Thermal decomposition of Solid Fuels
Fire Dynamics

Thomas Rogaume

and many persons

Thermal decomposition of solid fuels

Introduction

Introduction – Challenge of the thermal decomposition

The modeling of thermal decomposition permits to describe:

- The mass loss and the mass loss rate of the solid

  → So, the devolatilization flowrate: gaseous combustible products kept into the gas phase (quantity and composition)

Source Term

Are depending of the thermal decomposition:

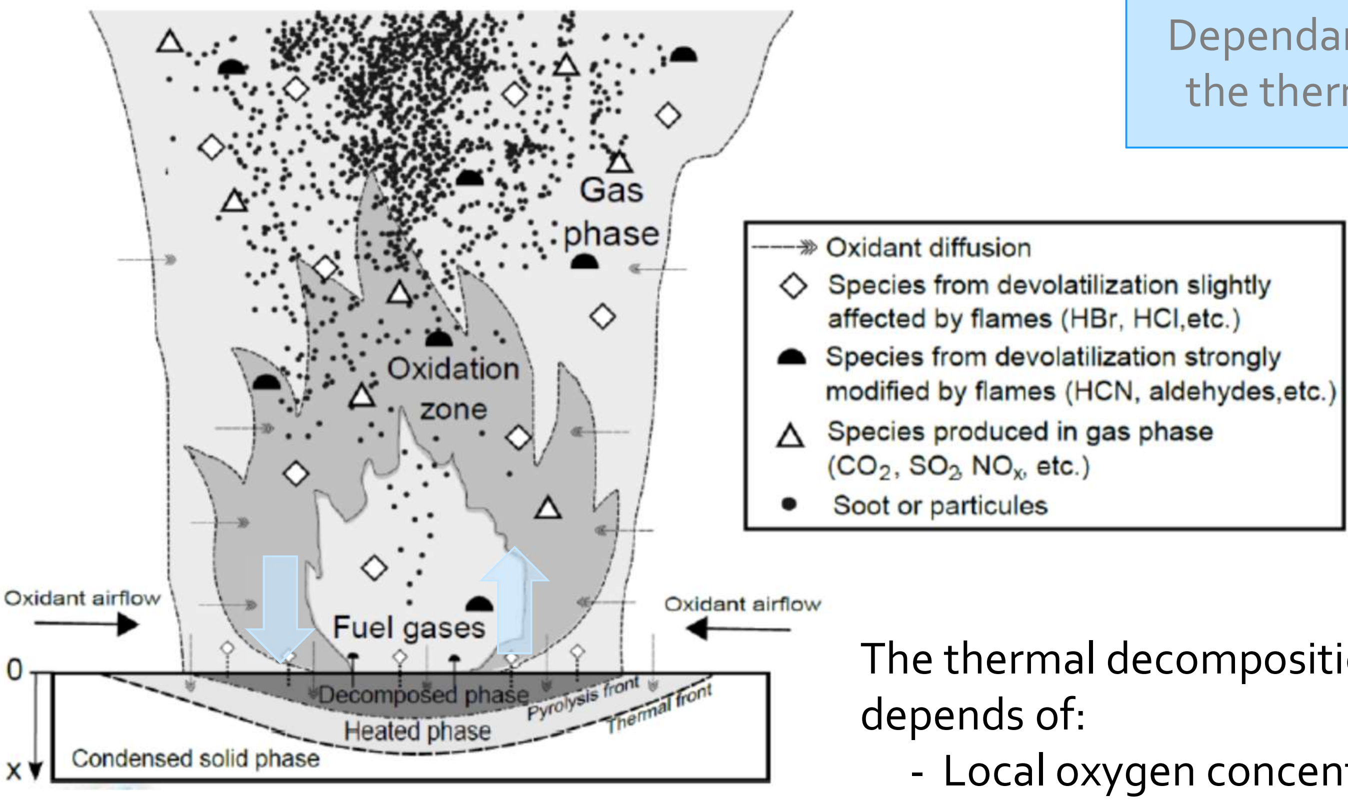
- The ignition and extinction process (time)
- The flame propagation
- The flame structure (height, growing, etc.) and characteristics (temperature, etc.)
- Heat Release Rate
- Etc.

So the Dynamics of the fire (ignition – propagation – extinction)

Big challenge now to describe with accuracy the thermal decomposition of the materials involved into a fire

Introduction – Challenge of the thermal decomposition

Dependance and Influence of the thermal decomposition



The thermal decomposition and gases production depends of:

- Local oxygen concentration
- Local temperature
- Structure and properties of the material (Intrinsic chemical and physical properties)

Introduction – Challenge of the Fire Safety Engineering

Improvement of the numerical models of behaviour

Composition of a CFD model:

- ✓ Different sub-models, for example:
  - Heat transfer
  - Radiation
  - Combustion: EDC, EBU, flamelet, etc.
  - Turbulence
  - etc.
  - **Pyrolysis model**
- ✓ A correlation between those sub-models: FDS, Firefoam, etc.

Our subject… (partially…)

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Introduction – What is a pyrolysis model

Model of pyrolysis:

- ❑ Relation between temperature, atmosphere and kinetic of thermal decomposition of a material
- ❑ Limit: volume element d*V* wich is considered at each step homogeneous in term of temperature and of composition.

So, a **pyrolysis model permits to describe the chemical evolution (reactions) of a small volume element as a function of temperature and of the atmosphere (%O_2)**

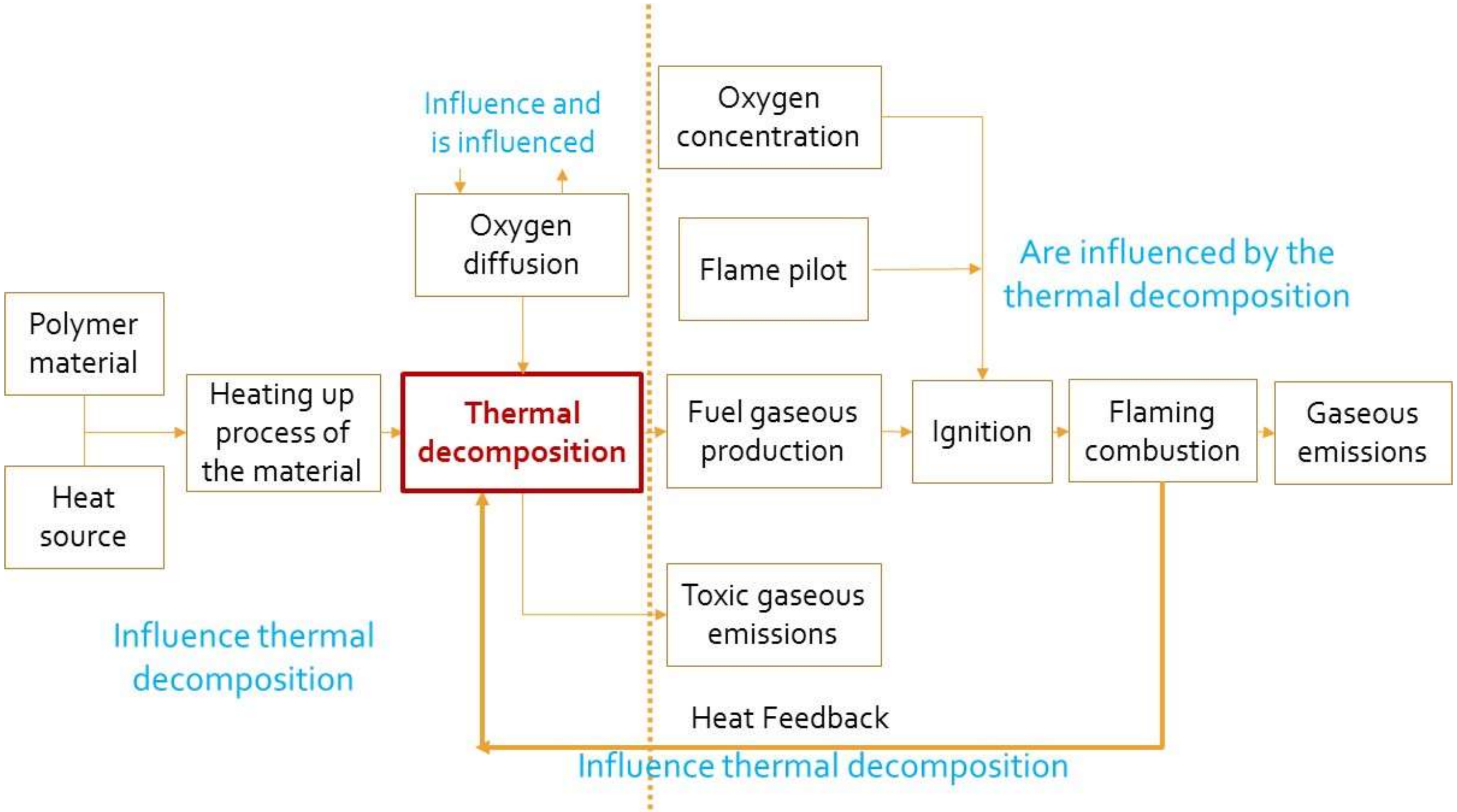
Then, the pyrolysis model:

- Is **a part** of the description of thermal decomposition process.
- Must be coupled to other ones to describe heat transfers (temperature), mass transfer (%O_2, devolatilization transfer, reactive mixture, etc.) and the boundary conditions of the volume element.

Introduction – Thermal decomposition

The description of the thermal decomposition of a solid fuel reclaims 3 aspects:

- A model of pyrolysis
- The physical, chemical and thermal properties
- The coupling of the model of pyrolysis with other submodels



Introduction – Thermal decomposition

The description of the thermal decomposition of a solid fuel reclaims 3 aspects:

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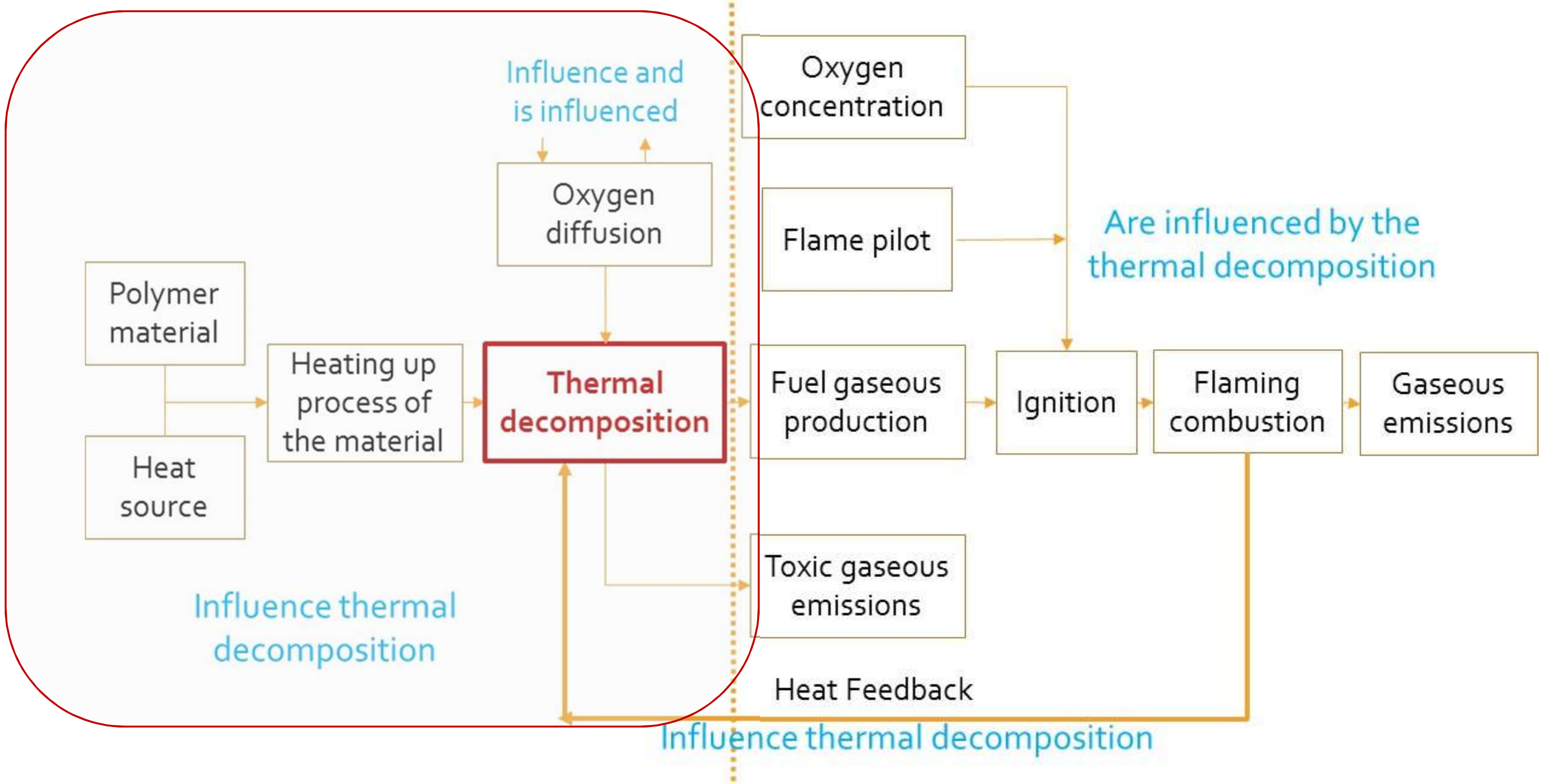
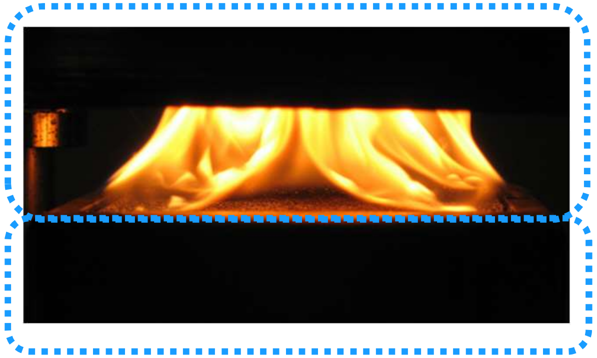
Our Challenge

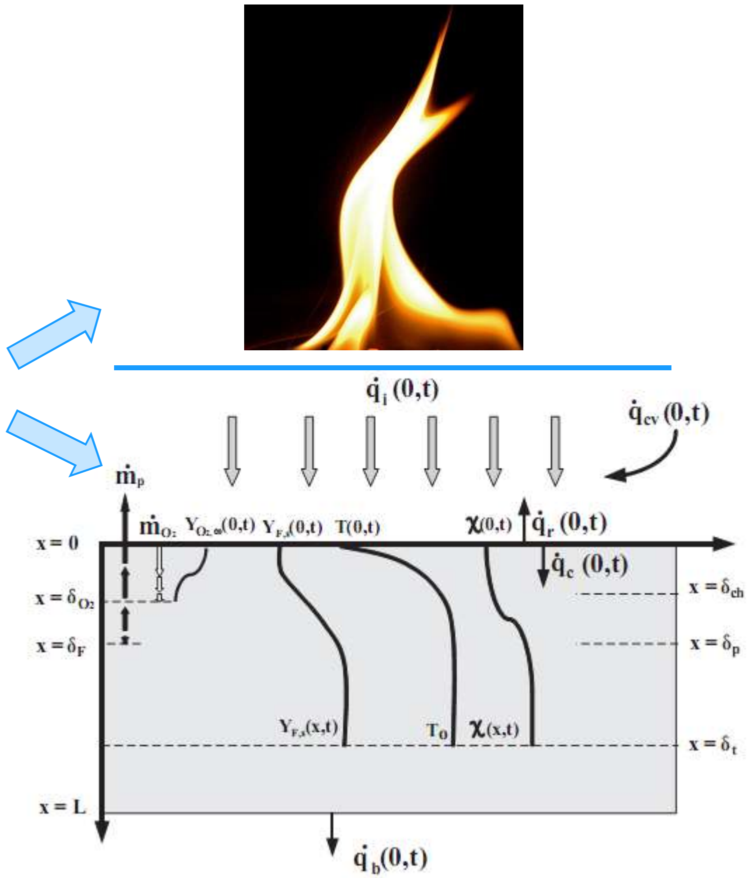


Challenge and complexity of thermal decomposition description

Thermal decomposition aspects

Problem – Strong coupling between the condensed and the gas phases





Coupling
Description of the interactions

Simplified processus (1D) of thermal degradation of a solid - Torero.

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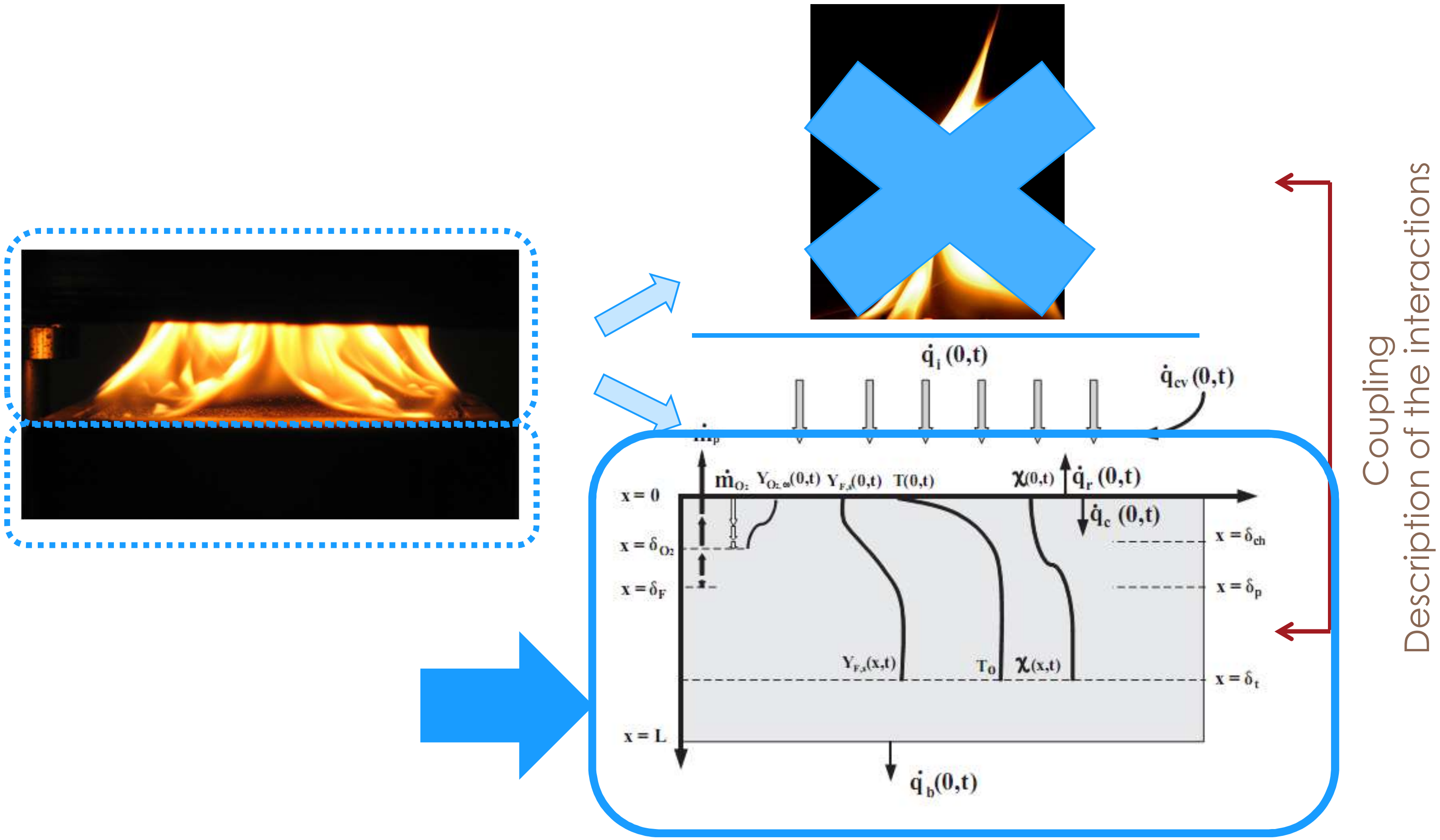
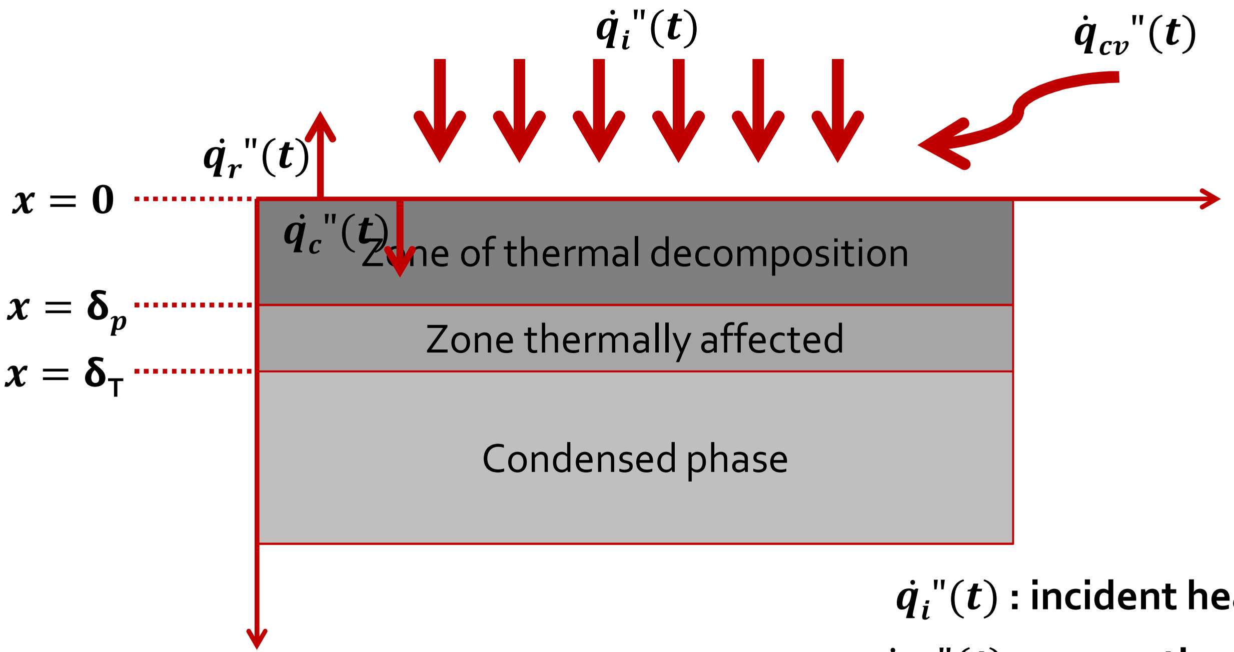
Problem – Strong coupling between the condensed and the gas phases



Simplified processus (1D) of thermal degradation of a solid - Torero.

Problems into the Condensed phase

Pyrolysis is the simultaneous **chemical decomposition and phase change** that provide the gaseous fuel feeding the flame burning over a solid



$x = \delta_p$ **: Position of the front of decomposition**

$x = \delta_t$ **: Position of the heat front**

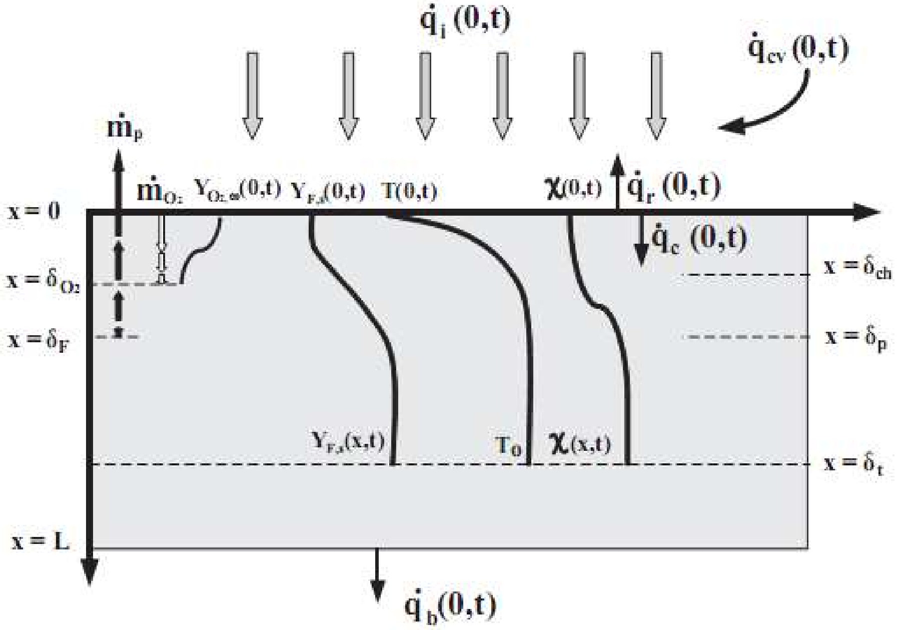
$\dot{q}_i''(t)$ **: incident heat flux**

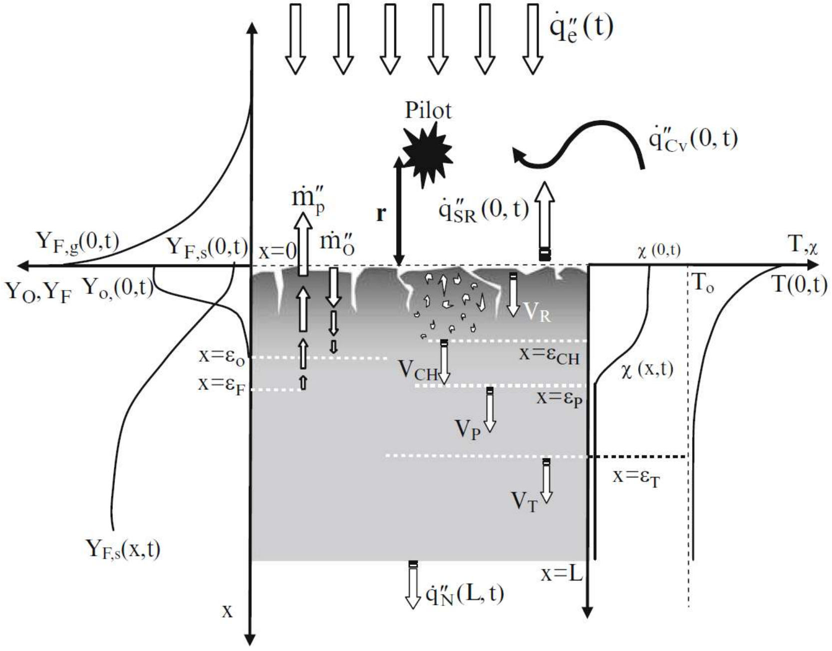
$\dot{q}_{cv}''(t)$ **: convective heat flux**

$\dot{q}_c''(t)$ **: conductive heat flux**

$\dot{q}_r''(t)$ **: re-radiative heat flux**

Problems into the Condensed phase





Simplified processus (1D) of thermal degradation of a solid – Torero, SFPE Handbook.

- External radiation
- Thermal transfer into the solid
- Mass transfer (gaseous emissions and air)
- Kinetic reactions of thermal decomposition and of combustion of the solid fuel
- Char production…

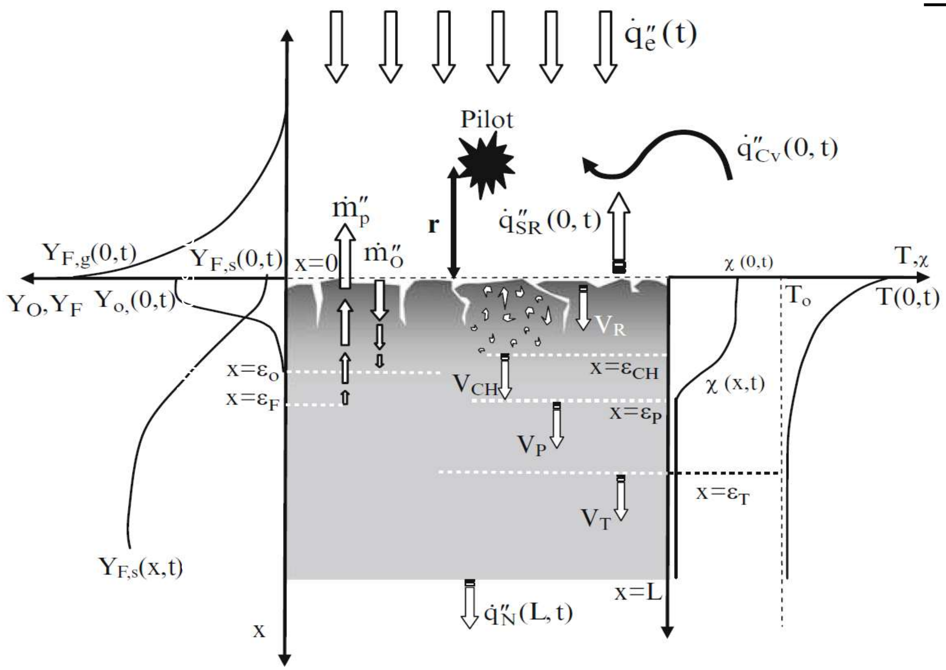
Energy conservation

$$\frac{\partial[\rho_S C_S T]}{\partial t} = \frac{\partial}{\partial x}\left[k_S \frac{\partial T}{\partial x}\right] + \frac{\partial[\dot{m}''_P C_{P,P} T_P]}{\partial x} - \frac{\partial[\dot{m}''_O C_{P,O} T_O]}{\partial x} + \frac{\partial[\rho_S V_R C_S T]}{\partial x} + \dot{q}'''_{RAD} + \sum_{i=1}^{i=N} \Delta H_{P,i} \rho_S \left[A_i Y_O^{m_i} Y_S^{n_i} e^{-E_i/RT}\right]$$

Chemical reactions

[J.L. Torero, SFPE Handbook]

Problems into the Condensed phase

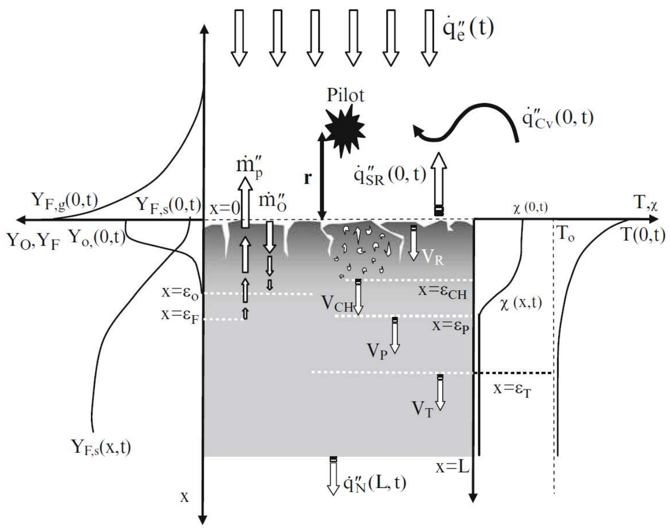


<u>The thermal degradation depends of - 1D approach - :</u>

- Temperature T(x,t).
- Local mass fraction of combustible, $Y_s(x,t)$.
- Local mass fraction of oxygen, $Y_{O2}(x,t)$.
- Mass fraction of residual solid fuel, $Y_{F,s}(x,t)$.
- Permeability, $\chi(x,t)$.
- Thickness of oxygen diffusion into the solid, $\delta_{O2}(t)$.
- Thickness of the reactive zone, $\delta_F(t)$.
- Kinetic parameters values of each reaction, A_i, n_i, m_i, E_i.

[J.L. Torero, SFPE Handbook]

Problems into the Condensed phase



The mass loss rate is determined (sum of the i reactions):

- Locally by:

$$\dot{m}'''_p(x,t) = Y_{F,s}(\mathbf{x},t)\sum_{i=1}^{N}\left[A_i Y_{0_2}^{m_i}(\mathbf{x},t)Y_s^{n_i}(\mathbf{x},t)e^{-E_i/RT(\mathbf{x},t)}\right]$$

- For a surface unit, taking into account the thickness and so the permeability (volumic element dV) by:

$$\dot{m}''_p(\mathbf{x},t) = \int_0^L \chi(\mathbf{x},t)\left[Y_{F,s}(\mathbf{x},t)\sum_{i=1}^{N}\left(A_i Y_{0_2}^{m_i}(\mathbf{x},t)Y_s^{n_i}(\mathbf{x},t)e^{-E_i/RT(\mathbf{x},t)}\right)\right]dx$$

[J.L. Torero, SFPE Handbook]

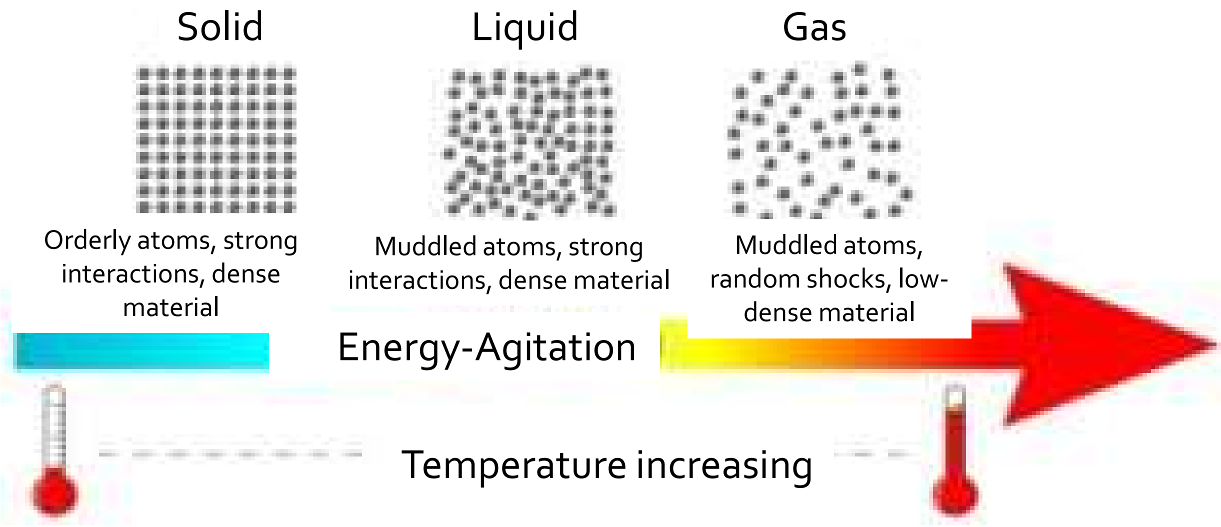
Problems into the Condensed phase – Special Focus

Thermal decomposition: transformation of the solid into gases by the breaking of the molecules into smaller ones – breaking of the chemical linkage

In a molecule, the atoms are linked the ones to the others by an energy = linkage energy

It is necessary to provide a sufficient energy in order to break this linkage

Energy of activation



To conclude: required parameters for the modeling of thermal decomposition *(Initial and boundary Conditions)*

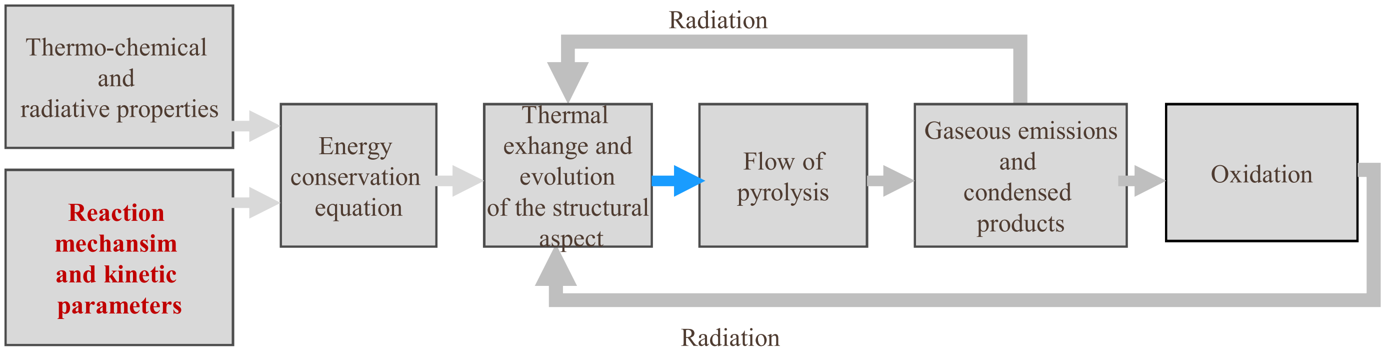
- Ambiant conditions: temperature, humidity, flows (rate), pressure…)
- Conditions of ventilation: Y_{O_2}
- Properties of the materials: physical, chemical, thermal (ρ, C_p, k, ε…) for each condensed phase
- Heat of each reaction and of combustion (ΔH_i)
- Kinetic model of thermal decomposition
- Kinetic parameters of each reaction: μ, A, Ea, n
- Heat flux received
- …

In space (x, y, z) and as a function of t and T

How to determine Them ?

- Experimental investigations
- Inverse method of optimization
- Numerical approaches
- Different empirical laws

Thermal decomposition
1st phase: development of the pyrolysis model



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Thermal decomposition
Development of the pyrolysis model

Special focus on the experimental benchscales

Focus: Experimental Investigations – Thermal decomposition

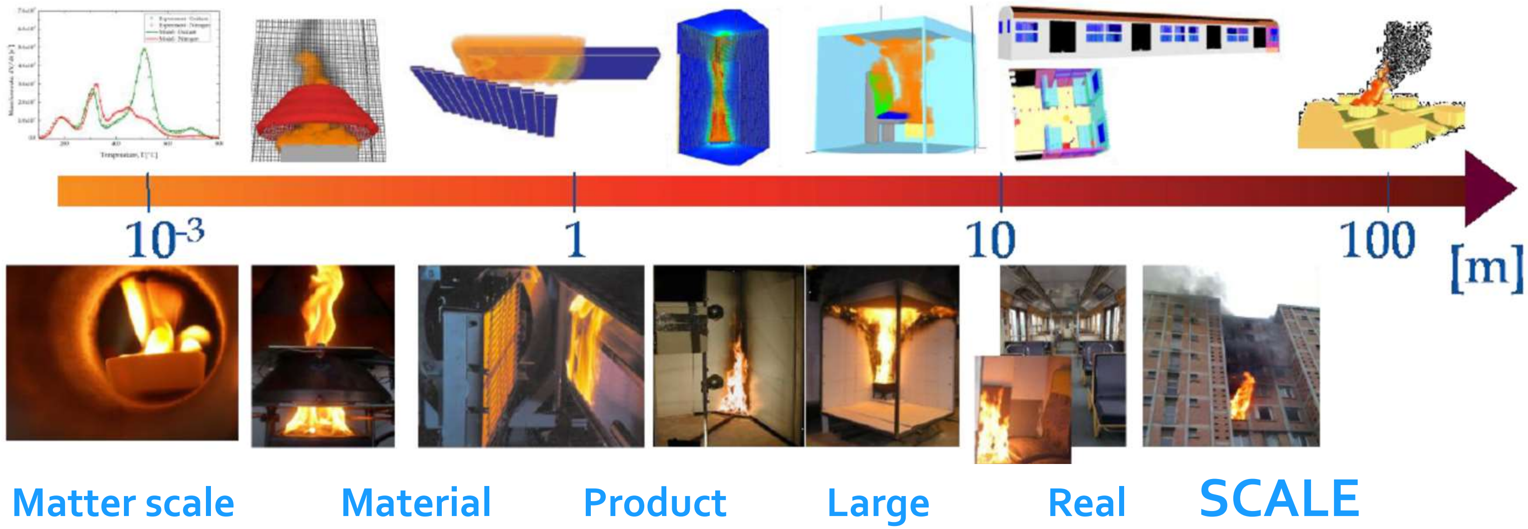
4 scales are classicaly used

Matter scale	mm mg	Thermal analysis: Thermo Gravimétric Analysis (TGA), Differencial Scanning Calorimetry (DSC), TDA, etc.
Small scale	cm g	Calorimetry: Cone Calorimeter (CC) and Fire Propagation Apparatus (FPA)
Product scale	10^n cm - m kg	IMO-LIFT, Medium Burning Item, Single Burning Item, room corner test
Real size scale	m kg - t	Rooms, House, real objects (train waggon, plane…)

The objective is to determine real properties and models avalaible for each scale and conditions

Focus: Experimental Investigations – Thermal decomposition

Multi scale approach



Focus: Experimental Investigations – Thermal decomposition

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Multi-scale appoach

Knowledge of the phenomenon and control of the conditions (simplification)

Building scale

Room scale

Furniture scale

Object scale

Matter scale

Focus: Experimental Investigations – Thermal decomposition

Multi-scale appoach

Complexity of the phenomenon involved into the process – reality of the conditions

Building scale

Room scale

Furniture scale

Object scale

Matter scale

Focus: Experimental Investigations – Thermal decomposition

Process studied and hypothesis

Matter Scale	Small Scale	Product scale	Real Scale

0D process

- No thermal diffusion
- No mass transfer

- « Perfect » control of the boundary conditions
- Controlled conditions: imposed by the user

- Intrinsic properties

1D process

- 1D Thermal transfer
- Radiative properties
- 1D mass transfer

- We try to control the boundary and the experimental conditions
- No flame propagation

- Simplified characterization of the diffusion aspects

2D or 3D process

- Thermal transfer
- Radiative properties
- Mass transfer

- Uncontrolled or difficulty to control the boundary conditions and the experimental ones
- Flame transfer-propagation

- Real diffusion aspects but… many process invoved and difficulty to determine the « conditions »

Focus: Experimental Investigations – Thermal decomposition

Parameters studied

Matter Scale	Small Scale	Product scale / Real Scale
•Mass Loss •Mass loss rate •Enthalpy of the reactions •Heat of combustion •Specific heat •Model of pyrolysis (mechanisms and parameters)	•Delays of inflammation, extinction •Mass loss •Mass loss rate •HRR •Temperatures •Gaseous emissions concentrations •Thermal inertia •Effusivity	•Delays of inflammation, extinction, flash-over •Mass loss •Mass loss rate •Gaseous emissions •HRR •Flame propagation •Temperatures

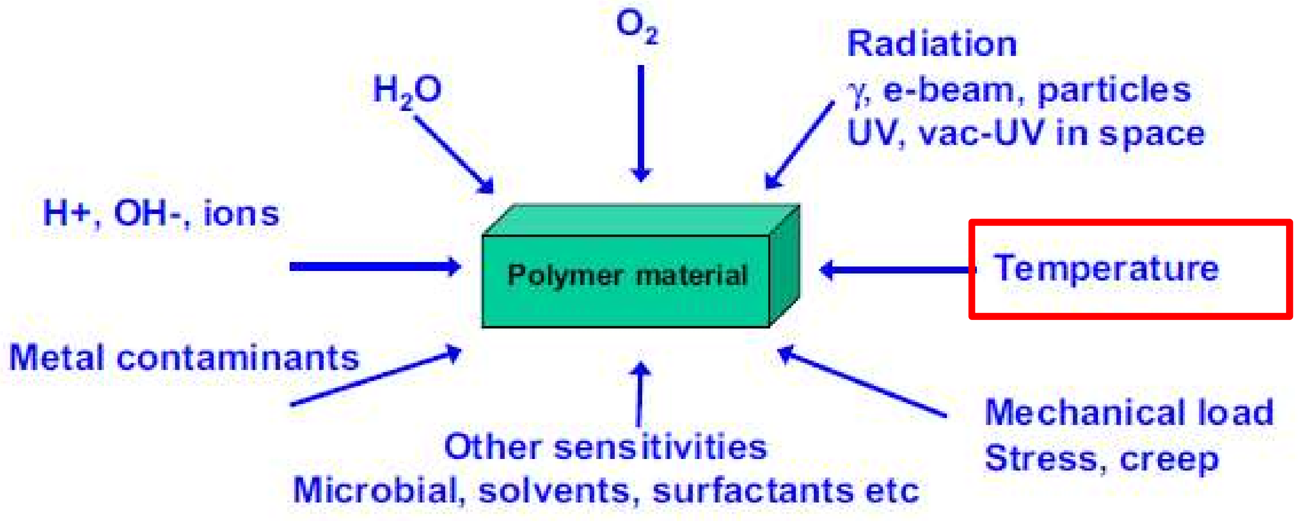
Thermal decomposition
Development of the pyrolysis model

The pyrolysis model

Determination of a model of pyrolysis - Matter scale investigations

Mechanism of degradation of polymers – what are the effects of temperature?

Polymeric materials will, during their lifetime, be exposed to different environments leading to their degradation.



Example: Ageing of PE

Example: Ageing of rubber

Example: Yellowing

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The pyrolysis model

The different approaches to determine the model of pyrolysis:

- Modelistic approach – Model fitting method:
  - Uses a define reaction mechanism with an Arrhenius formulation
  - Requires the definition of A, E_a and n for each reaction. A, E_a and n are defined as properties of the reaction → use of optimization inverse methods

- Isoconvertionnal approach – Free model method:
  - Permits to determine the evolution of the activation energy as a function of the degree of conversion of the reaction. E_a is dependant of α and T.
  - Does not use a reaction mechanism (just one reaction) but is based on an Arrhenius form. The evolution of E_a permits to represent the MLR
  - Are available in the case of 1 reaction of thermal decomposition, or when the steps are clearly separated and chronologics (not parallel – no competition)

- Hybrid approach: combination of the modelistic and the isoconversionnal ones. Each peak of MLR is treated with a Kissinger method

The pyrolysis model

The different approaches to determine the model of pyrolysis:

Software	Modelistic approach	Isoconvertionnal approach
Component Kinetic		X
Thermokinetics	X	X
Thermo-Calc	X	X
Gpyro	X	
Thermakin	X	
FDS (V6)	X	

- **Special Focus Here** on the Modelistic approach – Model fitting method

Determination of a model of pyrolysis - Matter scale investigations

The modeling of the kinetic of thermal decomposition at matter scale **with an imposed model**

Kinetic law

$$\dot{\omega} = A\, e^{-\frac{E_a}{RT}}\, m^n$$

Law of variation of the rate $(k(T))$

Function of conversion $(f(\alpha))$

Reaction mechanism

$$+ \quad m_1 \xrightarrow{\dot{\omega},\,\nu} m_2 \Longrightarrow$$

Kinetic model – Model of Pyrolysis

The pyrolysis model is formed by:
- A kinetic mechanism of thermal decomposition: kinetic reactions
- A kinetic model: rate of the reactions descrition
- Kinetic parameters for each reactions considered

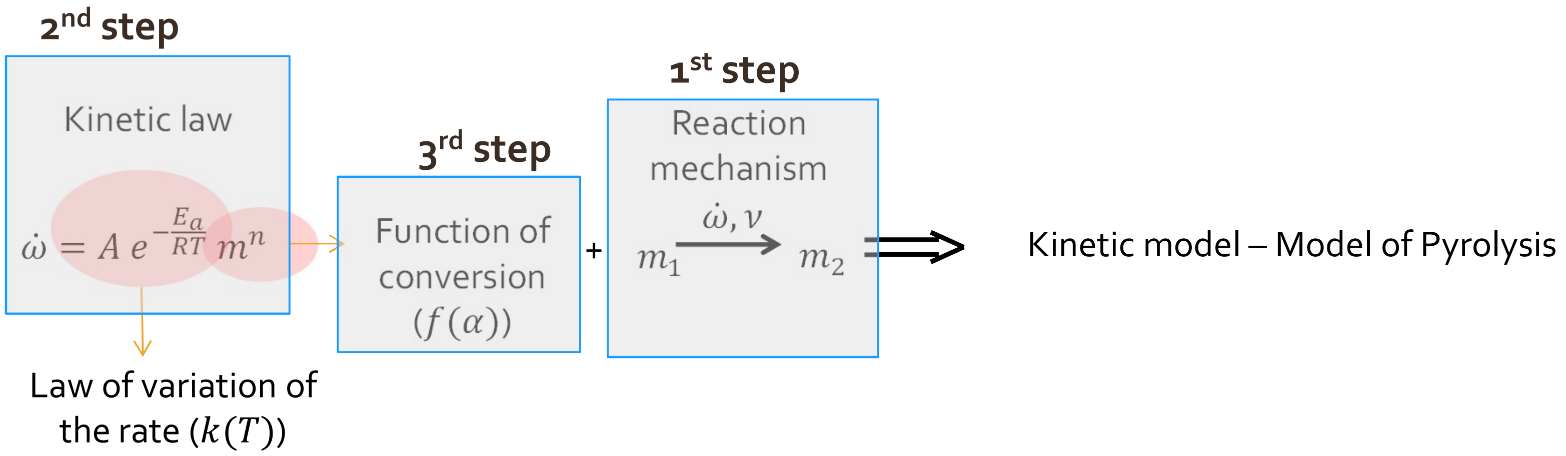
- Intrinsic properties
- Intrinsic kinetic reactions and parameters
- In known and controlled conditions

I work at the matter scale – In 3 steps

How to describe and to determine them ?

Determination of a model of pyrolysis - Matter scale investigations

The modeling of the kinetic of thermal decomposition at matter scale



Focus: Experimental Investigations – Thermal decomposition

Matter Scale

- Mass Loss
- Mass loss rate
- Enthalpy of the reactions
- Heat of combustion
- Specific heat
- Model of pyrolysis (mechanisms and parameters)

Small Scale

- Delays of inflammation, extinction
- Mass loss
- Mass loss rate
- HRR
- Temperatures
- Gaseous emissions concentrations
- Thermal inertia
- Effusivity

Product scale

Real Scale

- Delays of inflammation, extinction, flash-over
- Mass loss
- Mass loss rate
- Gaseous emissions
- HRR
- Flame propagation
- Temperatures

Determination of a model of pyrolysis - Matter scale investigations

Hypothesis of the analysis:

- The material is thermally thin
- Temperature and concentration around the sample are homogeneous
- Surface thermal decomposition
- No gaseous diffusion and mass transfers
- The sample does not affect the fluid flow (vector gas)
- No heat transfer: equilibium between the furnace and the particle
- Thermodynamical equilibrium between solid and gas phases
- No local pressure gradient
- Etc.

Matter Scale

Controled parameters

- Heating rate
- Temperature
- Atmosphere
- Diffusion and transfer

Unknown parameters

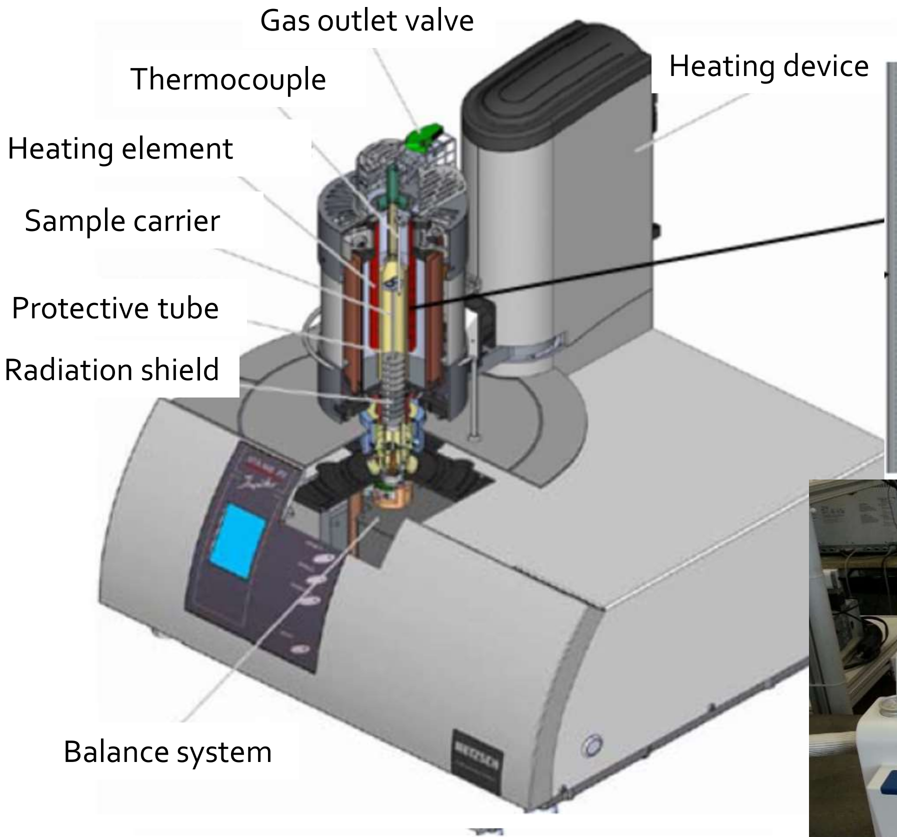
- /

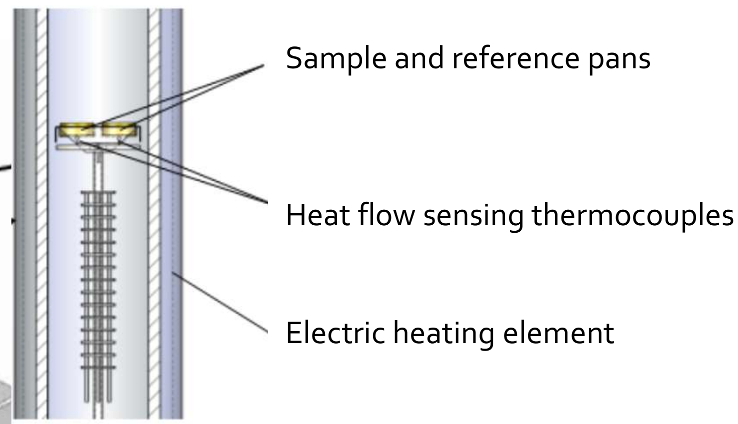
0D Investigation

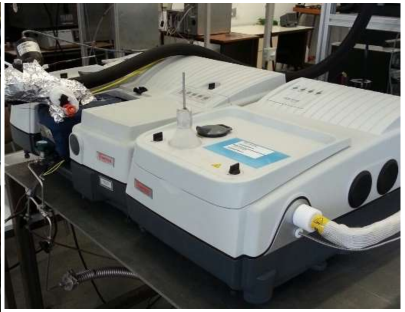
Determination of a model of pyrolysis - Matter scale investigations

TGA apparatus

1. A kinetic mechanism of thermal decomposition: kinetic reactions







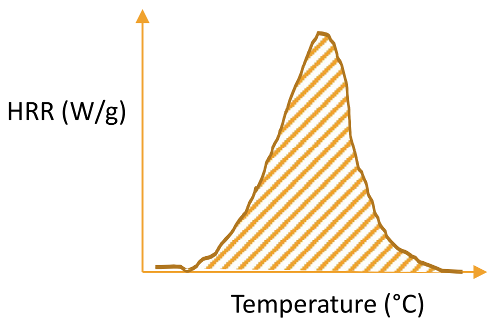
(TGA) – FTIR Apparatus

TGA can be coupled to gas analyzers (FTIR, GC, MS)

Determination of a model of pyrolysis - Matter scale investigations

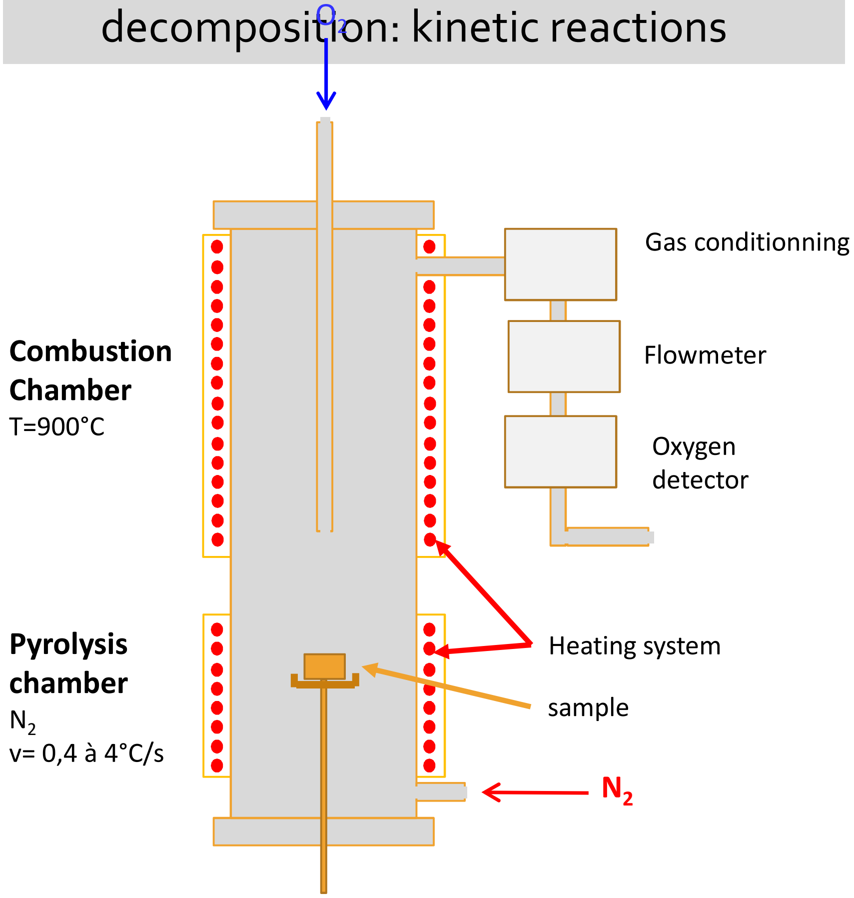
Pyrolysis Combustion Flow Calorimeter (PCFC-ASTM D7309) – Micro-scale Calorimeter

1) Measure the heat release rate of milligram-sized samples
2) Controlled pyrolysis of the sample in an inert gas stream
3) Followed by high-temperature oxidation (combustion) of the pyrolyzate in oxygen
4) The rate at which the sample releases its heat of combustion is calculated from the oxygen consumption history
5) The heat of combustion is obtained from the time integral of the heat release rate
6) Parameters: Peak of heat release rate (pHRR), total heat release (THR)



MSC can be coupled to gas analyzers (FTIR, GC, MS)

1. A kinetic mechanism of thermal decomposition: kinetic reactions

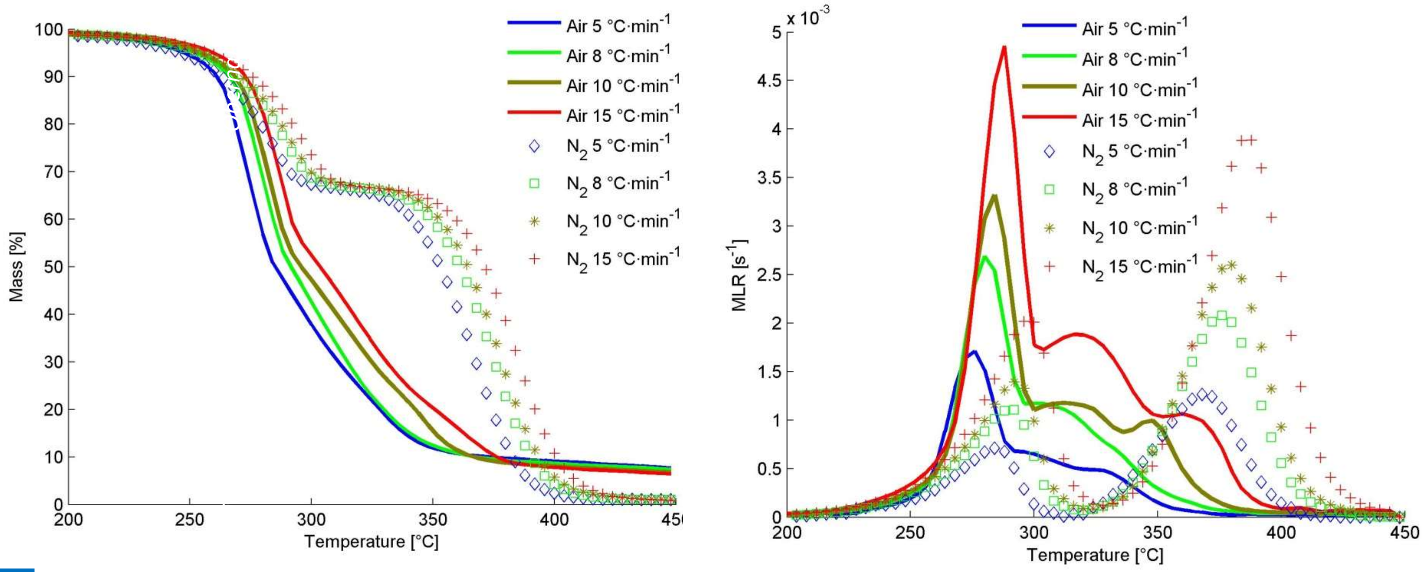


Determination of a model of pyrolysis - Matter scale investigations

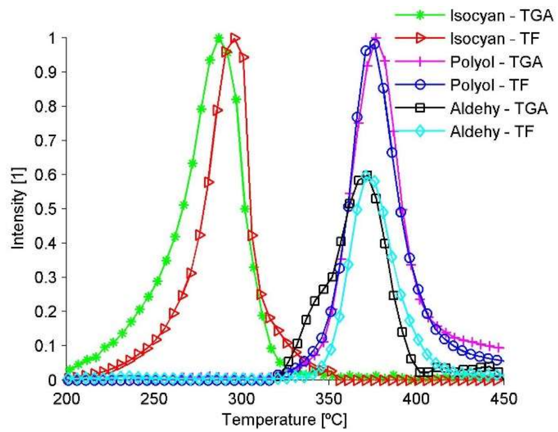
1. A kinetic mechanism of thermal decomposition: kinetic reactions

Results of TGA + FTIR$_{qlt}$

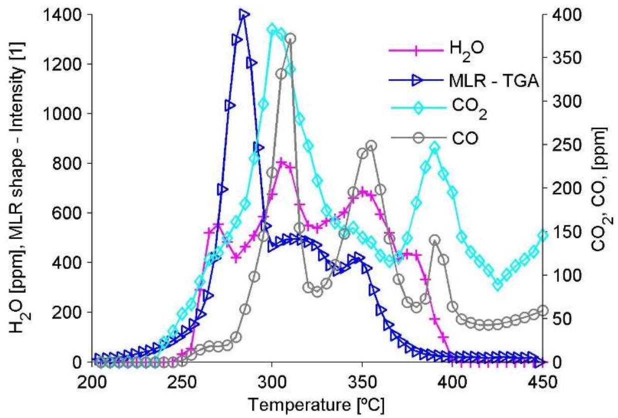
- Also possible with GC and MS system: knowledge of the gaseous emissions = tracker of what happen in the solid phase



Thermal degradation of a PU foam in TGA



Under inert atmosphere



Under air

[*T. Rogaume & al. Development of the thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase release data. Combustion Science and Technology, 2011*]

Determination of a model of pyrolysis - Matter scale investigations

1. A kinetic mechanism of thermal decomposition: kinetic reactions

From the TGA, TGA-FTIR, TGA-GC analysis → reaction mechanism

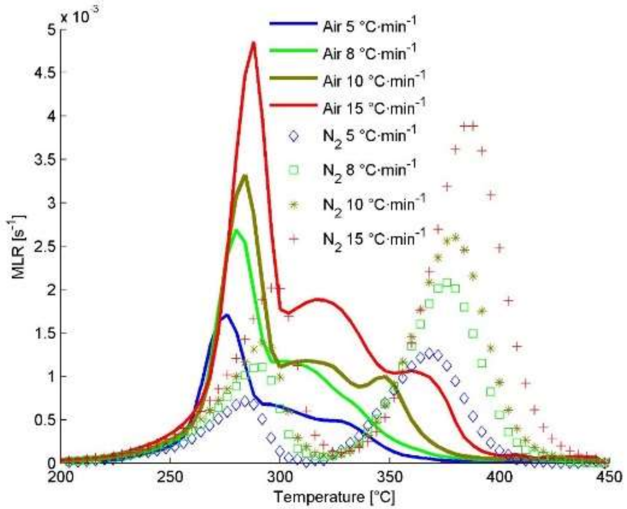
Different approaches are possible:

- ***Lumped parameter approach (LPA):*** considers that the material is one, homogeneous. The thermal decomposition is the one of this material.
- ***The constituant approach***: considers that a material is composed of several constituants and that the thermal decomposition is the sum of the one of each component – *Example: wood is composed of cellulose, hemicellulose and lignin.*
- ***The functional approach:*** the thermal decomposition is described as functional groups, due to the well known fragmentation of the polymers – *Done for some « simple » plastic polymers.*
- *The detailed model as for the gas emisisons*

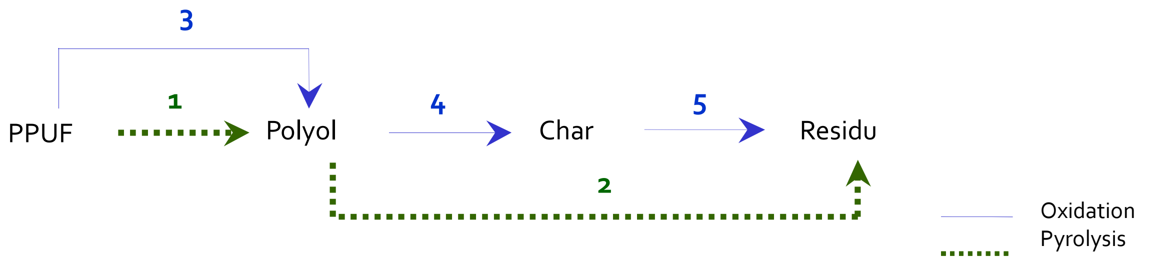
Determination of a model of pyrolysis - Matter scale investigations

1. A kinetic mechanism of thermal decomposition: kinetic reactions

Proposition of a reaction mechanism of thermal decomposition (LPA)



No	Type of reaction	Temp. [°C]	Reactives		Products solid or liquid		Products gas
1	Pyrolysis	200 – 340	PPUF	→	υ_1·Polyol	+	τ_1·[Isocyanate]
2	Pyrolysis	340 – 450	Polyol	→	υ_2·Residue	+	τ_2·[Polyol + H_2CO + H_2O + CH_4]
3	Oxidation	200 – 275	PPUF + O_2	→	υ_3·Polyol	+	τ_3·[Polyol + CO_2 + H_2O]
4	Oxidation	220 – 300	Polyol + O_2	→	υ_4·Char	+	τ_4·[Polyol + H_2CO + CH_4+ CO + CO_2 + H_2O]
5	Oxidation	300 – 450	Char + O_2	→	υ_5·Residue	+	τ_5·[Polyol + H_2CO + CH_4+ CO + CO_2 + H_2O]



[*T. Rogaume & al. Development of the thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase release data. Combustion Science and Technology, 2011*]

Determination of a model of pyrolysis - Matter scale investigations

2. A kinetic model: law of variation of the rate of the reactions

Considered here

The **model-fitting method** is expressed in terms of the degree of conversion: equal to 0 at the beginning of the test and to 1 when all the mass has been decomposed.

The degree of conversion is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

Where, m_o is the mass of the sample at the beginning of the process, m_t is the mass of the sample at an arbitrary time, m_f is the mass of the sample at the end of the process.

Determination of a model of pyrolysis - Matter scale investigations

2. A kinetic model: law of variation of the rate of the reactions

Solid reaction rate = [k(T), the rate constant **+** f(α) the differential conversion function]:

- The rate constant is the Arrhenius equation

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

With A pre-exponential factor, E apparent activation energy, R universal gas constant, T absolute temperature

- The conversion function *f(α)* is the reaction model.

Rate of the reactions

2. A kinetic model: law of variation of the rate of the reactions

Steady rate in the gaseous phase

$$k_i(t) = A_i e^{\frac{-E_i}{RT(t)}}$$

k: Steady rate, s^{-1}
A: pré-exponentiel factor, s^{-1}
E: activation energy, $J.kg^{-1}$
R: Constant of the perfect gases

Arrhenius

Rate of variation of a concentration A, B and C

$$A \xrightarrow{k_1,\upsilon_1} B \xrightarrow{k_2,\upsilon_2} C$$

$$\upsilon_1 = k_1 \cdot [A] \qquad \upsilon_2 = k_2 \cdot [B]$$

$$-\frac{d[A]}{dt} = \upsilon_1 = k_1 \cdot [A]$$

$$\frac{d[B]}{dt} = \upsilon_1 - \upsilon_2 = k_1 \cdot [A] - k_2 \cdot [B]$$

$$-\frac{d[C]}{dt} = \upsilon_2 = k_2 \cdot [B]$$

[B. Batiot, Étude et modélisation de la cinétique de décomposition thermique des matériaux solides. Application à la dégradation du bois. Thèse de Doctorat ISAE-ENSMA, 2014]

Determination of a model of pyrolysis - Matter scale investigations

Rate of the reactions (solid phase)

2. A kinetic model: law of variation of the rate of the reactions

Rate of the reaction

$$\dot{\omega}_i = k_i Y_j^{ni} Y_{O2}^{\delta}$$

$$k_i(t) = A_i e^{\frac{-E_i}{RT(t)}}$$

$\dot{\omega}_i$ reaction rate (s^{-1}),
A : pré-exponential factor (s^{-1}),
E_i : activation energy, (J/kg),
n_i : order of the reaction
Y_j : mass fraction of a specie j into the reaction i,
T : temperature,
R perfect gas constant,
: mass fraction of oxygen into the reaction zone
δ : equal to 1 under oxidative atmosphere and to 0 under inert atmosphere

Mass loss rate of a specie j

Difference between the rate of production and of consumption of the specie j

$$\frac{d}{dt} Y_j = \sum_{\gamma \in Hj} Y_{r_\gamma} \dot{\omega}_\gamma - \sum_{\xi \in Gj} \dot{\omega}_\xi$$

Y_r Residual mass fraction
H_j all the reactions producting j and G_j, the ones consuming j

Total mass loss rate

$$\frac{d}{dt} Y_t = \sum_{j=1}^{M} \frac{d}{dt} Y_j$$

[Rein G. *Computational model of forward and opposed smoldering combustion with improved chemical kinetics*. Thèse de doctorat, University of California, Berkley, 2005]

Determination of a model of pyrolysis - Matter scale investigations

2. A kinetic model: law of variation of the rate of the reactions

Mass balance of the species:

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

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

Each equation has an Arrhenius reaction rate

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

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

$$\frac{dm(t)}{dt} = \sum_{i=1}^{n} (v_i - 1)\dot{\omega}_i$$

Calculation results are compared to experiments

Different conversion function

Model		$f(\alpha)$
Reactional Order	ordre 0	1
	1er ordre	$1 - \alpha$
	2nd ordre	$(1 - \alpha)^2$
	ordre 3	$(1 - \alpha)^3$
	ordre n	$(1 - \alpha)^n$
Exponential law		α
Power function	$P = 3/2$	$\frac{3}{2}\alpha^{-\frac{1}{3}}$
	$P = 2$	$2\alpha^{\frac{1}{2}}$
	$P = 3$	$3\alpha^{\frac{2}{3}}$
	$P = 4$	$4\alpha^{\frac{3}{4}}$
	$P = n$	$n\alpha^{(1-\frac{1}{n})}$

Classically used

The choice depends of the thermal decomposition

Determination of a model of pyrolysis - Matter scale investigations

4. The determination of the kinetic parameters

$$\frac{dm}{dt} = \sum_{b=1}^{i} MLR_b$$

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

$$\frac{dm(t)}{dt} = \sum_{i=1}^{n} (v_i - 1)\dot{\omega}_i$$

k: Steady rate, s^{-1}
A: pré-exponentiel factor, s^{-1}
E: activation energy, $J.kg^{-1}$
R: Constant of the perfect gases
n: reaction order
υ: stoichiometric coefficient
δ=0 under inert, and =1 under air

Are unknown parameters – How to determine them?

- Experimentally, it is not possible
- Then, we use inverse optimization methods: Genetic Algorithms, Particle Swarm Optimisation, Shuffled Complex Evolution, etc.

Determination of a model of pyrolysis - Matter scale investigations

Inverse methods of optimization (Genetic algorithms, particle swarm…)

- Use an evaluation function
- This one defines a fitness ϕ which evaluates the adequation between the experimental and the numerical results of ML or/and MLR.
- Different evaluation functions:

$$\phi = \sum_{\beta=1}^{c}\left[\left(\int\left|\frac{dm}{dt}^{Calc} - \frac{dm}{dt}^{Exp}\right|dT\right)^{-1} + \psi\left(\int\left|m^{Calc} - m^{Exp}\right|dT\right)^{-1}\right]_{\beta}$$

[Rein & al.]

$$\phi = \sum_{\beta=1}^{c}\sum_{j=1}^{k}\left(\frac{dm_j}{dt}^{Calc} - \frac{dm_j}{dt}^{Exp}\right)_{\beta}^{-2}$$

[Esperanza & al.]

$$\phi = \sum_{\beta=1}^{c}\left[\cos[\angle(\vec{x},\vec{y})]\cdot\left[\frac{\|\vec{x}-\vec{y}\|}{\|\vec{x}\|}\right]^{-1}\right]_{\beta} \qquad \vec{x} = \frac{dm}{dT}^{Exp} \qquad \vec{y} = \frac{dm}{dT}^{Calc}$$

[Bustamante Valencia & al.]

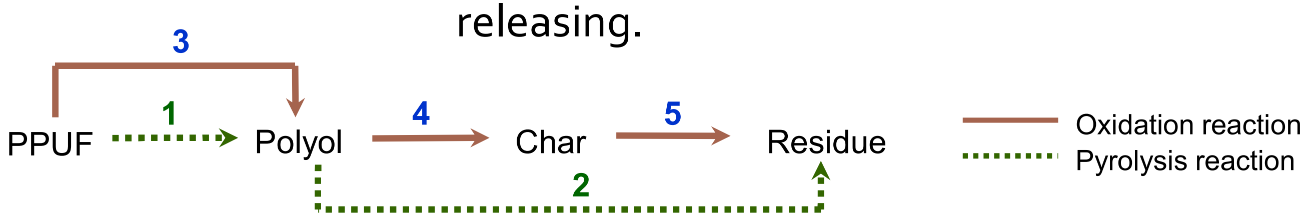
Determination of a model of pyrolysis - Matter scale investigations

One example of application: PU Foam

The mechanism includes the species of solid and gas phases

No	Type of reaction	Temp. [ºC]	Reactives		Products solid or liquid		Products gas
1	Pyrolysis	200 – 340	PPUF	→	υ_1 ·Polyol	+	τ_1 ·[Isocyanate]
2	Pyrolysis	340 – 450	Polyol	→	υ_2 ·Residue	+	τ_2 ·[Polyol + H_2CO + H_2O + CH_4]
3	Oxidation	200 – 275	PPUF + O_2	→	υ_3 ·Polyol	+	τ_3 ·[Polyol + CO_2 + H_2O]
4	Oxidation	220 – 300	Polyol + O_2	→	υ_4 ·Char	+	τ_4 ·[Polyol + H_2CO + CH_4+ CO + CO_2 + H_2O]
5	Oxidation	300 – 450	Char + O_2	→	υ_5 ·Residue	+	τ_5 ·[Polyol + H_2CO + CH_4+ CO + CO_2 + H_2O]

The **"chemically correct"** kinetic mechanism allow prediction of MLR and gas releasing.



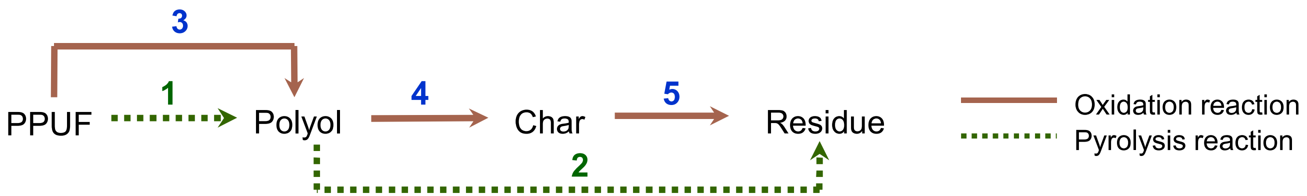
[Bustamante Valencia & al.]

Determination of a model of pyrolysis - Matter scale investigations

Special attention

The **"chemically correct"** kinetic mechanism allow prediction of MLR and gas releasing.

However, it is often essential to **consider other parameters** as the char thickness, the gradient of temperature, etc.



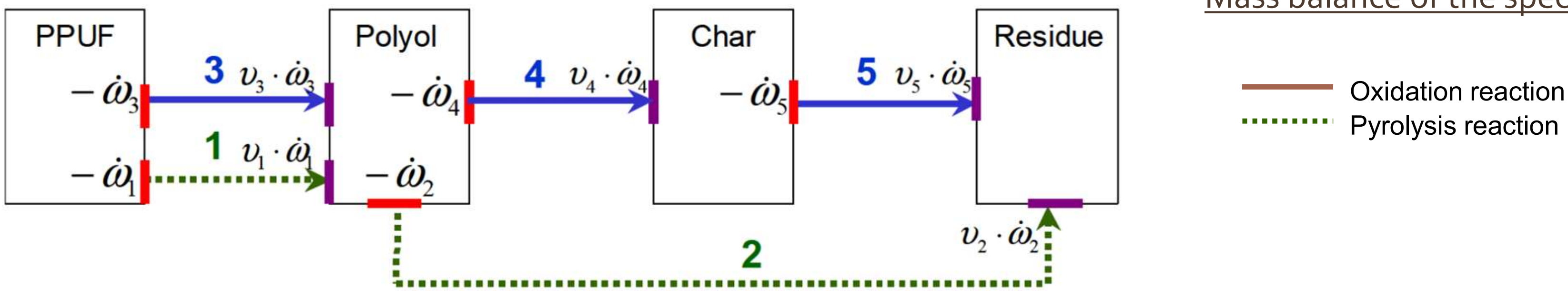
[Bustamante Valencia & al.]

Determination of a model of pyrolysis - Matter scale investigations

One example of application: PU Foam

Mass loss description

Mass balance of the species:



$$\frac{dm_{PPUF}}{dt} = -\dot{\omega}_1 - \dot{\omega}_3$$

$$\frac{dm_{Polyol}}{dt} = +\upsilon_1 \cdot \dot{\omega}_1 \quad \upsilon_3 \cdot \dot{\omega}_3 \quad -\dot{\omega}_2 - \dot{\omega}_4$$

$$\frac{dm_{Char}}{dt} = \upsilon_4 \cdot \dot{\omega}_4 \quad -\dot{\omega}_5$$

$$\frac{dm_{Residue}}{dt} = \upsilon_2 \cdot \dot{\omega}_2 \quad +\upsilon_5 \cdot \dot{\omega}_5$$

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

$$\frac{dm}{dt} = \sum_{b=1}^{4} MLR_b = \frac{dm_{PPUF}}{dt} + \frac{dm_{Polyol}}{dt} + \frac{dm_{Char}}{dt} + \frac{dm_{\mathrm{Residue}}}{dt}$$

$$\frac{dm}{dt} = (\upsilon_1 - 1)\dot{\omega}_1 + (\upsilon_2 - 1)\dot{\omega}_2 + (\upsilon_3 - 1)\dot{\omega}_3 + (\upsilon_4 - 1)\dot{\omega}_4 + (\upsilon_5 - 1)\dot{\omega}_5$$

[*T. Rogaume & al. Development of the thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase release data. Combustion Science and Technology, 2011*]

Determination of a model of pyrolysis - Matter scale investigations

One example of application: PU Foam

The unknown kinetic parameters determined are:

Calculation using Genetic Algorithms and a fitness function

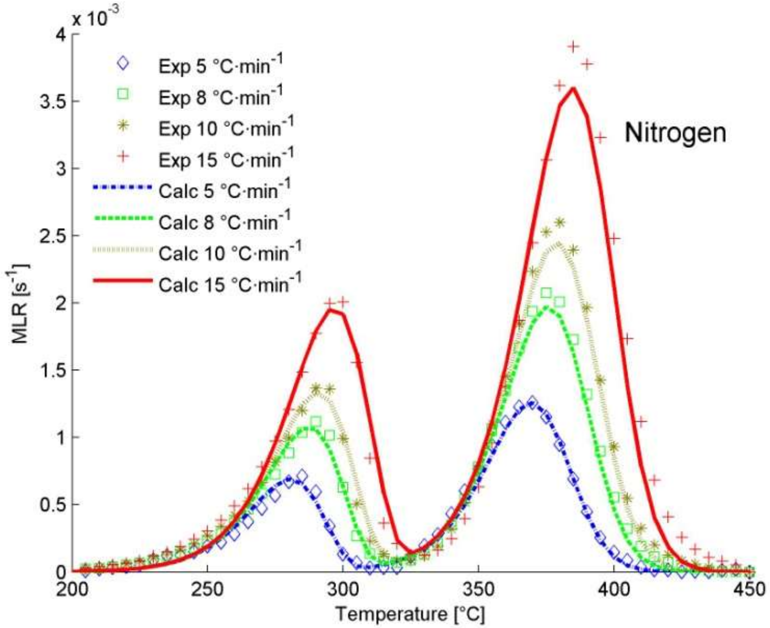
Reaction	Parameter	Value	Range		Units
			High	Low	
PPUF pyrolysis	E_1	169.9	190	150	kJ·mol^{-1}
	A_1	6.09 x 10^{13}	1 x 10^{22}	1 x 10^{7}	s^{-1}
	$_1$	0.91	1	0.1	_
	υ_1	0.69	0.9	0.1	Kg·kg^{-1}
	τ_1	_	9 x 10^{9}	1.5 x 10^{9}	_
Polyol pyrolysis	E_2	243.9	260	100	kJ·mol^{-1}
	A_2	4.42 x 10^{17}	1 x 10^{19}	1 x 10^{7}	s^{-1}
	n_2	1.26	1.5	0.1	_
	υ_2	0.10	0.81	0.1	kg·kg^{-1}
	τ_2	4.9 x 10^{9}	9 x 10^{9}	1.5 x 10^{9}	_
PPUF oxidation	E_3	214.1	240	161	kJ·mol^{-1}
	A_3	3.07 x 10^{18}	1 x 10^{20}	1 x 10^{7}	s^{-1}
	n_3	0.48	3	0.2	_
	υ_3	0.44	0.7	0.1	kg·kg^{-1}
	τ_3	8.9 x 10^{4}	1.5 x 10^{5}	3 x 10^{4}	_
Polyol oxidation	E_4	213.6	240	161	kJ·mol^{-1}
	A_4	1.26 x 10^{18}	1 x 10^{22}	1 x 10^{7}	s^{-1}
	n_4	0.95	3	0.3	_
	υ_4	0.56	0.7	0.1	kg·kg^{-1}
	τ_4	8 x 10^{5}	2.2 x 10^{6}	2 x 10^{4}	_
Char oxidation	E_5	160.8	240	160	kJ·mol^{-1}
	A_5	4.30 x 10^{12}	3 x 10^{15}	1 x 10^{11}	s^{-1}
	n_5	1.64	3	0.5	_
	υ_5	0.25	0.8	0.1	kg·kg^{-1}
	τ_5	3.4 x 10^{6}	9 x 10^{6}	1.7 x 10^{5}	_

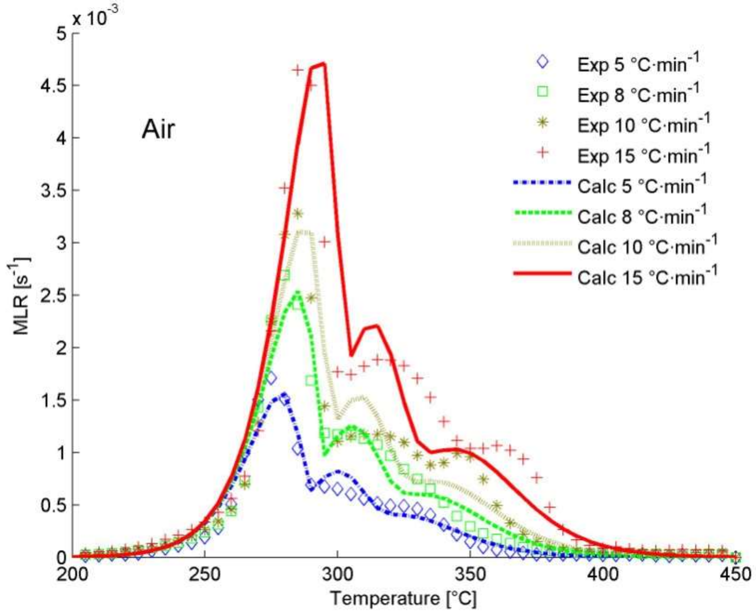
[*T. Rogaume & al. Development of the thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase release data. Combustion Science and Technology, 2011*]

Determination of a model of pyrolysis - Matter scale investigations

One example of application: PU Foam

Validation of the pyrolysis model:





Comparison of numerical and experimental MLR curves in TGA

[*T. Rogaume & al. Development of the thermal decomposition mechanism of polyether polyurethane foam using both condensed and gas phase release data. Combustion Science and Technology, 2011*]

Validation of the pyrolysis model:

- The pyrolysis model has been developed from matter scale experiments
- The mechanism of thermal decomposition is proposed from TGA and gas analysis measurements
- The kinetic is described from a modified Arrhenius law and a conversion function
- The unknown kinetic parameters of each reaction are determined using inverse methods of optimization
- The objective is to fit, at matter scale, the experimental and numerical mass loss and MLR curves using a fitness function.

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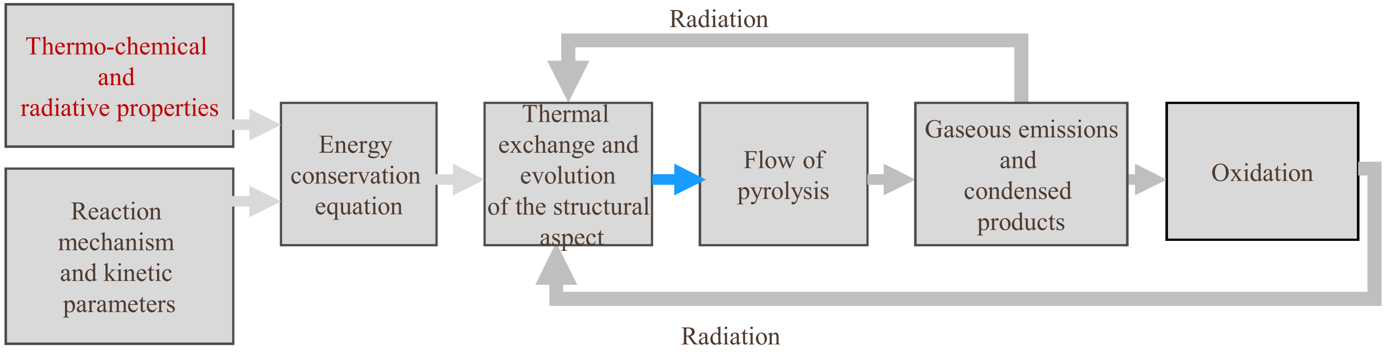
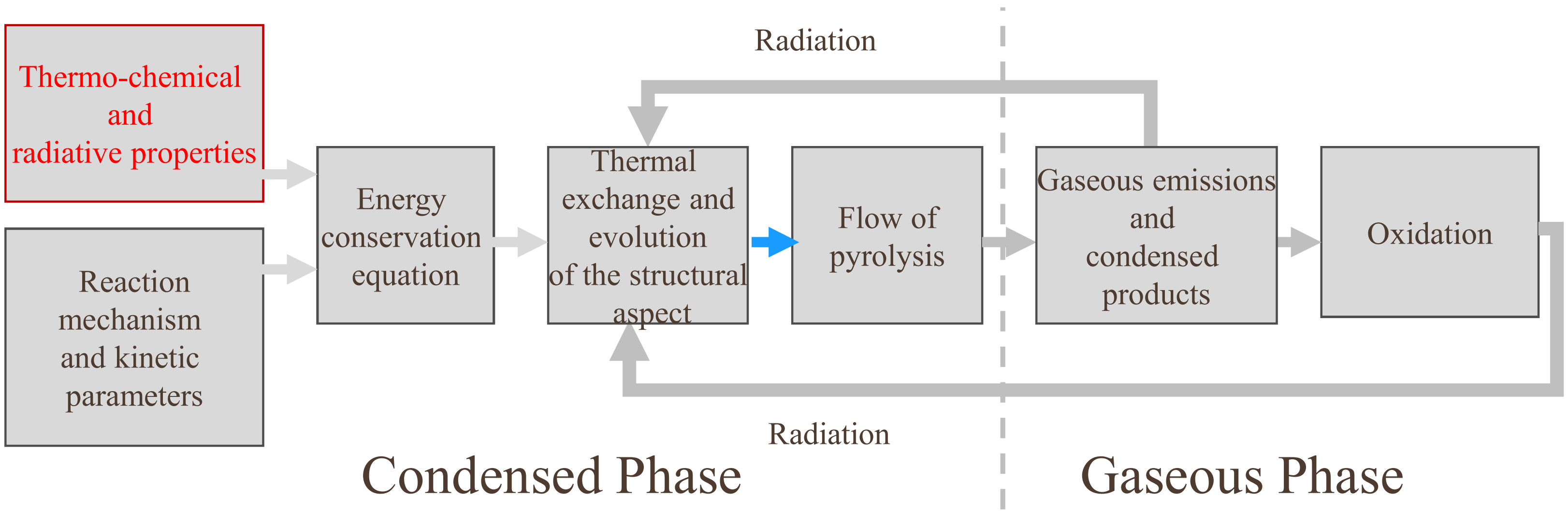
Thermal decomposition 2nd phase: Thermochemical and radiative properties



Determination of the thermochemical properties of the condensed phase

- k, ρ, Cp, ε…
- [C, H, O…] - Y_i
- Enthalpies of the reactions

- Experimental investigations
- Inverse optimization



Determination of the thermochemical properties of the condensed phase

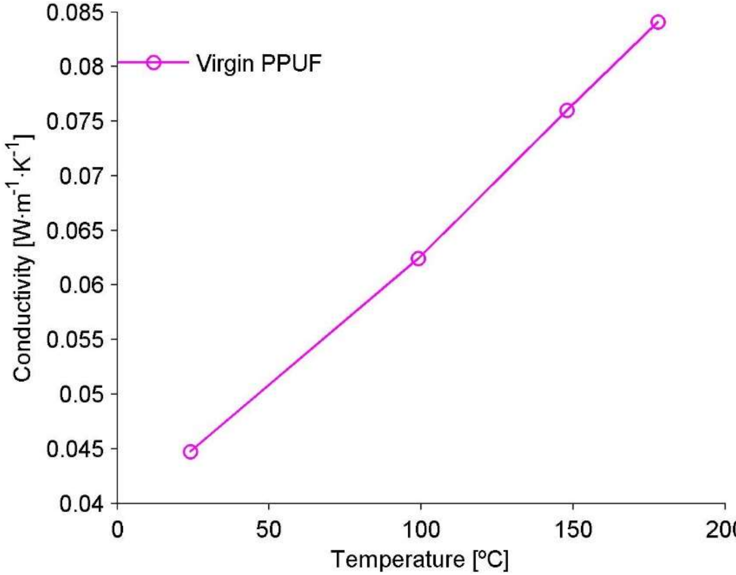
Determination of k – Different methodologies:
- Flash method (with a laser)
- Guarded hot plate

Superior calorific power: bomb calorimeter

Chemical properties:
- Elementary analysis: [C], [H], [O], [N], [S], [Cl],[H_2O], [ash], etc.
- Nuclear Magnetic Resonance: chemical linking.

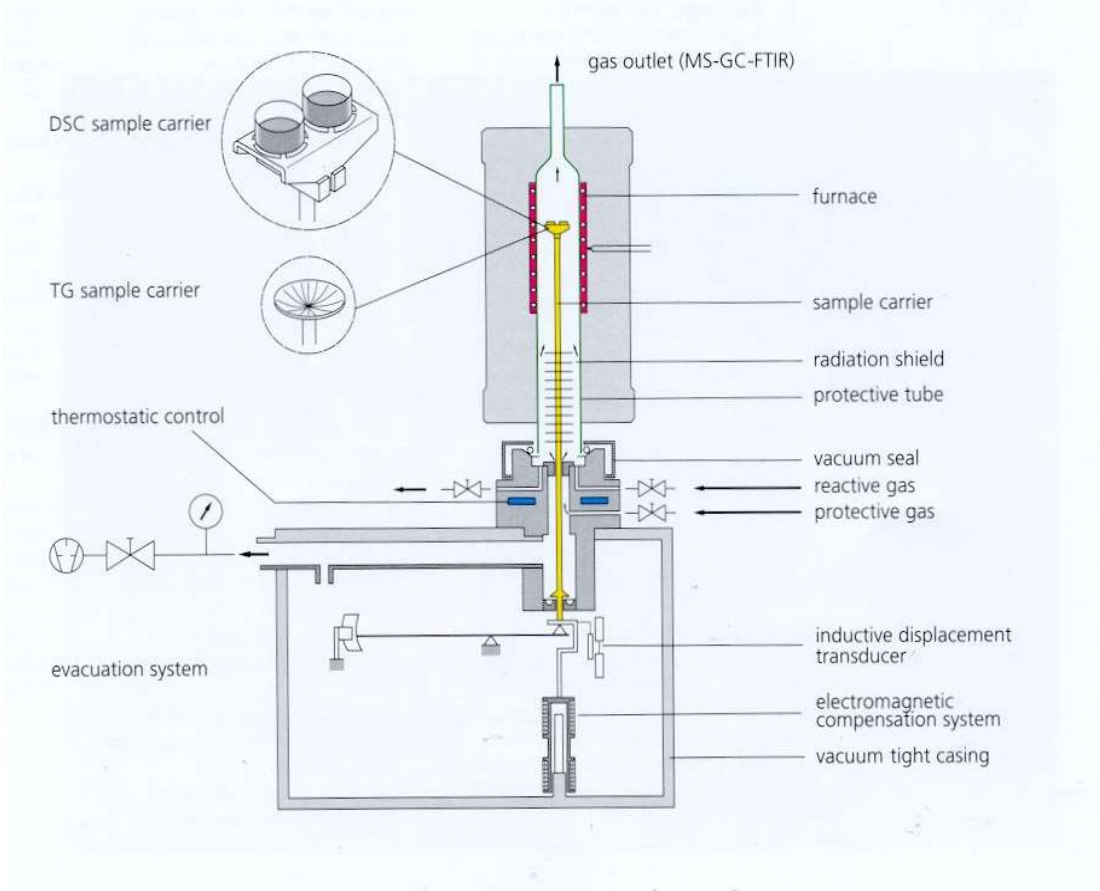
Determination of Cp and ΔH
- Differencial scanning calorimetry (DSC)

Determination of the radiative properties
- IR and thermal camera approach



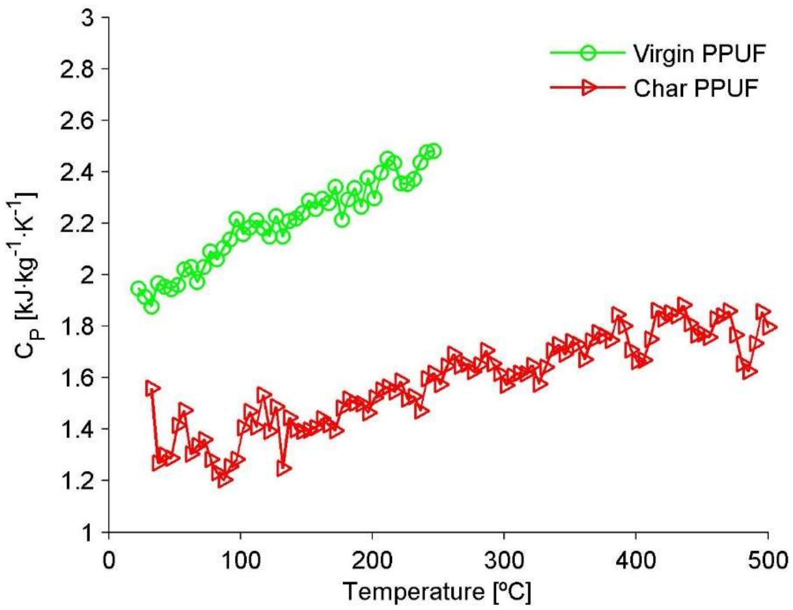
Example of k measurement of a PU Foam with a guarded hot plate apparatus

Differential Scanning Calorimetry (DSC)

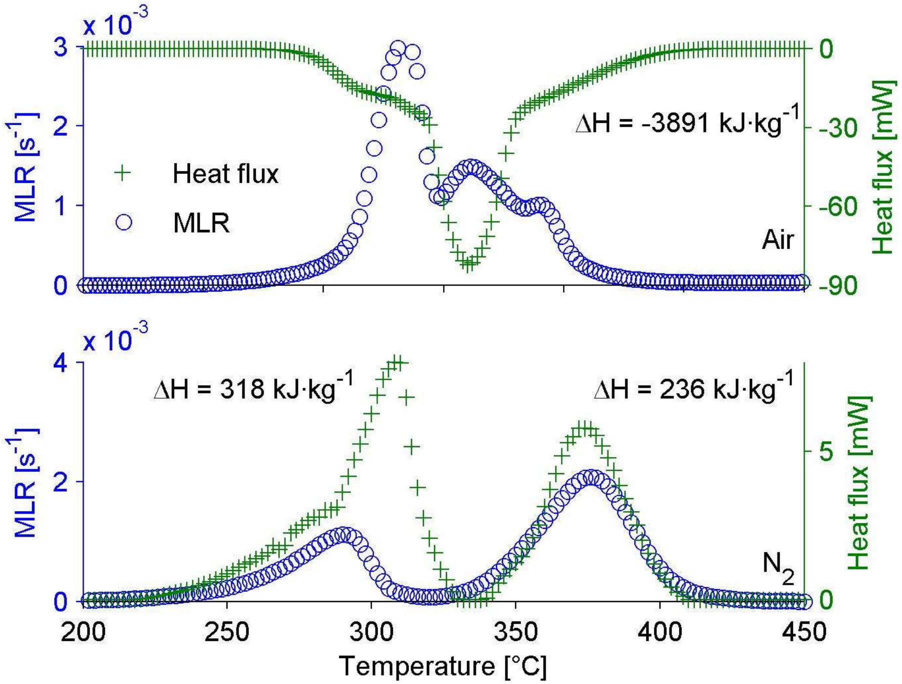


Determination of the thermochemical properties of the condensed phase

Differential Scanning Calorimetry (DSC)



Example of Cp measurement of a PU Foam in DSC

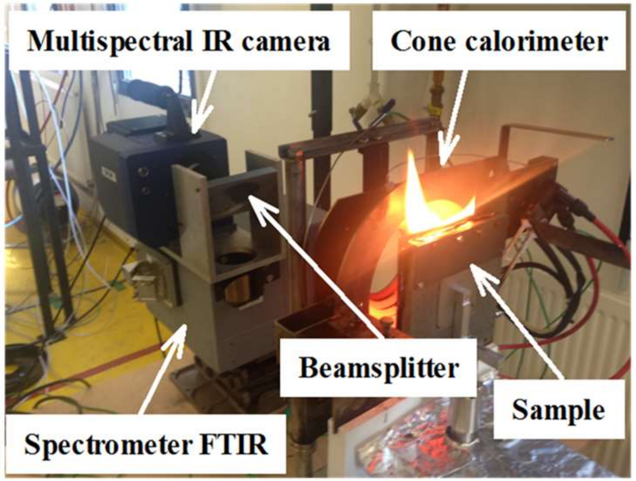


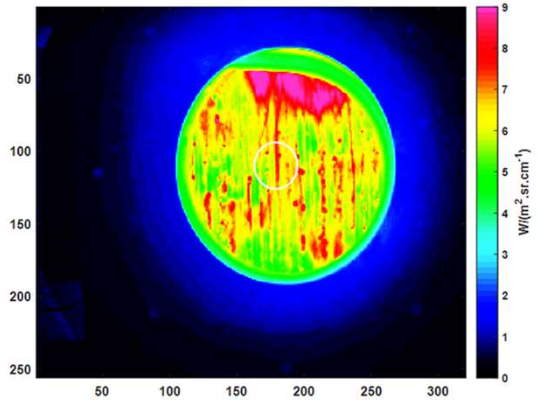
Example of ΔH measurement of a PU Foam in DSC

[Bustamante Valencia & al.]

Determination of the thermochemical properties of the condensed phase

Radiative properties – IR spectrometer and thermal Camera





IR image at 2353 cm⁻¹, converted in intensity. Composite - Incident flux 50 kW/m², time t = 80s

Mean absorptivity of the plywood samples as a function of the irradiation duration in the cone calorimeter. Averages based on Planck's means with reference temperature of 1000 and 1200 K respectively.

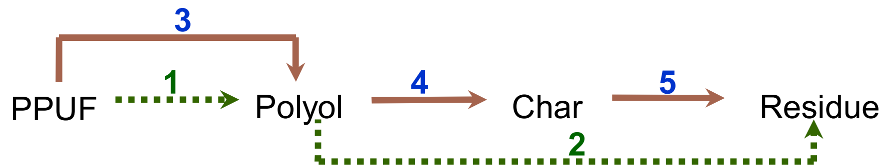
Sample and irradiation	Ref temp.	
	1000 K	1200 K
Virgin M1	0.87	0.84
M1 30 kW/m^2 during 1 min	0.85	0.83
M1 30 kW/m^2 during 10 min	0.94	0.94
M1 50 kW/m^2 during 2 min	0.93	0.93
M1 50 kW/m^2 during 10 min	0.95	0.95
Virgin M3	0.82	0.78
M3 30 kW/m^2 during 1 min	0.74	0.74
M3 30 kW/m^2 during 5 min	0.88	0.88
M3 50 kW/m^2 during 2 min	0.86	0.87
M3 50 kW/m^2 during 5 min	0.88	0.88

Plywood studied

[Team LEMTA - Boulet & al.]

Determination of the thermochemical properties of the condensed phase

Critical analysis of the experimental investigations of the thermochemical properties



The Thermochemical properties (k, ρ, Cp, ΔH) must be determined for each « condensed specie » formed, but:

- It is very difficult to « isolate » each condensed product in order to do the measurement required. A solution should be to degrade until a certain temperature and to stop the test. But when cooling, modification of the structure of the material… so impact on the measurements.
- It is classically done on virgin material, between 0 to 200°C
- No thermal degradation can occured in the setup used – destruction
- The measurement when there is some char is not possible (wrong), whatever the technique of measurement

Considering Cp and ΔH - In TGA-DSC apparatus:

- The furnace is not enough performant - thermal inertia and sensibility.
- The Cp value must be corrected by the mass loss

Determination of the thermochemical properties of the condensed phase

Critical analysis of the experimental investigations of the thermochemical properties

→The Thermochemical properties must be determined for each « condensed specie » formed

It is very difficult experimentally

What are the solutions:

Classically we use a « weighting (average) law », between the properties of the initial material and the final one :

- or, equivalent properties are taken for all the « materials » - as for just 1 equivalent material.
- or, a linear evolution of the properties between the initial and the final materials is considered

Other solutions of determination? Inverse optimization methods, but…
This is like some degrees of liberty, some mathematical fitting methods with more variables = the thermochemical properties

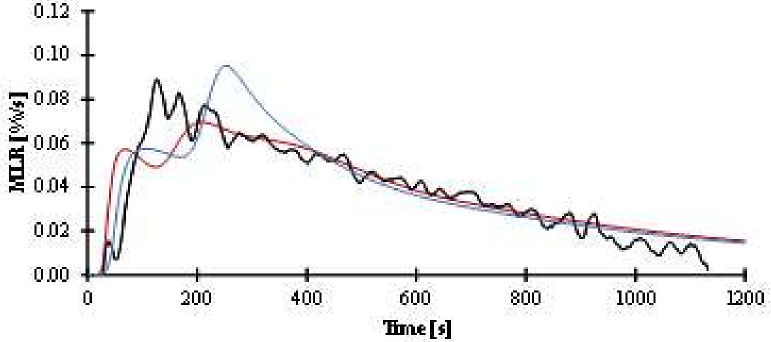
- The results obtained are not realistics and physics
- Compensation phenomenon are observed due to the large unknown parameters (the kinetics and the thermochemical ones)

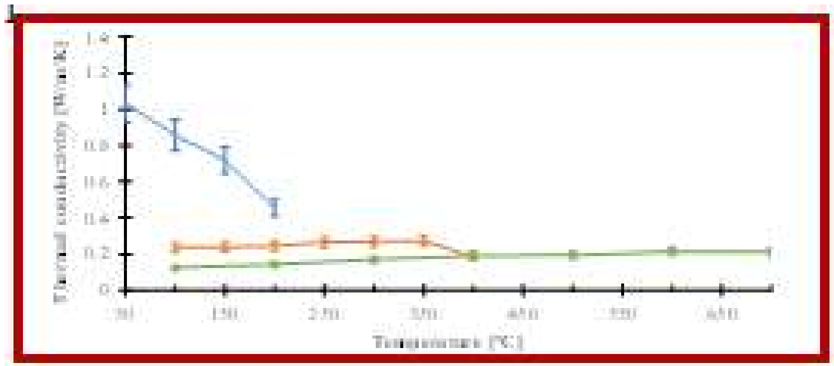
→ ***Determination of the thermochemical properties is a main actual challenge***

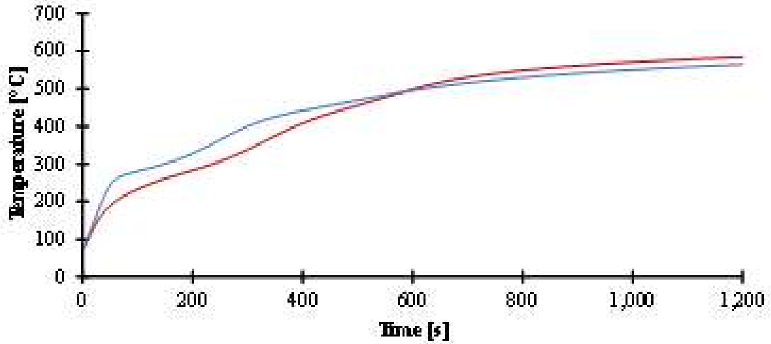
Determination of the thermochemical properties of the condensed phase

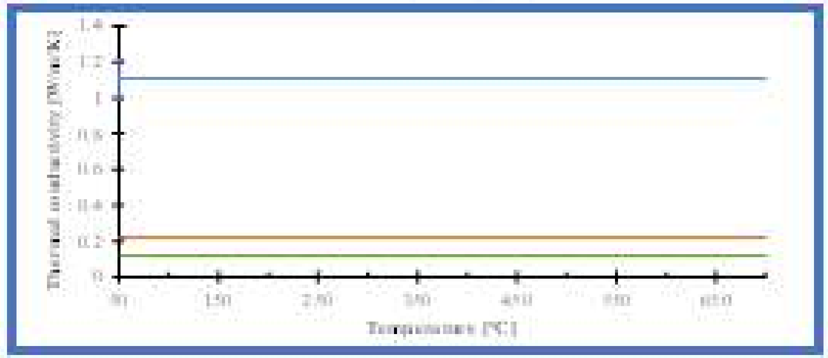
Examples of results:

$$k(T) = \frac{m_{Initial}}{m_{total}}.k_{Initial}(T) + \frac{m_{Intermediate}}{m_{total}}.k_{Intermediate}(T) + \frac{m_{Residue}}{m_{total}}.k_{Residue}(T)$$

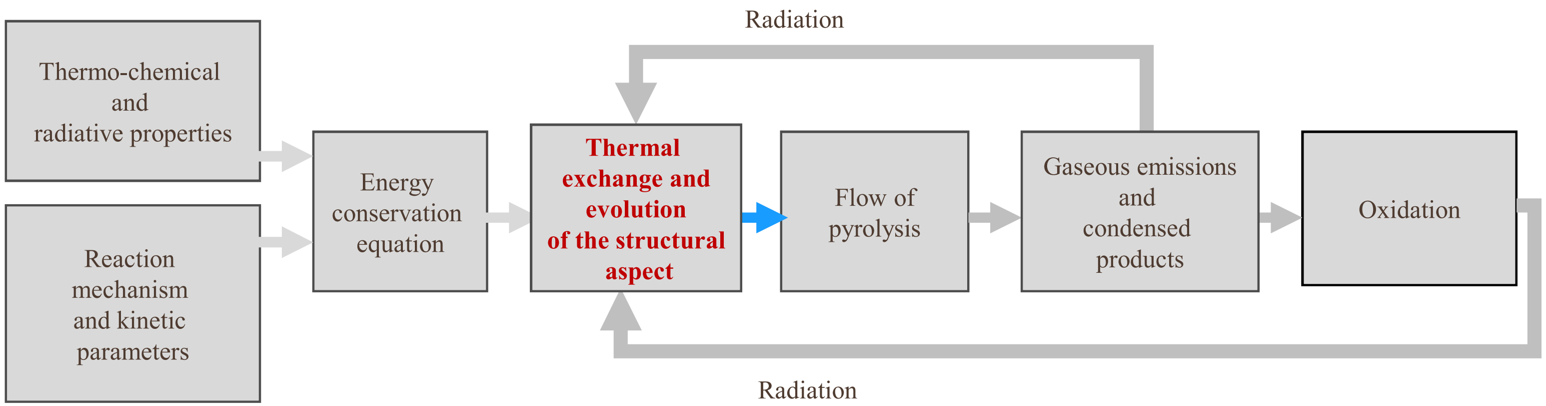




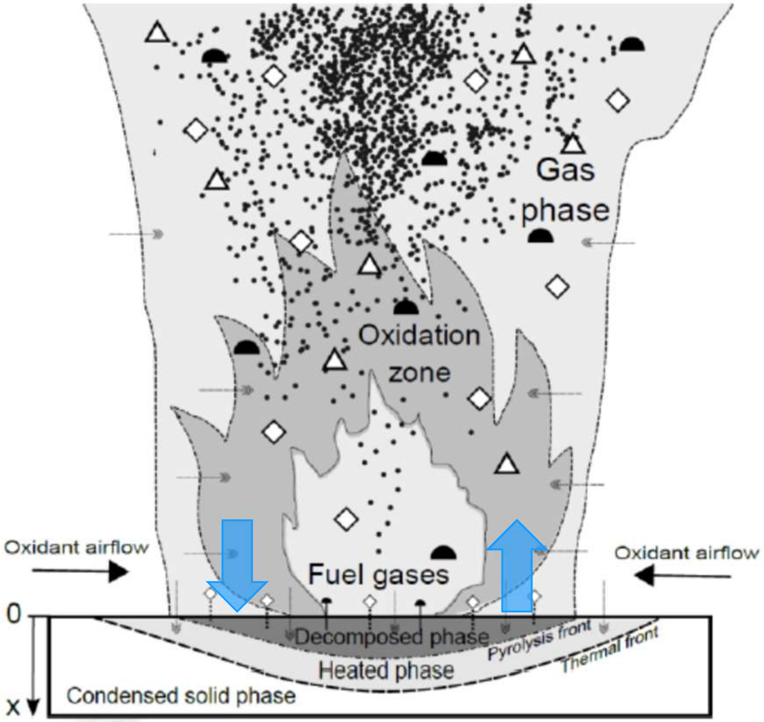




Thermal decomposition
3rd phase: Heat feedback and oxygen diffusion



Heat feedback and oxygen diffusion - Determination



In controlled and defined conditions

Multi-scale experimental investigations

This description requires the description of :

- What happen in the gas phase: flame, temperature.
- The MLR flow and the species diffusion.
- The mass transfer diffusion, from the condensed phase to the gas one, and from the gas phase to the solid.
- The thermal transfer between the gas phase and the solid one.

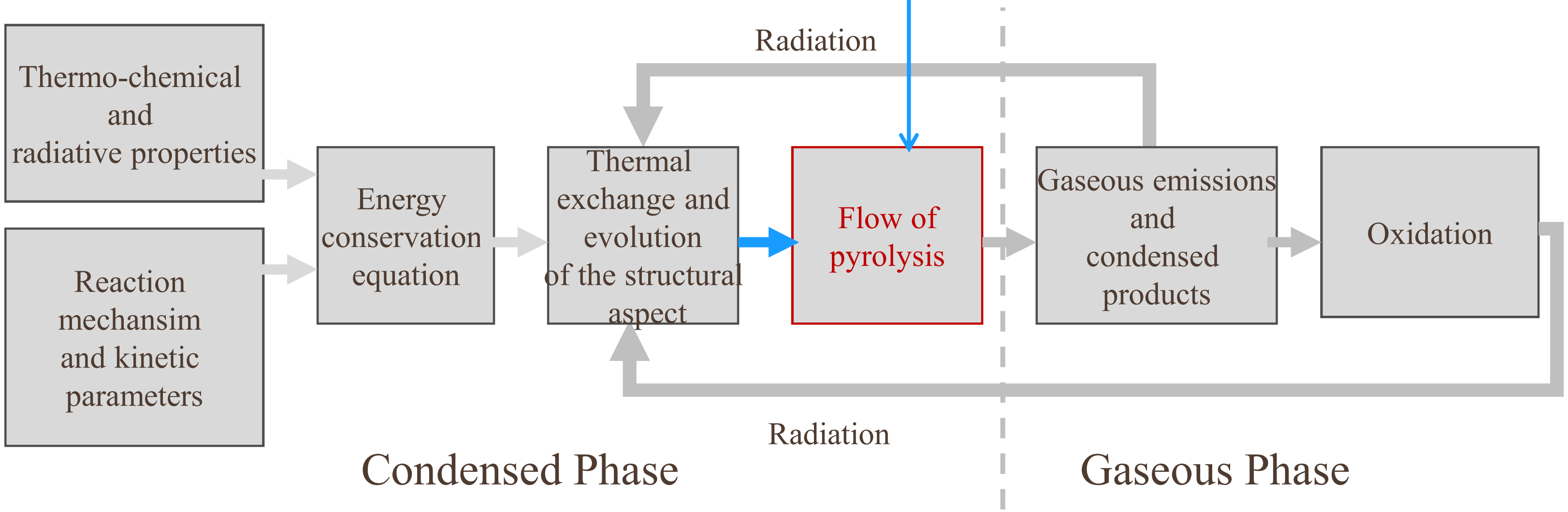
How to describe them ?
How to determine Them ?

Thermal decomposition
3rd phase: Heat feedback and oxygen diffusion

Special focus on the experimental benchscales

Modeling of Thermal decomposition – Required parameters

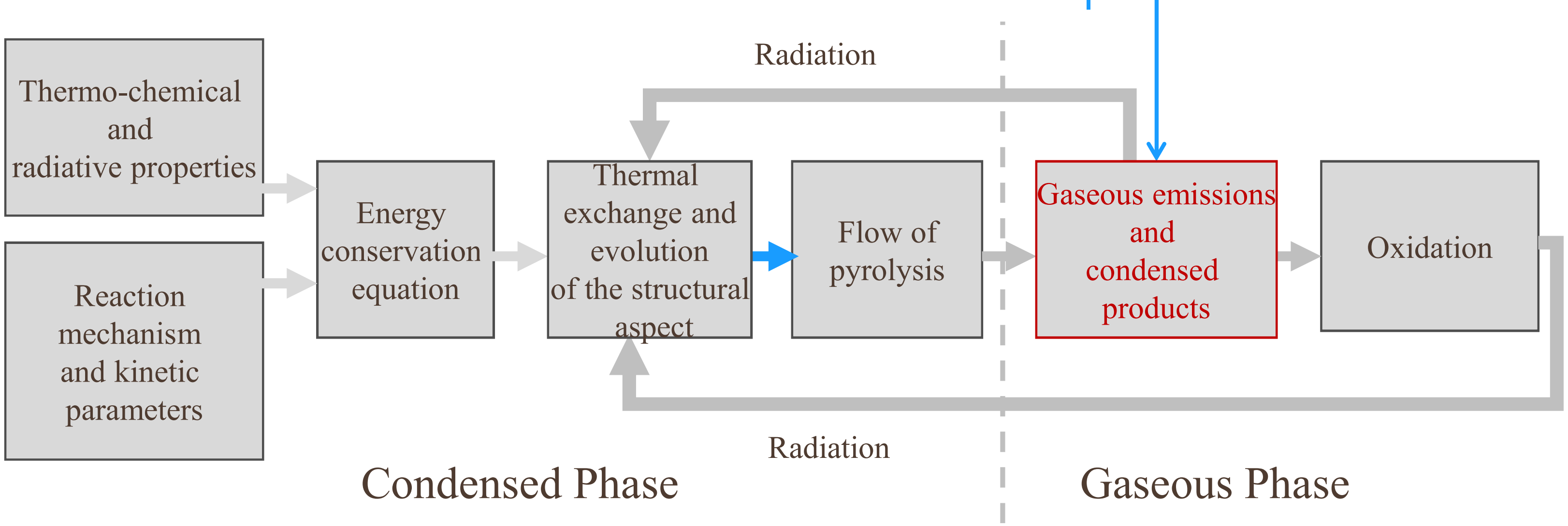
- Mass loss
- Mass loss rate- MLR
- Regression of the surface (thickness)



--> equ. of mass conservation
--> equ. of movement quantity conservation (rate)
--> equ. of energy conservation (T)
--> equ. of species conservation (mass fractions Y_i)

Modeling of Thermal decomposition – Required parameters

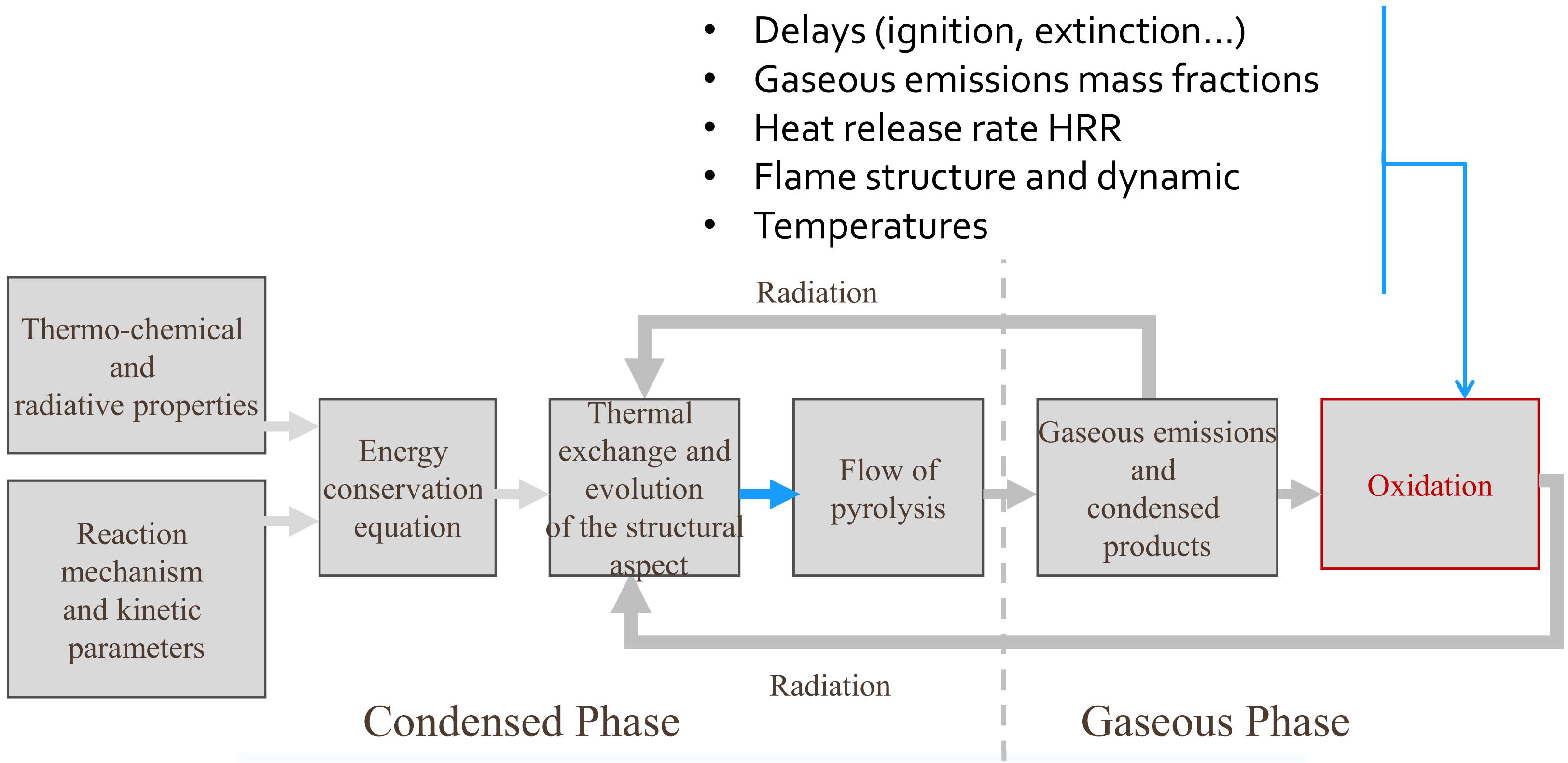
- Mass fractions of gaseous emissions
- Condensed products formed – mass fractions + properties
- Thicknesses of the condensed « phase »



--> equ. of mass conservation
--> equ. of movement quantity conservation (rate)
--> equ. of energy conservation (T)
--> equ. of species conservation (mass fractions Y_i)

Modeling of Thermal decomposition – Required parameters

- Delays (ignition, extinction…)
- Gaseous emissions mass fractions
- Heat release rate HRR
- Flame structure and dynamic
- Temperatures



--> equ. of mass conservation
--> equ. of movement quantity conservation (rate)
--> equ. of energy conservation (T)
--> equ. of species conservation (mass fractions Y_i)

Focus: Experimental Investigations – Thermal decomposition

Matter Scale	Small Scale	Product scale	Real Scale

0D process

- No thermal diffusion
- No mass transfer
- « Perfect » control of the boundary conditions
- Controlled conditions: imposed by the user
- Intrinsic properties

1D process

- 1D Thermal transfer
- Radiative properties
- 1D mass transfer
- We try to control the boundary and the experimental conditions
- No flame transfer-propagation
- Simplified characterization of the diffusion aspects

2D or 3D process

- Thermal transfer
- Radiative properties
- Mass transfer
- Uncontrolled or difficulty to control the boundary conditions and the experimental ones
- Flame transfer-propagation
- Real diffusion aspects but… many process invoved and difficulty to determine the « conditions »

Approach: to simplify the problem and to add complexity as we go along

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Focus: Experimental Investigations – Thermal decomposition

Matter Scale

- Mass Loss
- Mass loss rate
- Enthalpy of the reactions
- Heat of combustion
- Specific heat
- Model of pyrolysis (mechanisms and parameters)

Small Scale

- Delays of inflammation, extinction
- Mass loss
- Mass loss rate
- HRR
- Temperatures
- Gaseous emissions concentrations
- Thermal inertia
- Effusivity

Product scale

Real Scale

- Delays of inflammation, extinction, flash-over
- Mass loss
- Mass loss rate
- Gaseous emissions
- HRR
- Flame propagation
- Temperatures

Focus: Experimental Investigations – Thermal decomposition

<u>Cône Calorimeter (CC) or Fire Propagation Apparatus (FPA) :</u>

- Few g and (100*100*Thickness) mm^3 samples
- Heat flux: 0 to 100 kW/m^2
- Possible controlled atmosphere
- Coupling with gas analysis
- Piloted ignition or auto-ignition

✓ Determination of

  - t_{ig}, T_{ig}, CHF
  - ML and MLR
  - HRR
  - Gaseous emissions
  - Temperatures into the condensed and the gas phases
  - And other parameters can be deducted

Small Scale

<u>Controled parameters</u>

- Heat flux
- Global atmosphere

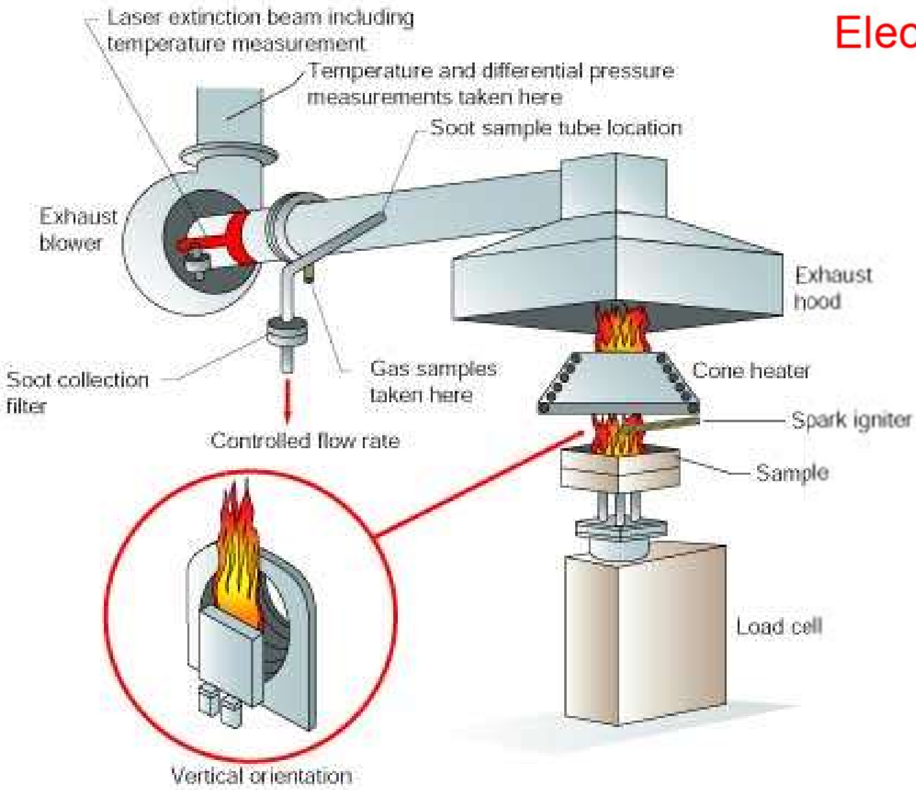
<u>Unknown parameters</u>

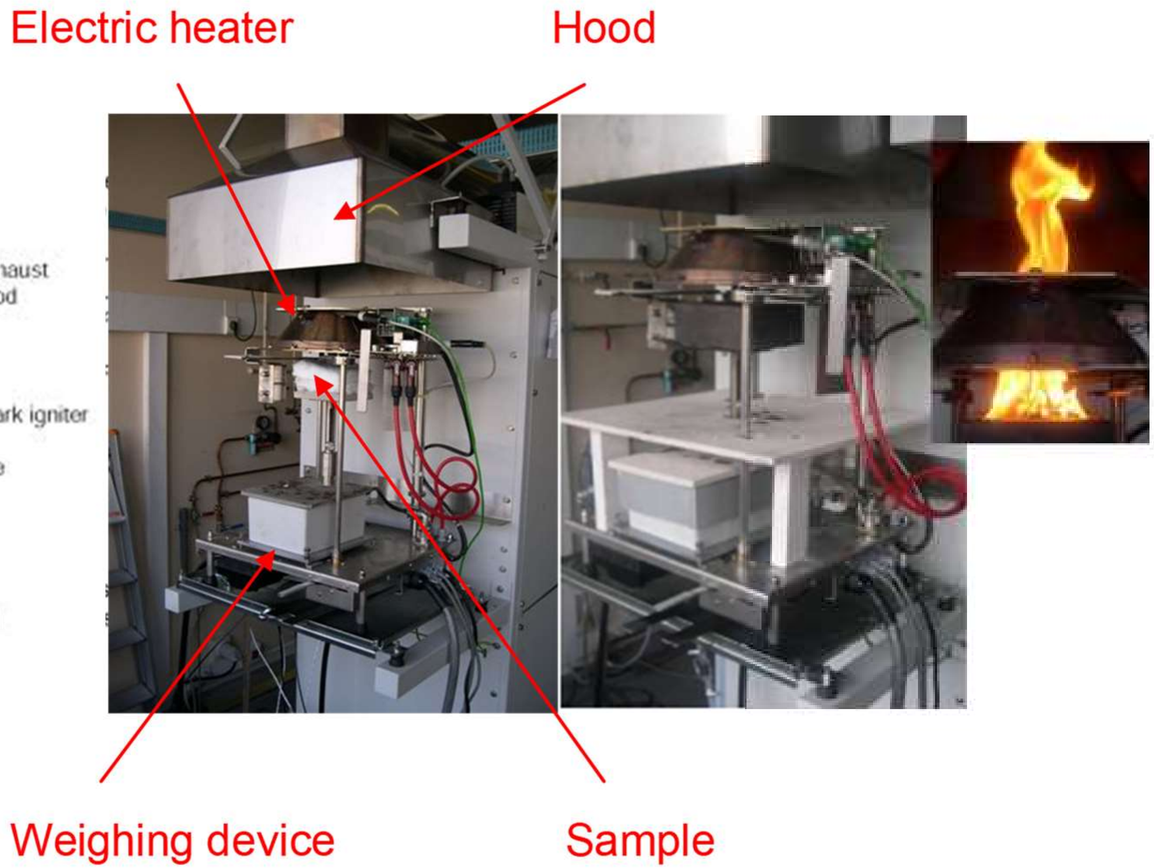
- Temperature
- Heating rate
- Local mass fraction of combustible and of oxygen
- Permeability of the solid
- Thickness of the reactive zone

Simplified « 1D » investigation, with a flame Heat and mass tranfers whithout a flame propagation

Focus: Experimental Investigations – Thermal decomposition

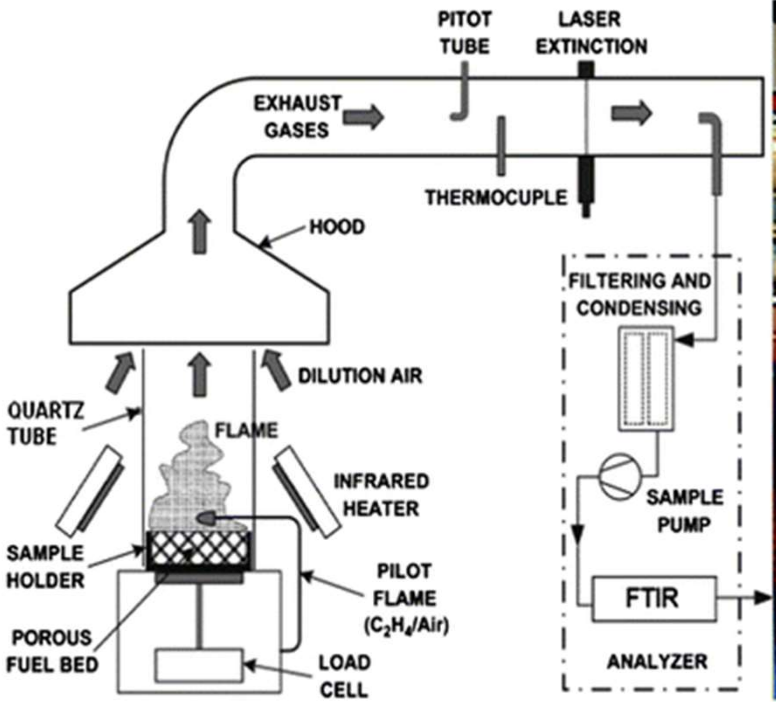
Cone Calorimeter (CC)





Focus: Experimental Investigations – Thermal decomposition

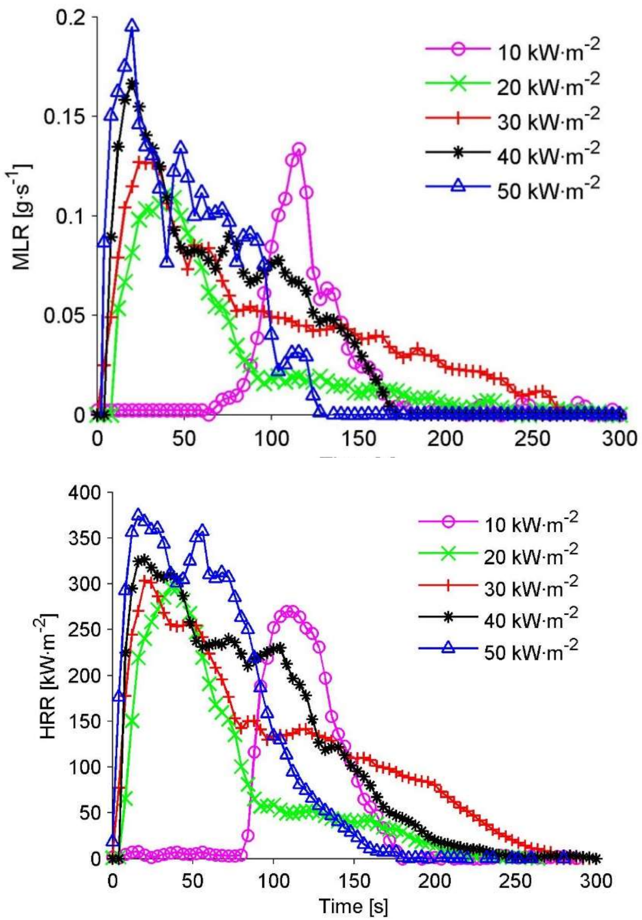
Fire Propagation Apparatus (FPA):

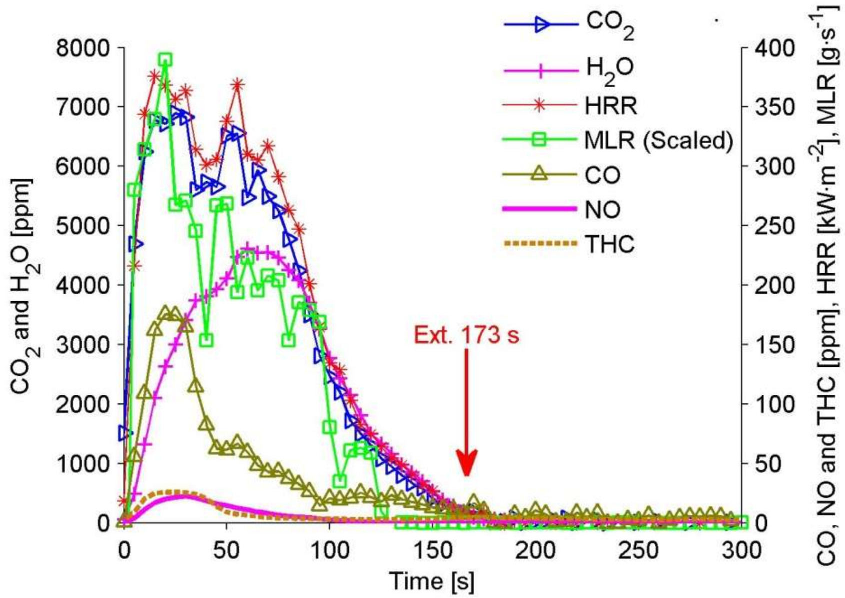


[*Diallo & al. An innovative experimental approach aiming to understand and quantify the actual fire hazards of ionic liquids, Energy and environmental science, 2013*]

Focus: Experimental Investigations – Thermal decomposition

Examples of results:





Thermal decomposition of a PU Foam

[*L. Bustamante Valencia & al. Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels. Fire Safety Journal, 2009.*]

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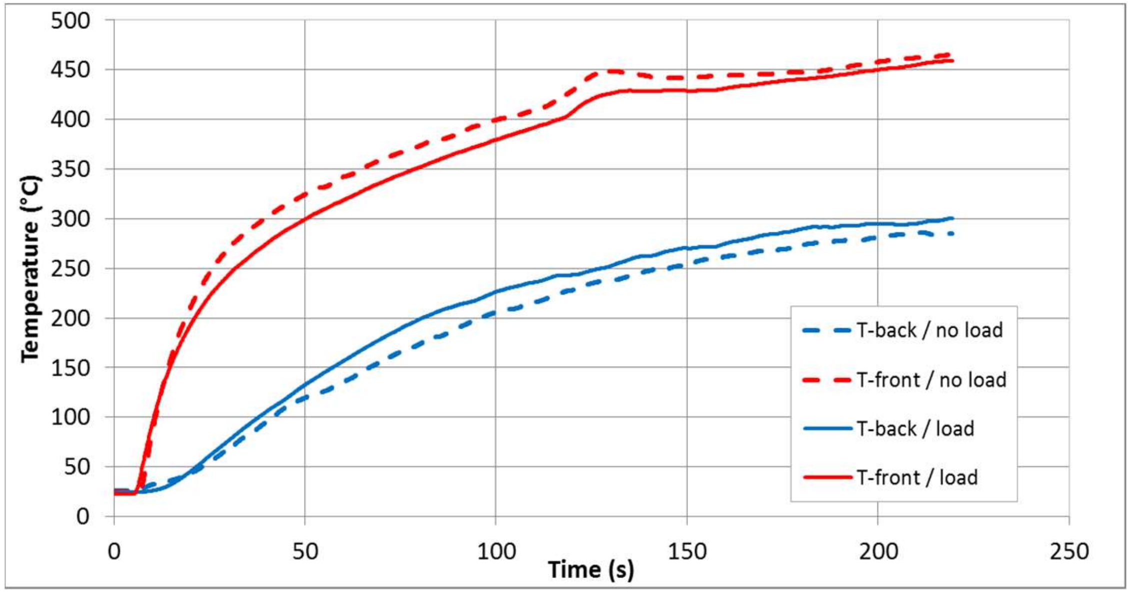
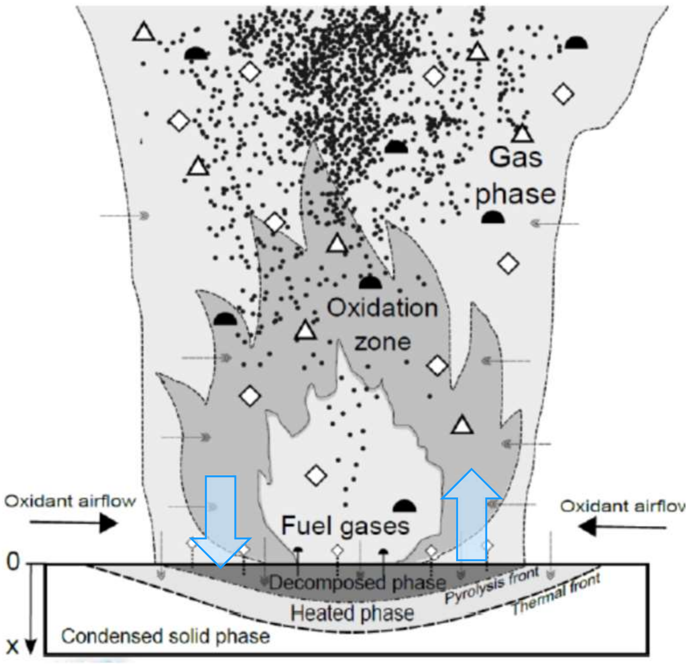
Examples of results:



Temperatures evolution during the thermal decomposition of a composite material in CC

[*A. Benelfellah & al. Effect of a coupled thermomechanical loading on the residual mechanical strength and on the surface temperature of wound carbon/epoxy composite, Journal of Composite Material, 2017*]

Heat feedback and oxygen diffusion - Modelling

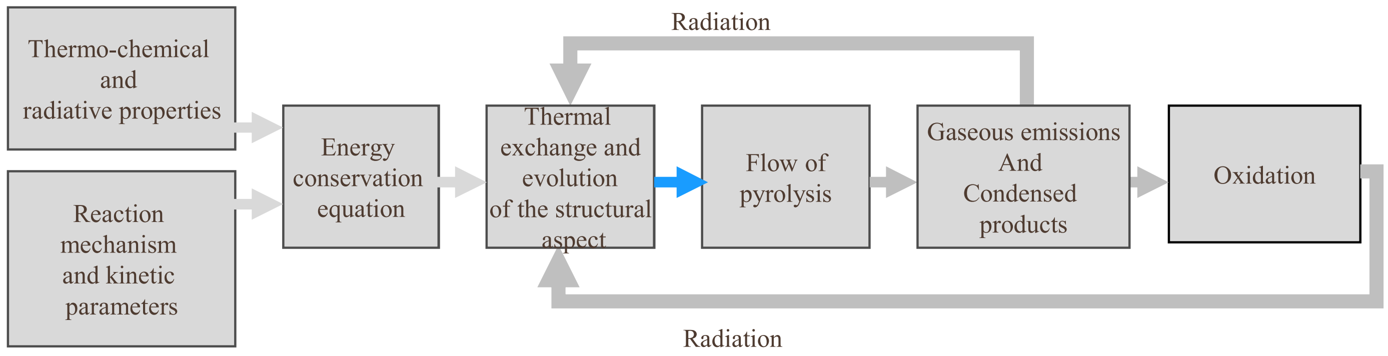


The **objective** is to describe the thermal decomposition and what happen at this scale:

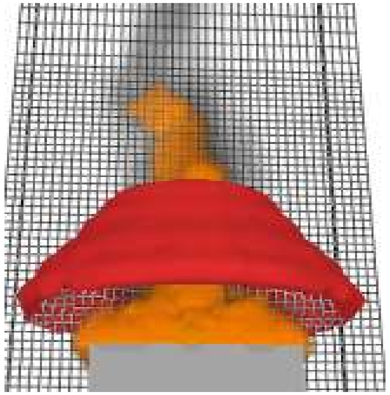
- CFD modeling
- Integration of the « model of pyrolysis » and the « thermochemical data » in the CFD model (as FDS or Firefoam)
- Modeling of the cone calorimeter or the FPA experiments

Validation of the model of pyrolysis at this scale, with thermal and mass transfers

Thermal decomposition
4th phase: validation of the thermal decomposition model



Validation of the thermal decomposition model



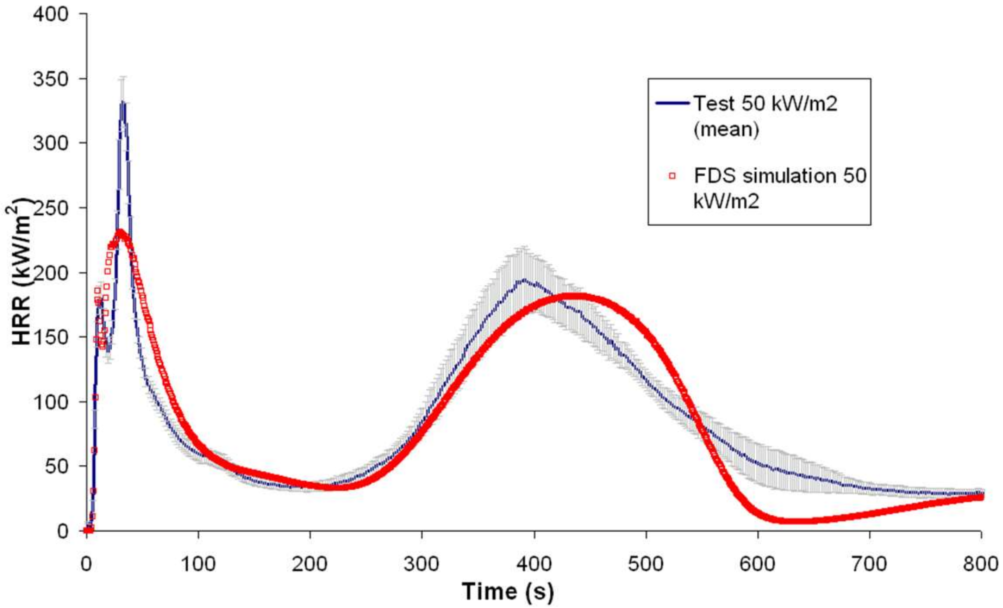
Small Scale

Model of pyrolysis

Thermo-chemical properties

Cone calorimeter results

Prediction of thermal decomposition at small scale



[A. Camillo & al.]

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Matter Scale | Small Scale | Product scale | Real Scale

0D process

- No thermal diffusion
- No mass transfer
- « Perfect » control of the boundary conditions
- Controlled conditions: imposed by the user

- Intrinsic properties

1D process

- 1D Thermal transfer
- Radiative properties
- 1D mass transfer
- We try to control the boundary and the experimental conditions
- No flame transfer-propagation

- Simplified characterization of the diffusion aspects

2D or 3D process

- Thermal transfer
- Radiative properties
- Mass transfer
- Uncontrolled or difficulty to control the boundary conditions and the experimental ones
- Flame transfer-propagation

- Real diffusion aspects but… many process invoved and difficulty to determine the « conditions »

Approach: to simplify the problem and to add complexity as we go along

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Product scale

Classical experimental investigations:

- IMO LIFT
- Medium Burning Item
- Single Burning Item

→ **HRR**
Rate of flame
Temperatures
Flame structure

- Open calorimeter (Nordtest NT Fire 032 calorimeter)
- Combustion chamber (ISO 9705 – room corner test)

→ **HRR**

[V. Brabauskas, Heat release rate, The SFPE Handbook of fire protection engineering 4th edition]

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Product scale

Single Burning Item (SBI), Medium and LIFT :

- Mass: kg
- Atmosphere: under air
- Piloted ignition by a burner or a piloted flame
- Gaseous analysis possible

Medium or LIFT: vertical or horizontal samples

SBI: possibility to « create » structures

Controlled parameters

- LIFT: incident heat flux
- SBI and medium : P_{burner}

Unknown parameters

- Temperature
- Heating rate
- Local mass fractions of combustible and oxygen
- Permeability
- Gradient of oxygen (diffusion) in the condensed phase
- Gradient of temperature
- Reactive zone thickness

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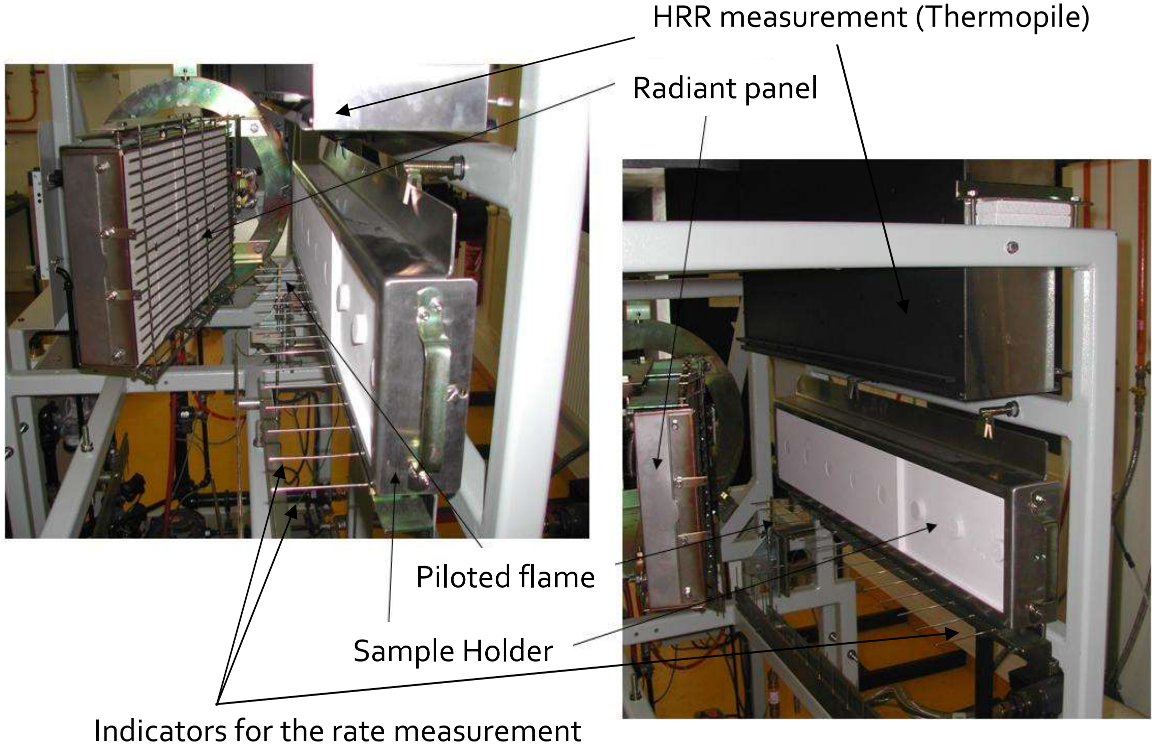
IMO – LIFT :

Product scale

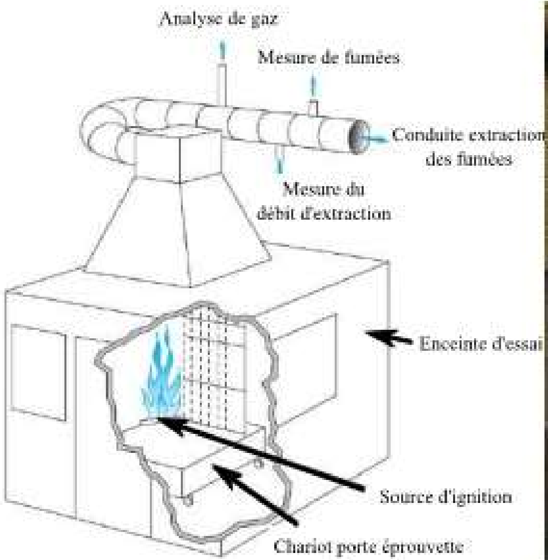


IMO/LIFT Spread Of Flame Apparatus (ISO 5658)

Medium and Single Burning Items:

Product scale

Medium Burning Item



Single Burning Item

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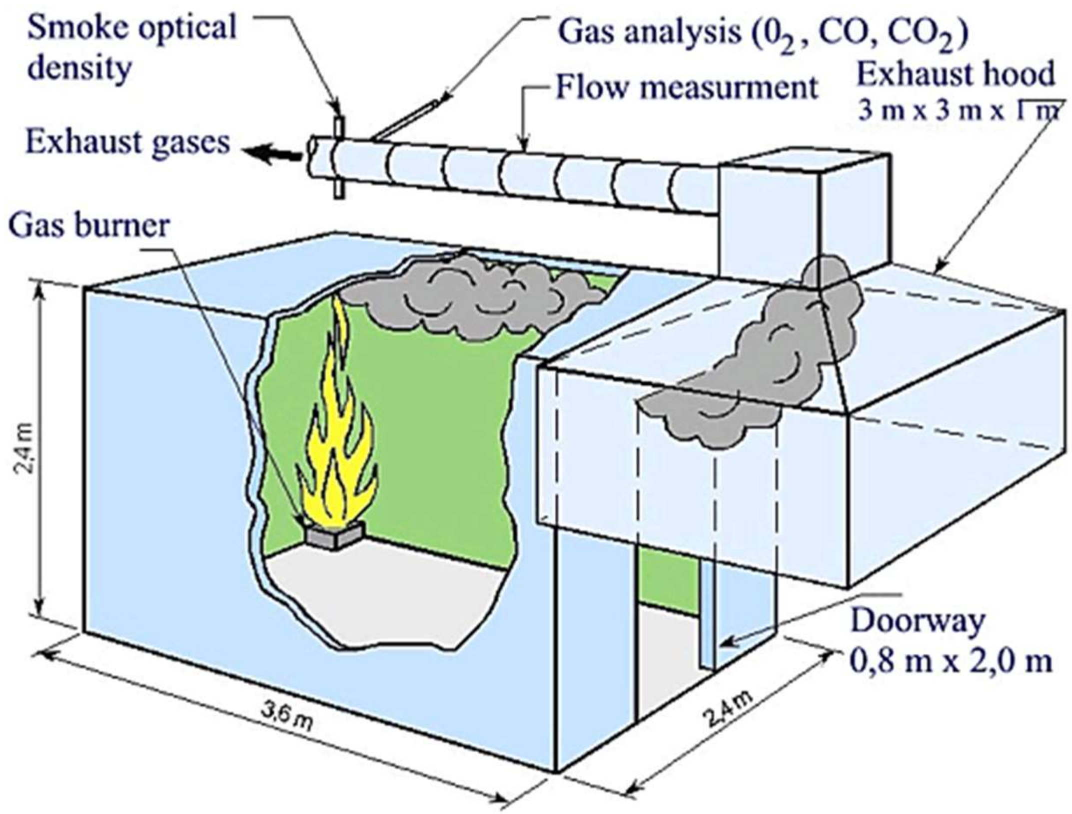
Product scale

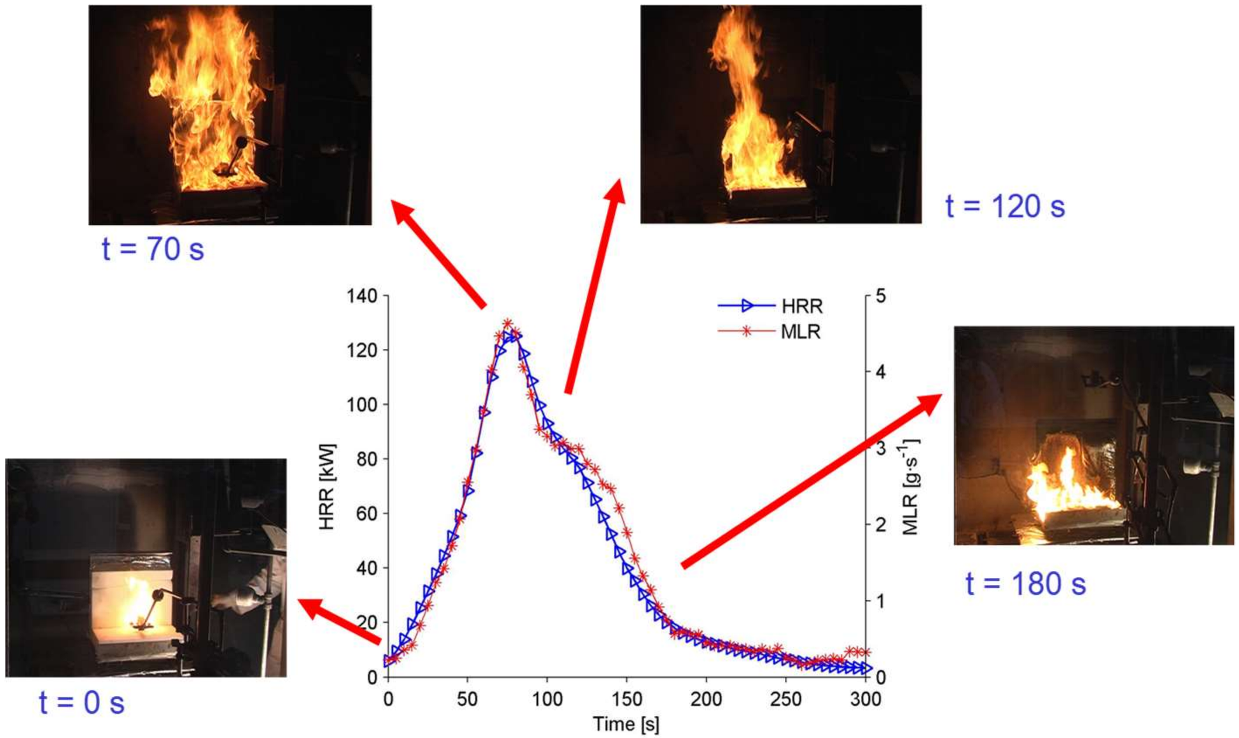
ISO 9705 - Room corner test:



Product scale

SBI et Medium:

- Example of results



Thermal decomposition and combustion of a PU Foam into a SBI

[L. Bustamante Valencia& al. Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels. Fire Safety Journal, 2009.]

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SBI:

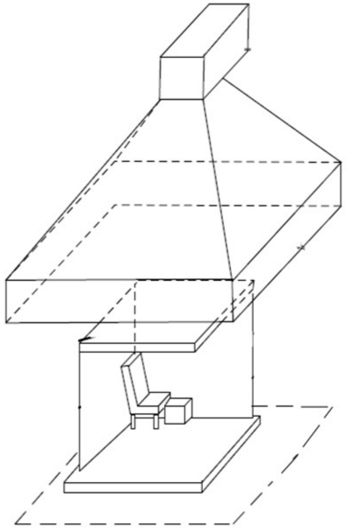
A : 30 s

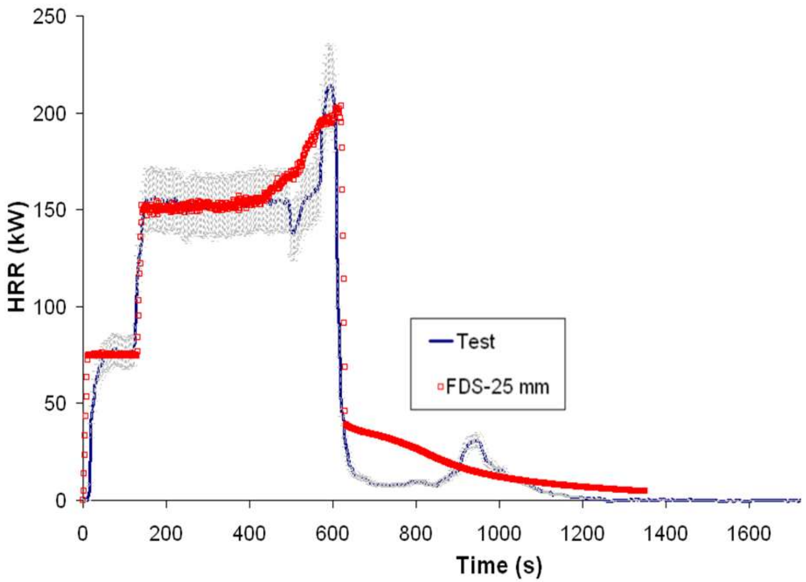
B : 270 s

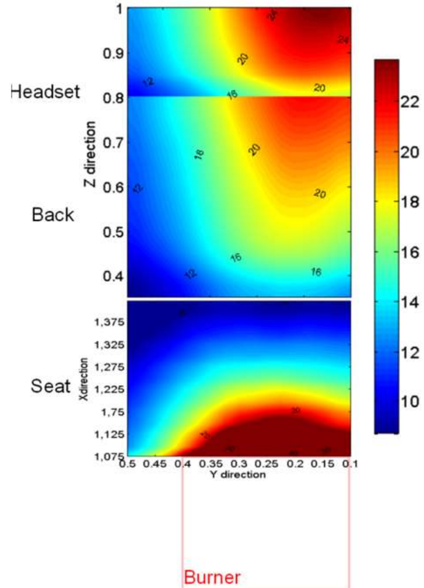
C : 480 s

D : 510 s

E : 600 s







Heat flux density distribution

[E. Guillaume & al. Application and Limitations of a Method Based on Pyrolysis Models to Simulate Railway Rolling Stock Fire Scenarios. Fire Technology, 50, pp. 317-348, 2014]

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Training device of the firemen (container)

Real scale

[Colloque national – Contraintes thermiques et performance des EPI des sapeurs-pompiers en caisson d'observation et d'entrainement aux phénomènes thermiques, Niort, 2014]

Rooms and building

Real Scale

[Essais Dalmarnock, Université d'Edinburgh]

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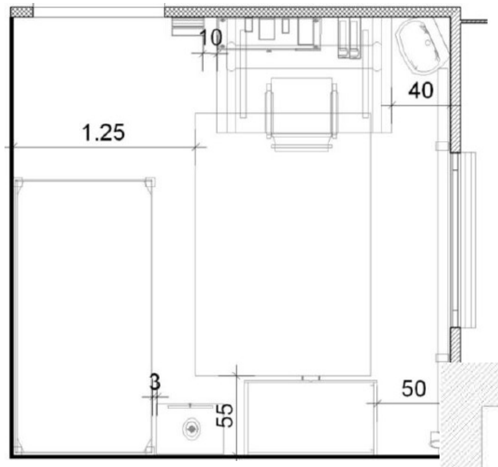
Rooms and building



Real Scale

[E. Guillaume & al. Real-scale Fire Tests of One Bedroom Apartments with Regard to Tenability Assessment, Fire safety journal, 2015]

Conclusions and perspectives

Conclusions and perspectives

One says (to do not cited him… Pr Torero) that the research on thermal decomposition will even require Hundreds of years !!!!

So, just a perspective: WE NEED YOU !!!!!