Effect of molecular structure of C1 – C7 hydrocarbons on PAH formation

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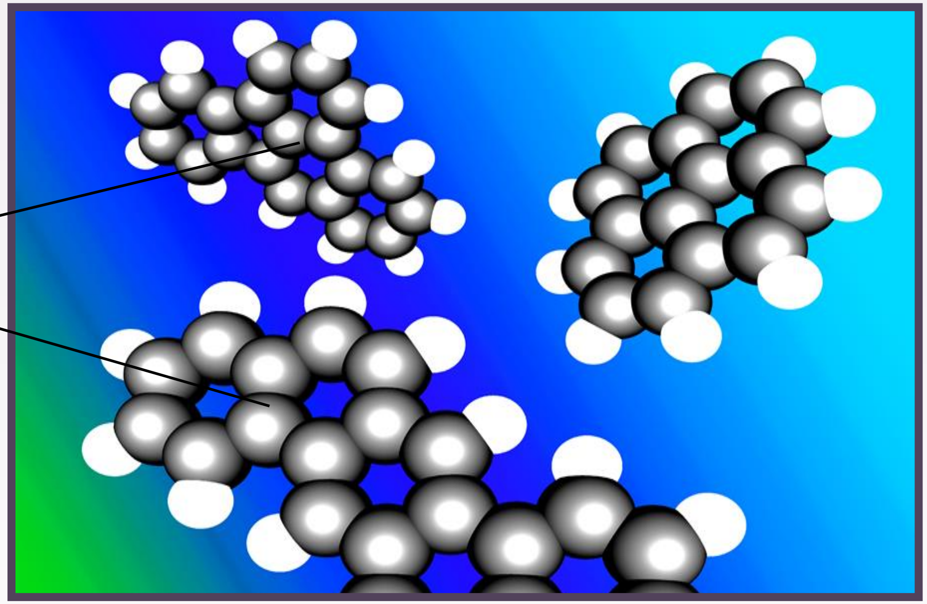
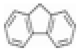
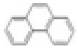
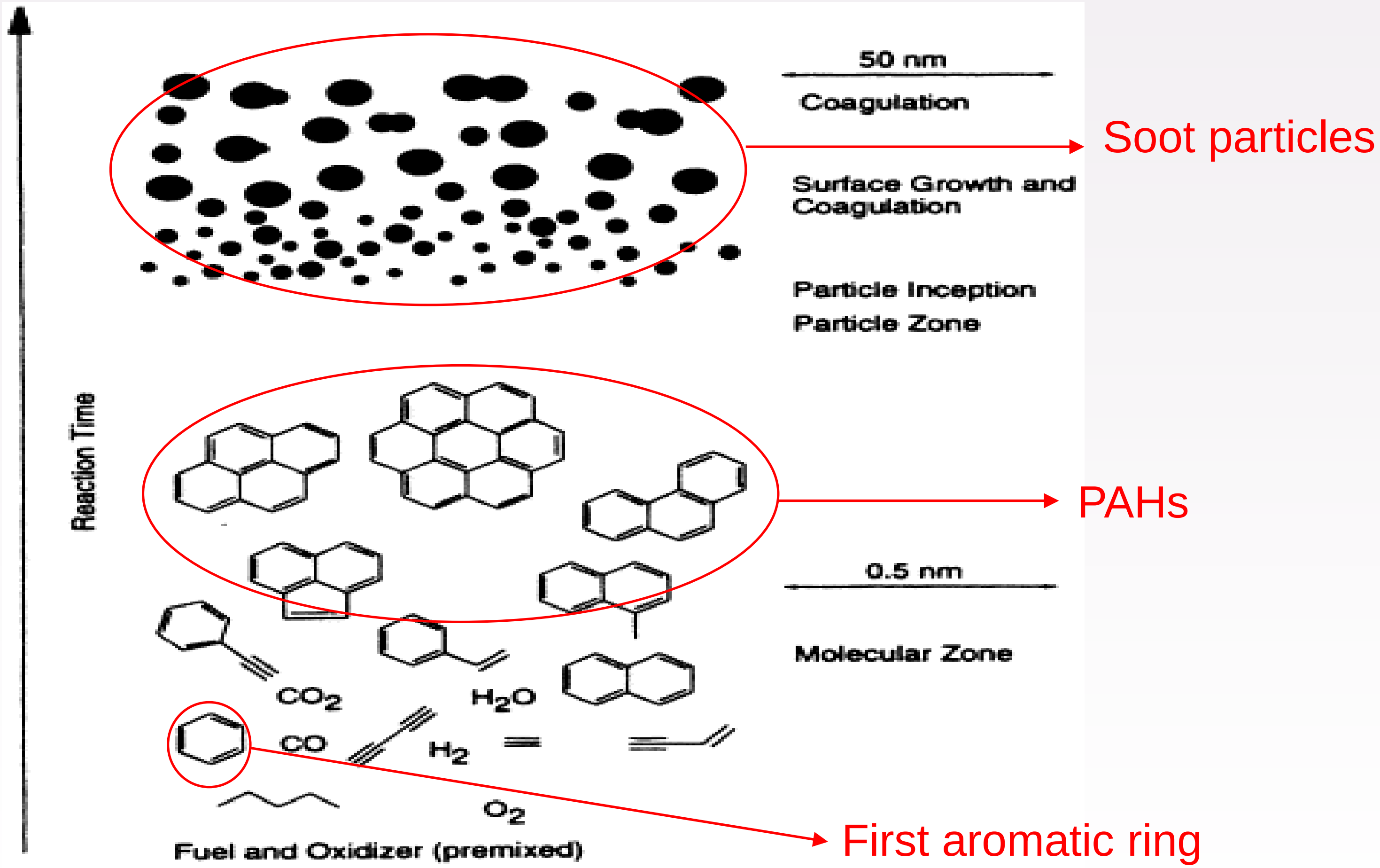
Introduction: Poly-aromatic hydrocarbons (PAHs)

PAHs



Sn	PAHs	PAH Abbreviation	Toxicity Group	Toxicity Factor	PAH Rings	Structure
1	Naphthalene	NPH	D	0.001	2	
2	Acenaphthylene	ACY	D	0.001	3	
3	Acenaphthene	ACN	NA	0.001	3	
4	Fluorene	FLU	D	0.001	3	
5	Phenanthrene	PHN	D	0.001	3	
6	Anthracene	ATR	D	0.01	3	
7	Fluoranthene	FLT	D	0.001	4	
8	Pyrene	PYR	NA	0.001	4	
9	Benzo[a]anthracene	B[a]A	B2	0.1	4	
10	Chrysene	CRY	B2	0.01	4	
11	Benzo[b]Fluoranthene	B[b]F	B2	0.1	5	
12	Benzo[k]Fluoranthene	B[k]F	B2	0.1	5	
13	Benzo(a)pyrene	B[a]P	B2	1.0	5	
14	Indeno[1,2,3-cd]pyrene	I[123cd]P	B2	0.1	6	
15	Dibenzo[a,h]anthracene	D[ah]A	B2	1.0	5	
16	Benzo[g,h,i]perylene	B[ghi]P	D	0.01	6	

Introduction: PAHs Vs Soot



Richter, H. and Howard, J. (2000) Prog. Energy and Combust Sci.

Motivation

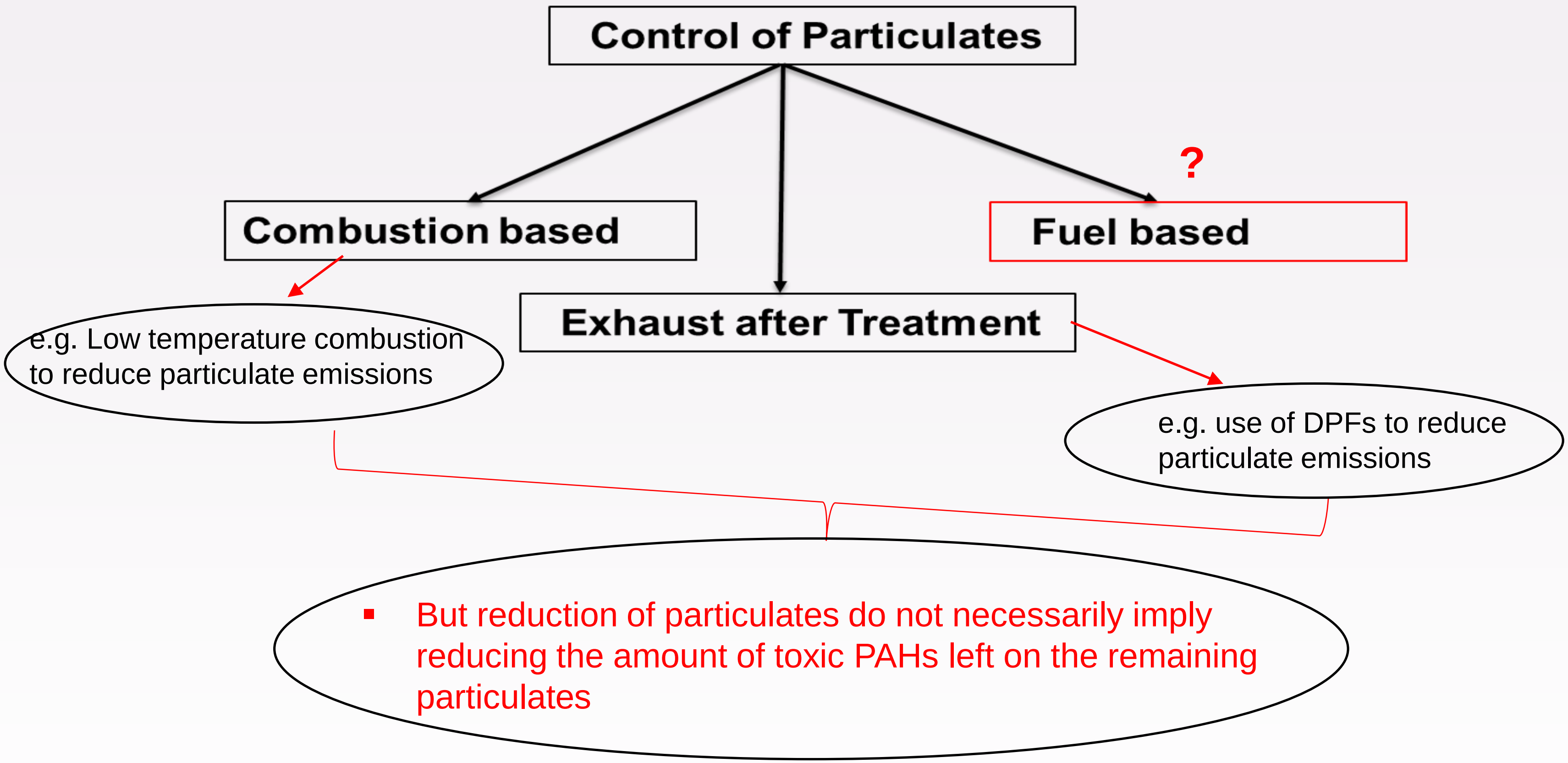
- Rise in human mortality rate ⟶ Stringent global particulate legislation

- Example of London Borough of Camden;

- Population = 165,000
- Number of annual deaths = 1126
- Particulate related deaths = 87
- Statistically, the 87 deaths caused a reduction of life average expectancy of 13.3yrs
- 1 in every 15 people will have their lifespan reduced by 13.3 years due to particulates

Gowers, M., Miller, B.G. & Stedman, J.R., 2014. *Estimating Local Mortality Burdens associated with Particulate Air Pollution, Public Health England*

Control of particulates

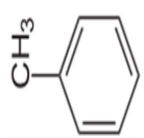


Two fuel-based approaches to eliminating the toxicity of particulates:

a) Eliminate the formation of carbon particles which act carriers of toxic substances such as PAHs

b) Reduce the formation of toxic substances on the particulates such as PAHs

Methodology

Fuel Molecules	Molecular Structures
Methane	CH_4
Ethane	CH_3CH_3
Ethylene	$H_2C = CH_2$
Acetylene	$HC \equiv CH$
Dimethyl-Ether (DME)	$H_3C-O-CH_3$
Propane	$CH_3\ CH_2CH_3$
Propene	$CH_3\ CH{=}CH_2$
Butane	$CH_3\ CH_2\ CH_2CH_3$
Iso-butane	$CH_3CH(CH_3)CH_3$
Toluene	

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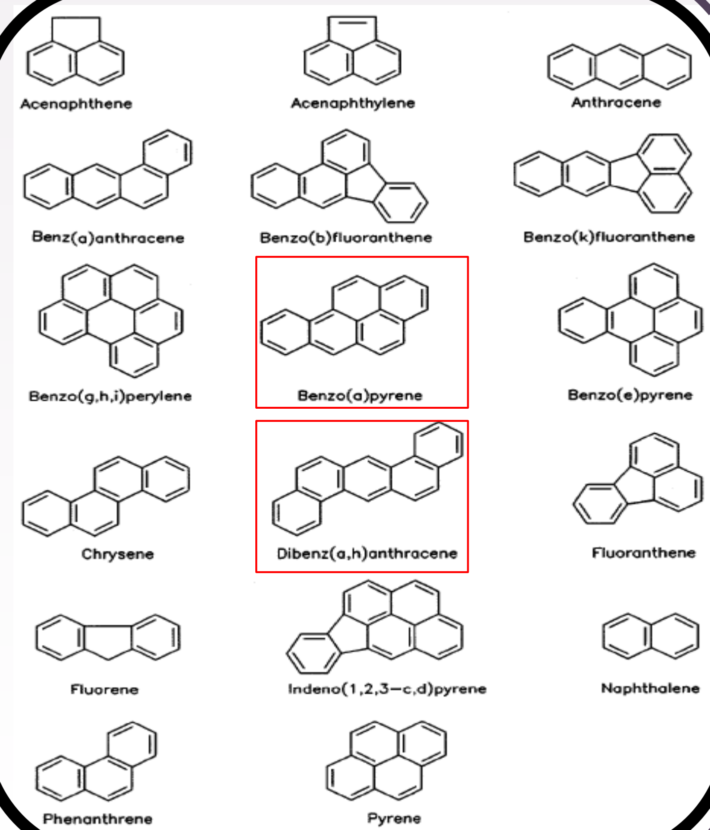
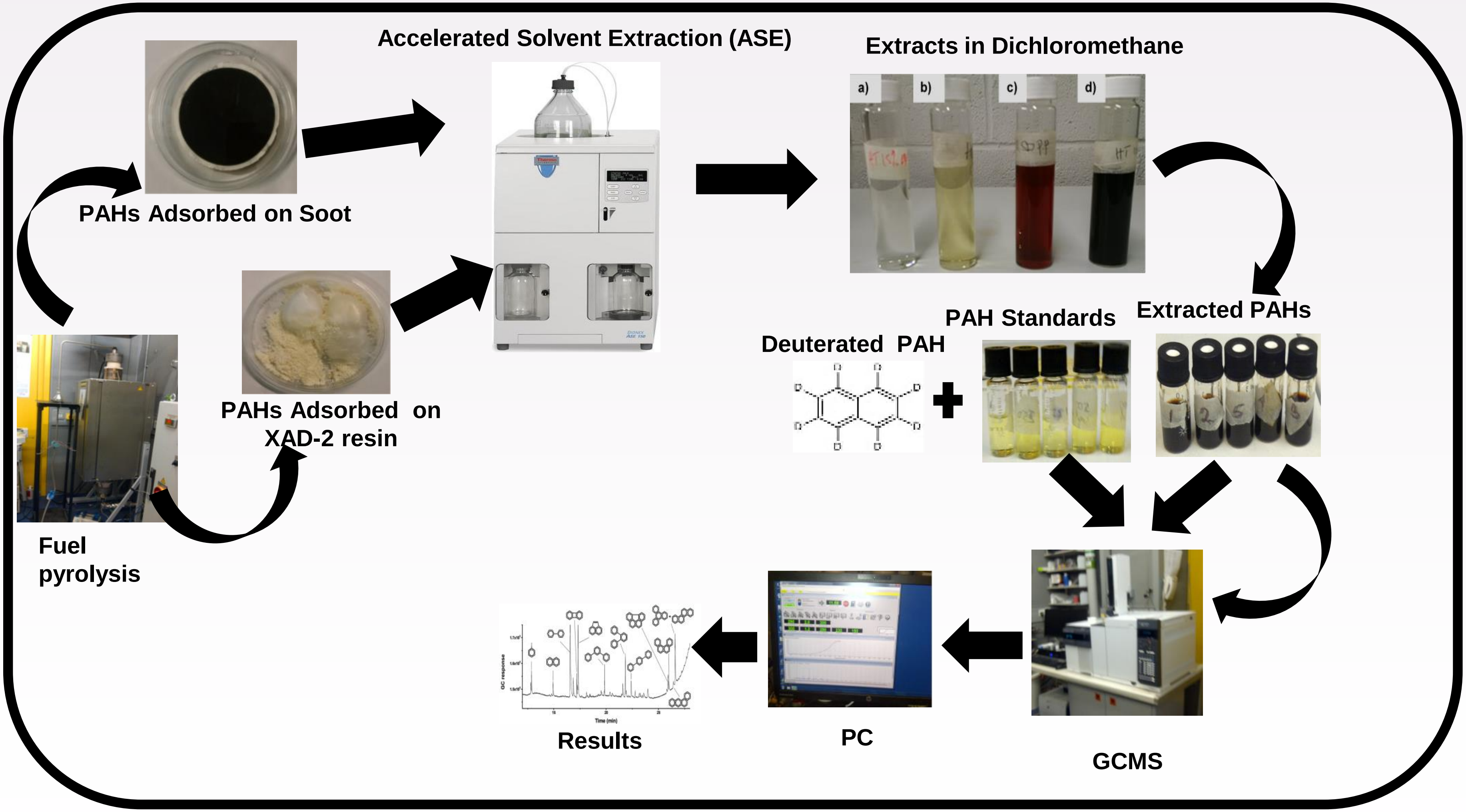
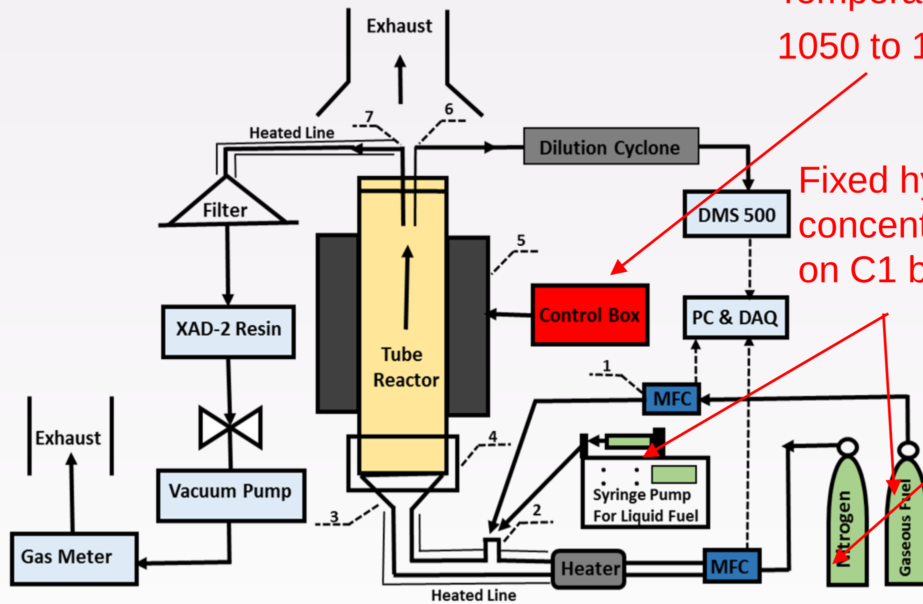


Methodology



Generation of particulates and gas phase PAHs



Temperature range of 1050 to 1350 ^{o}C

Fixed hydrocarbon concentration of 10,000 ppm on C1 basis

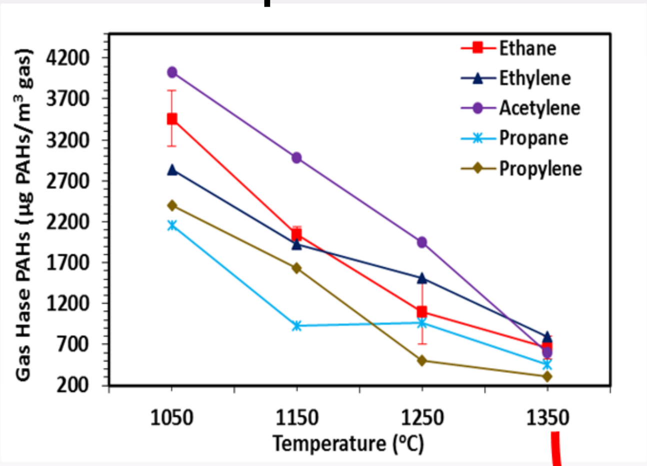
N_2 flowrate of 20L/min

Schematics of the experimental set-up: 1) mass flow controller (MFC) 2) vaporiser 3) static mixer 4) circulating cooling water 5) tube furnace 6) DMS 500 sampling probe 7) soot sampling probe

Results - effect of unsaturation on PAHs

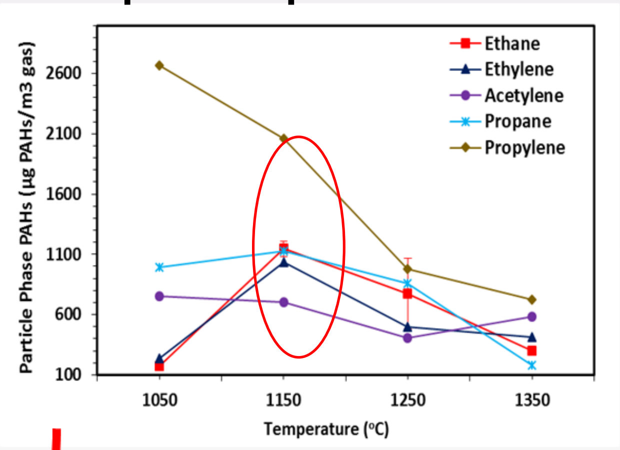
Gas phase PAHs

a)



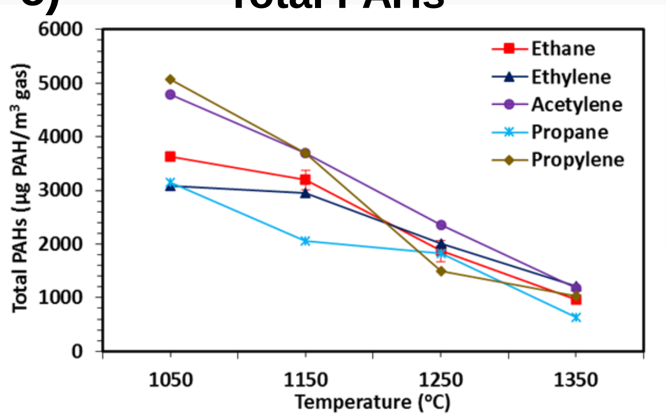
particle phase PAHs

b)



c)

Total PAHs



- ✓ Increase in Degree of unsaturation of fuels favoured GP PAHs in C2 fuels

- ✓ Increase in Degree of unsaturation of fuels favoured PP PAHs in C3 fuels

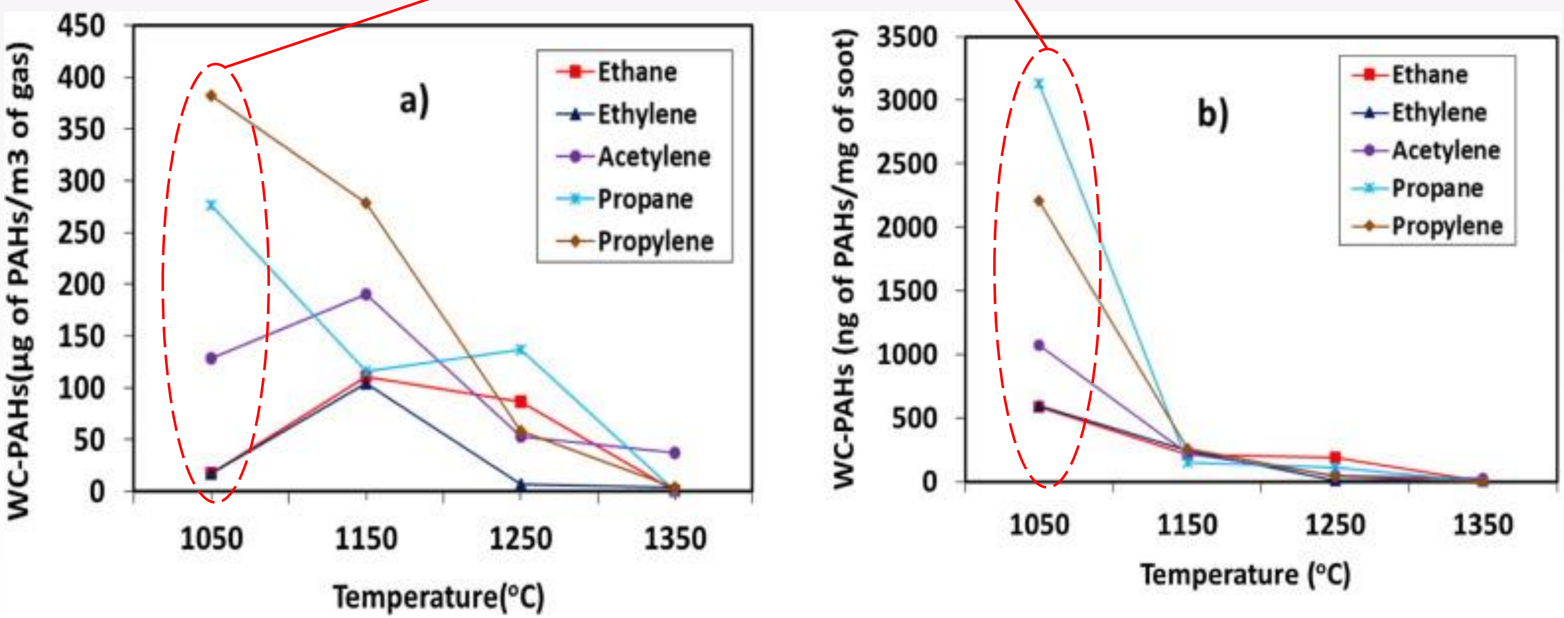
Results – Weighted carcinogenicity of PAHs (WC- PAHs)

$$\text{WC-PAHs} = \sum_{i=1}^{16} (\text{TEF}_i * \text{Ci})$$

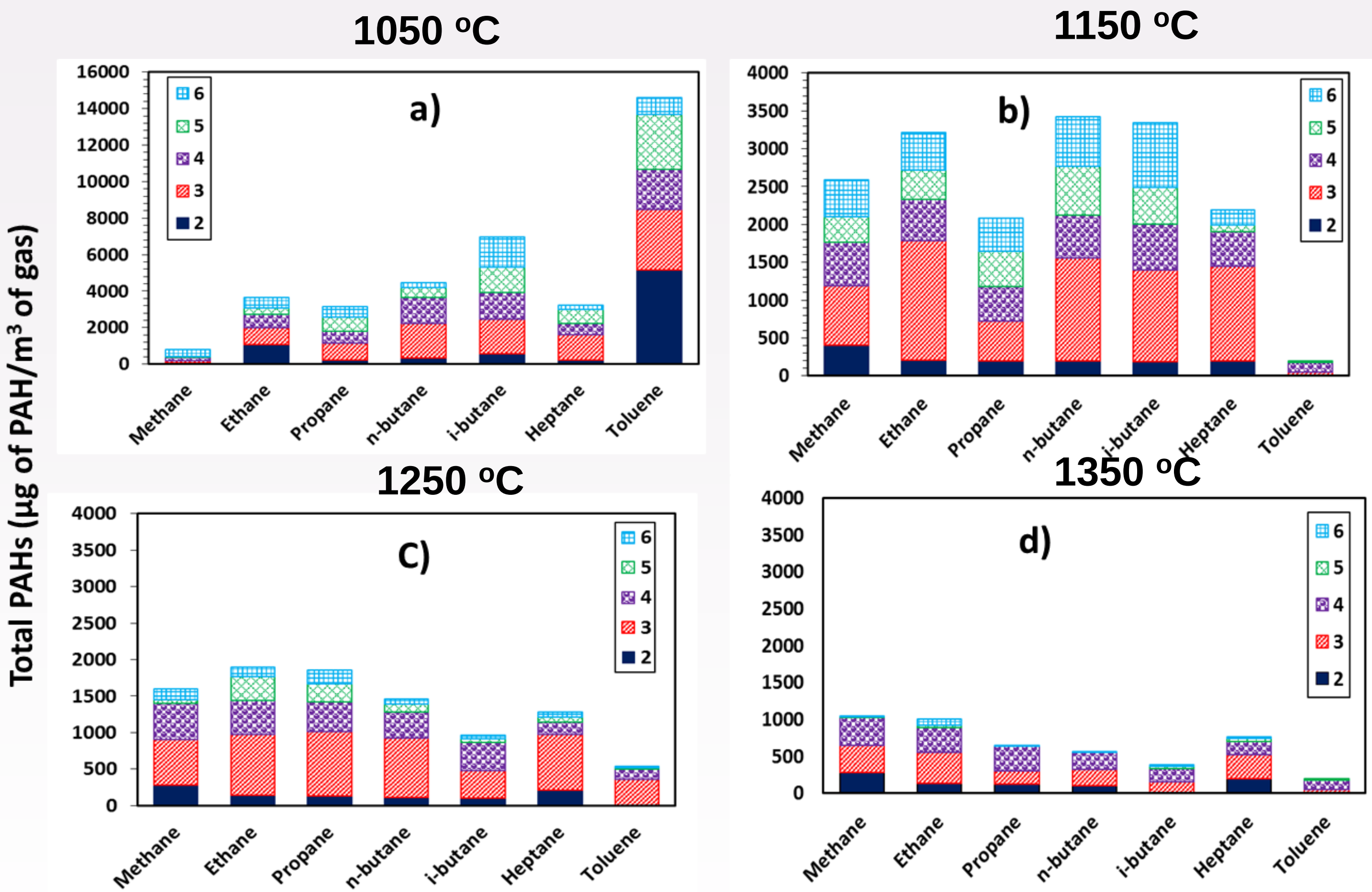
TEF = Toxicity equivalent factors

C_i = PAH concentrations

WC-PAHs is higher at low temperature



Results – effect of carbon number on PAHs

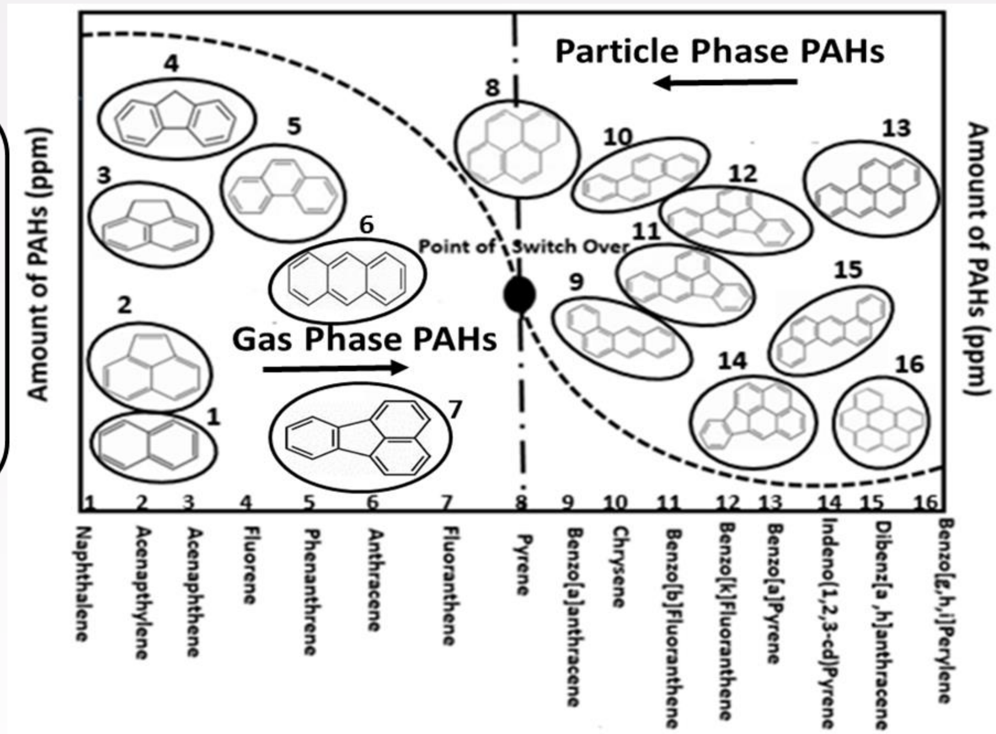


❑The total PAH concentrations tended to increase with increasing carbon number (excluding heptane) at the temperature of 1050 °C but an opposite (decreasing) trend was observed at 1350 °C.

Gas phase and particle phase PAH distributions - Summary

GP PAHs

- ✓ High vapour Pressure
- ✓ Low Boiling Point
- ✓ Hence, highly volatile

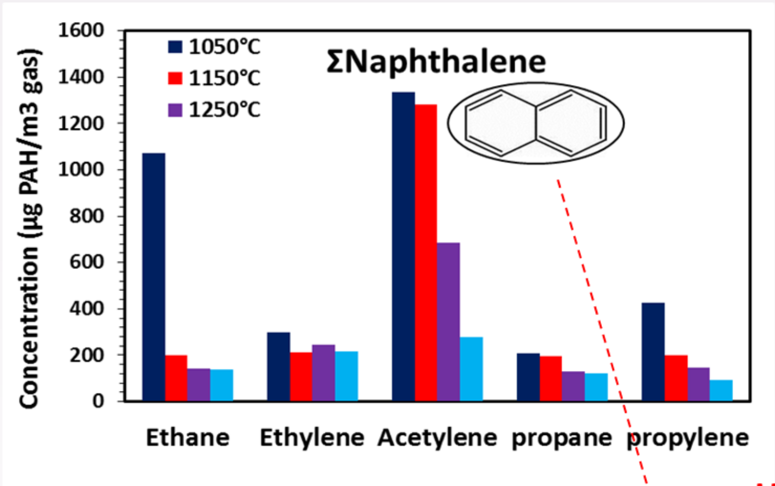


PP PAHs

- ✓ Low vapour Pressure
- ✓ High Boiling Point
- ✓ Hence, highly less volatile

- ❖ From Naphthalene to pyrene, the amount of gas phase PAHs (ppm) decreases
- ❖ From Pyrene to Benzo (g,h,i)Perylene, the amount of particulate PAHs (ppm) increases
- ❖ Pyrene was considered as vital PAH in transition from gas to particle phase
- ❖ Mojority of PAH growth passes through pyrene

Formation of a two ring naphthalene PAH via HACA mechanism



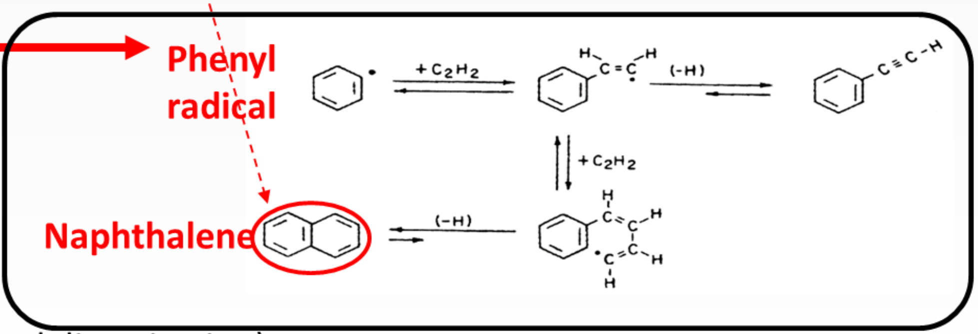
Naphthalene was the most abundant PAH found during the pyrolysis of a triple-bonded acetylene

HACA – Hydrogen Abstraction, Acetylene Addition

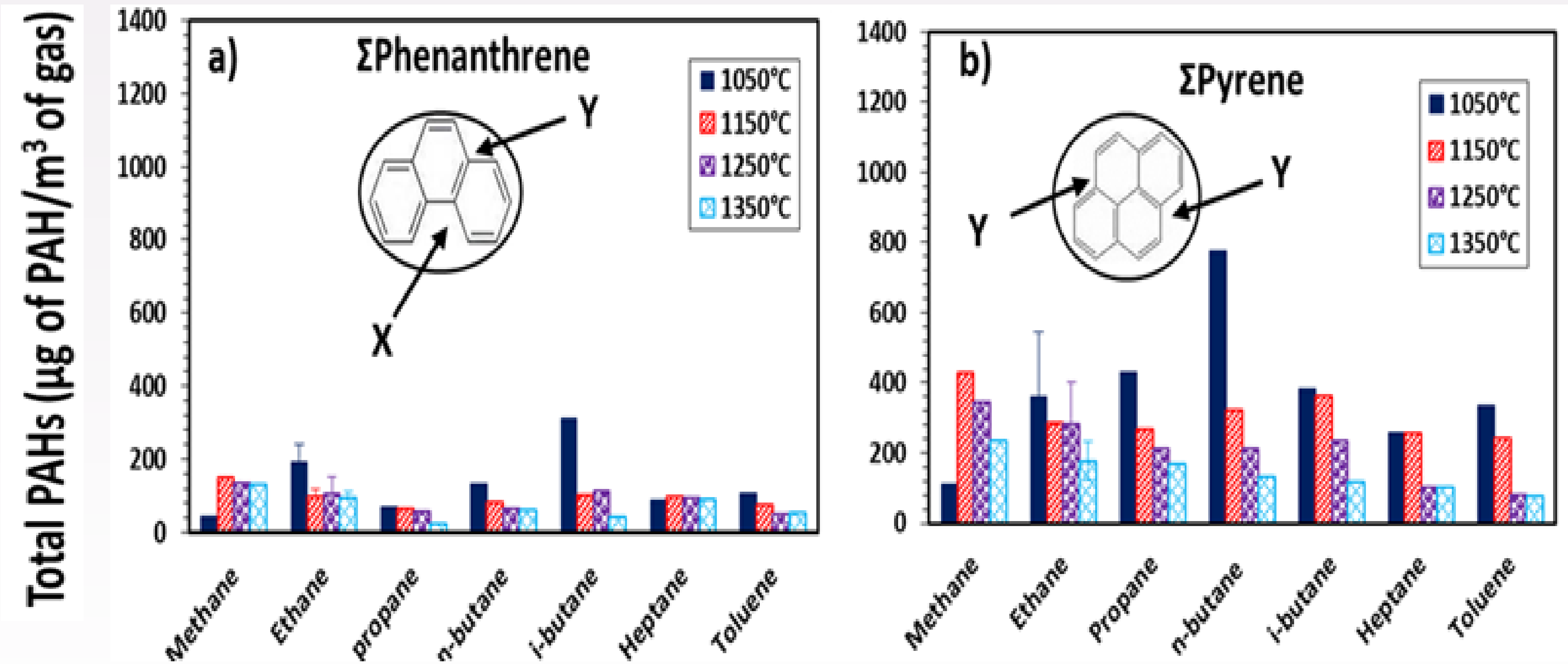
Possible Phenyl/benzene routes from acetylene

- ✓ $n\text{-}C_4H_3 + C_2H_2 \rightarrow C_6H_5$
- ✓ $n\text{-}C_4H_4 + C_2H_2 \rightarrow C_6H_6$

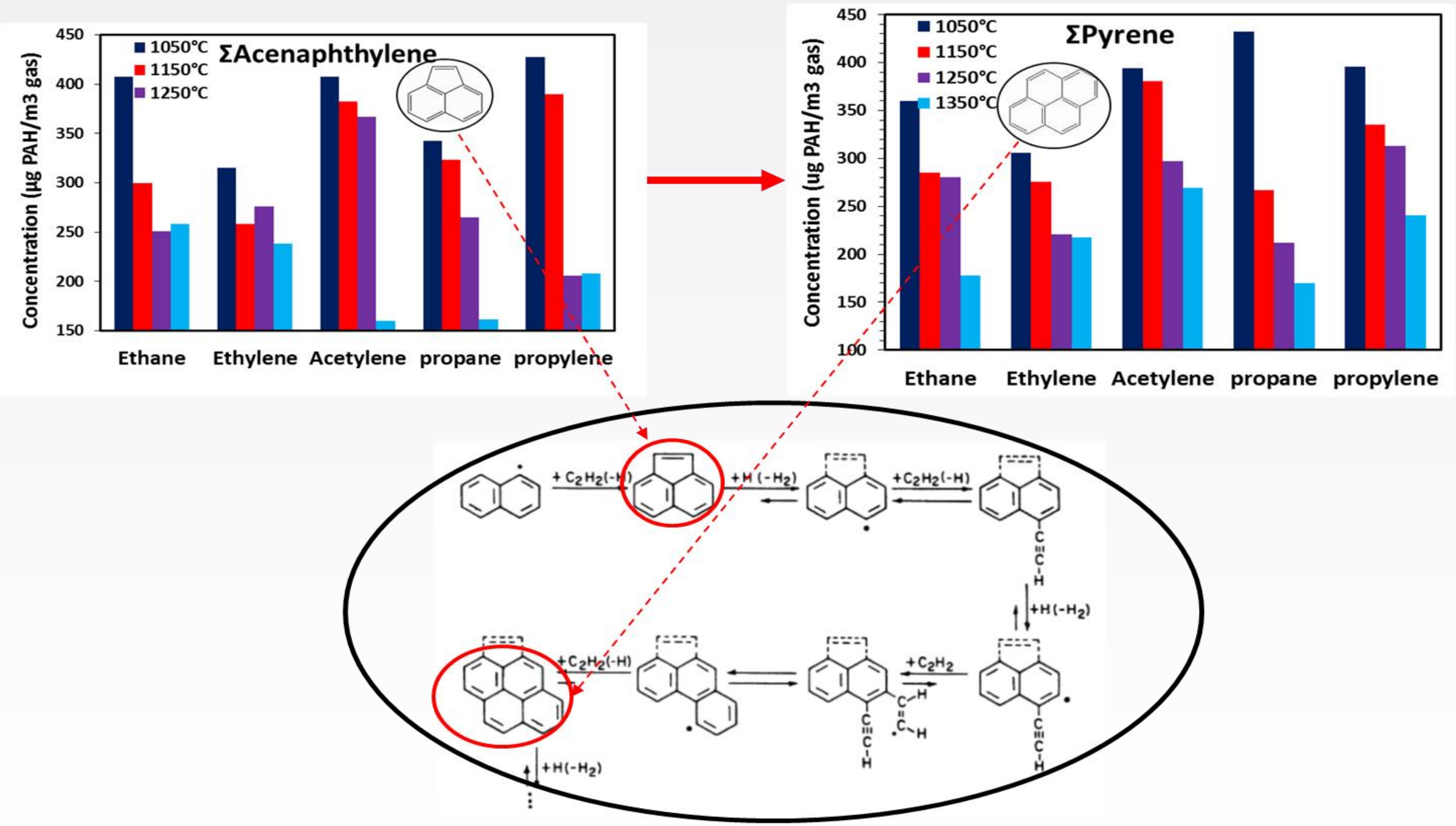
  ↑ $2(C_2H_2)$
- ✓ $3 (C_2H_2) \rightarrow C_6H_6$
- ✓ $2(C_3H_3) \rightarrow C_6H_6$ (Propargyl dimerization)



PAHs having 3 to 4 rings were detected in roughly similar concentrations regardless of the molecular structure of the hydrocarbon tested

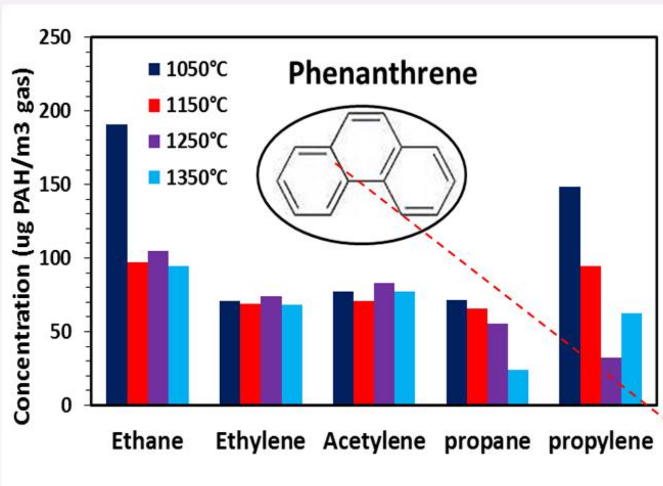


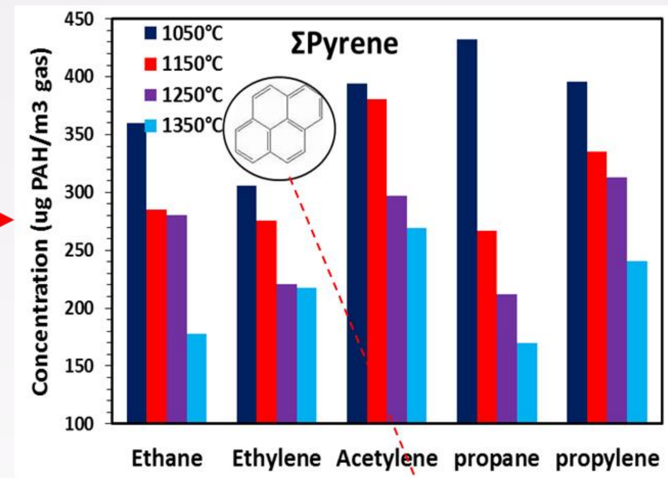
Growth of a five-membered ring acenaphthylene to Pyrene



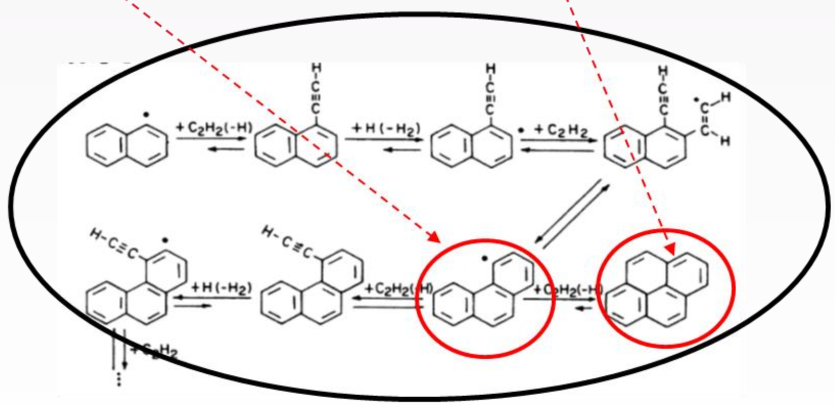
❖ PAH growth from Naphthalene → Acenaphthylene → Pyrene

Growth of a benzenoid phenanthrene to benzenoid Pyrene





- ❖ **Pyrene can also grow via Phenanthrene by HACA**



- ❖ PAH growth from Naphthalene → Phenatherene → Pyrene

- Further information on PAH formation of some C1 – C7 hydrocarbons can be found in:

Dandajeh, Hamisu Adamu, Nicos Ladommatos, Paul Hellier, and Aaron Eveleigh. 2017. “Effects of Unsaturation of C2 and C3 Hydrocarbons on the Formation of PAHs and on the Toxicity of Soot Particles.” *Fuel* 194. Elsevier Ltd: 306–20. doi:10.1016/j.fuel.2017.01.015

Conclusions

- Increasing pyrolysis temperature of the tube reactor decreased the total PAH concentration regardless of the carbon number and degree of unsaturation of the hydrocarbons

- The concentration of gas phase PAHs generated from the C_2 and C_3 fuels increased with increasing unsaturation in the fuels tested

- The total PAH concentrations tended to increase with increasing carbon number of the hydrocarbons from C1 – C7 (excluding heptane) at the temperature of 1050 ^oC but an opposite (decreasing) trend was observed at 1350 ^oC.

- The weighted carcinogenicity of PAHs was found have the highest concentration for all the fuels at the lowest temperature tested and this concentration decreased with rise in temperature to 1350 ^oC.

Thank You