

Direct Soot Formation

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14th ETH Conference on Combustion Generated Particles
August 1st – 4th, 2010

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Measurements show, that inside an aircraft gas turbine combustor, the soot concentration can be much higher than at combustor exit. The high soot concentrations inside the combustor can not be explained by HACA soot formation mechanism (Hydrogen Abstraction Carbon Addition). Therefore a new soot formation mechanism is suggested and discussed. I call it "Direct Soot Mechanism".

Jet fuel contains aliphatic molecules from C8 to C16. In a gas turbine combustor, the fuel spray is injected into hot compressed air. Fuel molecules vaporize from the spray droplets and heat up by heat transfer and flame radiation, before reaching the flame zone. Some fuel molecules crack by pyrolysis and built radicals and ions. These radicals and ions can recombine and built first clusters. If this happens, soot formation can start before the fuel molecules reach the flame region!

But the main part of soot formation takes place inside the flame, in fuel rich zones. Fuel molecules are cracked by pyrolysis and oxidation. This results in high concentrations of fuel-radicals and fuel-ions. The recombination of this radicals and ions built first clusters (fig. 1). These first clusters have very low density. The formation of the first soot particles in the flame results from further cluster growth, cluster agglomeration and cluster densification. The densification is a result of

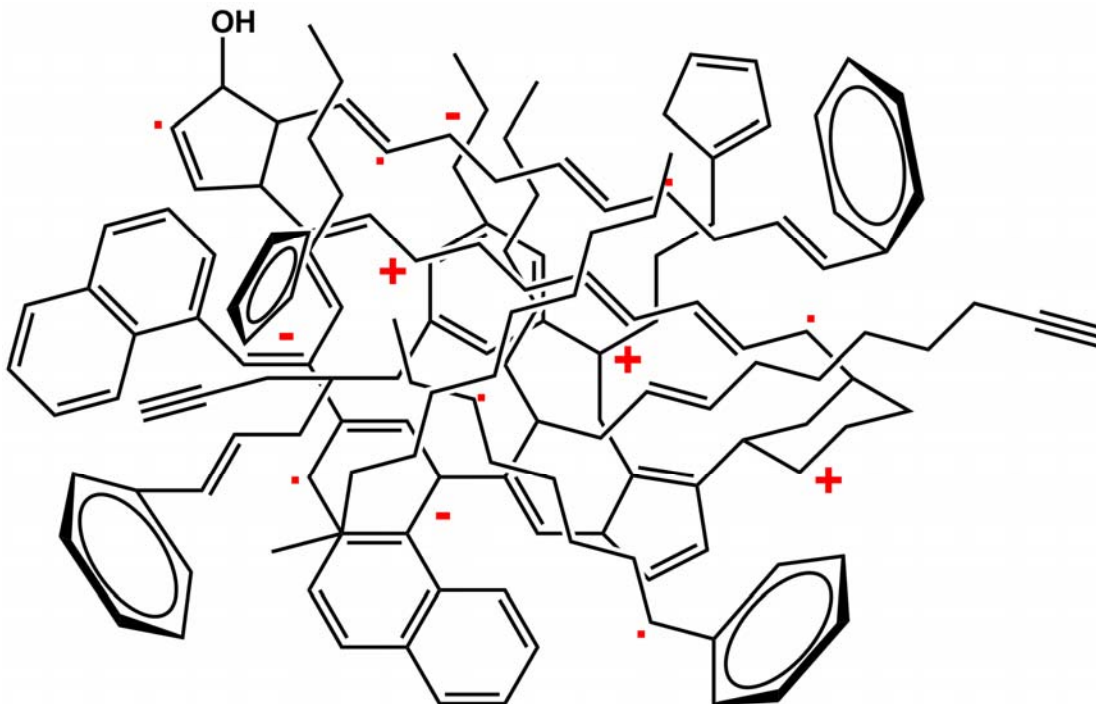


Fig. 1: Soot Cluster

the formation of more and more C=C double bonds and the formation of new C-C bonds inside the cluster. The aliphatic side branches of the particles are burned. At the end, the density and C/H ratio of the soot particles is a function of residence time, temperature and phi history. Densification and graphitization takes place on the way through the combustor. At combustor exit we see the well known soot particles.

In the direct soot formation mechanism, it is not necessary to crack the fuel down to acetylene to built the first aromatic rings. Aromatic rings can be formed directly via aliphatic rings (fig. 2).

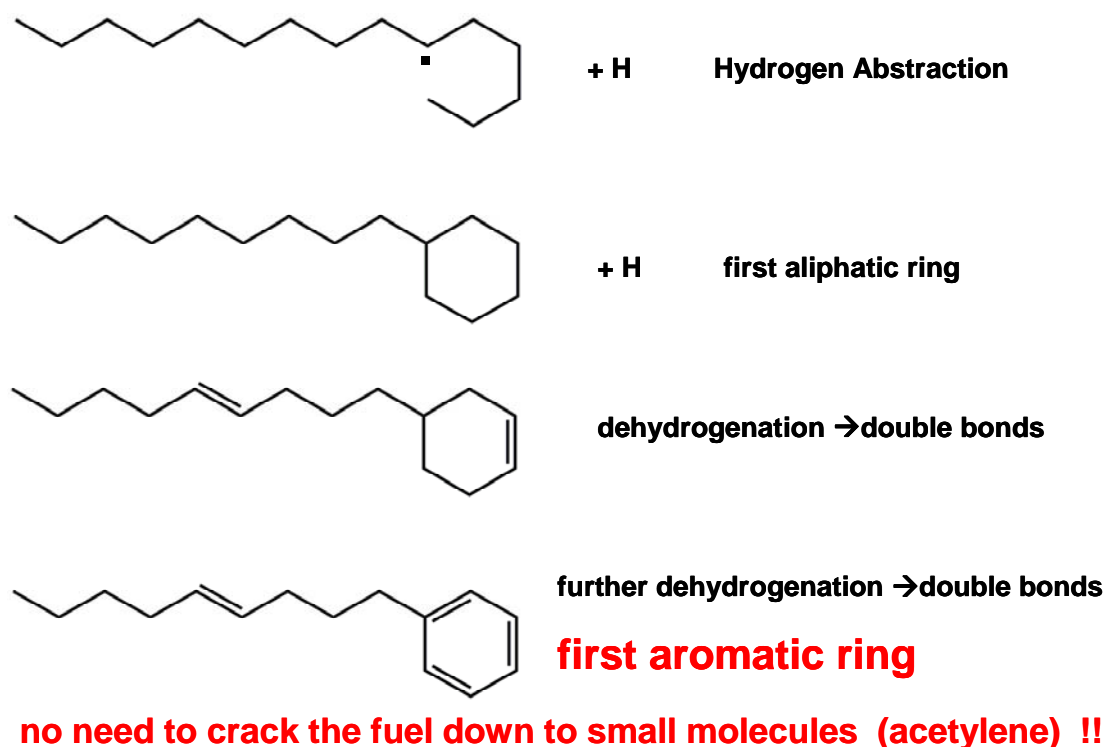
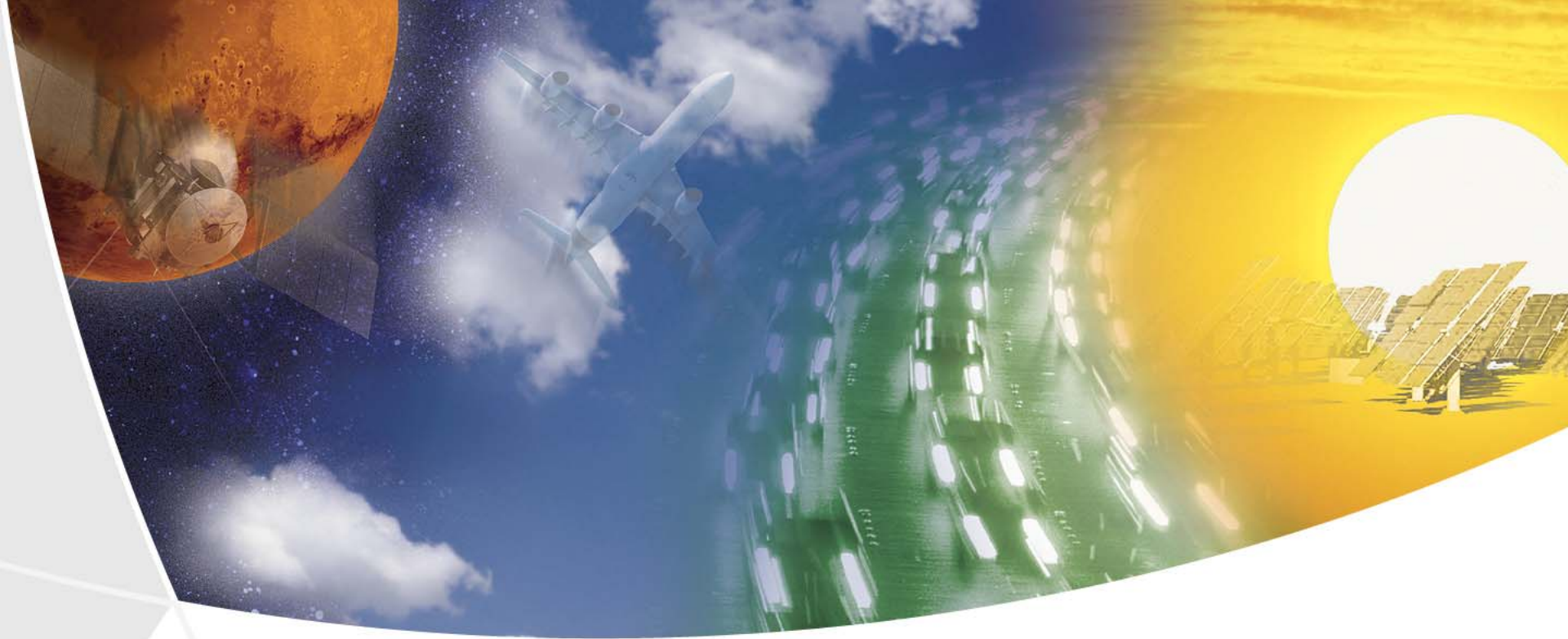


Fig. 2 Formation of first aromatic ring via aliphatic ring

“Direct Soot” is a complex, low density, three dimensional polymer of fuel molecules. During the way through the combustor, “direct soot” is transformed to soot particles. With the “Direct Soot Mechanism”, it is easy to explain fast soot formation from fuel molecules to soot particles.



Direct Soot Formation

in kerosene and diesel combustion

Claus Wahl

14th ETH Conference on Combustion Generated Nanoparticles

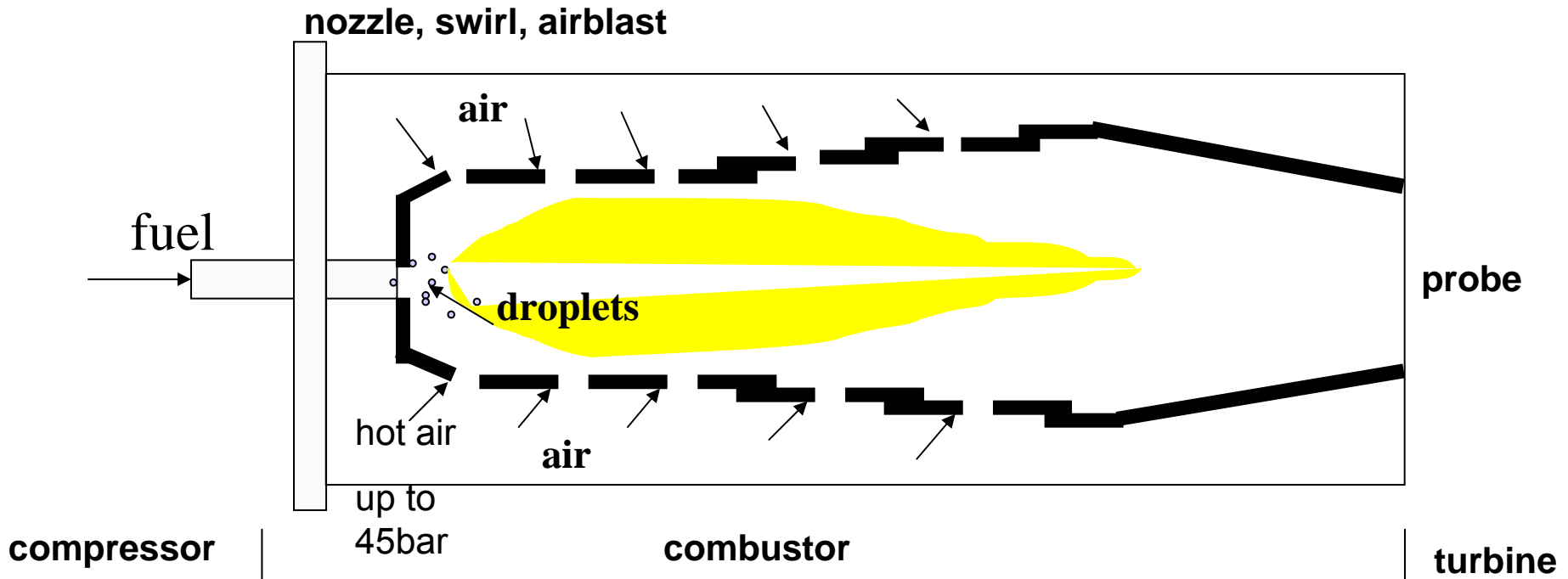


Deutsches Zentrum
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in der Helmholtz-Gemeinschaft

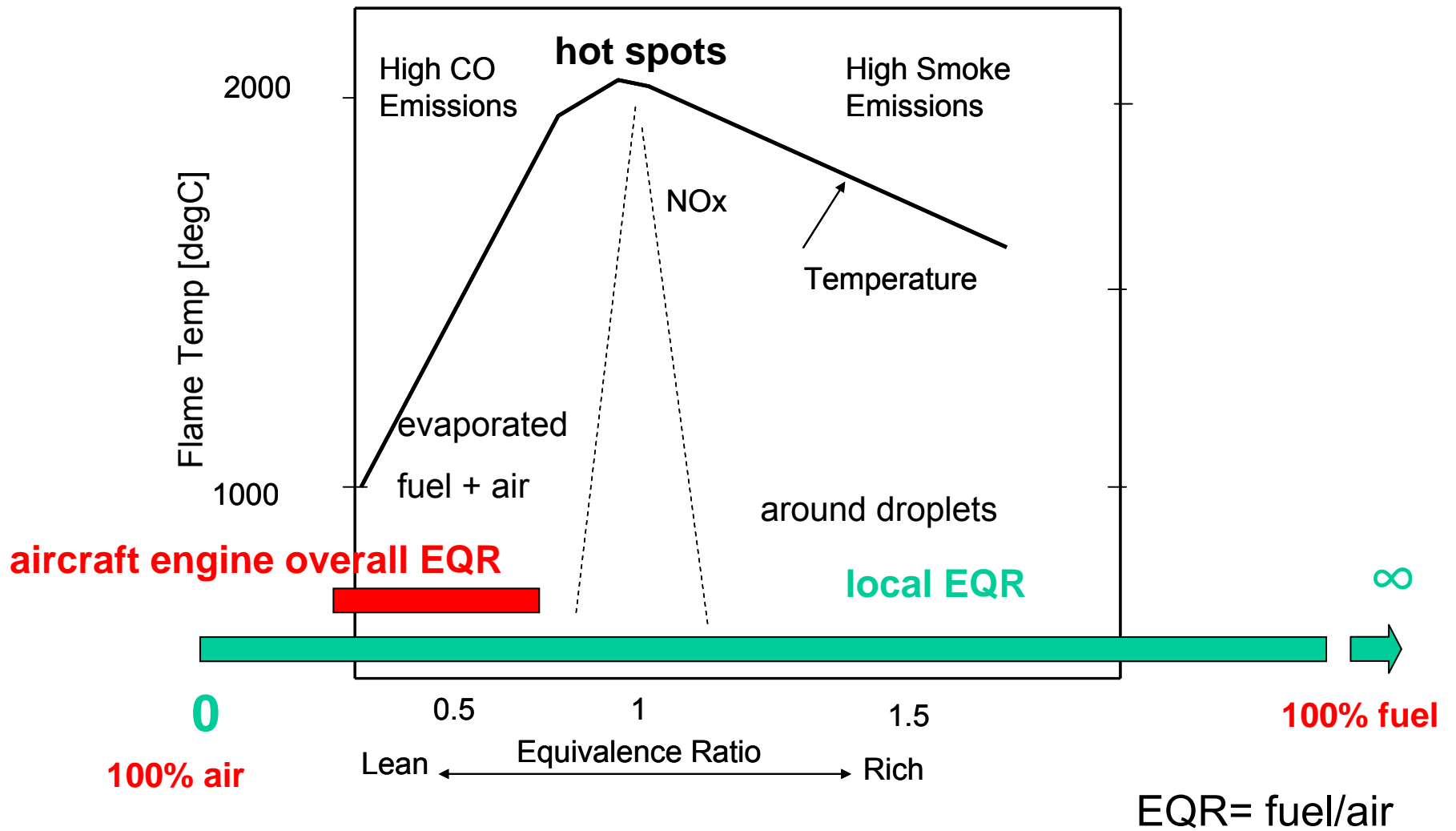
Gas Turbines show no visible soot, even at “Take Off”



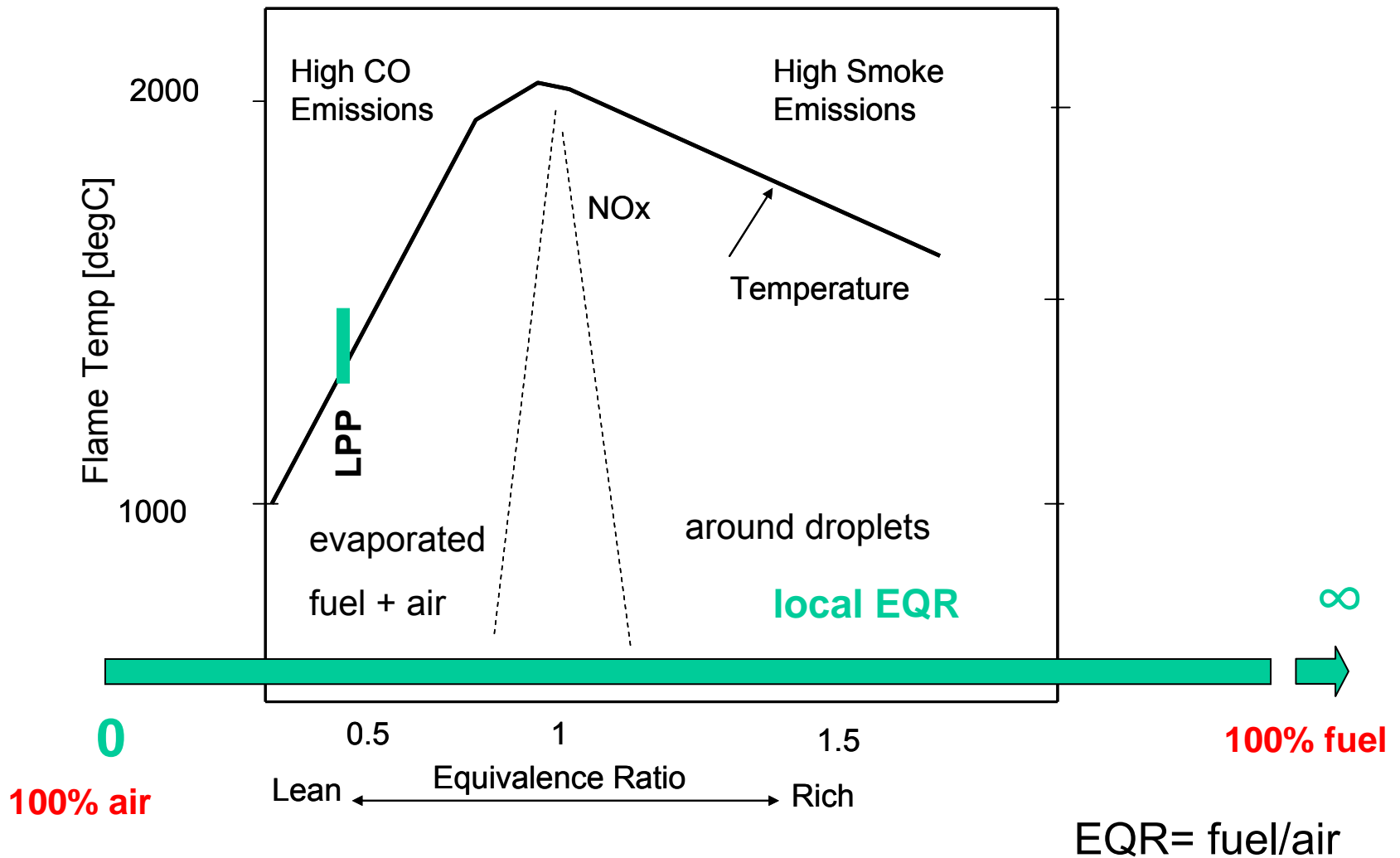
GT-Combustor tubular or annular



diffusion flame with local fuel rich flame zones



Diffusion Flame

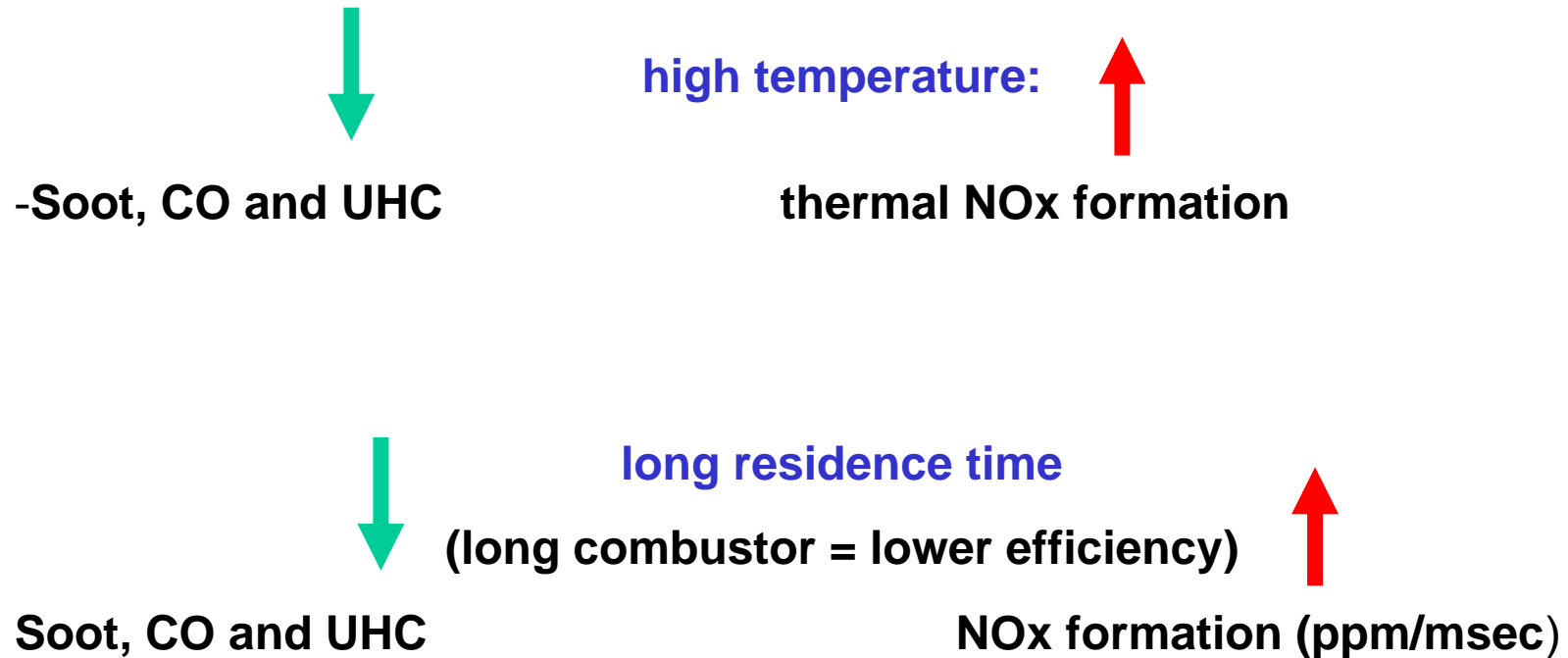




Soot is a Mixing Problem !

- liquid fuel is injected as droplet into the combustor
 - only the evaporated and air mixed fuel can be ignited
 - **soot is formed in local fuel rich flame zones around the droplets**
 - particles move on the **“coldest trajectory”** through the combustor
 - in the flame there is:
 - soot formation and surface growth
 - soot oxidation
 - soot agglomeration, aggregation
 - soot densification
 - pollutant formation
 - and fuel oxidation
- all in parallel

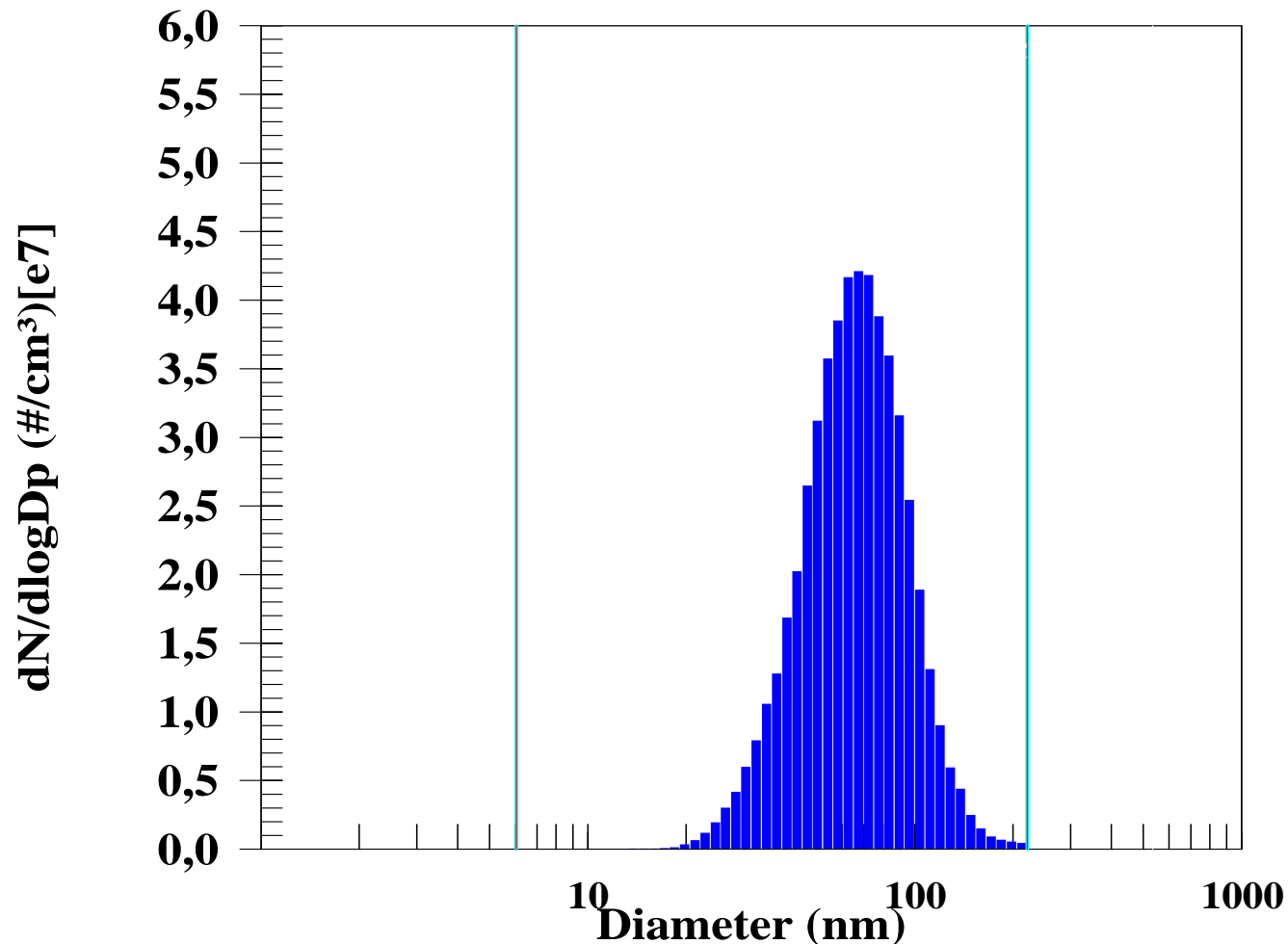
Pollutants as a Function of Combustor Design



combustor concepts: tubular, annular, dual annular, staged
LPP, RQL,



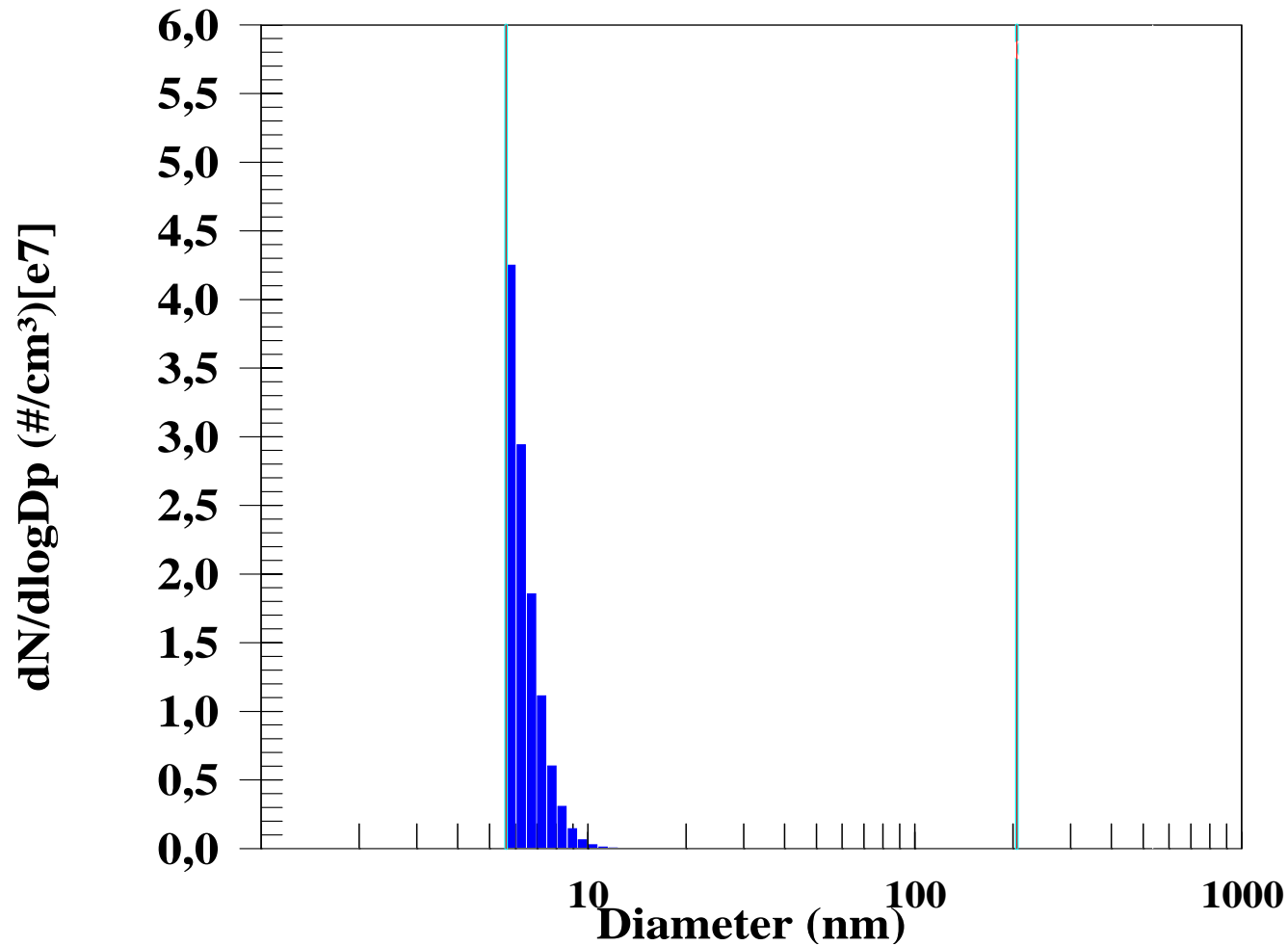
Candle / probe in the flame zone



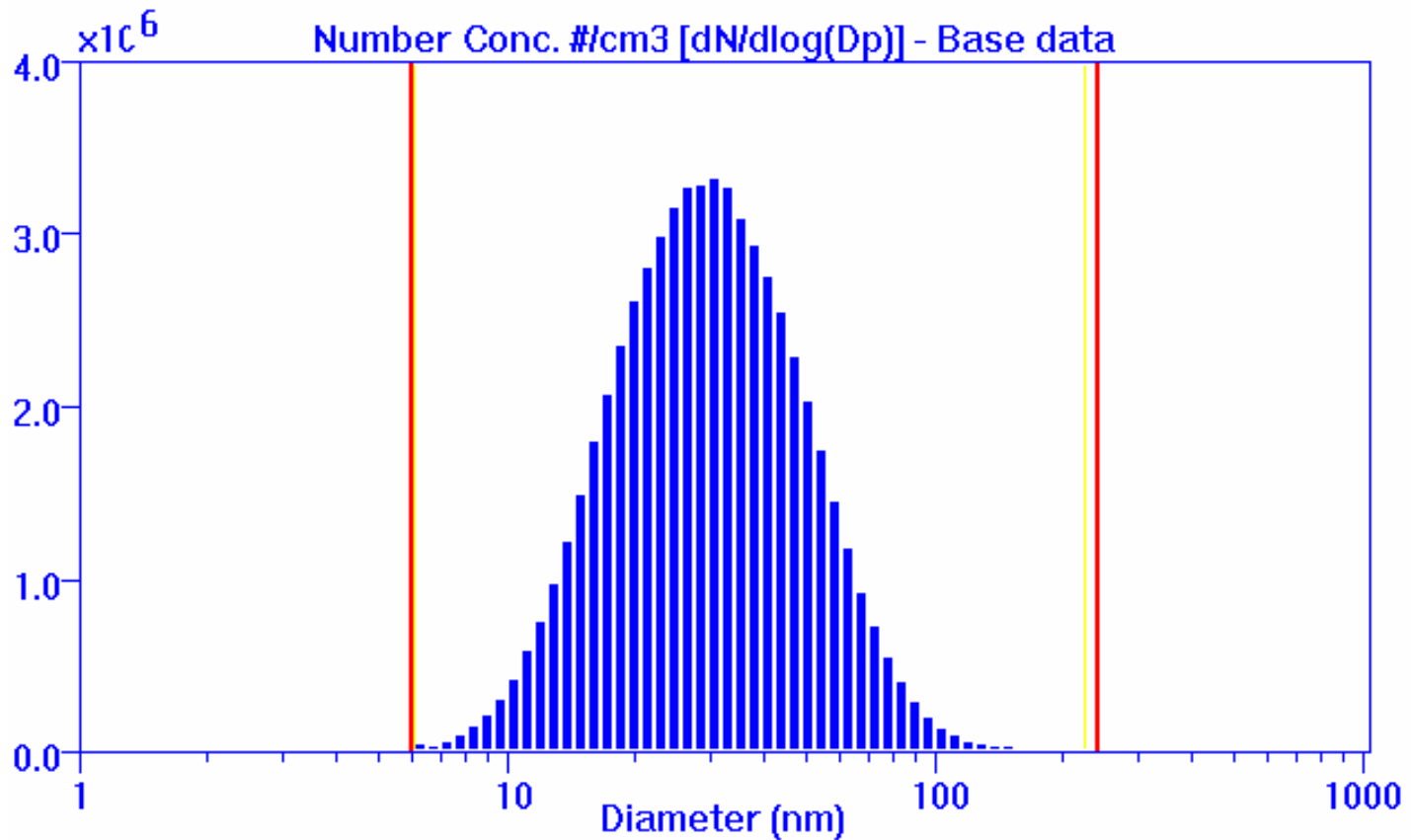
Candle with “ long combustor” (long residence time)



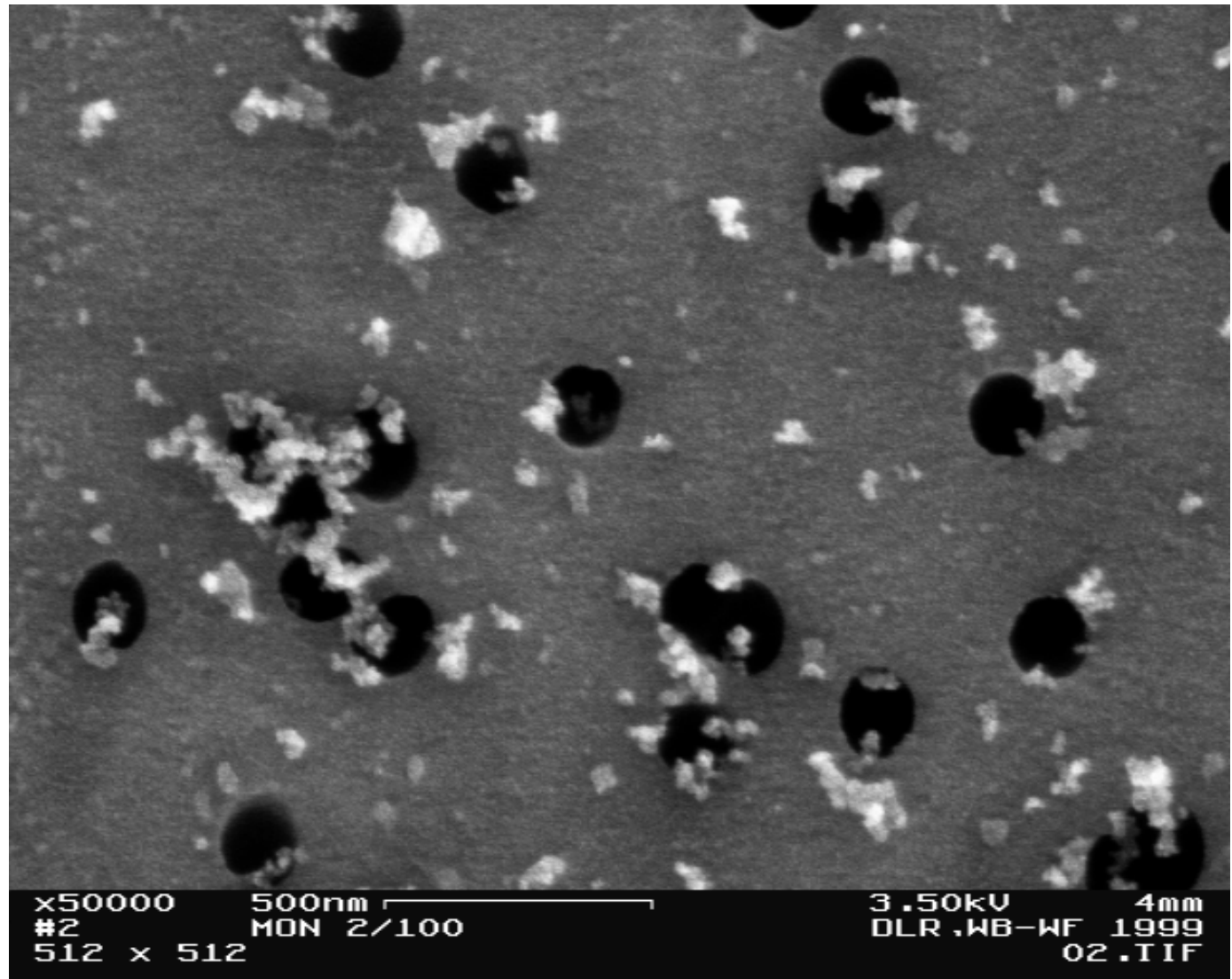
Candle with “ long combustor” (long residence time)



Particle Size Distribution / Approach



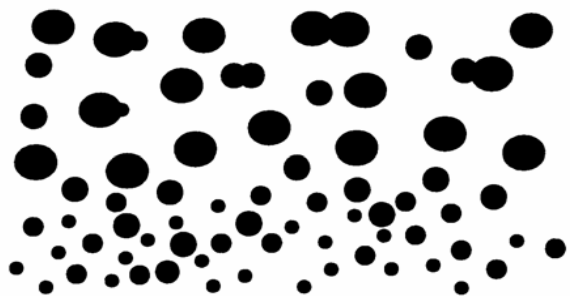
SEM picture / Approach



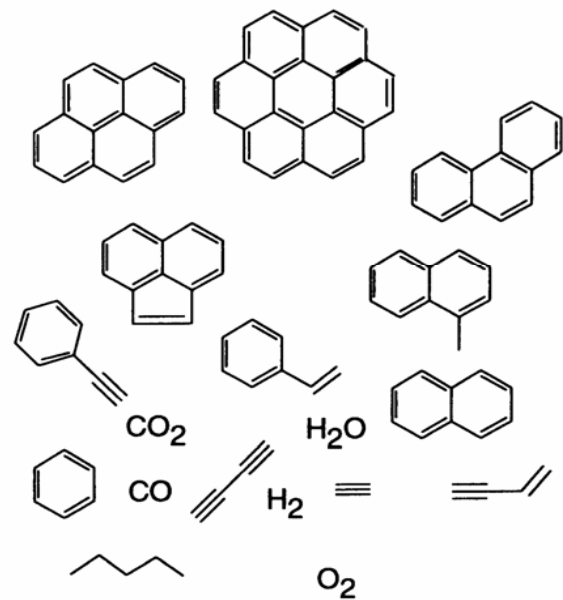
all SEM pictures
are done by

Roland Borath,
DLR, WB-WF





← soot formation gap



growth by HACA mechanism

formation of first aromatic ring

cracking of fuel to small molecules and radicals

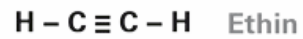
Bockhorn, H. 1994

time consuming steps

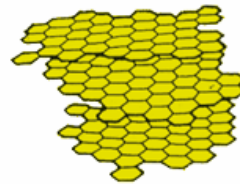


Kraftstoff

↓ **Verbrennung**

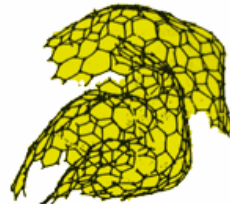


aromatische
Kohlenwasserstoffe



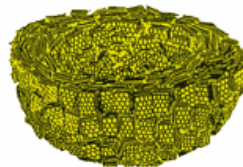
graphitähnliche
Rußteilchen

↓ **Koagulation**



Primärrußteilchen

↓ **Agglomeration**



Rußpartikel

Abbildung: Schematische Darstellung der Bildung von Rußpartikeln (nach Siegmann und Siegmann, 1999).



Existing Soot Formation Mechanisms

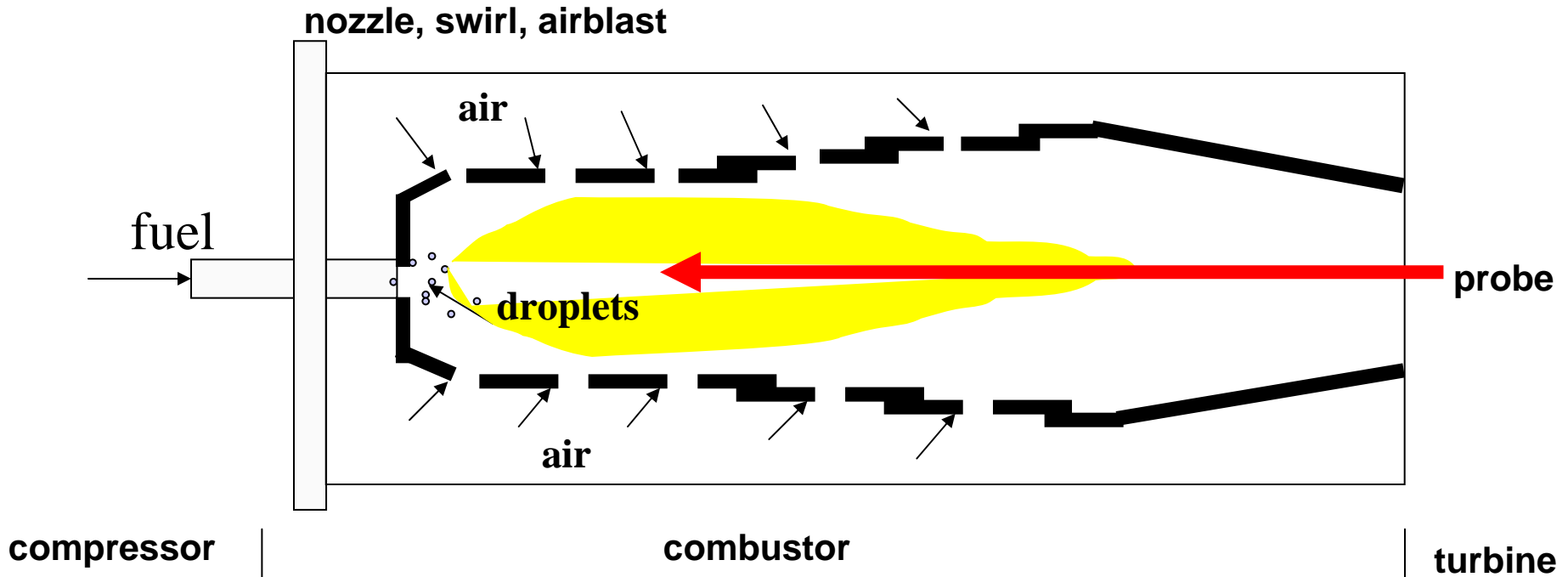
-all soot formation mechanisms “cut” fuel molecules down to small molecules like acetylene

- Soot formation starts with first aromatic rings made from acetylene

this may be true, but only for acetylene flames



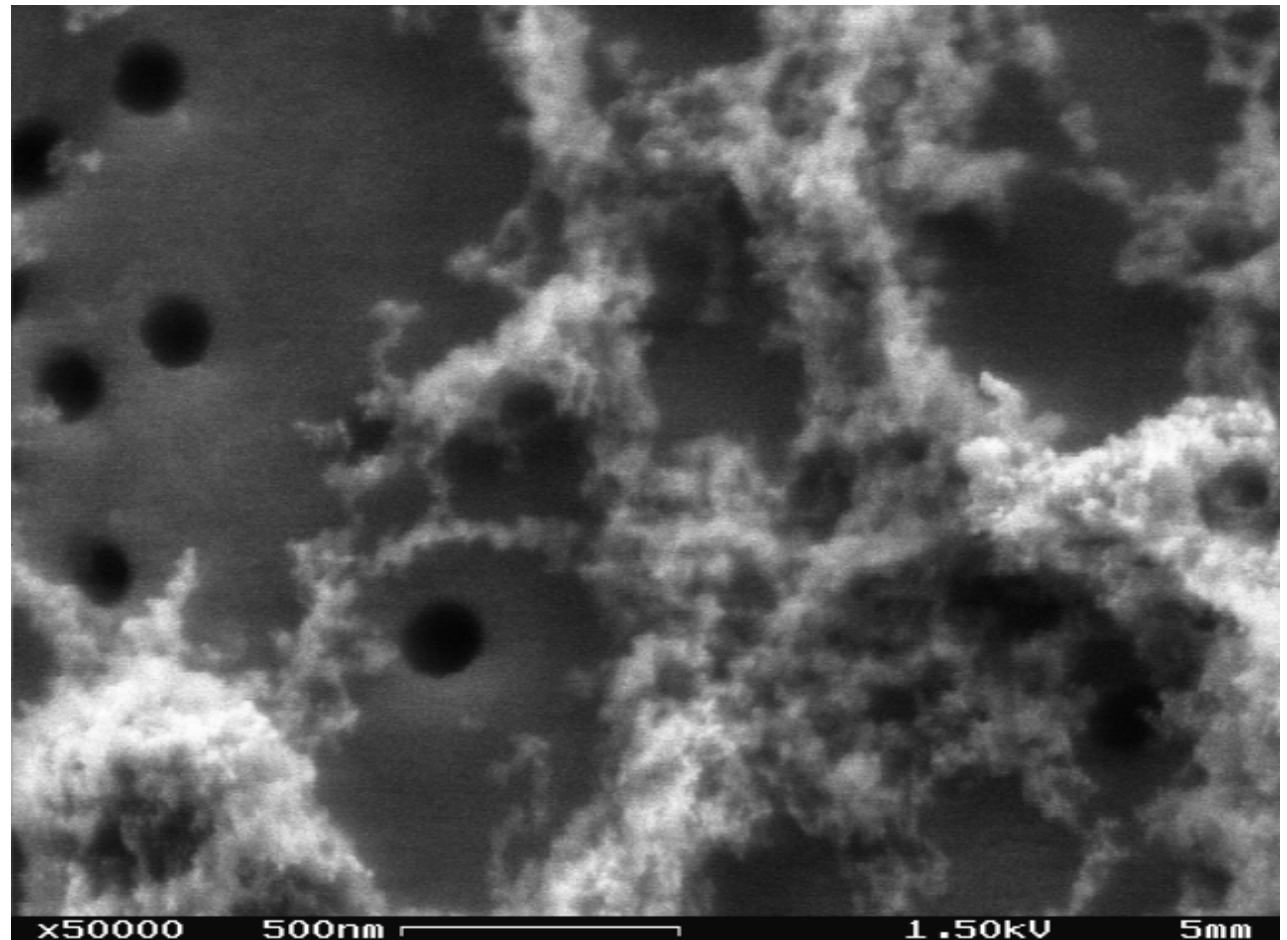
Combustor tubular or annular



diffusion flame with local fuel rich flame zones

Probe inside the Combustor

Soot concentration inside the combustor can be more than **1000 times higher** than at the combustor exit

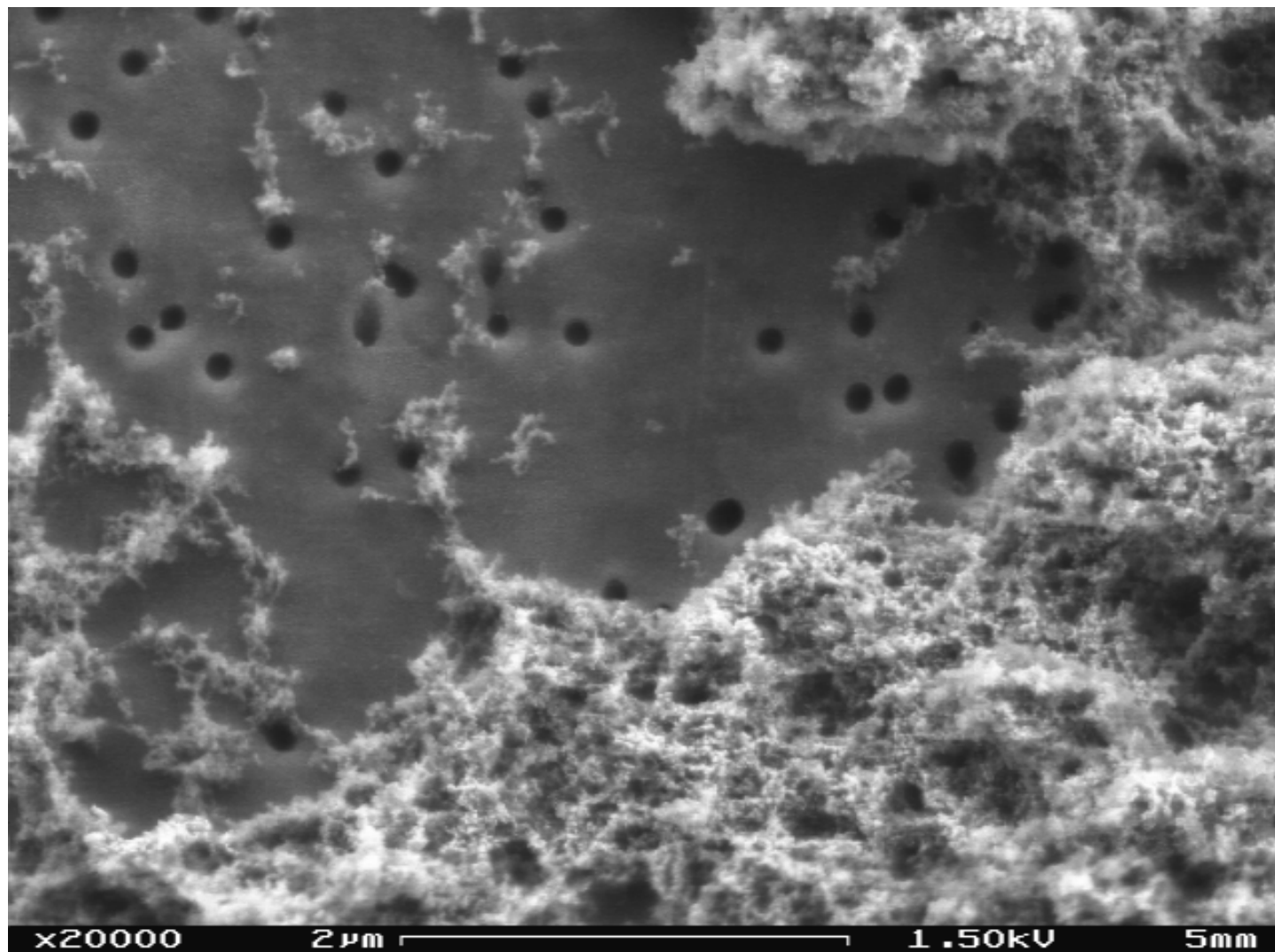


Probe inside Combuster

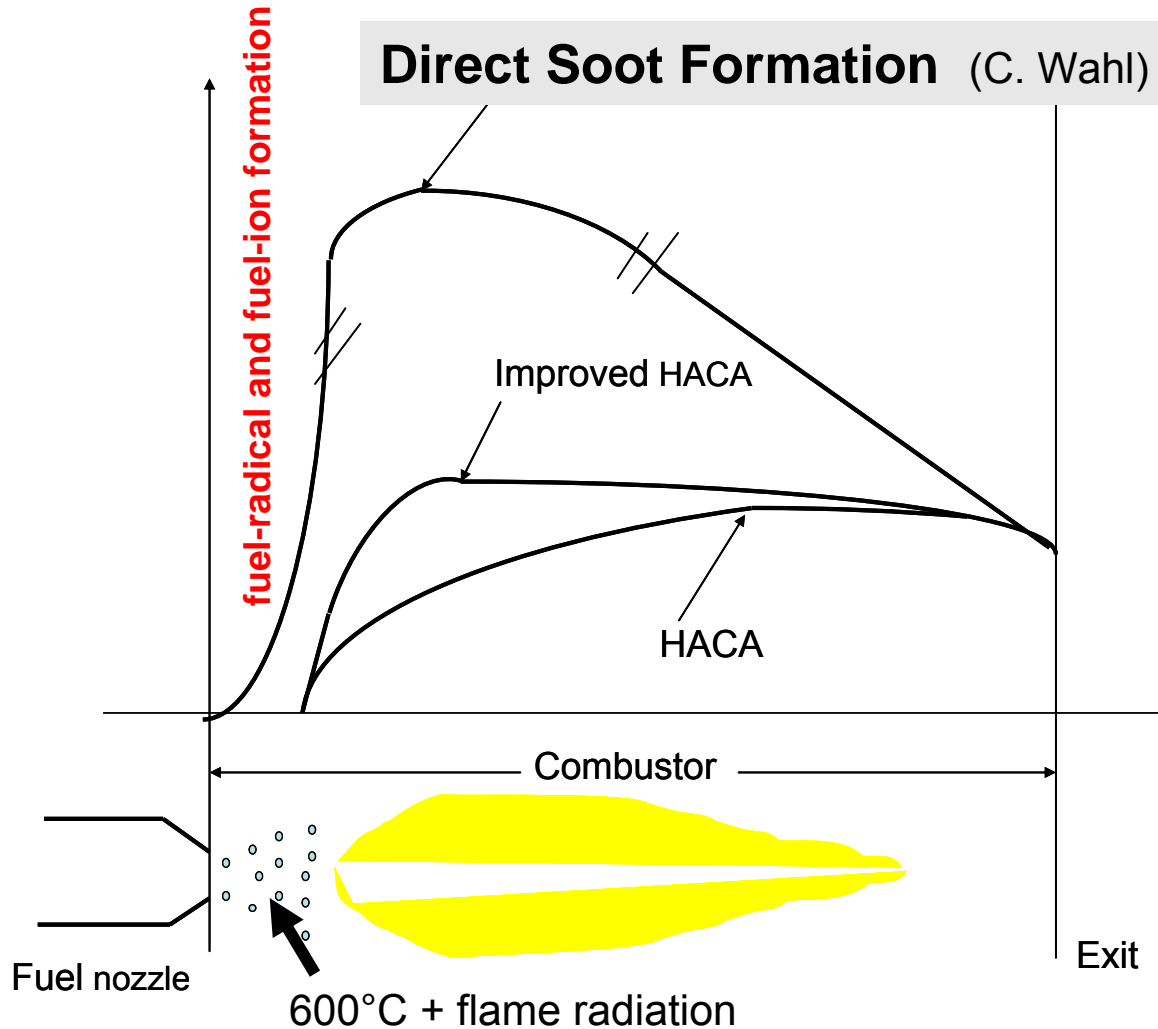
big Particles

high soot conc.

low density



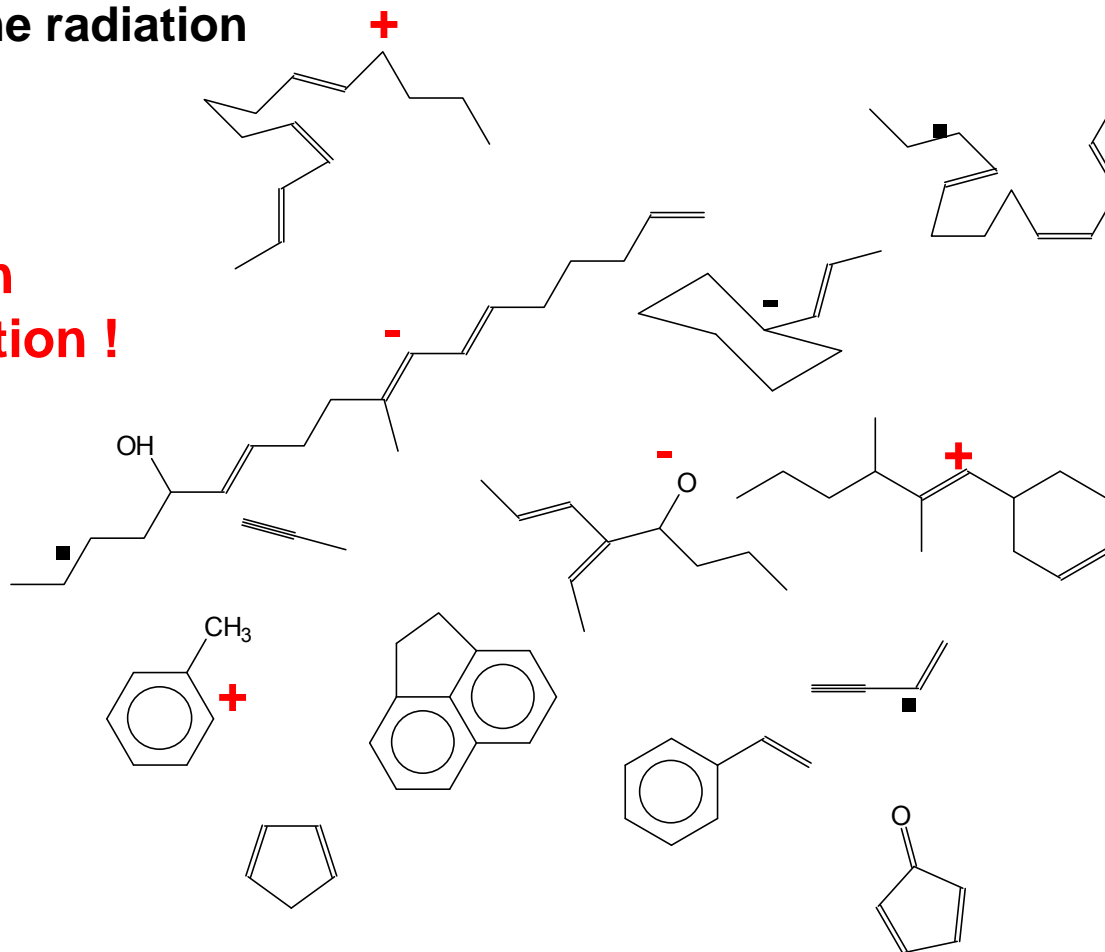
first clusters are formed by recombination of fuel-radicals and charged molecules (pyrolysis of fuel molecules)



Formation of Fuel-Radicals and Fuel-Ions

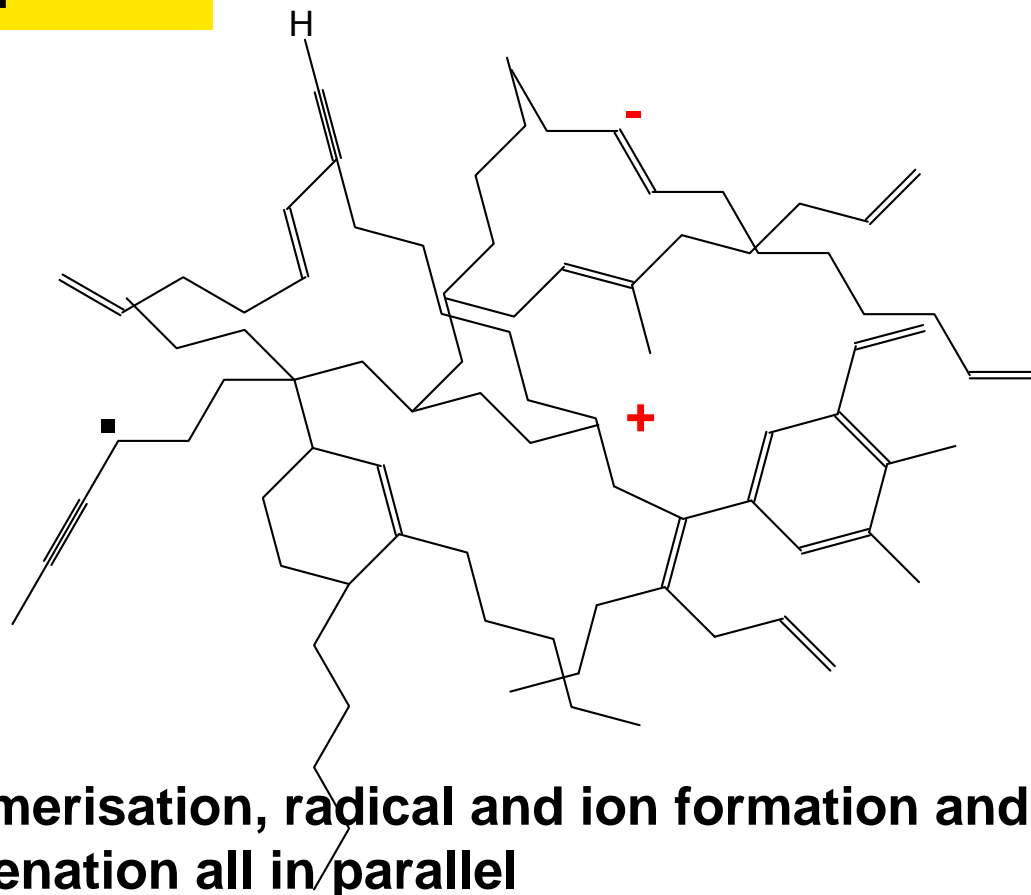
600°C + flame radiation

Pyrolysis:
can happen
before ignition !



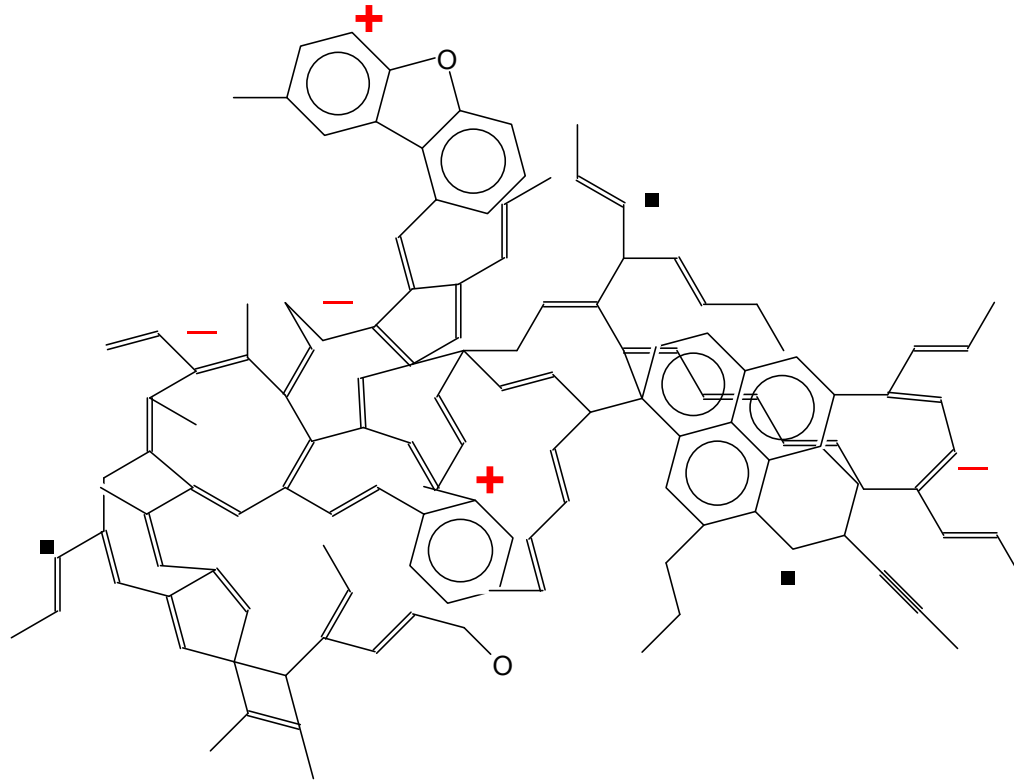
Recombination of Fuel-Ions and -Radicals

First Cluster

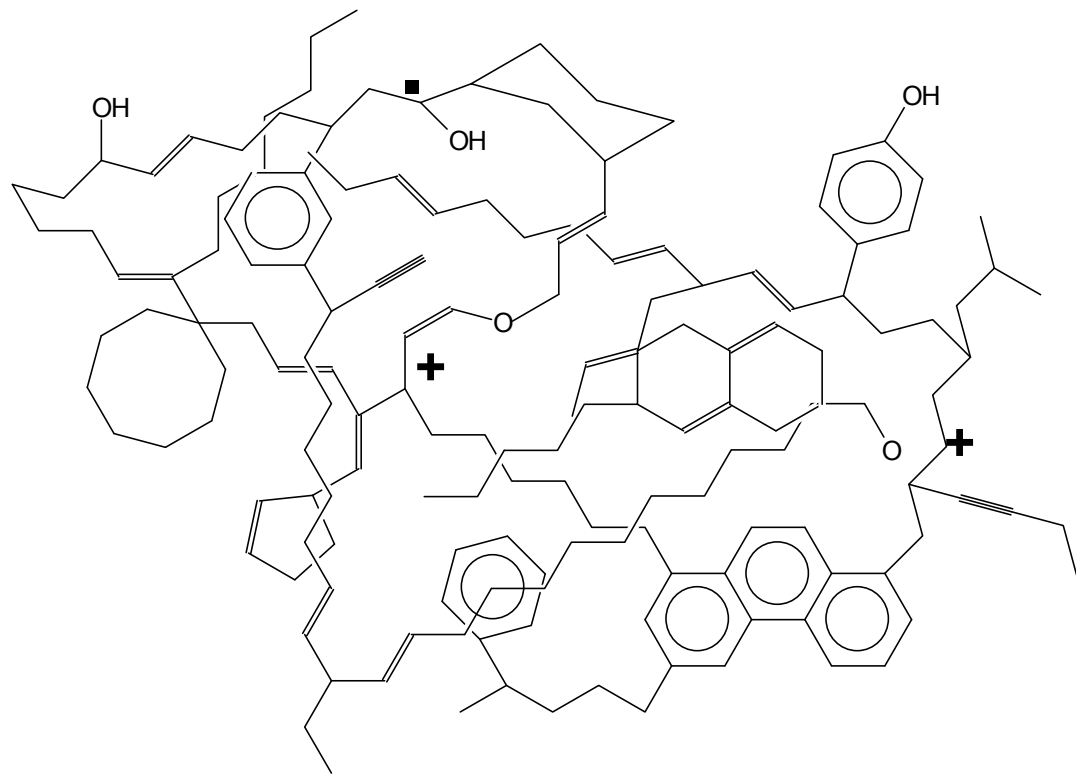


cluster dimerisation, radical and ion formation and dehydrogenation all in parallel

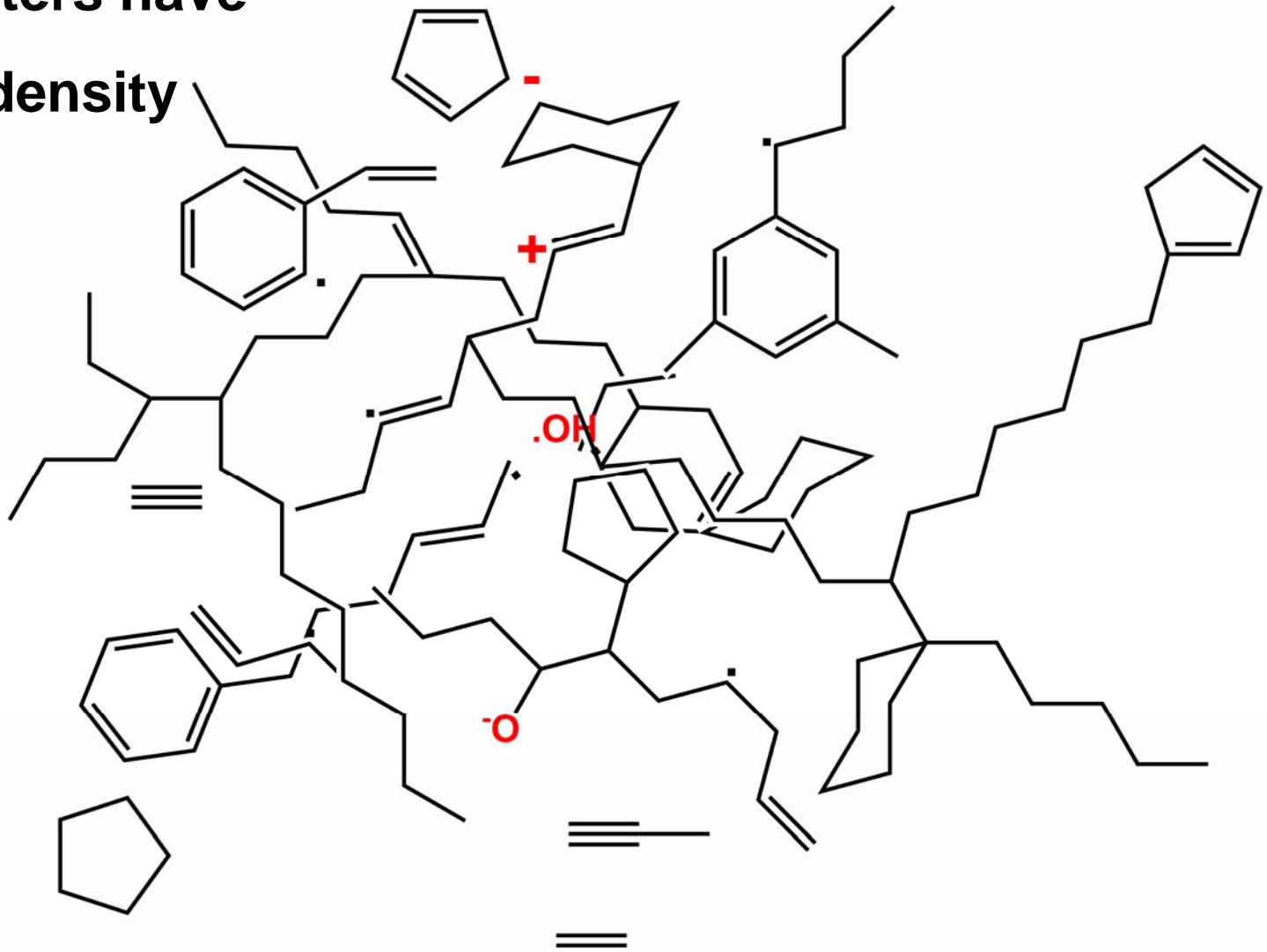
Further Cluster Growth in the Flame



cluster dimerisation, radical and ion formation and dehydrogenation all in parallel, more and more double bonds and aromatic rings → graphene structures



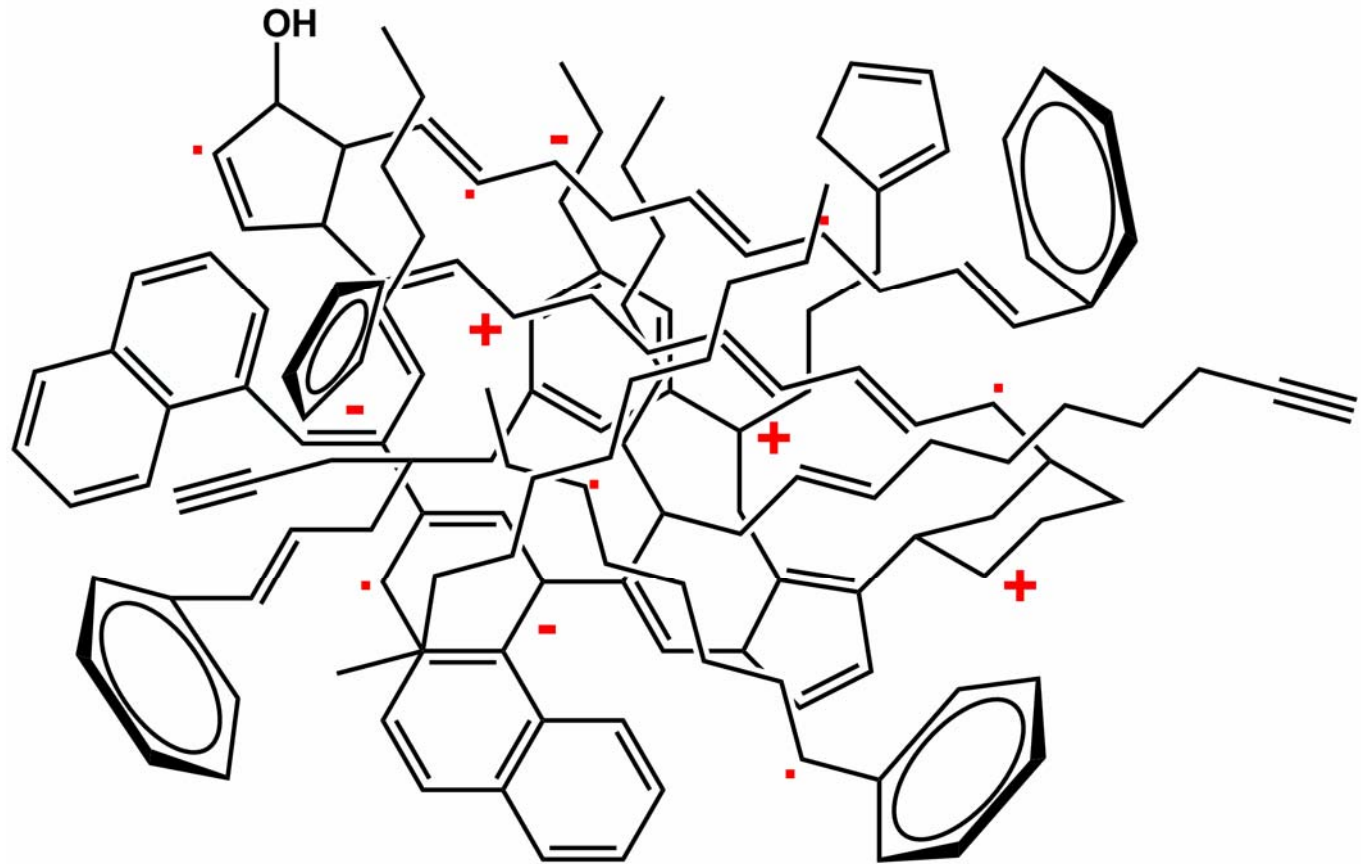
**First Clusters have
very low density**





- radical formation
- oligomerization and aliphatic ring formation
- cluster growth
- agglomeration
-
- **dehydrogenation** **OH** **O₂**
- **densification** more and more **C-C** bonds inside the cluster
- **oxidation** (preferably side branches → spherical)

Cluster densification, more and more double bonds and new C-C bonds

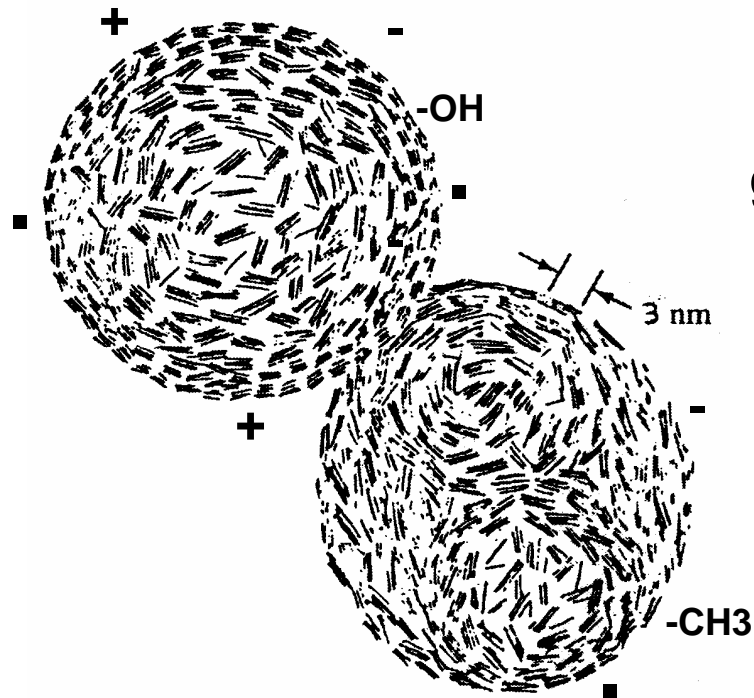




Soot Particle Properties at Exit depend on:

- residence time
- temperature history
- fuel composition
- residual aliphatic parts (sp³) inside particles (not UHC!)
- densification
- functional groups
- formation of graphene structures
- **at the end the well known soot particles can appear**

Soot structure, developed from Hres TEM pictures



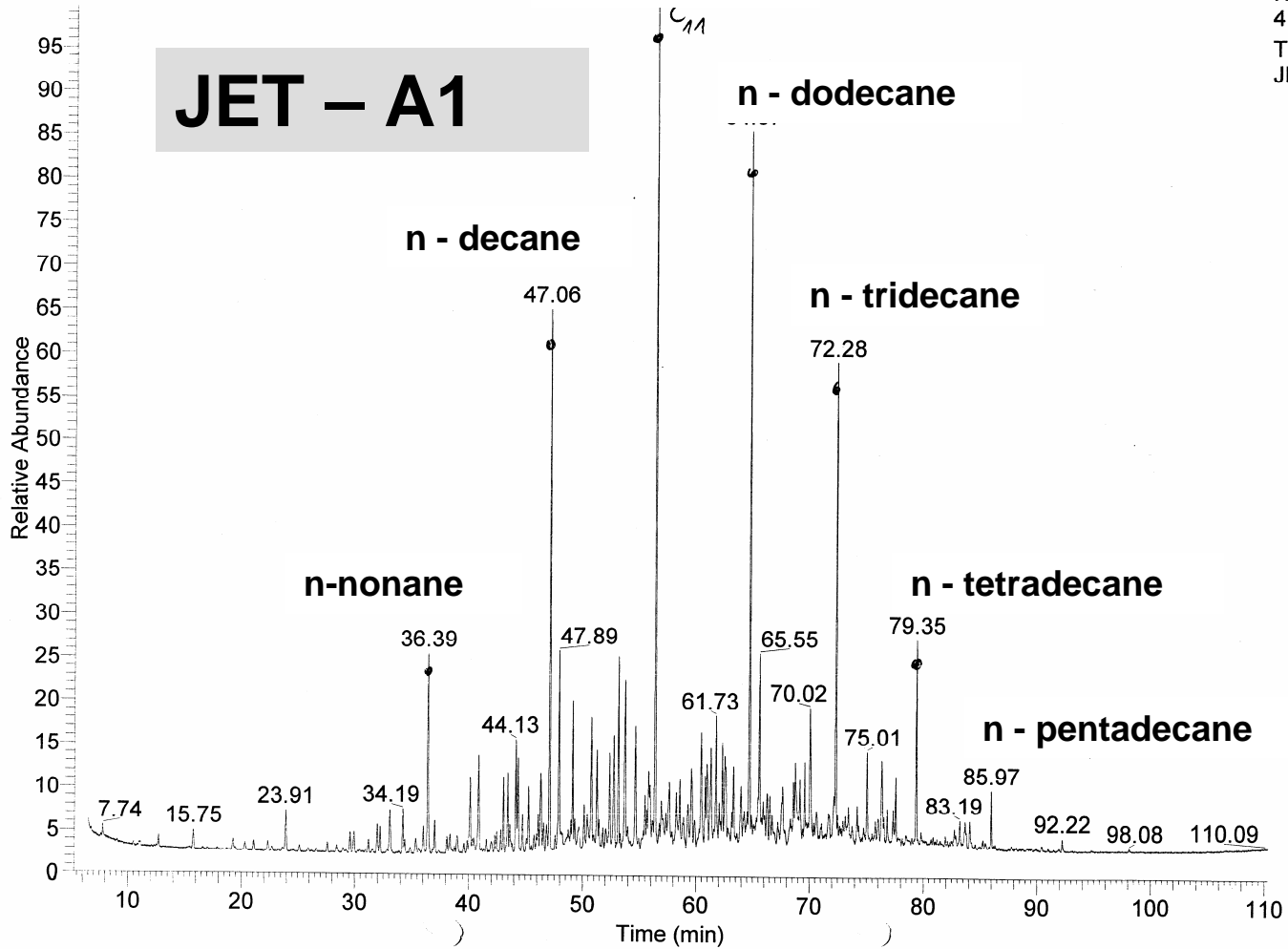
graphene layers

Radicals, pos. and neg. charges and functional groups on the surface

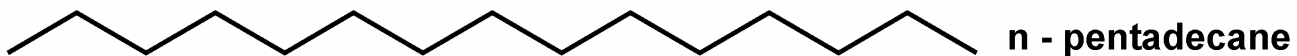
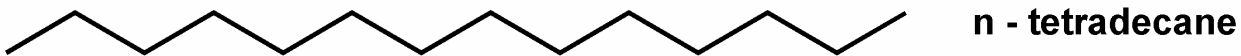
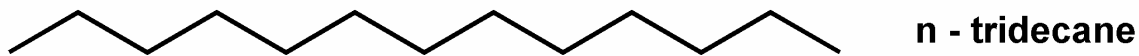
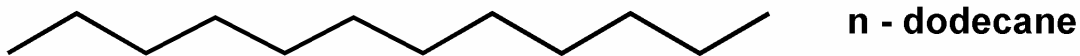
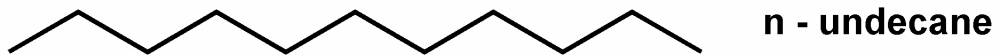
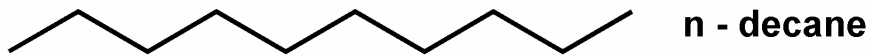
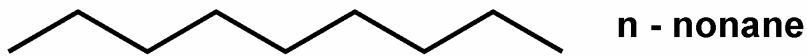
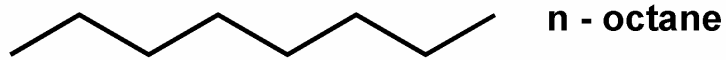
n - undecane

NL:
4.97E7
TIC F: MS
JET-A1

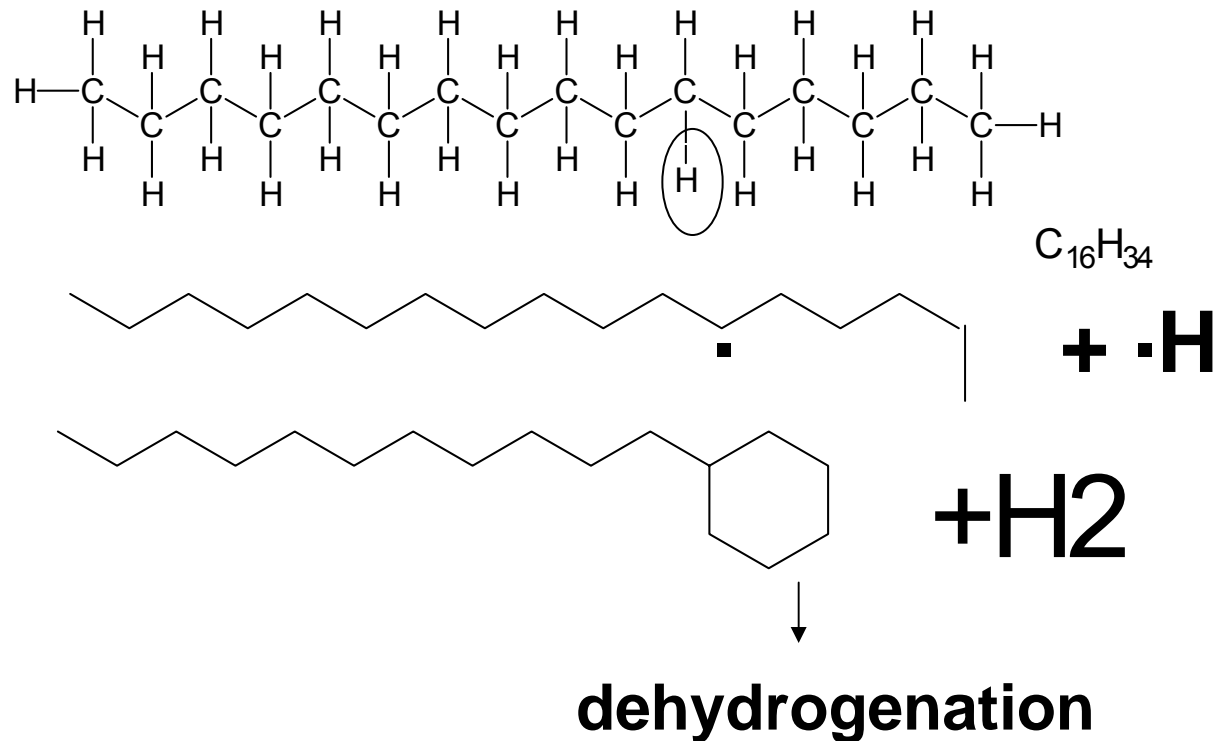
JET – A1



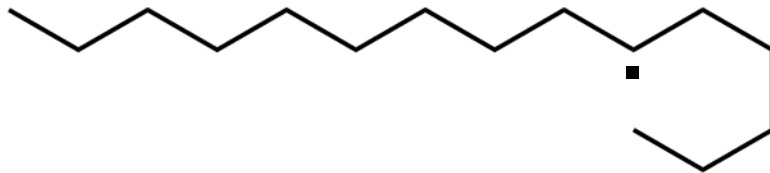
Main Compounds of Jet-A1 (C8 to C15)



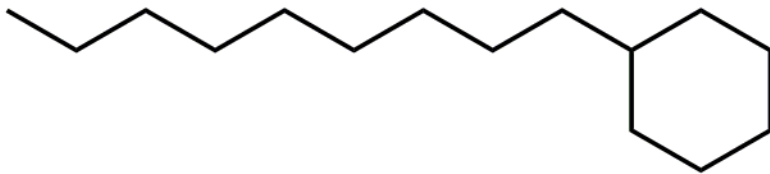
Direct Formation of first aliphatic Ring



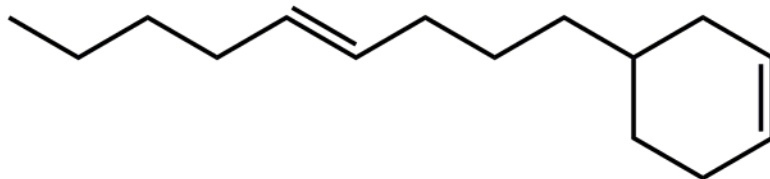
..



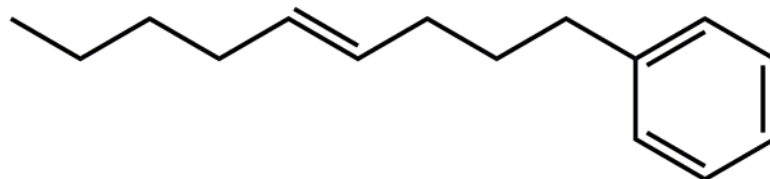
+ H Hydrogen Abstraction



+ H first aliphatic ring



dehydrogenation → double bonds



further dehydrogenation → double bonds

first aromatic ring

no need to crack the fuel down to small molecules (acetylene) !!



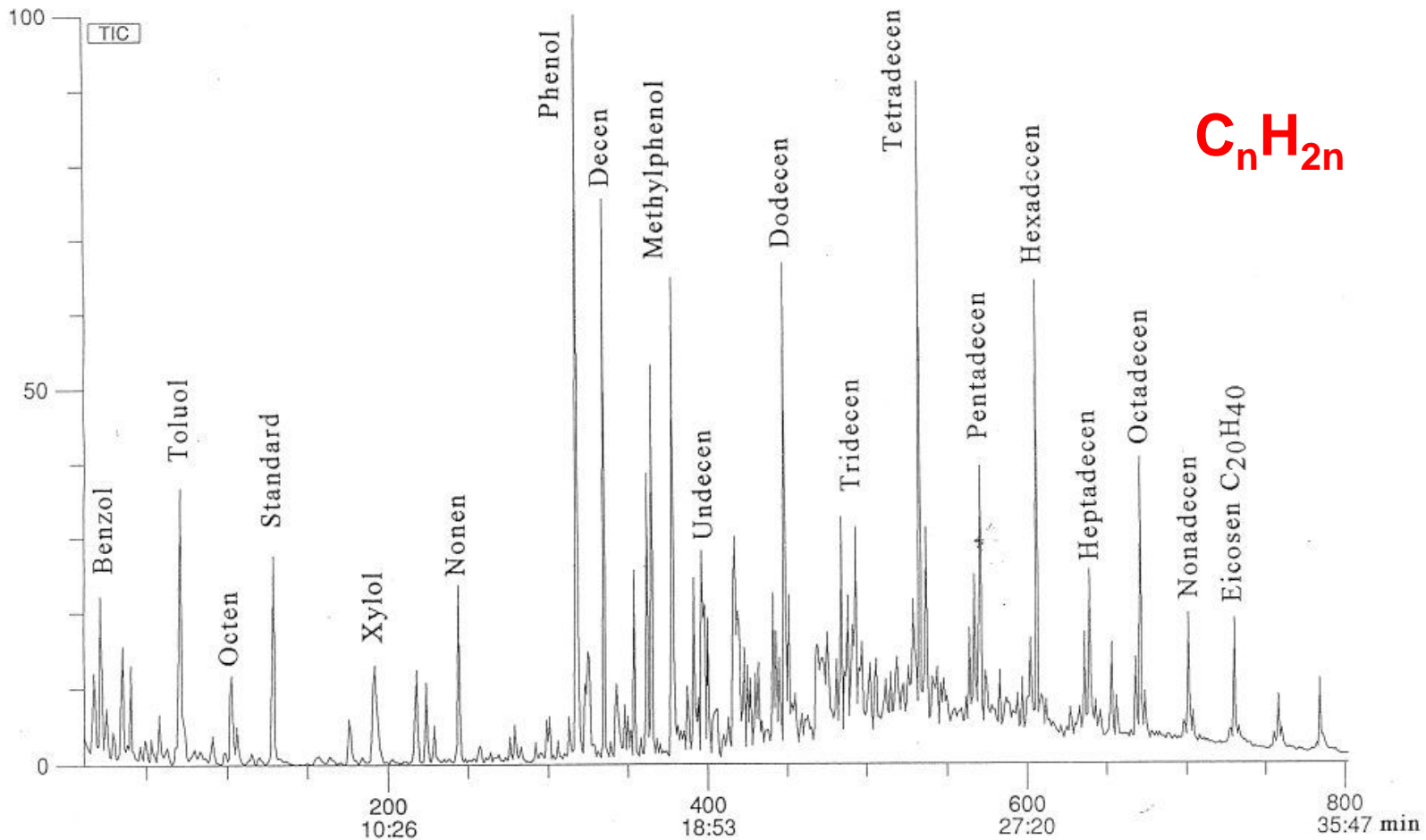
Flash pyrolysis experiment can support aromatic ring formation



Flash Pyrolysis

650°C

Lignite



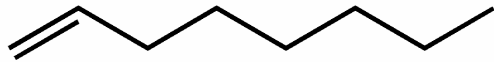
Flash Pyrolysis

650°C

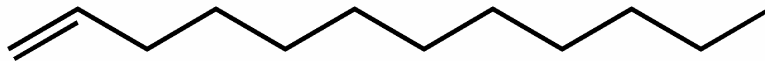
Lignite

main compounds

C_nH_{2n} all from C_8 to C_{22}



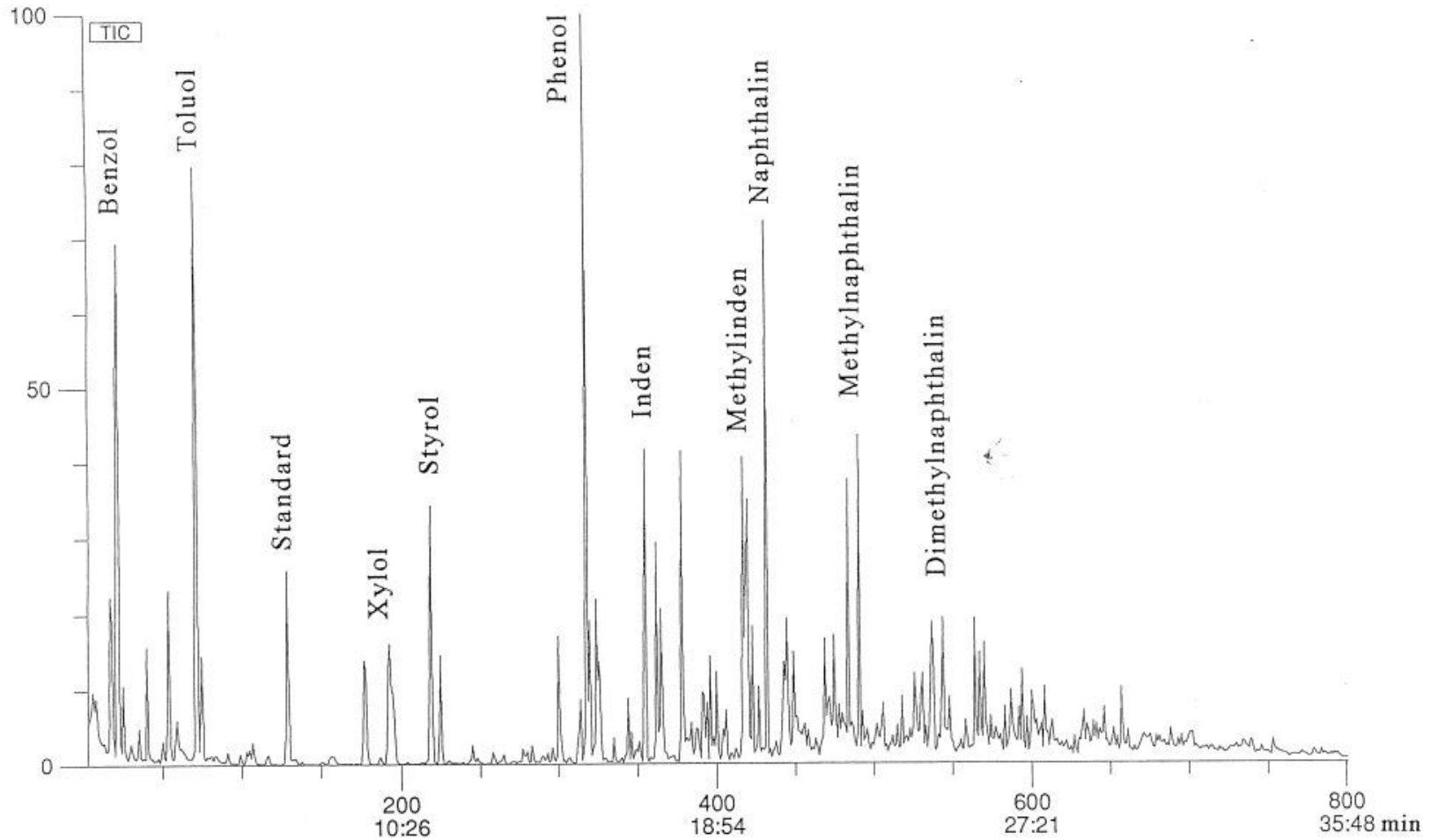
C_8H_{16} to $C_{22}H_{44}$



Flash Pyrolysis

750°C

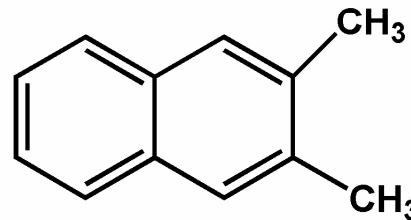
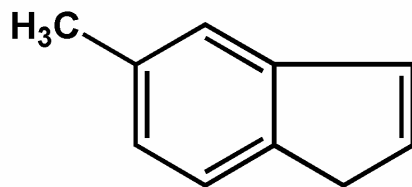
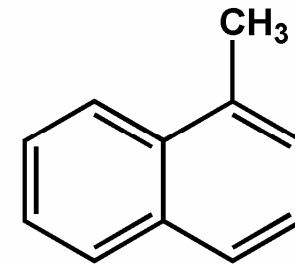
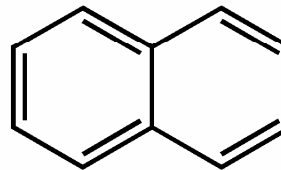
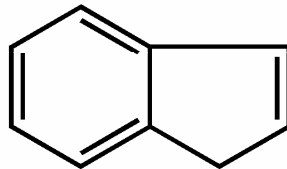
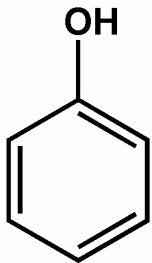
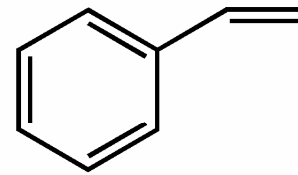
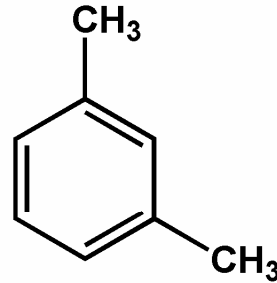
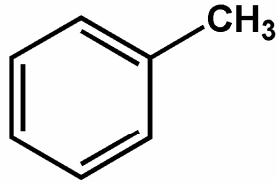
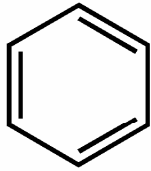
Lignite



Flash Pyrolysis

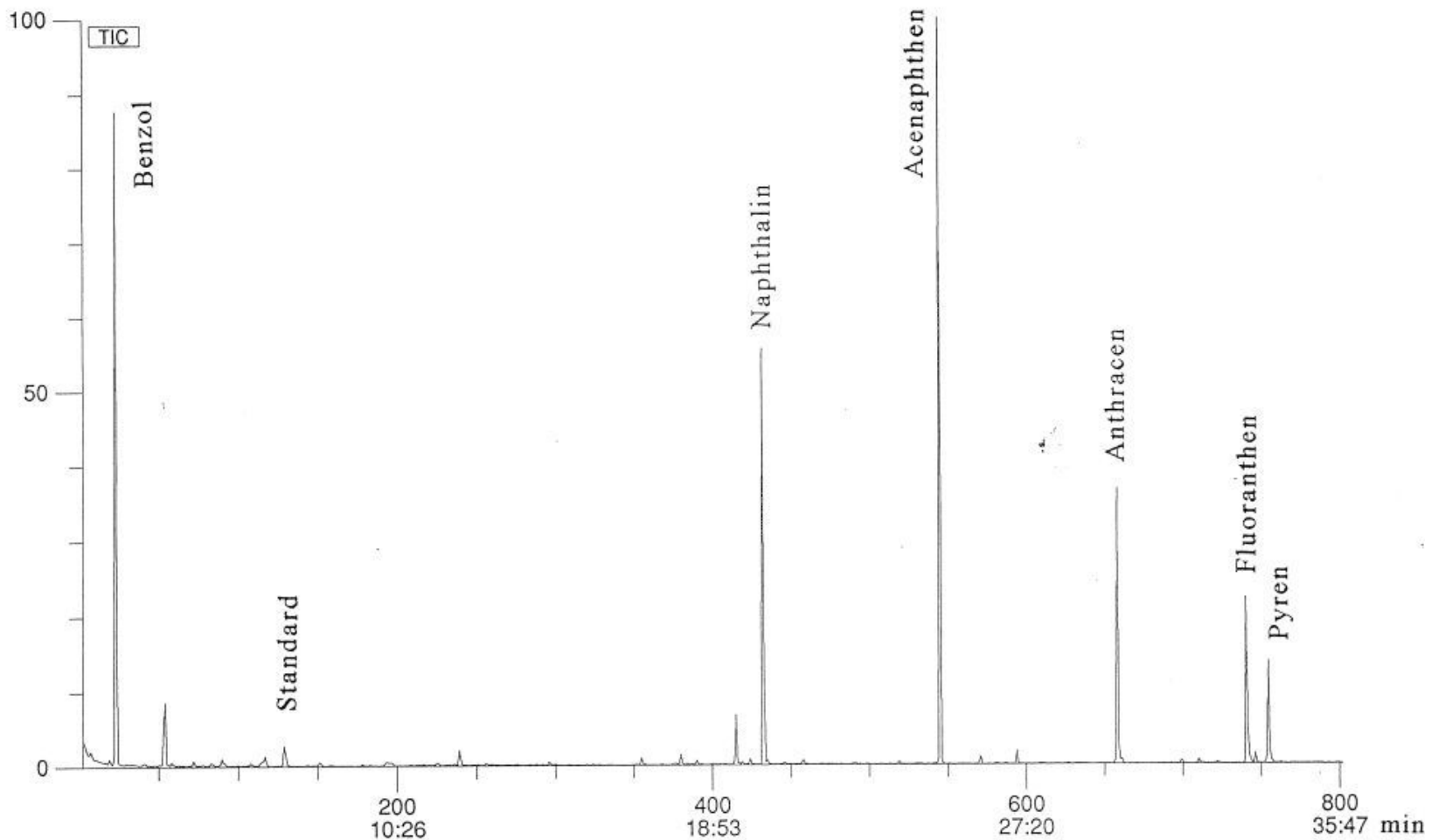
750°C

Lignite



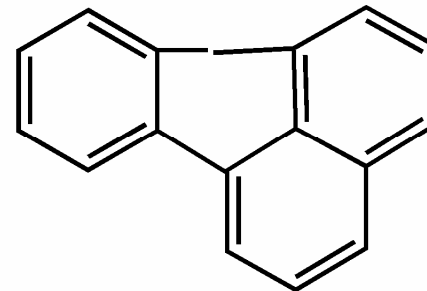
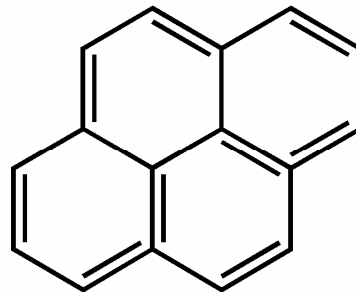
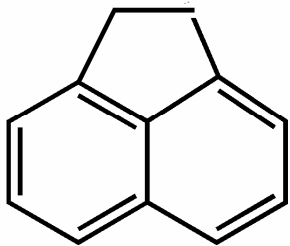
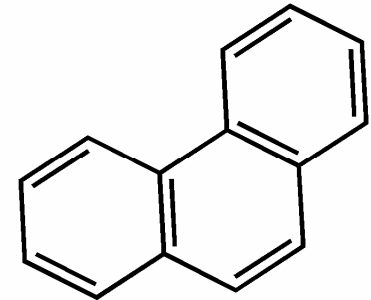
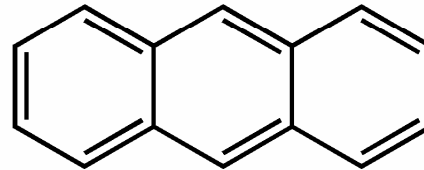
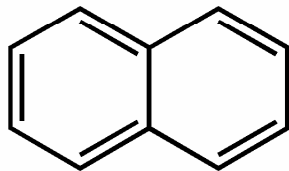
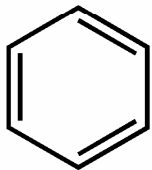
Flash Pyrolysis 1100°C

Lignite



Flash Pyrolysis **1100°C**

Lignite





Conclusion

- **Direct Soot Formation** is a possibility to explain high soot concentrations
- **Fuel molecules must not be broken down to acetylene**
- **Direct Soot Formation** is a fast pathway to soot, **in addition to HACA**
- Flash pyrolysis experiments support the theory
- Ion reaction may also play a role
- **More basic research is necessary** (shock tube and flow reactor experiments)



Soot is a mixing problem

**Lean, Premixed, Prevaporized Combustors (LPP)
produce **no soot****

GE-nx

Thank you for your attention

El's for existing Engines:

NOx 1 – 9 g/kg_{fuel}

CO 1 – 67 g/kg_{fuel}

Soot 10 – 400 mg/kg_{fuel} # ~ E16 / kg_{fuel}

UHC 0 - 30 g/kg_{fuel}

Aldehyde 0 - 6,2 g/kg_{fuel}





DLR

Deutsches Zentrum
für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

Pyrolysereaktor (300 - 1400K)

Aufheizgradient $> 1000\text{K/sec}$

Verweilzeit der Produkte : 0.3 - 0.8 sec

Bettmaterial : Quarzsand

