Modelling particulate formation in premixed flames using a CHEMKIN based approach

A. D'Anna
Dipartimento di Ingegneria Chimica
Università degli Studi di Napoli "Federico II", Italy

The problem

- The formation of combustion-generated particles is a central theme of many research activities in the field of combustion of fossil fuels

- In the past, it was motivated by fuel economy considerations

- Today it is driven by the adverse effects that combustion-formed particulate have on human health and on climate

The problem

- Most of the modeling work has concentrated on the prediction of the flame structure (concentration profiles of pyrolysis and oxidation products), and mean properties of particulates, including volume fractions, and mean particle sizes

- A few works have focused the attention on the prediction of Particle Size Distributions and on the testing of the sensitivity of PSDs with respect to operating parameters

Objective of the work

- to develop a detailed kinetic model of particulate formation

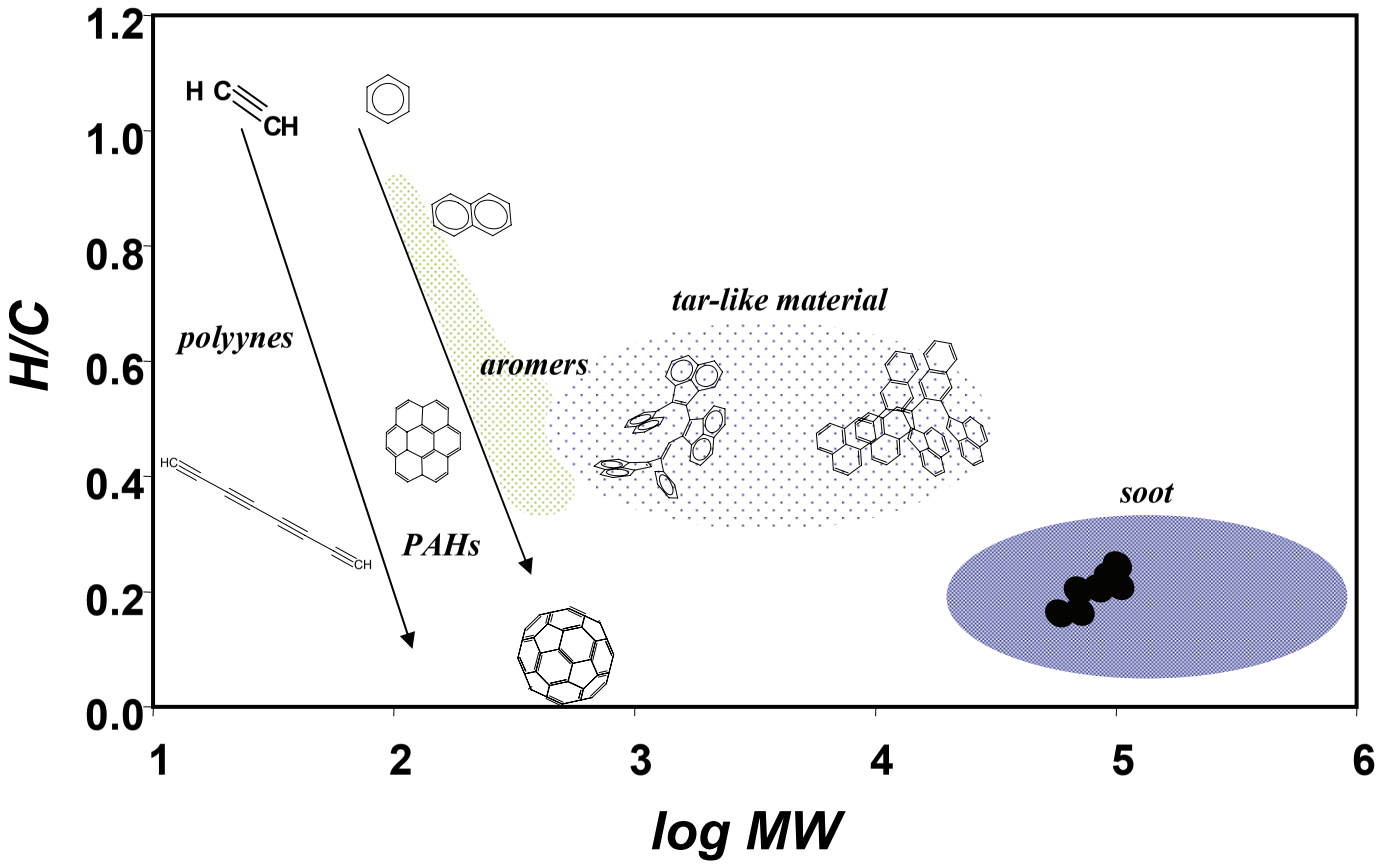
- to predict the concentration profiles of trace pyrolysis products involved in the process of particulate formation and the details of PSDs

Method

- the model is used in different flame conditions in order to:
  - ✓ test its capability to catch the main experimental evidences
  - ✓ test the sensitivity of particulate PSDs with respect to processes and parameters in particulate formation

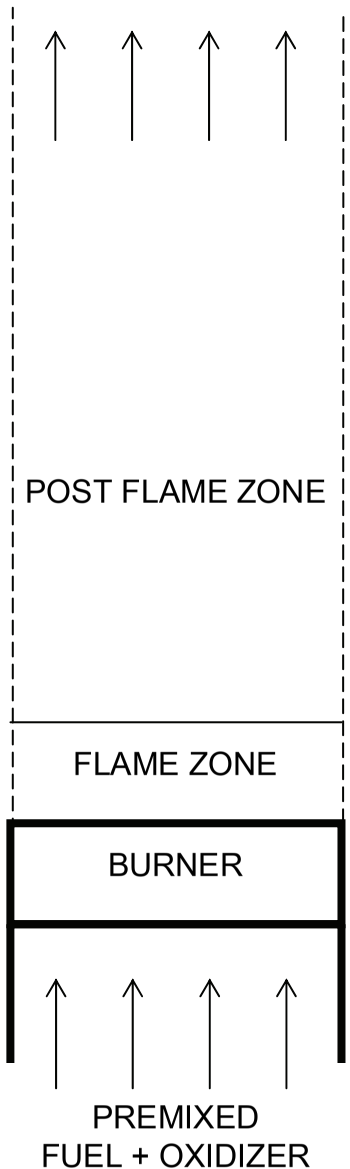
comparison of model predictions with experimental data have assisted in the model development

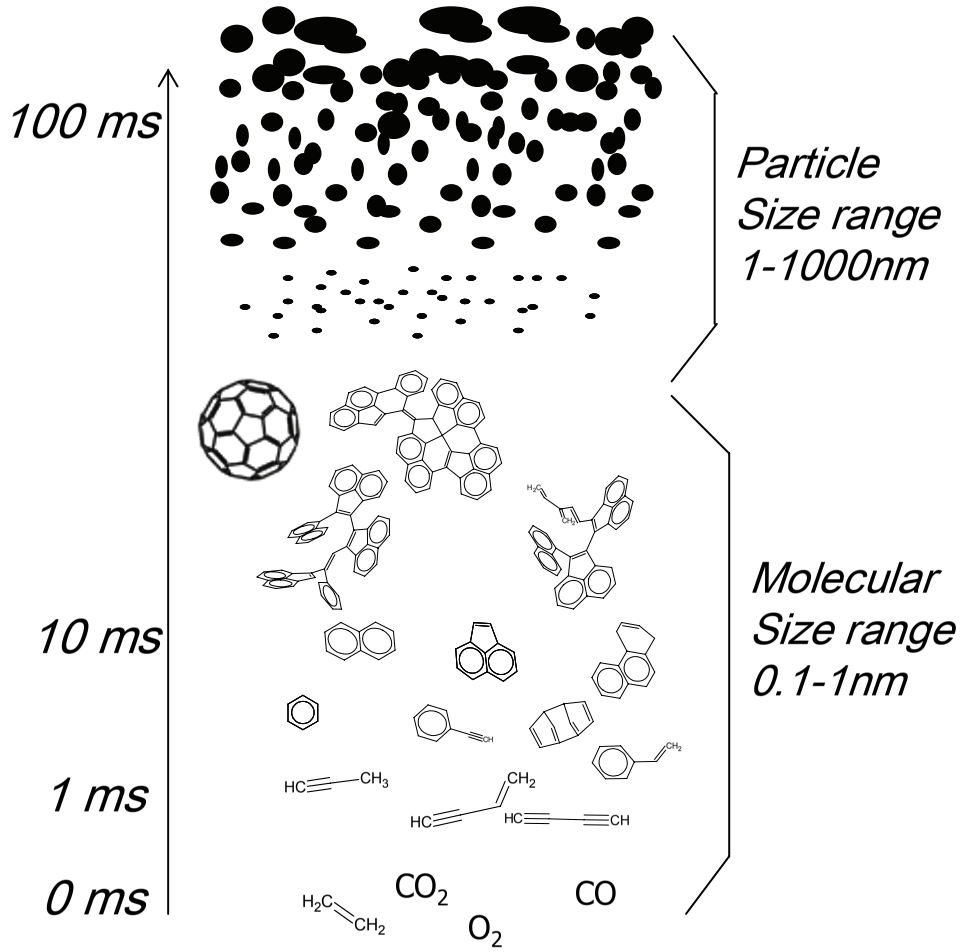
Chemical complexity



Adapted from: H.Gg.Wagner (1981)

Fuel-rich combustion

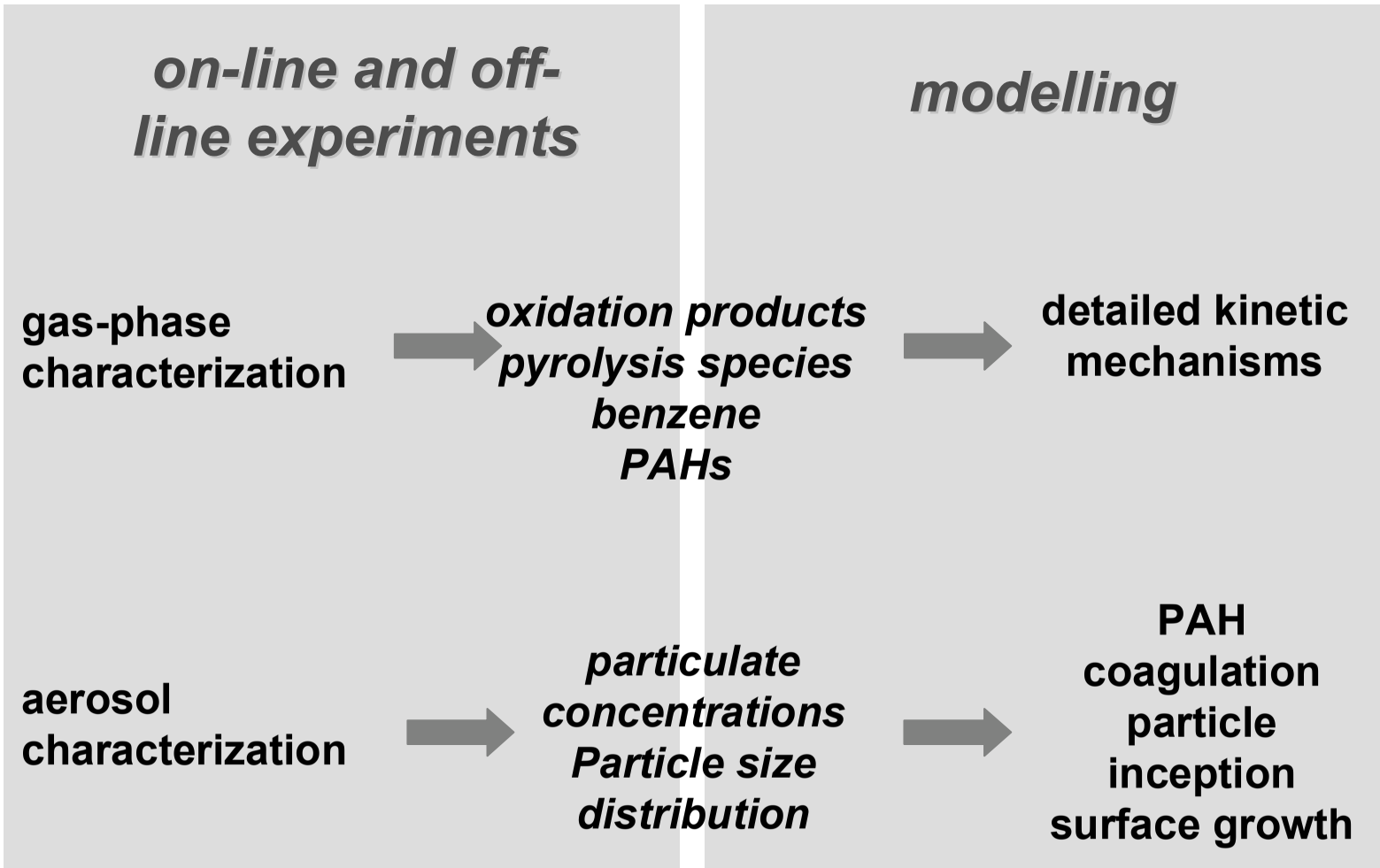




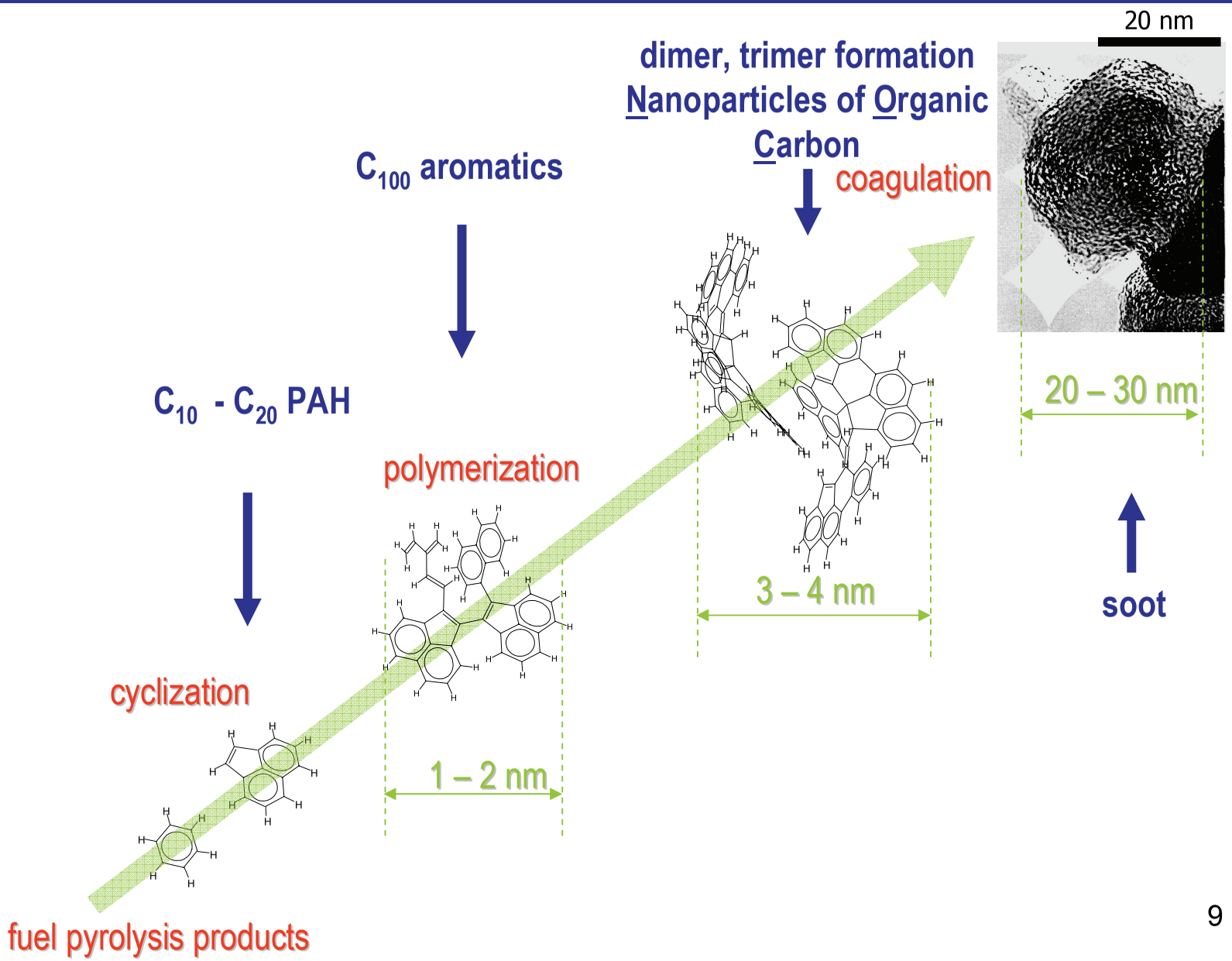
Adapted from:
H.Bockhorn (1994)

Modelling

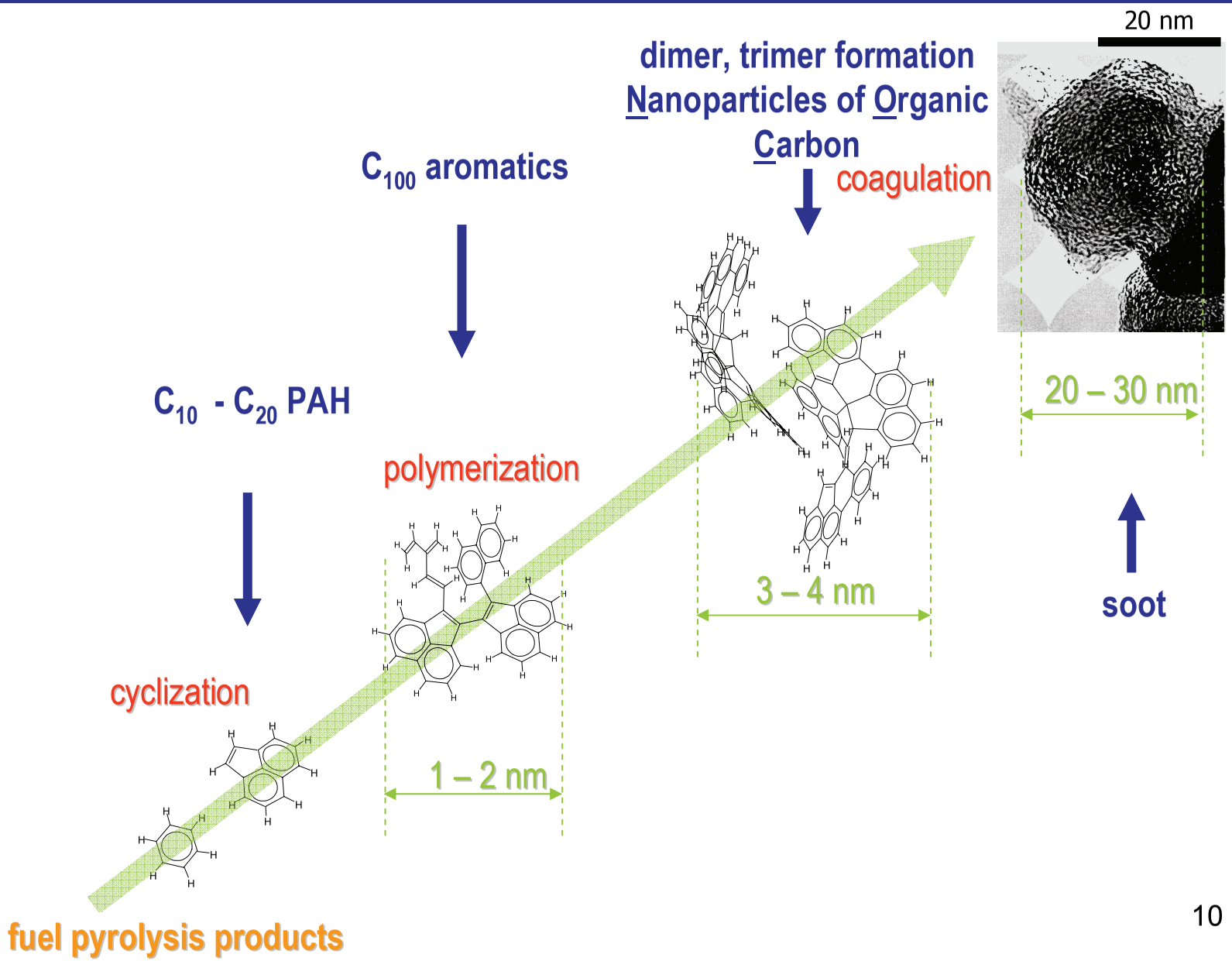
experimental results have oriented the development of fuel-rich combustion modelling



Modelling


20 nm
dimer, trimer formation
Nanoparticles of Organic Carbon
coagulation
C_{100} aromatics
C_{10} - C_{20} PAH
polymerization
cyclization
fuel pyrolysis products
1 – 2 nm
3 – 4 nm
20 – 30 nm
soot

Modelling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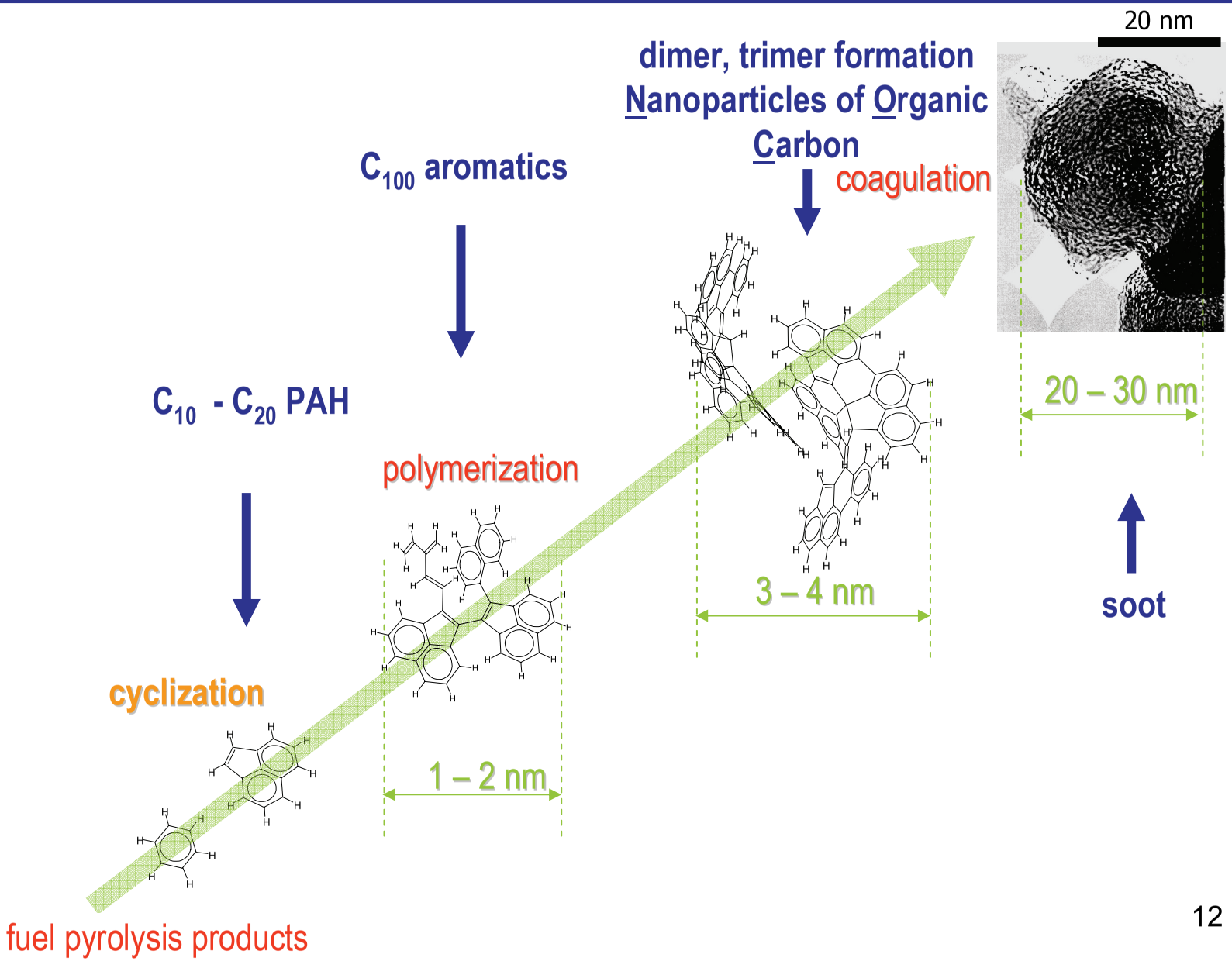
Fuel pyrolysis and oxidation

- GRI mechanism for C1 – C2 species
- Miller and Melius (1992) for C3 – C4 chemistry

the kinetic mechanism of C1 – C4 species includes 50 species and 250 elementary reactions

Modelling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Cyclization

Benzene formation

C_2H_2 addition to nC4H3 and nC4H5

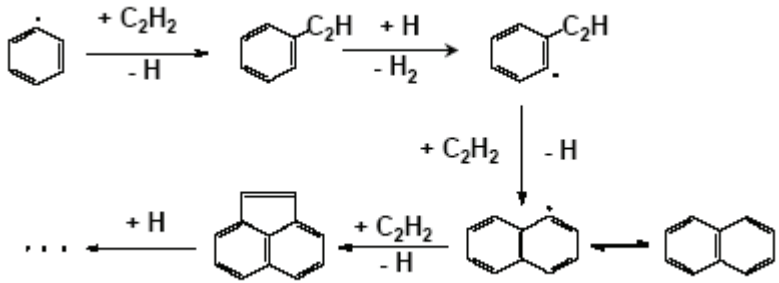
propargyl self-combination

propargyl and methyl-allenyl combination

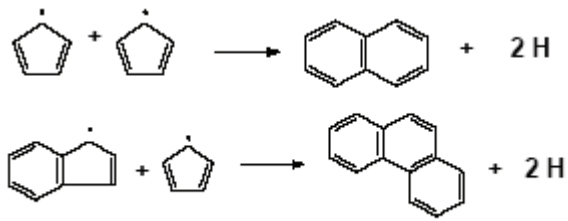
Cyclization

PAH formation

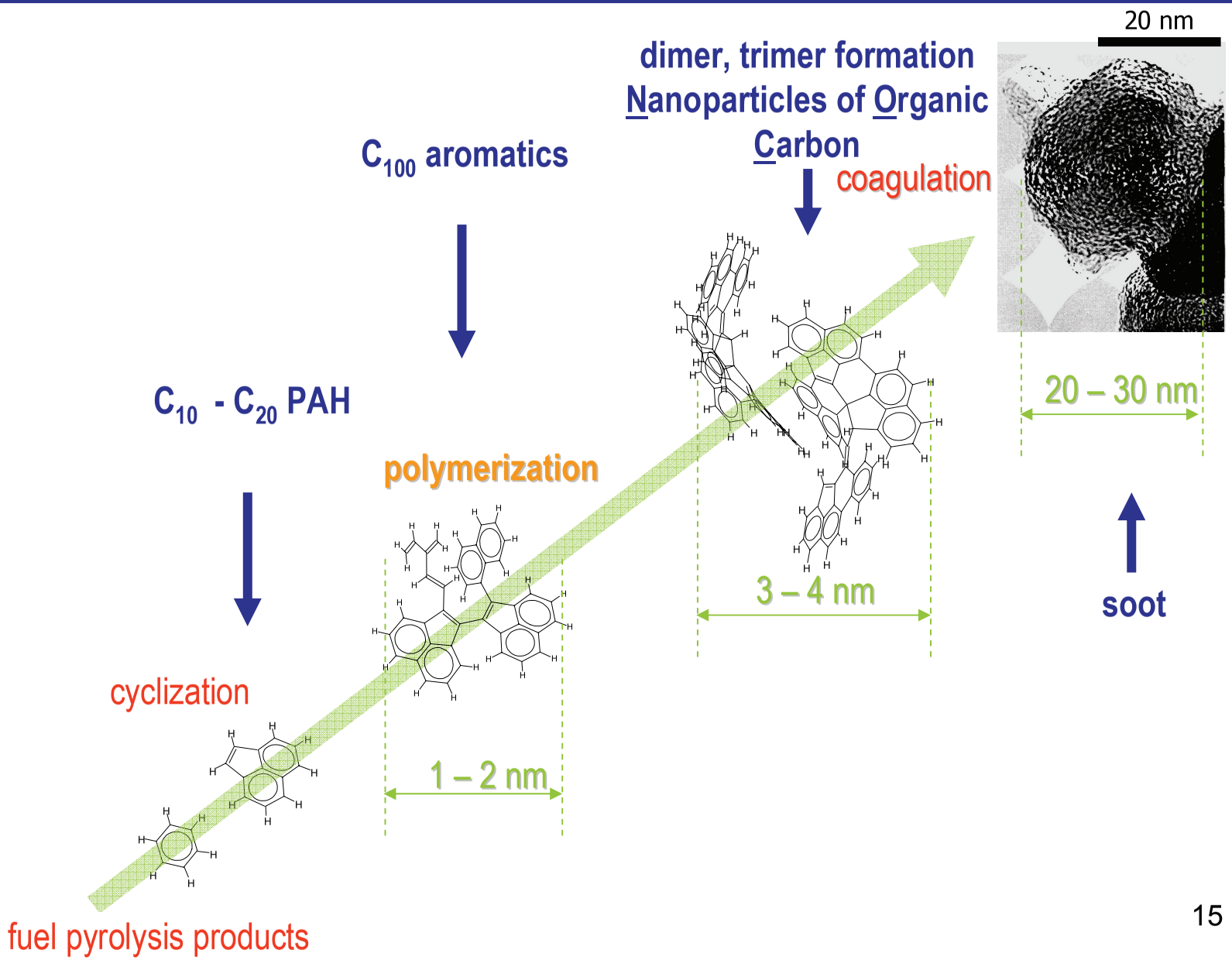
C_2H_2 addition to aromatic rings (HACA mechanism)



resonantly-stabilized free radical combination



Modelling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soot

Polymerization

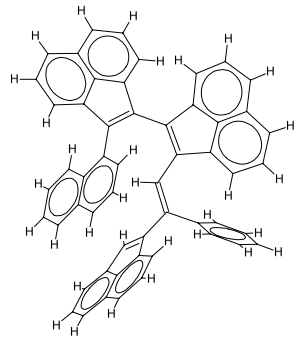
Aromatic growth

Radical-molecule addition reactions

$$Arm_i + H \Leftrightarrow Arm^*_i + H_2$$

$$Arm^*_i + Arm_j \Leftrightarrow Arm_{i+j} + H$$

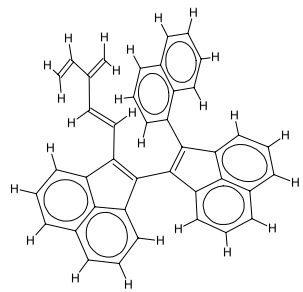
$$Arm^*_i + Arm^*_j \Leftrightarrow Arm_{i+j}$$



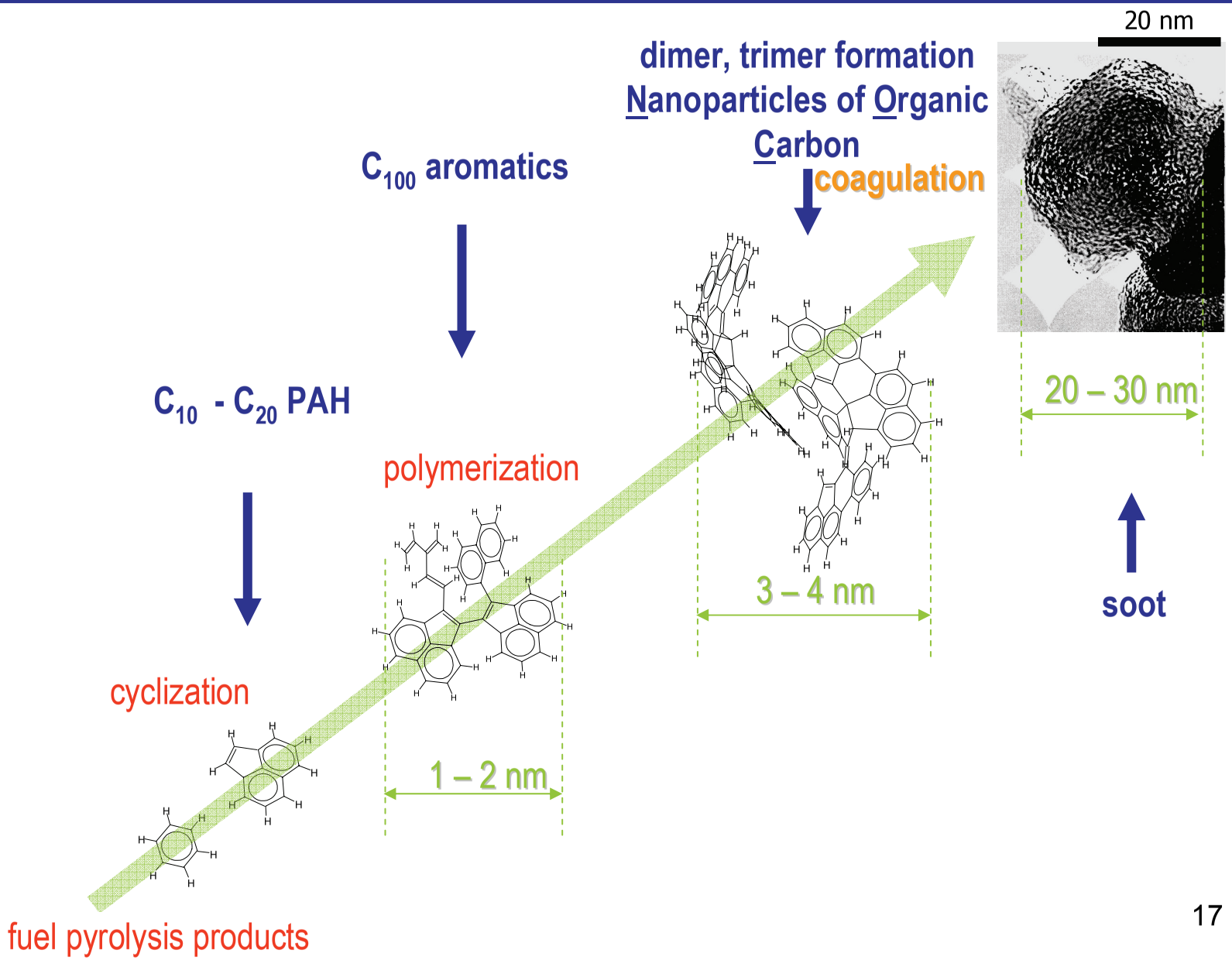
Surface growth

acetylene addition on activated molecule sites

$$Arm^*_i + C_2H_2 \Leftrightarrow Arm_i + H$$



Modelling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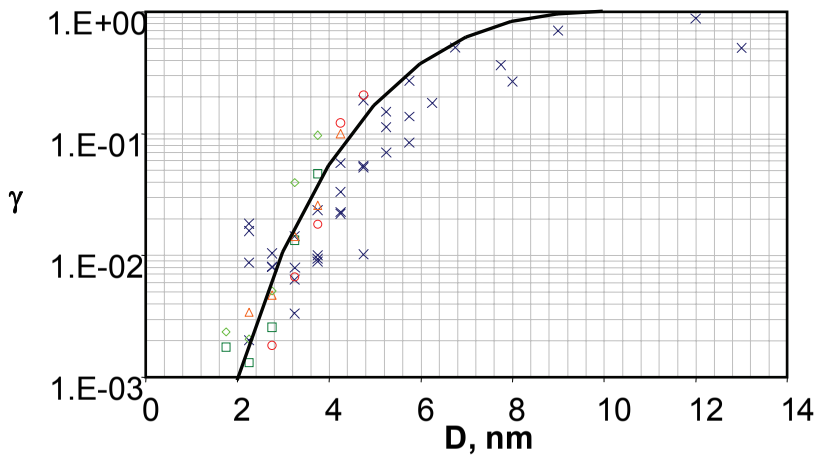
Coagulation

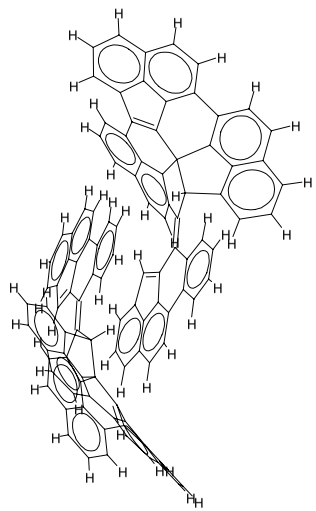
Collisional coagulation

van der Waals interactions between particles

$$Arm_i + Arm_j \Leftrightarrow Arm_{i+j}$$

Size-dependent coagulation efficiency





D'Alessio et al. *Proc. Combust Inst.* 30(2):2595-2603 (2004)

Numerical approach

Gas-phase chemistry modelling is performed by using the CHEMKIN software package

Transport and thermodynamic properties for the gas-phase species are from the Chemkin data base

A sectional approach is used to follow the transition from gas-phase species to nascent particles

A modified version of the gas phase *Interpreter* is used which allows for the handling of molecules with molecular masses sufficiently large to follow soot particle inception

Sectional approach

- Particle size distribution is defined by a range of sections, each containing a nominal hydrocarbonspecies in order of increasing atomic mass.
- There are two bins for each particle size, one for the stable species and the other for the radical.
- Twenty six sections ($\times$ 2) are used in a geometric series with a carbon number ratio of 2.2 between sections.
- The carbon number range is 20 - 7.2×10^9 which represents a particle size range of 1 – 500nm.

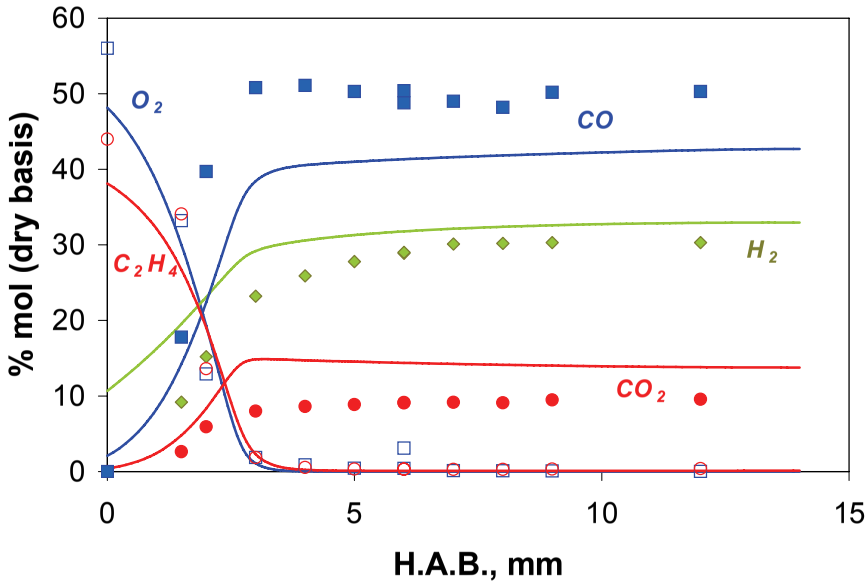
Sectional approach

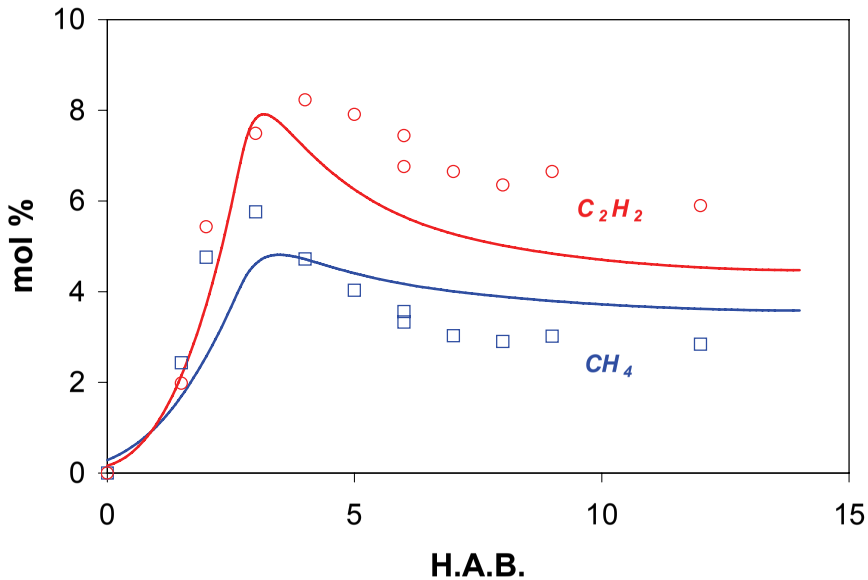
Section	C_xH_y	Mass (amu)	σ (nm)
1	$C_{20}H_{15}$	255	0.75
2	$C_{44}H_{34}$	562	0.98
3	$C_{96}H_{76}$	1240	1.27
4	$C_{213}H_{169}$	2725	1.65
5	$C_{468}H_{374}$	6002	2.15
6	$C_{1030}H_{824}$	13196	2.80
7	$C_{2267}H1_{813}$	29029	3.64
8	$C_{4988}H_{3990}$	63858	4.73
9	$C_{10975}H_{8779}$	140479	6.15
10	$C_{24145}H_{10315}$	309055	8.00
11	$C_{53119}H_{42495}$	679935	10.40
12	$C_{116863}H_{93490}$	1495858	13.52
13	$C_{257100}H_{205679}$	3290879	17.58
14	$C_{565620}H_{452495}$	7239935	22.86
15	$C_{1244364}H_{995490}$	15927858	29.72
16	$C_{2737601}H_{2190080}$	35041292	38.65
17	$C_{6022723}H_{4818177}$	77090853	50.25
18	$C_{13249990}H_{10599991}$	169599883	65.34
19	$C_{29149979}H_{23319982}$	373119730	84.96
20	$C_{64129954}H_{51303963}$	820863411	110.47
21	$C_{141085899}H_{112868719}$	1805899519	143.64
22	$C_{310388979}H_{248311183}$	3972978931	186.77
23	$C_{682855754}H_{546284603}$	8740553663	242.85
24	$C_{1502282660}H_{1201826127}$	19229218047	315.76
25	$C_{3305021853}H_{2644017481}$	42304279717	410.57
26	$C_{7271048076}H_{5816838460}$	93069415372	533.84

Sectional approach

- Diffusivities of the large sectional species are obtained from Stokes friction with Cunningham correction factors based on the Knudsen number.
- Thermophoretic flux is included for particles.
- Enthalpies of the sectional species are made the same per unit mass as that for naphthalene and thus sectional species reactions have no heat of reaction.

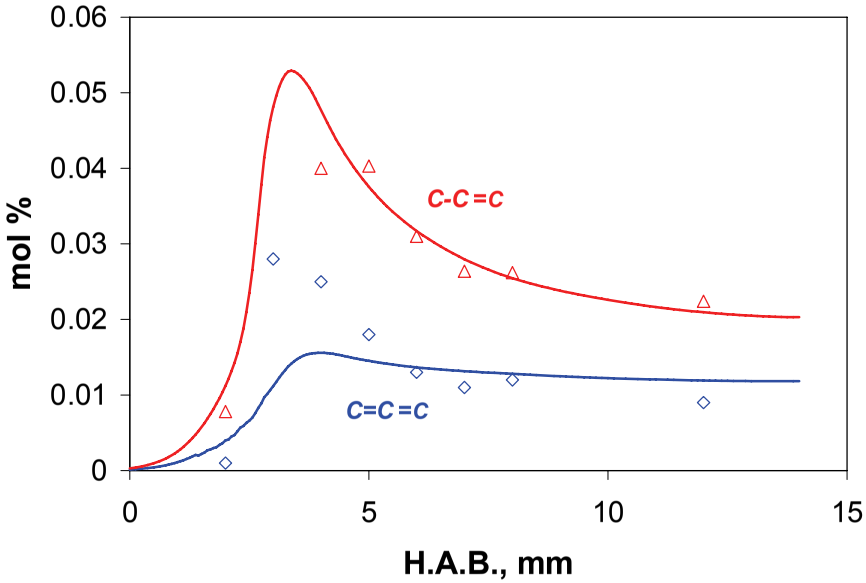
Premixed ethylene flame C/O=0.80

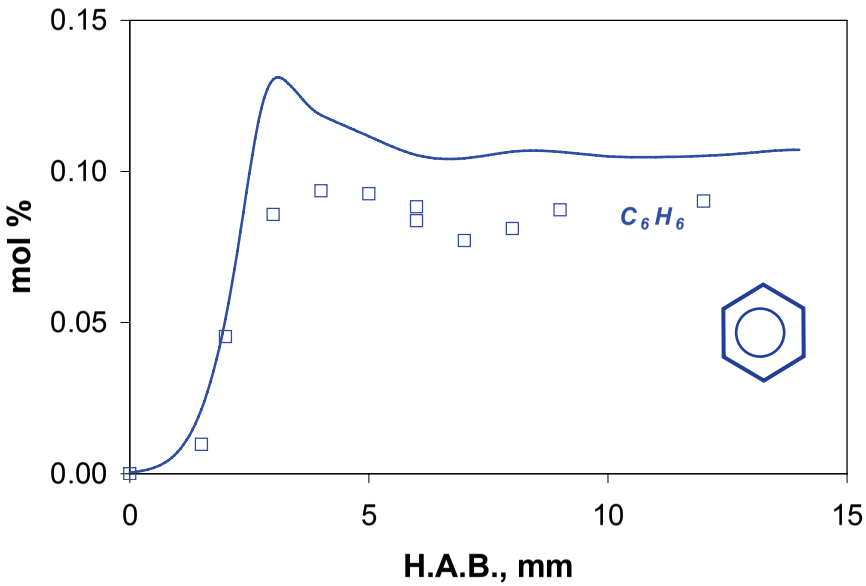




C2H4/O2 flame
C/O=0.80 v=4cm/s

Premixed ethylene flame C/O=0.80





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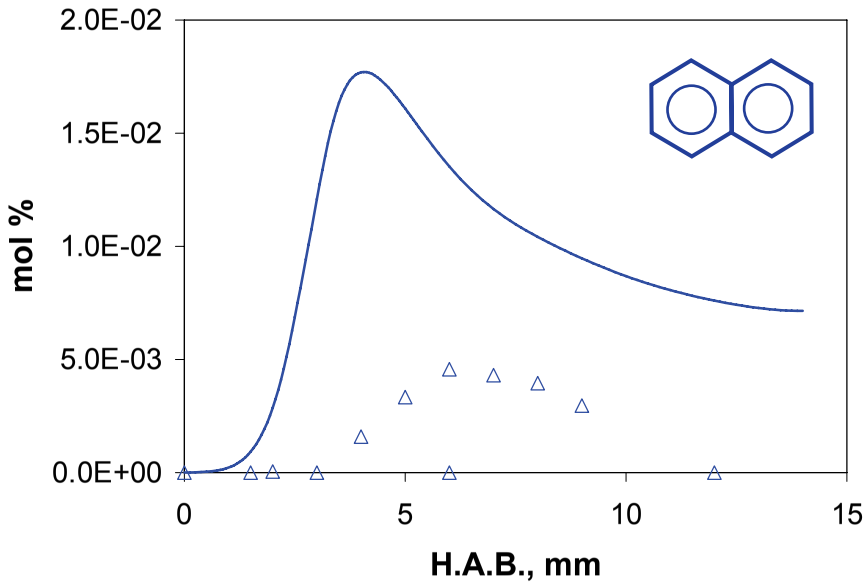

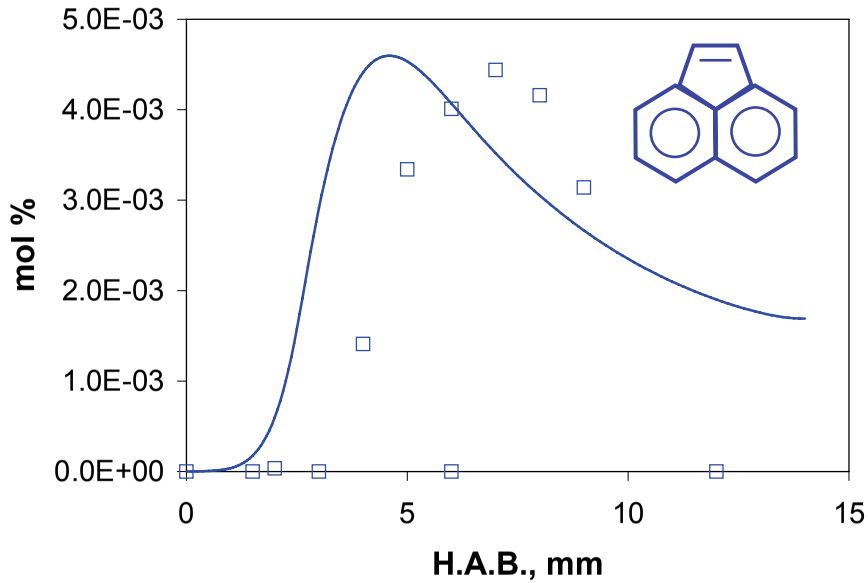

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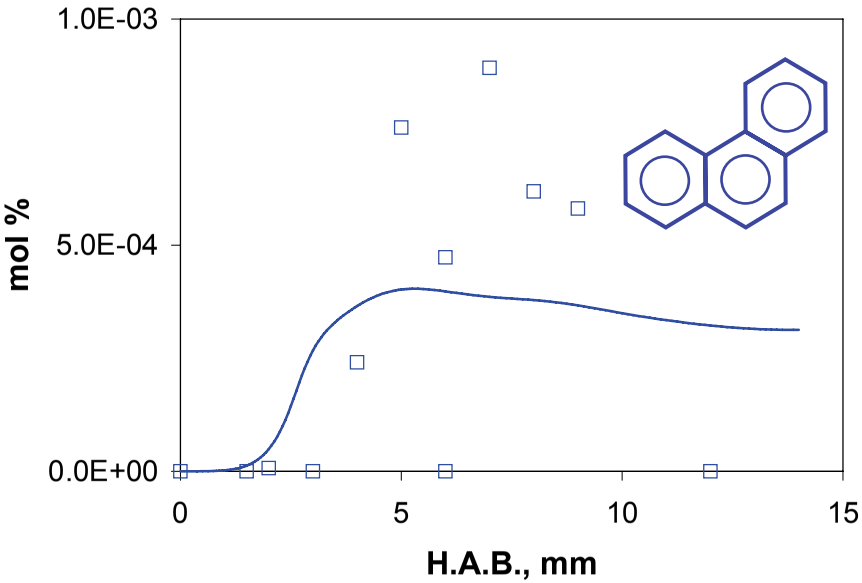

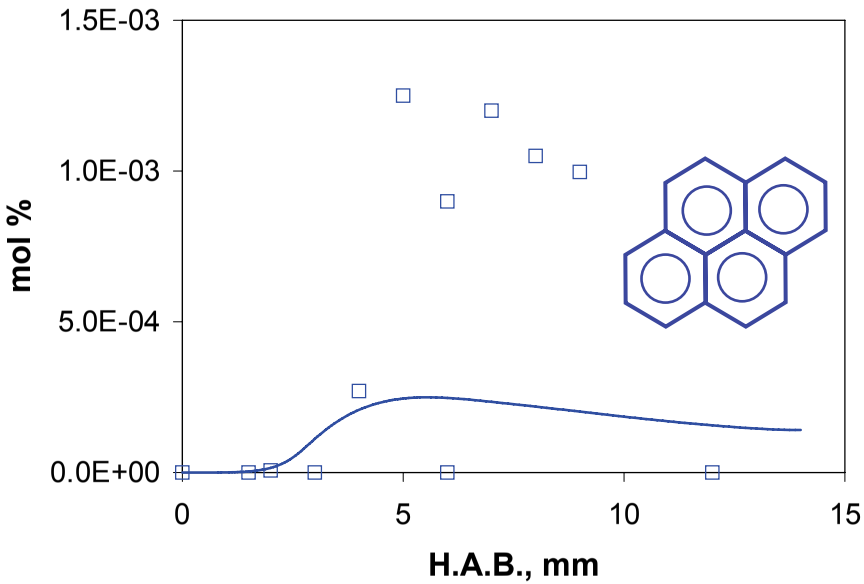

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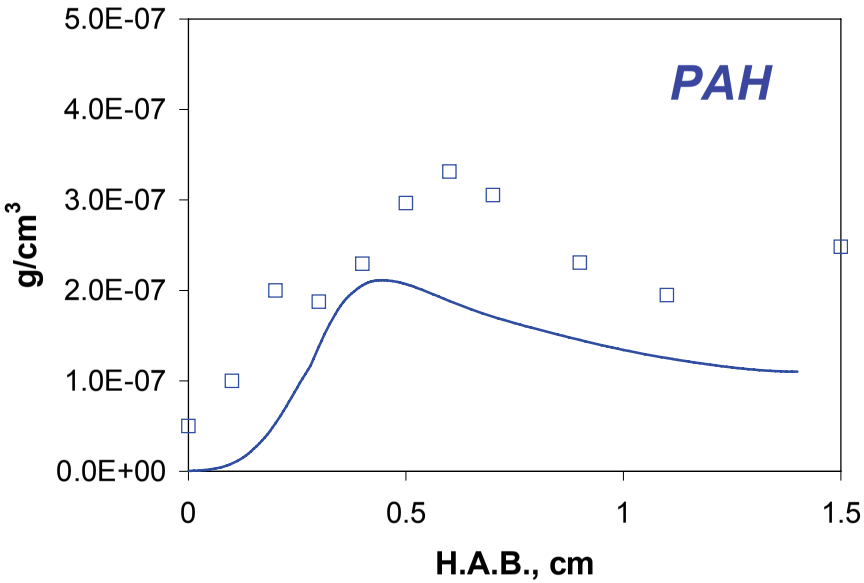

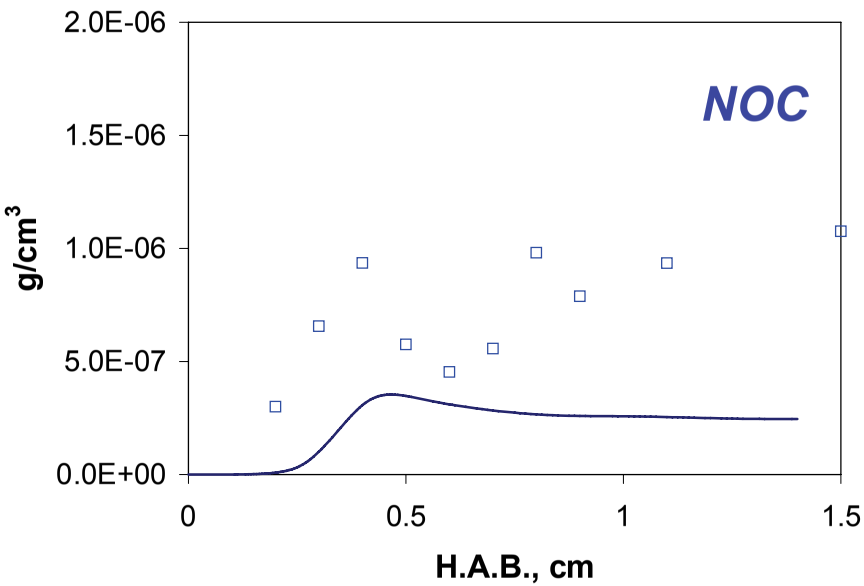

C2H4/O2 flame
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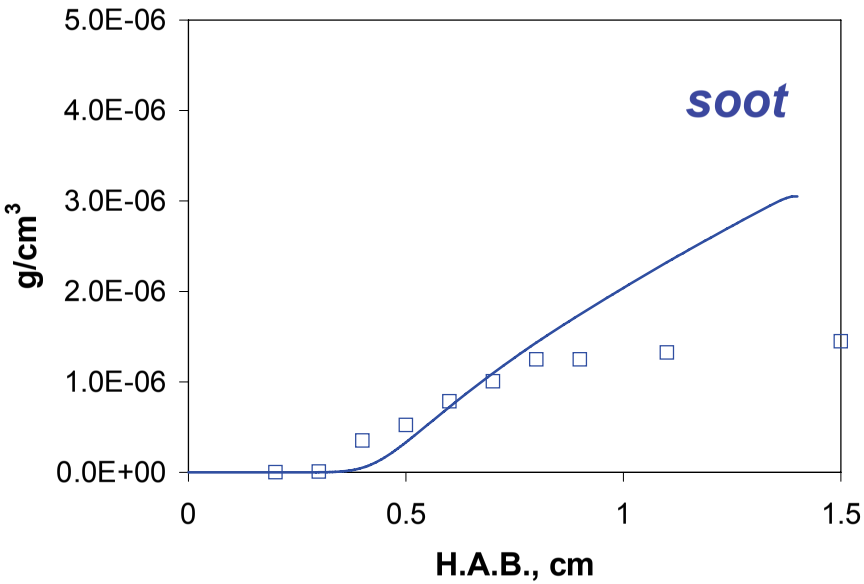
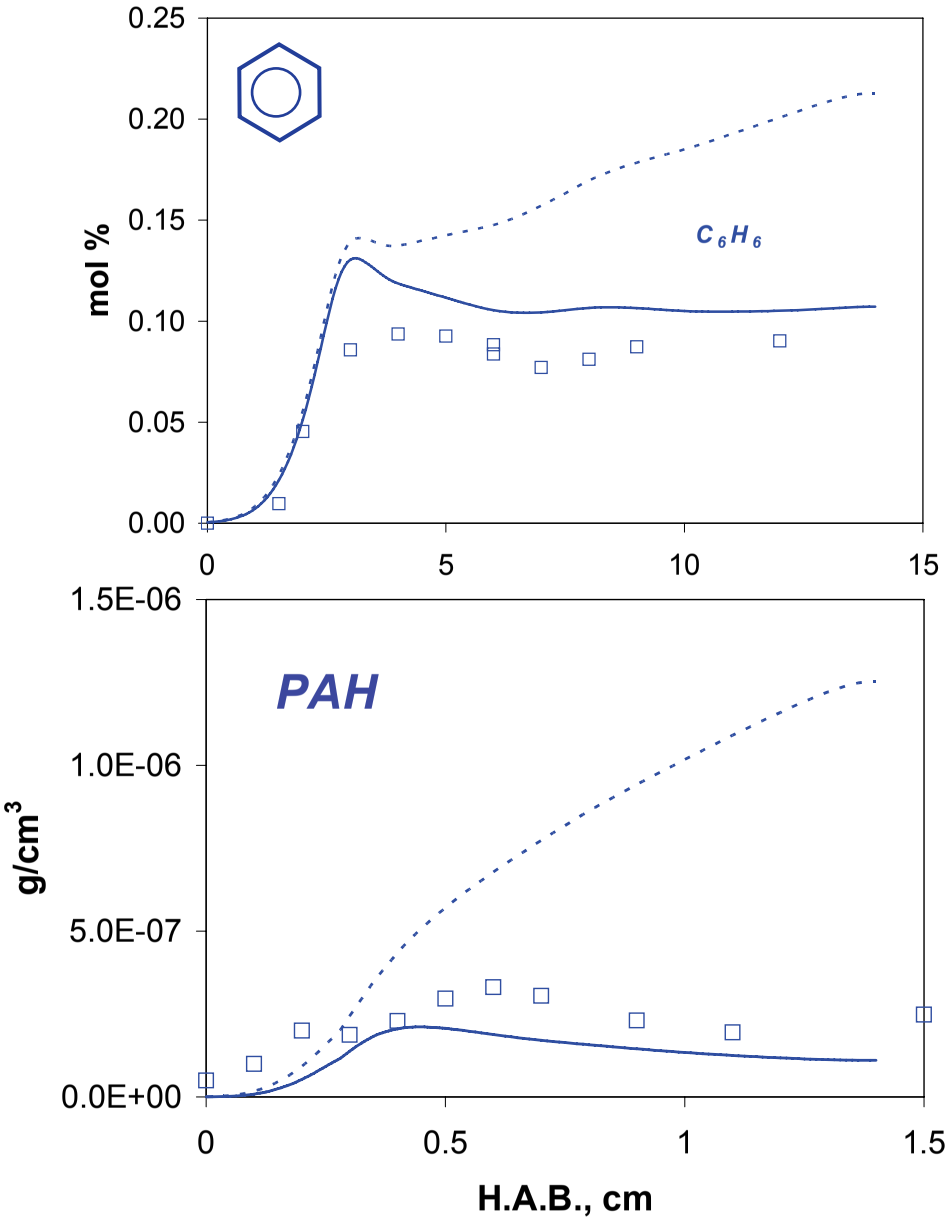
Premixed ethylene flame C/O=0.80



C2H4/O2 flame
C/O=0.80 v=4cm/s

Premixed ethylene flame C/O=0.80 (w/o soot)



C2H4/O2 flame
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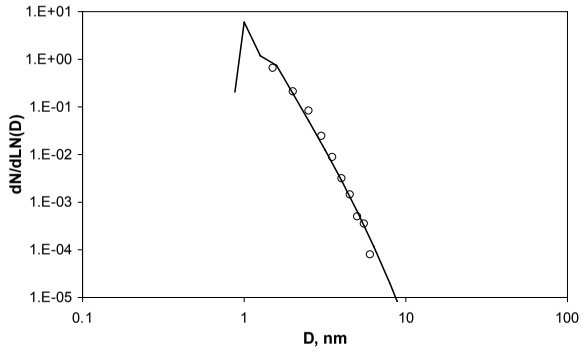
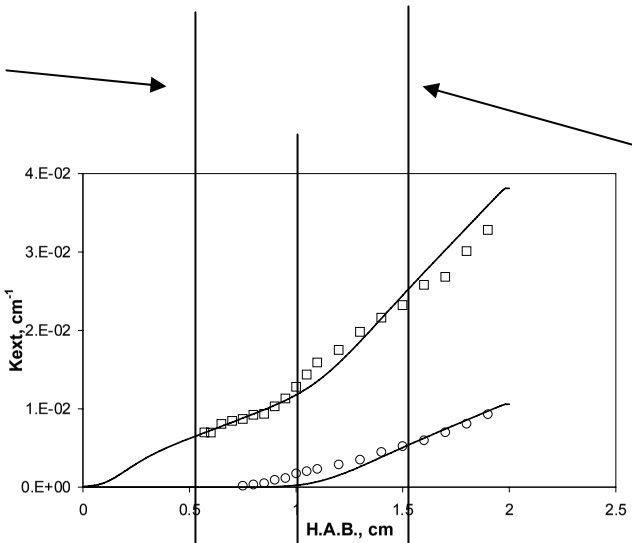
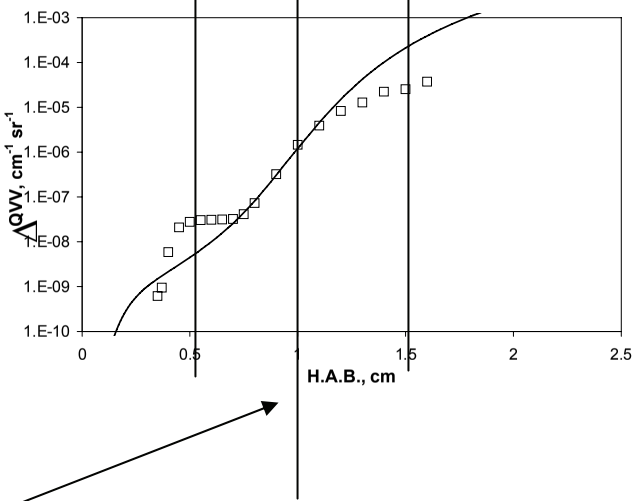
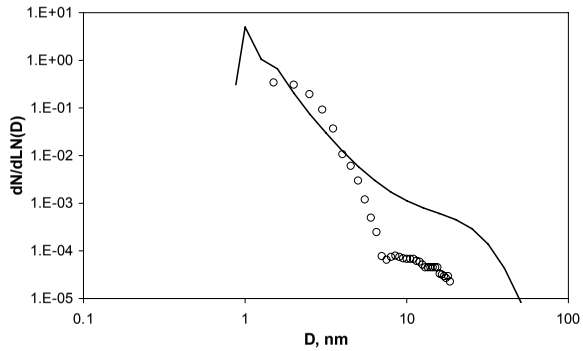
Premixed ethylene flame C/O=0.77

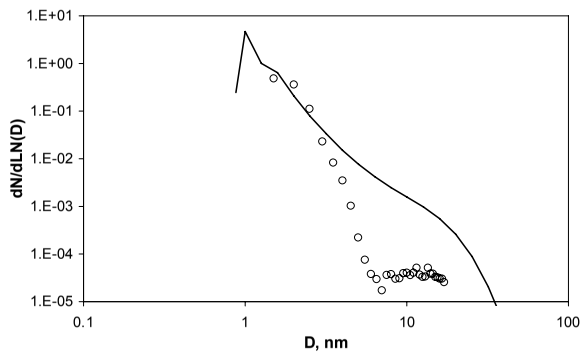






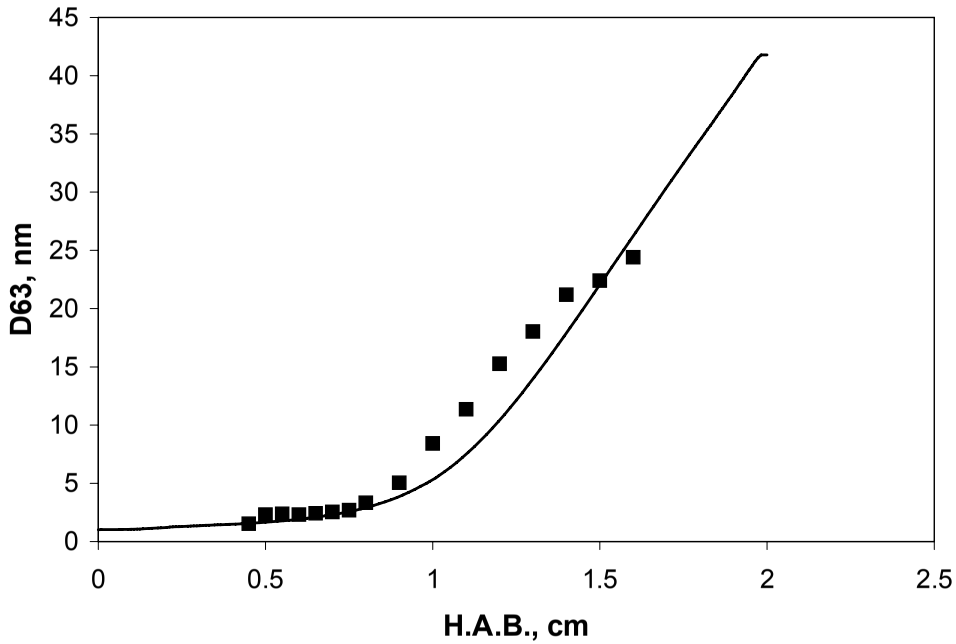


C2H4/air flame
C/O=0.77 v=10cm/s

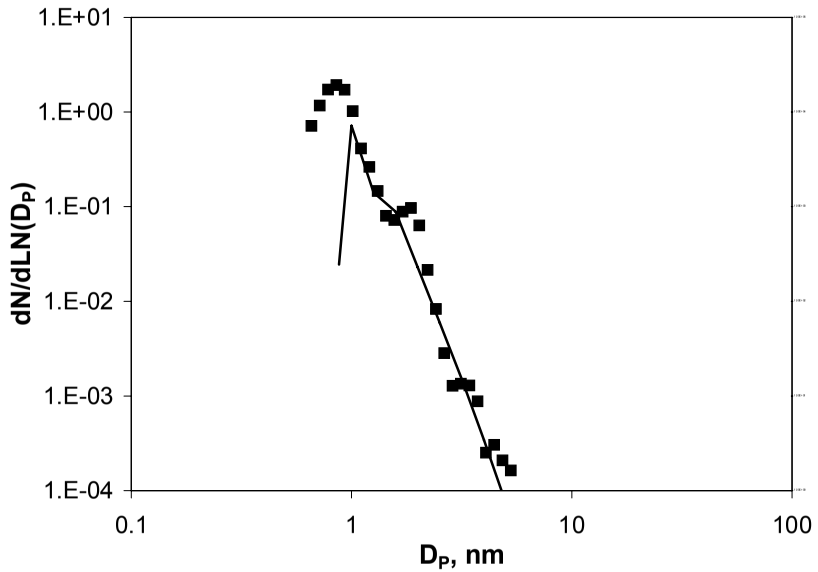


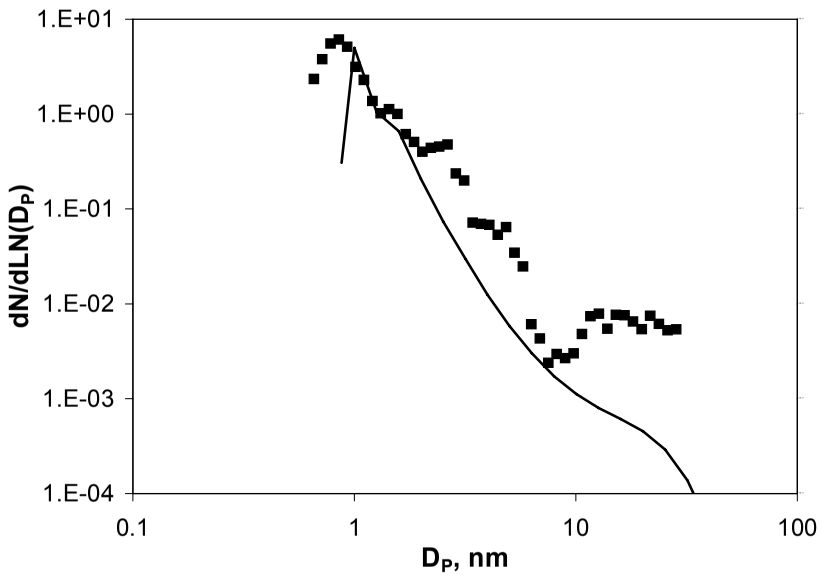
Premixed ethylene flame C/O=0.77

C2H4 flame
C/O=0.77 v=10cm/s



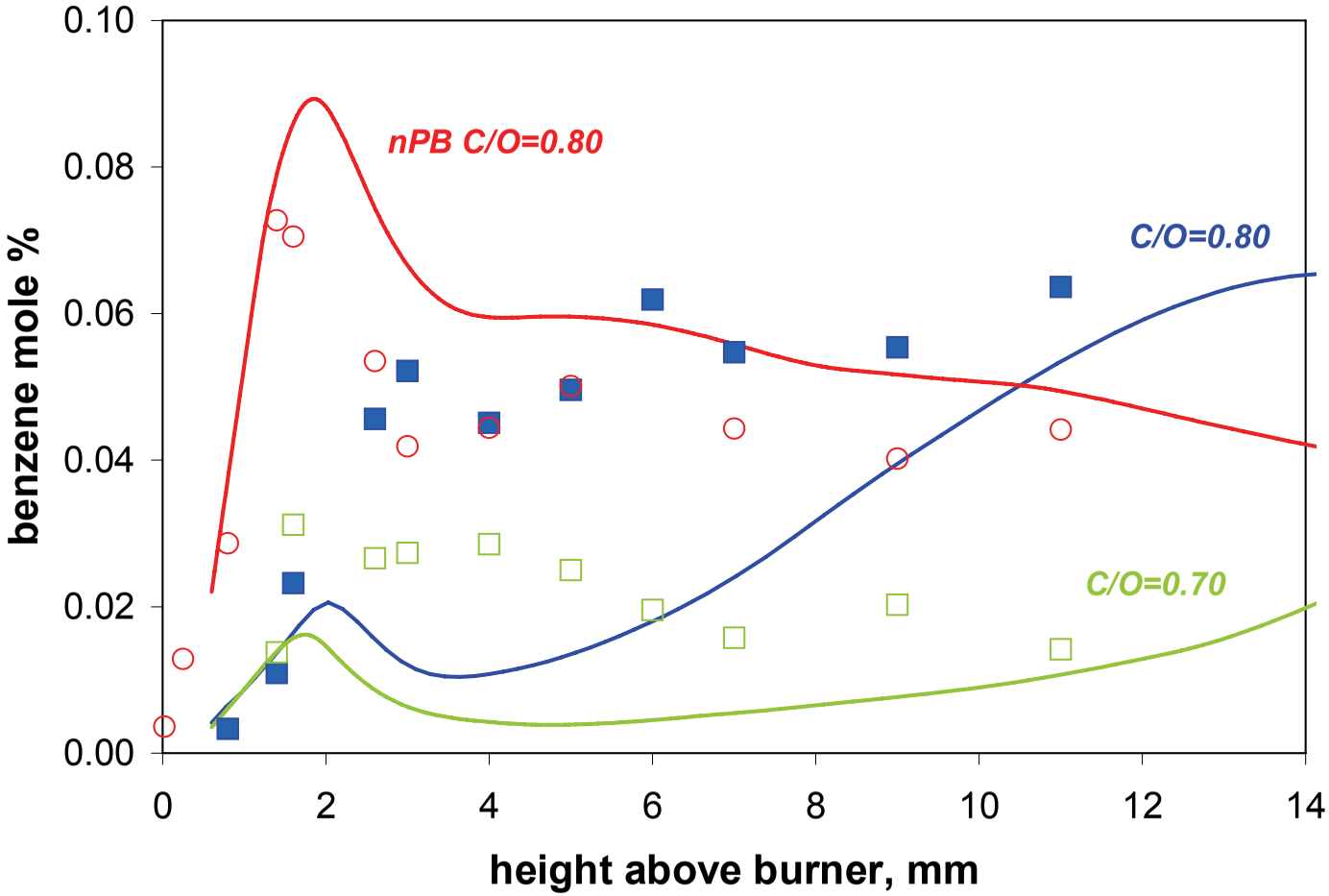
Premixed ethylene flame C/O=0.77





C2H4 flame
C/O=0.77 v=10cm/s

Premixed n-heptane/propylbenzene flames



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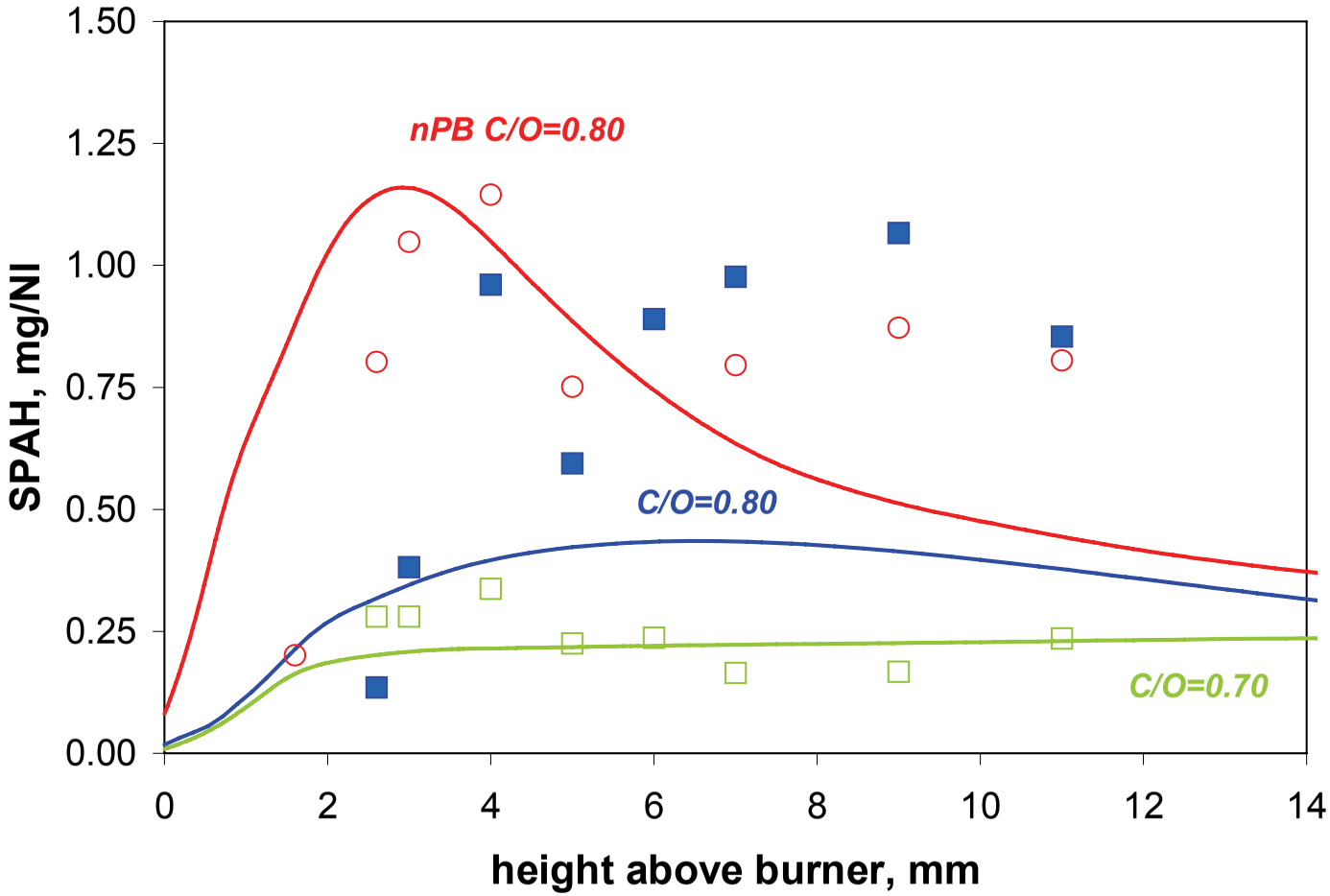

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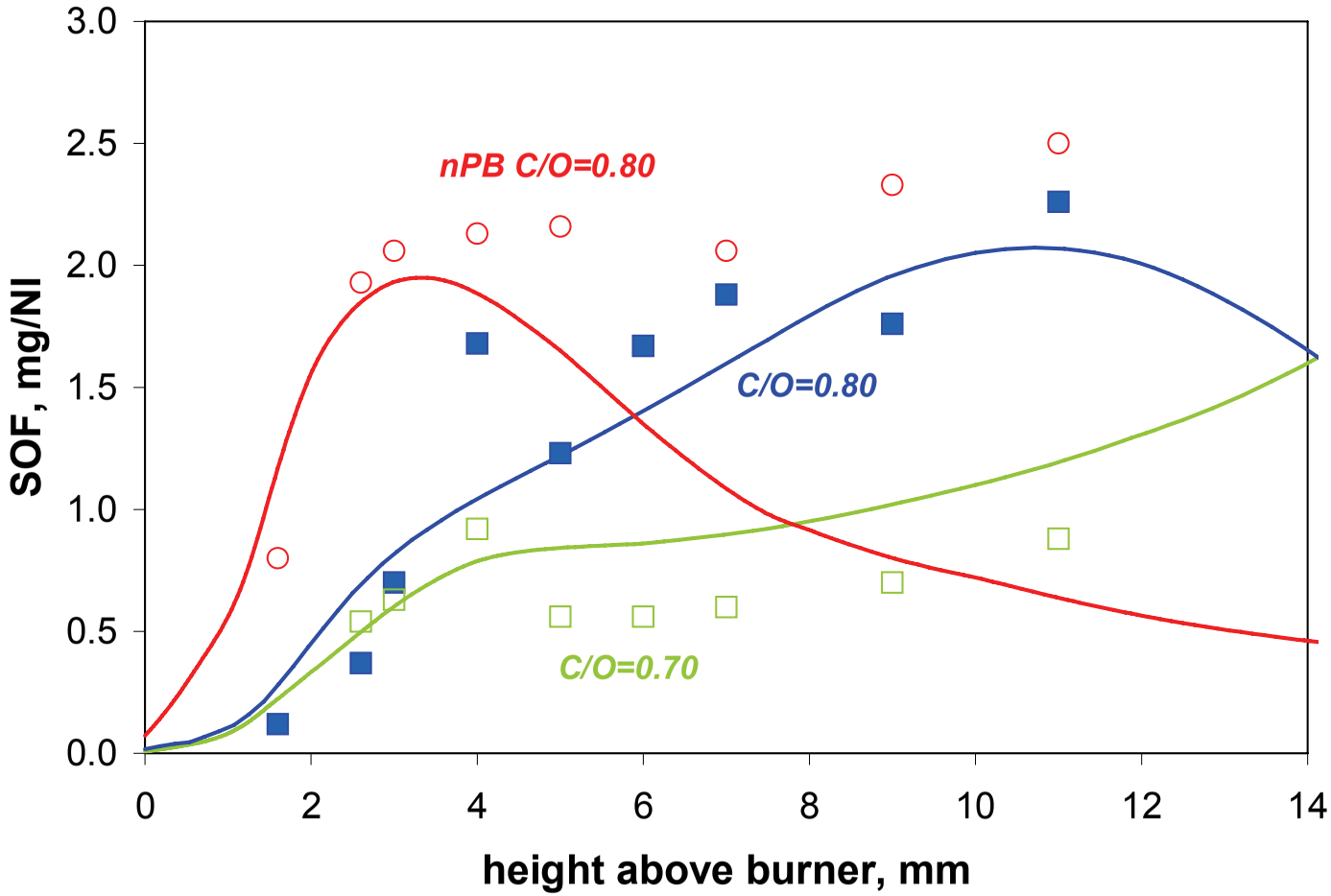

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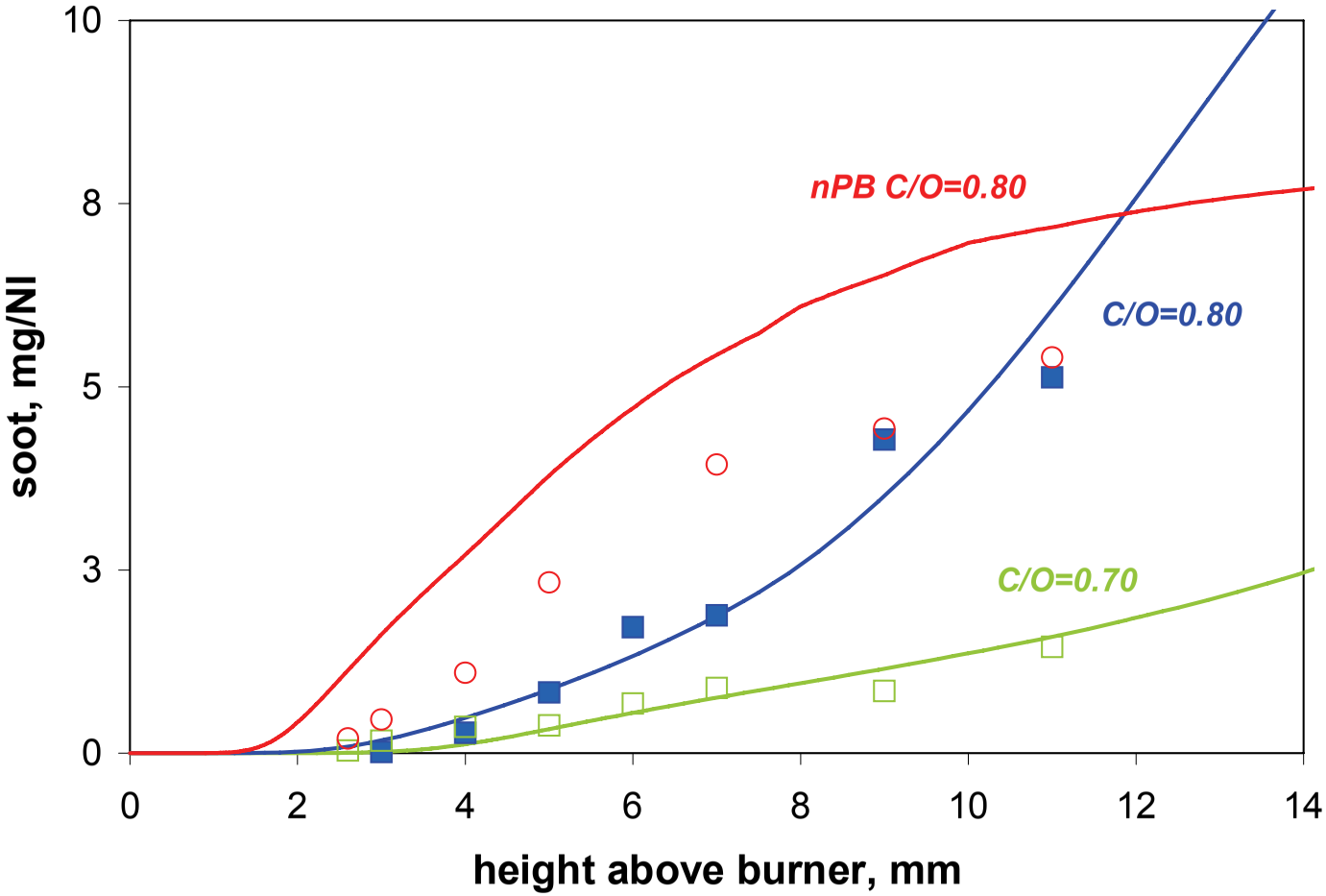

Summary

- a detailed kinetic model of particulate formation in premixed flames has been presented

- the model has the aim to predict the concentration profiles of trace pyrolysis products involved in the process of particulate formation as well as the details of PSDs.

- the model is a development of a previous polycyclic aromatic hydrocarbon (PAH) formation model which now includes also reaction pathways responsible for nano-sized particle nucleation, i.e. the transition from gas-phase species to nascent particles, and their coagulation to larger soot particles.

Summary

• a discrete-sectional approach is used for the modelling of the gas-to-particle process; the ensemble of aromatic compounds is divided into classes of different molecular mass and all reactions are treated in the form of common gas phase chemistry by using the compound properties such as mass, the numbers of carbon and hydrogen atoms averaged within each section.

• in the sectional method approach, the molecular mass distribution of the species is obtained from the calculation and not hypothesized *a priori*.

Summary

• premixed flame modelling is performed by using the CHEMKIN software package.

• a modified version of the gas phase *Interpreter* was used allowing the handling of molecules with molecular masses sufficiently large to follow soot particle inception.