggregates present in the trapped residual gases.

consecutive cycles. The recirculated aggregates can be clearly identified as the ones larger than about 20 nm.

Figure 9: More simulated in-cylinder soot aggregate size distributions.



(a) *C/H* ratio distribution shortly after igni- (b) *C/H* ratio distribution later in the cycle. *tion.* 



(c) Approximate PAH ring count distribution (d) Approximate PAH ring count distribution shortly after ignition. later in the cycle.

Figure 10: Simulated soot aggregate composition PDFs at two different crank angles.

without any soot present in the residual gases as mentioned above. We observe that the distribution has stabilized and the statistical noise has decreased substantially by the tenth cycle. Most importantly, we readily identify the aggregates larger than about 20 nm as being recirculated for possibly several times before being emitted from the engine.

Figure 10 shows aggregate composition PDFs, in particular carbon to hydrogen ratio and approximate PAH ring count versus aggregate collision diameter. Two distributions each are shown: shortly after the start of ignition (Figs. 10(a) and 10(c)), and about 20 CAD later (Figs. 10(b) and 10(d)). We observe that shortly after ignition, a noticeable fraction of PAH molecules within soot aggregates have increased in size significantly, whereas later in the formation phase, the composition of aggregates both in terms of C/H ratio and PAH ring count is much more similar to that of pyrene. These results suggest that condensation of pyrene is the main pathway of mass transfer from the gas phase to the particulate phase in this case.

## **5** Conclusions

We have developed a PDF-based engine simulation code which includes a detailed soot population balance solver called SWEEP, describing soot aggregate morphology and chemical composition. The engine code includes detailed chemical kinetics, a turbulent mixing sub-model, and accounts for inhomogeneities in composition and temperature as a consequence of convective heat losses.

Coupling the gas-phase to the particulate phase required the inclusion of soot precursor species, i.e. small Polycyclic Aromatic Hydrocarbons (PAHs), into a gas-phase kinetic mechanism for Primary Reference Fuels (PRFs). This lead to a detailed reaction scheme with 208 species, which has been validated against premixed fuel-rich flame data.

The new model, being computationally relatively cheap, enables the study of size distribution, morphology, and composition of soot aggregates formed over the course of several engine cycles.

We used the integrated code to simulate an n-heptane fuelled, fully premixed HCCI engine operated at an equivalence ratio of 1.93. We found that our simulated aggregate size distributions as well as their time evolution qualitatively agree with those obtained experimentally. It is also seen both in the experiment and in the simulation that, in the considered case of about 20% EGR, soot emissions in terms of mass stem mostly from recirculated aggregates, whereas in terms of number mostly from newly formed ones. The simulation also shows that the largest aggregates are recirculated in the trapped residual gases for possibly several cycles before being emitted from the engine.

Future work includes extending the combined model to operating modes using direct injection. The engine model on its own has already been applied to a number of direct injection cases [19, 21].

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