Experimental and Numerical Investigation of the Thermal Decomposition of Materials at Three Scales: Application to Polyether Polyurethane Foam Used in Upholstered Furniture

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CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

THE UNIVERSITY OF EDINBURGH

Presentation layout

1. **Background and methodology**
2. Proposition of possible kinetic mechanisms
3. Determination of the kinetic mechanism and calculation of kinetic parameters
4. Small scale analysis (cone calorimeter)
5. Fire of simplified upholstered furniture
6. Conclusions and perspectives

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The current numerical approaches of fire

The physics of fire

- Take only into account a **single stage** global decomposition **kinetic**
- **Extrapolate** the **phenomena** observed at the small scale to the large scale
- **Neglect** the **influence** of solid decomposition **kinetics** in the dynamic of combustion

The chemistry of fire

- Consider **infinitely** fast chemical **reactions**
- **Restrict** strongly the number of species and **pollutants** entering into reaction
- **Tabulated** chemistry
- **Lack** of knowledge of the **transformation** of species in the **region** between the solid and the flame

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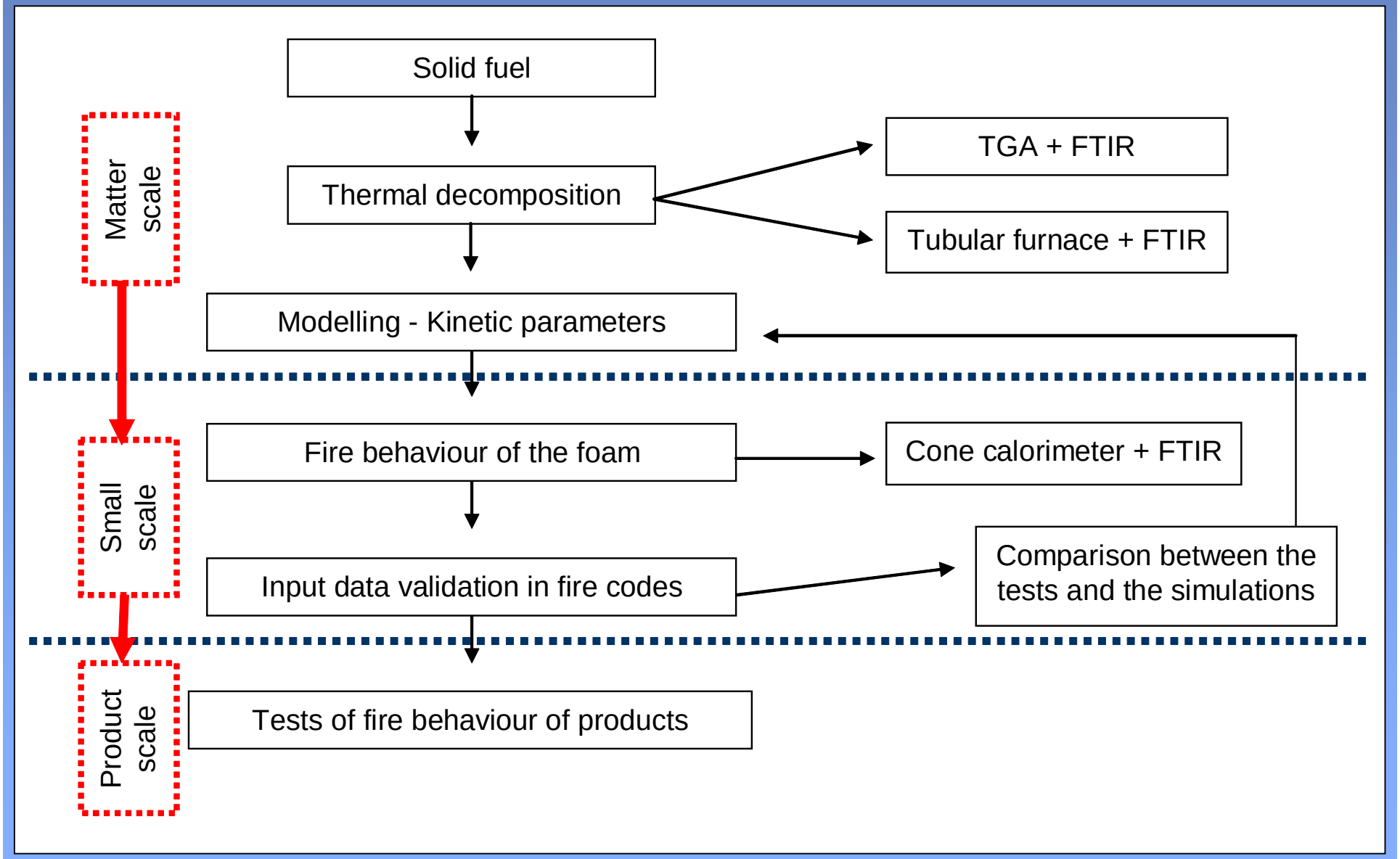
Goal

To develop a **general method** for establishing the **multi-stage** decomposition mechanism of **solid** materials based in a **multi-scale** analysis. The method is allowed to take into account the **chemistry** of the process (**pollutants** release).

Methodology of the work



Characterisation of the virgin foam

$$n\,\underbrace{OCN - R - NCO}_{Polyisocyanate} + n\,\underbrace{HO - R' - HO}_{Polol} \longrightarrow \underbrace{(R - NHCOO - R' - NHCOO)}_{Polyurethane}{}_{n}$$

Source: Ohtani H. et al. (1987)

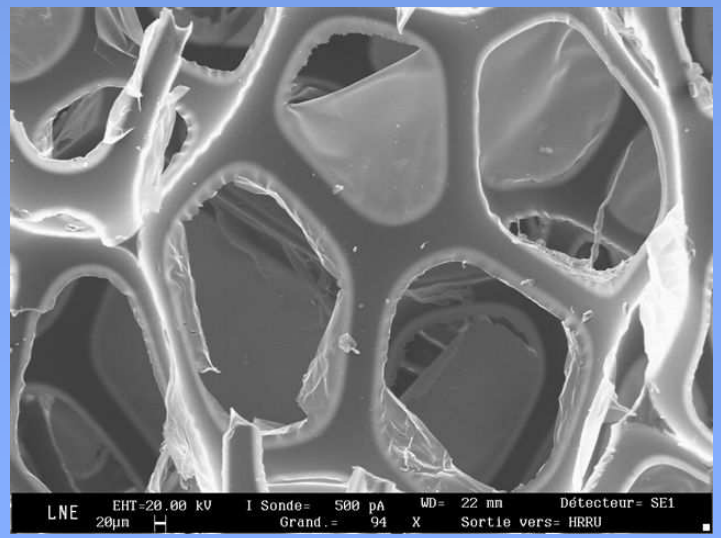
Element	Content
C	61.9%
H	8.5%
O	22.5%
N	5.9%
S	< 0.2%
Cl	< 10 ppm

Performed in Service central d'analyse

Molecule formula

$$C_1H_{1.53}O_{0.27}N_{0.08}$$

Structure of virgin foam



Density = 22 kg•m^{-3}

Raw components from the manufacturer

Performed in LNE

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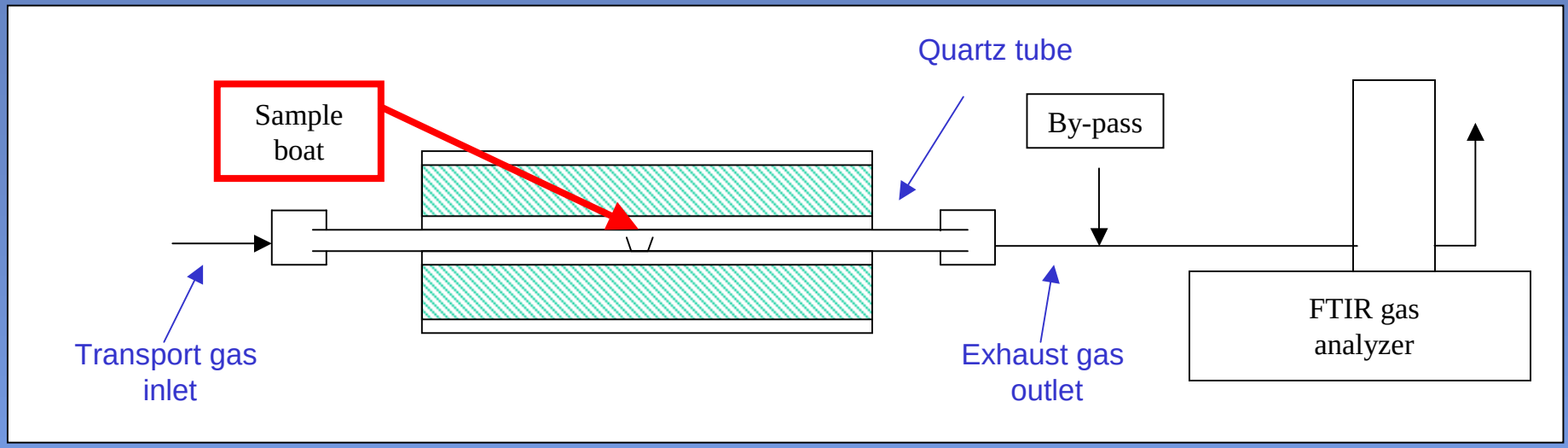
Tubular furnace and FTIR



Calibrated product		Quantification limits [ppm]	
Component	Symbol	Low	High
Carbon monoxide	CO	2.5	8802
Carbon dioxide	CO_2	260.4	101100
Water	H_2O	21.1	22560
Nitrogen monoxide	NO	4.9	883
Nitrogen dioxide	NO_2	1.0	639
Nitrous oxide	N_2O	8.5	1005
Hidrogen cyanide	HCN	5.0	1020
Hidrogen chloride	HCl	2.1	5290
Hidrogen bromide	HBr	2.0	1000
Methane	CH_4	0.3	4990
Acetylene	C_2H_2	2.1	994
Ethylene	C_2H_4	2.7	995
Formaldehyde	H_2CO	21.7	131
Sulfur dioxide	SO_2	1.0	852
Ammonia	NH_3	1.0	1085

Matter scale hypotheses

Particles

- Masses **< 110 mg**
- **No** gradients of **concentration** of oxygen and pyrolysis products
- **No** gradient of **temperature**
- No **aerodynamics** effects around the particle
- **Isotropic** structure
- **No** solid phase **transport** effects
- **Homogeneous** decomposition of samples

Alveolar matrix of PPUF, high **effective** exchange area

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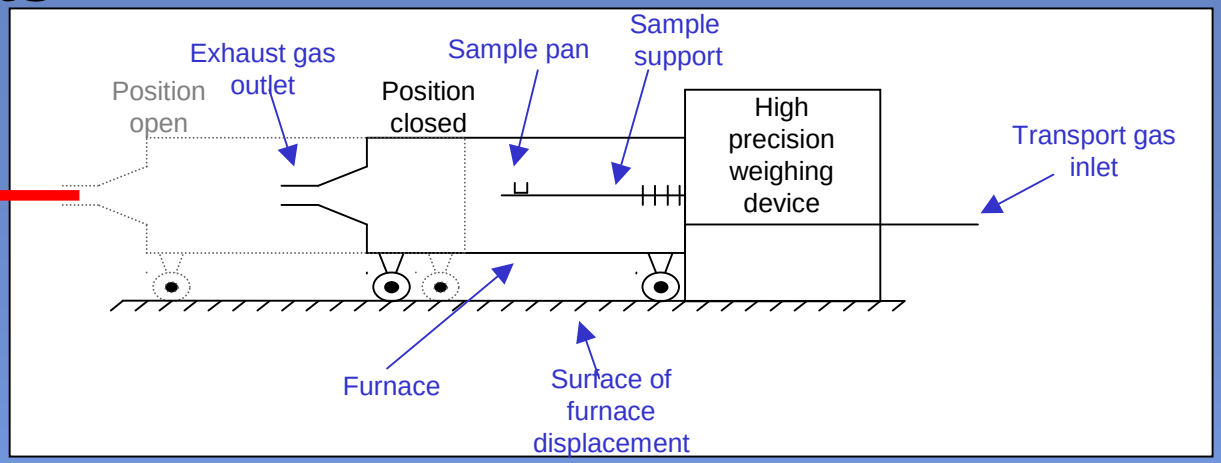
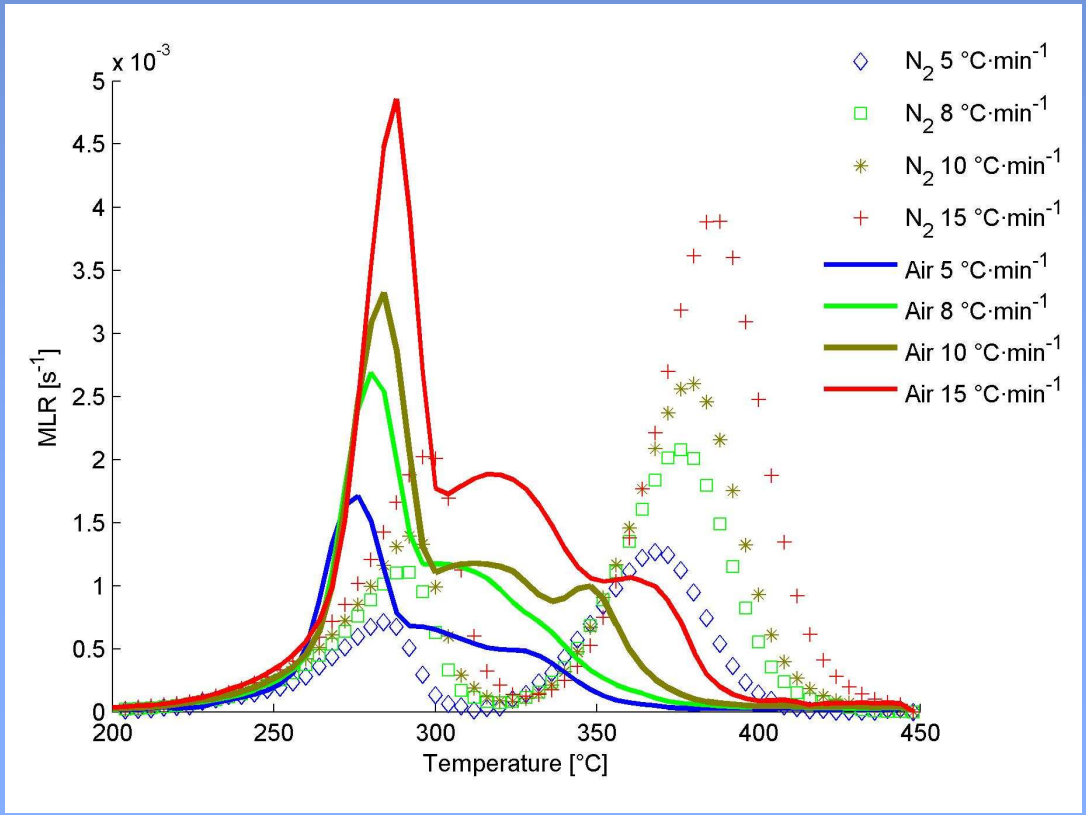
TGA experiments

To FTIR

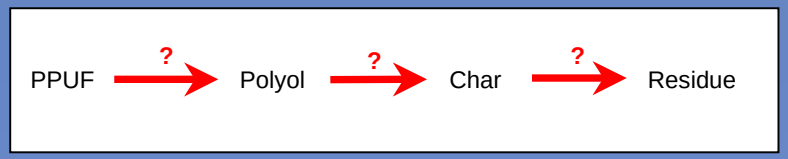


Heating rates:
- Found in literature
- Stages separation
- No gradients*

*Source: Lachaud J. et al. (2008)



Methodology of Modelling



Total mass at time t, is the sum of remaining mass of each condensed phase species

$$\frac{dm(t)}{dt} = \frac{dm_{PPUF}}{dt} + \frac{dm_{polyol}}{dt} + \frac{dm_{char}}{dt} + \frac{dm_{residue}}{dt}$$

Each equation has an Arrhenius reaction rate

$$\dot{\omega}_i = A_i e^{-\frac{E_i}{RT}} \left(\frac{m_i}{m_o}\right)^{n_i} Y_{O_2}^{\delta}$$

$$MLR_i = \frac{dm_i}{dt} = \upsilon_i \cdot \omega_i$$

Mass balance is expressed in terms of reaction rates and stoichiometric coefficients (υ_i)

$$\frac{dm(t)}{dt} = \sum_{i=1}^{5} (\upsilon_i - 1)\,\dot{\omega}_i$$

Calculation results are compared to experiments

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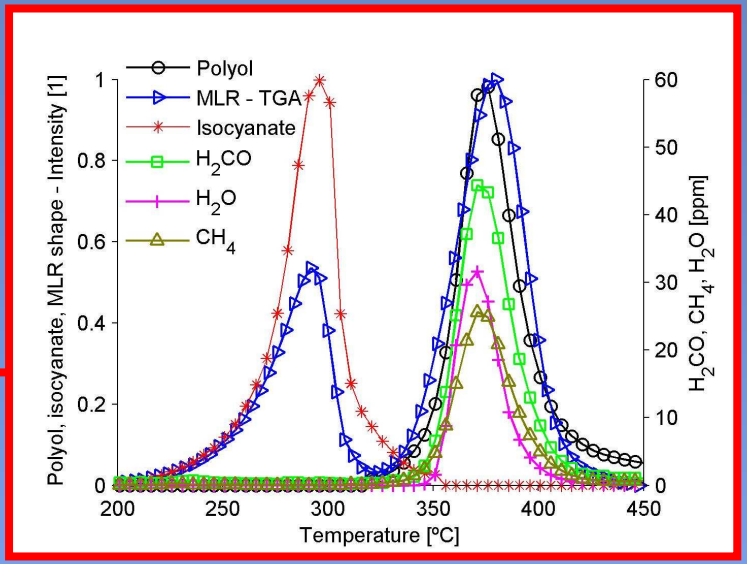
Coupling of solid and gas phases

TGA data (**solid** phase)

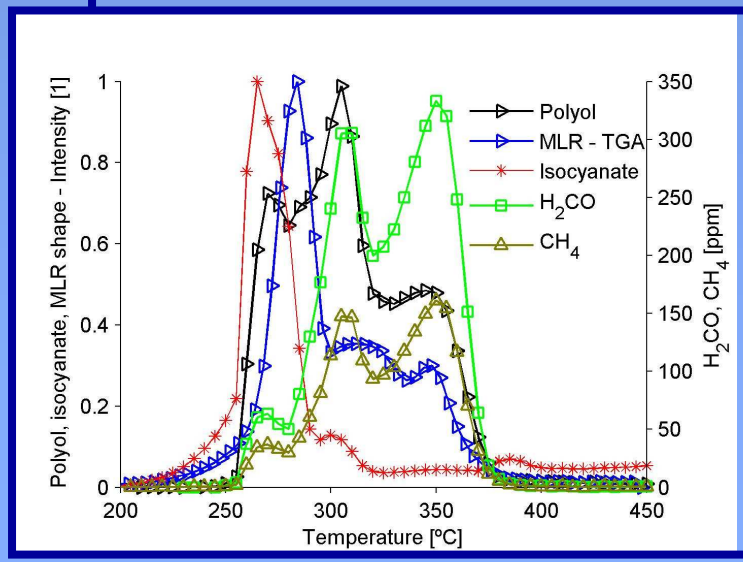
+

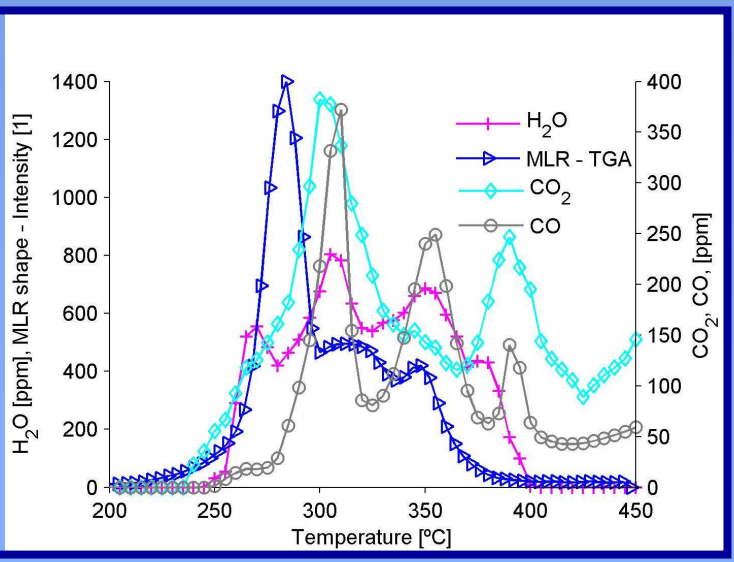
FTIR data (**gas** phase)

Nitrogen



Air





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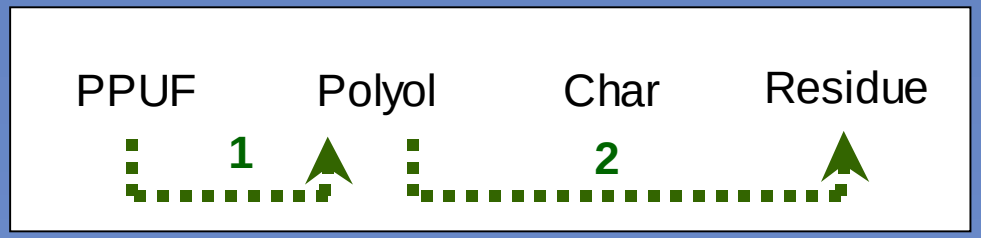
Mechanism



Pyrolysis reactions

- **Isocyanate** is released during the **collapse** of PPUF
- **Polyol** remains in the holder as a **semi-liquid**
- The **residue** of the second reaction is **negligible**

Oxidization reactions

- The virgin PPUF decomposition is **shifted towards low temperature** in comparison to pyrolysis one, releasing gases formed only by diphasic reactions.
- The **gas products** evidence that the second oxidization reaction occurs in **lean O_2 atmosphere**
- **CO and CO_2** appears during the **third** oxidization reaction. They are **not** present in the **pyrolysis** at a similar temperature (347 °C).

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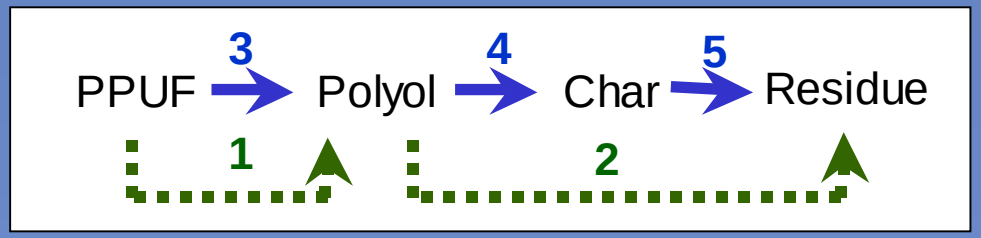
Mechanism



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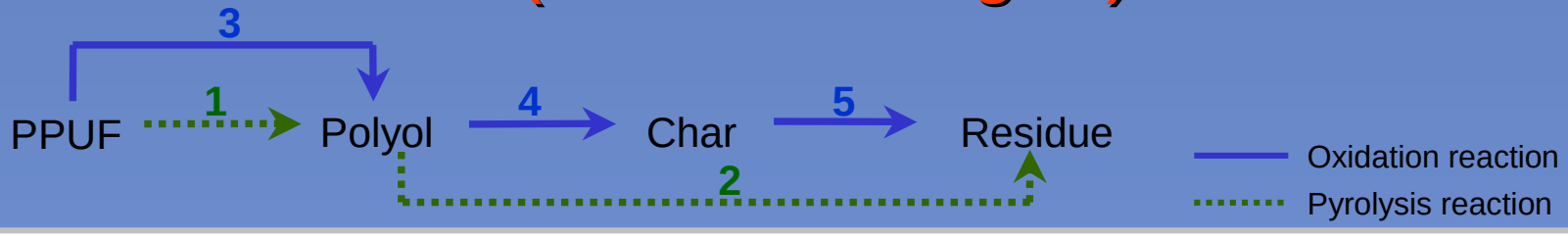
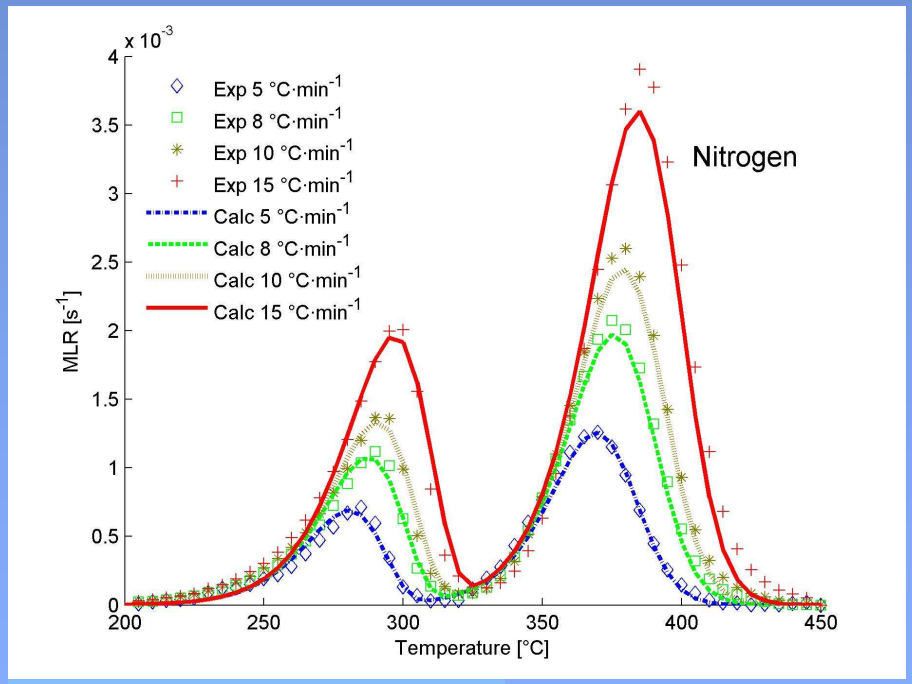
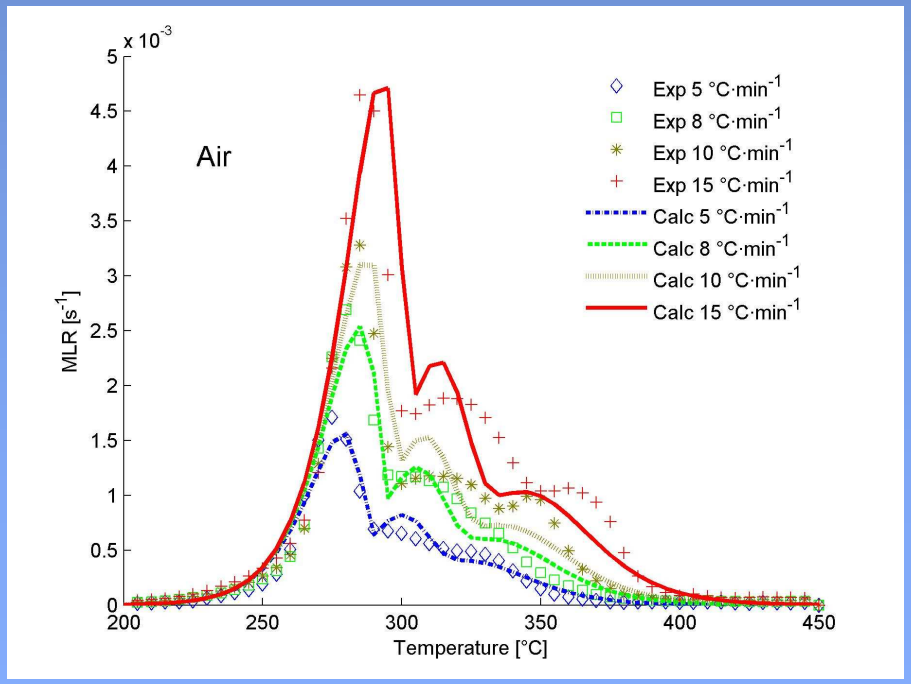
Prediction of MLR (air and nitrogen)



The kinetic parameters are dependent of the **evaluation function** and the decomposition **mechanism**.

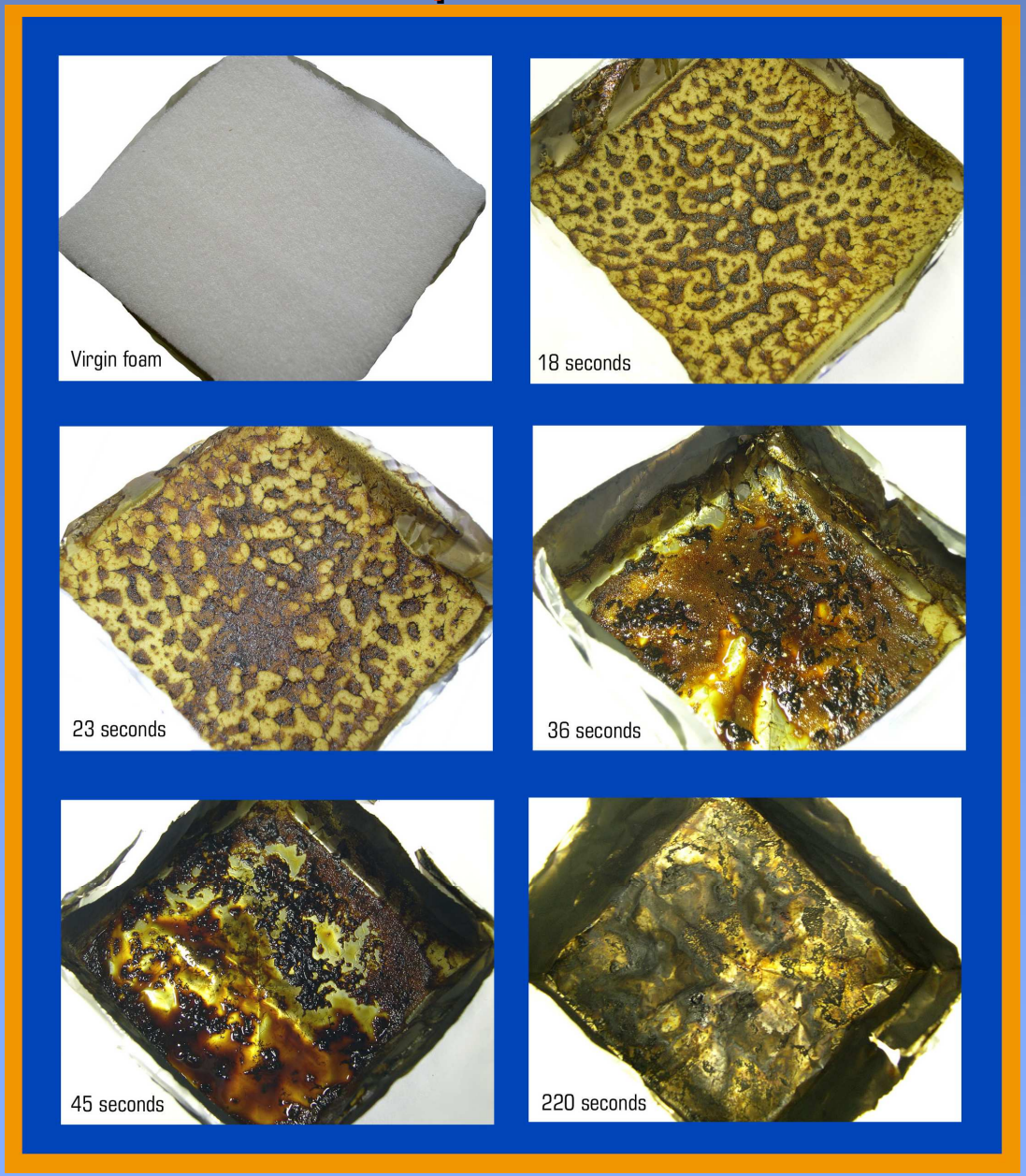




The **kinetic parameters** that allows prediction of TGA experimental results are calculated using genetic algorithms.

The change of the solid phase

30 kW·m^{-2}



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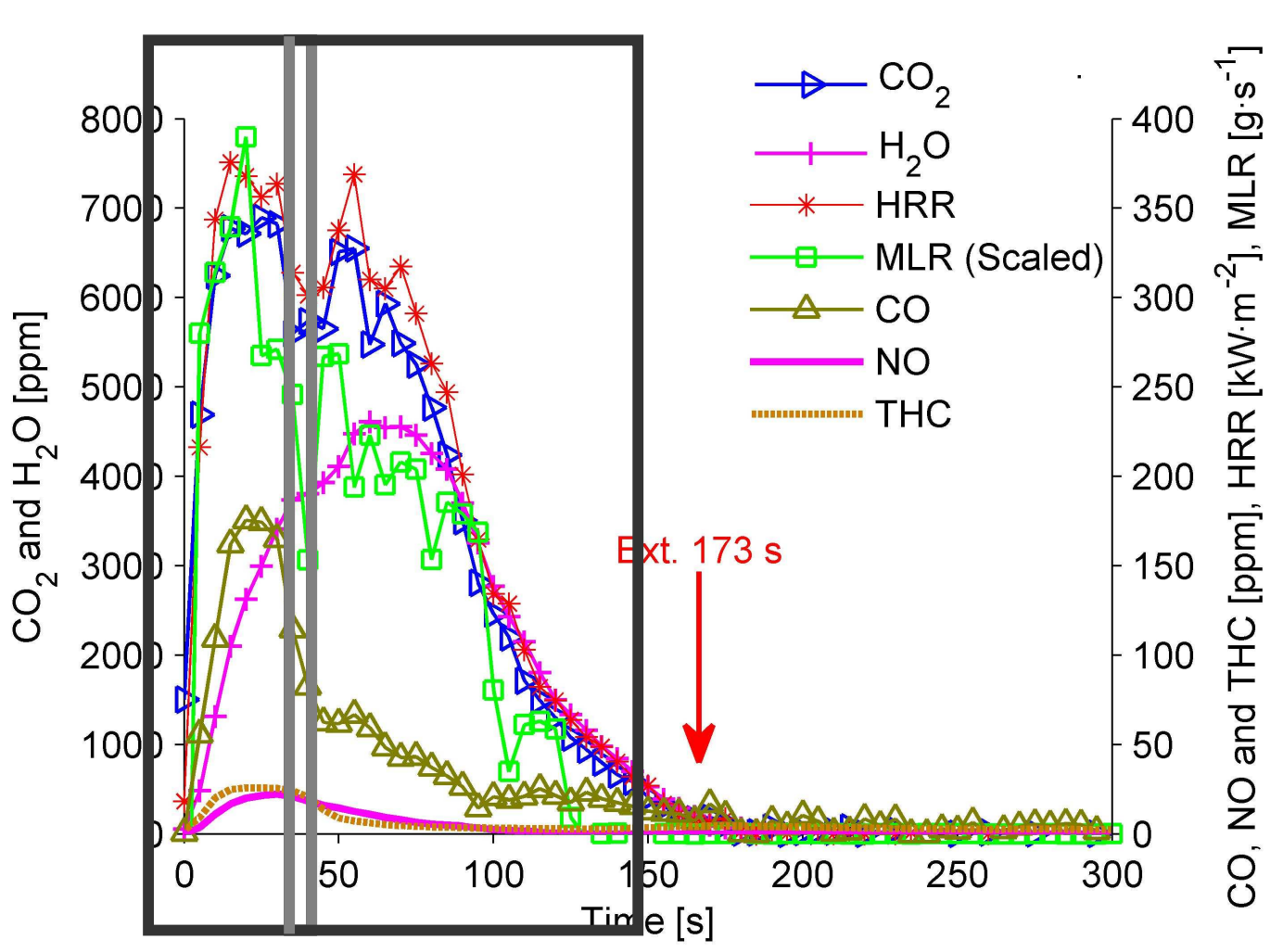
MLR & HRR coupled to toxic gases release

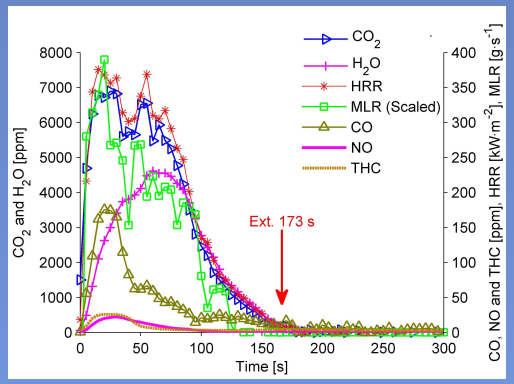
50 kW·m^{-2}



The release of **toxic gases** in function of time allows **analysis** of decomposition **mechanism** in CC

Source: Bustamante Valencia L. *et al.* Fire Safety Journal 44 (2009) 933 - 940

Decomposition mechanism of PPUF in CC



32%Wt

68%Wt

PPUF

↓

Isocyanate

+

Polyol

→ **First** pyrolysis and combustion stage. Yellow smoke

→ **Second** pyrolysis and combustion stage Semi-liquid polyol

- The decomposition mechanism is in **accordance** to data from **matter scale and literature**
  Saunders *et al.* (1961), Woolley *et al.* (1972), Rogers *et al.* (1981).
- The combustion of isocyanate and polyol are **not** completely **separated** in time.

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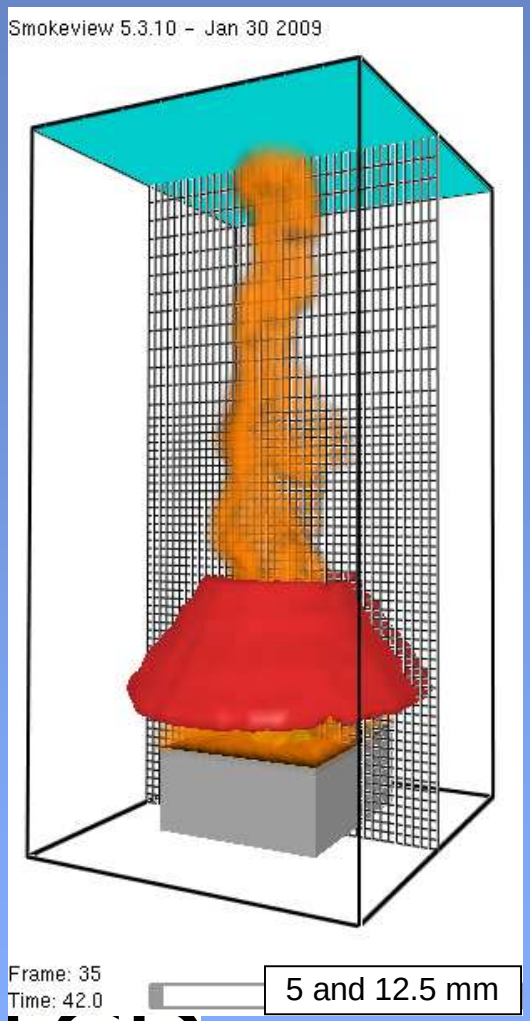
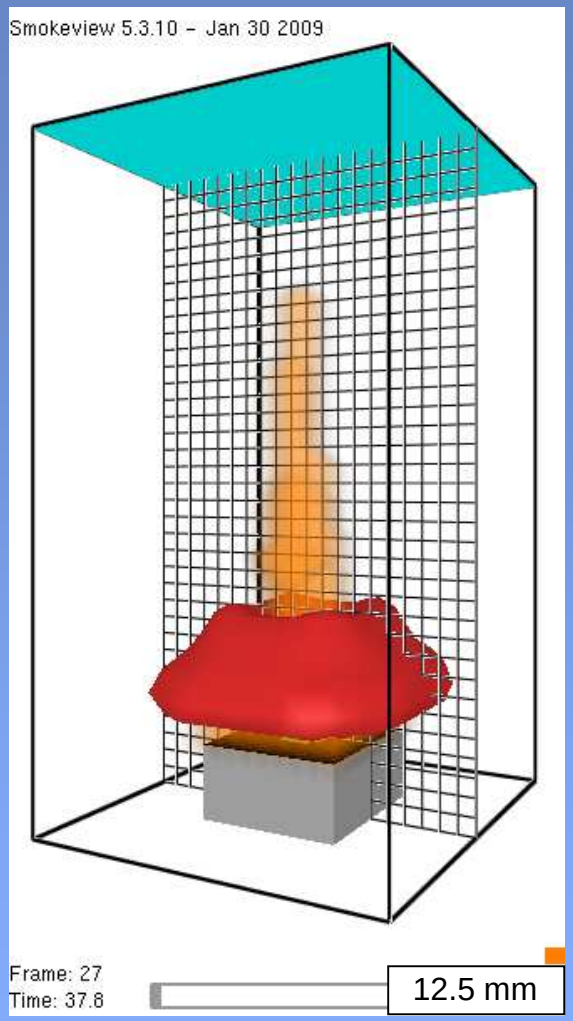
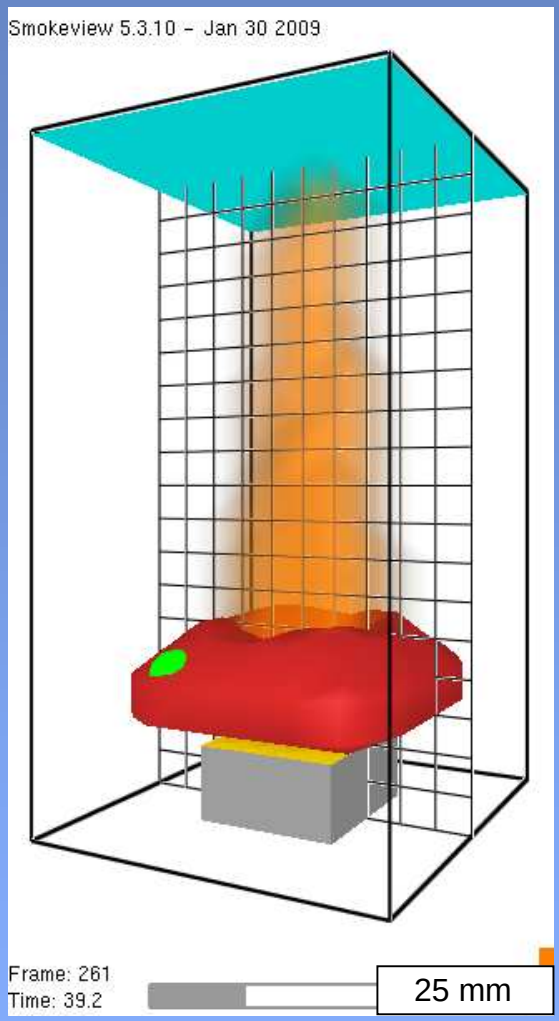
FDS simulations



5 and 12.5 mm



12.5 mm



25 mm

Three grid sizes have been analysed, nevertheless the uncertainty of **input data** is prioritary.

FDS simulations (2)

Input data

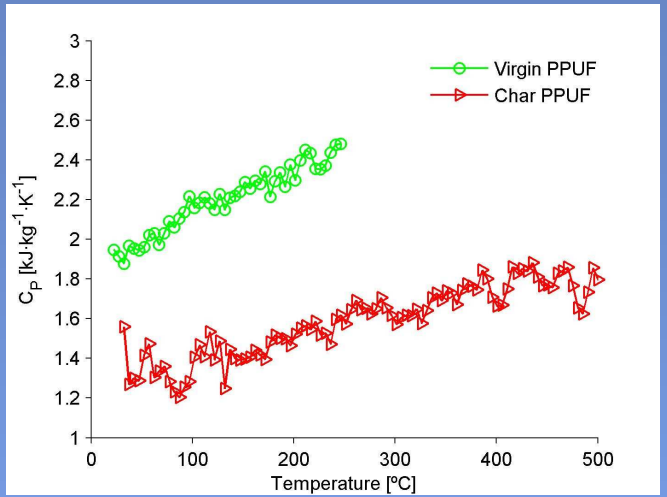
- The pyrolysis calculated numerical simulations require as input data the **kinetic parameters** of the reaction and the **thermal properties**
- Very **few** pyrolysis calculated numerical simulations are find in the **literature**.
- The **thermal properties** can be specified as **vectors** in function of the temperature.
- A great **uncertainty** exists about how to **specify** the input data for the pyrolysis submodels.

Thermal properties

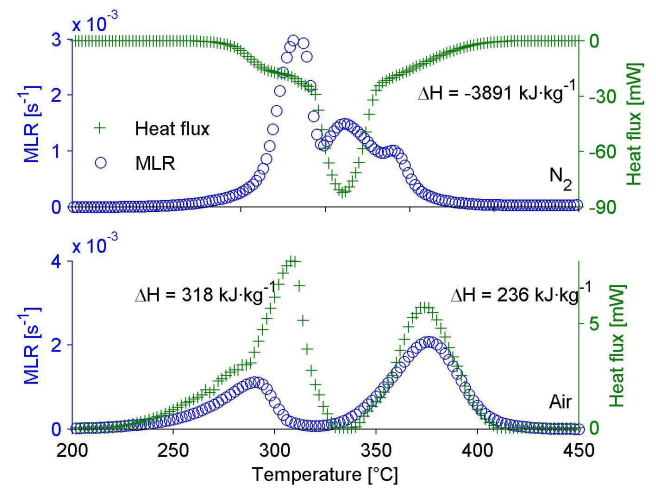
Input data for numerical simulations

ΔHc gross = 29.8 MJ•kg^{-1}

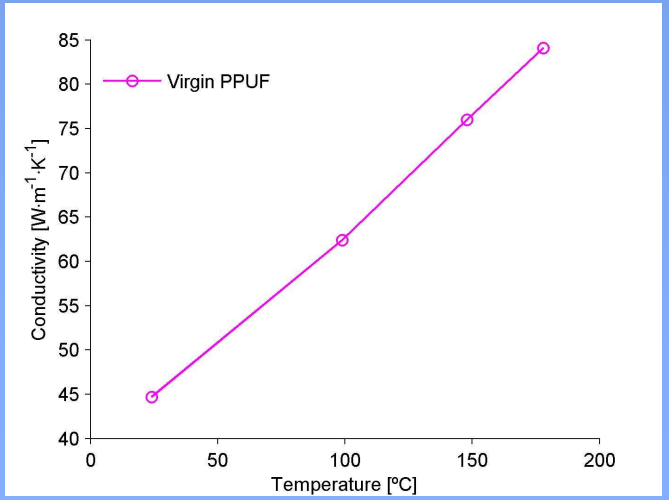
Specific heat



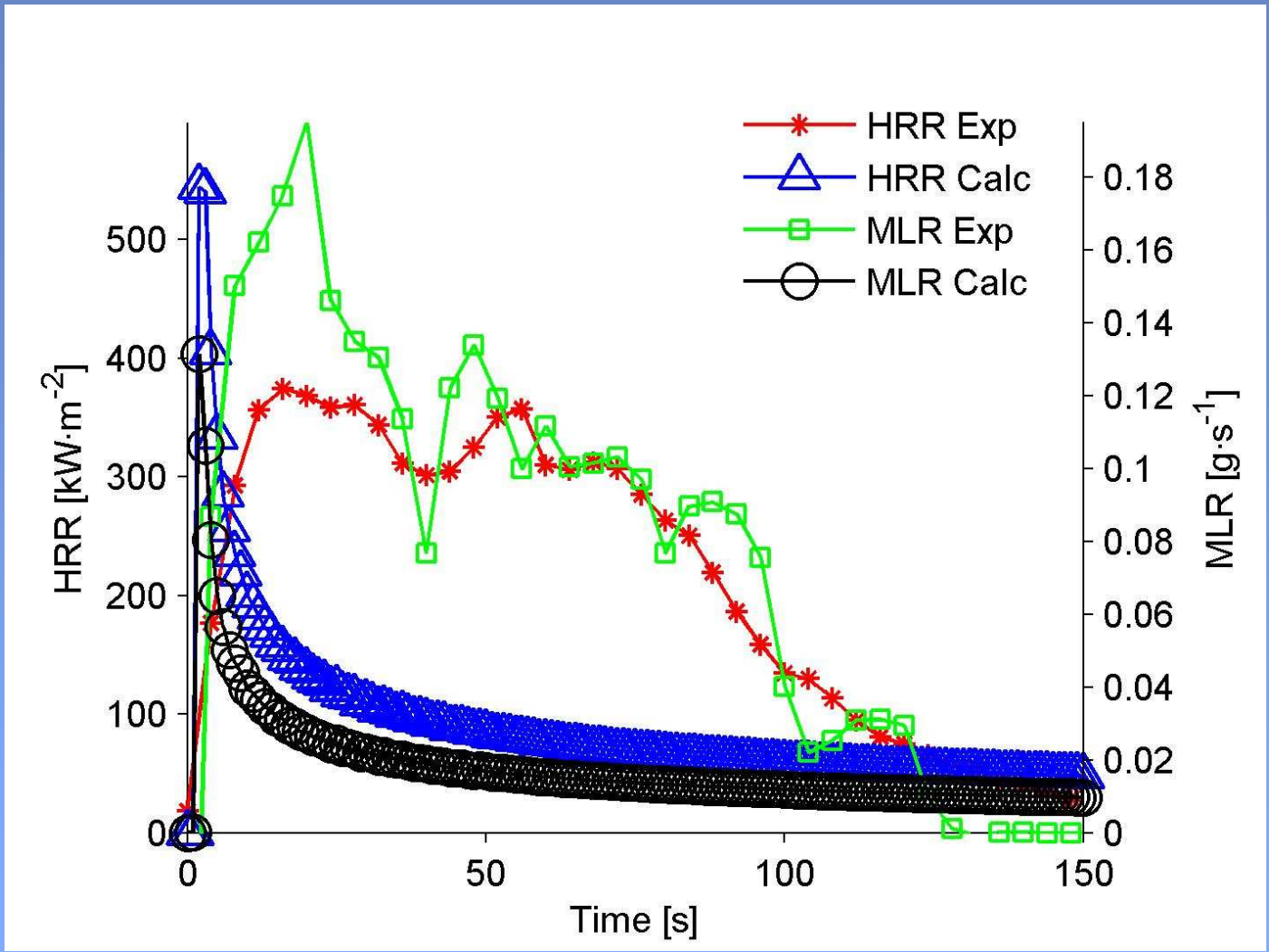
Heat of reaction



Thermal conductivity



Experimental and calculated MLR and HRR



- Input data found in this research
- Simulations highly sensible to remaining **residue**

Discussions

Lack of accuracy of the simulations

- **Sensitivity** analyses of multi-stage decomposition schemes are required.
- **No** diphasic reactions with **oxygen** are allowed
- The **conduction model** does not take into account the change of state of the intermediary species
- Combined **uncertainty** about the kinetic parameters and the variable thermal properties
- Strong influence of the **properties of the residue** remained in the holder on the MLR output
- The **effective heat of combustion** per individual reaction is difficult to be determined (up to date)

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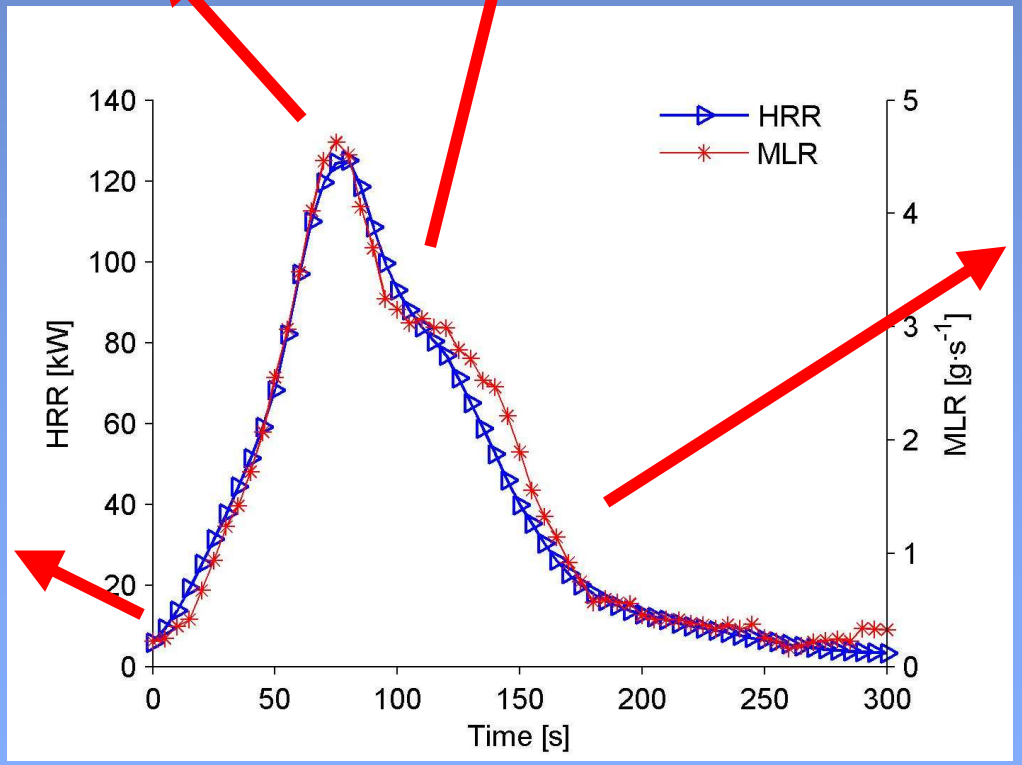
Fire of a piece of upholstered furniture

t = 70 s

t = 120 s

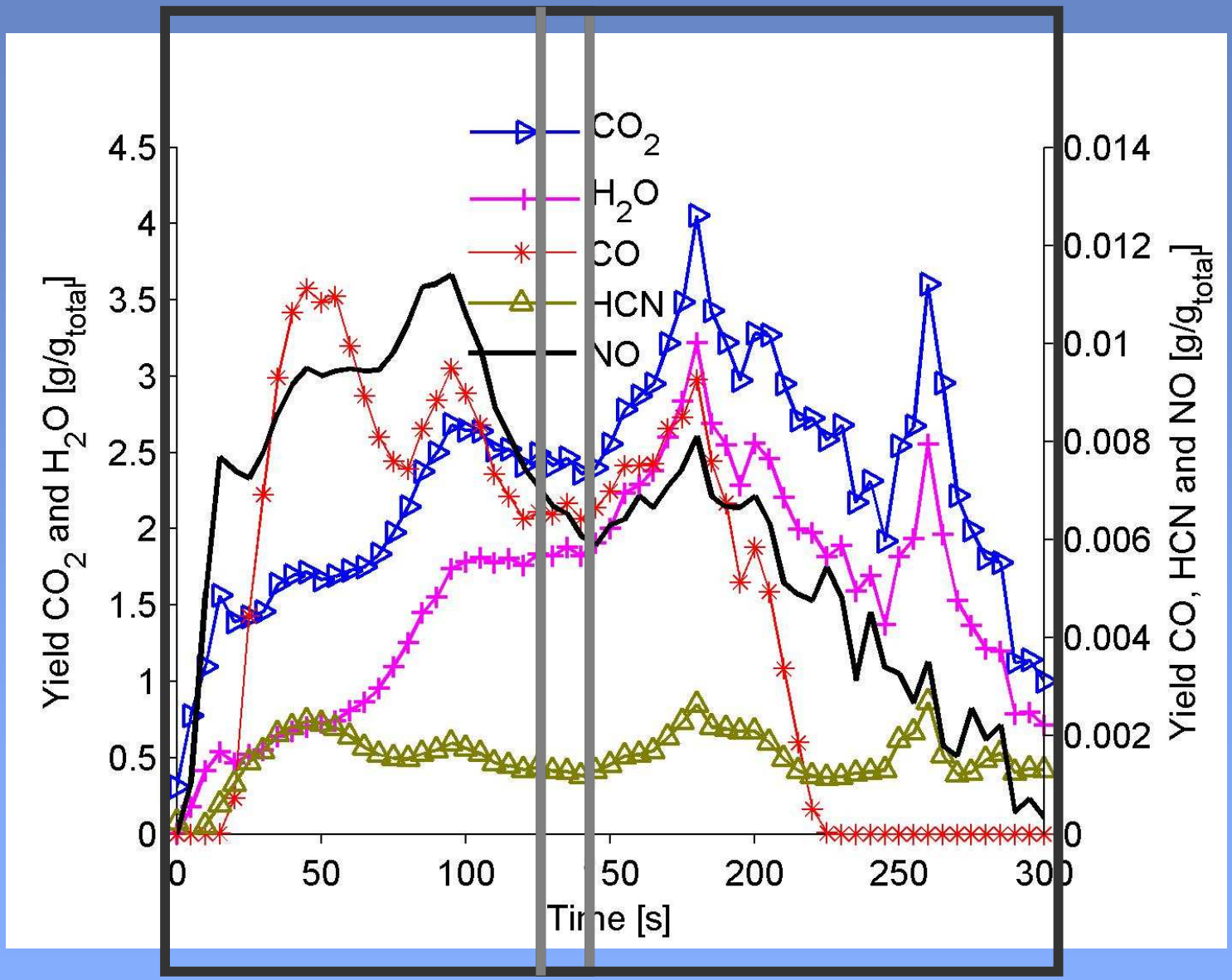


t = 0 s

t = 180 s

The **same** decomposition **mechanism** of CC

Fire of a piece of upholstered furniture



Conclusion

- Information from the **solid and gas phase** was used to determine the **multi-stage** decomposition mechanism of PPUF
- The decomposition mechanism remained **unchanged** independently of the scale considered
- The **kinetic parameters** of the decomposition process were calculated allowing prediction of MLR
- The **pyrolysis models** of fire simulation codes need to be **improved** in order to predict accurately the behaviour of complex materials
- The **sensitivity** of input data need to be verified at various scales

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Perspective

- The **temperature distribution** in the matrix and in the surface (pyrolysis front) need to be determined accurately
- The influence of **oxygen** in the kinetic of decomposition need to be studied
- The **prediction** of the kinetic of release of **toxic gases** need to be improved
- Improvement of the **procedures** that allow the **measuring the input data** of fire simulation codes are required

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Thank you very much!

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