Detailed Kinetics Modeling of Soot Formation

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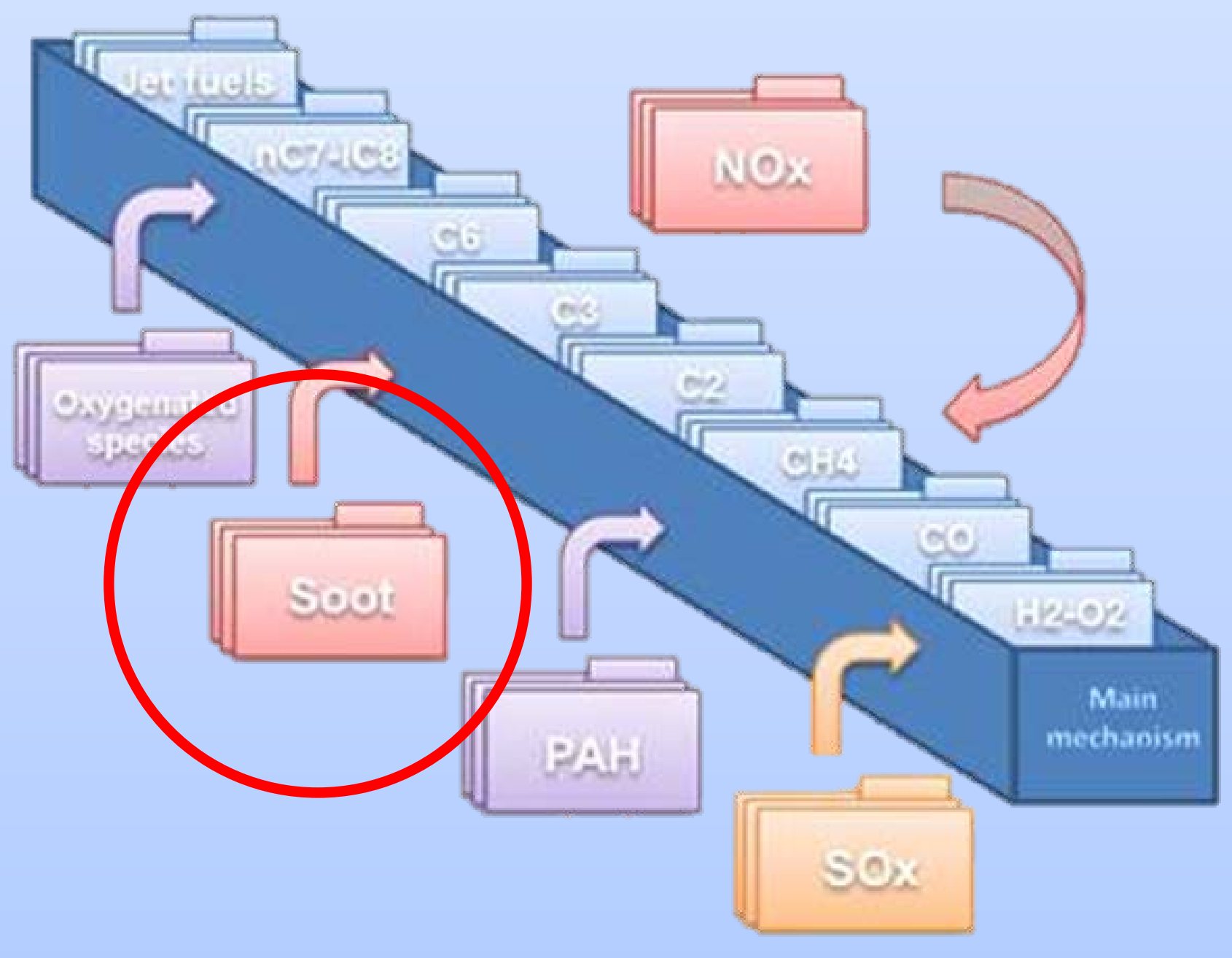
Motivation

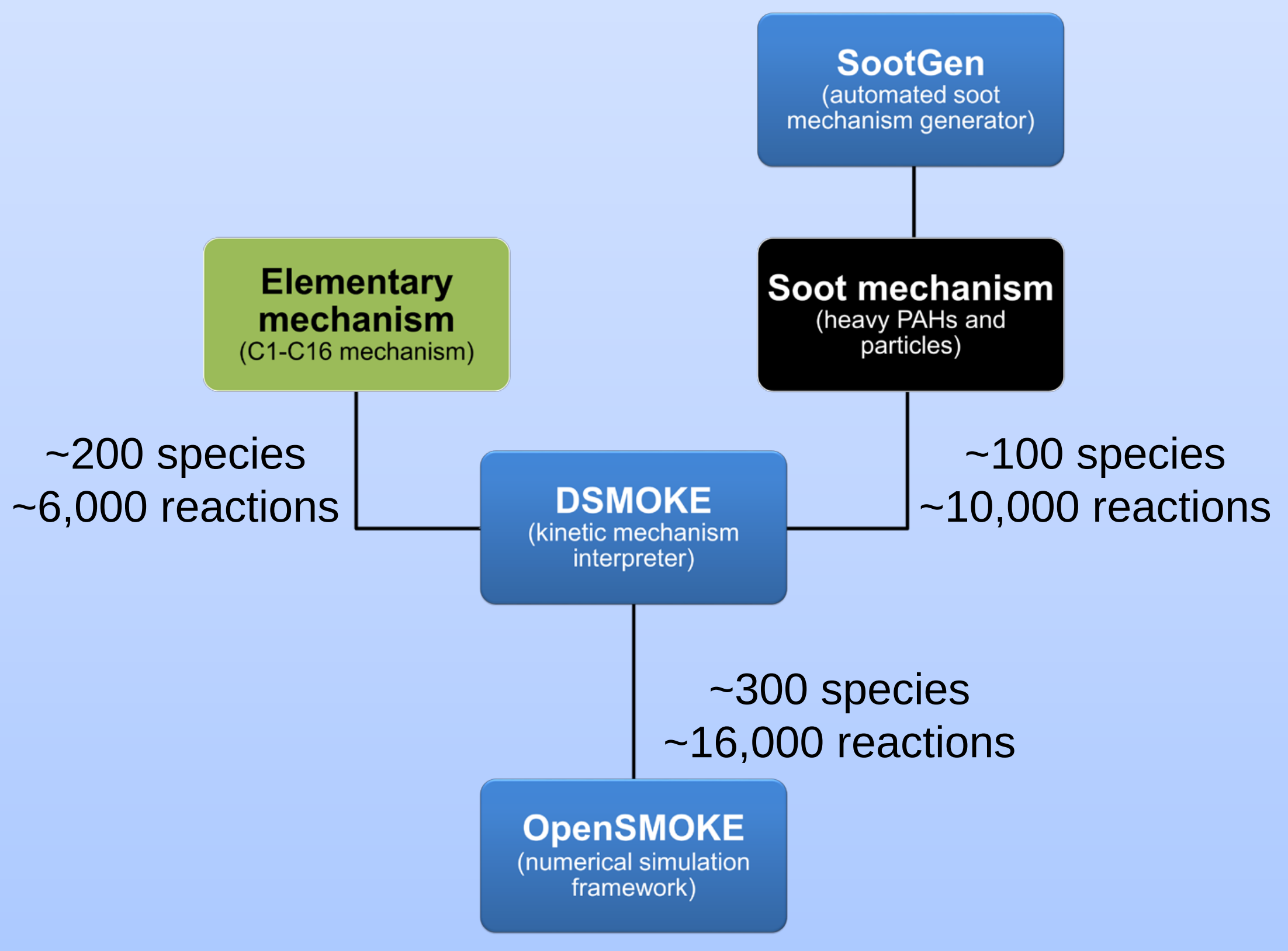
The present work addresses the study of the detailed kinetic modeling of soot formation process, with the aim to compare different number of classes of lumped pseudo-species (BIN).It is well known that soot carbonaceous particles cause adverse effects to health and environment and also reduce the combustion efficiency. The accuracy in predicting particle sizes and number density of soot particles is essential in addition to mass yield prediction. It is necessary to understand the chemical and physical pathways controlling the soot formation in combustion. The final goal of this activity is to investigate the appropriate models and simplifications which allow to predict carbonaceous particle formation from incepted to mature soot particles.

Kinetic Scheme and Numerical Method

Detailed kinetic model has proven to be a valuable tool to understand and describe the complex chemical systems. Specifically, it is able to explain chemical mechanisms for wide range operating conditions. Soot kinetic mechanism defines the particle kinetic in analogy with the gas-phase chemistry following the aerosol dynamic principal. Reactions involved in soot formation starting from large polycyclic aromatic hydrocarbon (PAH) and soot are generated by SootGen, an automated mechanism generator tool. Soot kinetic mechanism is the sub-module coupled with “C1-C16” mechanism following the hierarchy and modular of POLIMI kinetic schemes. Reactions from all modules are interpreted using DSMOKE into CHEMKIN format for executing numerical calculation using OpenSMOKE code [1].



The detailed kinetic mechanism is available at
http://creckmodeling.chem.polimi.it/



SootGen
(automated soot mechanism generator)

Elementary mechanism
(C1-C16 mechanism)

Soot mechanism
(heavy PAHs and particles)

~200 species
~6,000 reactions

~100 species
~10,000 reactions

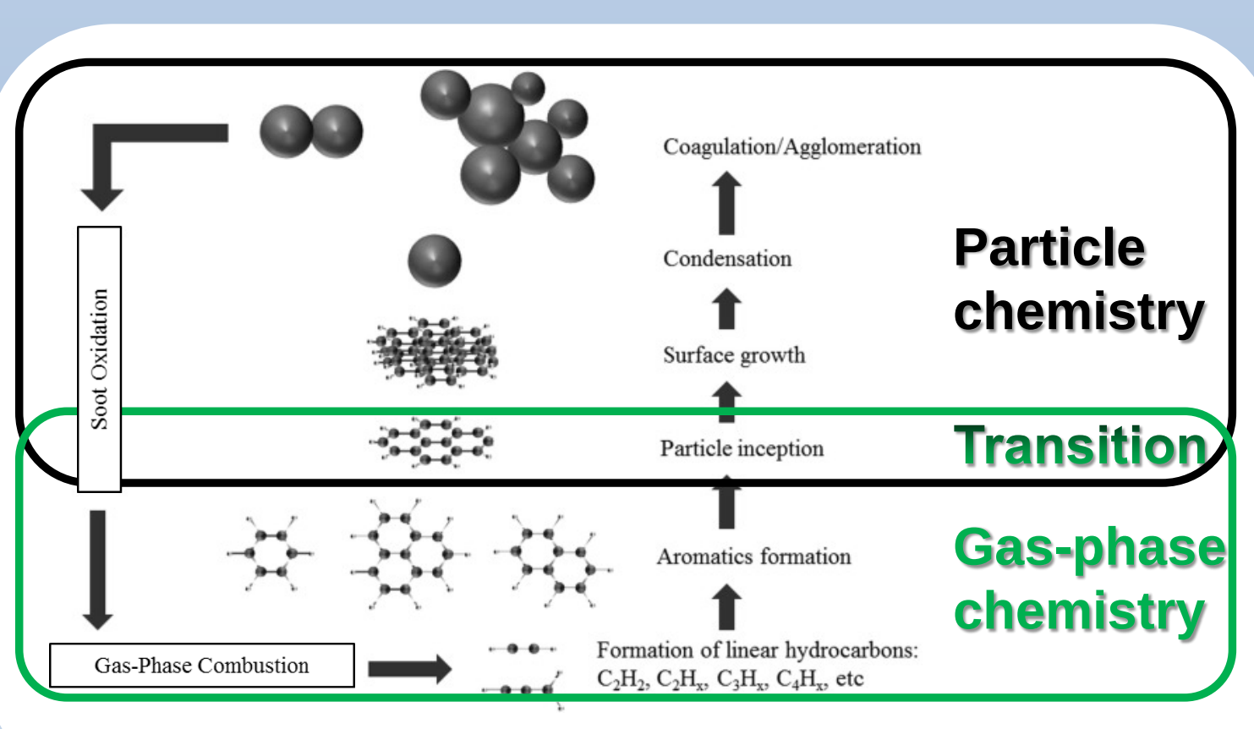
DSMOKE
(kinetic mechanism interpreter)

~300 species
~16,000 reactions

OpenSMOKE
(numerical simulation framework)

Soot Reaction Classes [2]

1. ***HACA mechanism***
   - ***1a. H-abstraction***
     $H + BIN_i \rightarrow H_2 + BIN_i•$
   - ***1b. Acetylene addition***
     $C_2H_2 + BIN_i• \rightarrow$ *products*
2. ***Soot inception (i,n < 5)***
   - $BIN_i• + BIN_n• \rightarrow$ *products*
   - $BIN_i + BIN_n• \rightarrow$ *products*
   - $BIN_i + BIN_n \rightarrow$ *products*
3. ***Surface growth***
   - ***3a. Small RR• addition***
     $RR• + BIN_i \rightarrow$ *products*
     $RR• + BIN_i• \rightarrow$ *products*
   - ***3b. PAH condensation***
     - ***i ≥ 5***
       $PAH• + BIN_i• \rightarrow$ *products*
       $PAH• + BIN_i \rightarrow$ *products*
       $PAH + BIN_i• \rightarrow$ *products*
     - ***i < 5 and n ≥ 5***
       $BIN_i• + BIN_n• \rightarrow$ *products*
       $BIN_i + BIN_n• \rightarrow$ *products*
       $BIN_i + BIN_n \rightarrow$ *products*
4. ***Dehydrogenation reactions***
   - ***4a. H-abstraction***
     $BIN_i• \rightarrow H• + BIN_i$
     $BIN_i \rightarrow H_2 + BIN_i$
   - ***4b. Demethylation*** (for H/C >0.3)
     $H• + BIN_i \rightarrow CH_3• +$ *products*
   - ***4c. C-H fission/recombination***
     $BIN_i \rightarrow H• + BIN_i•$
     $H• + BIN_i• \rightarrow BIN_i$
5. ***Particle coalescence and aggregation***
   - ***5a. Particle coalescence (5 ≤ i,n < 13)***
     $BIN_i + BIN_n \rightarrow$ *products*
   - ***5b. Particle coalescence on aggregates (5 ≤ i < 13 and n ≥ 13)***
     $BIN_i + BIN_n \rightarrow$ *products*
   - ***5c. Particle aggregation (i,n ≥ 13)***
     $BIN_i + BIN_n \rightarrow$ *products*
6. ***Oxidation***
   - ***6a. Oxidation with OH•***
     $OH• + BIN_i \rightarrow$ *products* $+ CH_2CO$
     $OH• + BIN_i \rightarrow$ *products* $+ CO + CH_3•$
     $OH• + BIN_i• \rightarrow$ *products* $+ CO + H•$
     $OH• + BIN_i \rightarrow$ *products* $+ HCO•$
   - ***6b. Oxidation with O•***
     $O• + BIN_i \rightarrow$ *products* $+ HCCO•$
     $O• + BIN_i \rightarrow$ *products* $+ CO$
   - ***6c. Oxidation with O_2***
     $O_2 + BIN_i• \rightarrow$ *products* $+ CO + HCO•$
     $O_2 + BIN_i• \rightarrow$ *products* $+ O• + CO$
     $O_2 + BIN_i \rightarrow$ *products* $+ 2CO$



Soot Formation Processes. Adapted from [3]

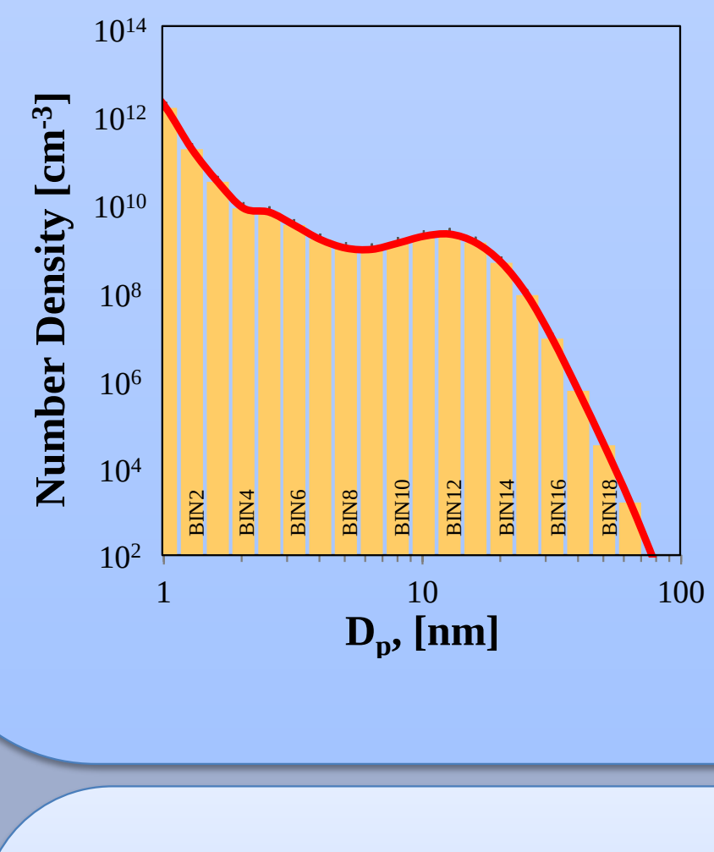
Pseudo-species

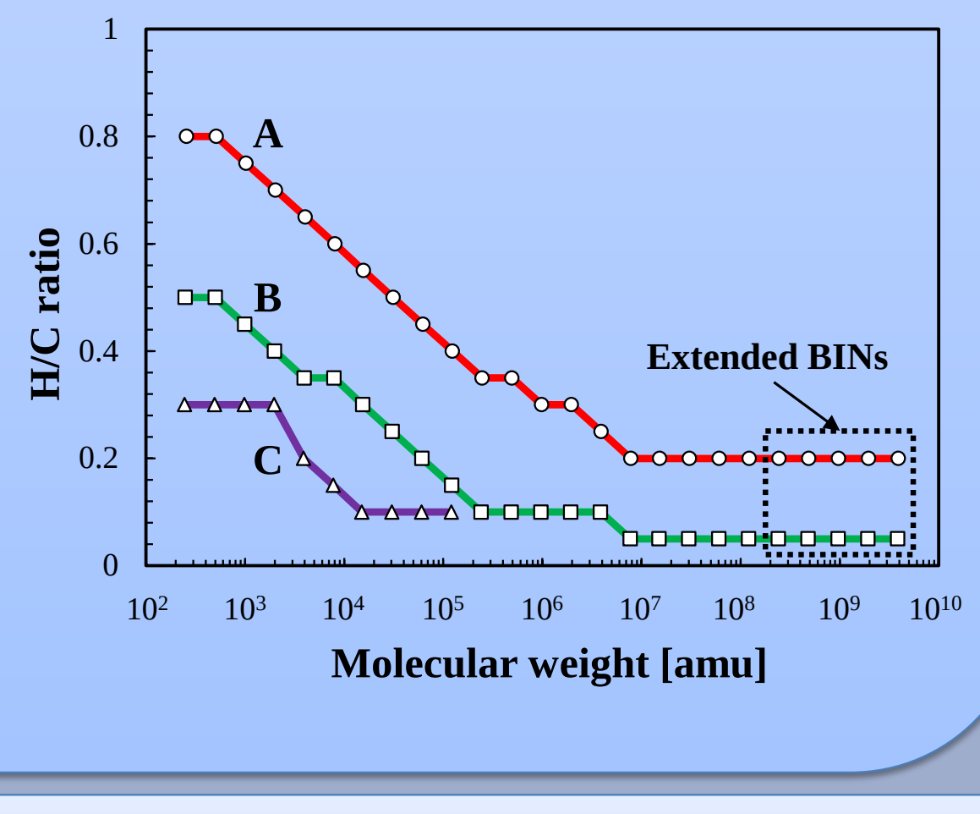
Discrete section method is adopted to discretize soot particle into each BIN with the assigned molecular mass representing each particle size.

Heavy PAHs						
				H/C ratio		
BIN_i	n_C	Mass [amu]	Diameter [nm]	A	B	C
BIN1	20	~ 250	0.81	0.8	0.5	0.3
BIN2	40	~ 500	1.02	0.8	0.5	0.3
BIN3	80	~ 1000	1.28	0.75	0.45	0.3
BIN4	160	~ 2000	1.62	0.7	0.4	0.3
Soot particles						
BIN5	320	~ 4×10^3	2.04	0.65	0.35	0.2
BIN6	640	~ 8×10^3	2.57	0.6	0.35	0.15
BIN7	1.25×10^3	~ 1.55×10^4	3.21	0.55	0.3	0.1
BIN8	2.5×10^3	~ 3×10^4	4.04	0.5	0.25	0.1
BIN9	5×10^3	~ 6×10^4	5.09	0.45	0.2	0.1
BIN10	1×10^4	~ 1.2×10^5	6.4	0.4	0.15	0.1
BIN11	2×10^4	~ 2.45×10^5	8.05	0.35	0.1	-
BIN12	4×10^4	~ 4.9×10^5	10.14	0.35	0.1	-

Aggregates						
					H/C ratio	
BIN_i	n_C	Mass [amu]	Collision diameter [nm]	Equiv. spherical diameter [nm]	A	B
BIN13	8×10^4	~ 9.7×10^5	13.27	12.74	0.3	0.1
BIN14	1.6×10^5	~ 1.95×10^6	19.5	16.05	0.3	0.1
BIN15	3.2×10^5	~ 3.9×10^6	28.63	20.20	0.25	0.1
BIN16	6.4×10^5	~ 7.8×10^6	41.98	25.42	0.2	0.05
BIN17	1.25×10^6	~ 1.51×10^7	60.89	31.78	0.2	0.05
BIN18	2.5×10^6	~ 3.02×10^7	89.19	40.04	0.2	0.05
BIN19	5×10^6	~ 6.02×10^7	131.53	50.44	0.2	0.05
BIN20	1×10^7	~ 1.21×10^8	193.32	63.55	0.2	0.05
BIN21	2×10^7	~ 2.41×10^8	282.8	80.07	0.2	0.05
BIN22	4×10^7	~ 4.82×10^8	414.18	100.88	0.2	0.05
BIN23	8×10^7	~ 9.64×10^8	608.73	127.11	0.2	0.05
BIN24	1.6×10^8	~ 1.93×10^9	894.67	160.14	0.2	0.05
BIN25	3.2×10^8	~ 3.86×10^9	1,314.92	201.77	0.2	0.05

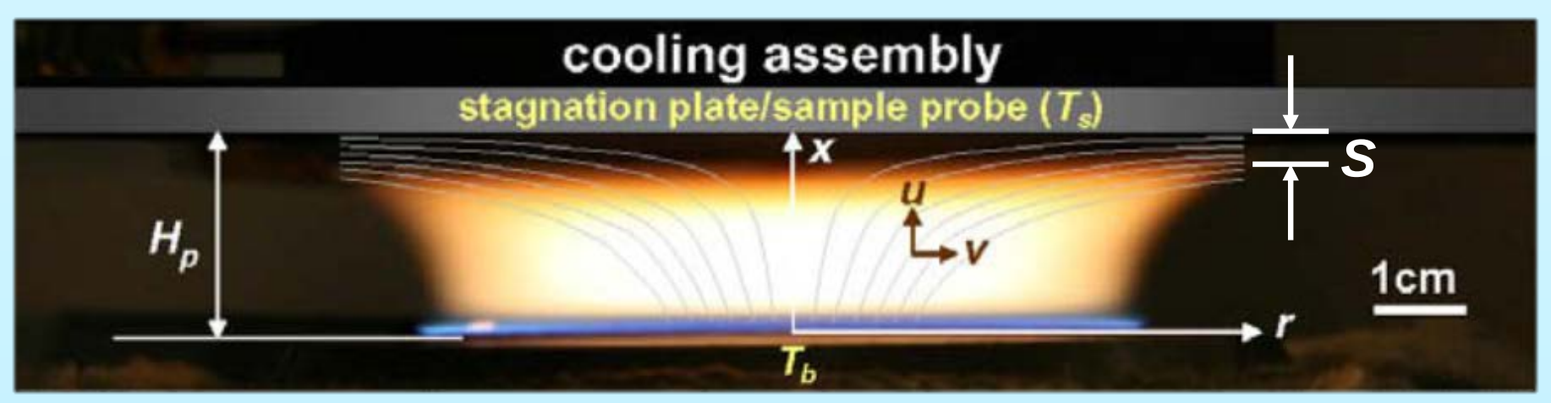
Extended





Comparison between Model Predictions and Experimental Data

Soot mechanism with 20-BIN proposed by [2] and the 25-BIN that presents in this work are used to predict burner-stabilized stagnation (BSS) flame of premixed ethylene-oxygen-argon [4]. The extension of BIN21 to BIN25 results from the mobility diameter of BIN20, the largest particle in 20-BIN mechanism, is not sufficient to predict aged soot particle. Therefore, 25-BIN mechanism is able to predict the mobility diameter up to 200 nm.



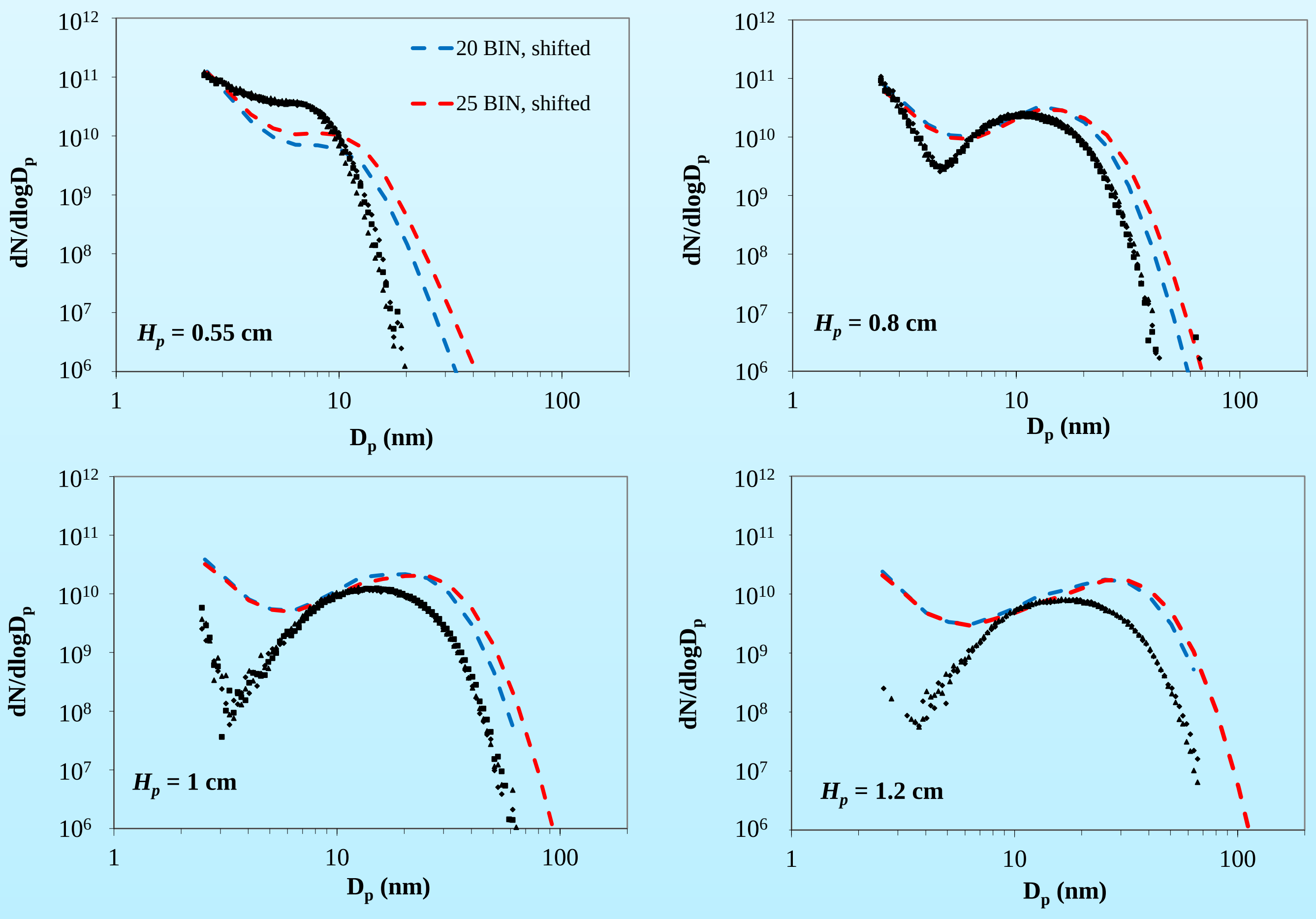
Burner-Stabilized Stagnation (BSS) Flame. Adapted from [6]

Flame details

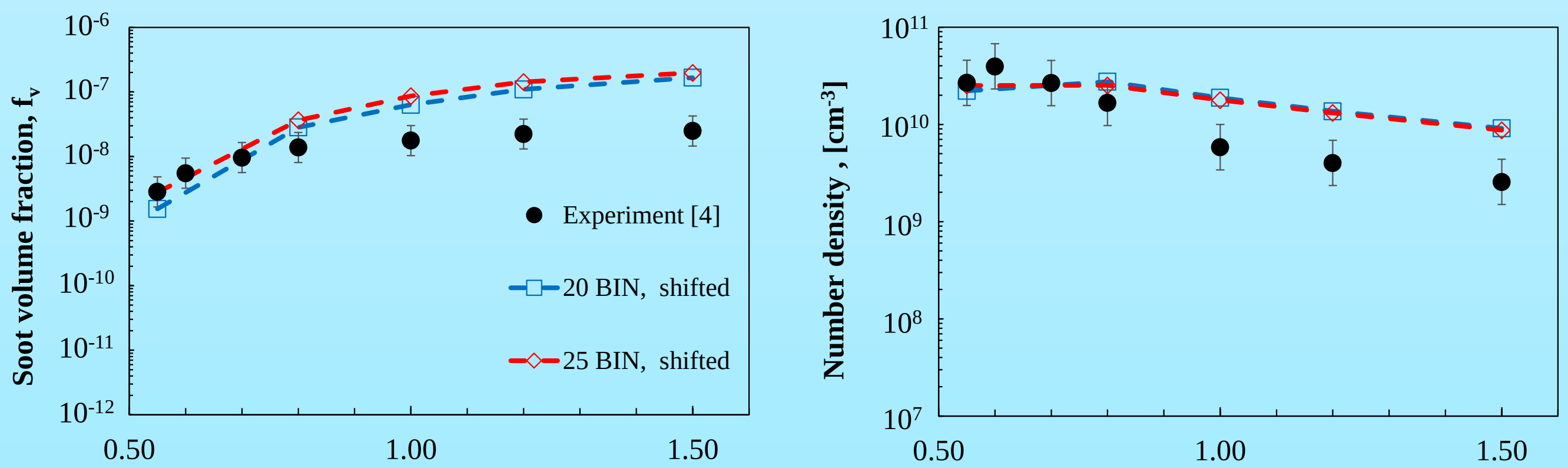
Fuel: 16.3% C_2H_4 - 23.7% O_2 - 60% Ar
Equivalent ratio: 2.07
V_{inlet}: 8 cm/s (at STP)
Pressure: 1 bar
Burner temperature, *T_b*: 473 K
Plate temperature, *T_s*: 555 K

The probe effect that deviates BSS flame from one dimensional problem. Correction by spatial shift, *S*, at the upstream of the probe calculated using regression correlation proposed by [5] allows the quasi-one dimensional model to be performed. Pressure drop across the orifice is assumed as 84 mmH_2O, calculated from dilution ratio of 700.

Burner-to-probe separation distances, H_p [mm]	Shifted distance, *S* [mm]
5.5	1.17
8	1.33
10	1.40
15	1.30



Particle Size Distribution Functions (PSDF) at each H_p



Soot Volume Fraction and Number Density

Conclusions

The developed soot kinetic mechanism with 25-BIN exhibits the continuation from the 20-BIN for larger particle size. The model prediction of this scheme shows the good agreement with the experimental data. However, it still overestimates soot formation especially for mature soot. The results express the improvement potential to further study the soot formation of mature soot. The modeling of mature soot or soot produced by other fuels should be considered in order to understand the soot formation specifically aggregates.

[1] Cuoci, A., et al. (2011). XXIV Meeting of the Italian Section of the Combustion Institute
[2] Saggese, C., et al. (2015). Combustion and Flame
[3] Yuen, A.C.Y., et al. (2016). International Journal of Heat and Mass Transfer
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