Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili

From primary pyrolysis products to carbon particulate: relevance of parent fuels, heating rate and gaseous atmosphere

Osvalda Senneca, Barbara Apicella, Francesca Cerciello, Carmela Russo
osvalda.senneca@stems.cnr.it

Consiglio Nazionale delle Ricerche, Naples, Italy

LEAT, Ruhr-University Bochum, Bochum, Germany

Soot in coal pyrolysis

Brigham Young (Tom Fletcher)

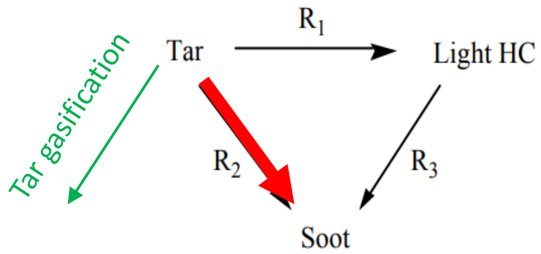


Figure 2.5. Possible reaction pathways for soot generation in coal pyrol (Suggested by Chen, et al., 1992).

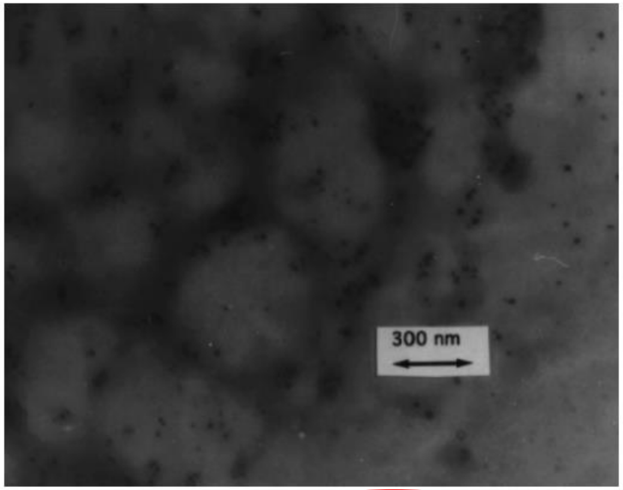


Figure 4.9. TEM micrograph of solid particles inside tar droplet from Utah coal, collected at 20.5 cm above the burner (103 ms).

It was clear that soot in coal pyrolysis largely comes from tar.

tar molecules may react with molecules or radicals in the gas phase such as H_2O, CO_2 or OH

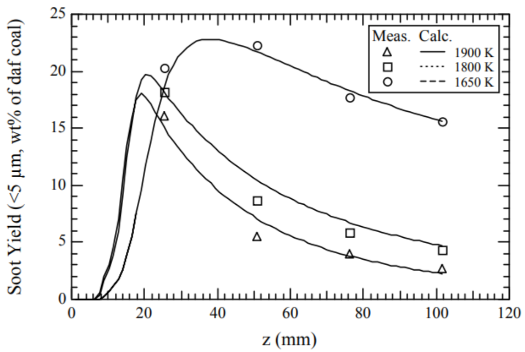
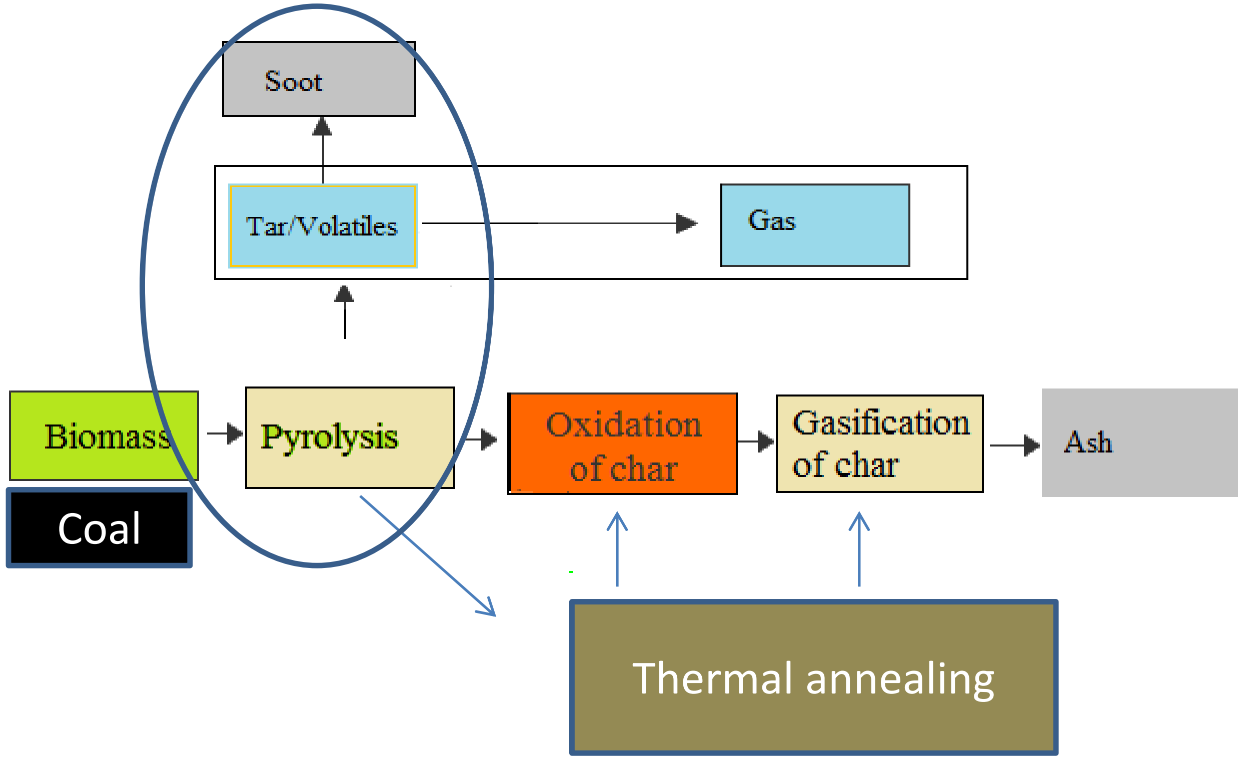


Figure 5.9. Calculated soot yield profiles for Pittsburgh #8 coal using the optimized kinetic coefficients in Table 5.2.



Novelty:

Coal→Biomass
Inert→CO_2 rich (oxyfuel)
Heating: fast/slow; severe/mild

Reactors used for heat treatment

Reactor type	FixBR	DTR	WMR/HSR
Process type	Batch	Continuous	Batch
Temperature (K)	973	900-1573	1573-2073
Particle size (mm)	0.1	0.1	0.1
Heating rate (K/s)	0.08	10^4	10^4
Heat treatment time (s)	18000	0.02-0.1	3 s

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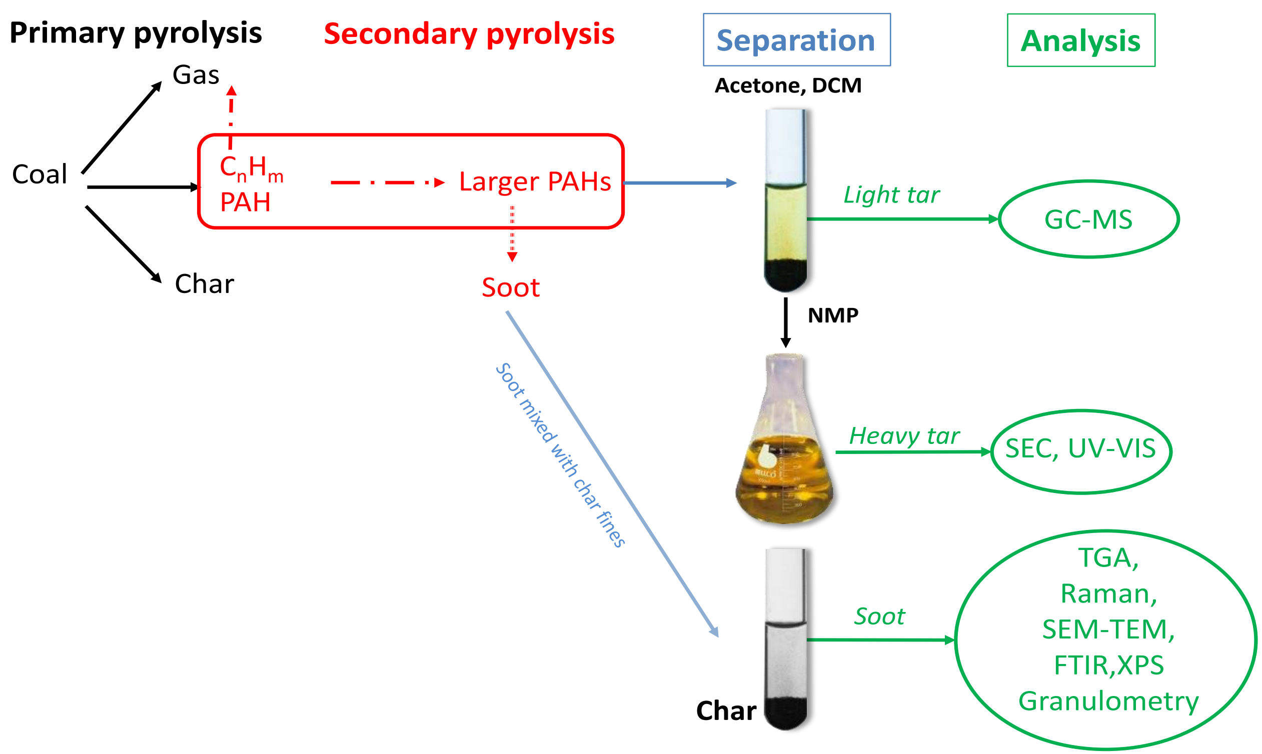
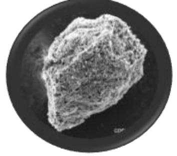
Challenges and progresses in the chemical investigation of high molecular weight species in condensed pyrolysis products of coal and biomass

Carmela Russo[a,*,1], Francesca Cerciello[b], Osvalda Senneca[a], Barbara Apicella[a]

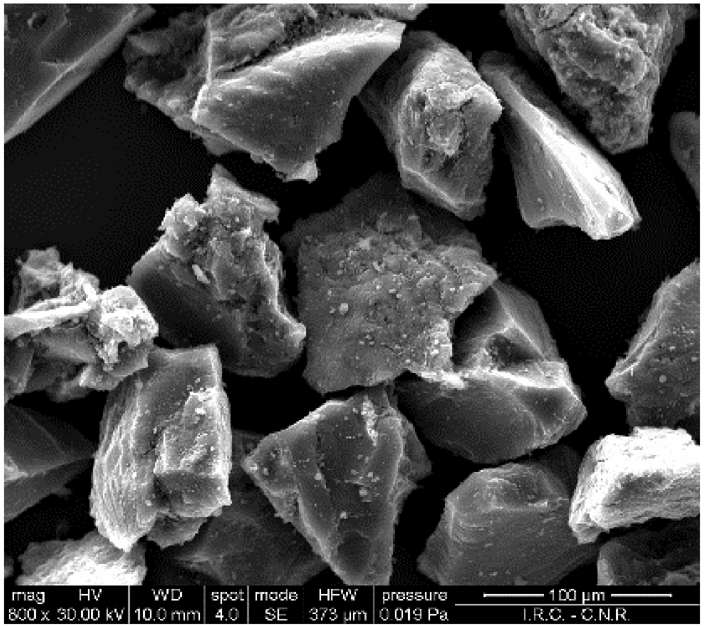
[a] Istituto di Scienze e Tecnologia per l'Energia e la Mobilità Sostenibili (STEMS)-CNR, 80125 Napoli, Italy
[b] Laboratory of Industrial Chemistry, Ruhr University Bochum, 44801 Bochum, Germany



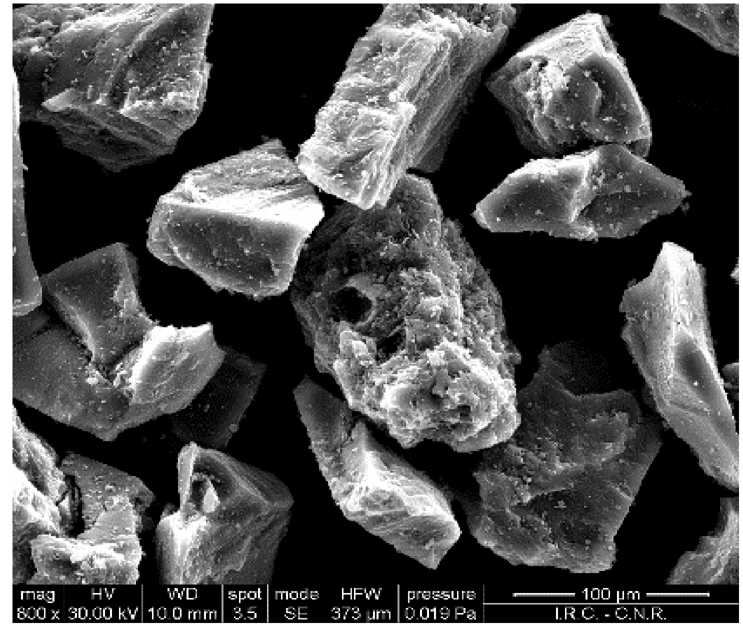


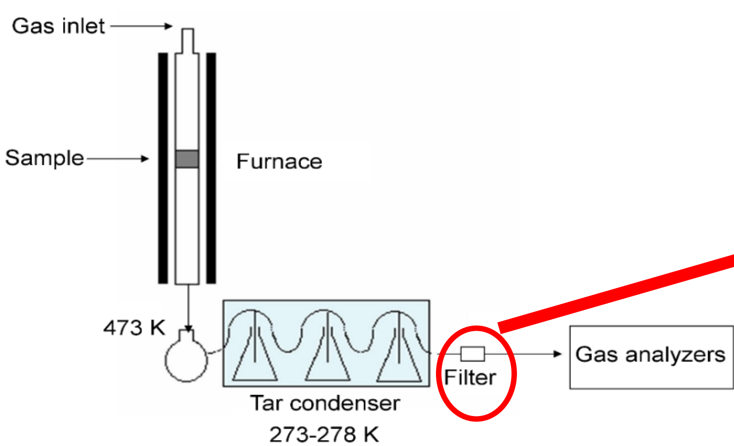
COAL slow

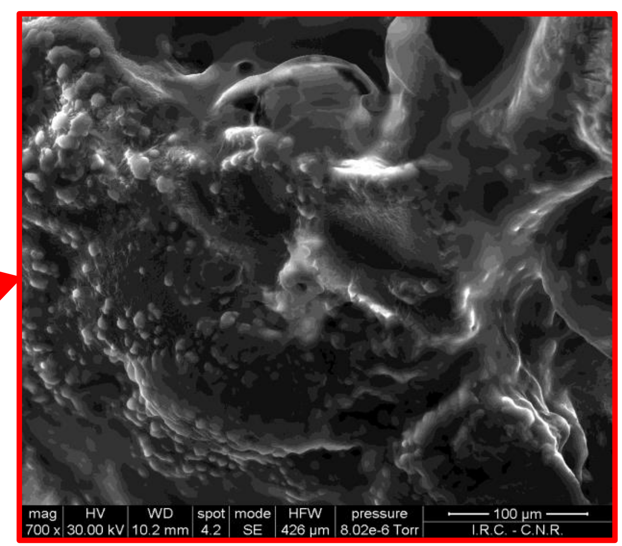
Fix-Bed-N_2

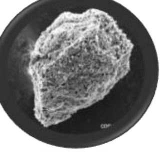


Fix-Bed-CO_2



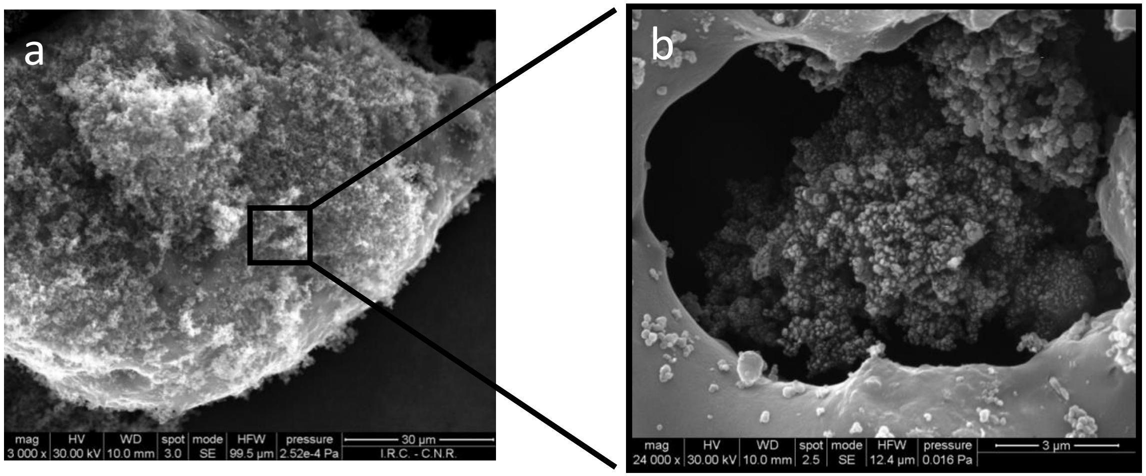


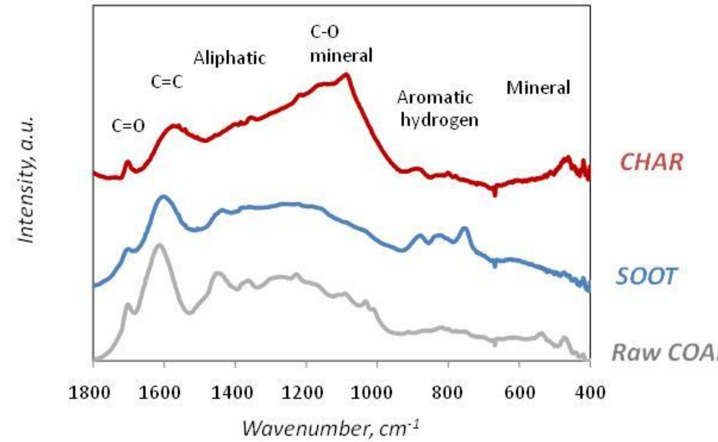




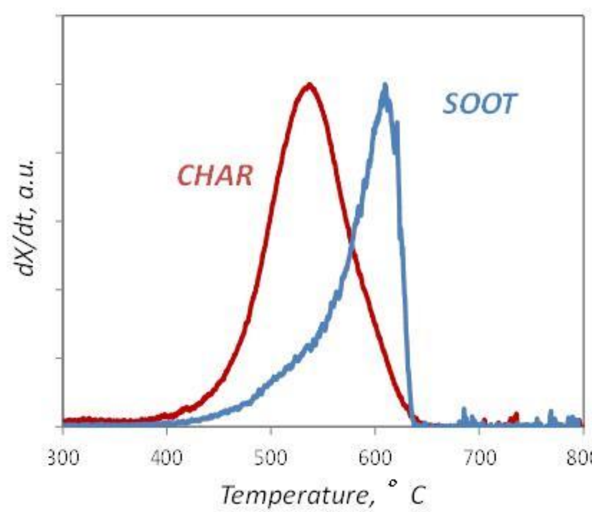
COAL fast (DTR)

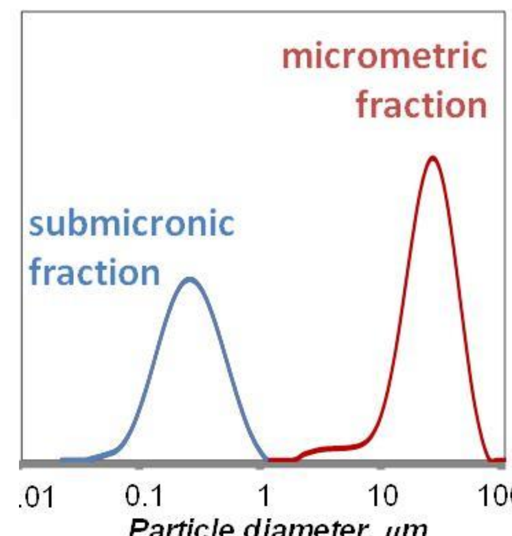
In CO_2 Soot is 3 times more abundant than in N_2





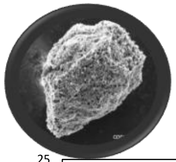
	Soot	Char
Reactivity (TGA)	Less reactive	More reactive
Functional groups (FT-IR, XPS)	Richer in hydrogen and oxygenated functionalities	Poorly functionalized
Ash (TGA)	Ash-free	Presence of inorganics
Aromatic layer extension, nm (Raman)	0.88-1.17	0.95-1.19
Laser Granulometry	0.1-1 µm	10-100 µm

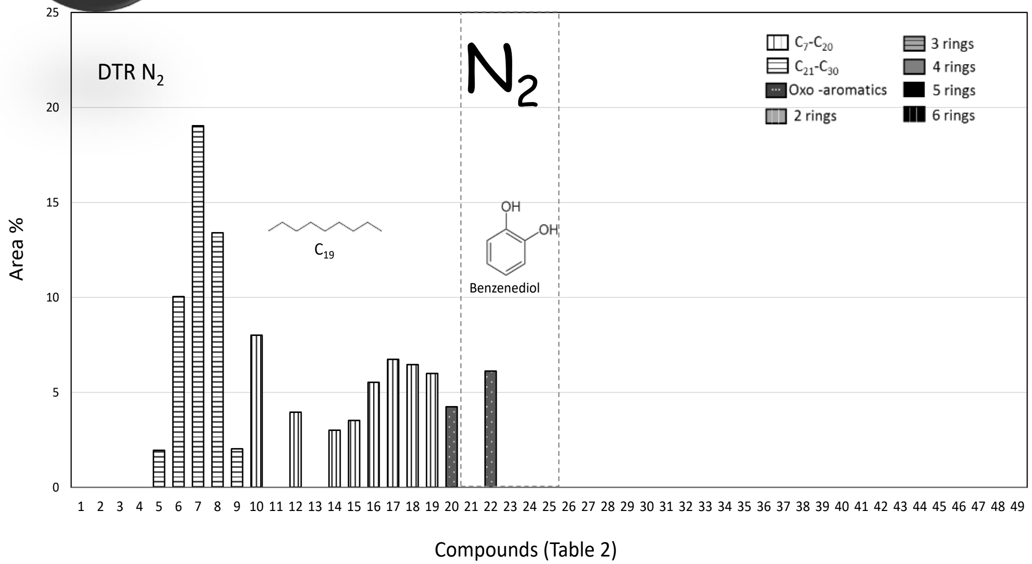


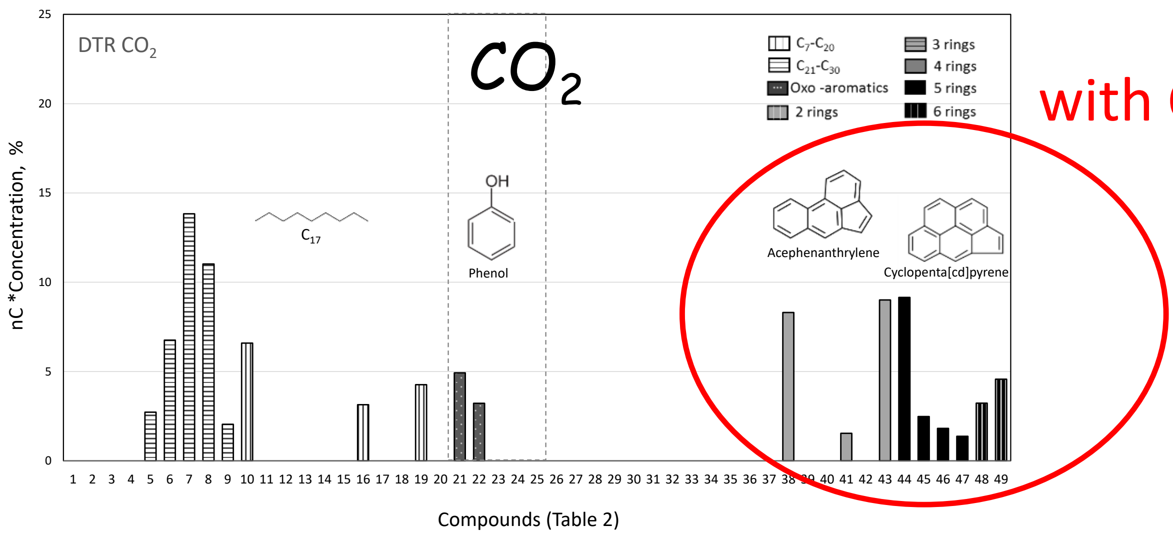


Bimodal distribution of the PDS curve

Coal tar N_2/CO_2

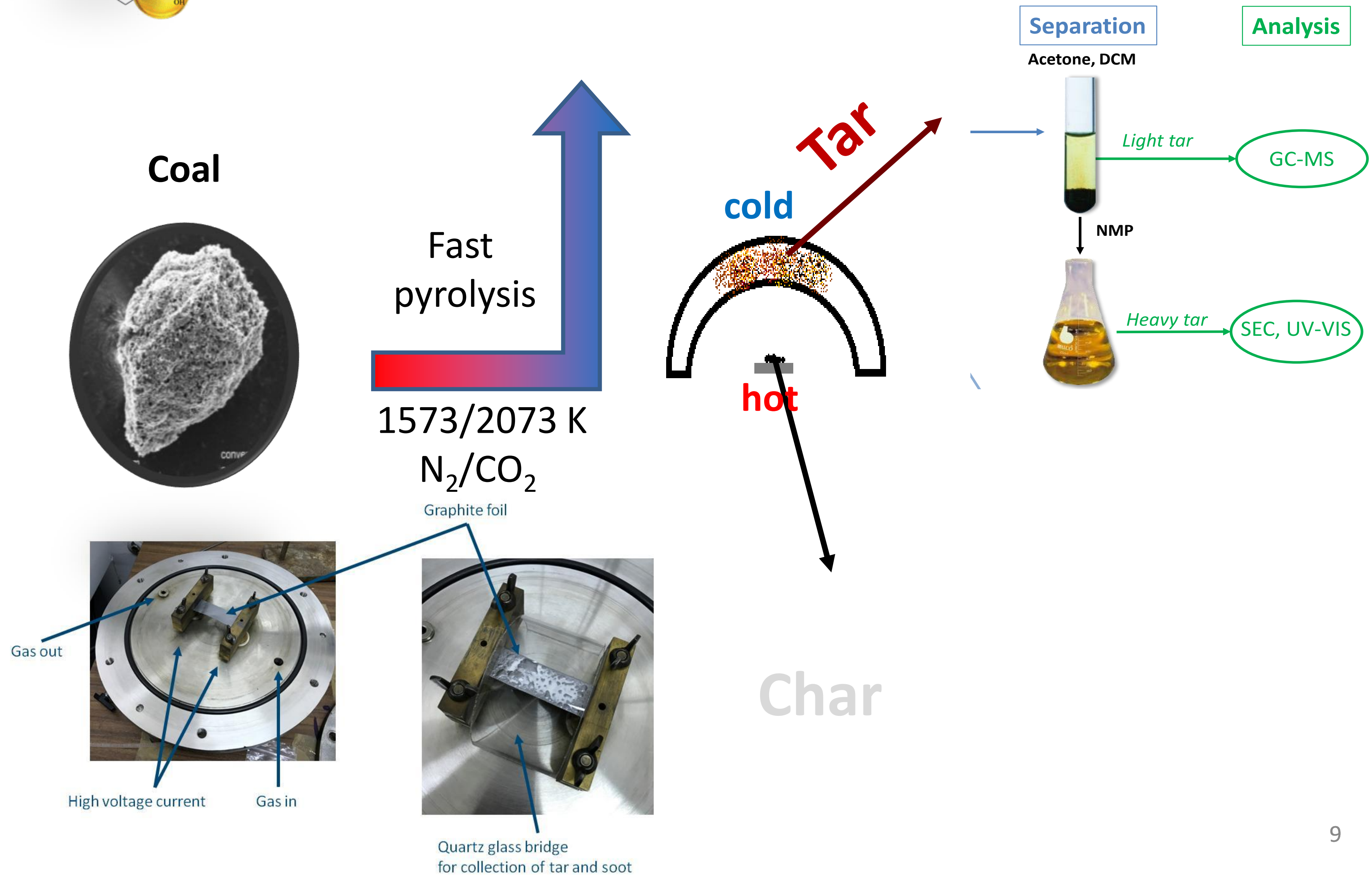


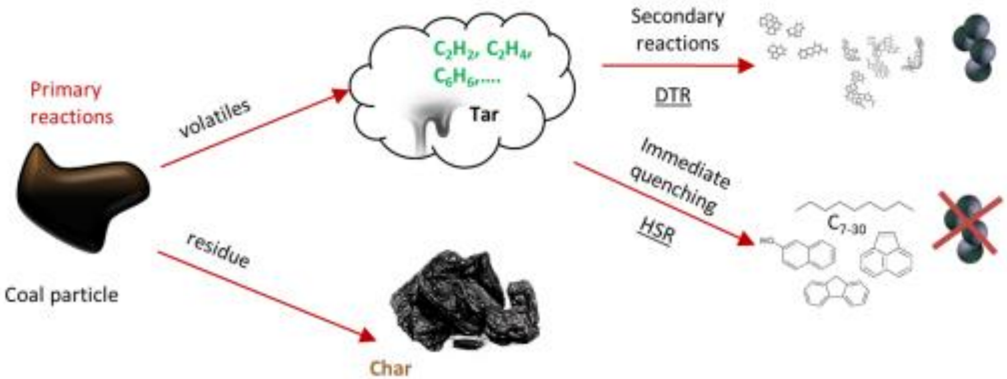




with **CO_2** tar is more aromatic

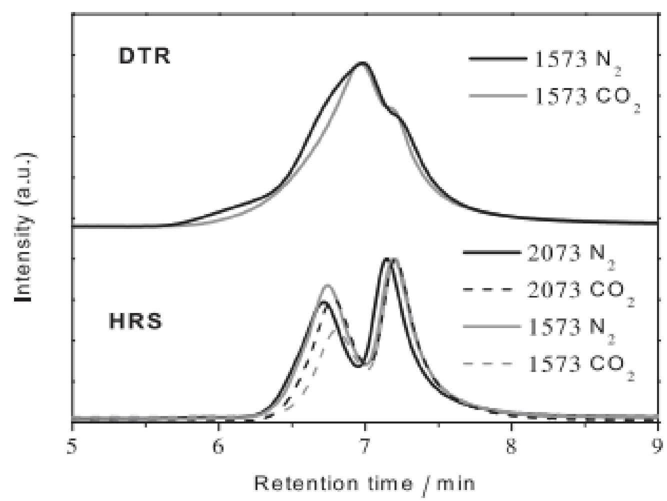
Primary tar


Coal
Fast
pyrolysis
1573/2073 K
N_2/CO_2
Tar
cold
hot
Char
Separation
Analysis
Acetone, DCM
Light tar
GC-MS
NMP
Heavy tar
SEC, UV-VIS
Graphite foil
Gas out
High voltage current
Gas in
Quartz glass bridge
for collection of tar and soot

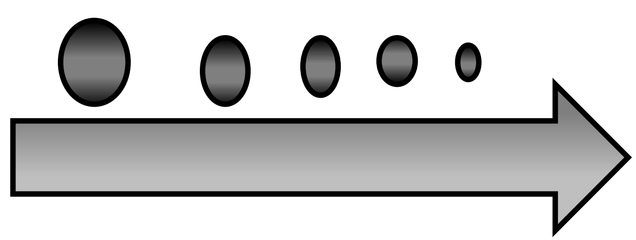


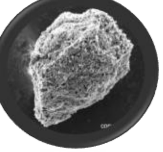
Soot not found in HSR conditions (“cold” volatile temperature), but…

SEC of the heavy tar shows “particles” > 10 nm.



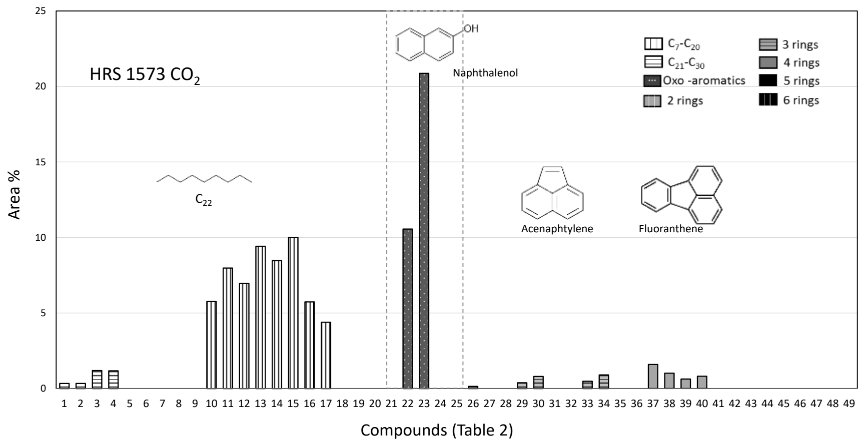
Size Esclusion Cromatography



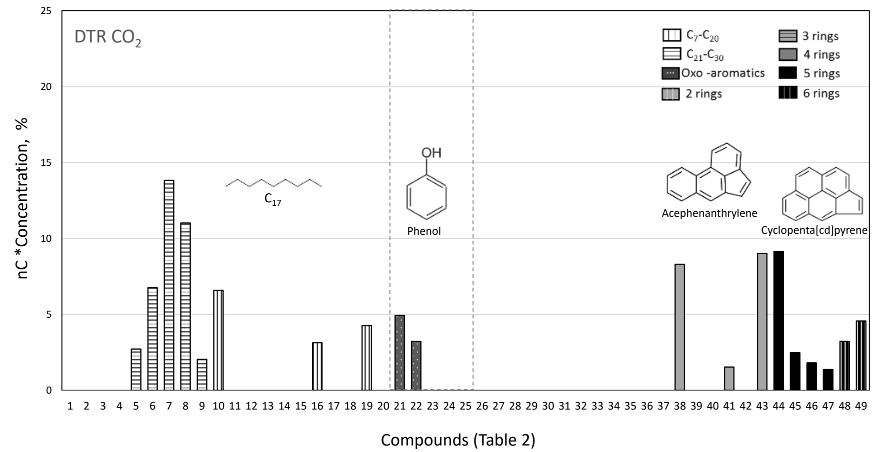


Light tar in cold and hot gas (primary vs secondary)

HSR: Cold gas /primary



DTR: Hot gas/secondary

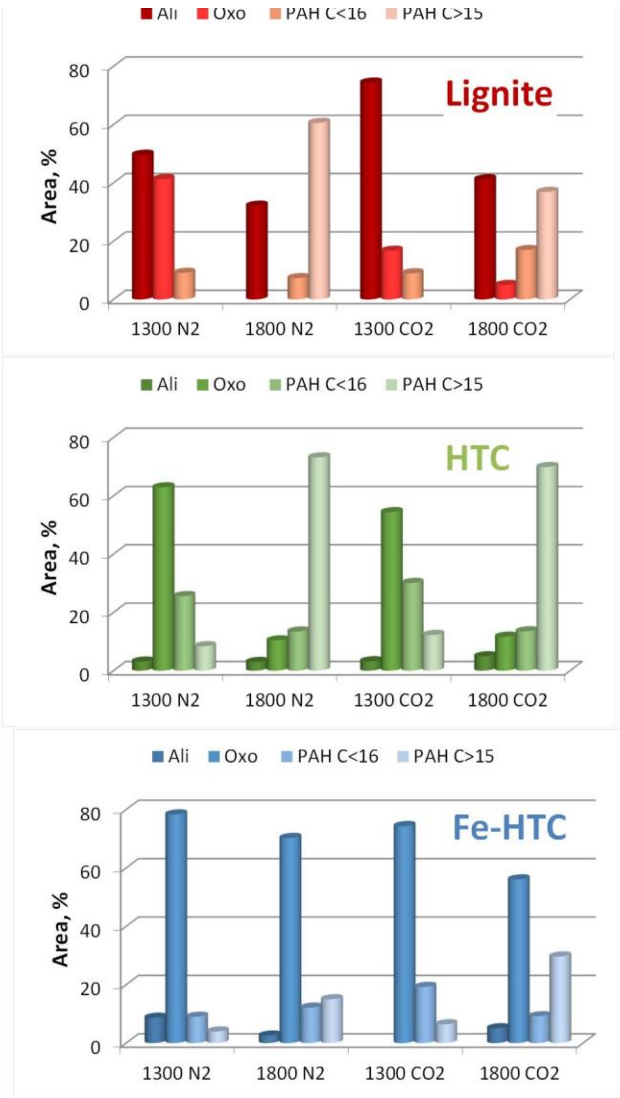


PAHs are favoured in hot gas

(Secondary tar has more PAHs)

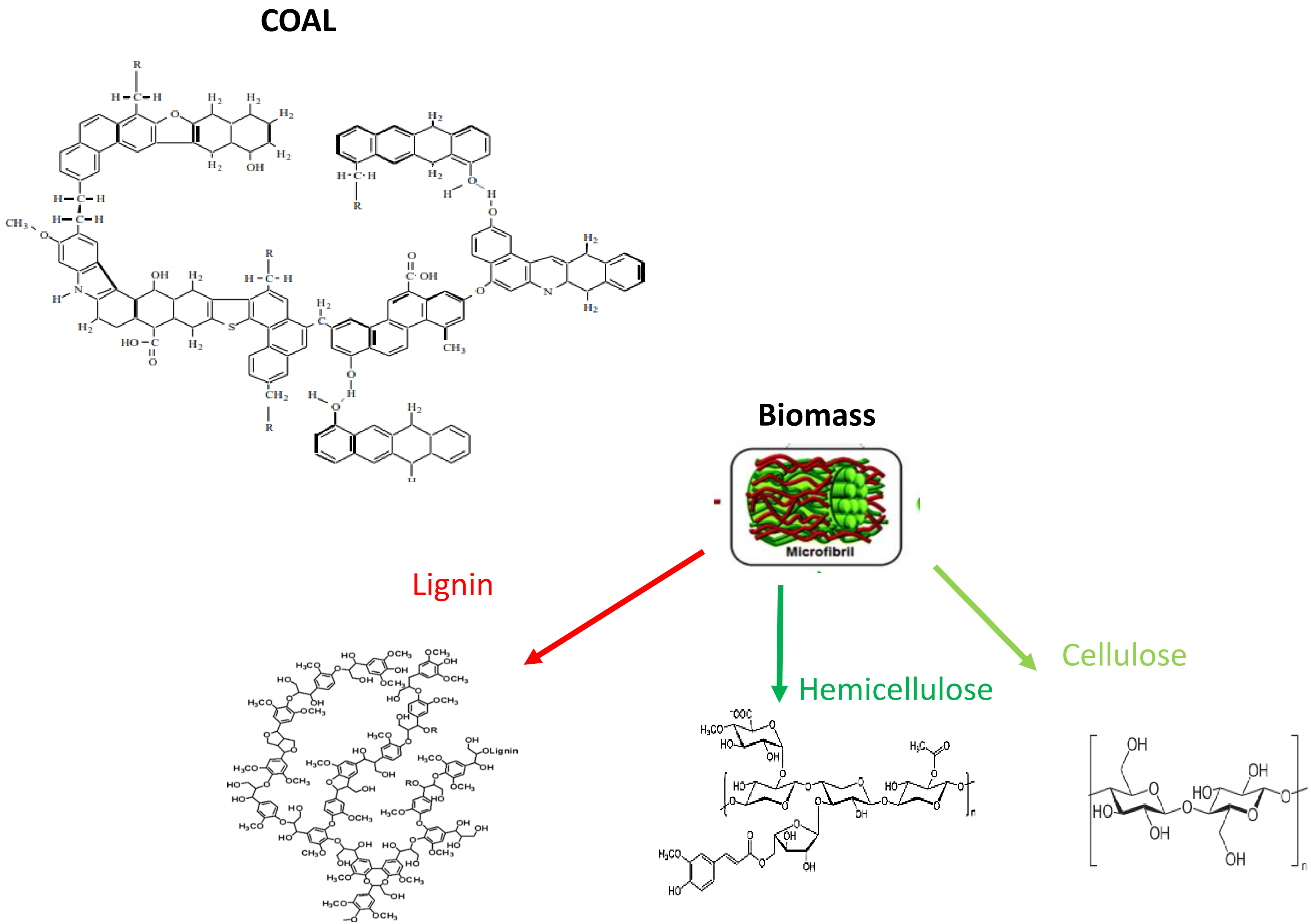
PAHs are favoured in CO_2

Let's move from coal to lignite to synthetic carbons (approaching biomass)

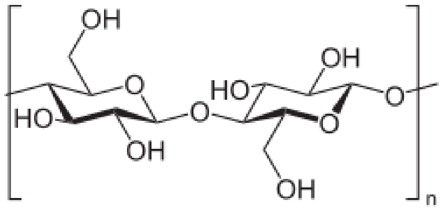


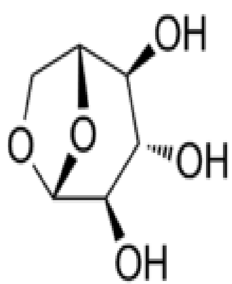
- Temperature favours PAHs
- CO_2 also favours PAHs (but less in the iron doped sample)

(catalytically activate tar gasification?)

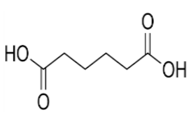

COAL
Biomass
Microfibril
Lignin
Hemicellulose
Cellulose

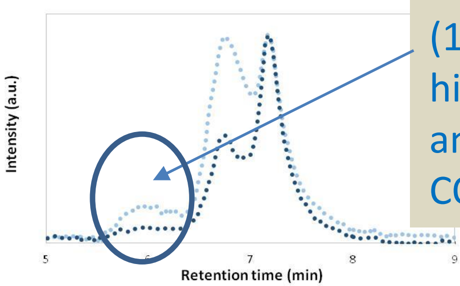
Cellulose





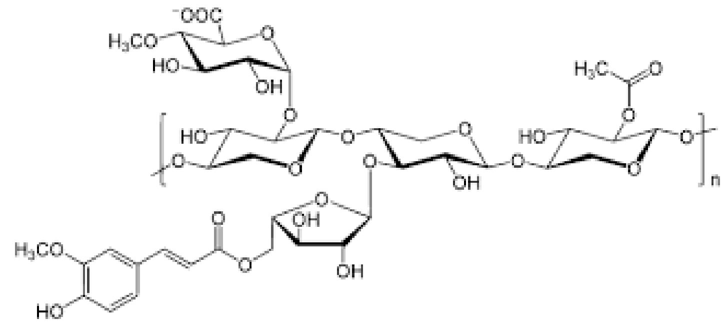
Light tar
is for > 90% composed of levoglucosan (unit block).
In CO_2 at high temperature there is an increase of phenol

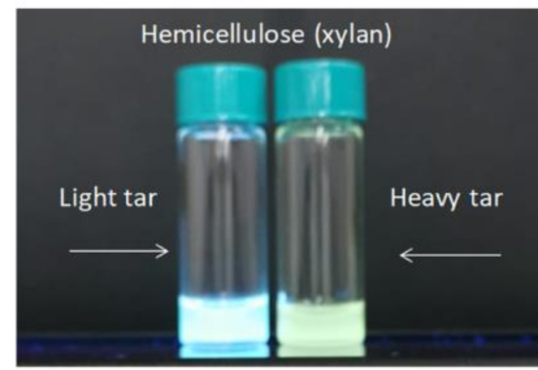


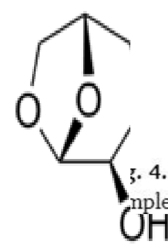


Hevy tar
the early SEC peak (100nm) appears at high temperature and increases with CO2

Xylane

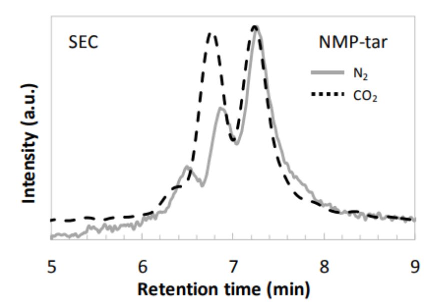




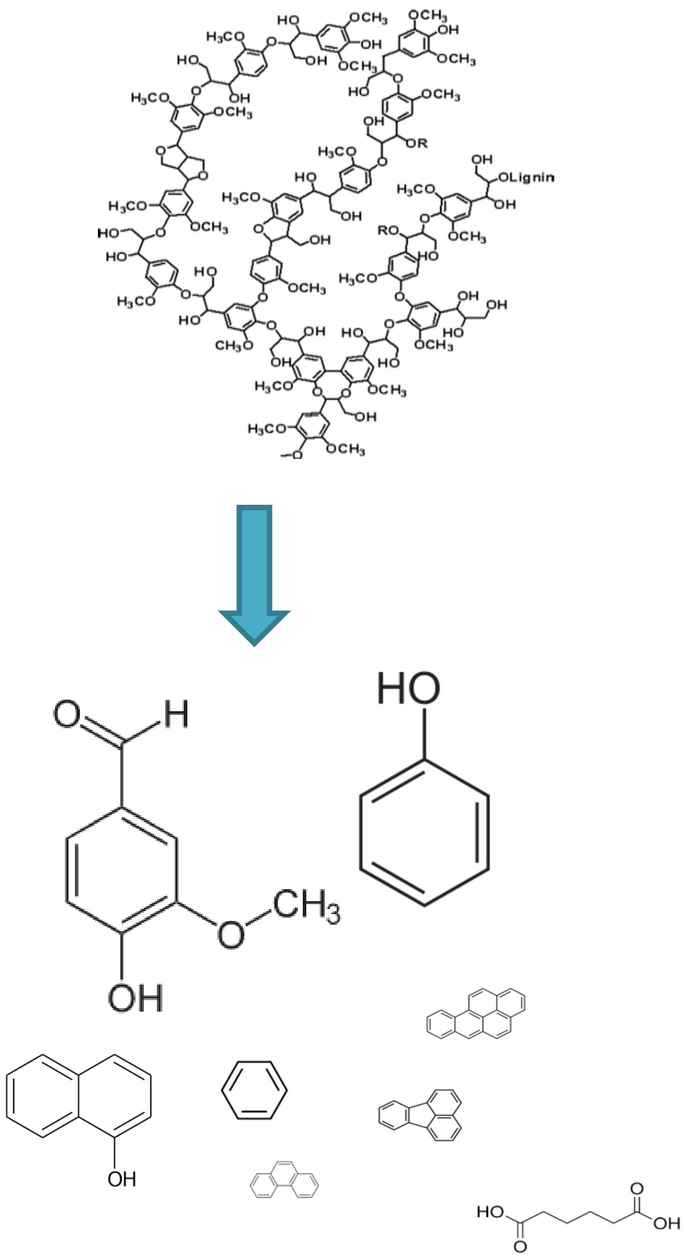


g. 4. Photo under blue light irradiation (365 nm) of hemicellulose (xylan
nples, dissolved in acetone and NMP [80].

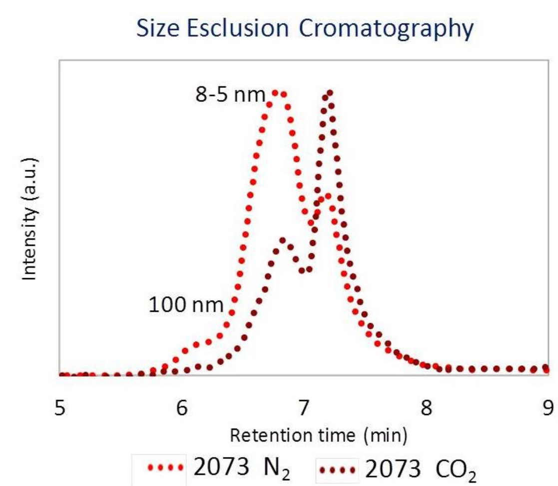
Hevy tar
The early SEC peak is not observed

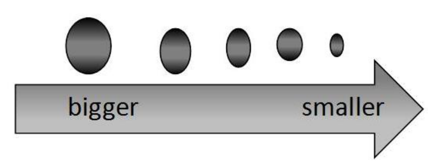


Lignin



N_2	1573	Oxo-aromatics: 50% Anhydrous monosaccharides: 30% Light PAHs: 20%	Bimodal distribution
CO_2	1573	Anhydrous monosaccharides: 40% Oxo-aromatics: 30% Light PAHs: 30%	
N_2	2073	Anhydrous monosaccharides:60% Aliphatics: 20% Light PAHs: 15% Oxo-aromatics: 10% Heavy PAHs: 5%	Trimodal distribution (higher MW)
CO_2	2073	Light PAHs: 40% Oxo-aromatics: 30% Aliphatics: 20% Anhydrous monosaccharides:10%	Bimodal distribution



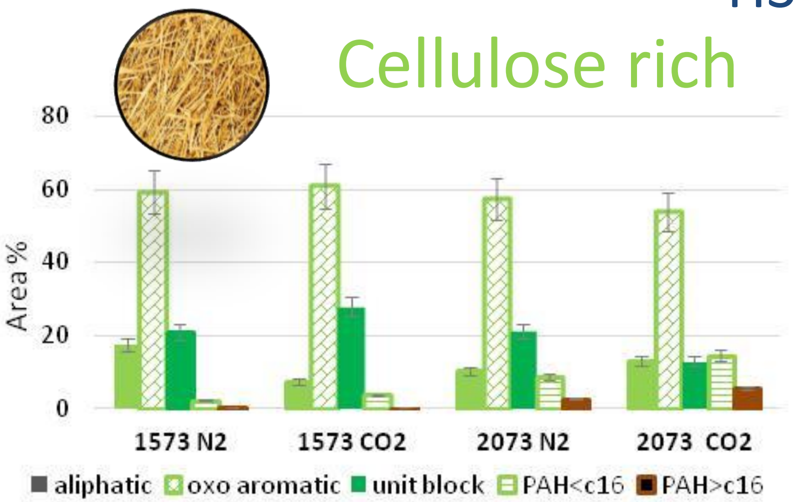


Cellulose rich vs *Lignin* rich biomass: opposite effect of CO_2 at high temperature

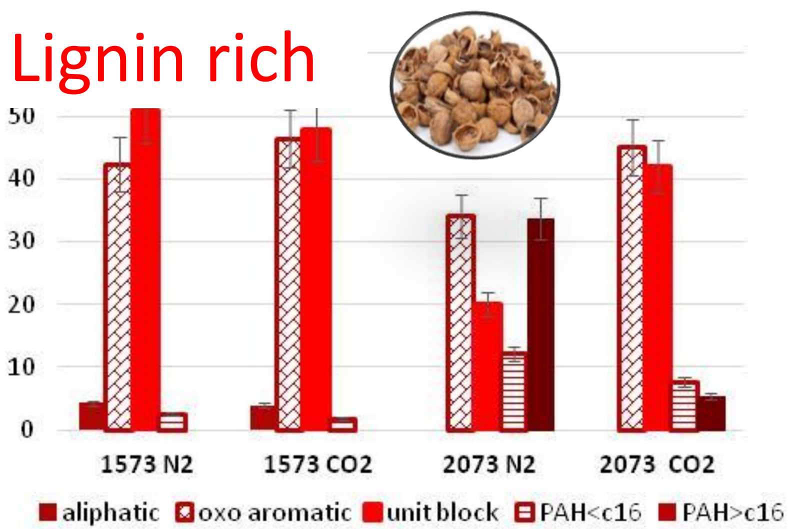
HSR: primary tar

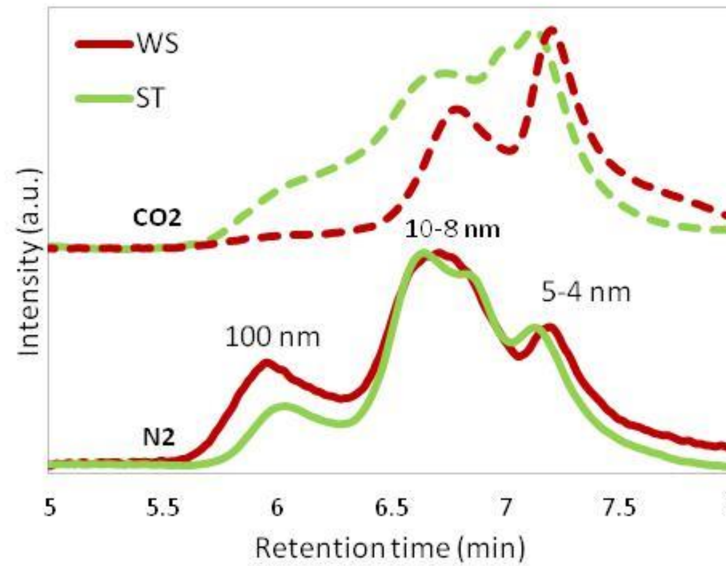
2073 K

Cellulose rich

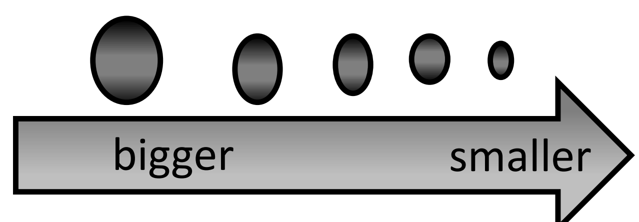


Lignin rich



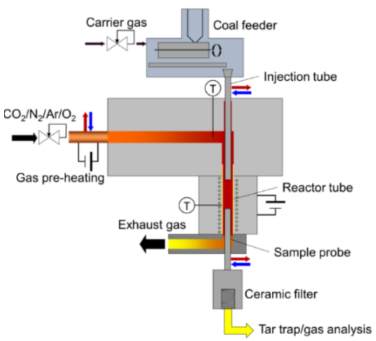


Size Esclusion Cromatography

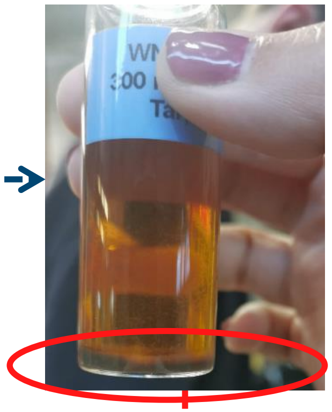


Secondary tar
WS (in DTR)

Drop Tube Reactor

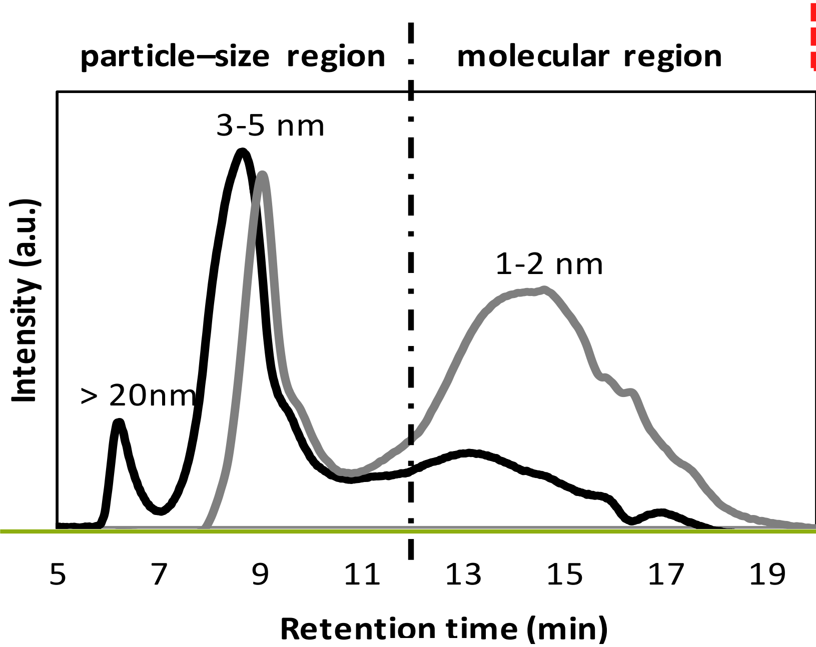


acetone



Sample	T(K)	t(s)	N_2	CO_2
Walnut shells	1125 K	0.1 s	no	
Walnut shells	1125 K	0.24 s	no	yes
Walnut shells	1125 K	0.38 s	little	yes
Walnut shells	1300 K	0.1 s	no	no
Walnut shells	1300 K	0.24 s	yes	n.a.
Walnut shells	1300 K	0.38 s	A lot	A lot

CO_2 and high temperature favor the formation of ***heavy tar***



Conclusions

- Secondary reactions, temperature and CO_2 in general favour formation of PAHs in tar and carbon particulates for both coal and biomass.
- In coal carbon particles are larger (soot), in biomass are very small (fluorescent carbon dots)
- At very high temperature (1800°C) CO_2 reduces the formation of carbon particulate in lignin rich biomasses

- **Open to discussion**

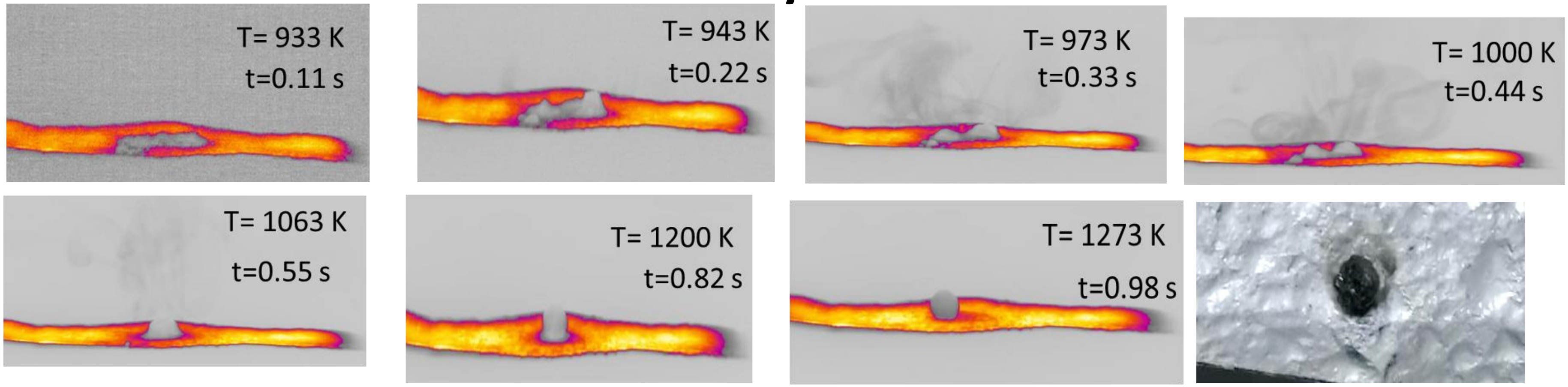
Why???

- One more question for further work:

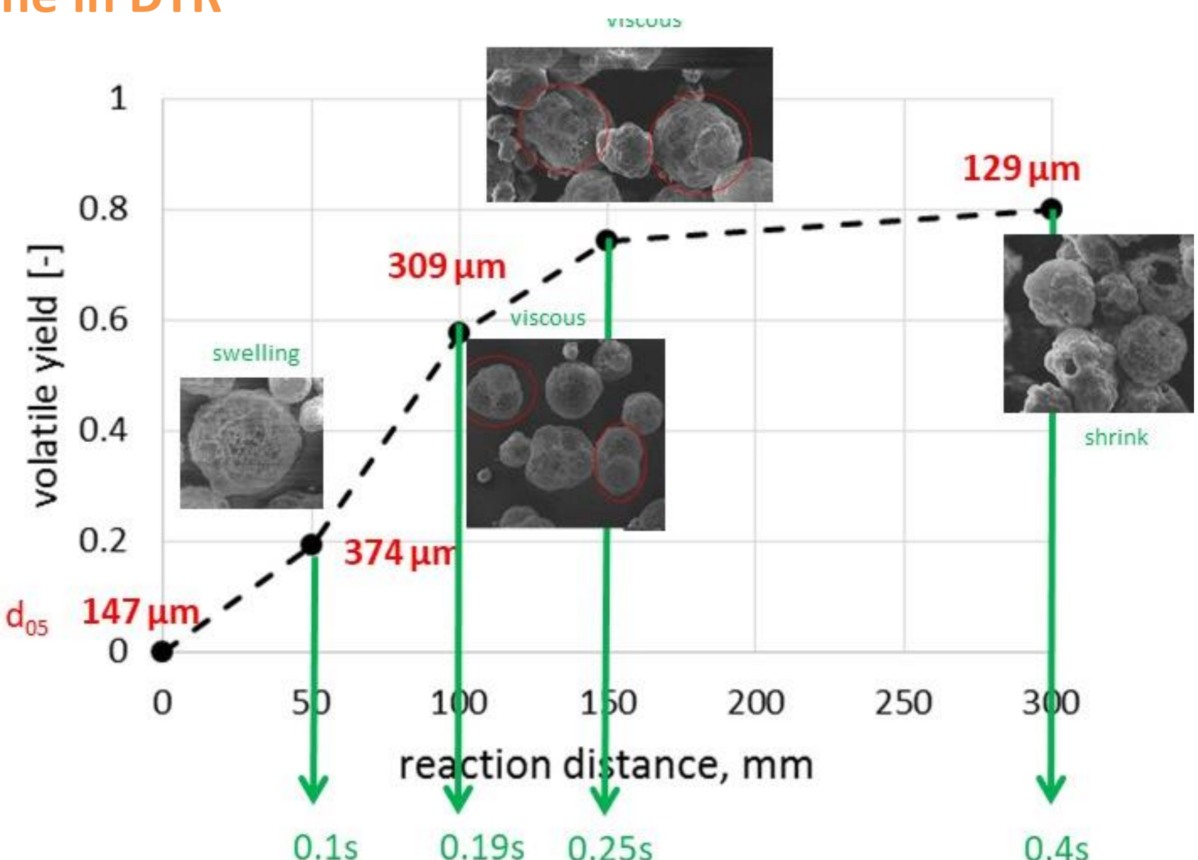
effects of plasticity on tar evolution and soot formation

Plasticity effects

Xylane in HSR



Xylane in DTR



During pyrolysis primary tars are entrapped in the melt.

Can this further influence soot formation?