Kinetic Modelling of Soot Oxidation

The Effect of Different Carbons on a Kinetic Model

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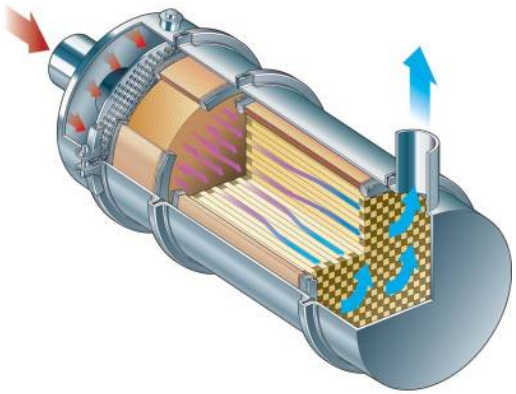
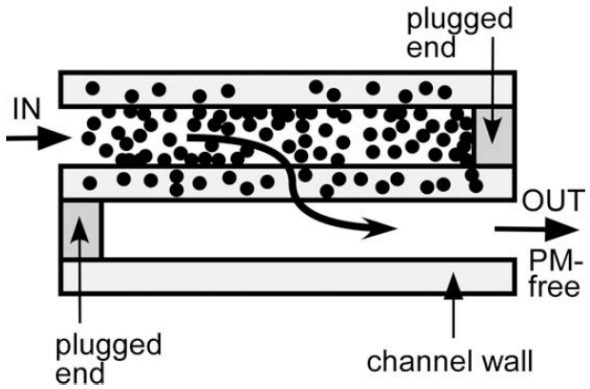
Introduction

- Regeneration in Diesel particle filters (DPFs)
  - Oxidation of accumulated soot
- Uncatalysed oxidation
- Efficiency of regeneration
  - reaction conditions
  - nature of the soot

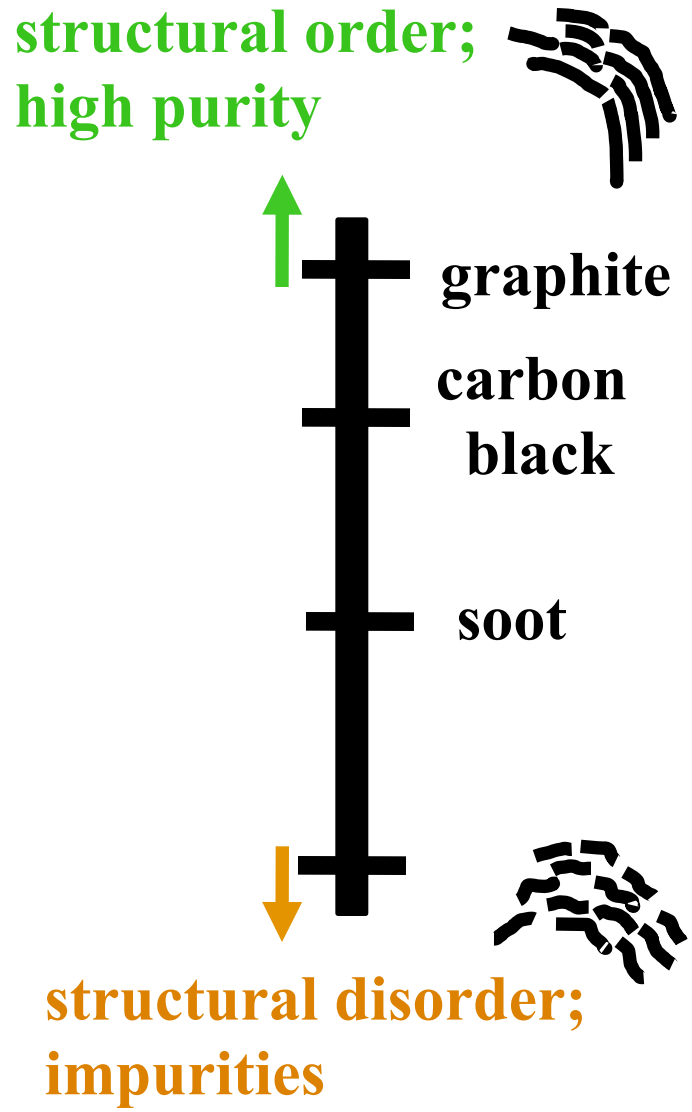




Structure of soot-like carbons

- Crystallinity and concentration of active sites
- Impurities

- oxidative reactivity
- kinetics



Scope

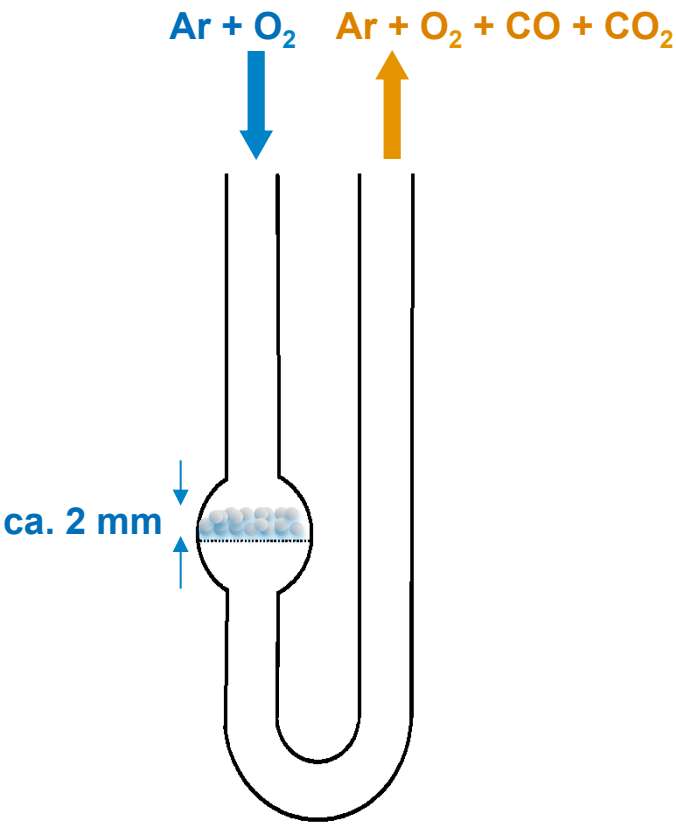
- Semi-global mechanism
  - soot + O_2

- Determine mechanistic parameters for a range of carbon materials
  - Experiments
  - Extract kinetic data
  - How do the kinetics depend on the nature of the material?

$$r_j = A_j \, e^{-\frac{E_{a,j}}{RT}} \cdot S_a \cdot C_{O_2}^{n_j}$$

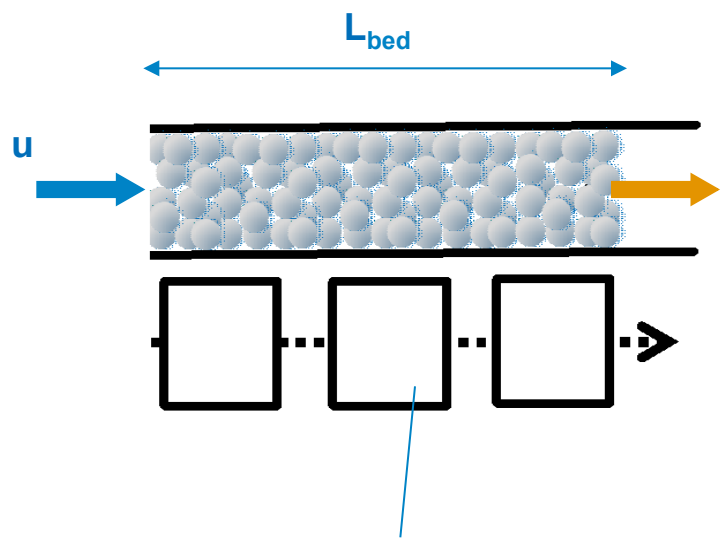
Reactor experiments

- Fixed bed of particles
  - diesel soot
  - graphite
- Conditions:
  - 100% Ar, 10 °C/min to T_{des}
  - 10% O_2 + 90% Ar at T_{des}
  - 250 ml/min at STP
- Experiments from the literature: coke, char, ethylene soot, carbon black, graphite



Reactor model

- Fixed bed of particles
  - described as a series of CSTRs
  - $Pe = u\,L/D_{ax} \rightarrow$ RTD
    $\rightarrow$ 1 CSTR required



$$\frac{dm_i}{dt} = \dot{m}_i^{in} - \dot{m}_i^{out} + \omega_i$$

- Flow through porous bed:

$$\frac{\Delta P}{L_{bed}} = 150\,\frac{(1-\varepsilon)^2}{\varepsilon^3}\,\frac{\mu\ \ v}{\bar{d}_p^{\,2}}$$

Reaction mechanism

1. $*C + \frac{1}{2}O_2 \rightarrow C(O)$
2. $C(O) \rightarrow CO + *$
3. $C(O) + \frac{1}{2}O_2 \rightarrow CO_2 + *$

- Reaction rates

$$r_j = k_j(T) \cdot C_{O_2}^{n_j}$$

$$= A_j \, e^{-\frac{E_{a,j}}{RT}} \cdot C_{O_2}^{n_j}$$

- Source tems

$$\omega_i = \sum_{j=1}^{3} \nu_{j,i} r_j \, S_a \, M_i$$

$$\frac{d\theta_k}{dt} = \frac{\sum_{j=1}^{3} \nu_{j,k} r_j}{\Gamma}$$

Diffusion limitations

- Thermal limitations
  - no noticeable exothermicity during experiments

- External diffusion
  - insignificant at low T
  - fraction of external resistance < $2.5 \cdot 10^{-3}$

- Internal diffusion

$$\Phi = L\sqrt{\frac{n+1}{2}\frac{k\ C^{n-1}}{D_{eff}}}$$

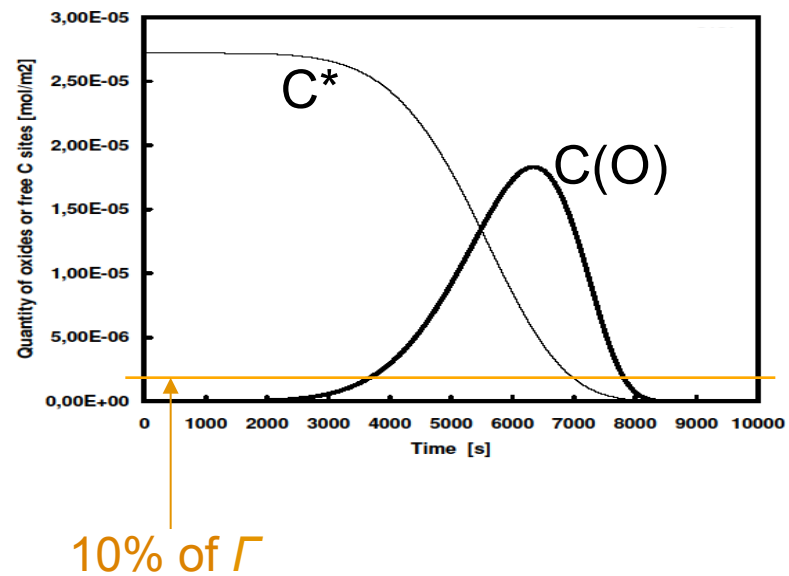
$$r_{\text{app}} = \left[\frac{1}{\Phi}\frac{1}{\tanh(3\Phi)} - \frac{1}{\tanh(3\Phi)}\right]\cdot r_{\text{int}}$$

  - $\Phi \ll 0.3$

Strategy of calibration

- Equations solved with the IFPExhaust library (AmeSim)

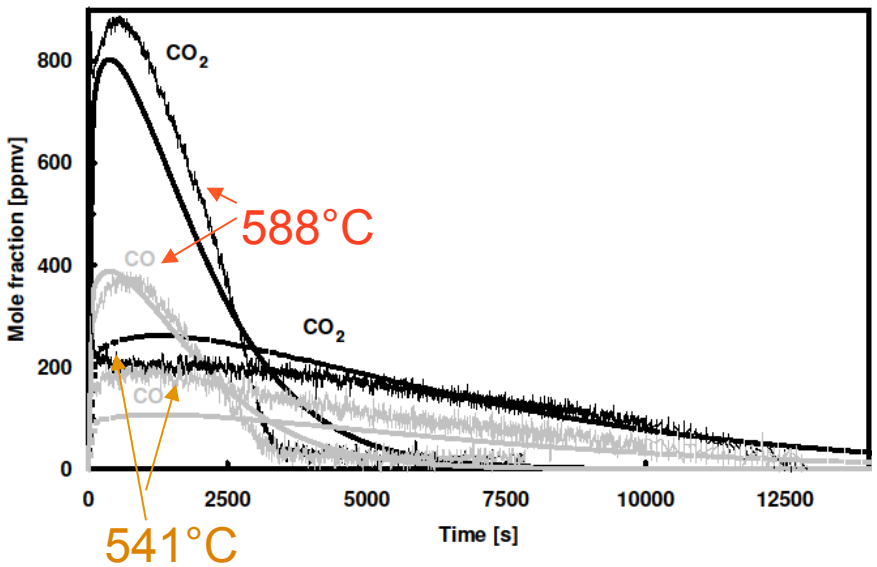
- Data used for calibration
  - TPO or IOs (2 different temperatures)
    - global mass consumption
    - reaction products
    - surface intermediates
      - no measurements available
      - > 10% of Γ *(Campbell&Mitchell, 2008)*

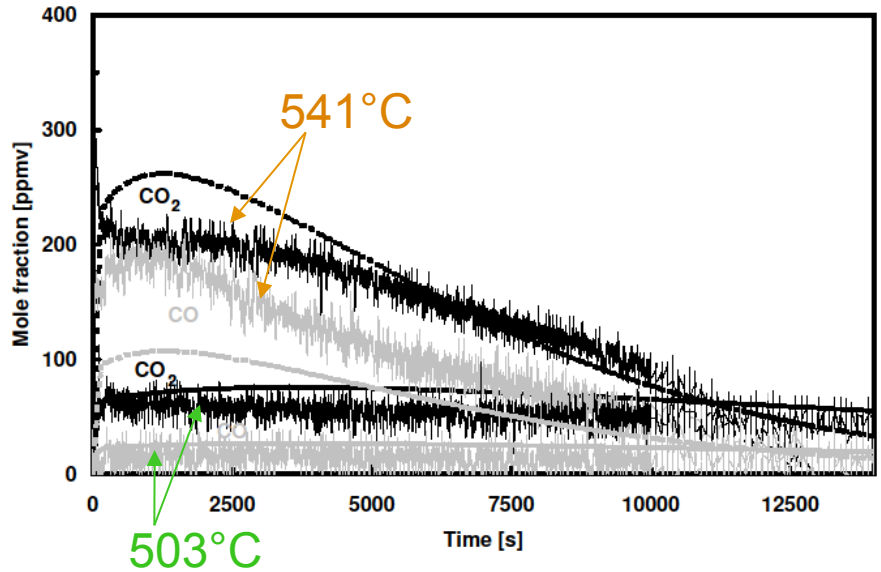


- Assumptions:
  - CO and CO_2 formation rate limiting
  - O_2 adsorption fast
  - $\Gamma \approx 2 \cdot 10^{-5}$ mol/m^2

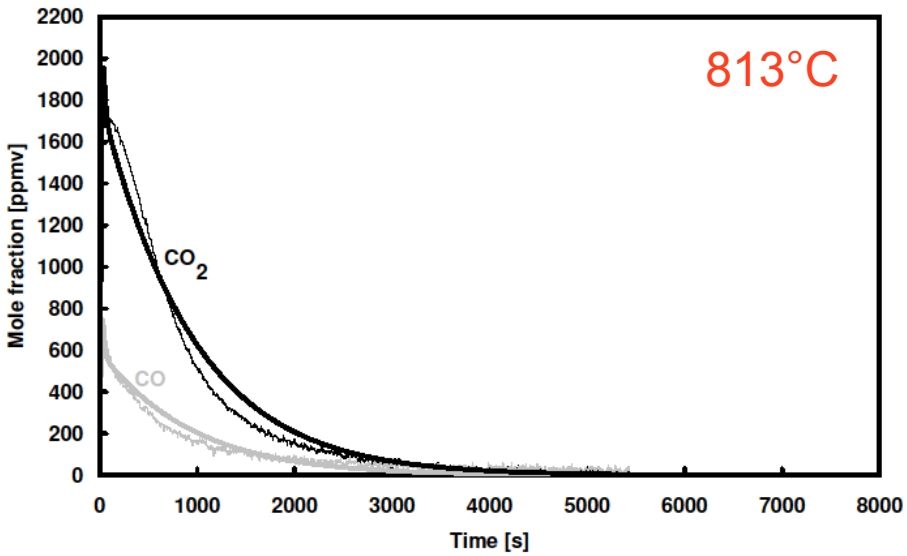
- S_a determined from mass balance
  - Random pore model

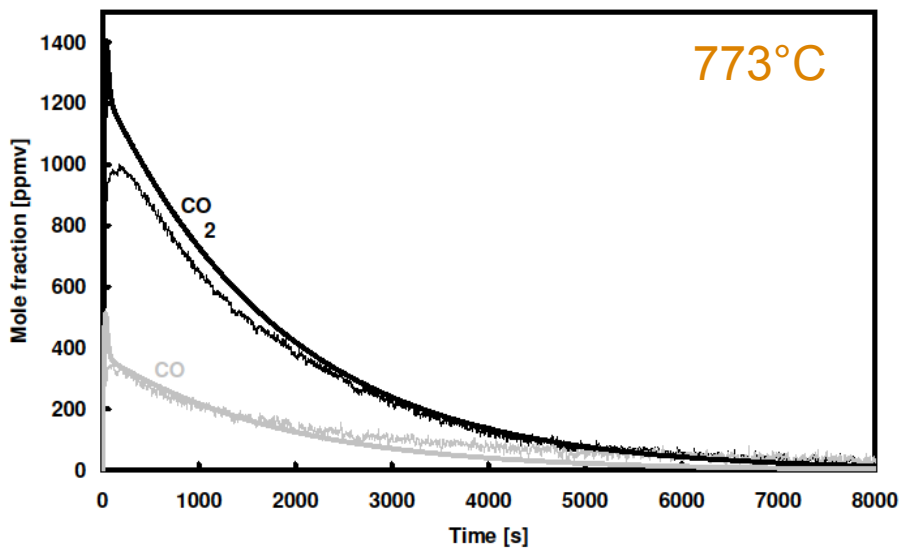
Oxidation of diesel soot (ψ = 5)



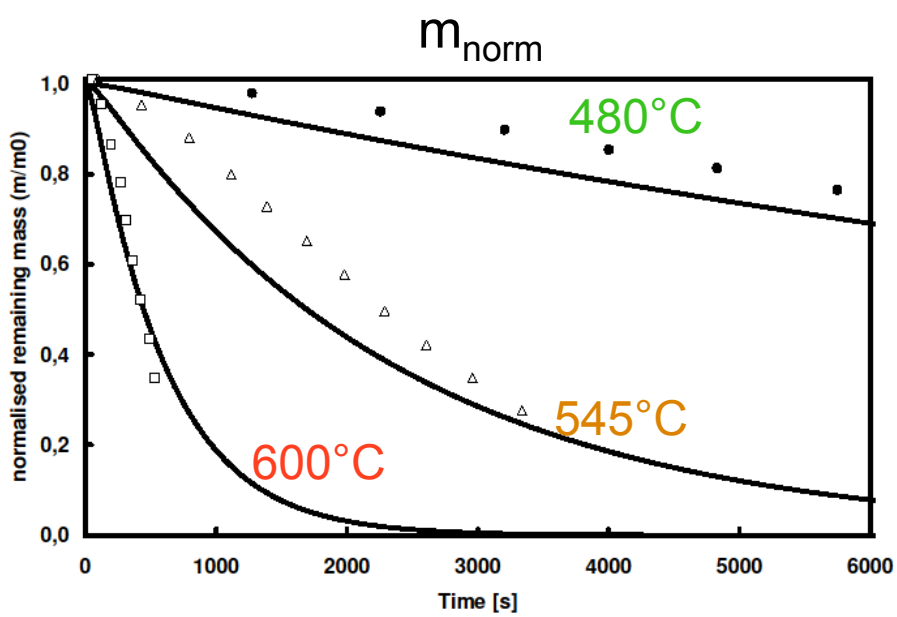


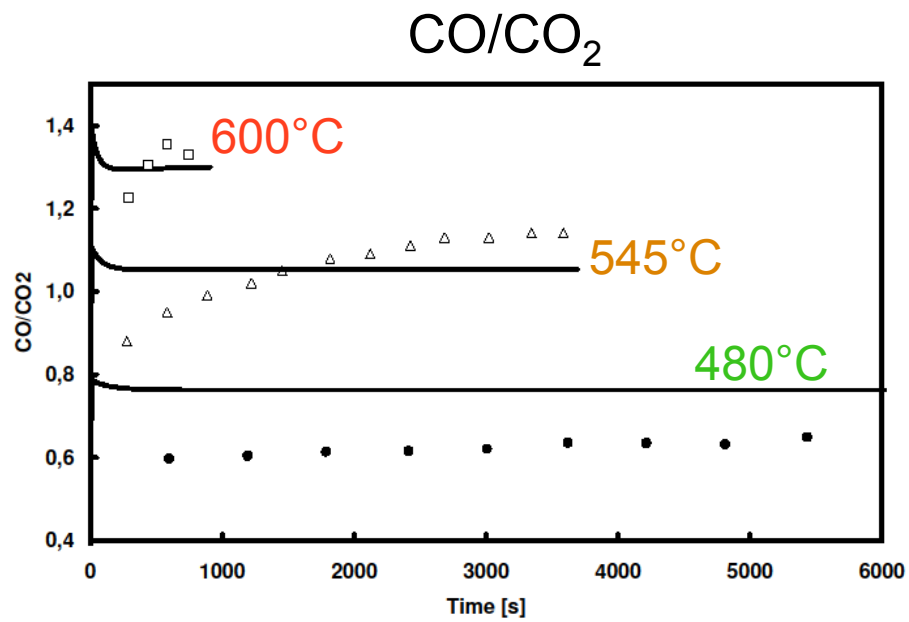
Oxidation of graphite (ψ = 0)





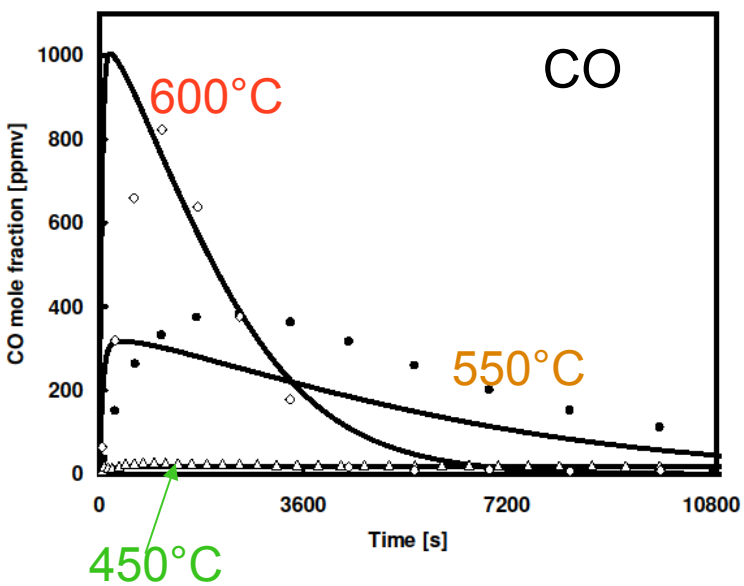
Oxidation of ethylene soot

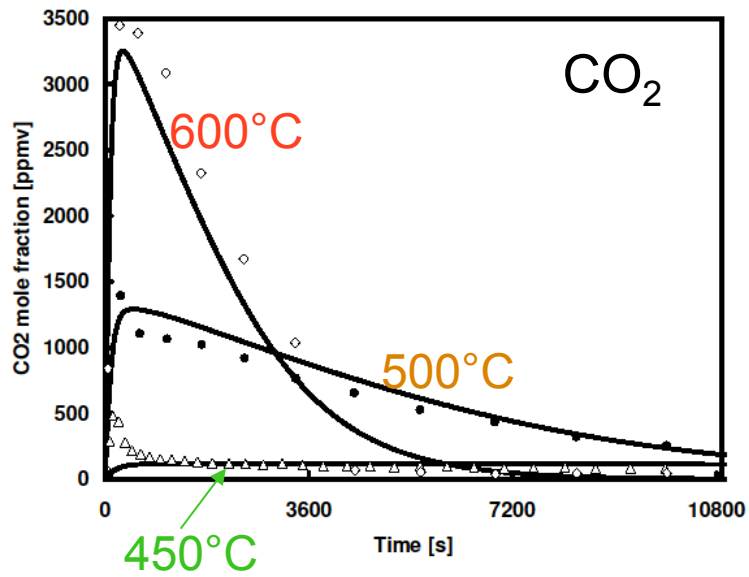


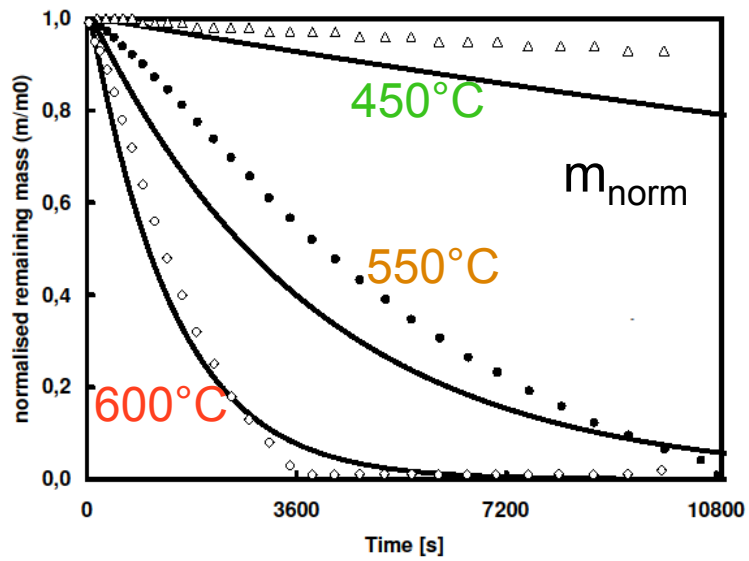


- $\psi = 0$
- experimental data: Du et al., 1991, Energy & Fuels, 5

Oxidation of char



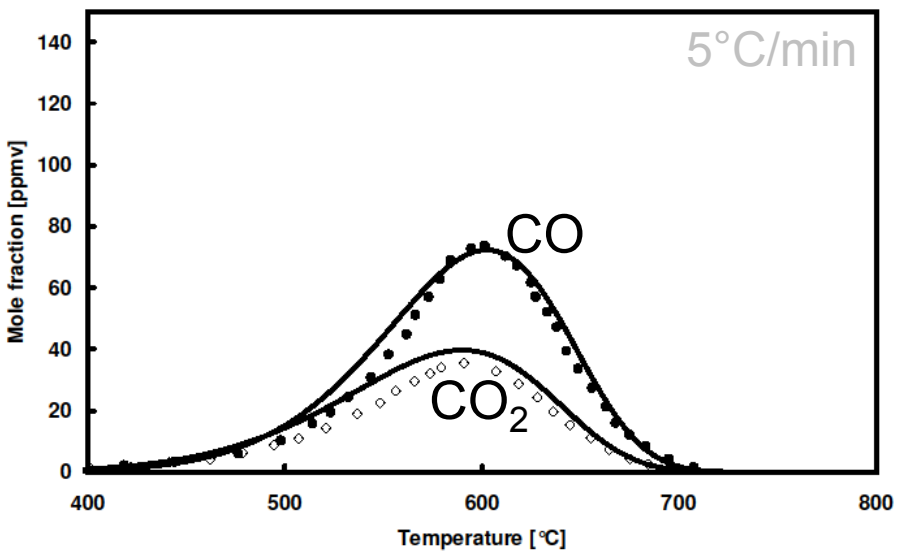


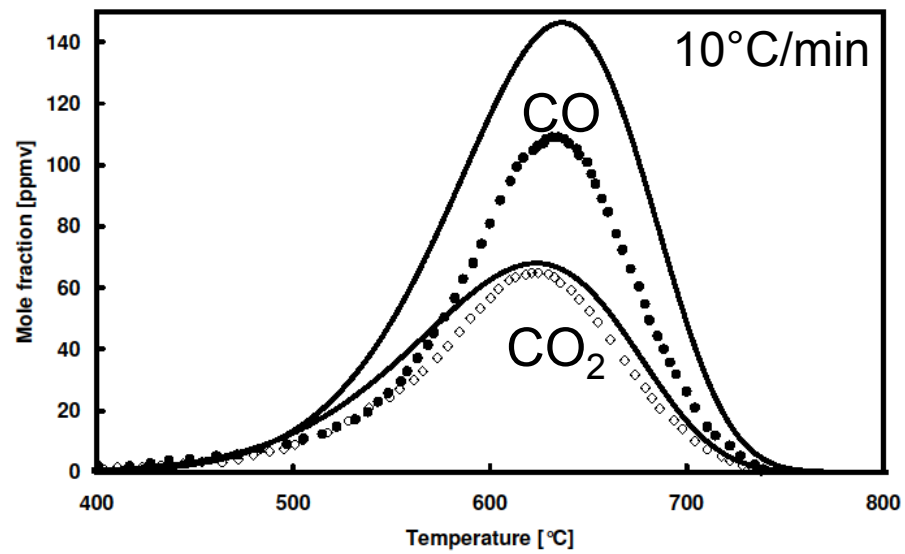


- ψ = 2 (fit by Campbell and Mitchell, 2008

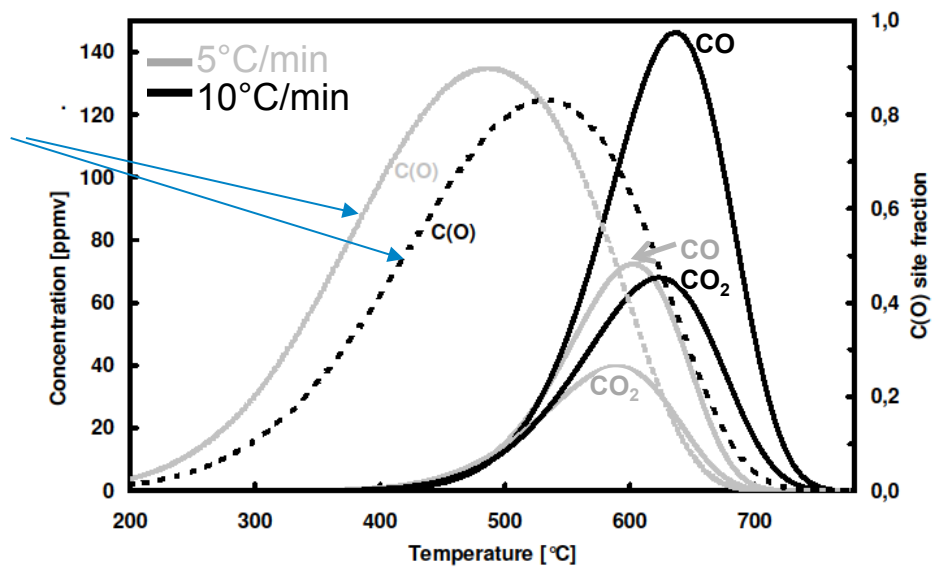
- experimental data: Campbell and Mitchell, 2008

Temperature-programmed oxidation of coke





surface evolution during TPO

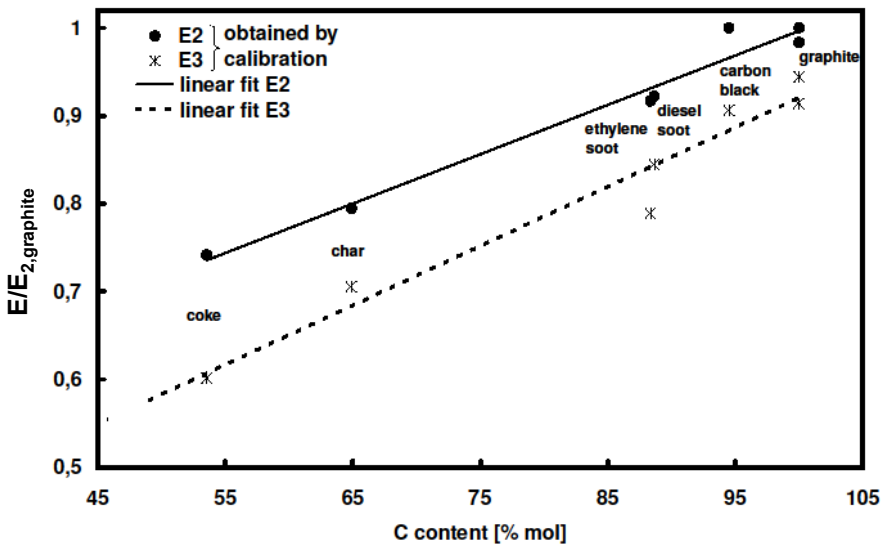


($\psi = 0$)

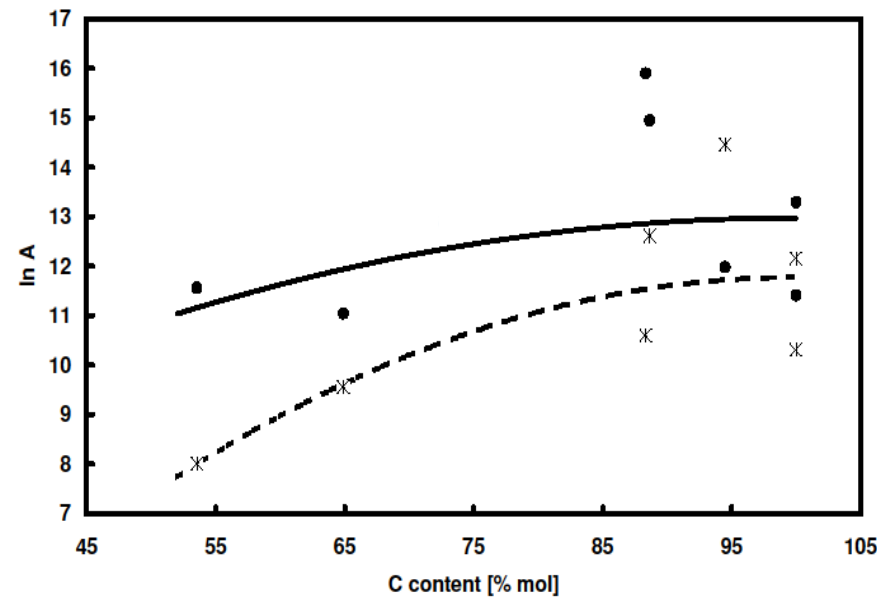
experimental data: Kanervo et al., 2001

Kinetics of different soot-like carbons

E_2 and E_3



$\ln A_2$ and $\ln A_3$



$$r_j = A_j\, e^{-\frac{E_{a,j}}{RT}} \cdot S_a \cdot C_{O_2}^{n_j}$$

surface chemistry
- f(%C)
- microkinetics

surface physics

Conclusions...

- Important trends of oxidation reproduced: Global reactivity and CO/CO_2 selectivity of different carbon materials
- Kinetic parameters used to distinguish between different types of soot-like carbon

... and future developments

- Confirm values
  - More experimental quantities (surface species...)
- Microkinetics
  - confirm link with %C
  - model using distributions of activation energies

Thank you for your attention

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Supplementary slide (1)

Generation of the diesel soot used in experiments

Engine	
Engine code	PSA DW10 BTED4 Euro 4
Displacement	1998 cm^3
Fuel injection	common rail direct injection
EGR	none
Max. rated power	100 kW at 4000 min^{-1}
Max. rated torque	320 Nm at 1750 min^{-1}
Compression ratio	18
Fuel	
Cetane number	50.7
Lower heating value	41.72 MJ/kg
Aromatic content	22 wt. %

- Common rail diesel engine (DW10, PSA)
- ECE urban driving cycle (1500 rev/min, 5 bar)
- Soot collected on a DPNR at 340 °C

Supplementary slide (2)

Bhatia-Perlmutter random pore model : evolution of surface area

$$\frac{S_a}{S_{a,0}} = \sqrt{1 - \psi \ln\left(1 - x\right)}$$

$$\psi = \frac{4\pi L_0 \left(1 - \varepsilon_0\right)}{S_{a,0}^2}$$