GDR Feux – Rencontres de Toulouse, 12-13 octobre 2017

QUELQUES RAPPELS SUR LA NATURE ET LES EFFETS DU FUEL GAZEUX LORS DE LA MODÉLISATION DE LA PYROLYSE

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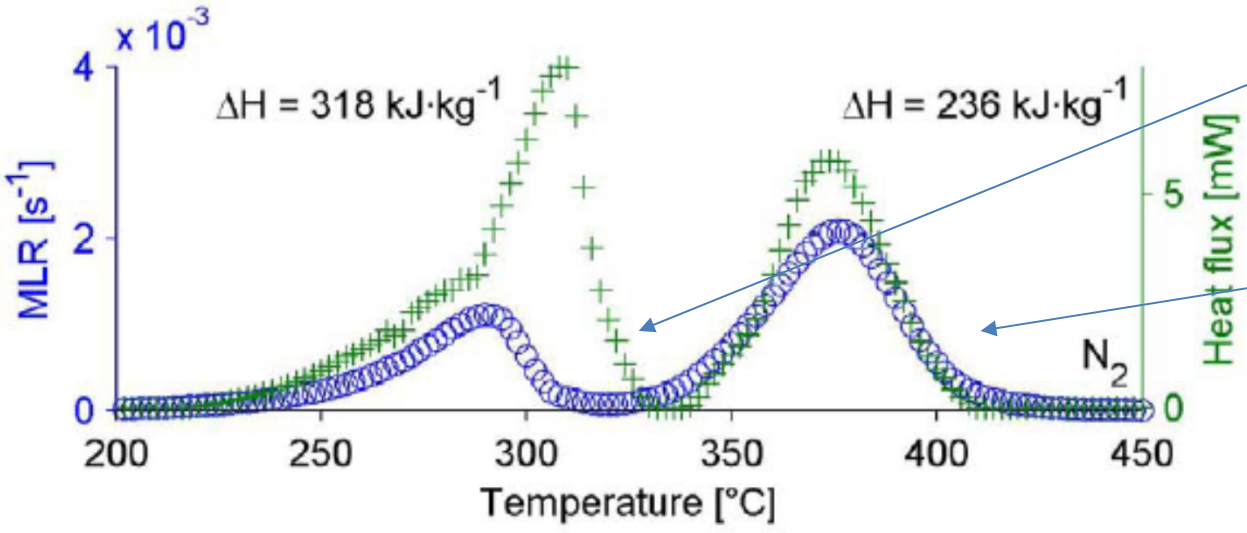
CHEMICAL APPROACH OF GASEOUS FUEL

- Need to study separately solid and gas phase
- Fire scientists often don't consider fuel as of importance
- Models often reduce gaseous FUELS to FUEL
- Accurate representation of flame requests proper knowledge of the gaseous fuel mixture
  - Turbulence calculation
  - Radiation

DIFFERENCES WITH SOLID PHASE (1)

- Description of solid phase based on mass loss rate as function of local temperature, i.e. using Arrhenius-like functions
- This is a very partial description:
  - Mass loss from the solid could correspond to various fractions simultaneously or consecutively
  - Combustibility domain of the fuels is a determining parameter.
  - Combustibility domains depend on pressure and temperature

Example case: polyurethane (from Bustamante thesis)



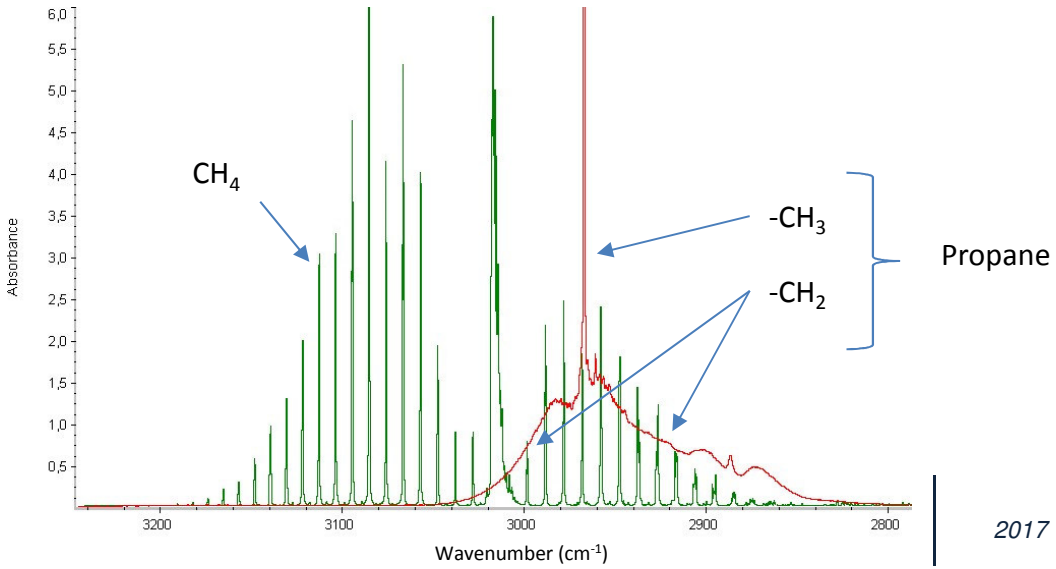
1st released, under 300°C, is made of isocyanates. This is not combustible under 400°C

2nd released, after 350°C, is polyols-based. This is combustible

DIFFERENCES WITH SOLID PHASE (2)

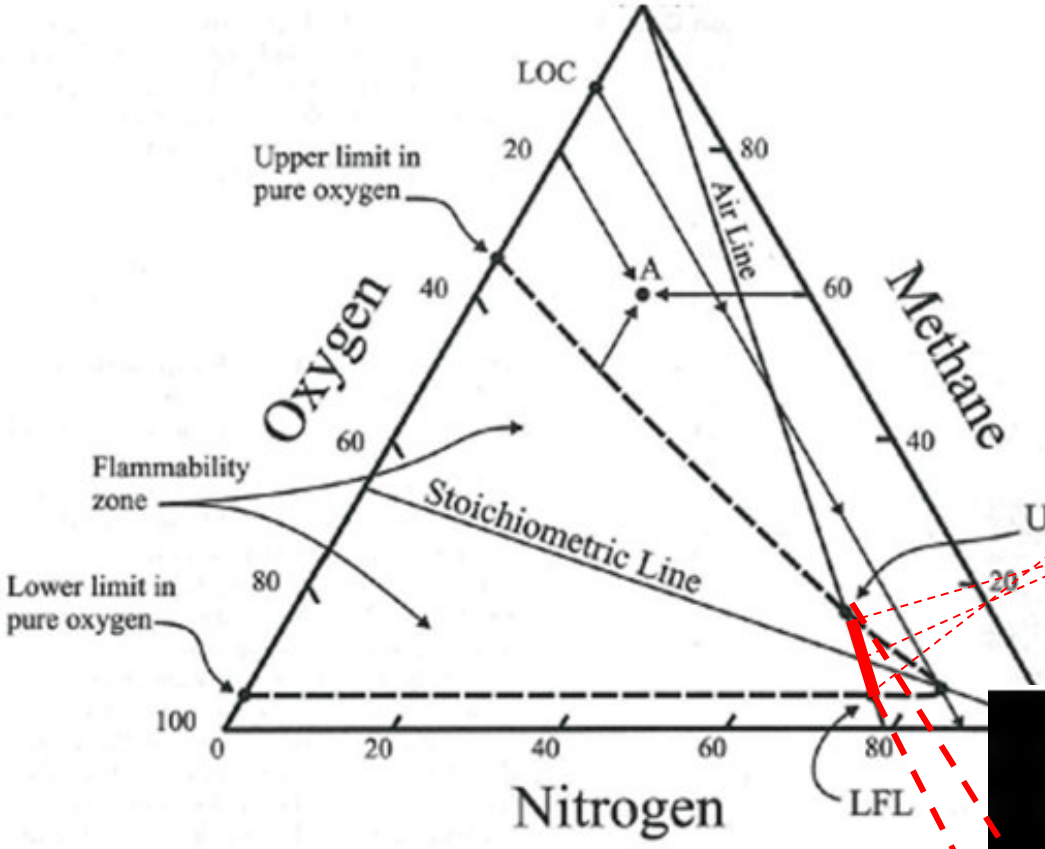
- Contrary to solid:
  - Gas phase reactions are not governed by their kinetic: too fast compared to the phenomena that interrest us in fires
  - The combustion in gas phase is driven by mixture, meaning **combustibility domains**

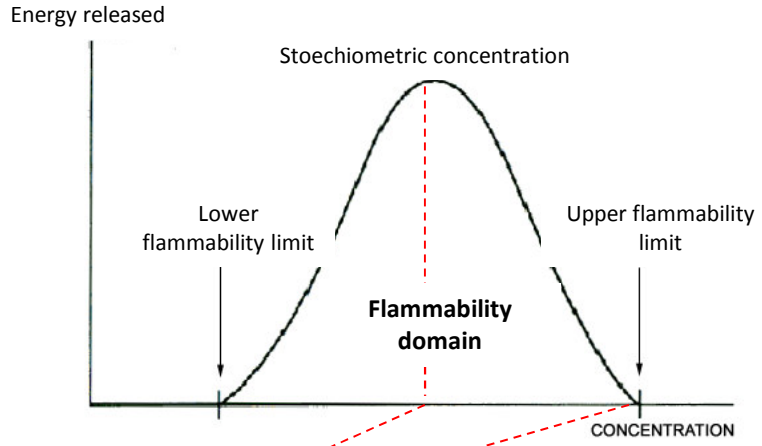
- Fuel species have several impacts on radiative balance:
  - Spectral dependance of emission / absorption down the flame
  - Influence on flame shape modifies view factors

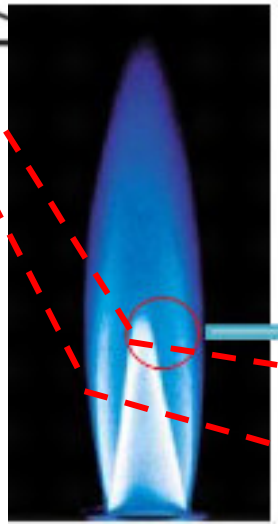


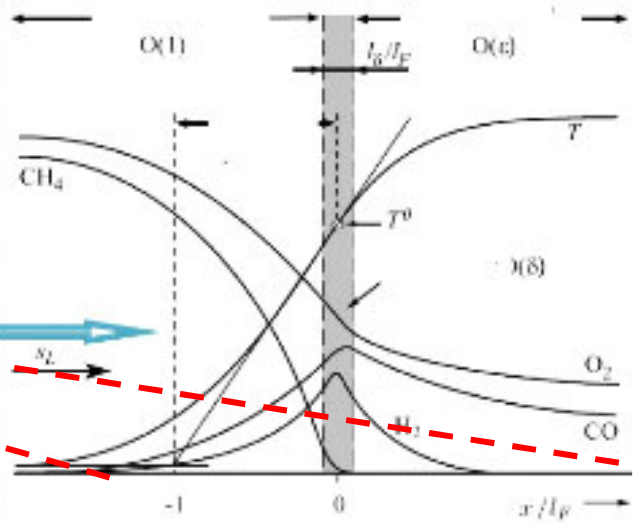
FTIR spectra of several fuels, showing radiative behaviour

COMBUSTIBILITY DOMAINS – EXAMPLE OF METHANE

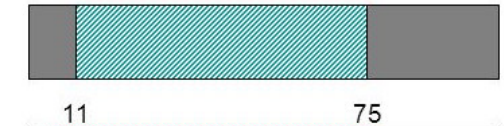
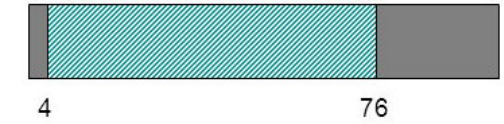








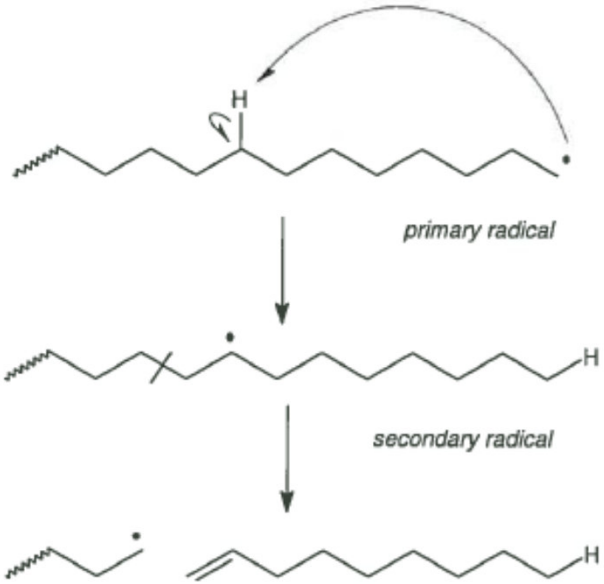
EXAMPLE OF COMBUSTIBILITY DOMAINS OF SEVERAL FUELS

Domain	Fuel	Density
	Methane	0.6
	Butane	2.01
	Propane	1.6
	Acetylene	0.9
	Carbon monoxide	0.97
	Hydrogen	0.07

FUEL SPECIES RELEASED DURING THERMAL DEGRADATION OF SELECTED SOLIDS

GENERAL CASE FOR THERMOPLASTICS

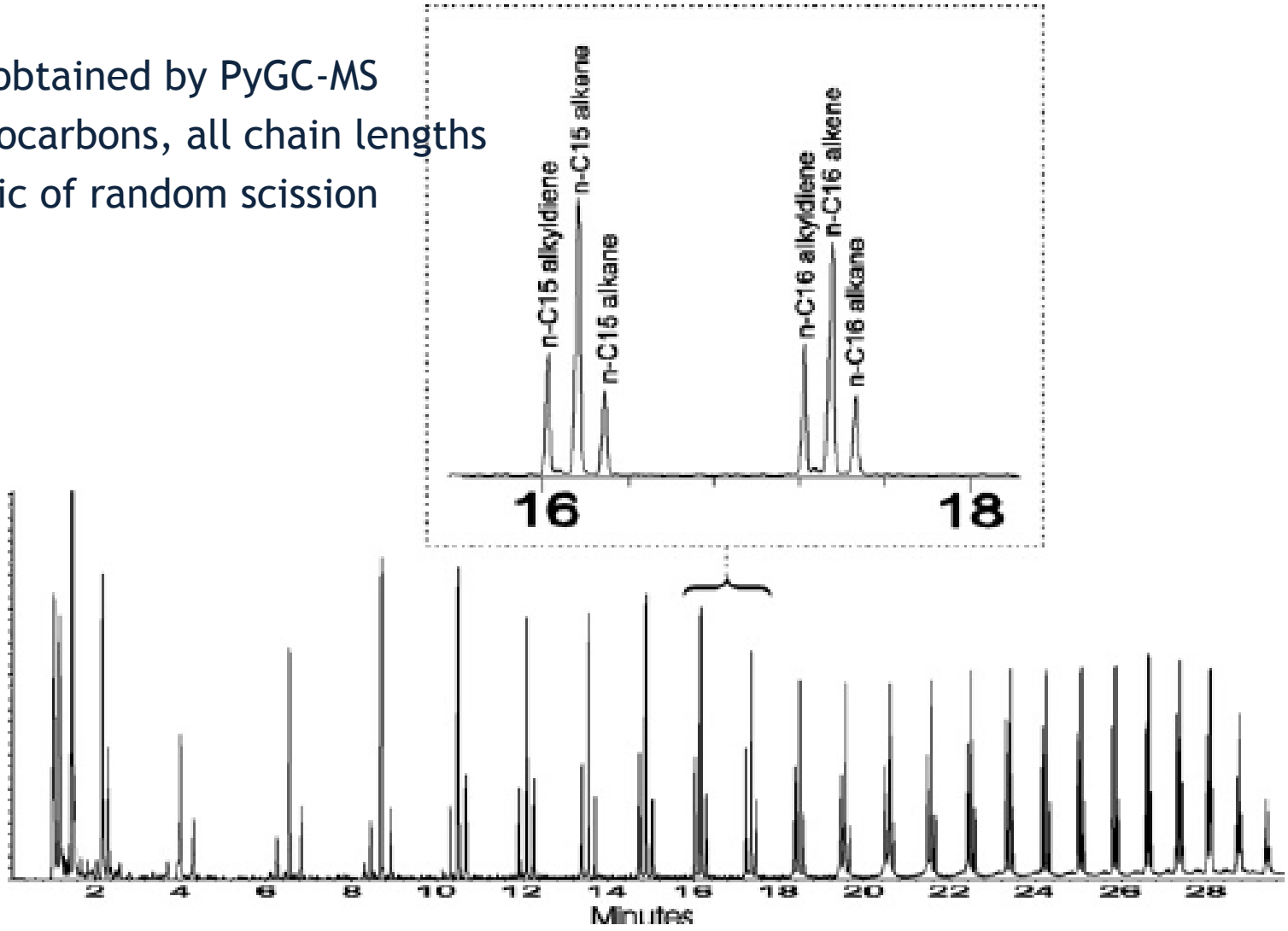
- Degradation occurs in 4 mechanisms (Bolland, 1947):
  - Random-chain scission
  - End-chain scission
  - Chain stripping
  - Cross-linking
- Scission may occur randomly, in weak points or in end of chain, resulting to the formation of lighter chain fragments
- If these chain fragments are light enough, they could be released as a gas



Typical example of scission process in a polyolefine

POLYETHYLENE (1)

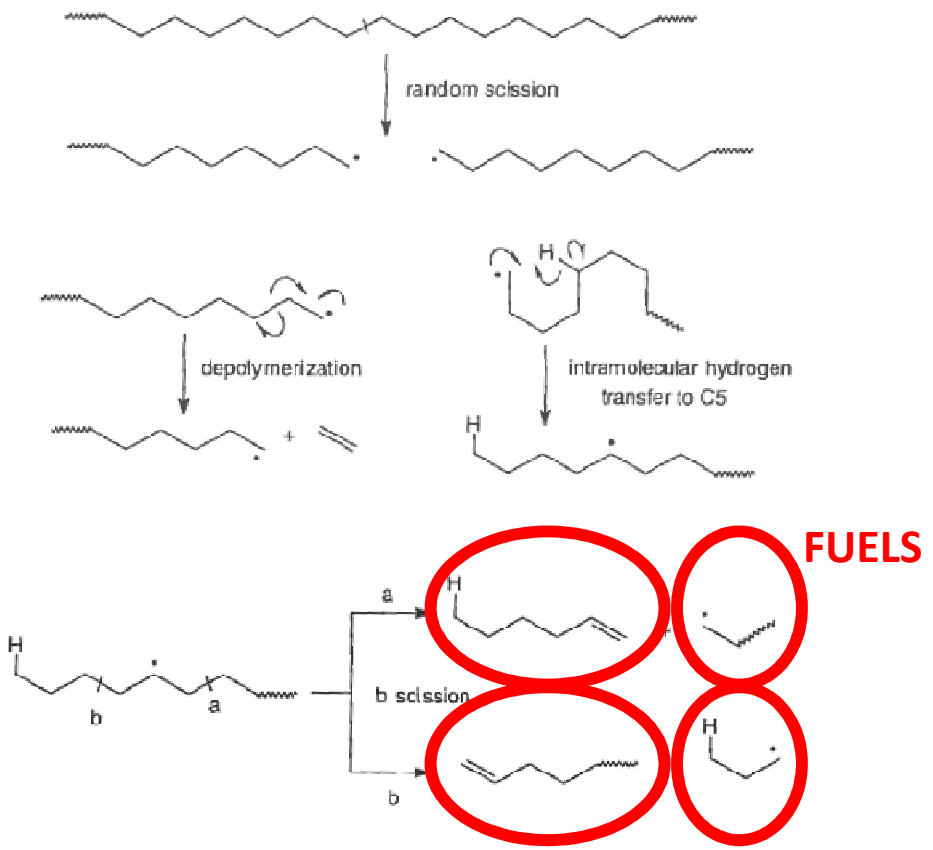
- Pyrogramm obtained by PyGC-MS
- Various hydrocarbons, all chain lengths
- Characteristic of random scission



POLYETHYLENE (2)

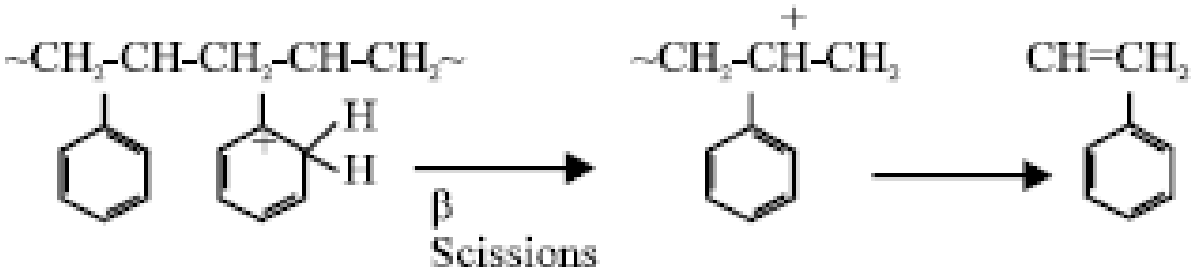
- What happens chemically ?

Thermal degradation of PE showing initial random scission, depolymerization, intramolecular hydrogen transfer and β-scission

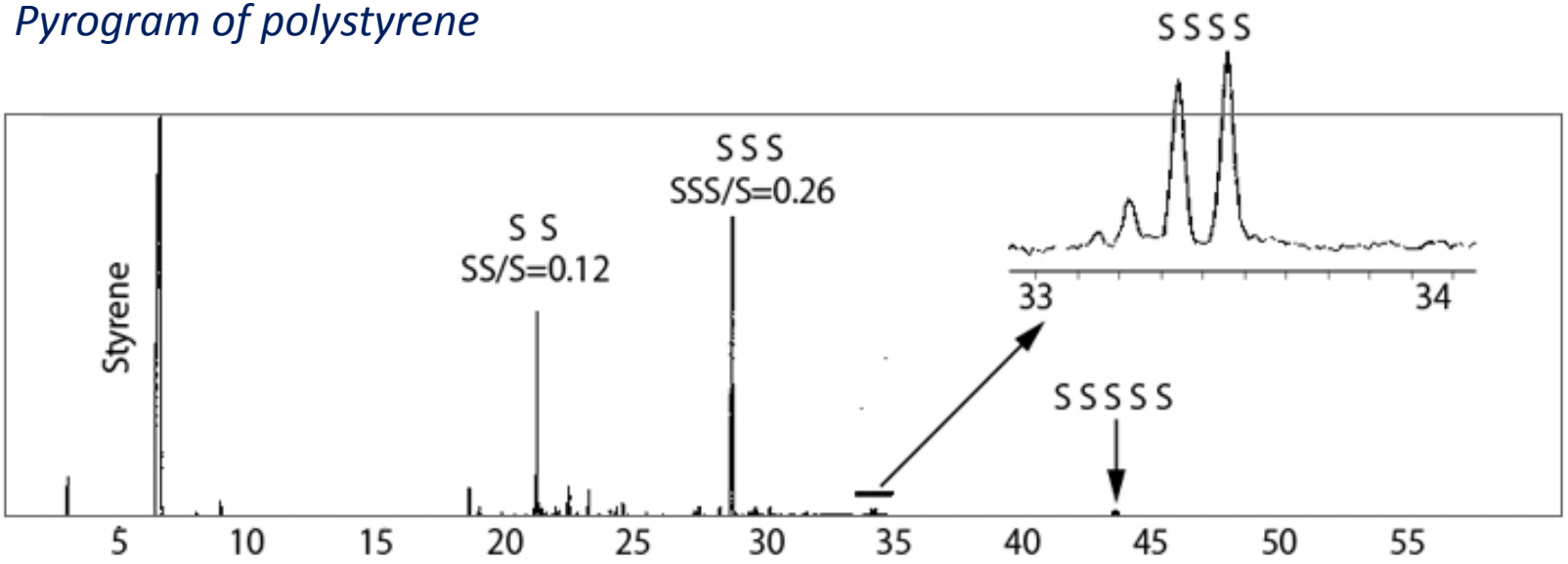


POLYSTYRENE (PS)

- Releases mainly its monomer, styrene, and in less proportions as dimers or trimers

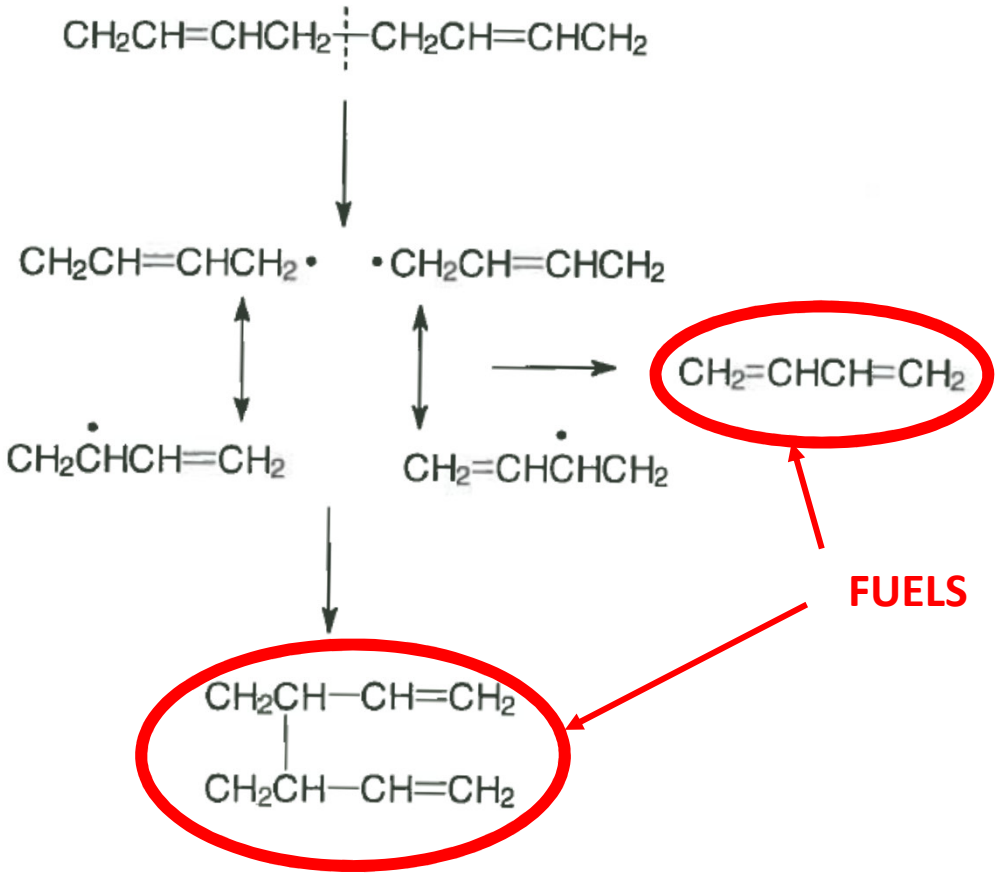


Pyrogram of polystyrene

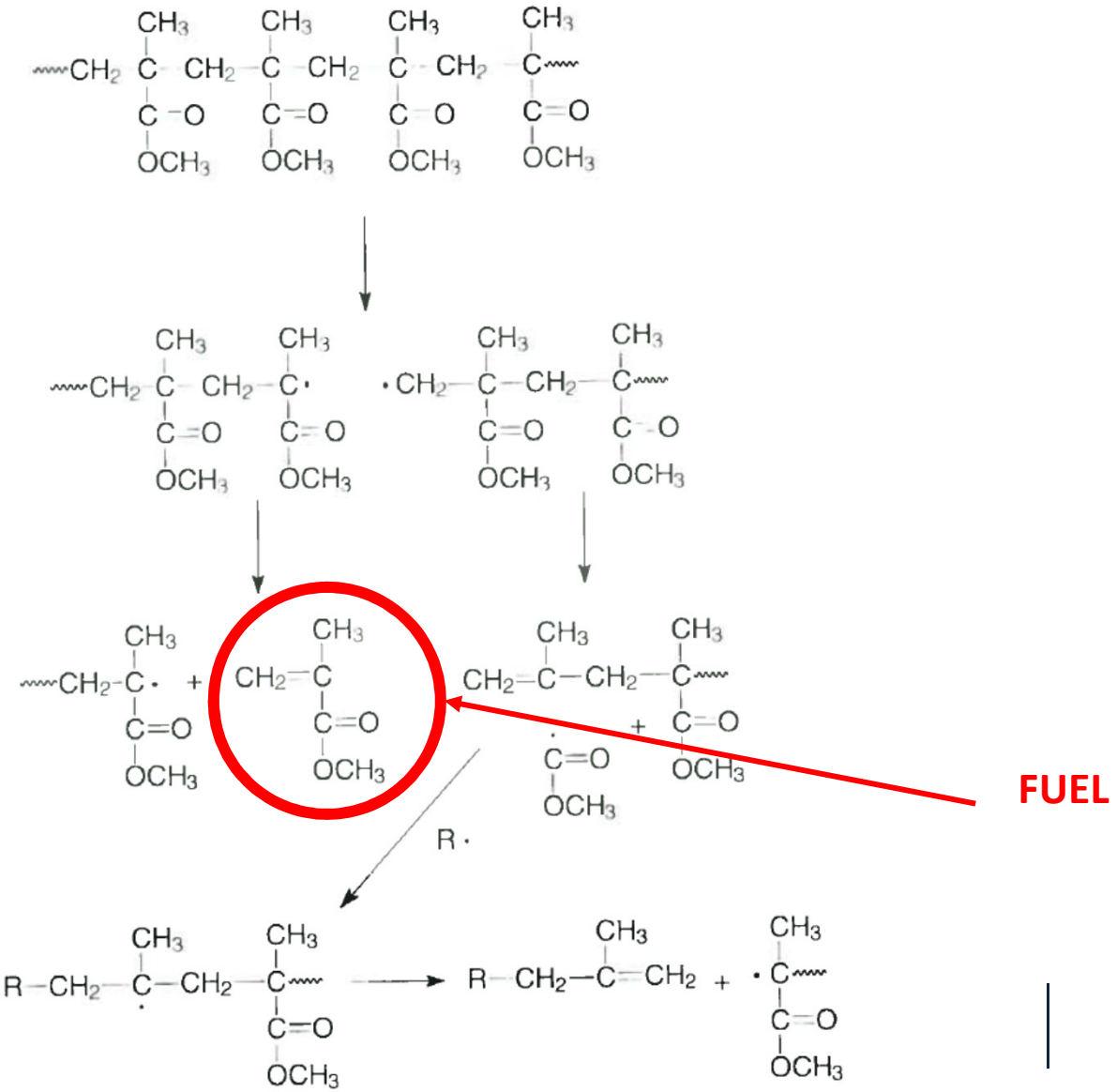


POLYBUTADIENE

- Formation of monomere and dimere by cross-linking



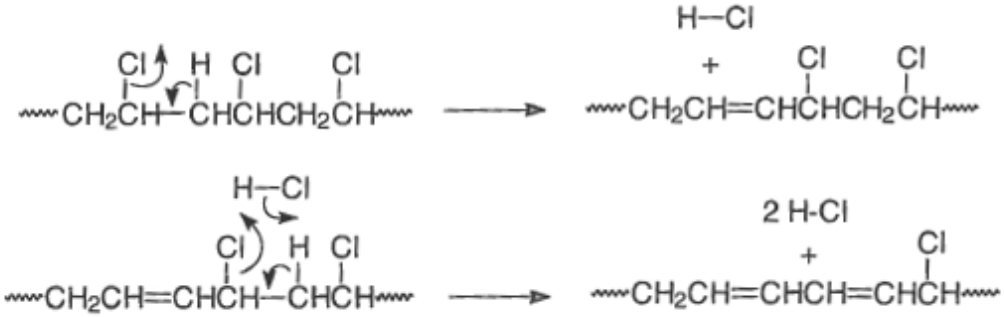
PMMA



POLYVINYL CHLOIRIDE (PVC)

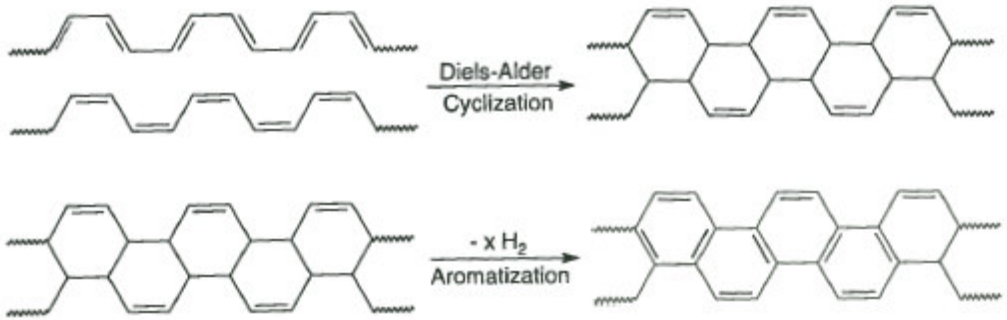
- 1st step: autocatalytic dehydrochlorination. Releases HCl.

1



- 2nd step: cyclation and aromatization, leading to the formation of a char

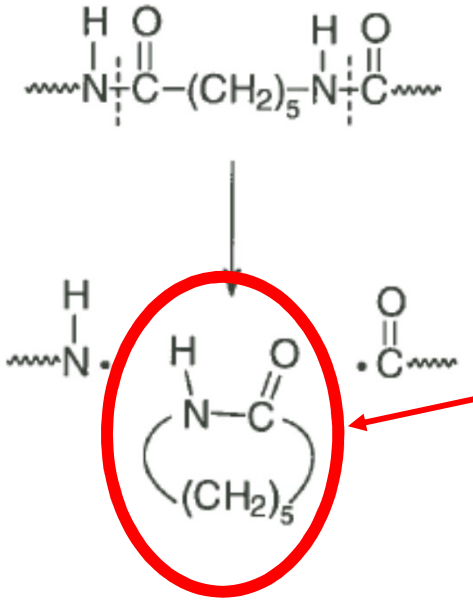
2



- It means no fuel released in gas phase, except additives such plasticizers. At 2nd step, production of dihydrogene. After, oxidation of char due to oxygen diffusion, producing CO

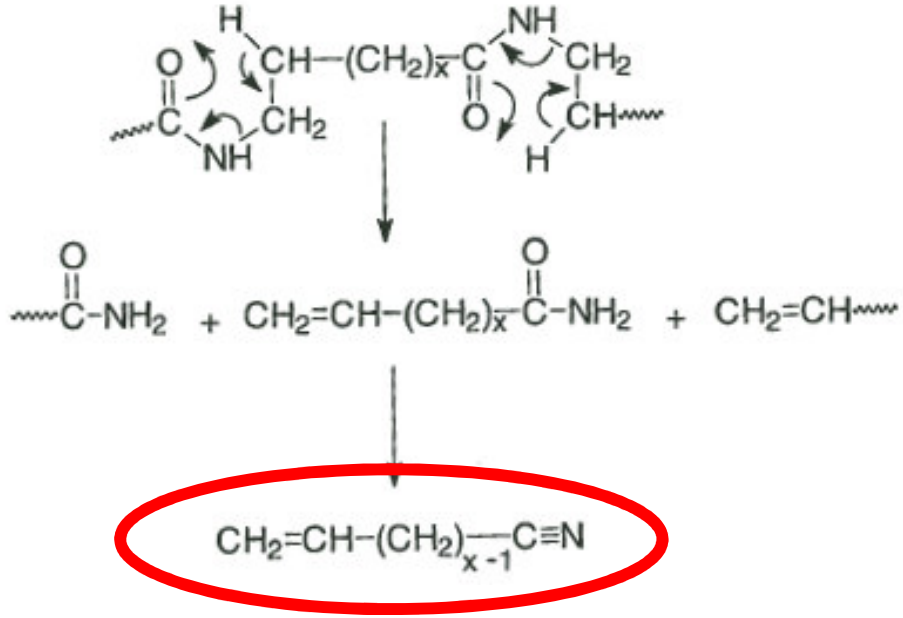
POLYAMIDES (1)

- In the case of PA-6, fuel is Caprolactame, quite heavy molecule



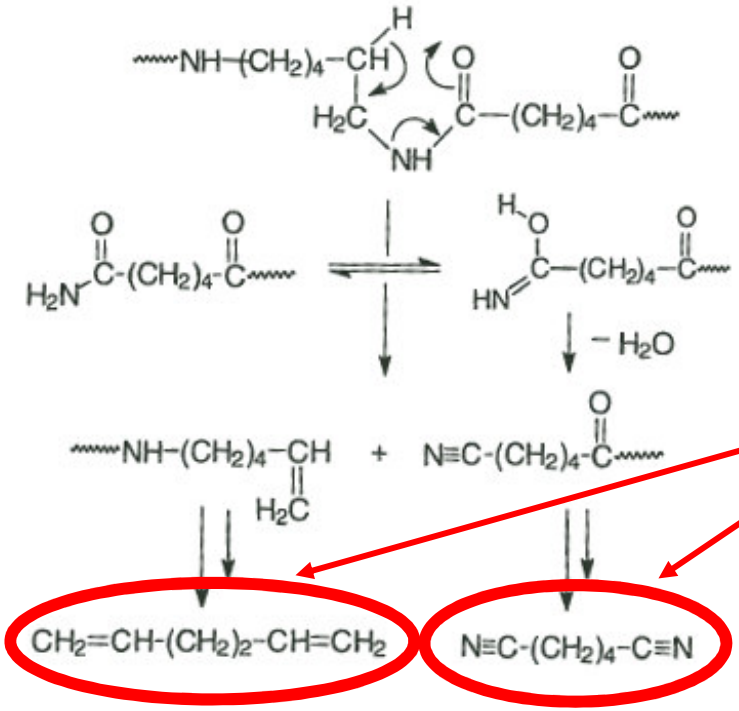
FUEL

- For larger polyamides such PA-10, the lactam is less important. Major products are nitriles and olefines (see right)



POLYAMIDES (2)

- In the case of PA-6-6, 2 fuels are produced, close to inital monomers

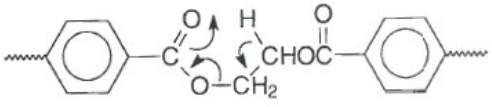


1,5-hexadiene

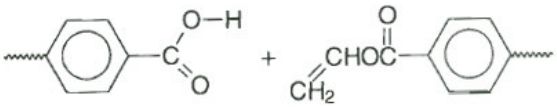
1,4-dicyanobutane

POLYESTERS – POLYETHYLENE TEREPHTALATE

1

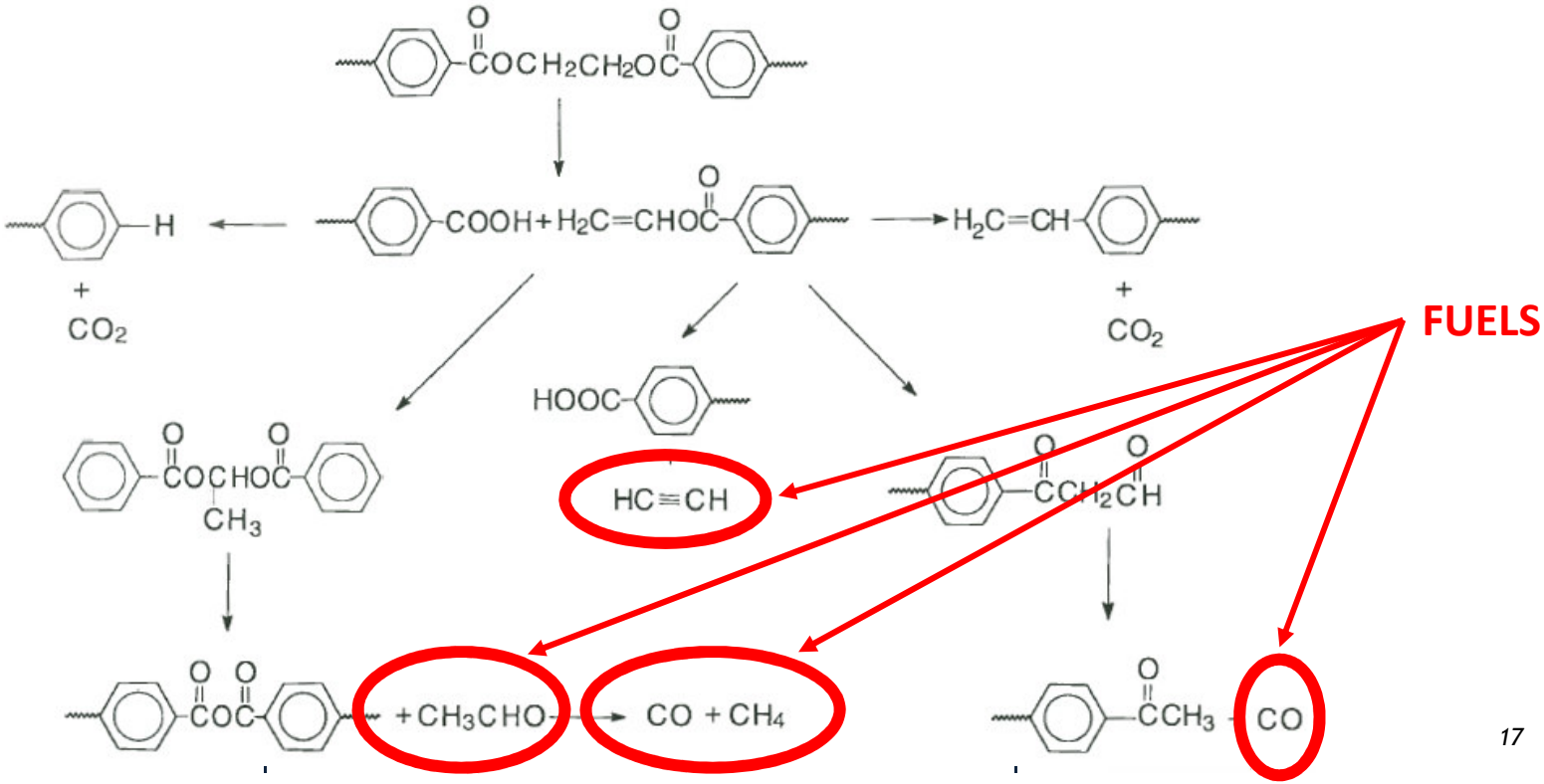


Carboxylic acid radical



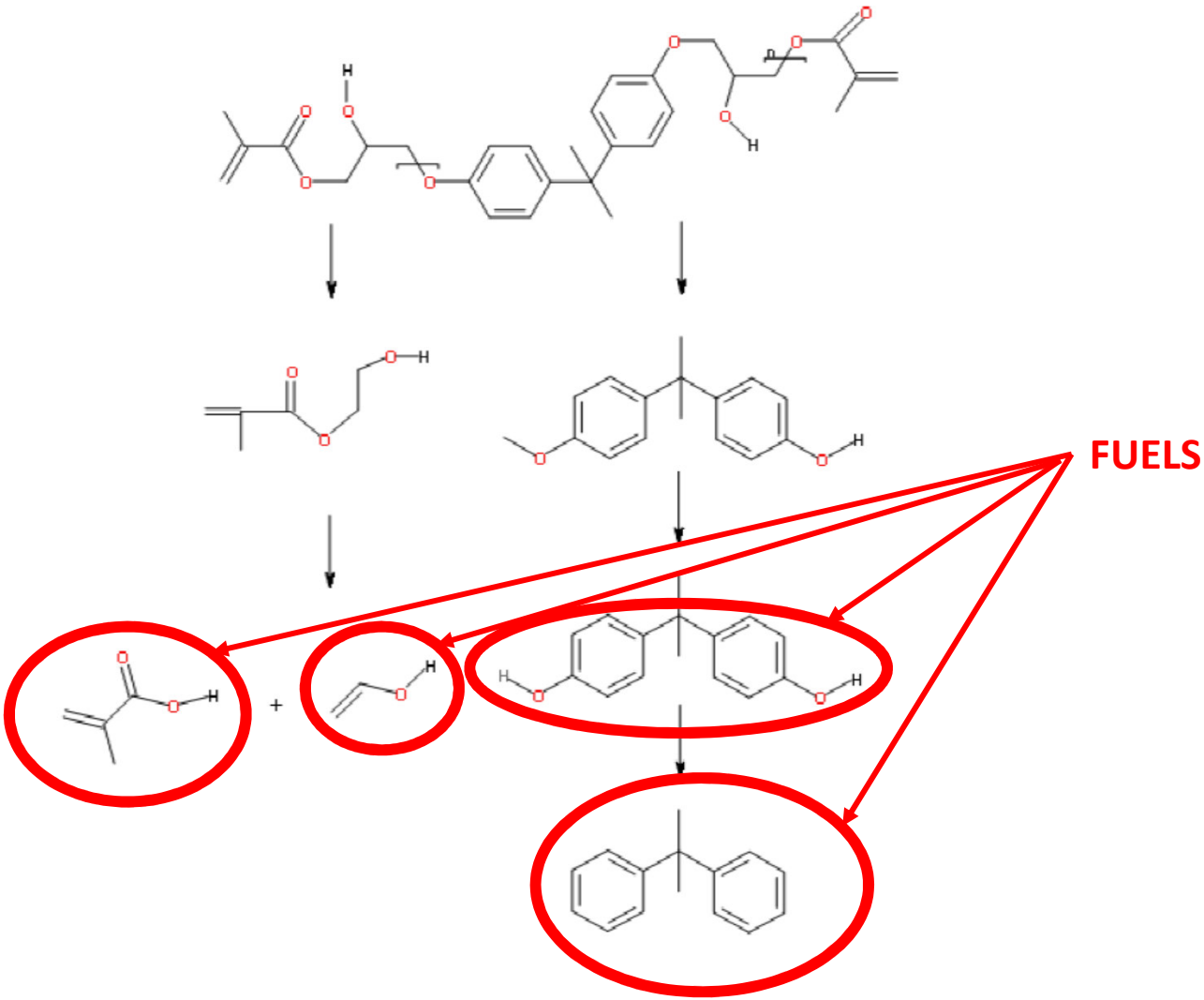
Vinyl ester radical

2



UNSATURATED POLYESTERS AND VINYLESTERS

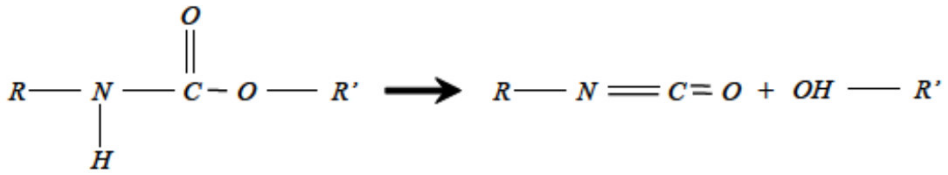
Vinylester



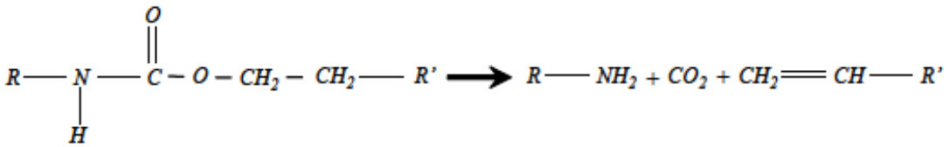
POLYURETHANES

- Typical dissociation mechanisms and examples of temperature influence in pyrograms

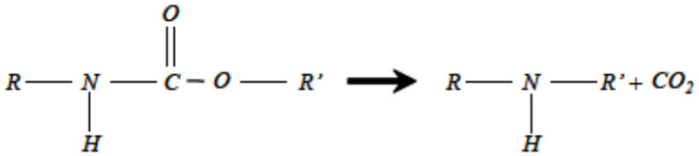
1) dissociation to isocyanate and polyol

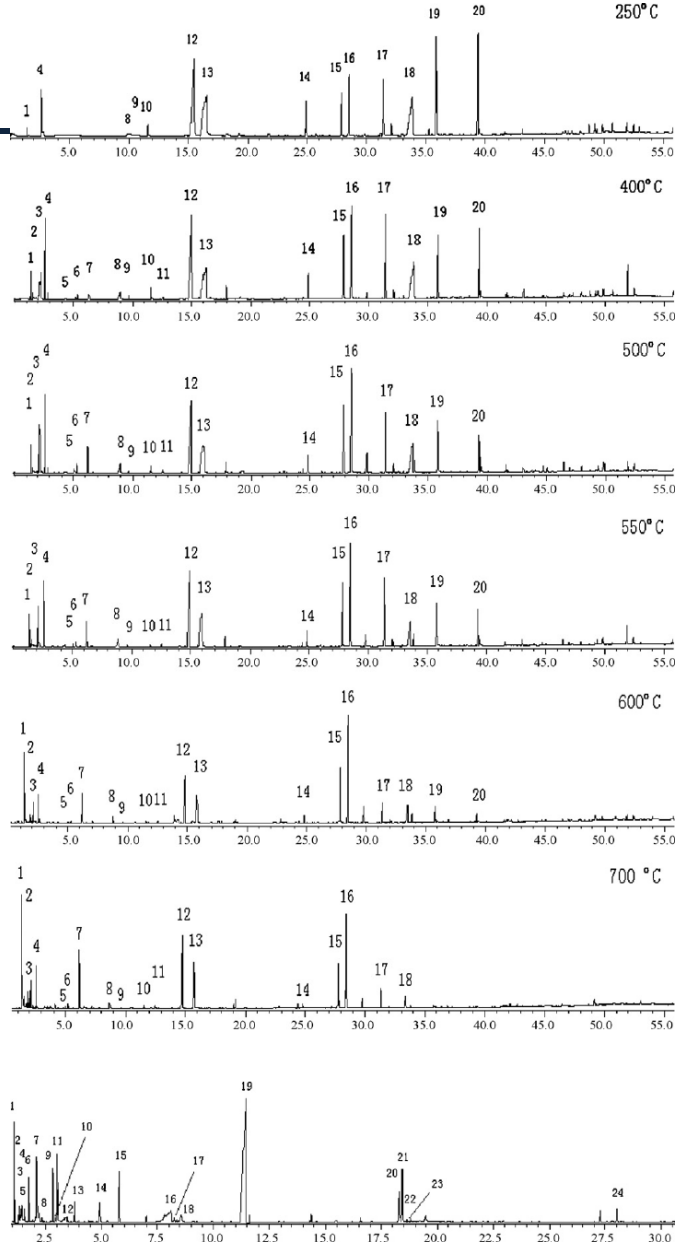


2) dissociation to primary amine, olefin and carbon dioxide

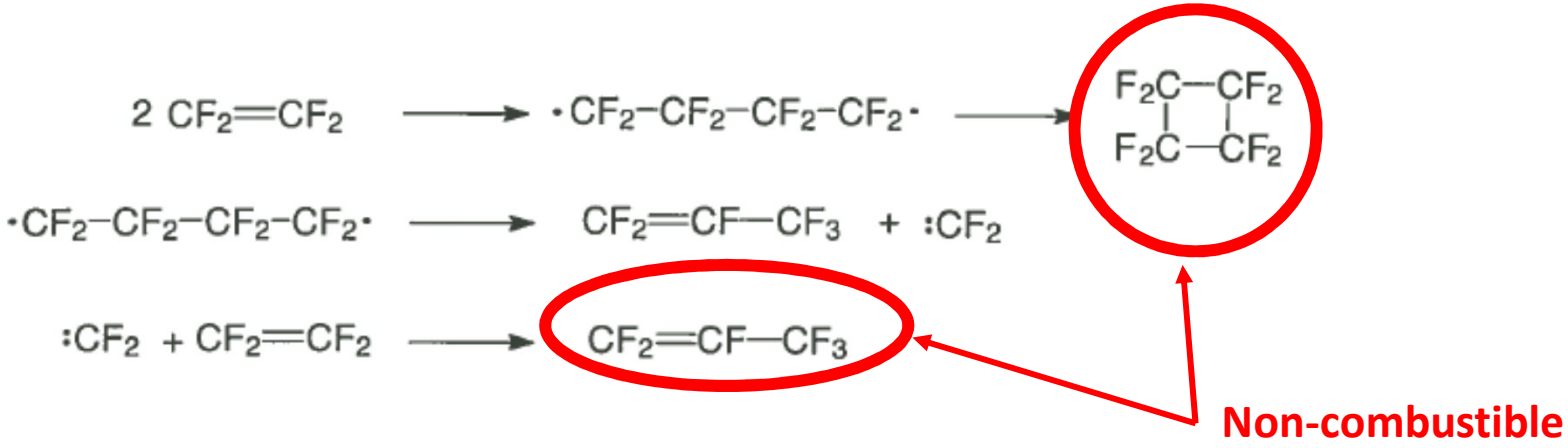


3) elimination of carbon dioxide, leading to formation of a secondary amine



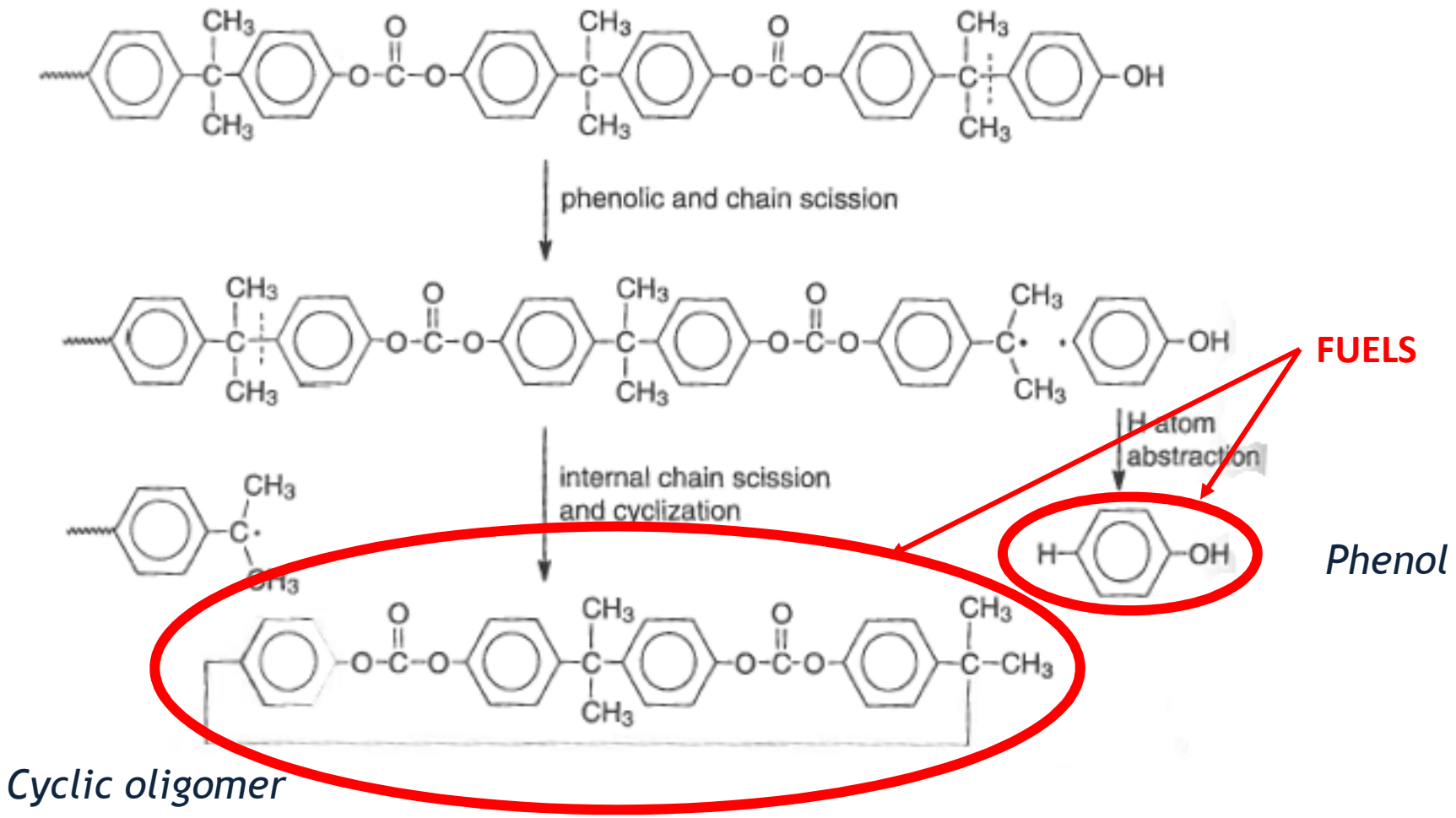


POLYTETRAFLUOROETHYLENE (PTFE)



POLYCARBONATES (PC)

- Bisphenol-A based Polycarbonate



THANKS FOR YOUR ATTENTION