



Training event “Anthropogenic activities and effects on the living environment and human health.”

Pollutants by anthropogenic activities:
mechanism of formation, strategies for reduction

Andrea D’Anna

anddanna@unina.it

3477603055

Mario Commodo

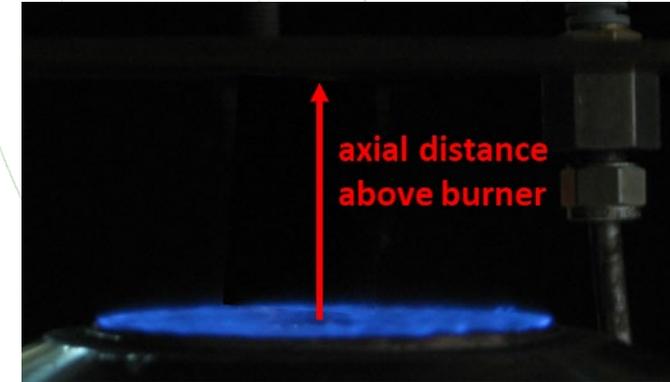
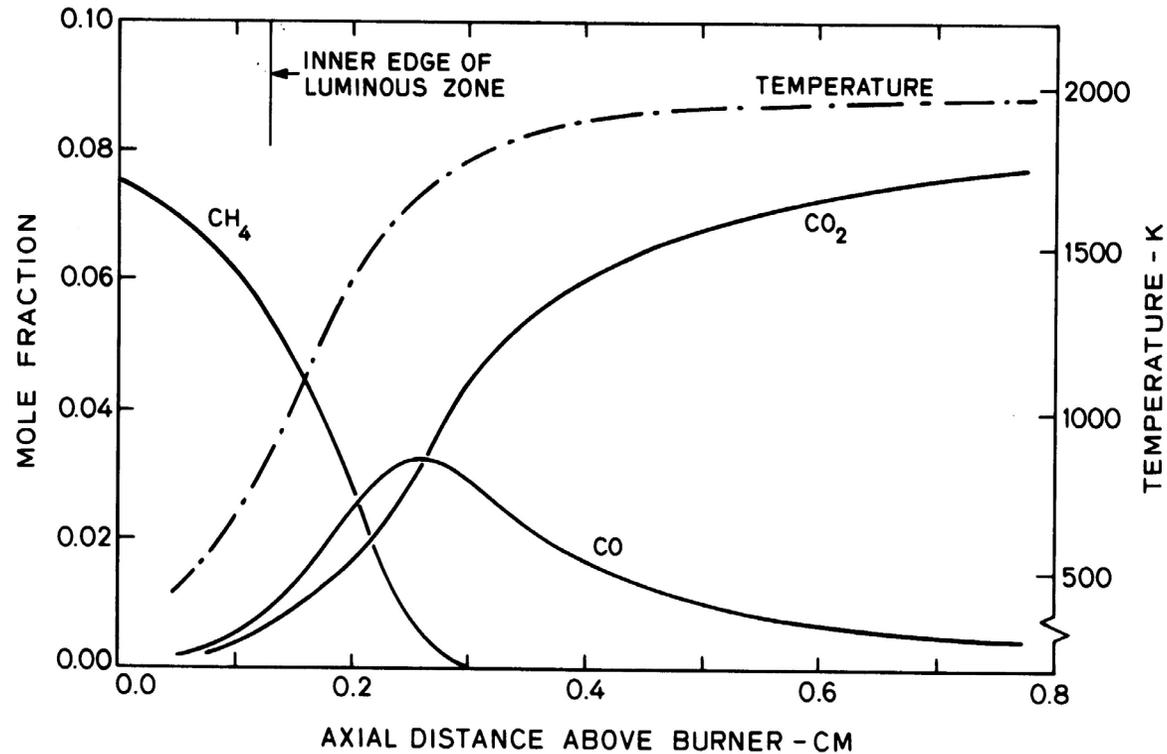
commodo@stems.cnr.it

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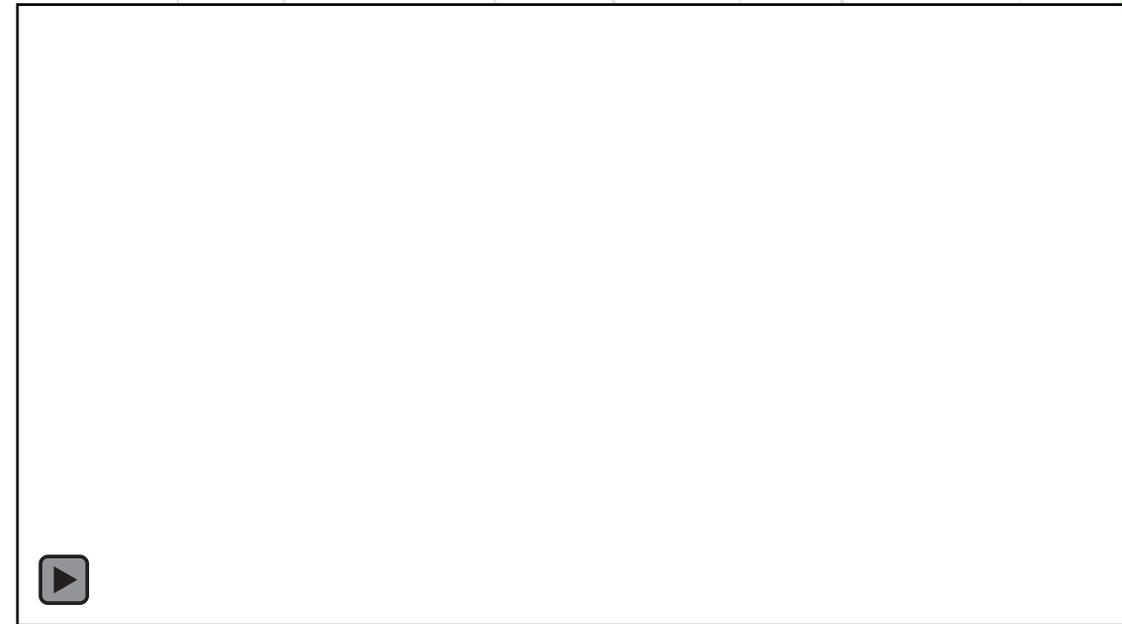
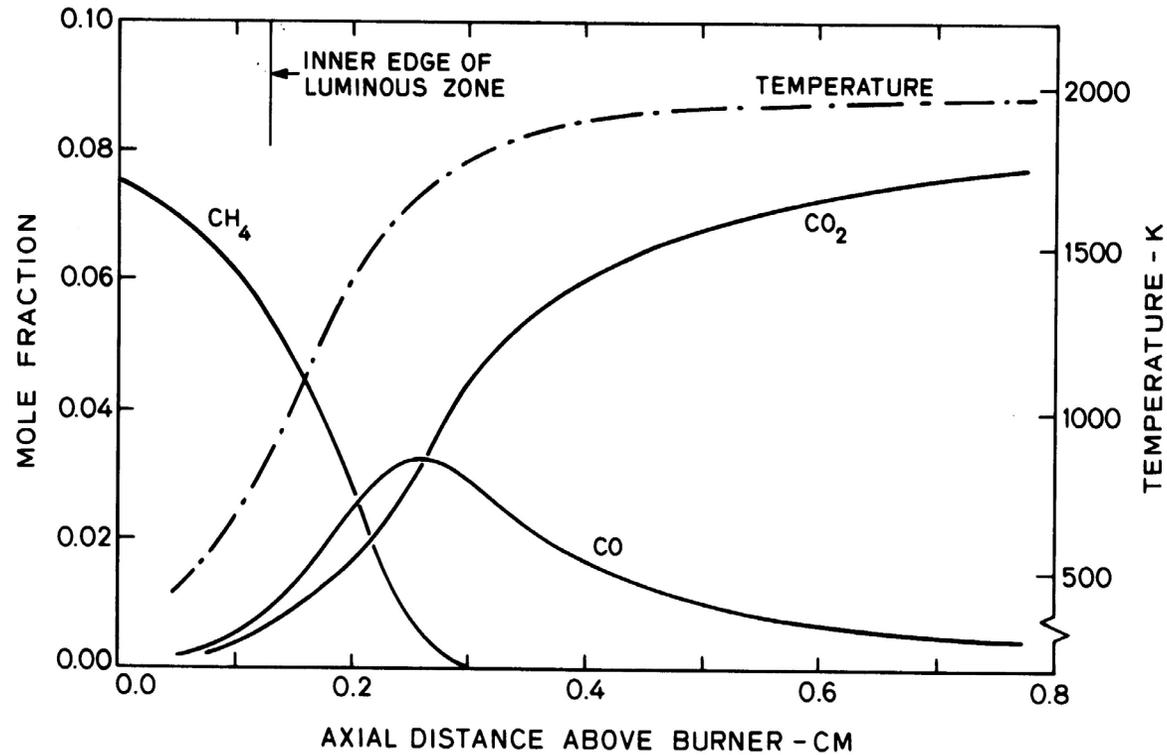
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Pollutant formation (CO, VOC, SVOC)



Pollutant formation (CO, VOC, SVOC)



Pollutant formation (CO, VOC, SVOC)

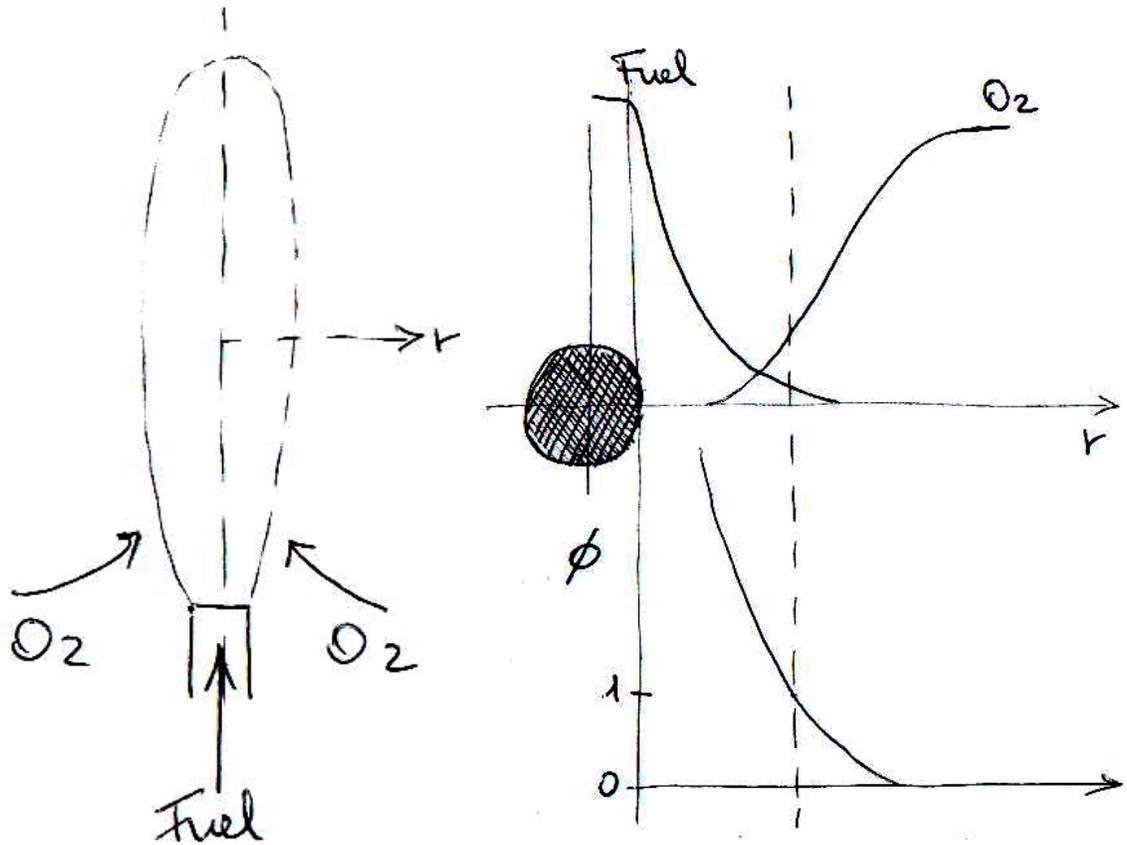
In fuel-rich combustion, O and OH are not available to fully oxidize C_xH_y to CO and consequently CO to CO_2

thus decreasing O_2 available to oxidize C_xH_y , the product of fuel oxidation is CO

Further O_2 decrease leads to the formation of unburned hydrocarbons

In fuel-rich combustion, acetylene C_2H_2 , ethylene C_2H_4 and H_2 are abundant products

Pollutant formation (CO, VOC, SVOC)



let define the equivalence ratio ϕ

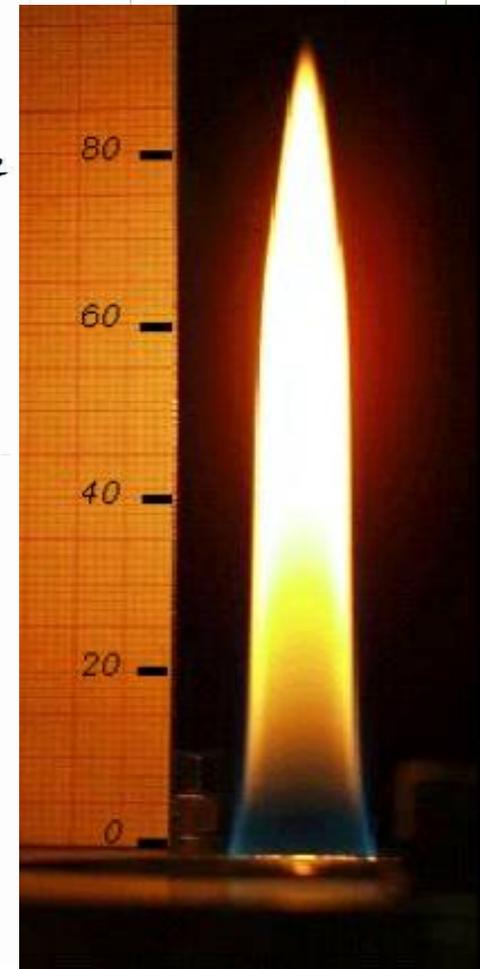
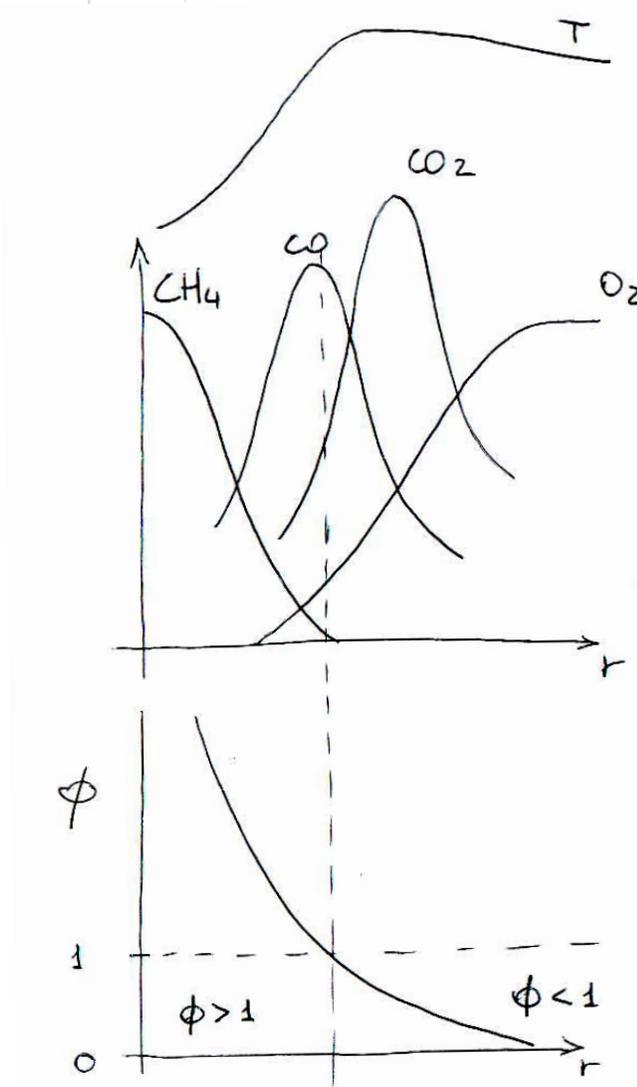
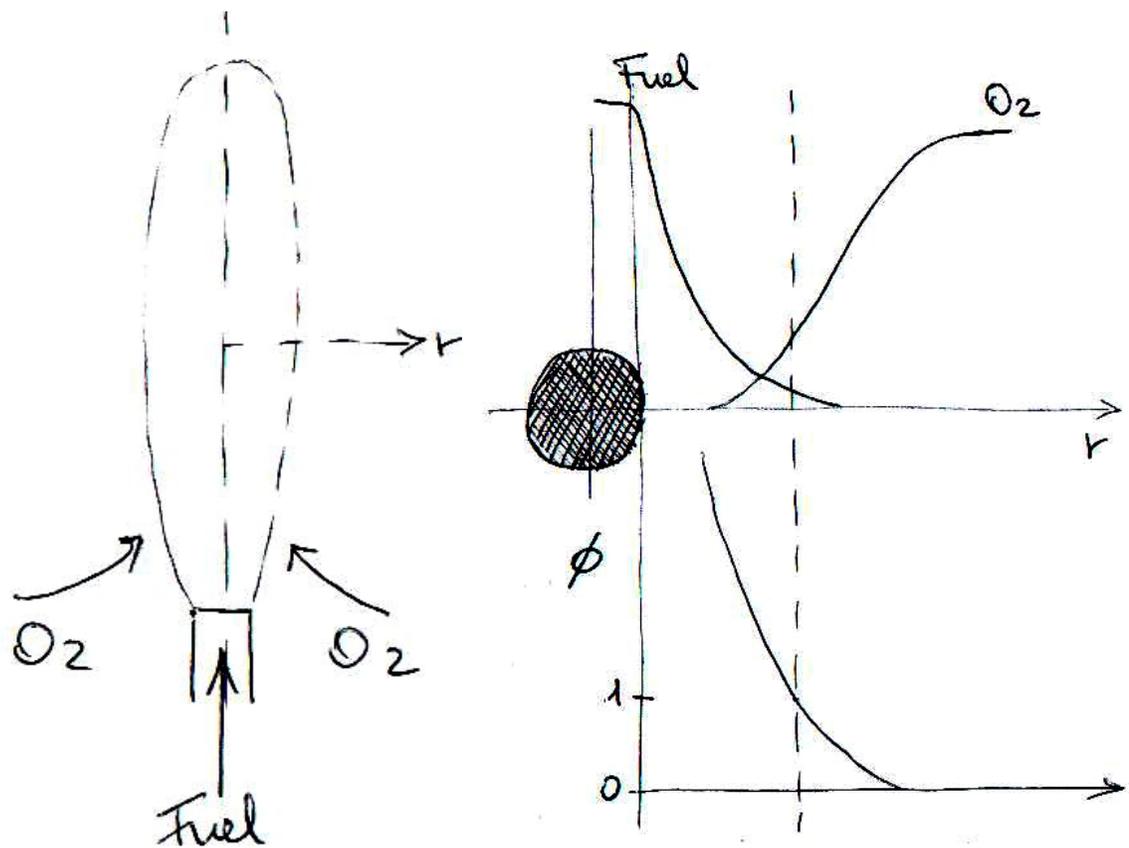
$$\phi = \frac{(C/O)}{(C/O)_{st}}$$

$\phi = 1$ stoichiometric conditions

$\phi > 1$ fuel-rich conditions

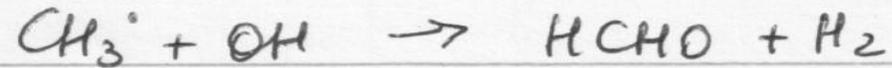
$\phi < 1$ oxygen-rich conditions

Pollutant formation (CO, VOC, SVOC)

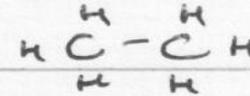
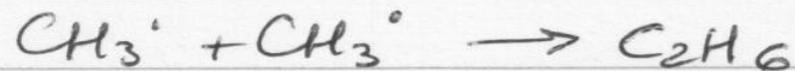


Pollutant formation (CO, VOC, SVOC)

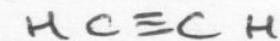
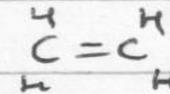
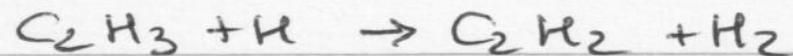
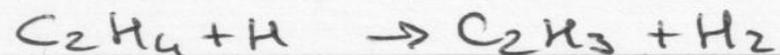
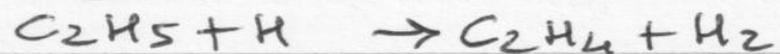
Oxidation:



radical recombination



H-atom abstraction



Pollutant formation (CO, VOC, SVOC)

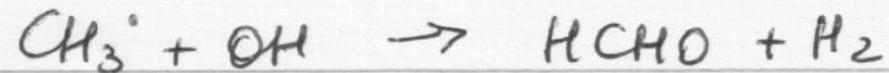
In fuel-rich conditions, parallel to oxidation some recombination reactions may occur

In fuel-rich conditions there are mainly three reaction types:

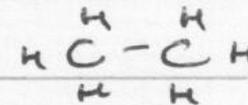
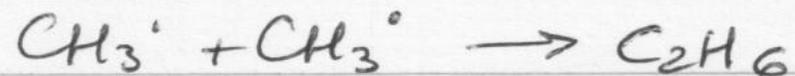
- i) oxidation
- ii) radical recombination
- iii) H-atom abstraction

Pollutant formation (CO, VOC, SVOC)

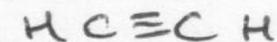
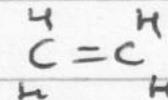
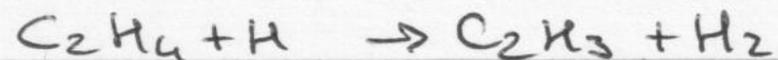
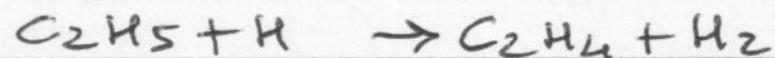
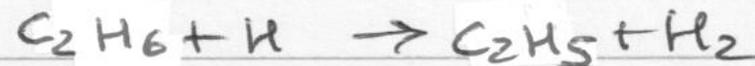
Oxidation:



Radical recombination



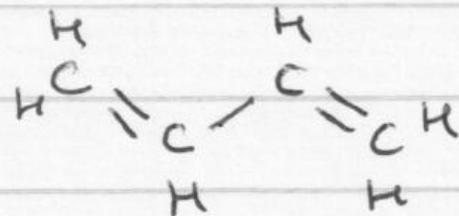
H-atom abstraction



Pollutant formation (CO, VOC, SVOC)

Molecular growth in fuel-rich conditions leads to the formation of large amounts of acetylene and ethylene, i.e. 2-C atoms species.

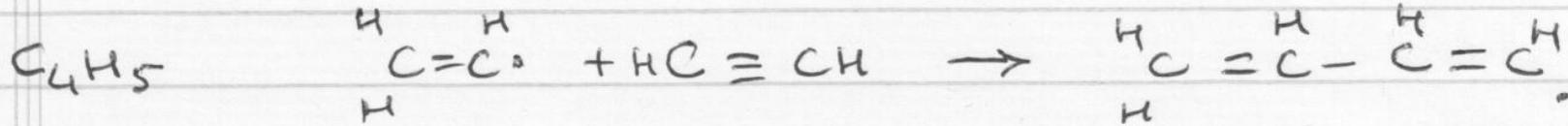
Combination of C₂ compounds leads to the formation of a pollutant 1,3 butadiene



short-term (acute) exposure to 1,3 butadiene results in irritation of eyes, nasal passages, throat and cardiovascular diseases

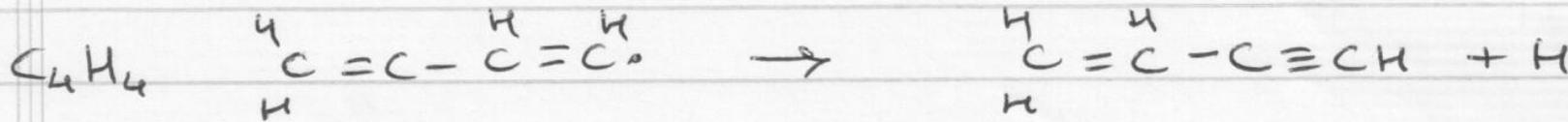
Pollutant formation (CO, VOC, SVOC)

it forms by recombination of ethenyl radical with acetylene

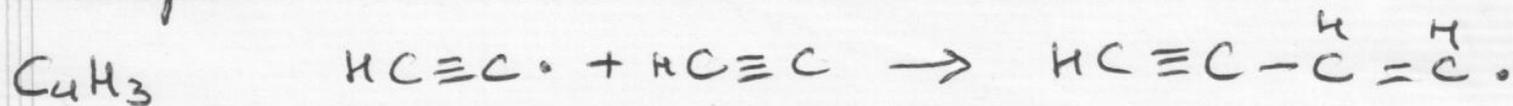


1,3 butadiene radical

by products might be vinyl-acetylene

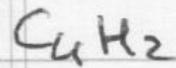


or by recombination of an acetylenic radical with acetylene



Pollutant formation (CO, VOC, SVOC)

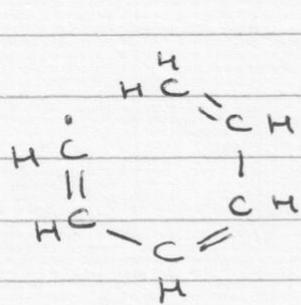
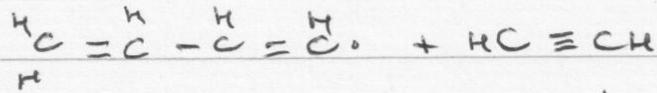
Vinyl acetylene can also form 1,3 butadiene
also known as di-acetylene



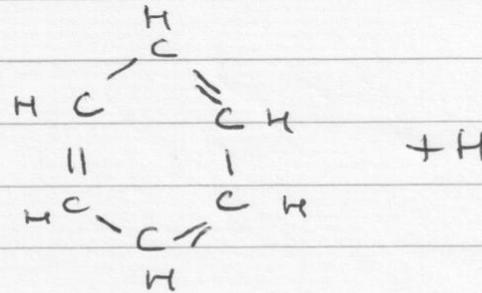
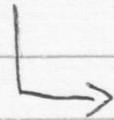
These C_4 compounds are quite stable due to the presence of conjugated double and triple bonds

Pollutant formation (CO, VOC, SVOC)

1,3 butadiene radicals and/or acetylenic radicals
can recombine with acetylene molecules forming
C₆ species



1,3,5 hexatrienyl radical



benzene

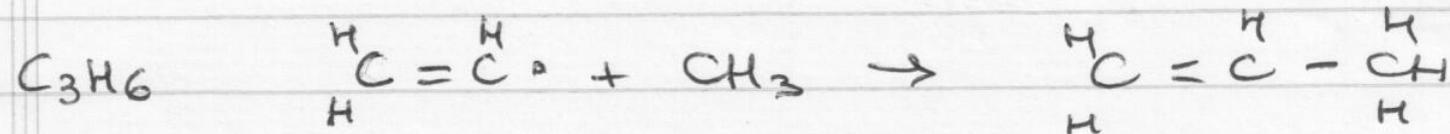
Pollutant formation (CO, VOC, SVOC)

The process of benzene formation requires three propagation reactions (bimolecular) and occurs in fuel-rich conditions when oxygen is not available for oxidation (pyrolysis)

Benzene formation has been detected also in moderately rich conditions close to the main oxidation region.

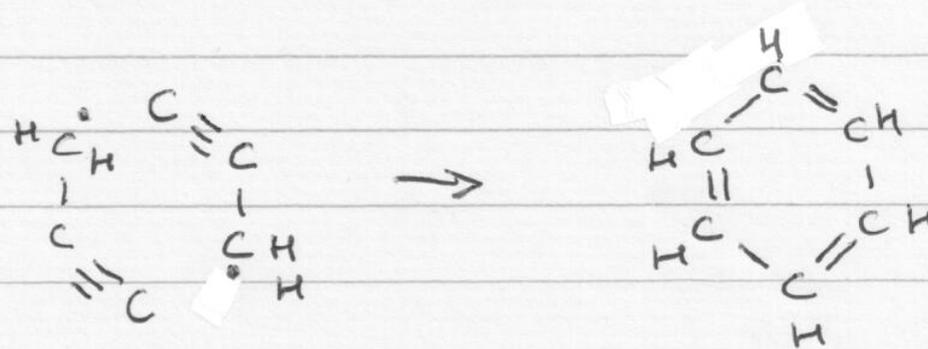
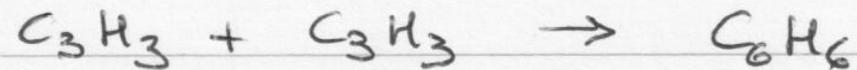
Pollutant formation (CO, VOC, SVOC)

Reaction of ethynyl radicals with methyl radicals
might form a C₃ species



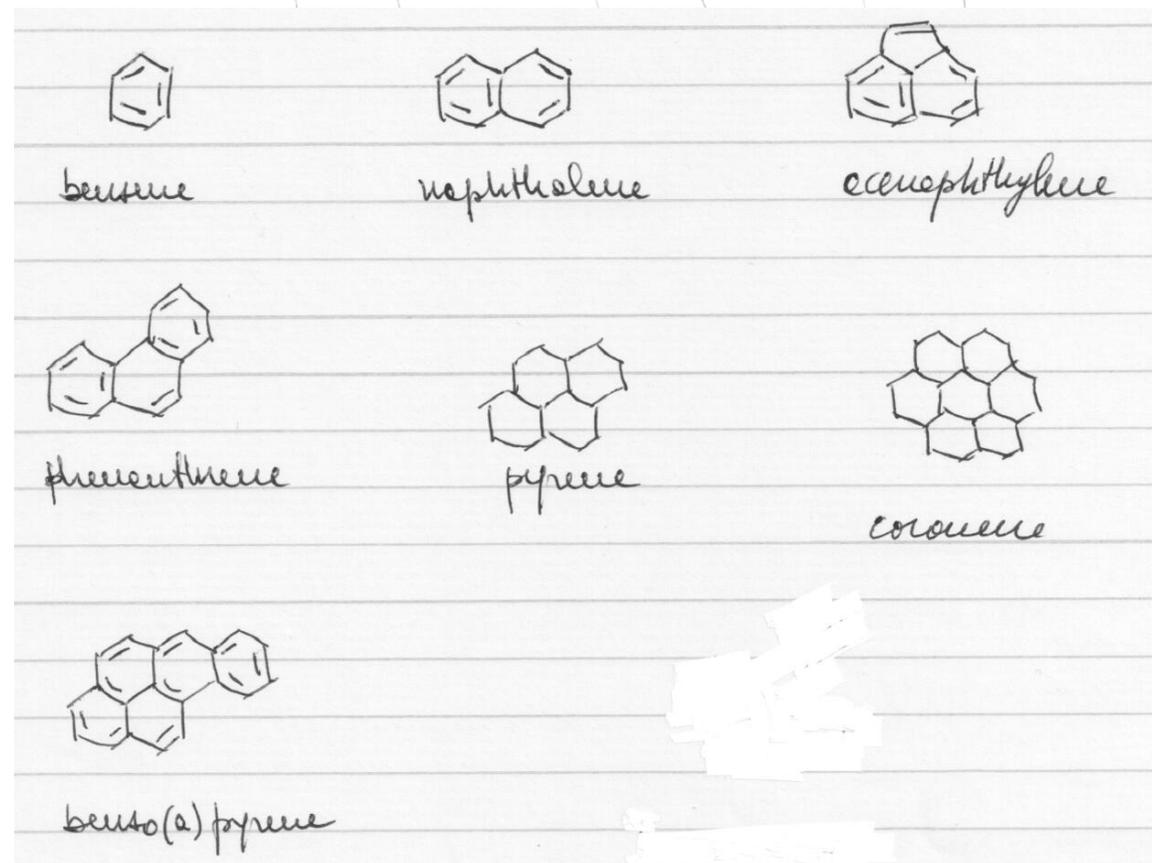
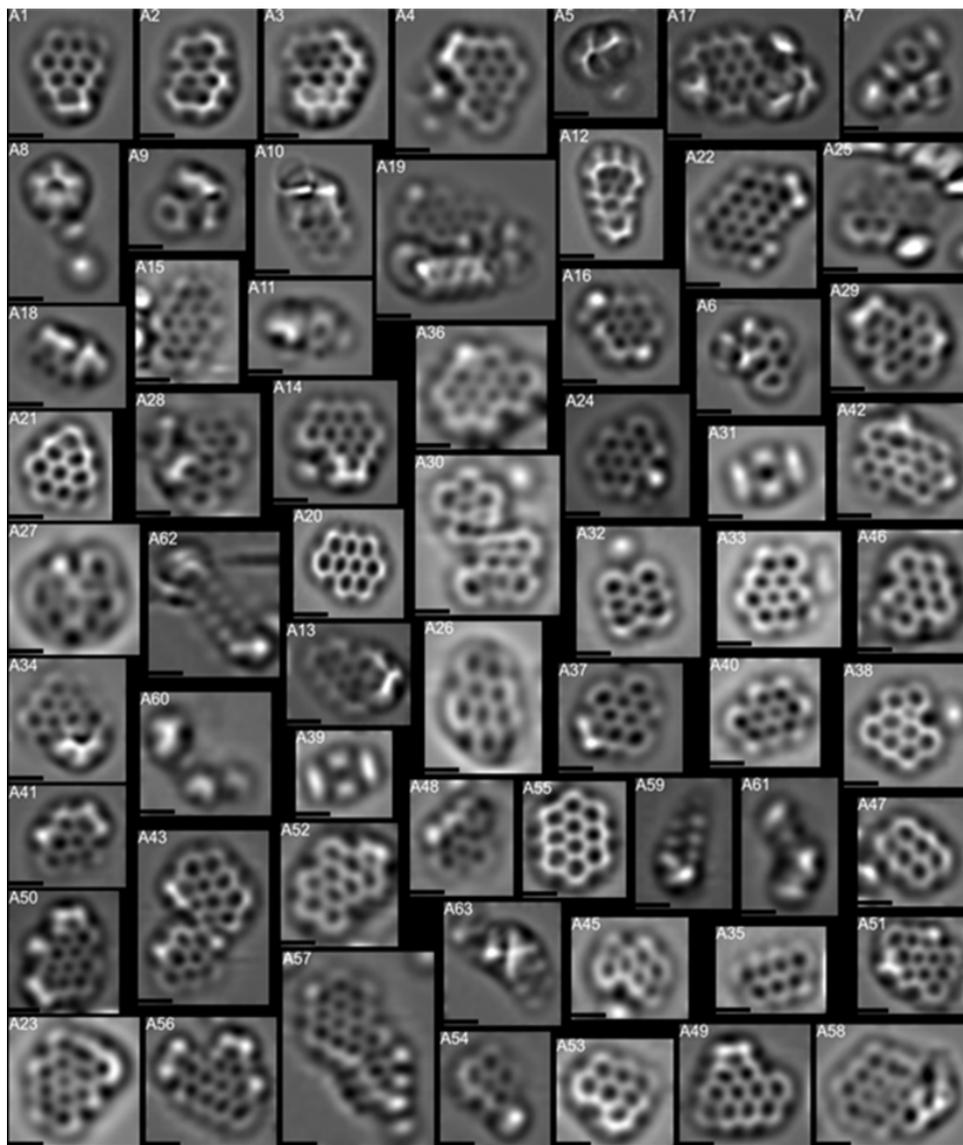
Pollutant formation (CO, VOC, SVOC)

C_3H_3 propargyl radical
it is a stable radical
it is resonance stabilized



Resonance stabilized radicals have an important role in molecular growth

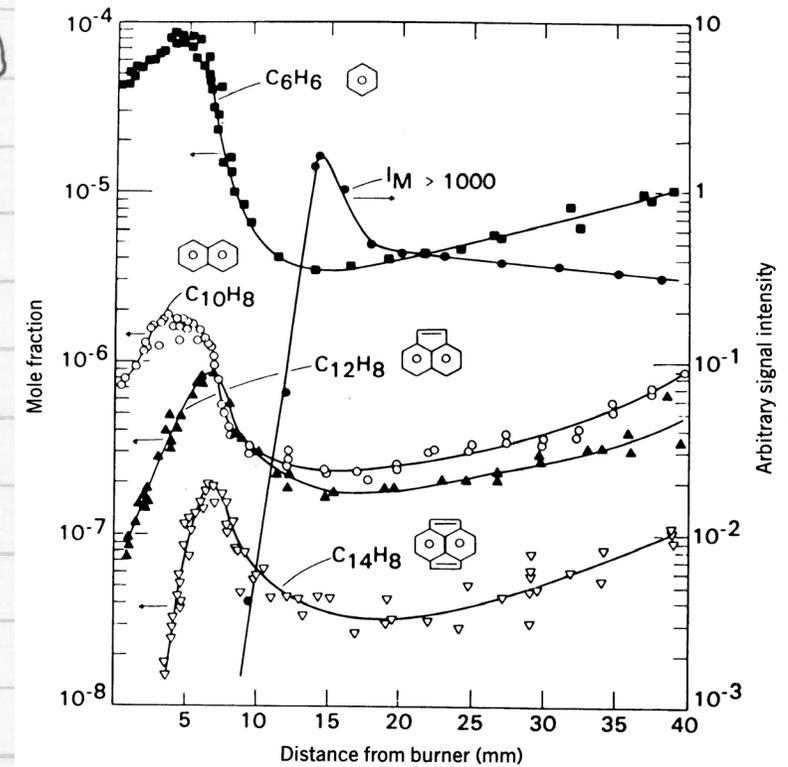
Pollutant formation (CO, VOC, SVOC)



Pollutant formation (CO, VOC, SVOC)

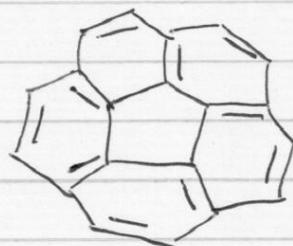
Typical concentrations in flames (rich-combustion)

| | % | toxicity |
|-----------------|-------|----------|
| naphthalene | 40 | 0.001 |
| acenaphthylene | 40 | 0.001 |
| fluorene | 10 | 0.001 |
| pyrene | 5 | 0.001 |
| coronene | 1 | |
| benzo(e) pyrene | <0.01 | 1 |
| others | 4 | |

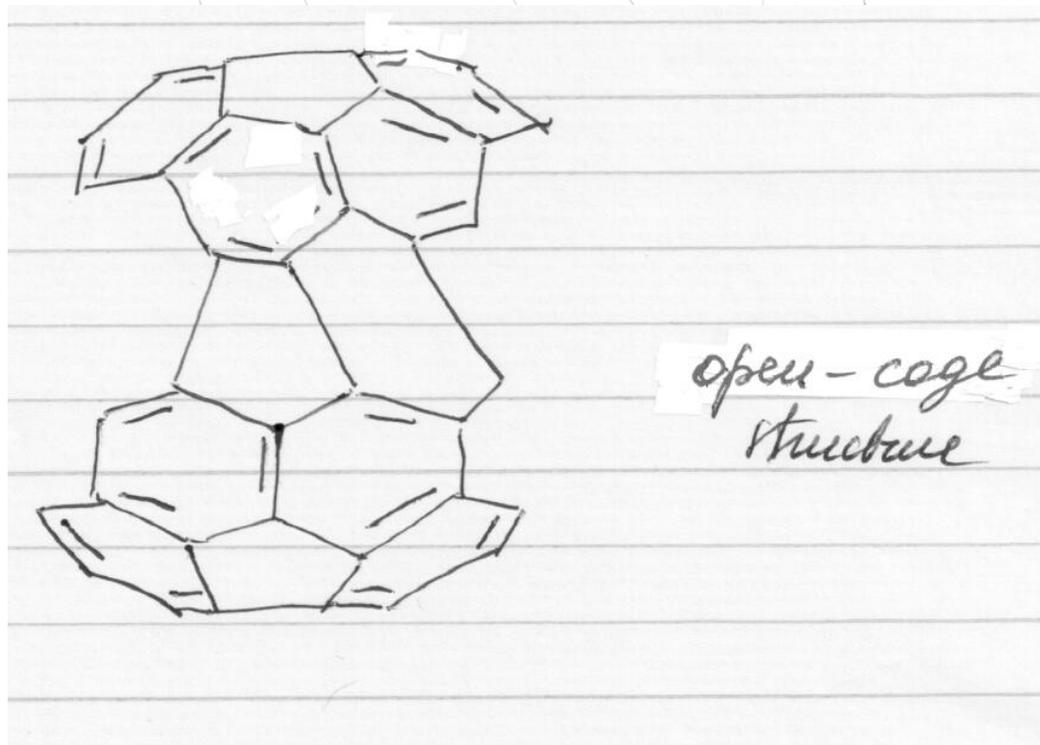
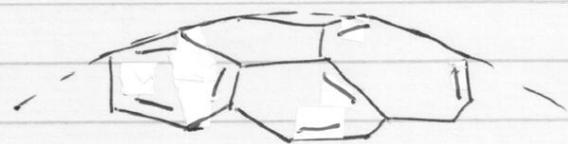


Pollutant formation (CO, VOC, SVOC)

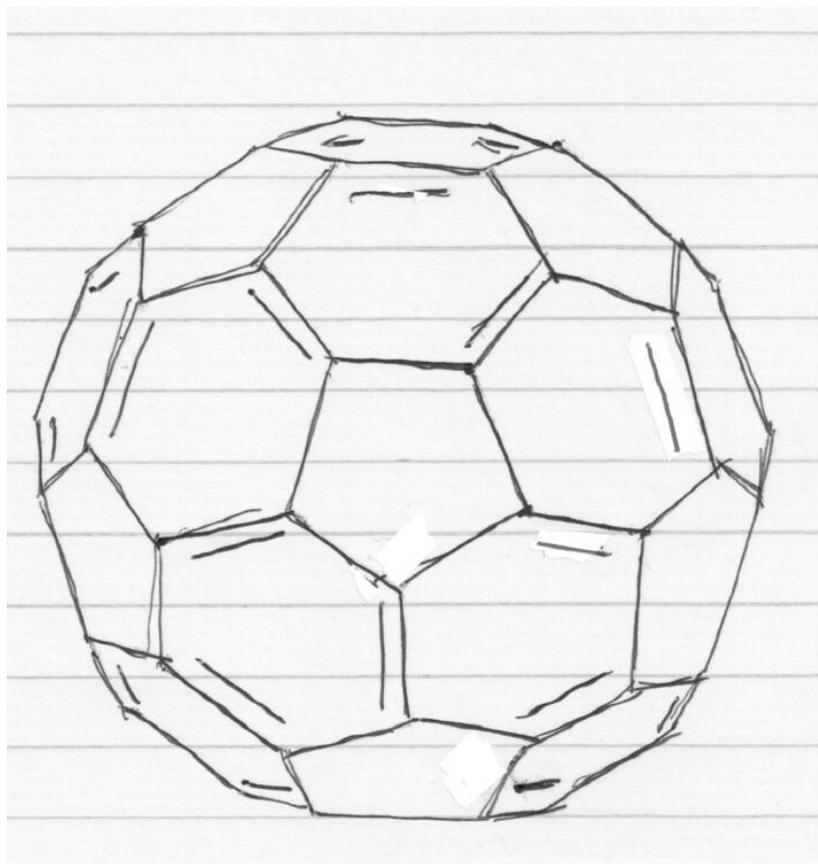
growth by hexagons → planar structure
growth by 5-member rings → 3D structures



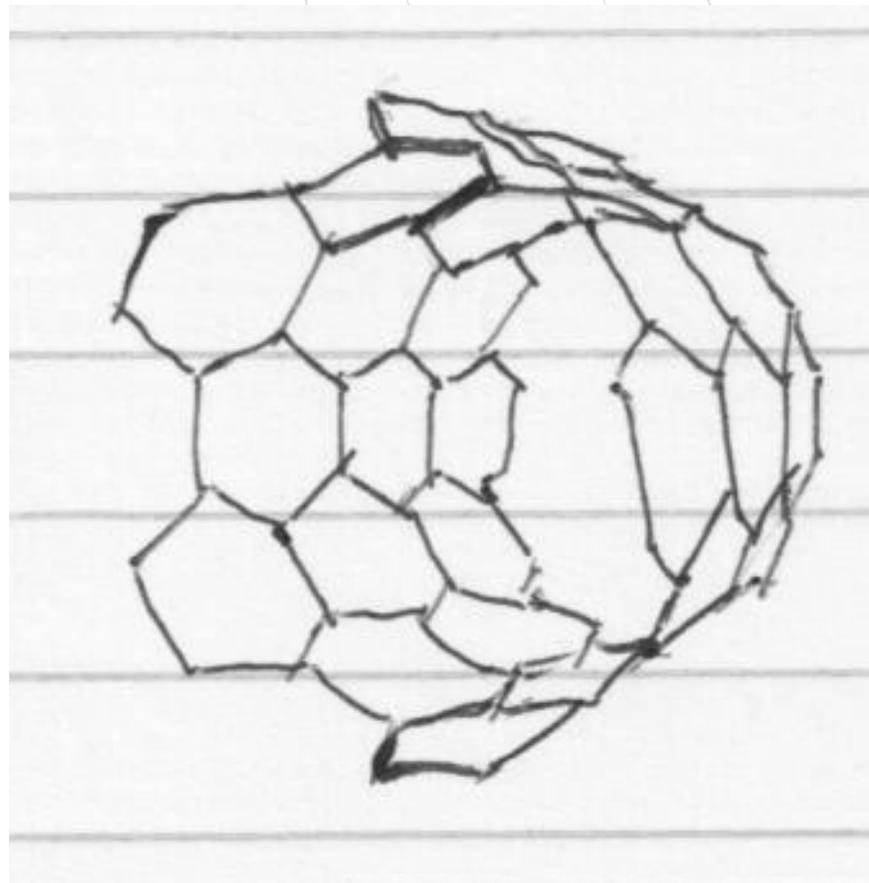
corannulene



Pollutant formation (CO, VOC, SVOC)



fullerenes



nanotubes

Pollutant formation (NO_x)

Commonly named NO_x they include NO, NO₂ and N₂O

NO formation is typically related to anthropogenic activities and in particular high temperatures combustion processes
"nitrogen oxide"

NO₂ is also a products of combustion processes at relatively low temperatures. But it is essentially formed photochemically in the atmosphere
"nitrogen dioxide"

Pollutant formation (NO_x)

N_2O has been measured in the products of combustion of nitrogen-containing fuels known as "laughing gas" is produced in small quantities in combustion and it has a biogenic origin (mainly agriculture, nitrification and denitrification; biological degradation of other nitrogen-containing pollutants)

Pollutant formation (NO_x)

The three principal sources of nitrogen oxide emissions in combustion are

- 1) oxidation of atmospheric (molecular) nitrogen, often termed the "thermal" NO formation mechanism
- 2) "prompt" NO formation
- 3) oxidation of nitrogen-containing fuels

Pollutant formation (NO_x)

In the combustion of "clean" fuels (fuels not containing nitrogen compounds) under lean and stoichiometric conditions the thermal mechanism is the principal source of nitrogen oxide emissions.

As the nitrogen content of the fuel increases, significant contribution from the fuel nitrogen mechanism to total nitrogen oxide emissions occurs.

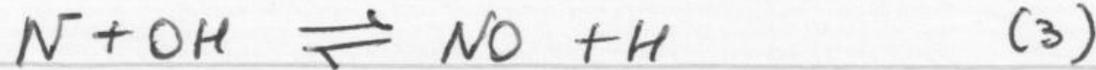
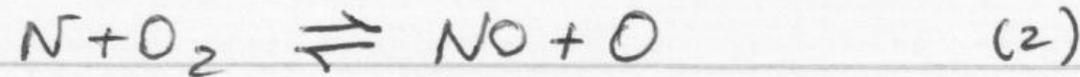
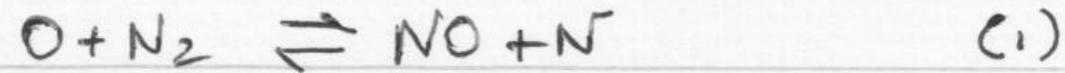
For nitrogen contents typical of fuel oils and pulverized coal, fuel nitrogen is the principal source of NO

Pollutant formation (NO_x)

| Fuel | Nitrogen (wt %) | Total Sulfur (wt %) |
|--------------------------------|-------------------|---------------------|
| <i>Petroleum Crude Oil</i> | | |
| Residual oil | 0.3–2.2 | 0.3–3.0 |
| Heavy distillates (# 3–5) | 0.3–1.4 | 0.2–2.5 |
| Light distillates (# 1, 2) | 0–0.4 | 0.01–0.4 |
| <i>Coal Liquids</i> | | |
| Crude (COED) | 1.1 | 0.02 |
| Utah heavy distillate | 0.2 | 0.05 |
| Utah light distillate | 0.1 | < 0.01 |
| Sea coal (COED) | 0.1 | 0.02 |
| Synthoil (PERC) | 0.8 | 0.2 |
| <i>Shale Liquids</i> | | |
| Residual oil | 1.5–2.5 | 0.2–0.5 |
| Heavy distillates | 1.4–2.0 | 0.1–0.5 |
| Light distillates | 0.25–1.4 | 0.01–0.2 |
| <i>Anthracite Coal</i> | | |
| Hazelton, Pennsylvania | 0.79 ^b | 0.47 ^b |
| <i>Bituminous Coals</i> | | |
| Black Creek, Alabama (MV) | 1.47 ^b | 1.3 ^b |
| Western Kentucky (HVA) | 1.55 | 3.2 |
| Pittsburgh Seam # 8 (HVA) | 1.65 | 0.84 |
| Price, Utah (HVB) | 1.54 | 0.66 |
| Cadiz, Ohio (HVB) | 1.07 | 7.40 |
| Illinois # 6 (HVC) | 1.18 | 3.77 |
| Four Corners, New Mexico (HVC) | 1.23 | 1.03 |
| <i>Subbituminous Coals</i> | | |
| Hardin, Montana (B) | 0.99 ^b | 1.07 ^b |
| Shell, Texas (C) | 1.13 | 1.02 |
| Rosebud, Montana (B) | 0.84 | 1.00 |
| Colstrip, Montana (B) | 1.38 | 0.63 |
| <i>Lignite</i> | | |
| Beulah, North Dakota (A) | 0.96 ^b | 0.37 ^b |
| Savage, Montana (A) | 1.00 | 0.42 |
| Scranton, North Dakota (A) | 0.83 | 1.52 |
| COED Char | 1.67 | 2.67 |

Pollutant formation (NO_x)

Thermal NO formation (Zeldovich)



Rx (1) is the controlling step because it involves breaking of the triple bond of N₂ molecule N≡N which bonding energy is of the order of 225 kcal/mol

Rx(1) has an activation energy of about 76 kcal/mol

Pollutant formation (NO_x)

NO formation rate has a strong dependence on the combustion gas temperature and a weaker dependence on oxygen-atom concentration

Conventional methods for control of NO emissions produced by thermal mechanism generally involve modifications of the combustion process to reduce combustion gas temperature

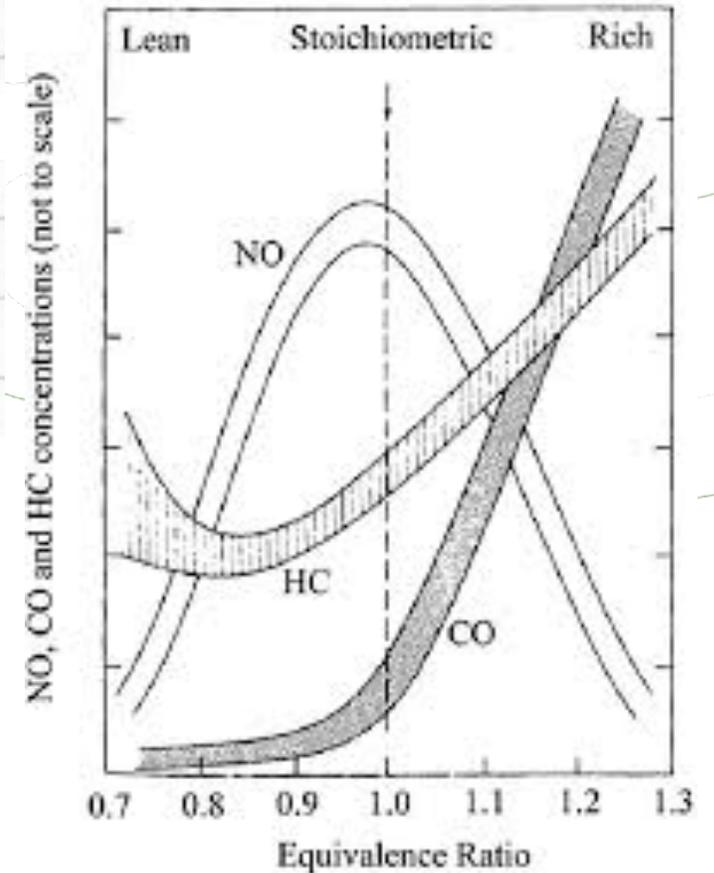
Pollutant formation (NO_x)

Temperature reduction can be obtained in various ways including:

- = exhaust gas recirculation (EGR)
- = introduction of dilution air downstream of the primary combustion zone
- = water injection
- = reduction in fuel-air ratio

Pollutant formation (NO_x)

While reduced temperatures can produce significant reductions in NO_x emissions, the reduced temperatures also may result in quenching of the CO oxidation reactions, thereby causing an increase in CO and HC emissions as well as operational problems introduced by temperature reduction, such as flame stability



Pollutant formation (NO_x)

Reduction of available oxygen can reduce thermal
NO formation

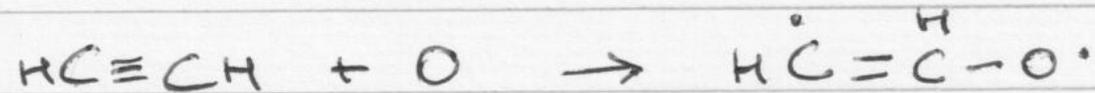
Although thermal NO emissions is generally reduced,
the products of rich combustion may cause the
increase of NO through the "prompt" NO mechanism

Pollutant formation (NOx)

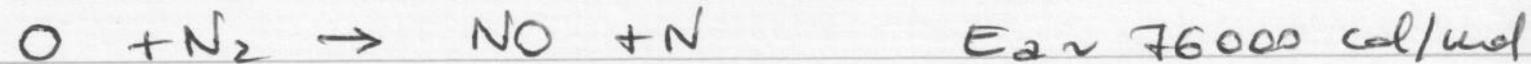
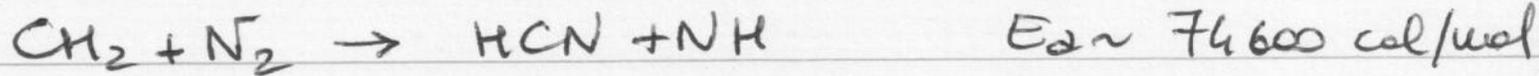
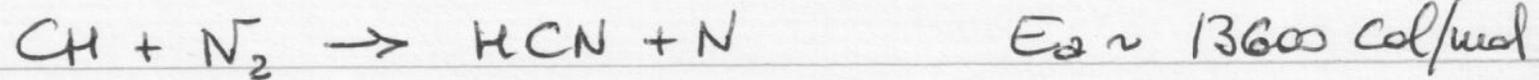
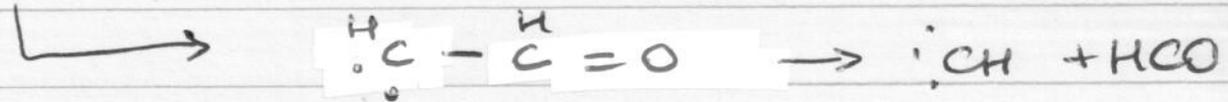
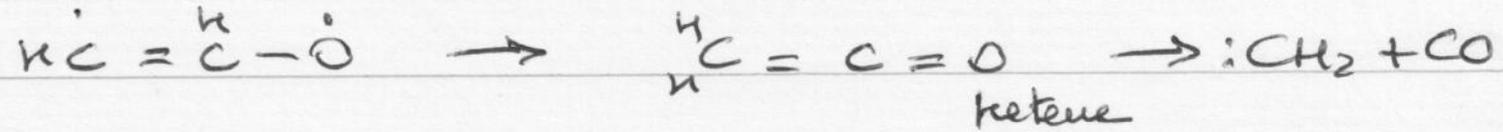
Prompt NO (Fenimore)

Prediction of NO formation rates in fuel-rich combustion requires coupling of the NO process to radical-producing reactions.

In fuel-rich combustion, CH and CH₂ radicals can be formed by acetylene oxidation through ketene formation



Pollutant formation (NO_x)



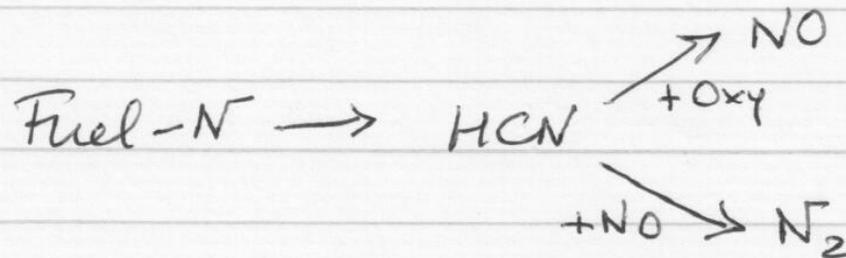
Reaction of N₂ with CH occurs with an activation energy very low with respect to the activation energy of the reaction forming N-atoms in the thermal mechanism

Pollutant formation (NO_x)

Fuel - NO

Fuel-nitrogen is a principal source of NO emission in combustion of fossil fuels.

The extent of conversion of fuel nitrogen to NO is nearly independent of the identity of the parent fuel nitrogen compounds but is strongly dependent on the local combustion environment (temperature and stoichiometry) and on the initial fuel nitrogen concentration in the reactants.



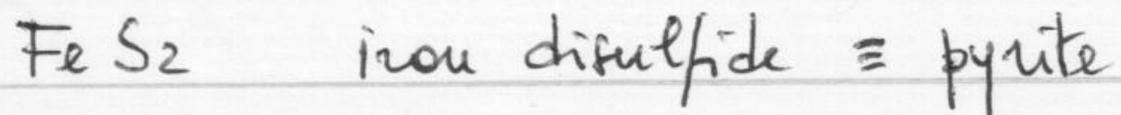
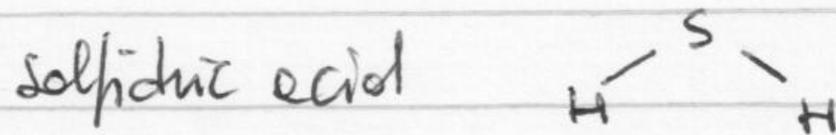
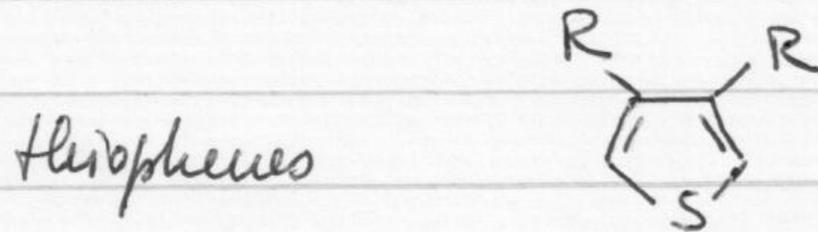
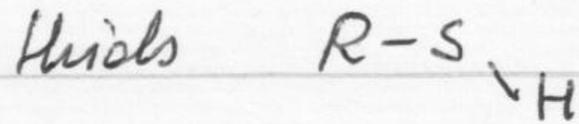
Pollutant formation (SO_x)

Coals contain high levels of sulfur.

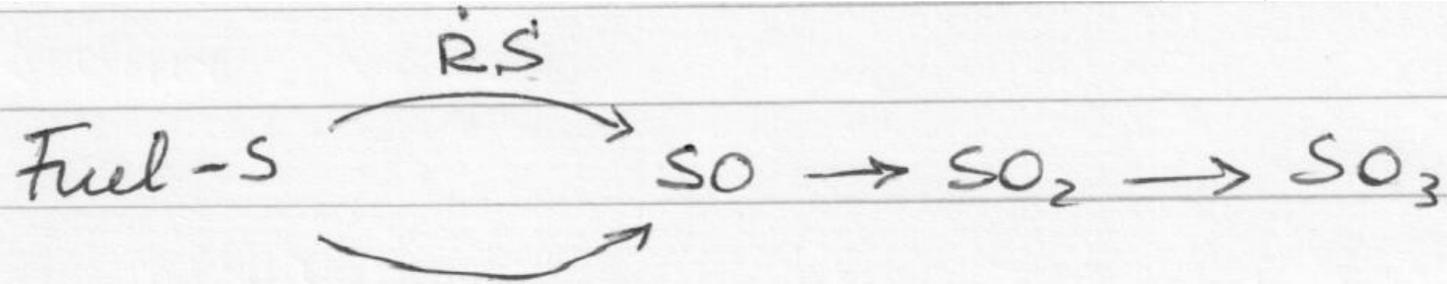
It exists in the form of inorganic, mainly FeS_2 , and organic, incorporated in the various organic structures present in coal.

The sulfur containing compounds in gaseous fuels, including natural gas and gas produced by coal and char gasification, include H_2S and thiols and thiophenes.

Pollutant formation (SOx)



Pollutant formation (SO_x)



R·S is a sulfur containing radical such as
HS, CS, CH₃S or S

Pollutant formation (dioxines)

Combustion of chlorinated hydrocarbons

Combustion of chlorinated hydrocarbons (CHC) is of practical interest

↳ management of toxic and hazardous wastes

↳ formation of toxic combustion by-products

↳ among others

= polychlorinated benzenes (PCB)

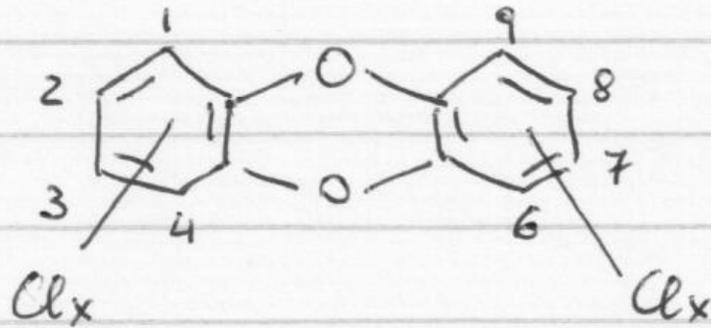
= polychlorinated dibenzo dioxins (PCDD)

= polychlorinated dibenzo furans (PCDF)

Pollutant formation (dioxines)

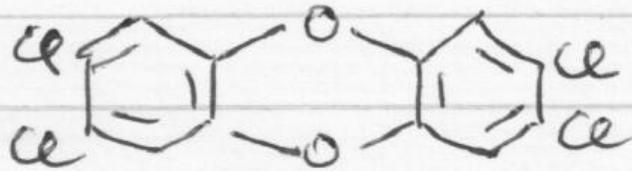
Some byproducts in CHC combustion are considered highly toxic to certain laboratory animals, particularly the 2,3,7,8-isomer of tetrachloro dibenzo dioxin and in general all the isomers having Cl atoms in positions 2,3,7,8

Pollutant formation (dioxines)



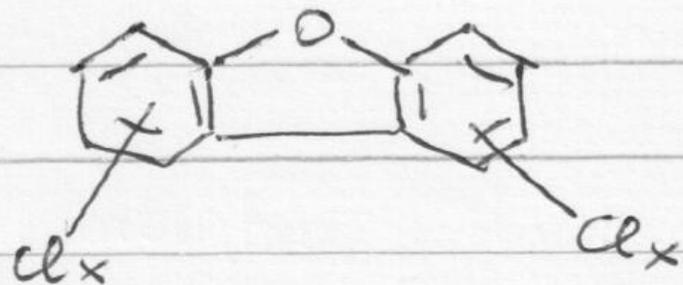
Poly Chlorinated Dibenzodioxin (PCDD)

Cl_x represent the Cl atoms substituted to H atoms in the molecule



2,3,7,8 Tetrachlorodioxin
2,3,7,8 TCDD

Pollutant formation (dioxines)

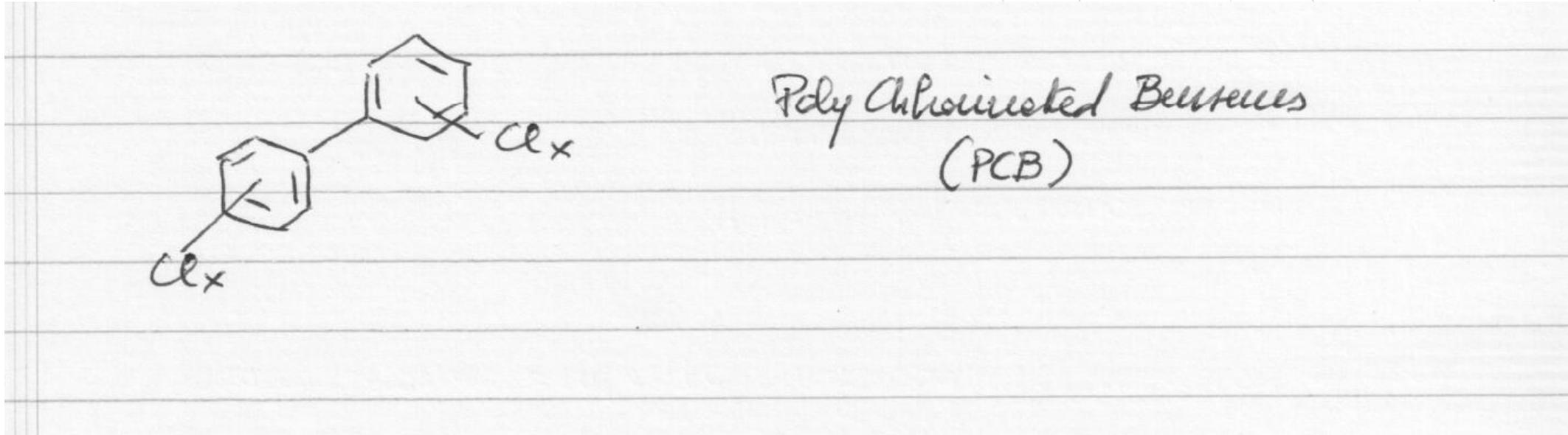


Poly Chlorinated Dibenzofuran (PCDF)



2,3,7,8 Tetrachloro Furan
2,3,7,8 TCDF

Pollutant formation (dioxines)



Pollutant formation (dioxines)

Toxicity rating chart

| <u>Toxicity rating or Class</u> | <u>Probable lethal dose for humans</u> |
|---------------------------------|--|
| Practically non toxic | > 15 g/kg |
| Slightly toxic | 5-15 g/kg |
| Moderately toxic | 0.5-5 g/kg |
| Very toxic | 50-500 µg/kg |
| Extremely toxic | 5-50 µg/kg |
| Supertoxic | < 5 µg/kg |

per kg of body weight

Pollutant formation (dioxines)

Although there are over 100 isomers of PCDD, the 2,3,7,8 TCDD has the highest toxicity in animal tests

Relative toxicity of some PCDD and PCDF

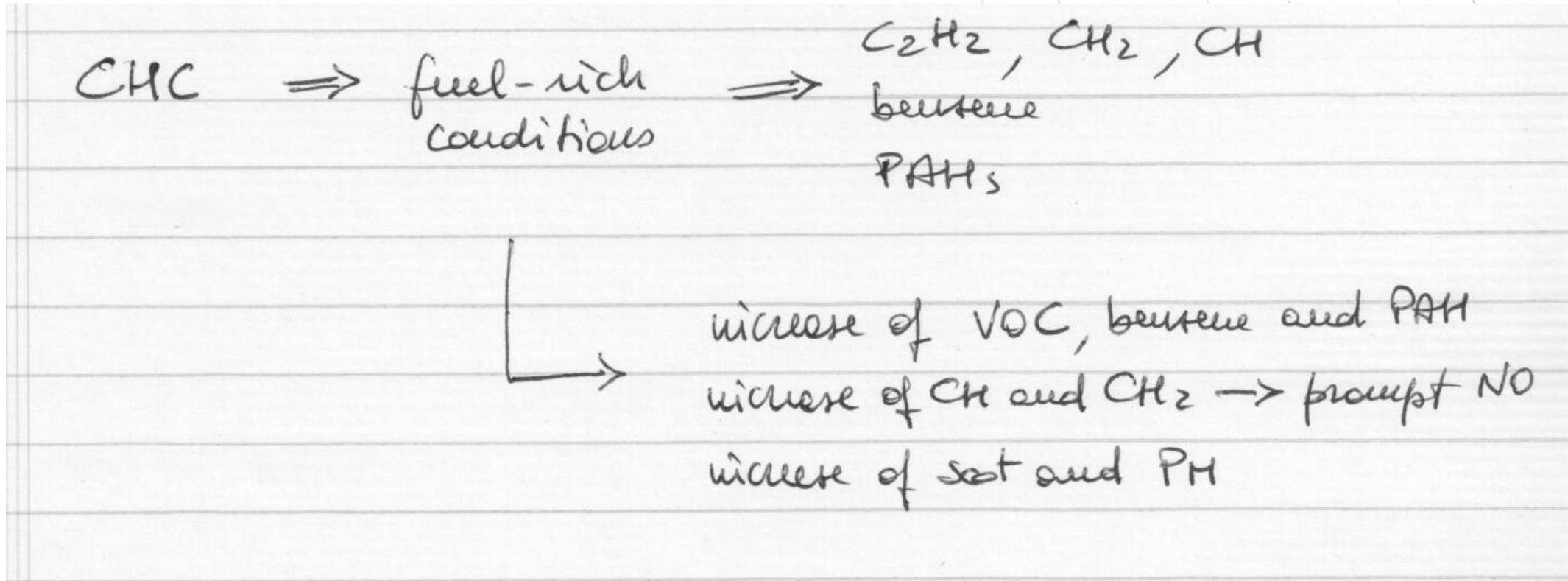
| <u>Chemical</u> | <u>Relative toxicity</u> |
|--------------------------|--------------------------|
| 2,3,7,8 TCDD | 1 |
| 2,3,7,8,x Penta CDD | 0.5 |
| 2,3,7,8,x,y Hexa CDD | 0.1 |
| 2,3,7,8,x,y,w Hepta CDD | 0.01 |
| 2,3,7,8,x,y,w,z Octa CDD | 0.001 |
| all the others | 0 |
| 2,3,7,8 TCDF | 0.1 |
| 2,3,7,8,x Penta CDF | 0.01 |
| 2,3,7,8,x,y Hexa CDF | 0.001 |

Pollutant formation (dioxines)

Because chlorinated compounds are effective in decreasing the concentrations of H and therefore OH and O radicals, they impact the formation of pollutants such as NO_x , hydrocarbons and soot in a complex manner.

Decreasing H and consequently OH and O, the system is fuel-rich also if the right combustion air is available due to the tendency of Cl to tie up H atoms.

Pollutant formation (dioxines)



Pollutant formation (dioxines)

The "richness" of the combustion mixture favors the formation of benzene and PAH and consequently PCB, PCDF and PCDD.

At present two mechanisms have postulated to explain the formation of PCDD and PCDF in practical facilities.

- 1) homogeneous synthesis from aromatic precursors such as chlorinated benzenes and phenols
- 2) heterogeneous and/or de novo synthesis from carbonaceous materials with particulate carbon and carbon species assisted by a surface

Pollutant formation (dioxines)

The mechanisms of formation of PCDD and PCDF in heterogeneous systems

Reactants: virtually any carbon source in gas phase

Surface: fly ash and metal/metal oxides, soot

Chlorine source: both organic and inorganic

Temperature: 200 - 550 °C

Reaction time: 5 min - 1 hour

Catalysts/Promoters: transition metals Cu and Fe

these conditions are typical of filters, particularly bag filters



THANKS!

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3.1: “Fund for the realisation of an integrated system of research and innovation infrastructures”

