

# **Modelling particle shape and composition of soot particles in laminar premixed flames**

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## **Flame Simulation**

A previously developed bivariate surface-volume model has been extended to a new particle structure and composition model (PSCM). The PSCM is capable of providing information about the shape of a soot particle by approximately tracking its aggregate structure and holding size information of the primary particles, of which a soot particle is comprised. Information about the aggregate composition is provided by counting the number of carbon and hydrogen atoms per aggregate particle. Thus, the new model makes it possible to produce representative TEMs for soot particles in a flame at different heights above the burner, with only a small increase in the computational expense.

A number of premixed ethylene flames, for which experimental observations are available in the literature [1,3,4], were simulated using the ABF/MoMIC model [2]. The simulation of the flames resulted in the concentration profiles of the key species, soot particle number density and the soot volume fraction as a function of height above the burner. The computed and the experimentally observed soot volume fraction profile for one of the flames from reference [4], hereafter referred to as the DLR flames, were compared and a large disagreement between the two profiles was observed. The agreement between the experimental and computational results was improved by adjusting the rate of the surface reactions. A scaled rate constant, suggested by this simulation, was used to simulate the other DLR flames, and a good agreement was observed between the computed and experimental results. The techniques developed for the simulation of the DLR flames were used for other

reported flames [1,3], and a good agreement between the computed and experimentally observed soot volume fraction profiles was observed.

The PSDFs for all the flames were obtained using the PSCM implemented in a Monte-Carlo population balance solver as a post-processing step.

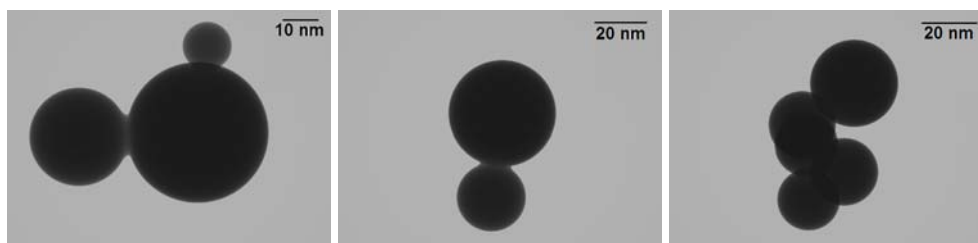
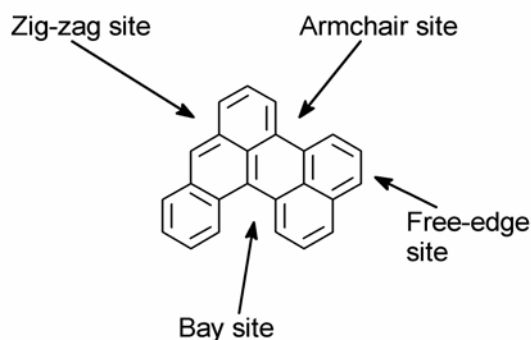


Fig 1. Computer generated TEM images for the top of HWC flame 5.

The primary particle size information can be used to generate representative TEM images (fig. 1) of the aggregate soot particles for all the ethylene flames. The images for the flames in reference 1, referred to as the HWC flames, are in line with the experimental observation that the average diameter of the (spherical) primary particles increases with decreasing flame temperature. These observations from the computed TEM images suggest that PSCM can form the basis for further analysis of coagulation and coalescence of primary particles, the effect on the interaction of the chemical species with soot particles and on the growth of soot particles. Since the aggregation of primary particles changes the surface structure of soot particles, there may be a change in the rate of surface growth through chemical reactions in the sterically hindered regions. There is a need to extend this model to account for the effect of alpha in the ABF model in order to achieve more predictive power. This may be achieved by incorporating the chemical composition of soot particles.

## Soot PAH modelling

Therefore a model which includes information about soot particle constituent PAHs is proposed. This model describes a soot particle by the number of different PAH site types, as well as their carbon and hydrogen atom counts. The model does not use alpha to account for the fraction of reactive sites on the soot particle. The hexagonal nature of PAH structures leads to the identification of four site types (fig. 2): Edges consist of two carbon atoms, zigzags consist of three, armchairs consist of four and bays consist of five.



**Fig 2. An example PAH structure showing site types.**

No PAH shape information is tracked per particle, that is the location of sites relative to other sites. The model merely tracks the number of each site type for every particle. Mechanisms for growth at these different sites are described in the literature, and include five-member ring addition to zigzags, ring growth with acetylene by the HACA mechanism at armchairs, ring growth at edges and five-member ring conversion at armchair and edge sites. The model proposed here includes these reactions and describes rules for updating reacting sites, as well as the neighbouring sites, for each process. These rules are based on the observation that each site must have two neighbouring sites, which change type when a reaction occurs. In general, for acetylene addition, neighbouring sites will gain one carbon atom and therefore move one site type up the chain: edge>zigzag>armchair>bay. This model generates a great deal of information about simulated soot particles and should provide some insight into soot particle PAH structure. It is intended to solve this model using a Monte-Carlo particle population balance solver (Sweep), as the complexity of the particle state space makes other methods computationally prohibitive.

## Soot Database

The Cambridge soot database is an effort to collect and provide a consistent source of experimental data and simulation results for a variety of premixed flames and shock-tubes. The present soot database is available at the following web link:

<http://como.cheng.cam.ac.uk/index.php?Page=Resources&Section=SootDatabase>

It is eventually intended to incorporate the data in this database into the PrIME database [5]. The PrIME data structure is currently being modified to include soot data for flames. This requires a systematic way of describing experimental results.

## References

- [1] A D Abid, N Heinz, E D Tolmachoff, D J Phares, and H Wang. Relation between Particle Size Distribution Function and Morphology of Soot Formed in Atmospheric-Pressure, Premixed Ethylene-Oxygen-Argon Flame. *5th US Combustion Meeting Organized by the Western States Section of the Combustion Institute and Hosted by the University of California at San Diego, March 25-28, 2007.*
- [2] J Appel, H Bockhorn, and M Frenklach. Kinetic modelling of soot formation with detailed chemistry and physics: Laminar premixed flames of C<sub>2</sub> hydrocarbons. *Combust. Flame*, 121:122–136, 2000.
- [3] B Öktem, M Tolocka, B Zhao, H Wang, and M Johnston. Chemical species associated with the early stage of soot growth in a laminar premixed ethylene-oxygen-argon flame. *Combust. Flame*, 142:364–373, 2005.
- [4] M Tsurikov, K Geigle, V Kruger, Y Schneider-Kuhnle, W Stricker, R Luckerath, R Hadeff, and M Algnier. Laser-based investigation of soot formation in laminar premixed flames at atmospheric and elevated pressures. *Combust. Sci. and Tech.*, 177:1835–1862, 2005.
- [5] M Frenklach. Transforming data into knowledge—Process Informatics for combustion chemistry, *Proceedings of the Combustion Institute*, 31(1):125-140, 2007.



# Advanced Soot Particle Modelling: Current and Future

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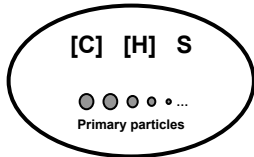


<http://como.cheng.cam.ac.uk>

An advanced soot particle model with an extended state space is introduced, which allows possible soot particle structures to be generated. This model is coupled to the ABF model to solve experimental systems. Future collaborative efforts are highlighted.

## 1 Particle Structure and Composition Model (PSCM)

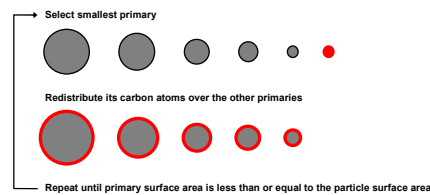
Soot particle state space: C atom count, H atom count, surface area, primary particle array.  
Primary particle state space: C atom count.



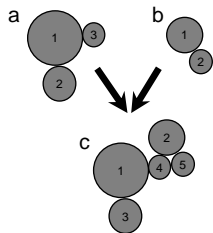
In addition to tracking size and shape (surface area) information, a list of spherical primary particles is stored for each aggregate particle. The primaries are tracked and updated during the simulation, but are not used to calculate aggregate properties.

**Inception**  
Newly incepted particles are assumed to be spherical, therefore have only one primary.

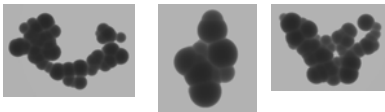
**Particle rounding by gas-particle interaction**



**Coagulation (a + b → c)**

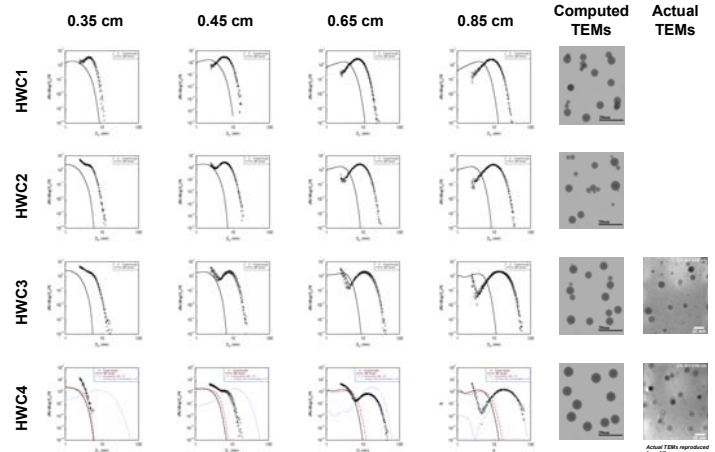


By randomising the list of primaries, TEM style images can be produced:

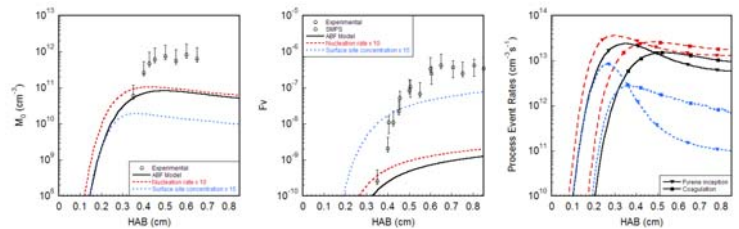


## 3 Premixed Laminar Flames

Simulations of the premixed laminar flames presented by Abid et al. [4] were carried out. The flame chemistry was solved using PREMIX with MoMIC for the soot. A Monte-Carlo solver implementing the PSCM was used to post-process the resultant flame profiles. The ABF soot model was used, and its limitations are shown by altering some of the accepted parameters.

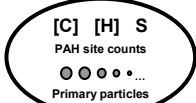


A closer look at HWC4:



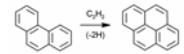
## 2 Soot Particle PAH Structure

A future refinement of the soot particle model is proposed, whereby particles are described in terms of their PAH structure. This requires a nomenclature to describe PAH structures, a set of reactions by which PAHs grow [3], and a set of rules to govern growth.

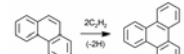


**PAH growth processes:**

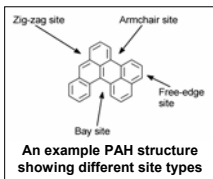
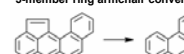
Armchair ring growth



Free-edge ring growth

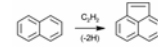


5-member ring armchair conversion

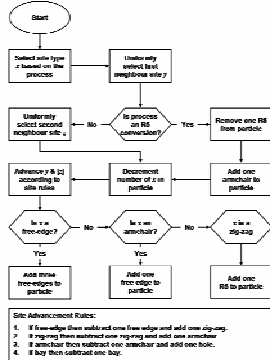
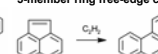


An example PAH structure showing different site types

5-member ring addition



5-member ring free-edge conversion

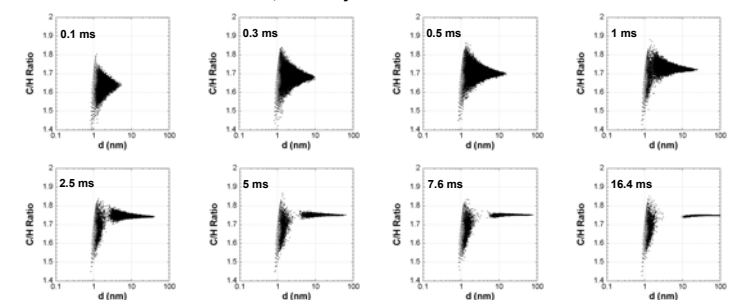


Site Advancement Rules:

- 1. If free-edge then add and one free edge and add one zig-zag.
- 2. If zig-zag then add and one zig-zag and add one armchair.
- 3. If armchair then subtract one armchair and add one bay.
- 4. If bay then subtract one bay.

## 4 Particle Composition

The PSCM allows composition data, such as C/H ratios, to be analysed. The following figures show C/H ratios for a plug-flow reactor [1,2]. The ABF soot model was used, assuming that pyrene addition added C/H in the ratio 1.6:1, and acetylene addition in the ratio 2:1.



## 5 The Soot Database & PrIme

**Aim:** To facilitate and automate

- Model validation
- Parameter estimation
- Model comparison

**Need:** Large database which is

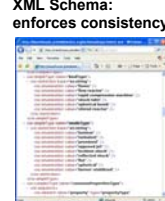
- Easy for computers to read
- Easy for humans to add to
- Consistently formatted for all data
- Available online

**Solution:** Use PrIme

- Agree keywords, ontology, and schema
- Add soot data to PrIme data warehouse

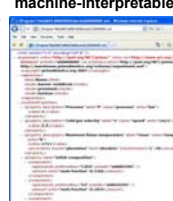
**XML Schema:**

enforces consistency



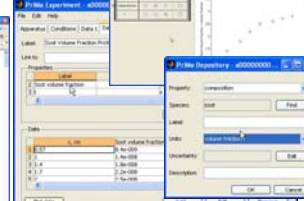
**XML Experiment data:**

machine-interpretable



**GUI:**

user-friendly



**Future: PrIme [5]**

Process Informatics Model: a collaborative, open source, effort led by M. Frenklach  
Available now, at <http://primekinetics.org>

## References

1. Kronholm and Howard, Analysis of soot surface growth pathways using published plug-flow reactor data with new particle size distribution measurements and published premixed flame data, *Proc. Combust. Inst.* 28, 2555-2561, 2000.
2. Celnik et al., Coupling a stochastic soot population balance to gas-phase chemistry using operator splitting, *Combust. Flame* 148, 158-176, 2007.
3. Frenklach et al., Migration mechanism of aromatic-edge growth, *Proc. Combust. Inst.* 30, 1389-1396, 2005.
4. Abid et al., Relation between particle size distribution function and morphology of soot formed in atmospheric-pressure, premixed ethylene-oxygen-argon flame, *5th US Combust. Meeting*, Paper F11, 2007.
5. Frenklach, Transforming data into knowledge - process informatics for combustion chemistry, *Proc. Combust. Inst.* 31, 127-140, 2007.