Kinetics of Soot Formation at Combustion Engines Conditions
A Decade of Research at ICARE

N. Chaumeix

Workshop on Techniques for High-Pressure Combustion, August 29 – September 1, 2001
Argonne National Laboratory, Argonne, Illinois, 60439 USA

Where is ICARE ?

ICARE is in Orléans,
125 km from Paris

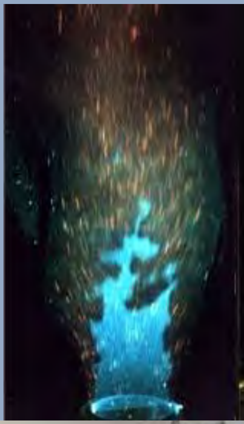
ICARE – CNRS
Institut de **C**ombustion, **A**érothermique
Réactivité et **E**nvironnement
1c, avenue de la Recherche Scientifique
45071 Orléans – Cedex 2 – France

Total staff : 110
35 Researchers
30 Engineers and technicians
30 PhD students and post-docs
15 Various trainees

Research domains of ICARE

Energy & Environment
Propulsion & Space

- Combustion
  - Chemical kinetics
    - Plasmas physics
      - Fluid mechanics, turbulence
        - Two phase flows
          - Supersonic, hypersonic flows
            - Ionized, rarefied flows










Application domains

- Aerospace propulsion
- Electric propulsion
- Liquid and solid propulsion
- Atmospheric reentry
- Atmospheric chemistry
- Energy production
- Alternative fuels, biofuels, hydrogen
- Pollutant emissions reductions
- Industrial risk prevention

Main cooperations

International co-operations: All EU countries, Russia, USA, Canada, China, Japon, Ukraine, Turkey, Argentine, etc

Research Activities of the S. W. Group

- **Combustion Chemistry**
  - Elementary Reaction Rates involving O and H atoms
  - Pollutant Formation from Gasoline Components
  - Reduced Mechanism of soot precursors from kerosene fuel
  - Soot Formation from fuels
    - Diesel, Gasoline, kerosenes
  - Soot Oxidation
    - In engine conditions behind shock waves
    - Particles Filter

Research Activities of the S. W. Group

- ✓ **Flame and Explosions Dynamics**
  - Laminar Flame properties and their instabilities
  - DDT using hot jet ignition
  - Flame acceleration in obstructed areas
  - Detonation criteria and industrial safety
  - Hypergolic limits of propellant agents
  - Propellants for PDE
  - Solid Explosives and their thermal aging

Main Objectives

COMBUSTION CHEMISTRY

Chemical Explosion

Premixed Flames

Laminar or turbulent

SLOW DEFLAGRATIONS

DETONATIONS stable & unstable

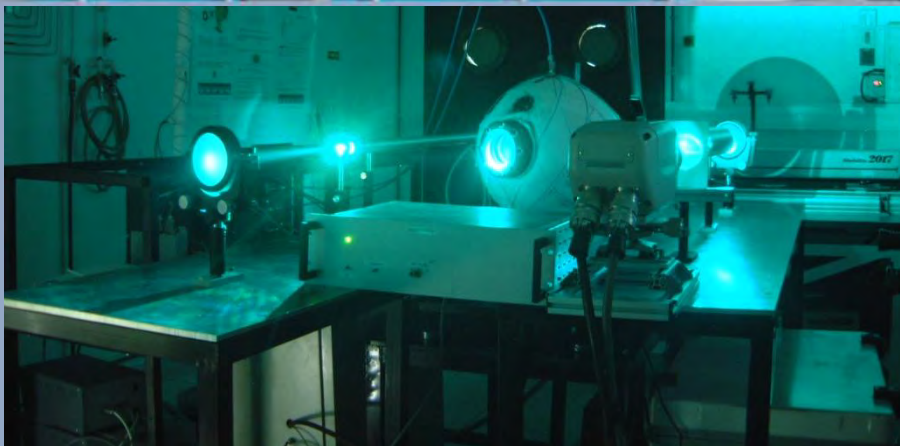
HIGHLY ACCELERATED DEFLAGRATIONS

Institut de Combustion, Aérothermique, Réactivité et Environnement • 1c, avenue de la Recherche Scientifique – 45071 Orléans – Cedex 2 • http://www.cnrs-orleans.fr/icare/

Methodology and Techniques

Several High Pressure Shock-Tubes

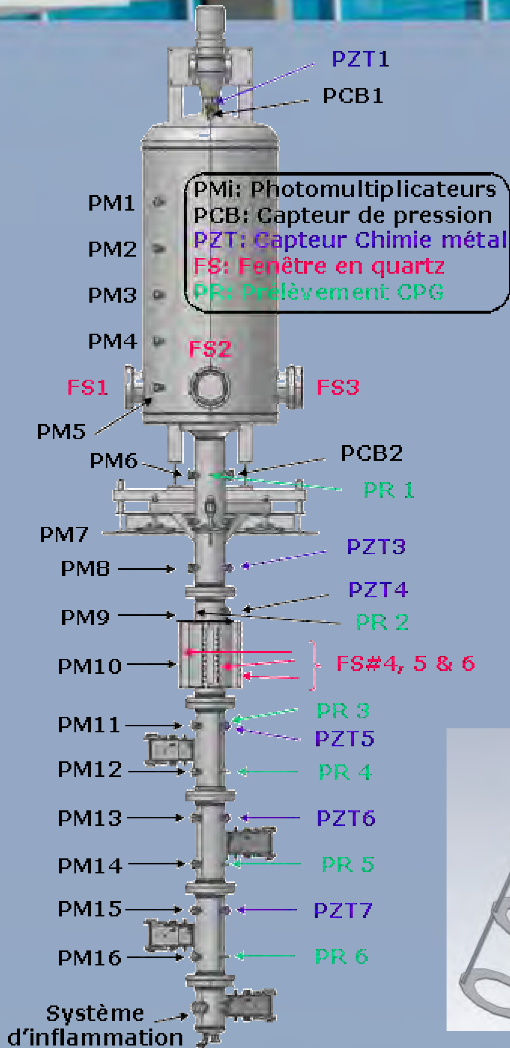
Laminar Flames



- ✓ **Spherical Bomb 8 l**
  - P_{max} = 75 bar
  - T_{max} = 353 K

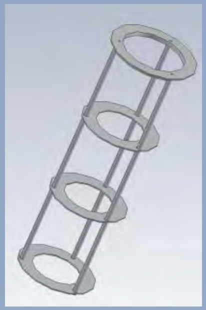
- ✓ **Spherical Bomb 56 l**
  - P_{max} = 75 bar
  - T_{max} = 520 K

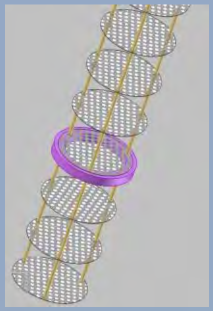
ENACCEF
Accelerated Flame Facility



- Volume = 850 l
- P_{max} = 45 bar
- T_{max} = ambiant

<u>Different obstacles</u>





Kinetics of Soot Formation at Combustion Engines Conditions
A Decade of Research at ICARE

N. Chaumeix

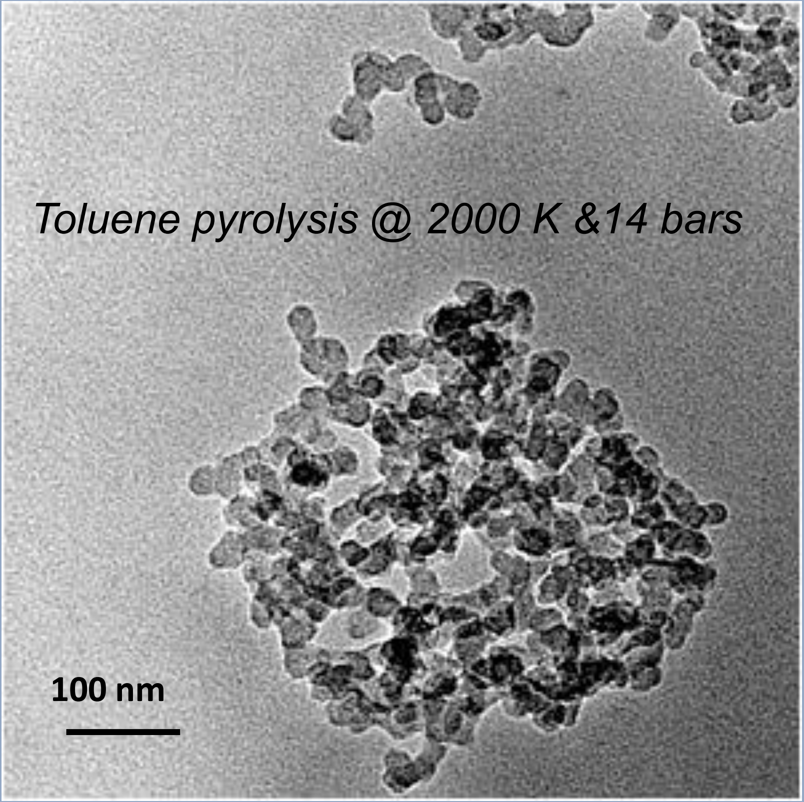
Workshop on Techniques for High-Pressure Combustion, August 29 – September 1, 2001
Argonne National Laboratory, Argonne, Illinois, 60439 USA

What is soot ?

- **Soot is:**
  - Solid phase with condensed molecules
  - Mainly carbon and H with a ratio 8/1
  - The density is roughly 1.85 g/cm^3
  - The primary particle is spherical
- **Soot is constituted of**
  - Soluble fraction that depends strongly on the combustion conditions (fuel, engine load, injection system
  - Dry fraction which is characterised by a turbostratic structure

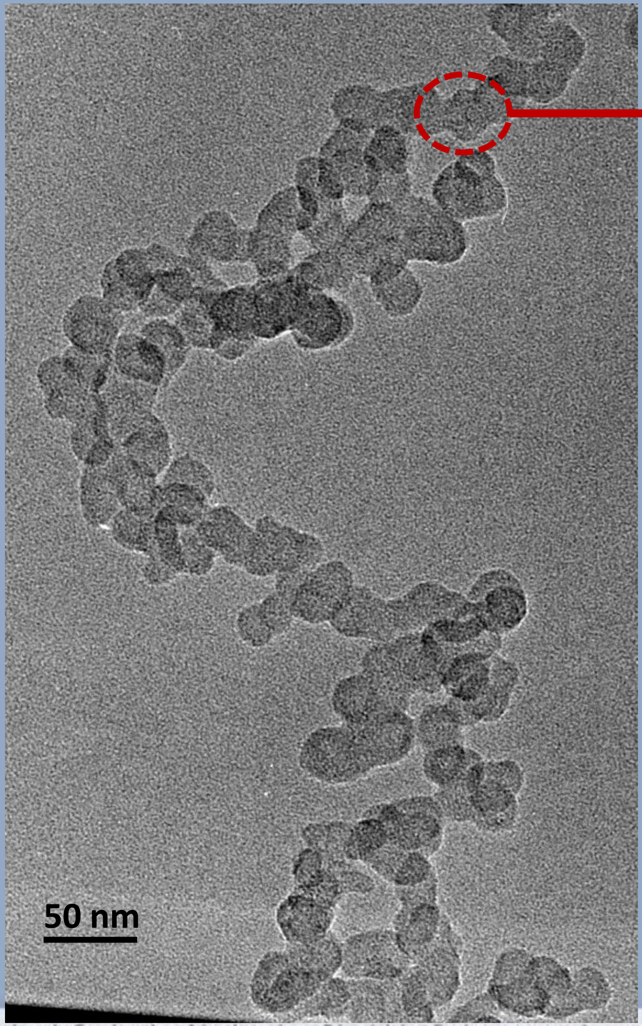
Soot Organization

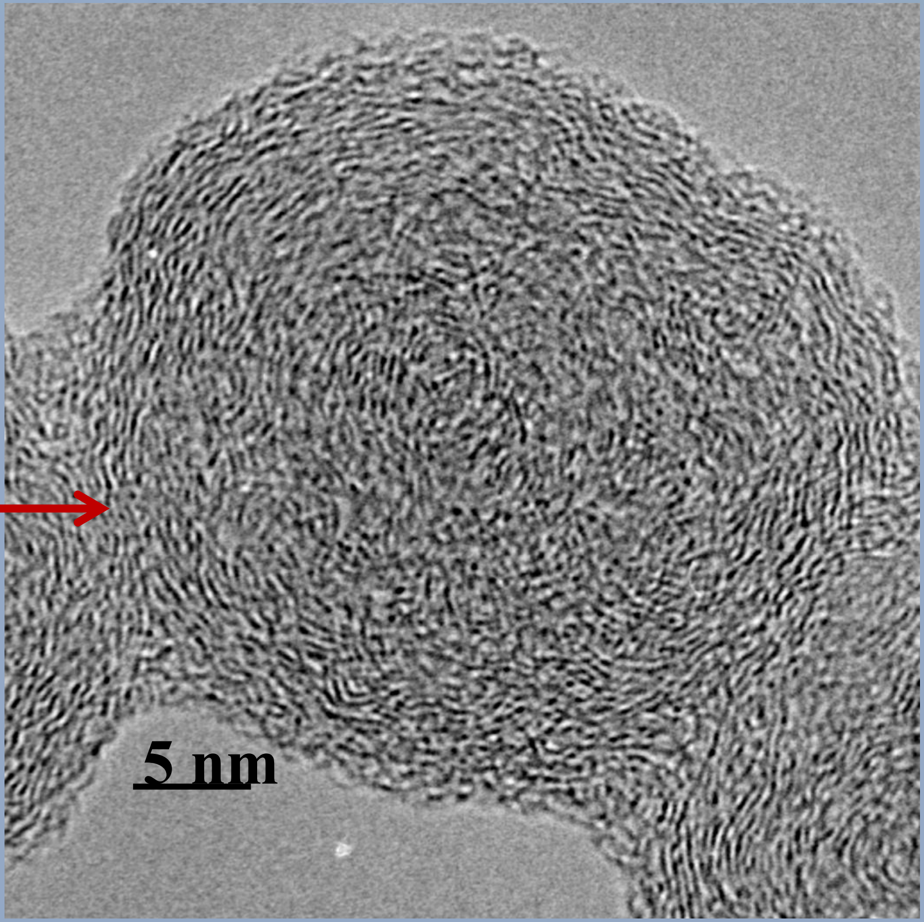
- ✓ **From the texture point of view**
  - soot is a particle of about a **micrometer size**
  - If one looks closer, they are in fact agglomerate of primary spheres with an average size about **10 & 40 nm**
  - Their number can be as high as 100s
- ✓ **The size is the main factor in the toxicity of soot particles**



Microtexture and structure

TEM @ low resolution x 50 000





TEM @ high resolution x 310 000

Objectives of the Study

✓ **Acquire fundamental data regarding soot formation**

- In a well defined conditions → P, T
- In homogeneous conditions
- For pure compounds → ideally heavy hydrocarbons
  → from major families
- For Surrogate Mixtures
- For Equivalence ratios > 1 and up to ∞

Objectives of the Study

- ✓ **How long does it take to form soot?**
- ✓ **How much soot can be formed?**
- ✓ **What is exactly formed?**
  - How do soot look like ?
  - What kind of species are adsorbed on the surface ?
- ✓ **How can these data be useful to the soot modeling?**

Soot Properties

✓ **Soot Optical Properties will depend on**

- Type of agregates
- Mean diameter of the primary spheres
- Micro-Structure

→ **Refractive Index**

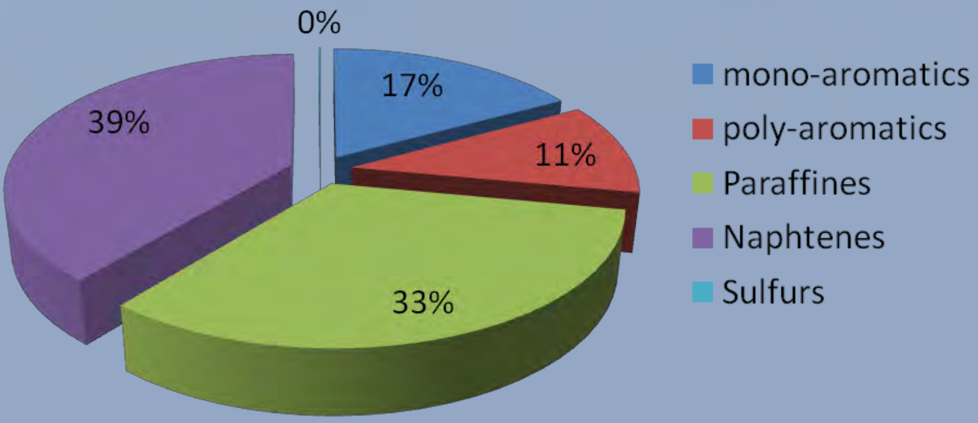
✓ **Soot Reactivity will depend on**

- Micro-Structure
- Adsorbed phase

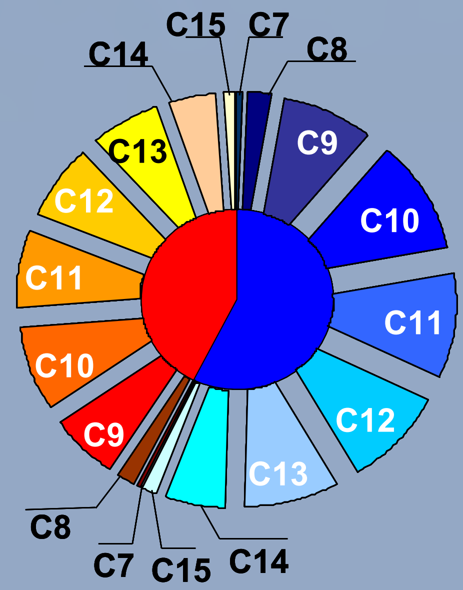
→ **Soot Oxidation Rate**

Real Fuels

Conventional Diesel Fuel



Fisher-Tropsch Cut at 403 K Fuel



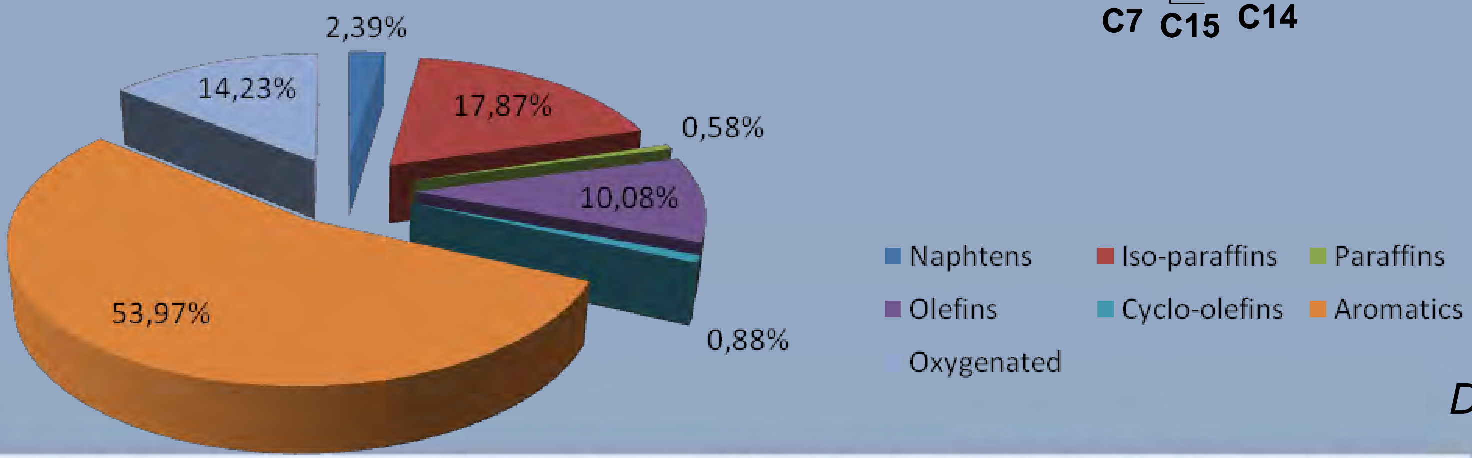
n-paraffins:

57.22 $\%_{mass}$

iso-paraffins:

42.78 $\%_{mass}$

Conventional Gazoline Fuel



Data source: TOTAL

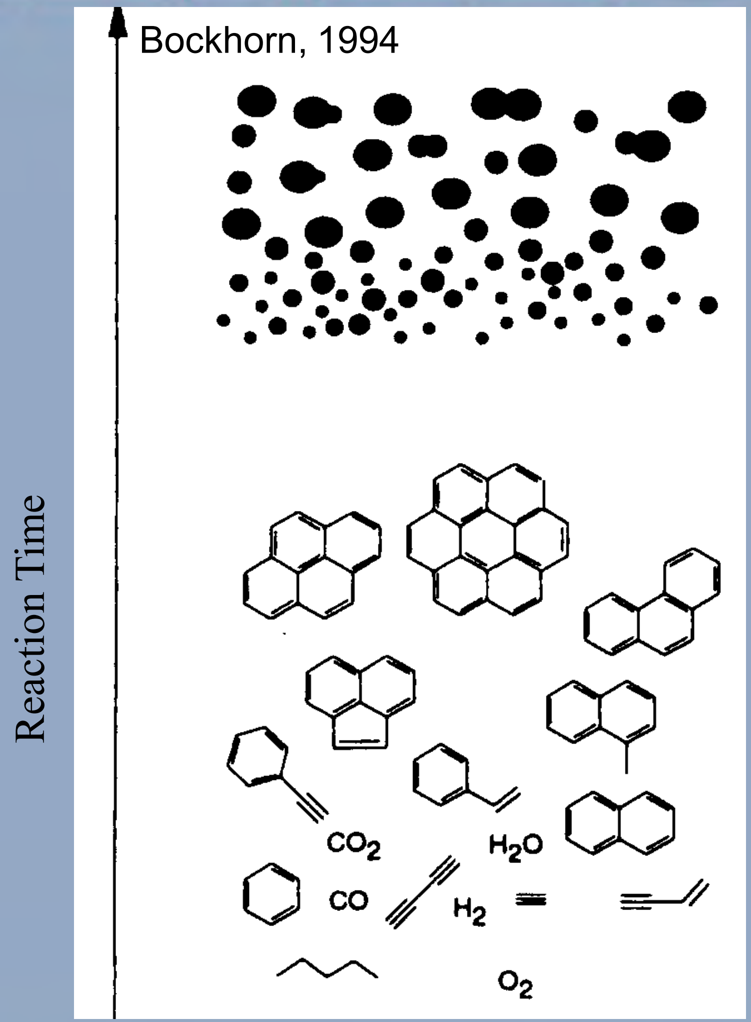
Studied Fuels

- **Hydrocarbons representing major component of the real fuel**
  - Diesel : n-hexadecane, butyl-benzene, n-heptyl benzene, decaline, α-methylnaphtalene, propyl-cyclohexane, butyl-benzene, 2,2,4,4,6,8,8 heptamethylnonane
  - Gazoline : iso-octane, toluene, 1-hexene, 2M2B
  - Kerosenes : n-decane, trimethyl-benzene, cyclohexane, n-propylbenzene
  - Fischer-Tropsch : propyl-cyclohexane, 2,2,4,4,6,8,8 heptamethylnonane
- **Additives**
  - ETBE , Thiophene, 3-methyl-thiophene

Studied Fuels

- ✓ **Diesel Surrogate**
  - 47 % Propyl-cyclohexane + 22 % Heptamethylnonane + 31 % Butyl-benzene
- ✓ **Gazoline Surrogate**
  - 50 % Iso-Octane + 35%Toluene + 15%1-Hexene
- ✓ **Kerosene Surrogate**
  - 80% n-decane + 20% n-propylbenzene
- ✓ **Real Fuel : Fischer-Tropsch**
  - Cut at 403 K

Main Soot Formation Mechanism



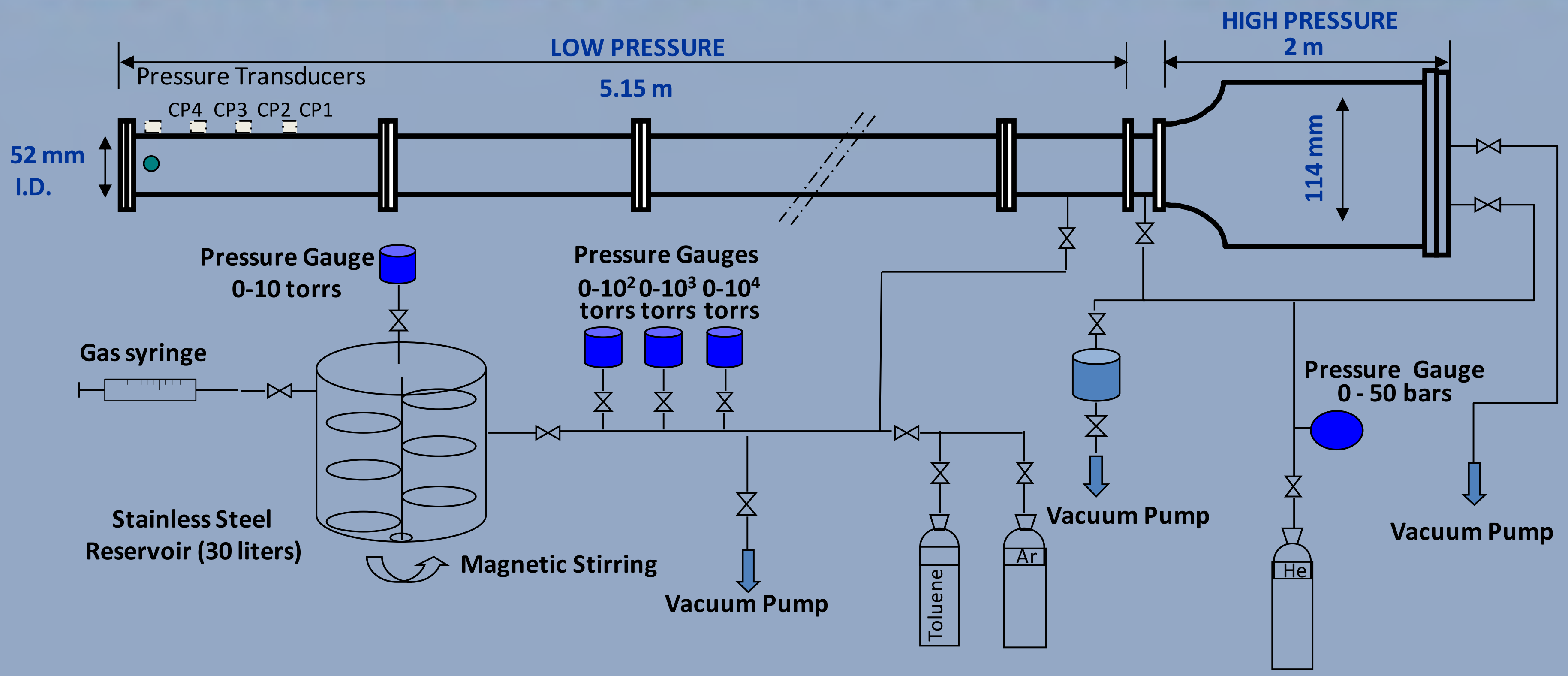
Soot Growth due to surface growth and coagulation

Soot Nucleation

Inception and Growth of PAHs

First Ring Formation

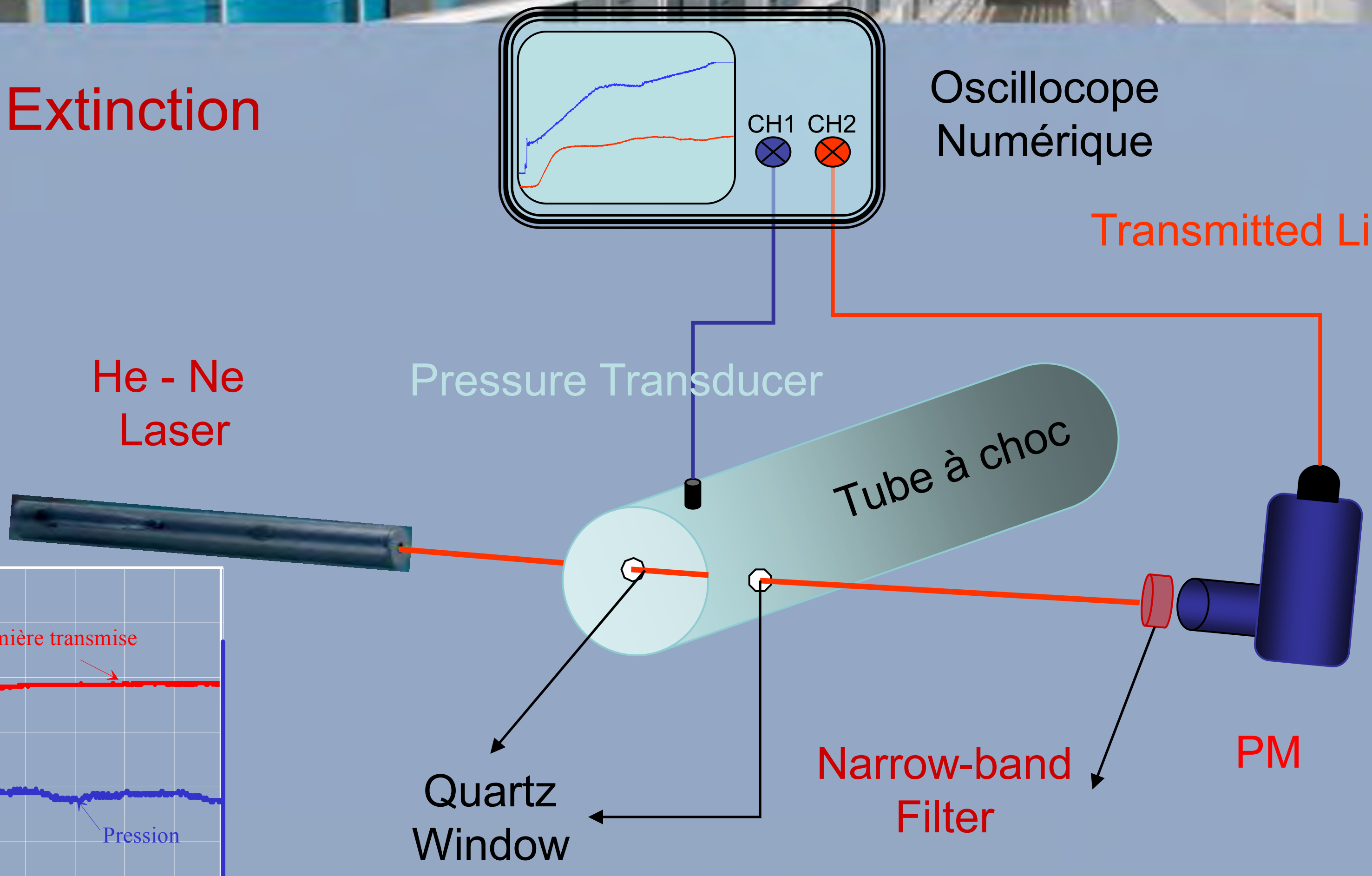
Experimental setup

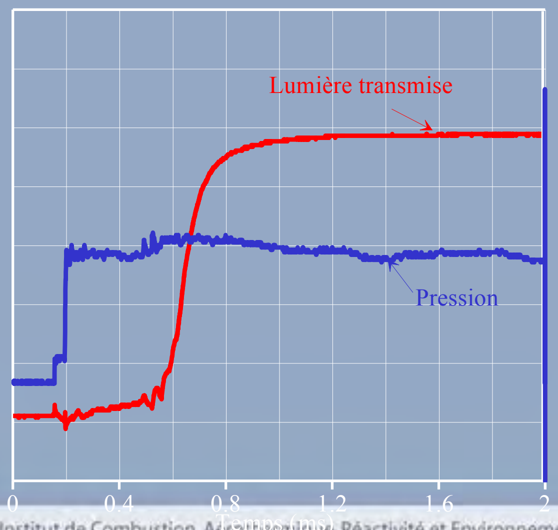


Setup (shock tube, pipes, tank) @ 405±2K

Diagnostics Coupled to the Shock Tube

► Laser Extinction

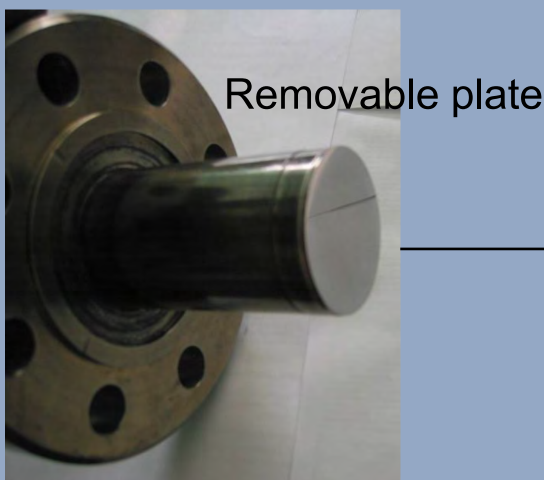


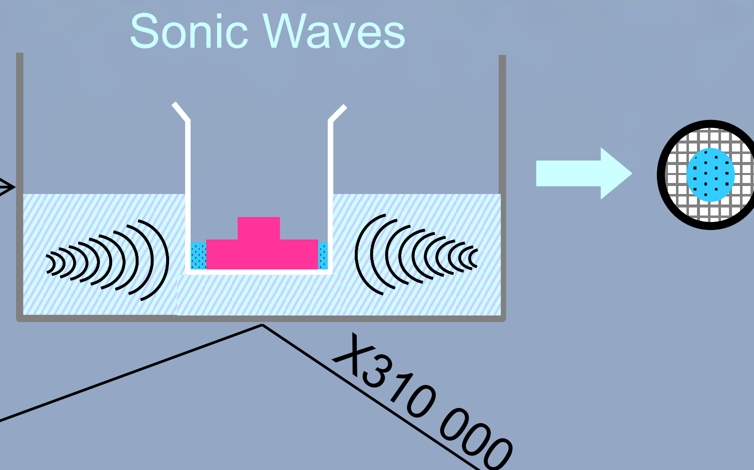


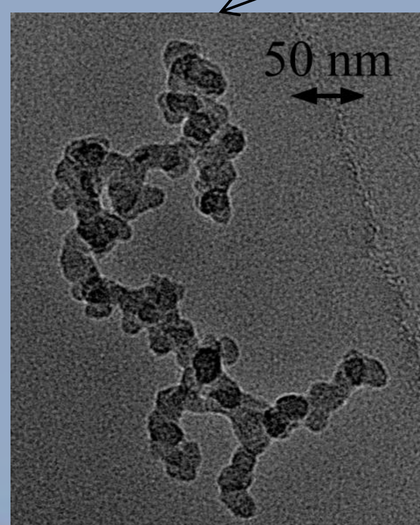
Diagnostics Coupled to the Shock Tube

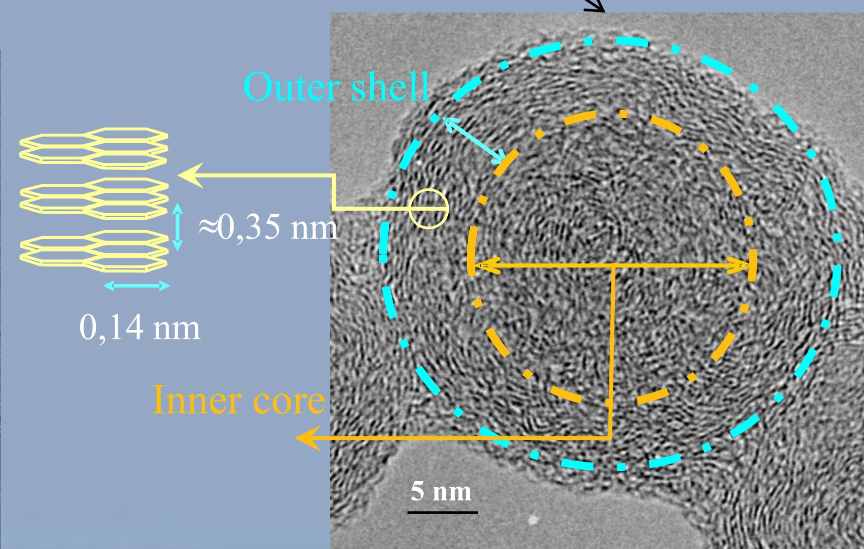
► TEM at low and High Resolution

Shock Tube End









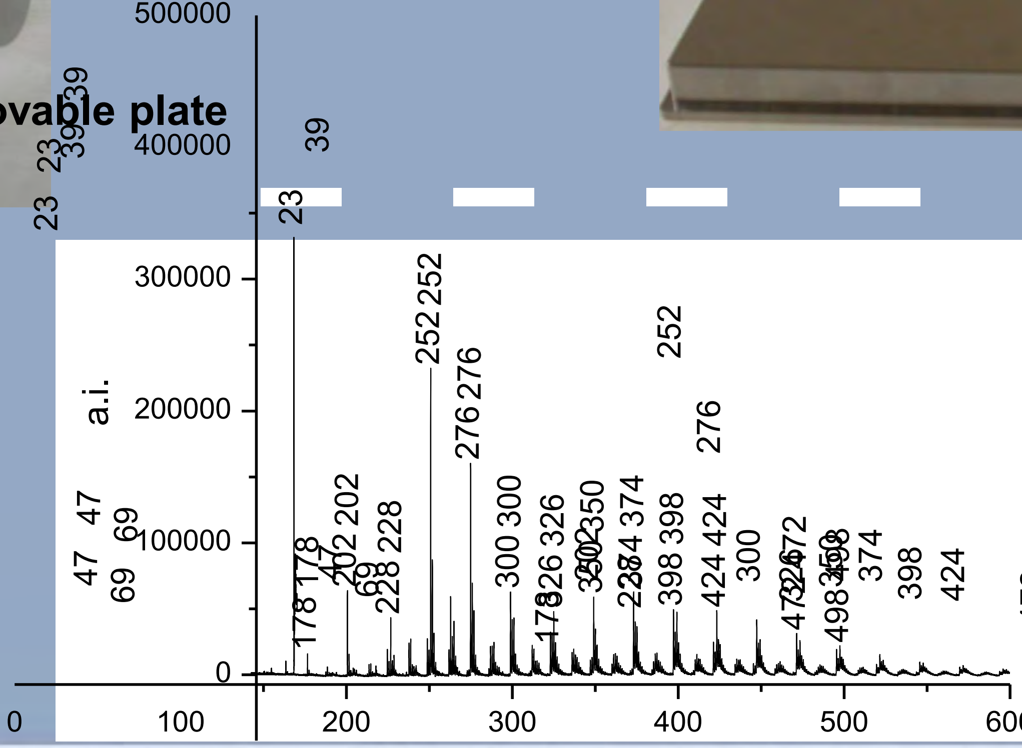
Diagnostics Coupled to the Shock Tube

Shock Tube End

Removable plate

Soot on the plate

LDIToFMS Sampling Holder

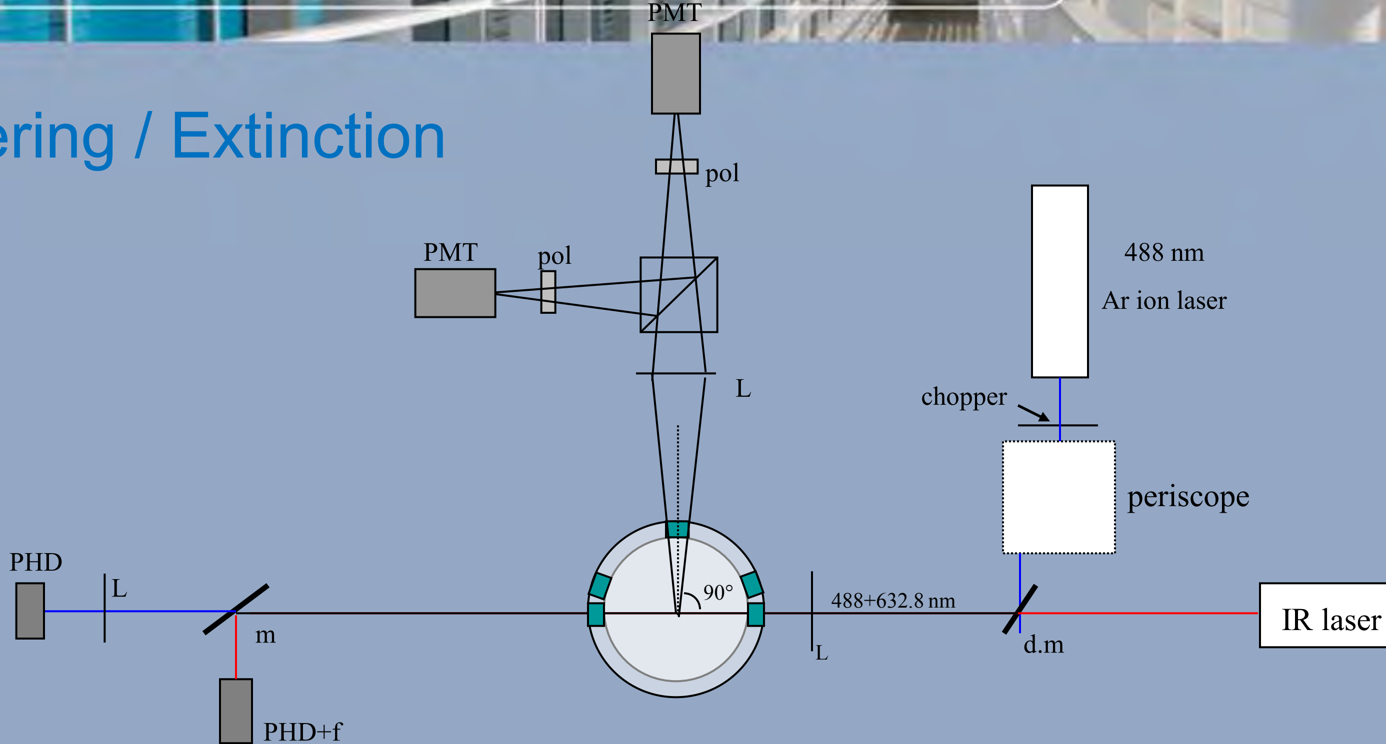


178 - 572 amu

Diagnostics Coupled to the Shock Tube

► Laser Scattering / Extinction

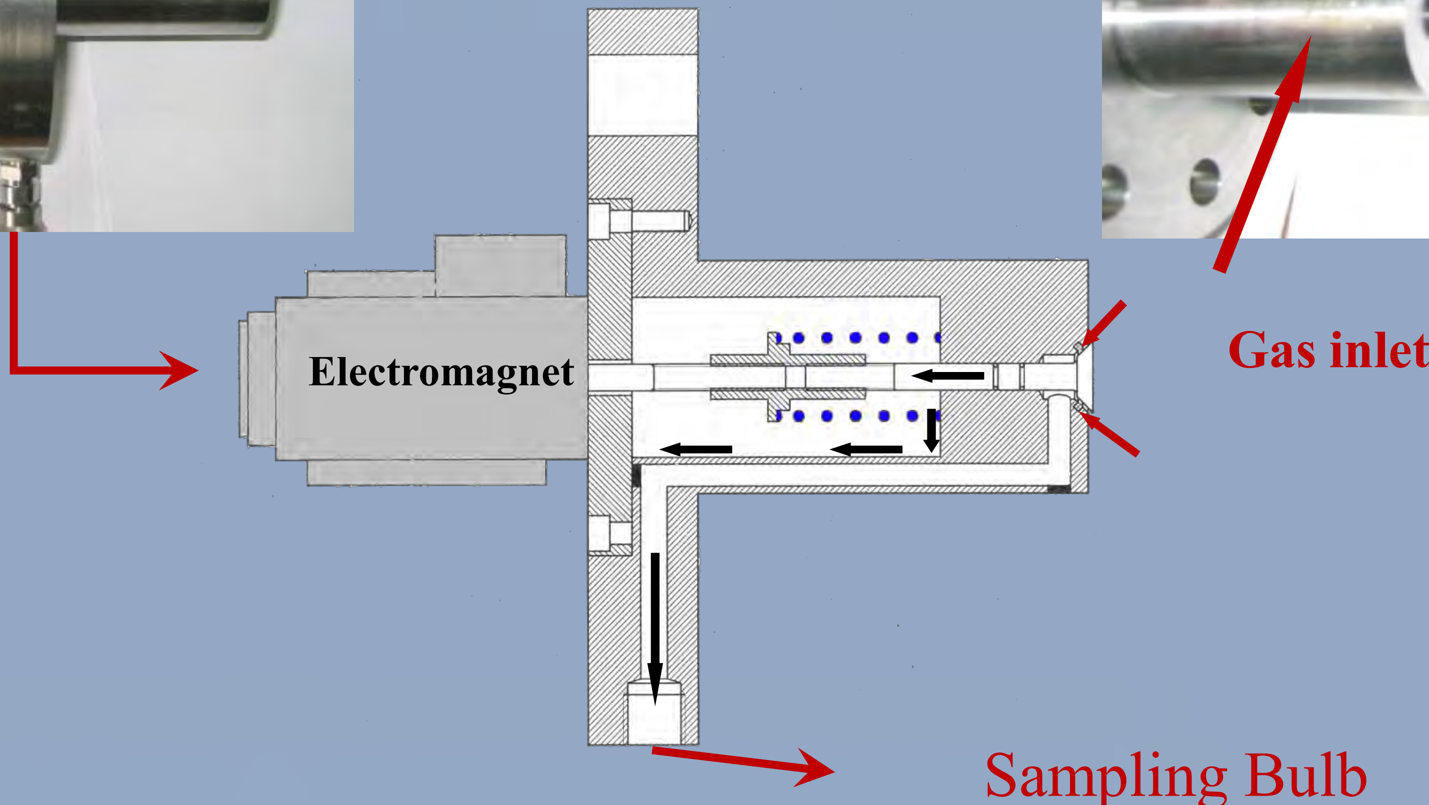
m = mirror
d.m.= dichroic mirror
f = interferential filter
pol=polarizator
M=monochromator
PMT = photomultiplier
L = lens
PHD = photodiode



Mechanical chopper at 40KHz

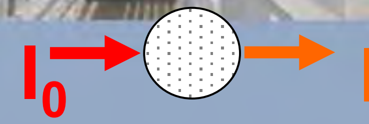
fv ⇦ I/I_0 ⇦	Extinction	diode laser λ = 800 nm	⇨ I_{scat} & I/I_0 ⇨ d_p
	Scattering	Ar^+ laser λ = 488 nm	

Gas Sampling Behind the RSW

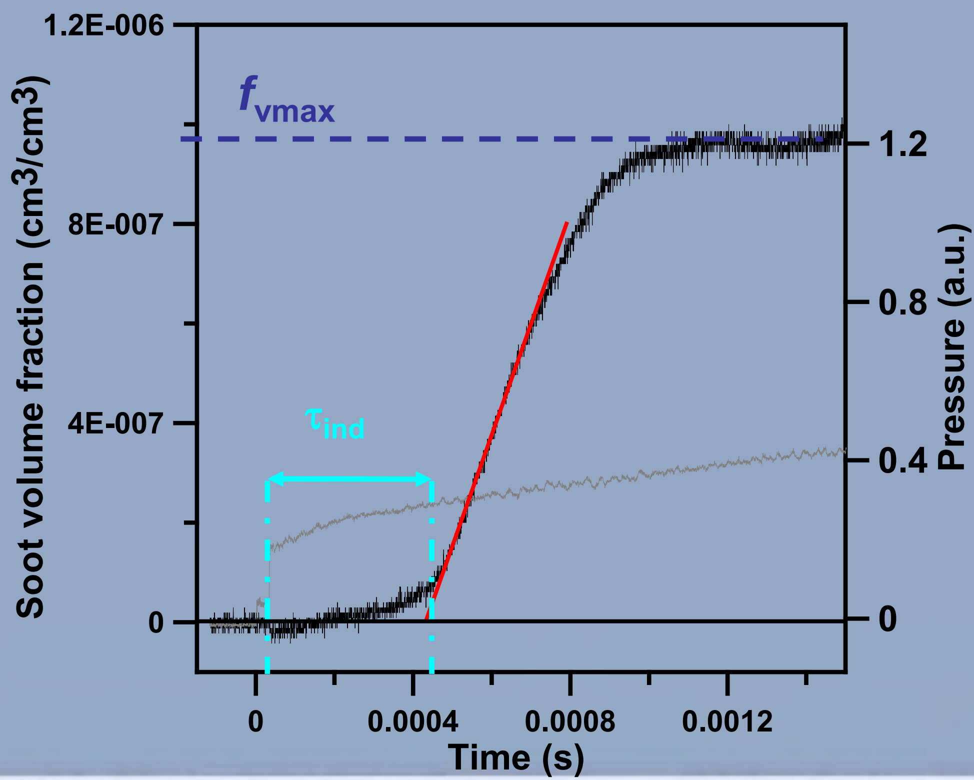


Soot Volume Fraction Measurement

BEER-LAMBERT Law & Graham's model (1975)



$$f_v = \frac{\lambda}{6 \cdot \pi \cdot L \cdot E(m)} \ln \frac{I_o}{I}$$



- **Induction Delay**

$$\tau_{ind} = A \cdot [HC]^a \cdot [Diluant]^b \cdot \exp\left(\frac{E_{ind}}{R \cdot T}\right)$$

- **Growth Constant**

$$\ln \frac{f_{v\infty}}{f_{v\infty} - f_v} = k_f t$$

- **Soot Yield**

$$Y = \frac{[C]_{suies}}{[C]_{total}} = \frac{N_{av}\rho\lambda}{72\pi E(m) l [C]_{total}} \ln \frac{I_0}{I}$$

Studied Parameters

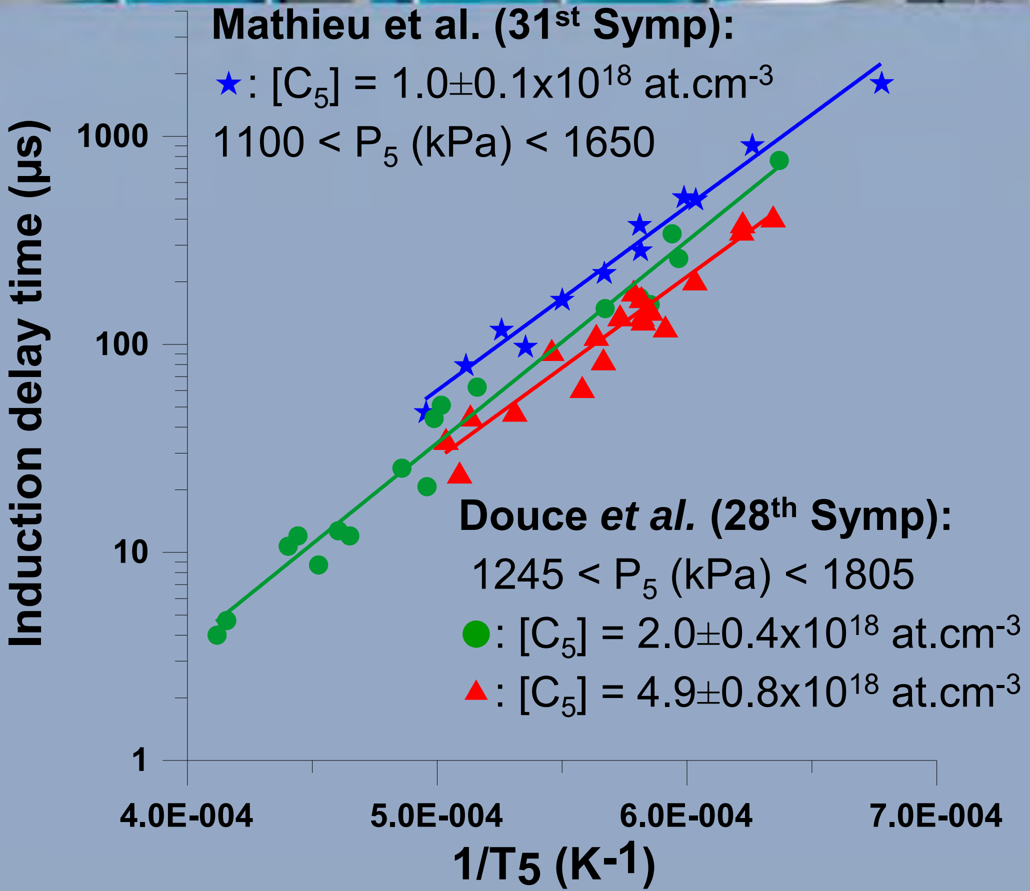
- ✓ **Morphology and structure of the soot (T.E.M.)** → CRMD
  - Low Resolution: Aggregates, diameter distribution
  - High Resolution: Arrangement of the carbon layers
- ✓ **Adsorbed Phase on soot** → LSMCL, Metz

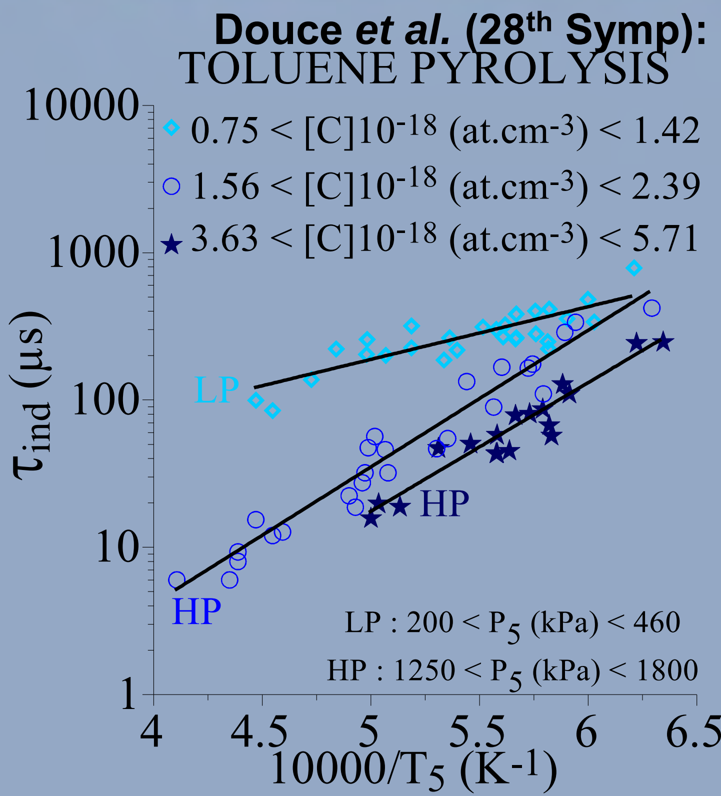
Experimental Conditions

FT ($C_{11.23}H_{24.46}$)	T_5 (K)	P_5 (MPa)	$[Carbon]_5$ (atoms.cm-3)	Eq. ratio (ϕ)	O_2% (mol.) in Ar
0.4% mol.	1675-2540	1.24-1.71	$(1{,}83\text{-}2{,}76).10^{+18}$	∞	0%
	1630-2325	1.51-1.65	$(2.11\text{-}2{,}50).10^{+18}$	18	0.42%
	1525-1920	1.05-1.48	$(2{,}17\text{-}2{,}49).10^{+18}$	5	1.33%
0.2% mol.	1500-2225	1.15-1.65	$(1{,}15\text{-}1.38).10^{+18}$	∞	0%

→ **Argon Dilution usually > 99 %**

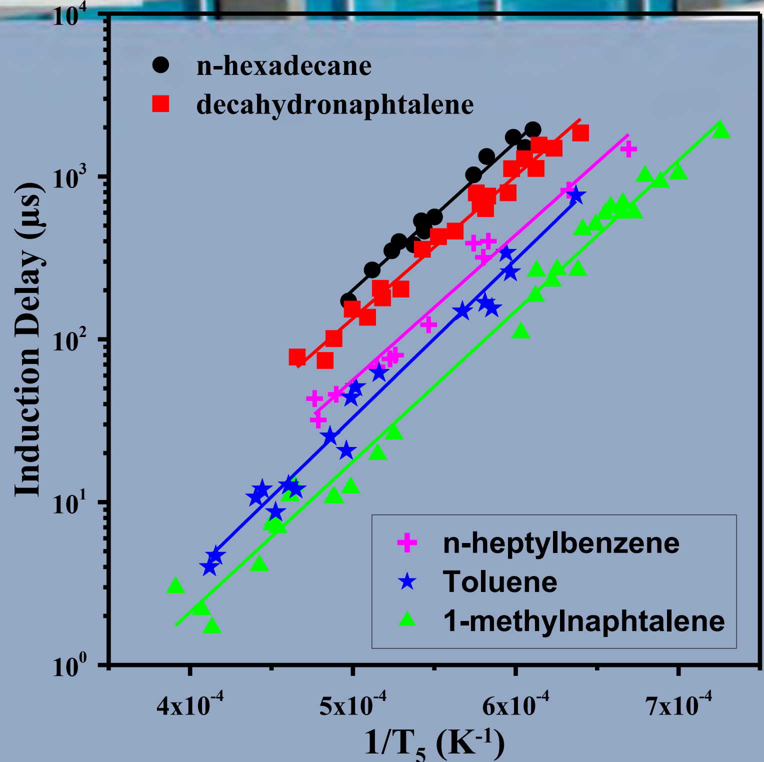
Induction Delay Times

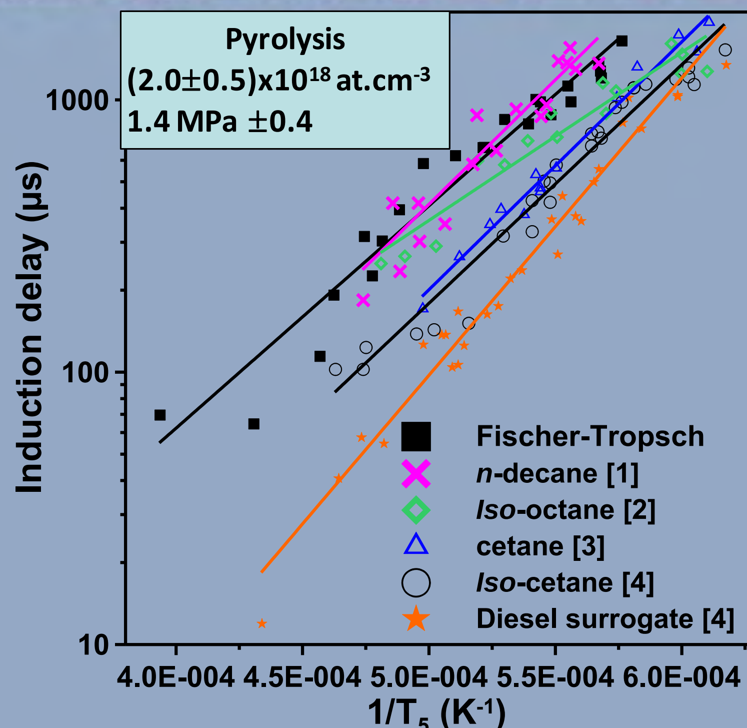




$$\tau_{ind}(\mu s) = 0.046 \cdot [x_{toluene}]^{-0.50} \cdot P^{-0.93} \cdot \exp\left(\frac{21690}{T(K)}\right)$$

Induction Delay Times





$$\tau_{ind}(\mu s) = 1{,}4 \cdot 10^{-3} \cdot \left[\frac{n_C}{n_H}\right]^{-3{,}04} \cdot \exp\left(\frac{165000}{8{,}314 \cdot T(K)}\right)$$

$R^2 = 0{,}9355$

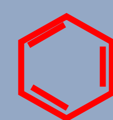
Summary

Aromatic — **Fast Route** →

Aliphatic — **Slow Route** →

C$_3$ Route:

$C_3H_3+C_3H_3 \rightarrow C_6H_5+H$

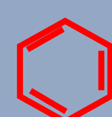
$C_3H_3+C_3H_4 \rightarrow$  $+H$

C$_4$ Route :

$C_2H_3+C_2H_2 \rightarrow C_4H_5$

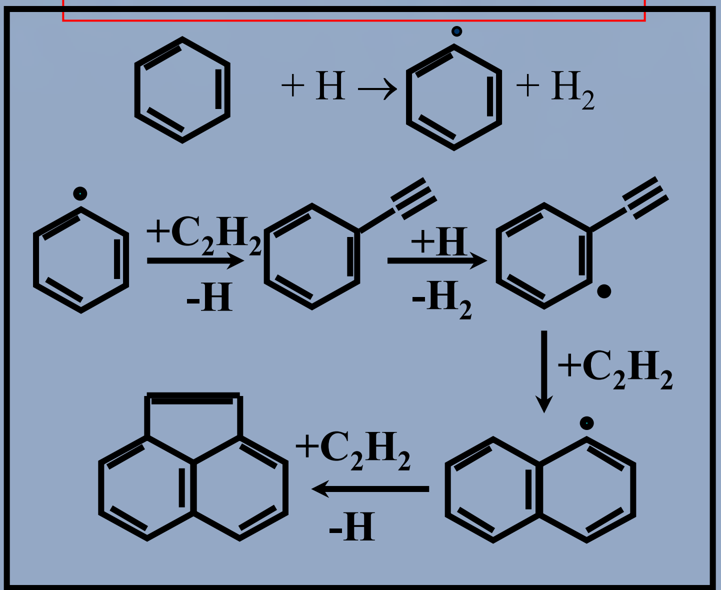
$C_2H+C_2H_2 \rightarrow C_4H_3$

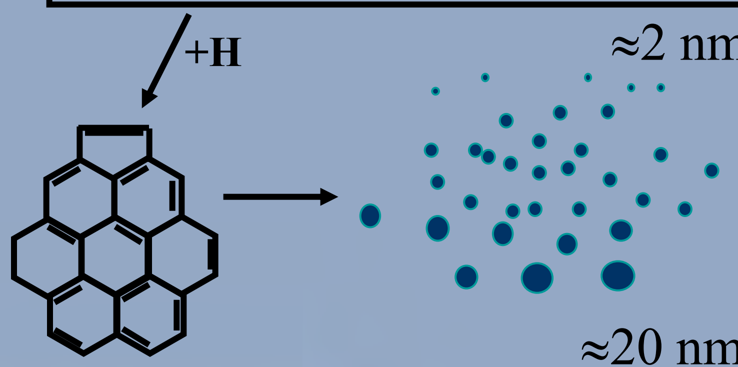
puis,

$C_4H_5+C_2H_2 \rightarrow$  $+H$

$C_4H_3+C_2H_2 \rightarrow C_6H_5$

HACA Mechanism





HAP

Institut de Combustion, Aérothermique, Réactivité et Environnement • 1c, avenue de la Recherche Scientifique – 45071 Orléans – Cedex 2 • http://www.cnrs-orleans.fr/icare/

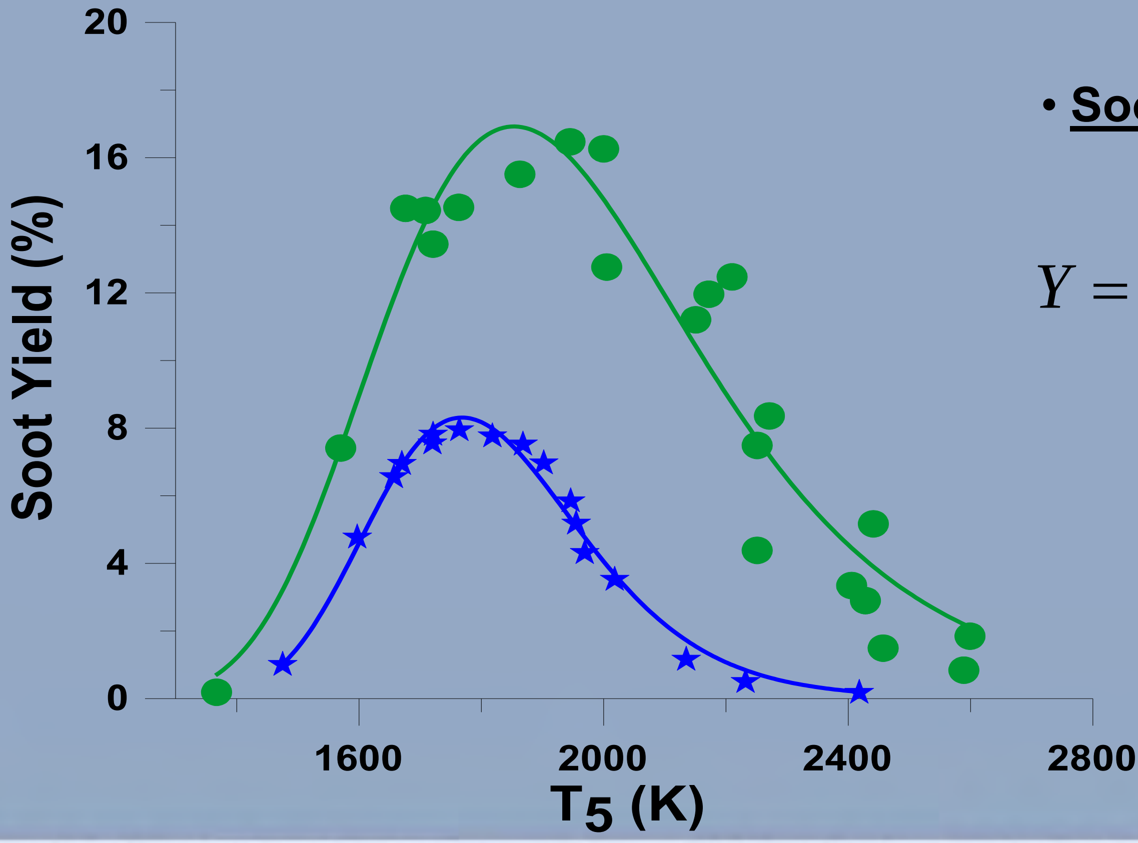
Soot Yield - Toluene

Douce *et al. (PCI, 2000)*:

●: $[C_5] = 2.0 \pm 0.4 \times 10^{18}$ at.cm^{-3}

Mathieu et al. (PCI, 2007) :

★: $[C_5] = 1.0 \pm 0.1 \times 10^{18}$ at.cm^{-3}



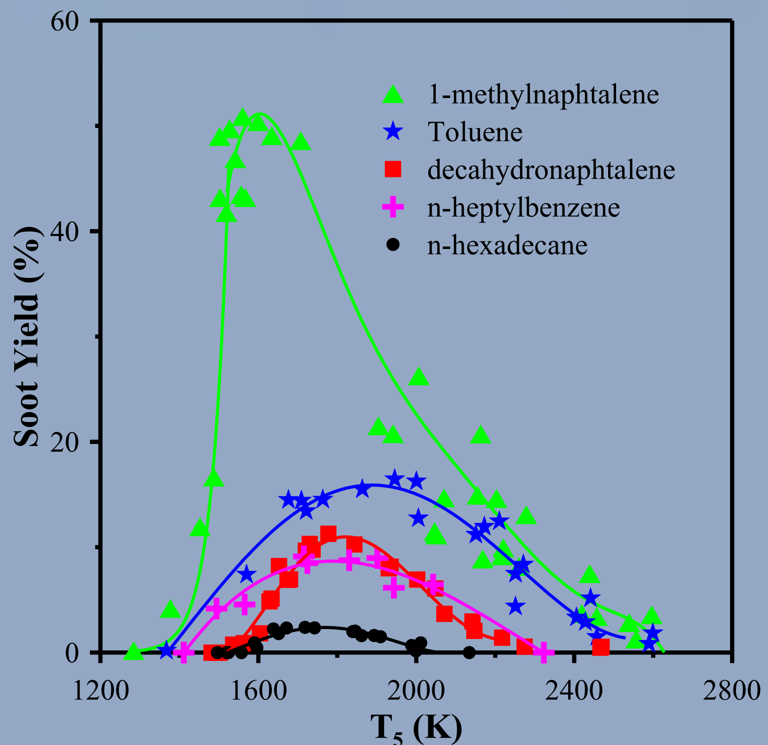
- **Soot Yield's definition**:

$$Y = \frac{[C]_{soot}}{[C]_{initial}} = \frac{N_{av}\rho}{12\pi[C]_{initial}} f_{v\infty}$$

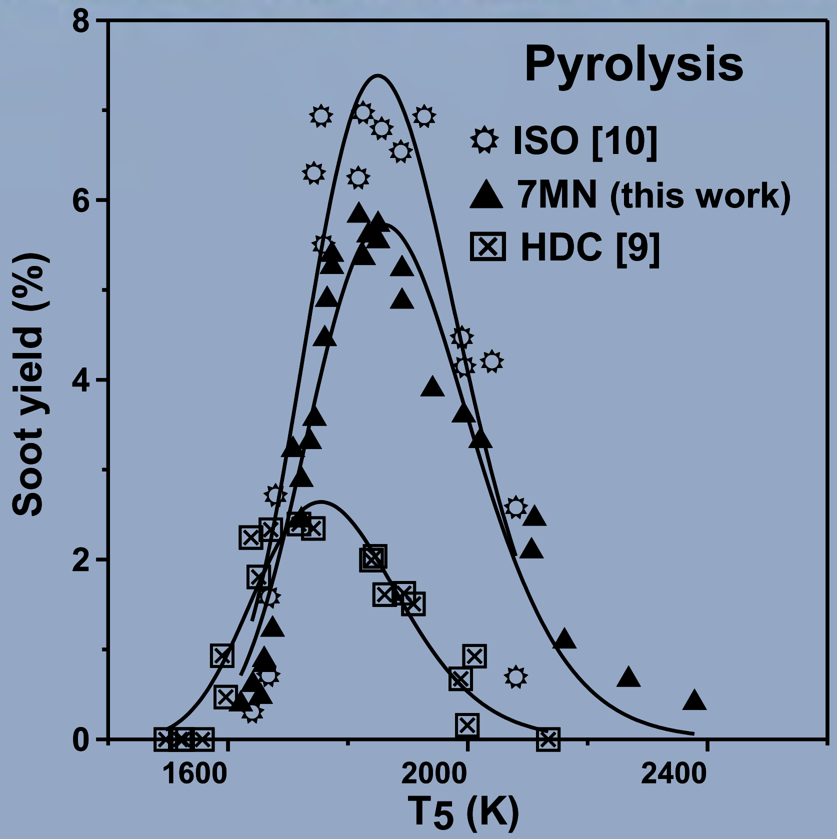
- **Soot Yield's representation**:

$$Y = Y_{\max} \cdot \exp\left(- A\left[\frac{T_{opt} - T}{T} \right]^2 \right)$$

Soot Yield

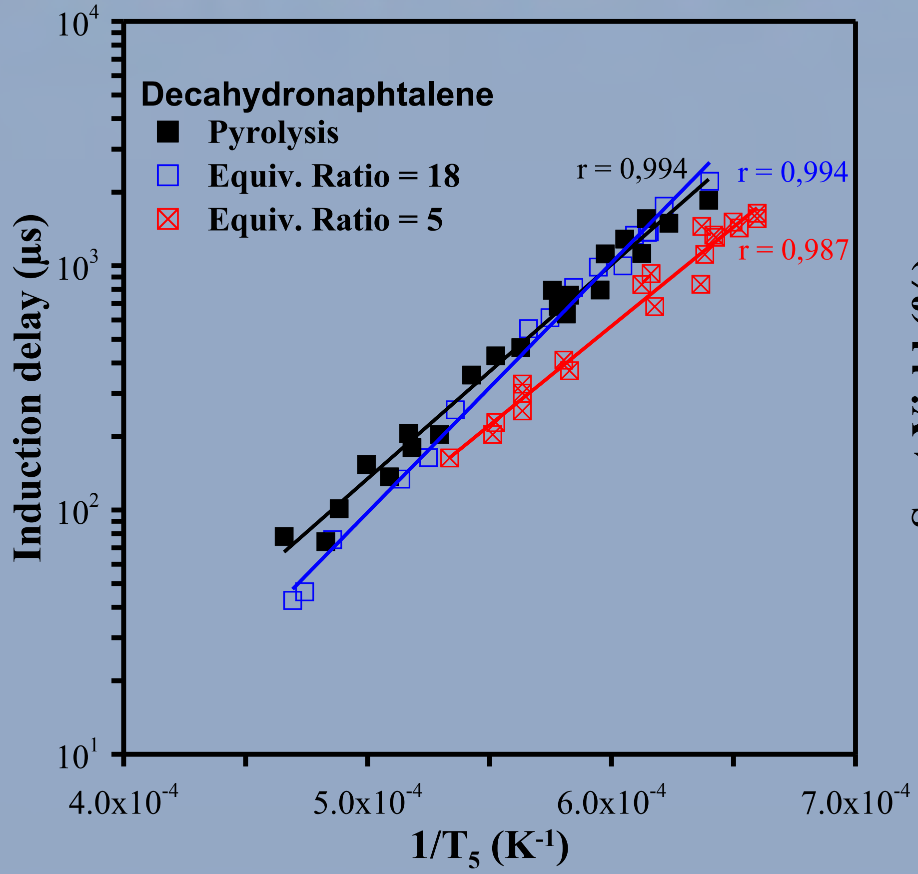


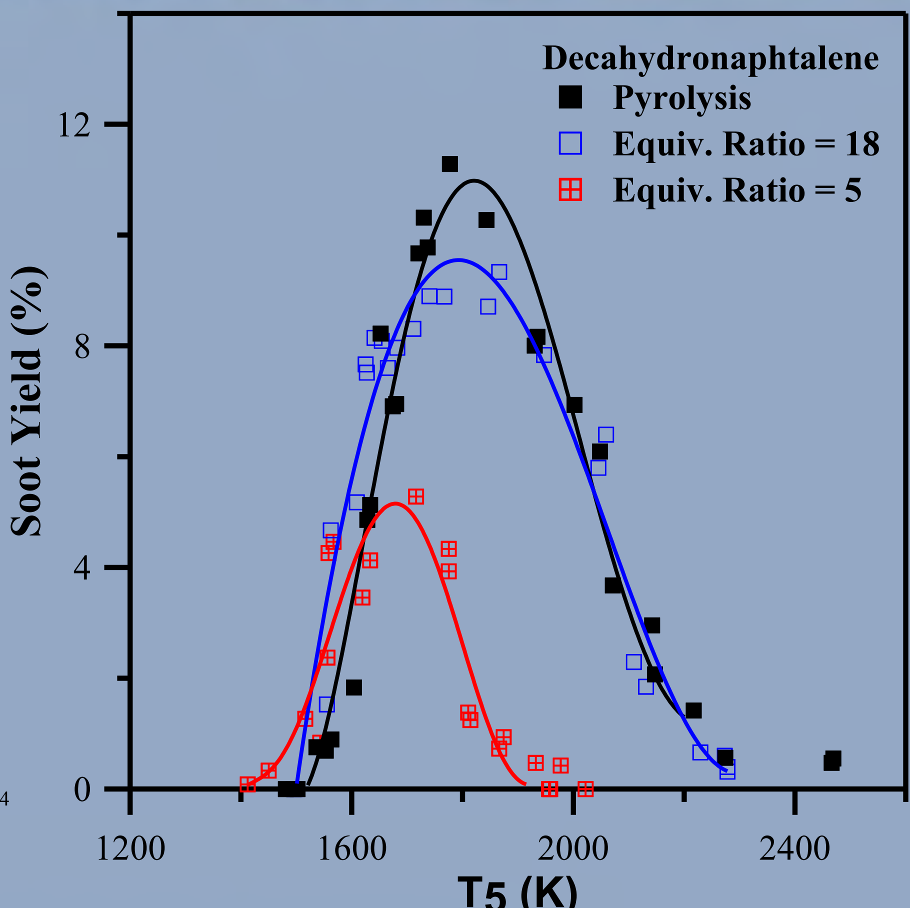
Douce *et al. (PCI, 2000)*



Mathieu et al. (Combst. Flame, 2009)

Effect of Oxygen

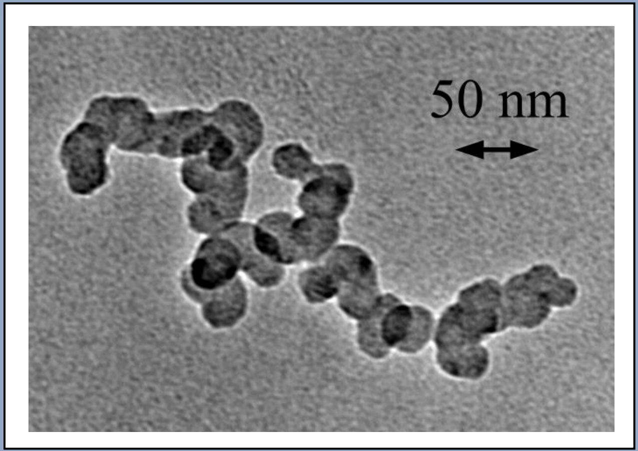


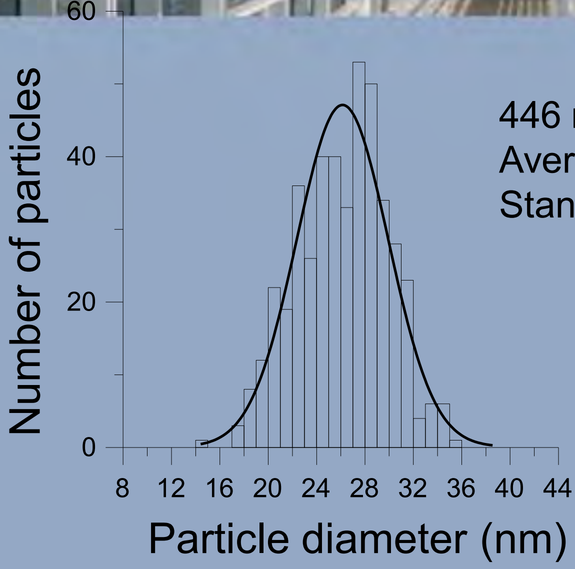


Douce ***et al.* (PCI, 2000)**

TEM - Toluene / Ar

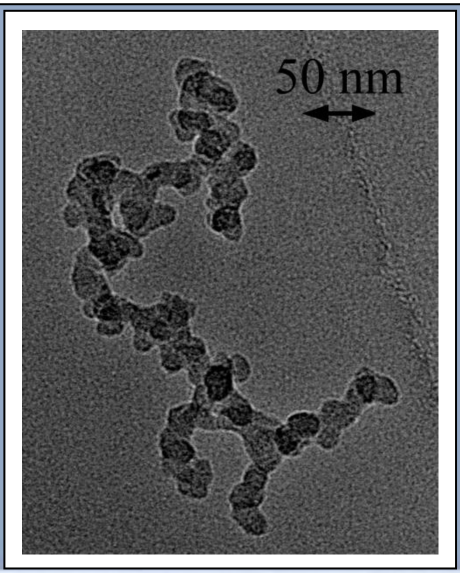
T_5 = 1700 K ; P_5 = 1714kPa

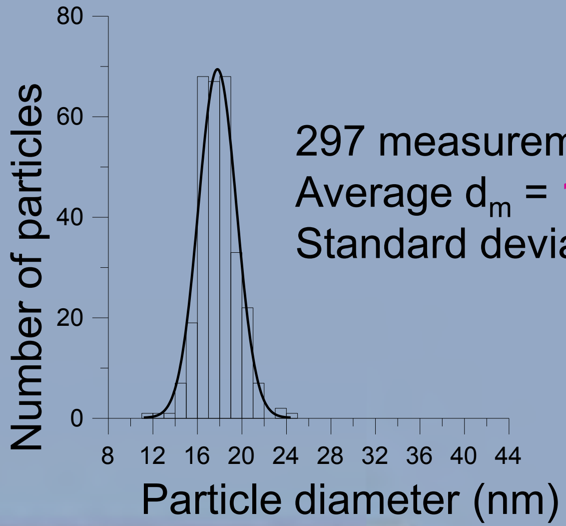




446 measurements
Average d_m = **26.2 nm**
Standard deviation = 3.78

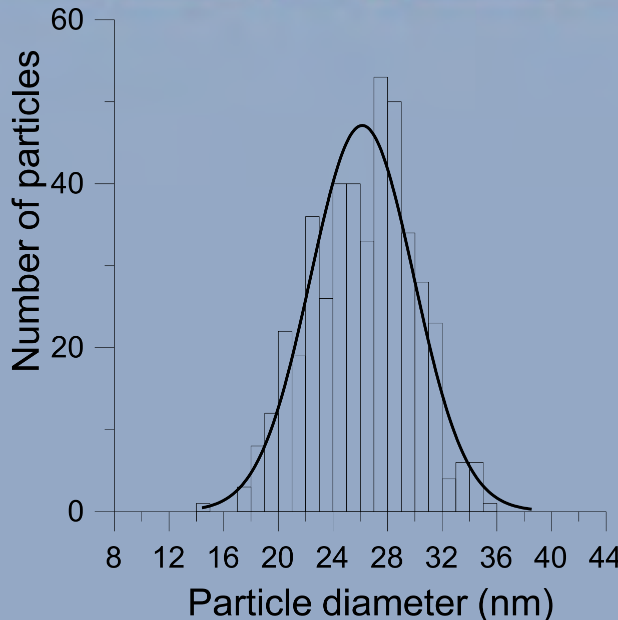
T_5 = 2000 K
P_5 = 1433kPa





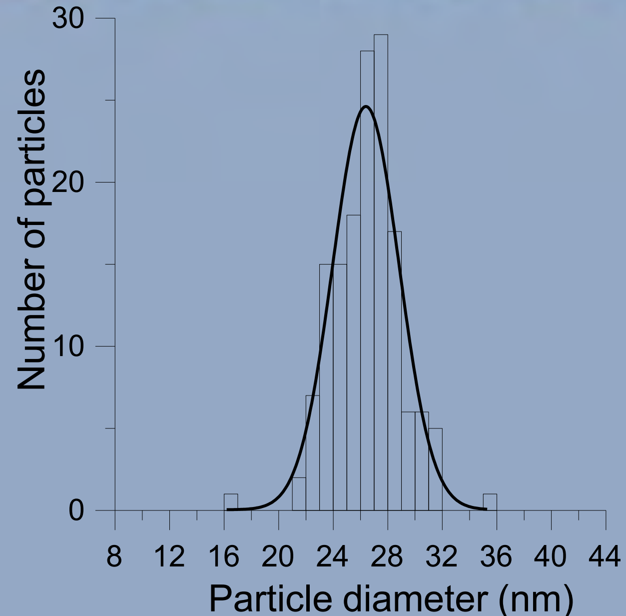
297 measurements
Average d_m = **17.9 nm**
Standard deviation = 1.71

TEM – Size distribution



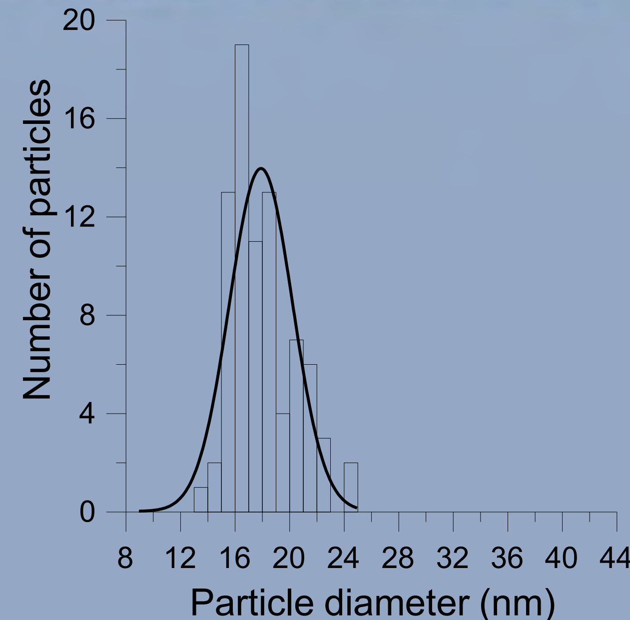
Toluene **Pyrolysis**
(T_5=**1700 K** ; P_5= 1714 kPa)

Nb of data points used : 446
Average d_m = **26.19 nm**
Standard deviation = 3.78



Toluene **Oxidation (ϕ=18)**
(T_5=**1685 K** ; P_5= 1802 kPa)

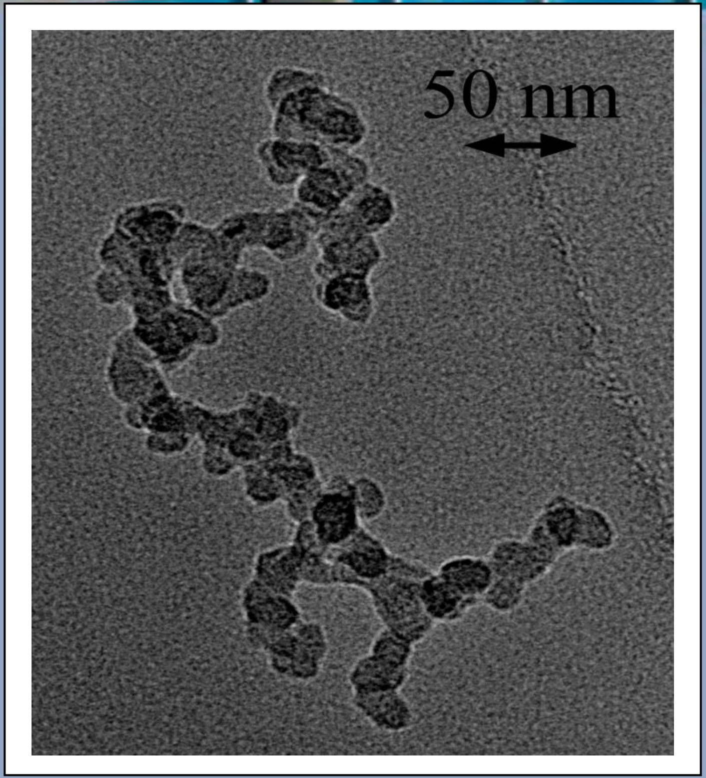
Nb of data points used : 150
Average d_m = **26.44 nm**
Standard deviation = 2.43

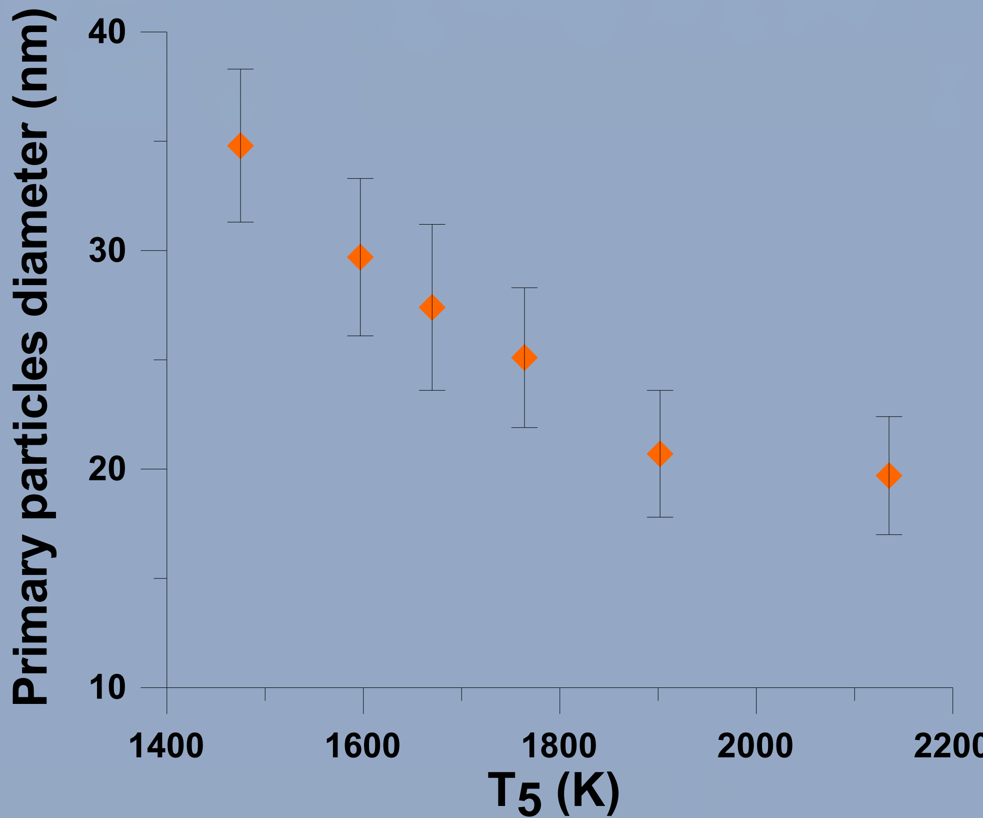


Toluene **Oxidation (ϕ=5)**
(T_5= **1685 K** ; P_5= 1266 kPa)

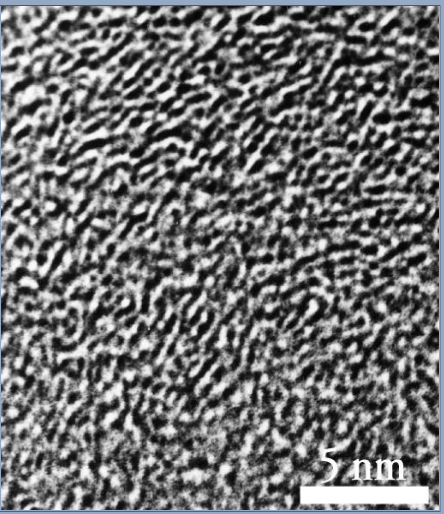
Nb of data points used : 81
Average d_m = **17.95 nm**
Standard deviation = 2.33

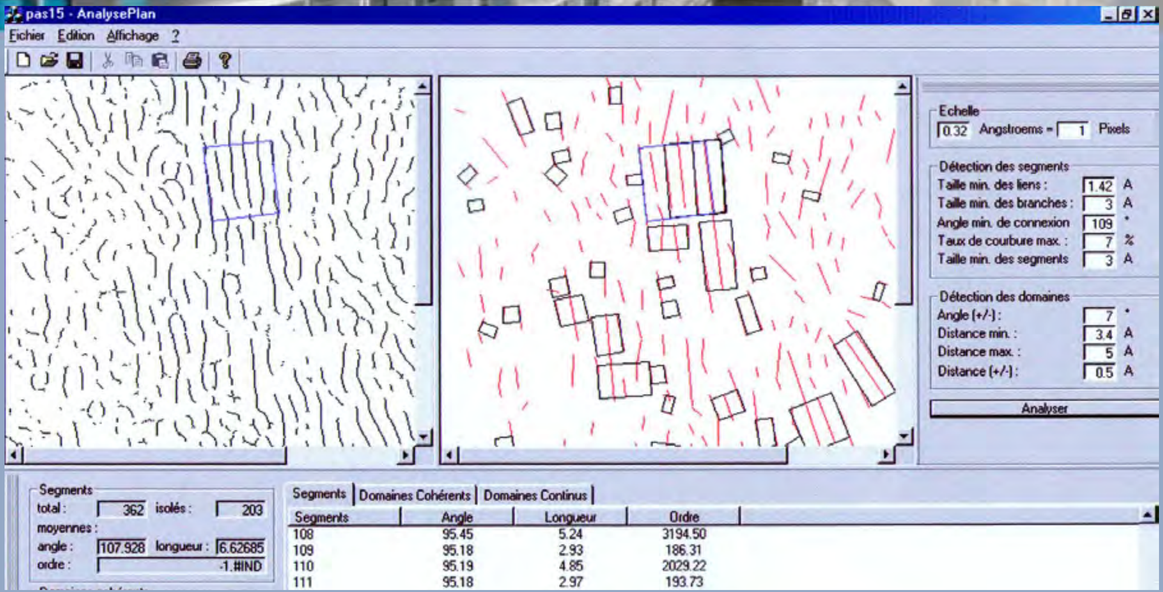
MET


50 nm


Primary particles diameter (nm)
40
30
20
10
1400
1600
1800
2000
2200
T_5 (K)

Microtexture and structure





Raw Image

% single layer

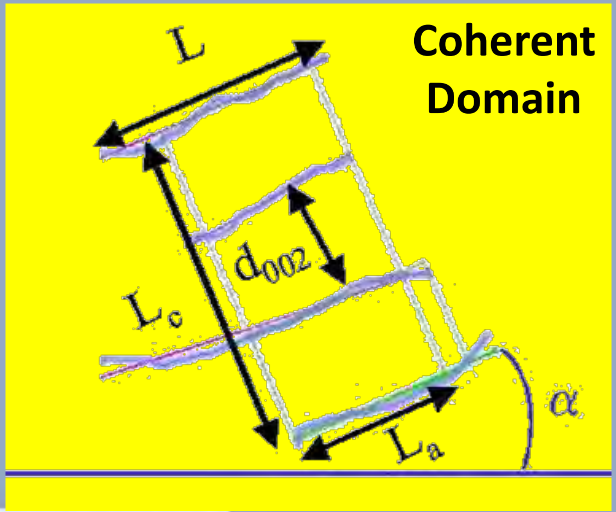
L : layer diameter

d_{002} : interlayer spacing

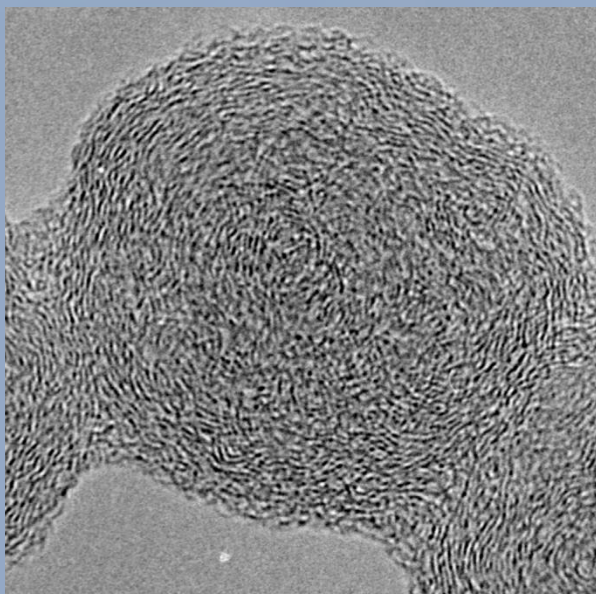
L_a : BSU diameter

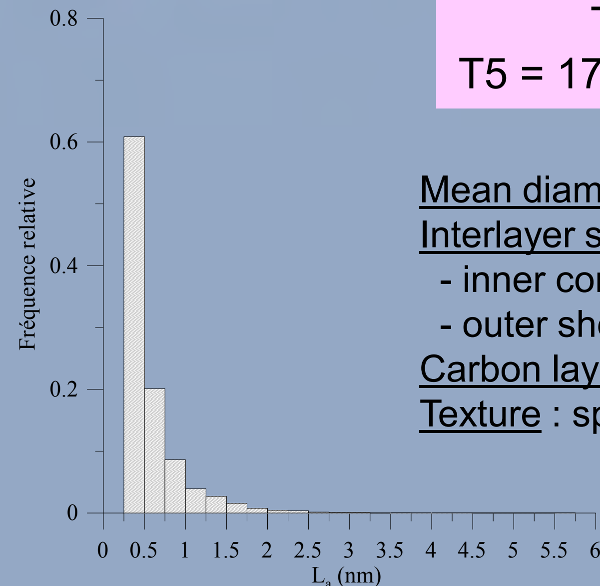
L_c : BSU height

α : desorientation degree



Layer Extension





Toluene/Argon
T5 = 1700 K ; P5 = 1714kPa

Toluene/Argon
1700 K, 1714 kPa
Thickness: 0.247 nm
La moy = 0.58 nm

Mean diameter : 26 nm
Interlayer spacing :
- inner core : 0.43 nm
- outer shell : 0.39 nm

Carbon layer : 0.58 nm
Texture : spherical, homogeneous

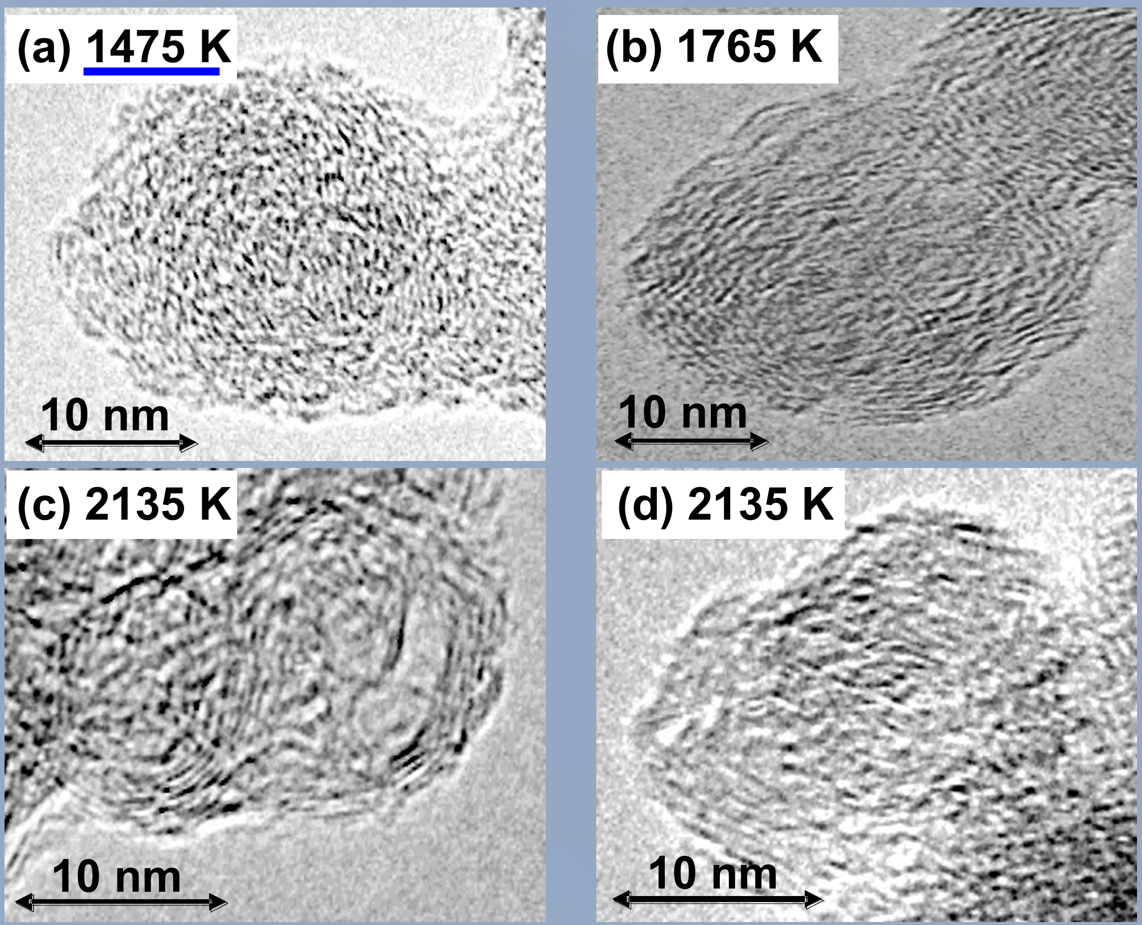
1% toluene + 99% Argon
T_5 = 1718 K, P_5 = 1720 kPa

Toluene/Argon
T5 = 2000 K ; P5 = 1433kPa

Mean diameter : 18 nm
Interlayer spacing :
- inner core : 0.39 nm
- outer shell : 0.39 nm

Carbon layer : 0.58 nm
Texture : spherical, homogeneous

5. Soot micro-structure



x 310 000

La = Lateral extension of the poly-aromatics layer.

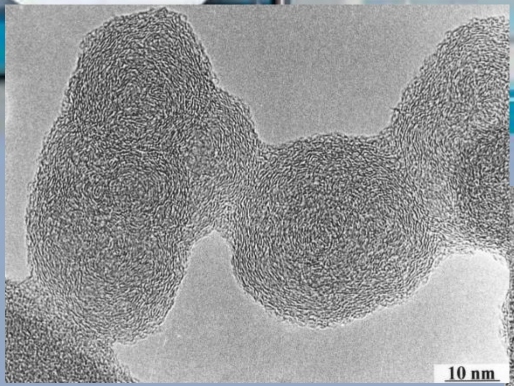
Interlayer spacing ➘ as the temperature of formation ➚ (Douce *et al*., *Proc. 4th Int. Conf. on Internal Comb. Engine*)

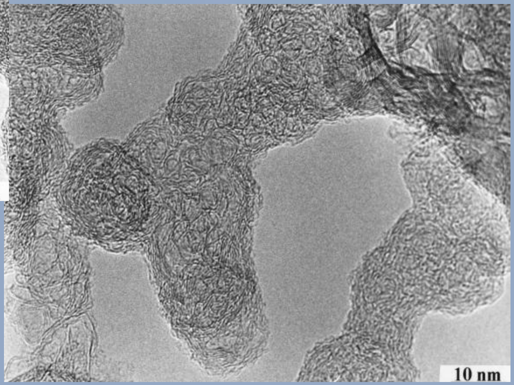
At 1475 K:

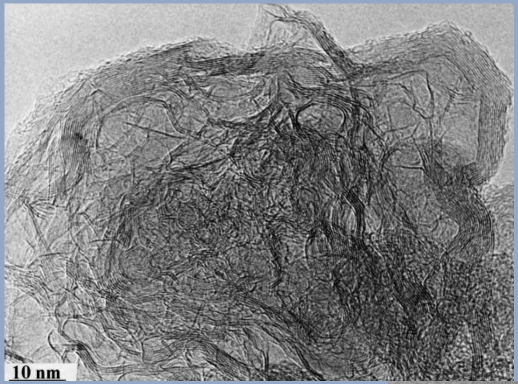
- Short La and low degree of organization

- Short La = important density of edge site carbon atoms ⇨ reactive surface (Vander Wal and Tomasek, *Comb. and Flame* 134, 2003)

Effect of Temperature on micr-structure







TEMPERATURE

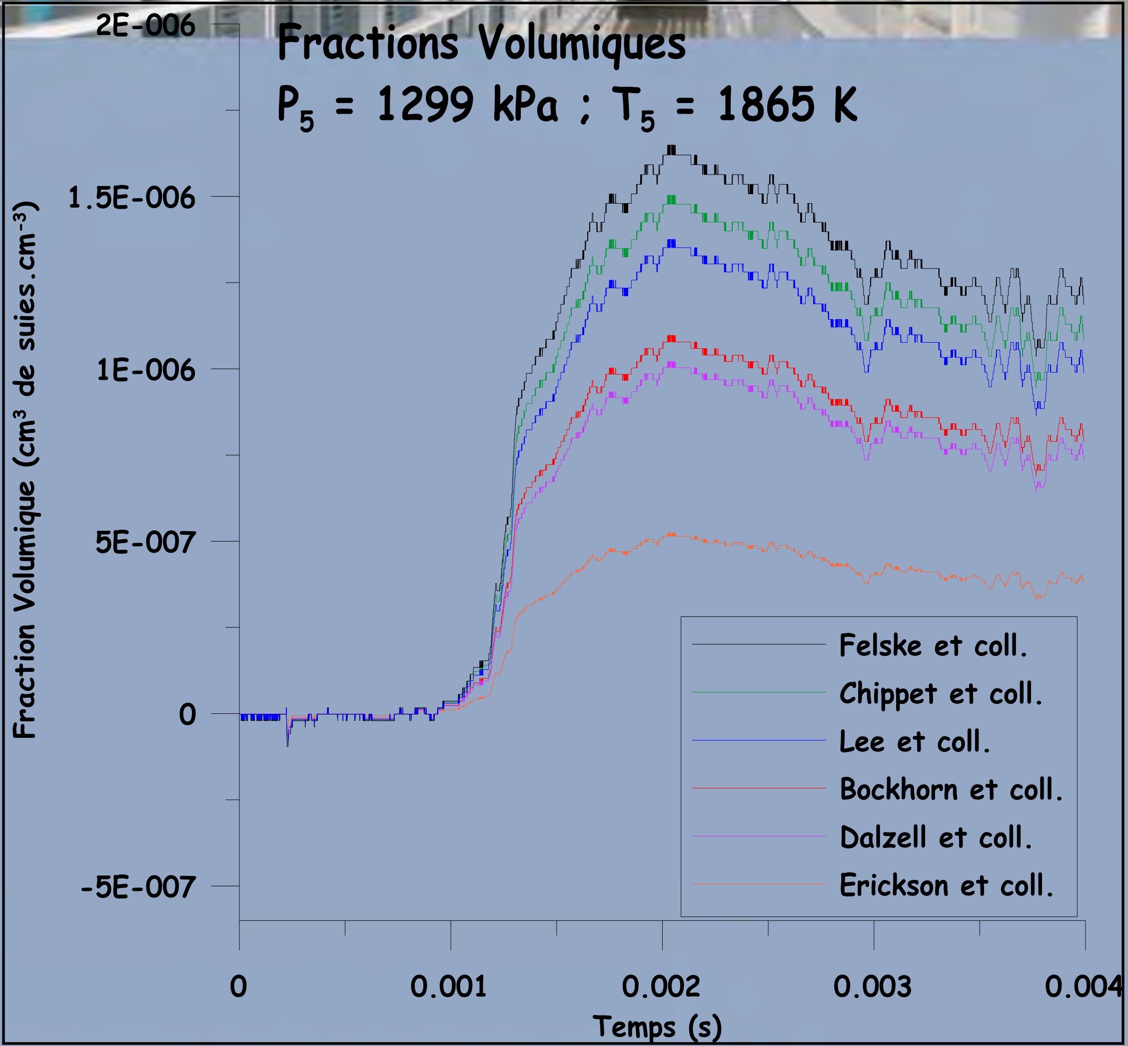
Optical Properties of Soot

Authors	Spectral Domain	Real Parti	Imaginary Part
Erickson et coll.	visible	1,4	1
Chippet et Gray	Visible	1,9-2,0	0,35-0,50
Bockhorn et coll.	Visible	1,1	0,37
Lee et Tien	Visible	1,8-2,0	0,45-0,65
Dalzel et Sarofim	Visible	1,57	0,56
Stagg et Charalampopoulos	633 nm	1,531±0,004	0,372±0,007
Mullins et Williams	633 nm	1,91±0,02	0,425±0,035
Chang et Charalampopoulos	Visible	1,94	0,6
Habib et Vervisch	600-650 nm	1,47	0,24±0,01
Vaglieco et coll.	637 nm	2,515	0,836
Felske et coll.	2-10 μ m	2,46±0, 15	0,8±0,14

Effect of soot refractive index on Fv

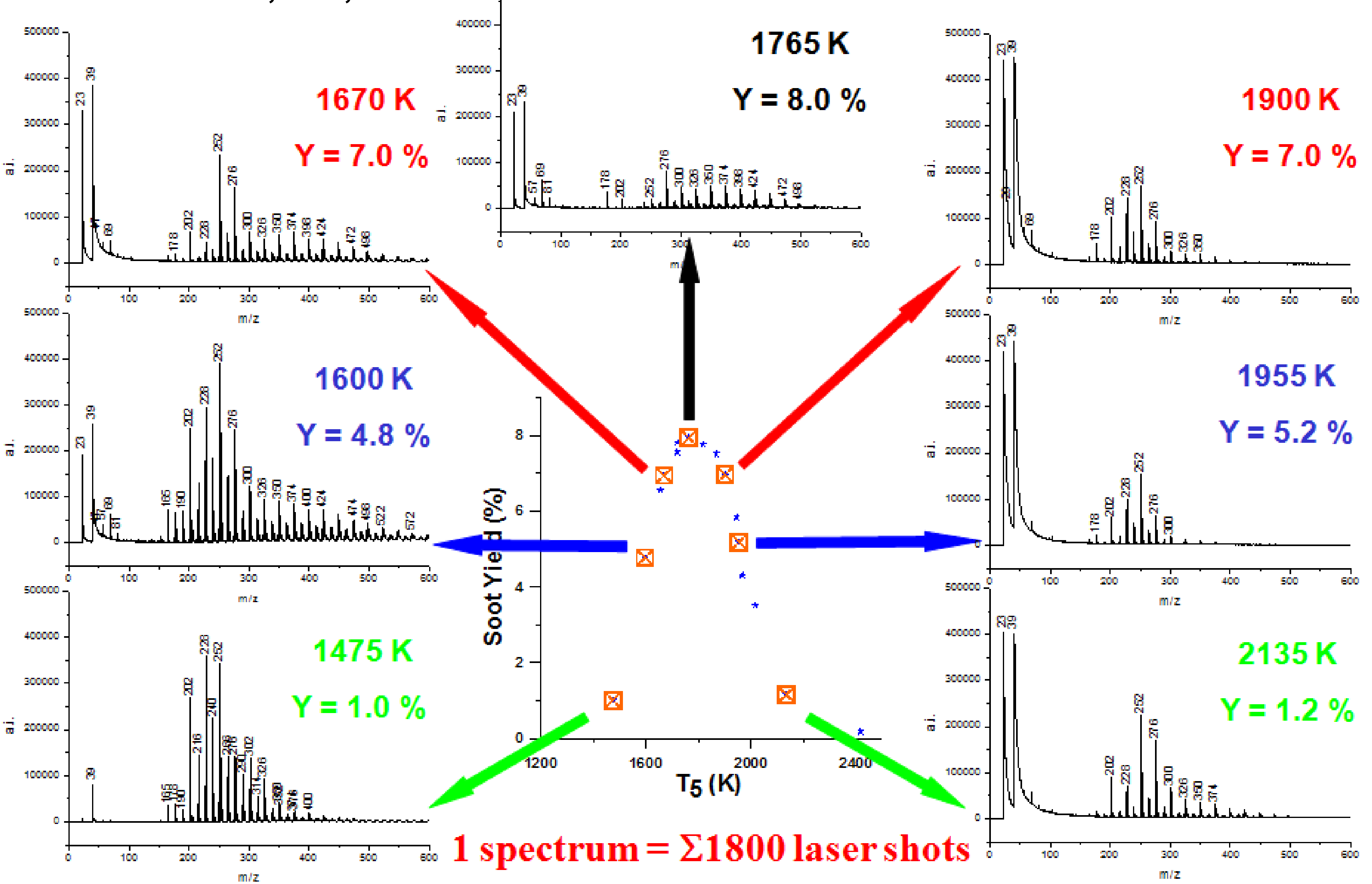
$$E(m) = -Im\left(\frac{m^2 - 1}{m^2 + 2}\right)$$

P_5 = 1299 kPa
T_5 = 1865 K
0,4% de n-décane
99,6% d 'argon
$[C]_{total} = 2{,}01.10^{18}$ at.C/cm^3



Species adsorbed on Soot

O. Mathieu et al, PCI, 2009



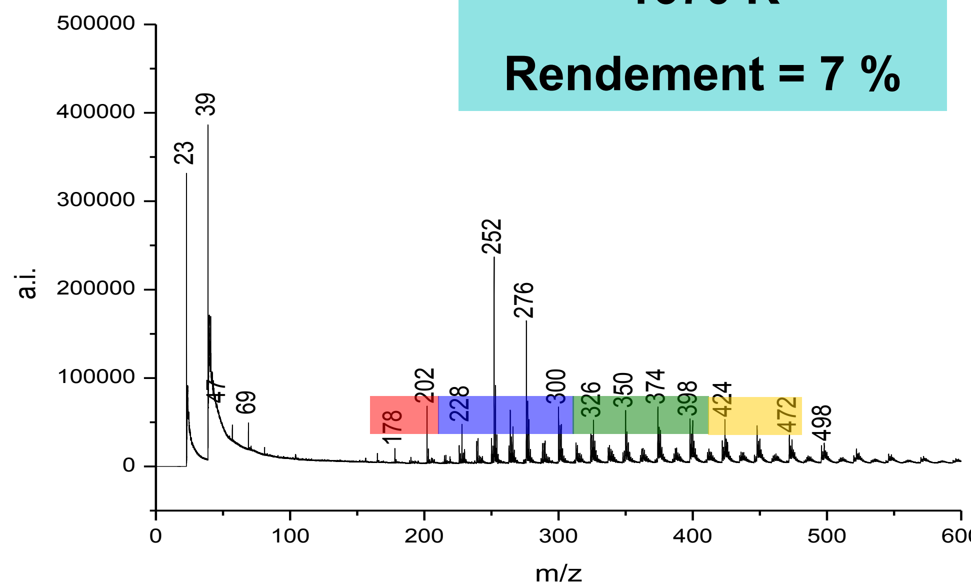
LDIToFMS Study

Mass increment sequences of 24 amu between major peaks interrupted by increment of 26 amu

Major Peaks are Benzenoïd

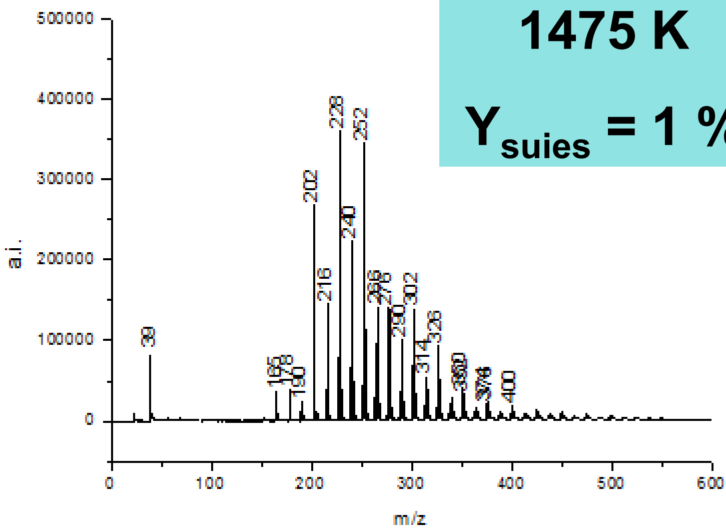
1670 K

Rendement = 7 %



1475 K

Y_{suies} = 1 %



Major Peaks:

- **Benzenoïd HAP : 202, 228, 252, 276…**
- **Non Benzenoïd HAP: 165, 190, 216, 240, 266, 290 & 314**

O. Mathieu et al, PCI, 2009

Orléans ICARE UPR n°3021 du CNRS

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Modeling Soot Formation in a Shock Tube

O. MATHIEU[1a], J. Z. WEN[2b], N. CHAUMEIX[1*], C.-E. PAILLARD[1] and M. J. THOMSON[2]

[1] C.N.R.S., France

[2]University of Toronto, Canada

[a] *Department of Mechanical Engineering, Texas A&M University, College Station, TX*

[b] University of Waterloo,

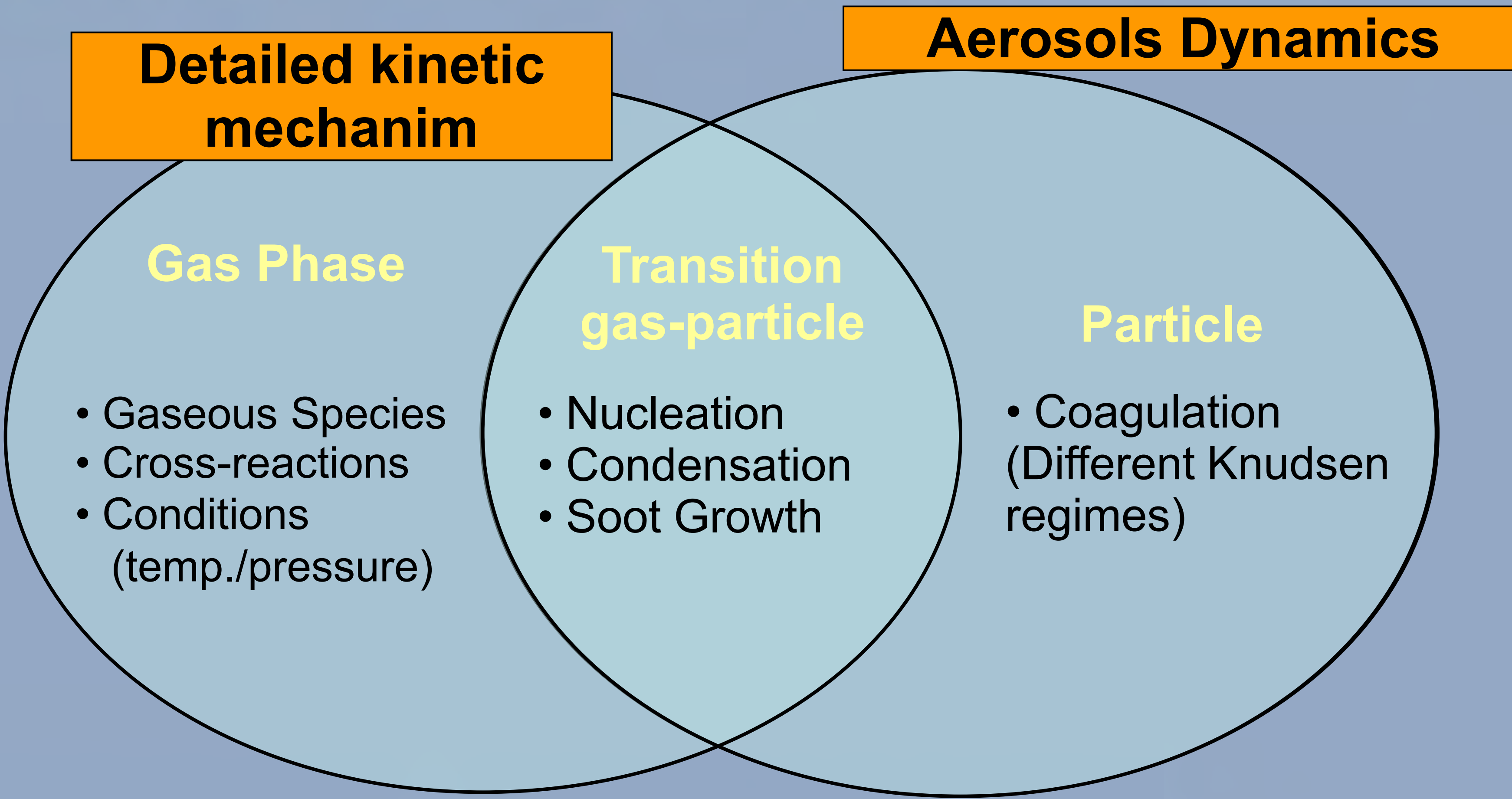
I nstitut de
C ombustion
Aérothermique
R éactivité et
E nvironnement

IENI

Consiglio Nazionale delle Ricerche

Istituto per l'Energetica e le Interfasi

Detailed kinetic model



J. Z. WEN et coll. *Energy and Fuels*, N° 20, 2006.

⇨ University of Toronto

Gas Phase

Initial gas phase mechanism includes the different possible pathways of soot formation [2]:

- **Complete set of Polycyclic Aromatic Hydrocarbons (PAH) formation pathways up to the pyrene,**
- **Reaction mechanism for acetylene pyrolysis**
- **Formation mechanism of polyynes molecules**
- **Formation mechanism of pure carbon cluster (C-C30).**

Initial mechanism: 151 species and 1123 reactions.

Modification (+ toluene sub-mechanism):

According to LDI-TOFMS, PAHs at least up to coronene ($C_{24}H_{12}$) are formed during toluene pyrolysis

⇨ addition of reactions from Richter et al. for benzenoid PAHS growth from pyrene to coronene.

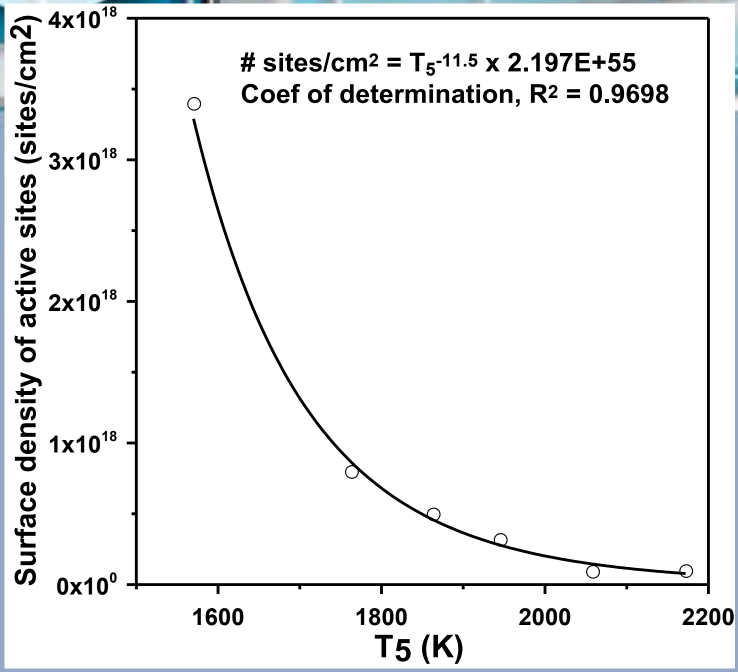
Coronene has a similar molecular formula than the first soot precursor (BIN1) ⇨ Continous PAH growth up to BIN1

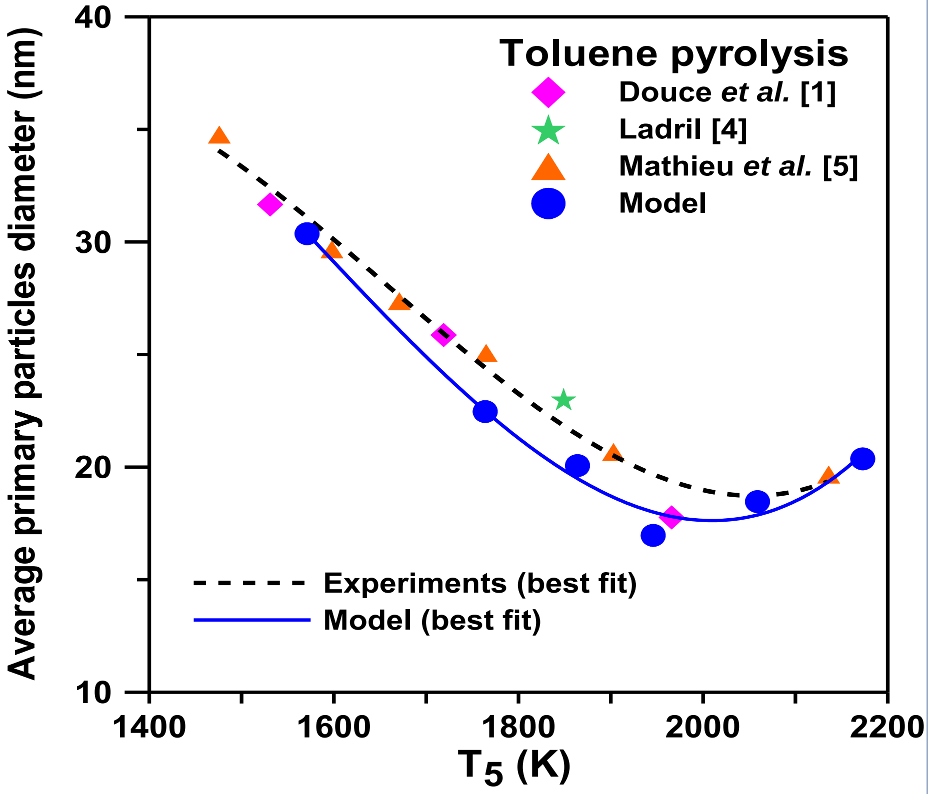
Final mechanism: 194 species and 1626 reactions.

No.	Mass (amu)	formula	Σ (nm)	H/C
BIN1	201-400	$C_{24}H_{12}$	0.85	0.5
BIN2	401-800	$C_{48}H_{24}$	1.07	0.5
BIN3	801-1600	$C_{96}H_{48}$	1.34	0.5
PIN1	195-390	$C_{24}H_{4}$	~0.85	0.167
PIN2	391-778	$C_{48}H_{8}$	~1.07	0.167
PIN3	779-1558	$C_{96}H_{16}$	~1.34	0.167

O. Mathieu et al, ECM, 2009

Evolution of the Active Sites

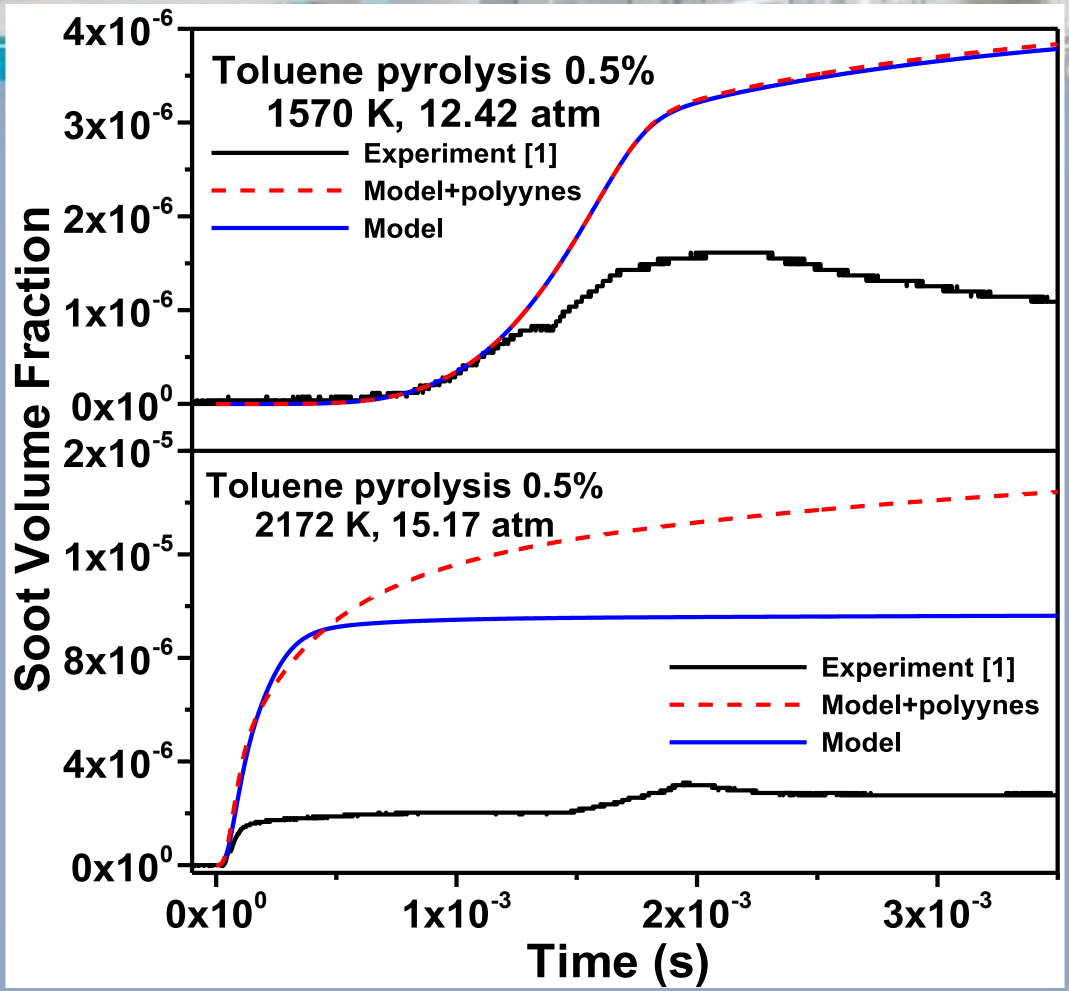




Number density of active surface sites adjusted to obtain values of induction delay time and mean primary particles diameter comparable with exp. measurements. Evolution of the active sites density with temperature in agreement with TEM observations [5].

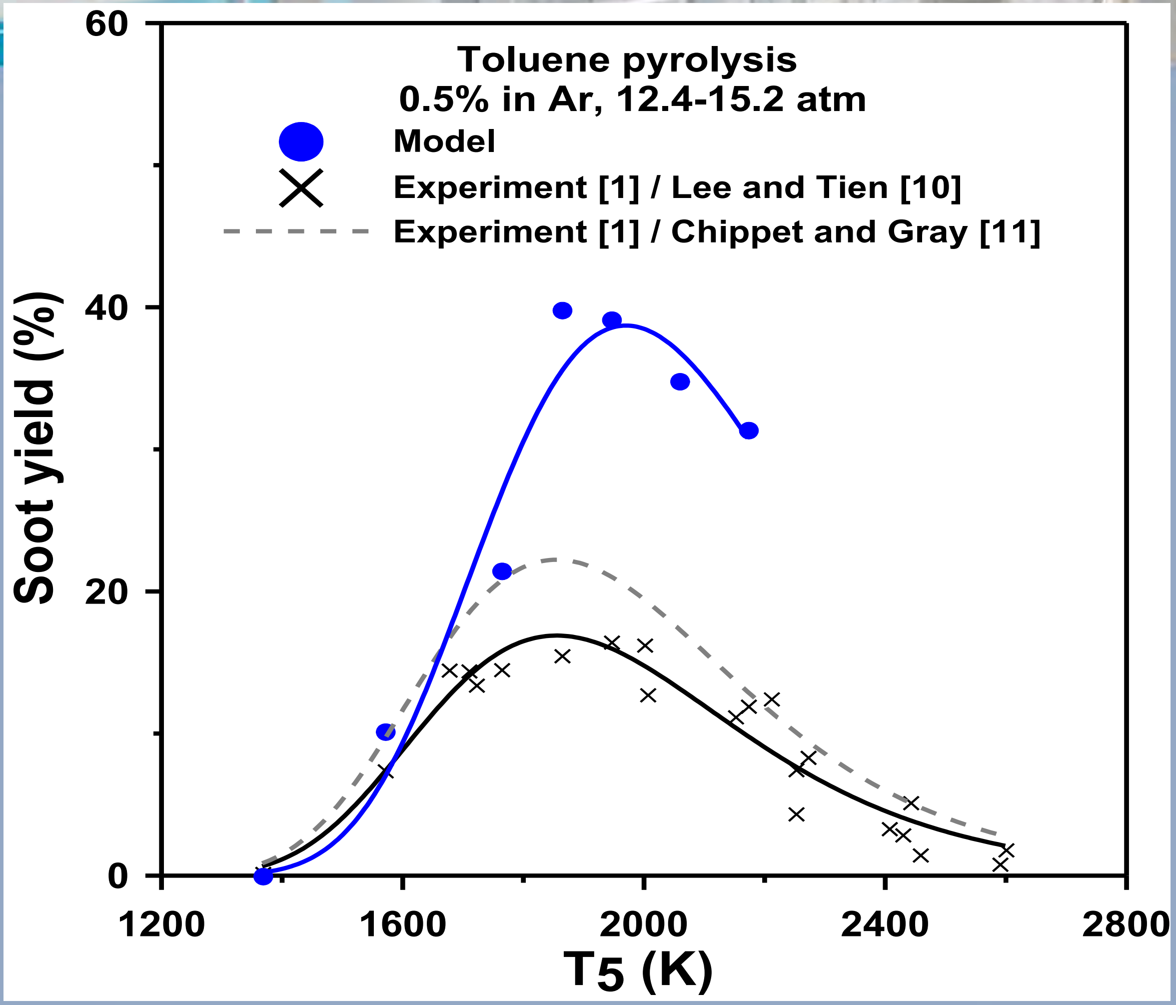
O. Mathieu et al, ECM, 2009

Main Results



O. Mathieu et al, ECM, 2009

Main Results



O. Mathieu et al, ECM, 2009

Effect of Hydrogen addition on Soot Formation in a Shock Tube

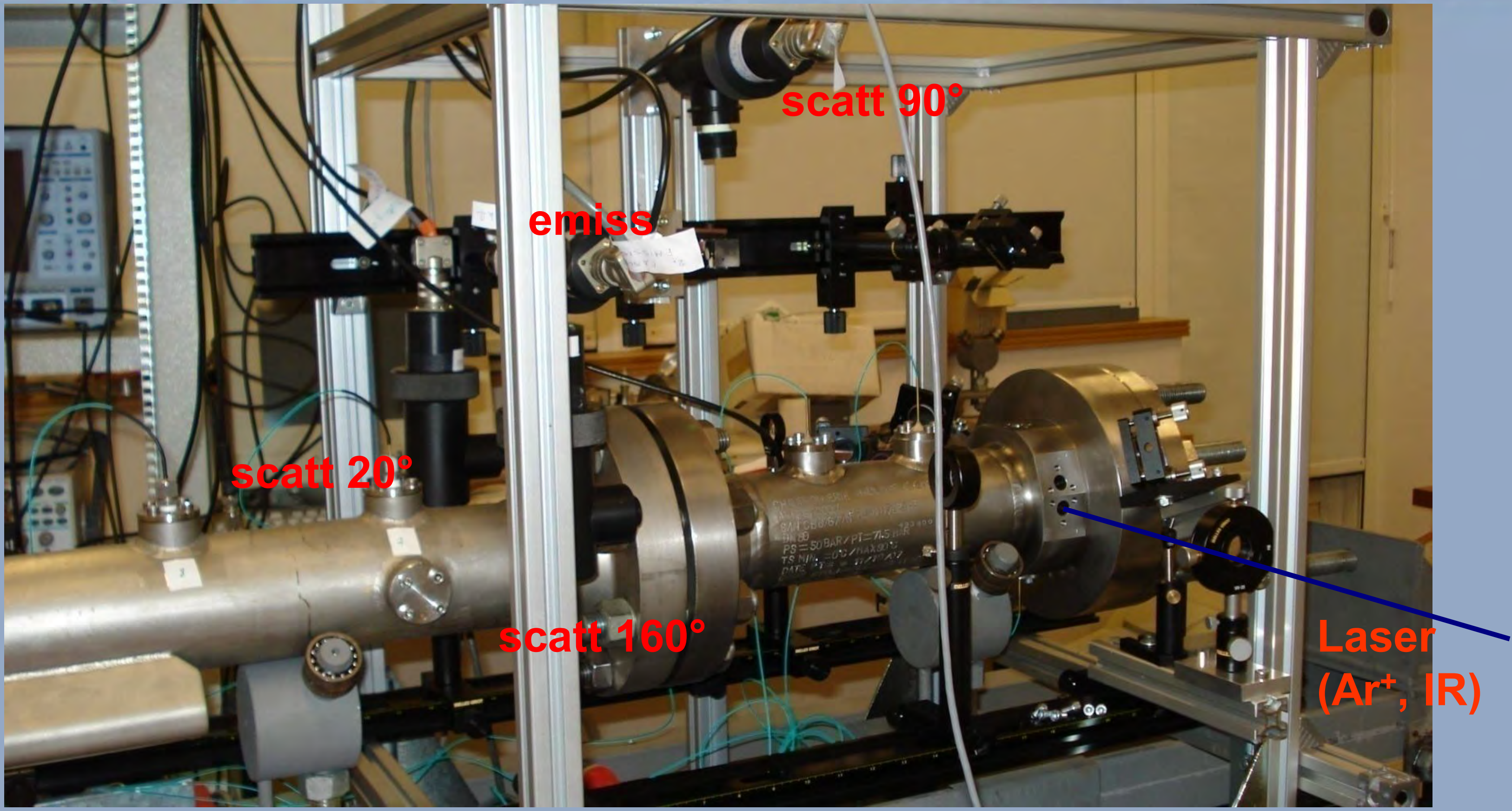
S. De Iuliis*, N. Chaumeix**, M. Idir**,
G. Zizak*, C.-E. Paillard**, A. Coghe***

*CNR-IENI, Milano, Italy
** CNRS-ICARE et Universitè d'Orleans, France
***POLIMI, Milano, Italy

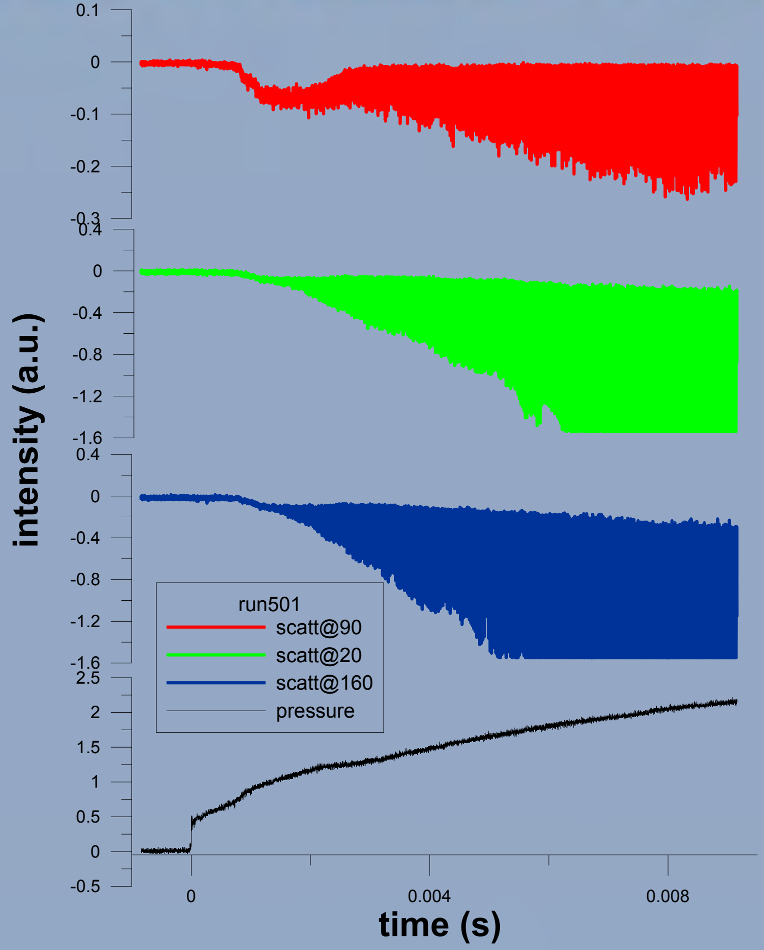
Consiglio Nazionale delle Ricerche
Istituto per l'Energetica e le Interfasi

I nstitut de
C ombustion
Aérothermique
R éactivité et
E nvironnement

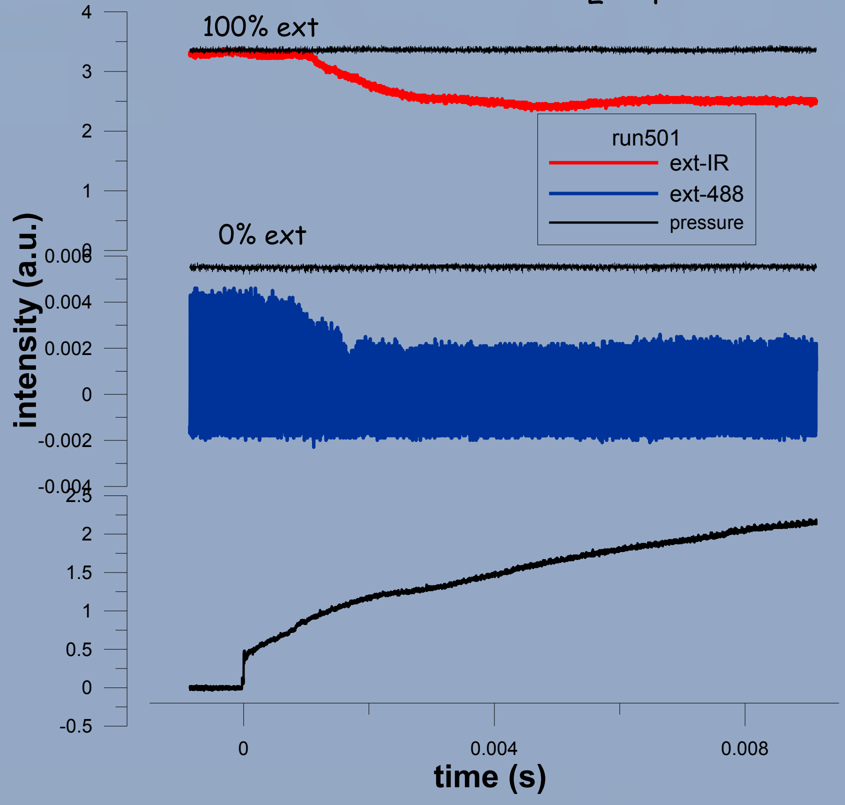
Shock tube with Ø = 87.4 mm



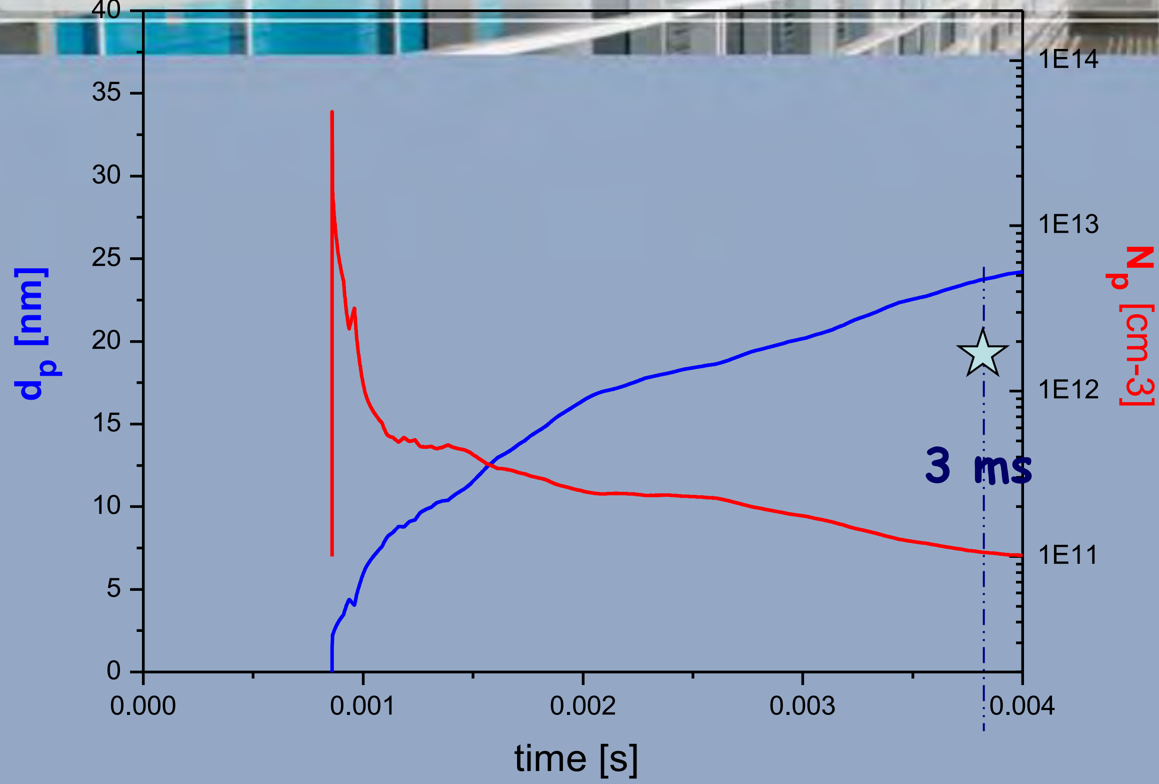
Typical time-resolved extinction/scattering measurements, raw data



2% C_2H_4 in Ar



Soot Particles Parameters : N_p, d_m



✓ Growth characterized by two different rates (the faster at the beginning of soot nucleation).

✓ The number density presents a fast increase due to soot nucleation, followed by a decrease due to coagulation mechanisms.

ICARE Orléans UPR n°3021 du CNRS

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

This work has been carried out thanks to
A. Barret, D. Darius, F. Douce,
D. Ladril, O. Mathieu, T. M'Boko,
J. Wen, M. Yahyaoui, S. De Iuliis, ….

Funded by

TOTAL, PSA-Peugeot Citroen, CNRS, European Community

Collaboration with

CNR-Milano, Polimi, U. of Totonto