Polyurethane Foam Pyrolysis and Combustion in Cone Calorimeter – Analysis of released heat and gases

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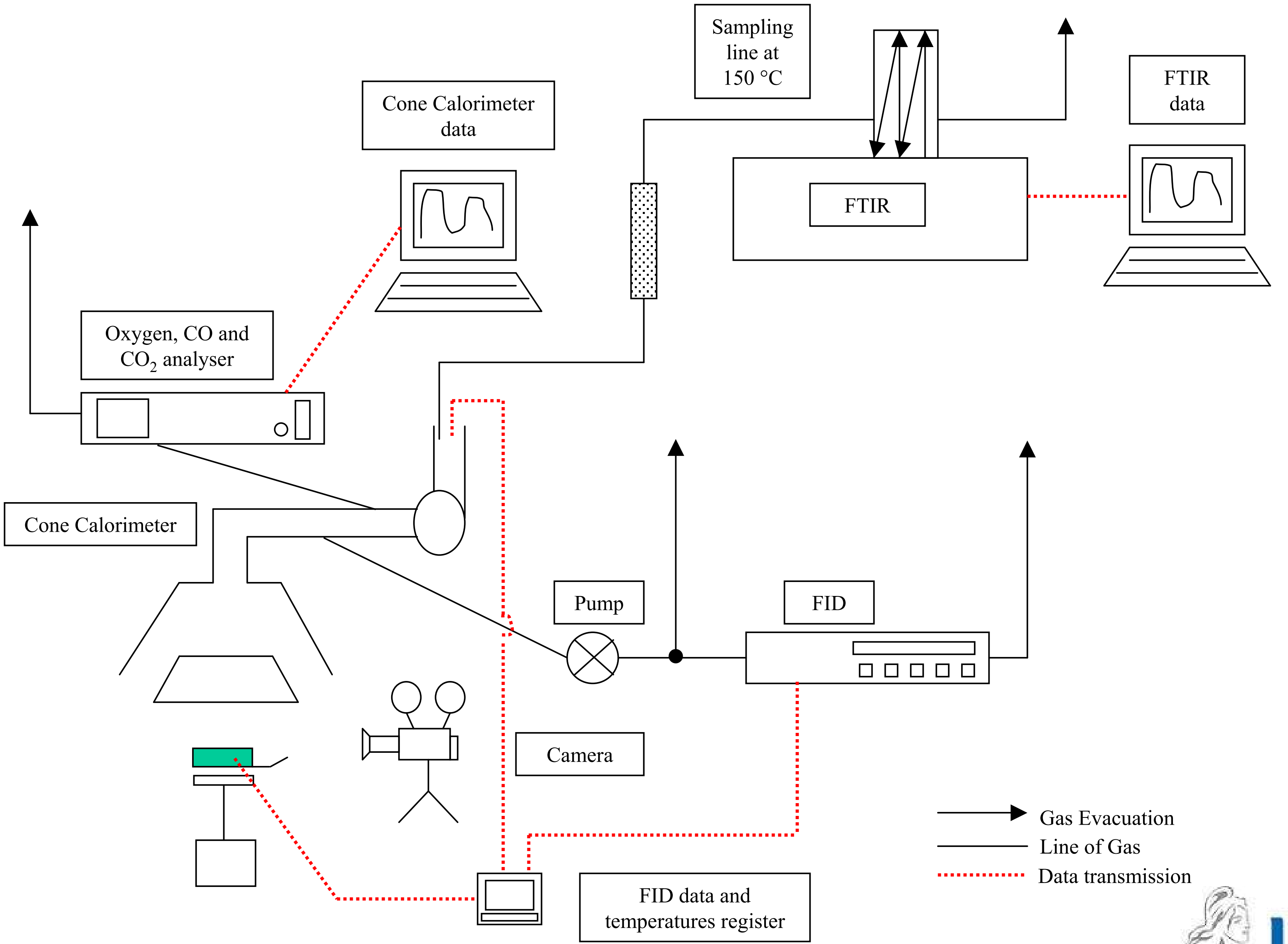
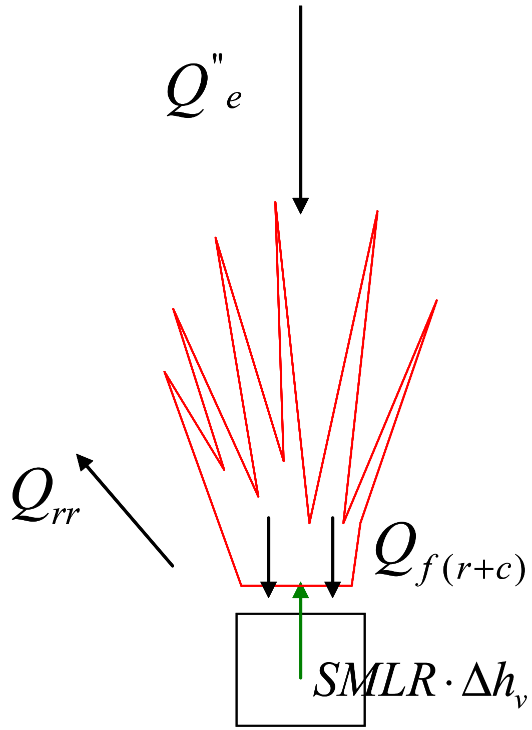
CNRS GDR « Feux » – Corte
6th to 8th June 2007

Scheme of apparatus distribution



PF “perfect” heat exchange balance in thermally-stable conditions



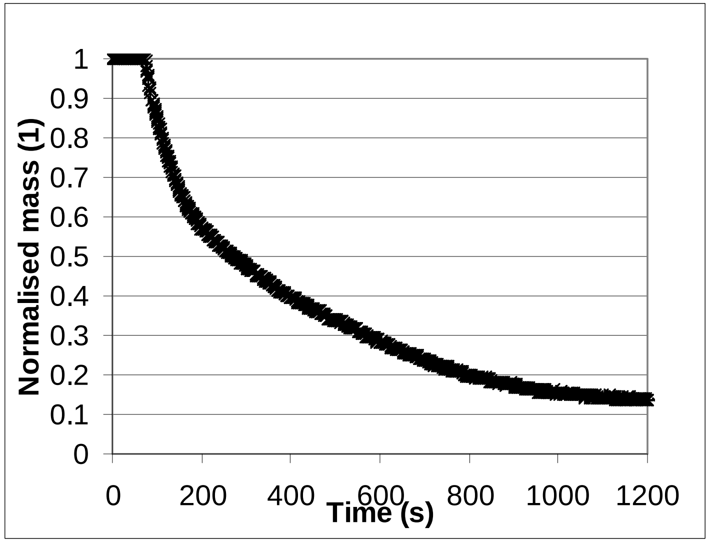
$$Q''_e + Q_{f(r+c)} - Q_{rr} - SMLR \cdot \Delta Hv = 0$$

PF chemical composition (elemental analyse)

Element	**Mean (%)**	Molar Mass (g/mol)	Molar proportion (mol)	Coefficients
C	**61.97**	12.01	5.16	1.00
H	**8.50**	1.01	8.43	1.63
O	**22.46**	16.00	1.40	0.27
N	**5.88**	14.01	0.42	0.08
S	**< 0.2**	32.06		
Cl	**< 10 ppm**	35.45		
Total	**98.81**	18.62		

Density 20.87 kg/m^3

$$C_1H_{1.63}O_{0.27}N_{0.08} + 1.17O_2 \rightarrow 0.92CO_2 + 0.77H_2O + 0.08HCN$$



Normalised mass evolution with time in non-flaming condition - 30 kW/m²

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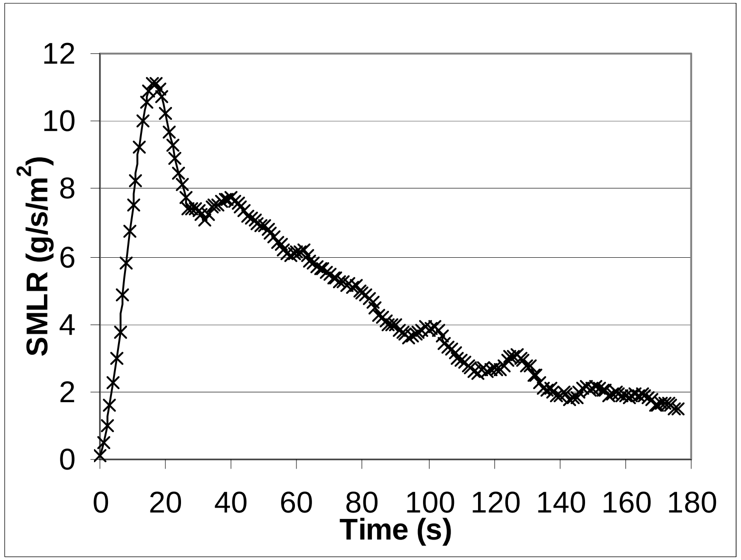
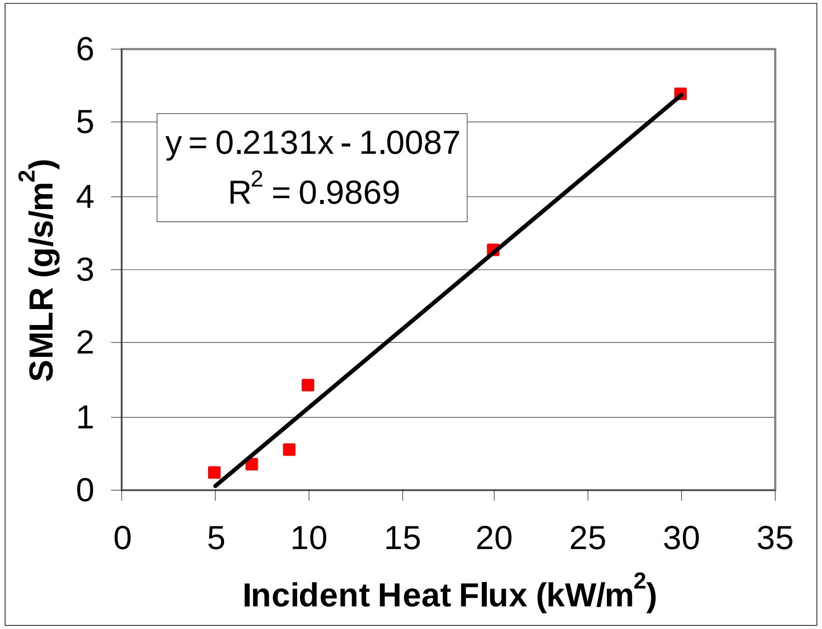
Specific mass-loss rate

Specific mass-loss rate until 180 s



$$SMLR = \frac{Q''_e - Q_{rr}}{\Delta Hv} = a \cdot Q''_e + b$$

$$a = \frac{1}{\Delta Hv} \qquad b = -\frac{Q_{rr}}{\Delta Hv}$$



SMLR vs incident heat flux

Where:

- $SMLR$ Specific mass-loss rate (kg/s·m²)
- Q''_e Incident heat flux (kW/m²)
- Q_{rr} Reflected heat flux (kW/m²)
- ΔHv Vaporisation enthalpy (kJ/kg)

Parameter	Calculated	Literature
Vaporisation enthalpy (kJ/kg)	4,692	2400*
Reflected heat flux (kW/m²)	4.73	16 - 19*

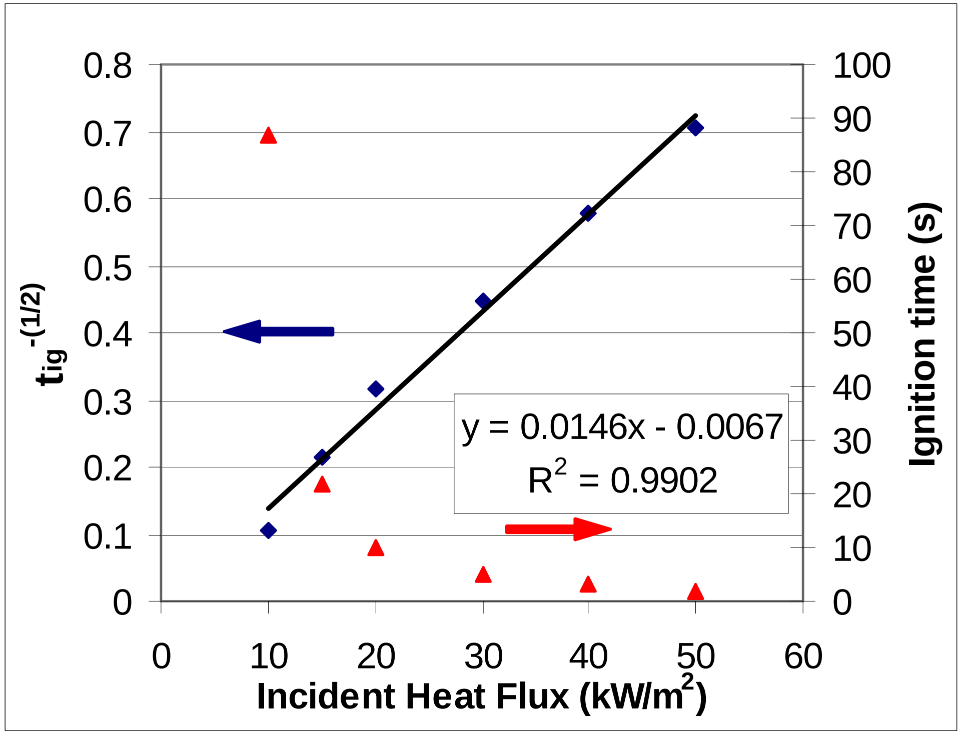
* Fire protection engineering – SFPE 2nd Ed.

Ignition time vs incident heat flux

$$\sqrt{\frac{1}{t_{ig}}} = \frac{\sqrt{\frac{4}{\pi}}\left(Q''_e - CHF\right)}{TRP}$$

$$TRP = \sqrt{\frac{4}{\pi}}\frac{1}{Slope}$$

$$CHF = -\frac{TRP \cdot y_{\text{intercept}}}{\sqrt{\frac{4}{\pi}}}$$



Ignition time vs incident heat flux

Where:

t_{ig} Ignition time (s)

Q''_e Incident heat flux (kW/m²)

CHF Critical heat flux, is also found in literature as $\dot{Q}''_{cr}$ (kW/m²)

TRP Thermal Response Parameter (kW·s$^{1/2}$/m²)

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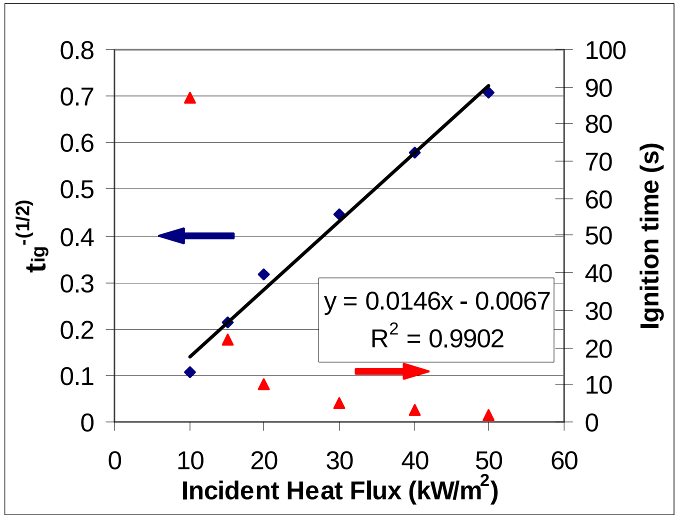
Thermal Parameters



$$CHF = h_c\left(T_{ig} - T_o\right) + \sigma \cdot \varepsilon\left(T_{ig}^4 - T_o^4\right)$$

Where:

h_c Coefficient of convective transfer = **15±2 W/m²·K**

T_{ig} Temperature of the surface at ignition

To Laboratory temperature = **293±1 K**

σ Material emissivity = **(0.9±0.07)**

ε Stephan Boltzmann constant = **5.67x10^{-8}W/m²·K^4**

$$TRP = \left(T_{ig} - T_o\right)\sqrt{\lambda \rho C_P}$$

Where:

λ Thermal conductivity (kW/m K)

ρ PF density (kg/m^3)

C_P Specific heat at constant pressure (kJ/kgK)

Parameter	Calculated	Literature
Thermal Response Parameter (kW·s$^{1/2}$·m^{-2})	75.23	55 - 221*
Critical Heat Flux (kW·m^{-2}) – Experimental	9.00	13 - 40*
Ignition Temperature (°C)	275	280**
Thermal Inertia ρλCp (kJ^2·s^{-1}·m^{-4}·K^{-2})	0.09	

* Fire protection engineering – SFPE 2nd Ed. (Data obtained in flammability Apparatus)

** Fire protection engineering – SFPE 2nd Ed.

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Heat Release Rate

$$HRR = 1.10\left(\frac{\Delta h_c}{r_o}\right) X^o_{O_2}\left[\frac{\Phi}{(1-\Phi)+1.105\Phi}\right]\dot{m}_e$$

Where:

$\left(\frac{\Delta h_c}{r_o}\right)$ Thornton factor = 13.1MJ/kgO_2

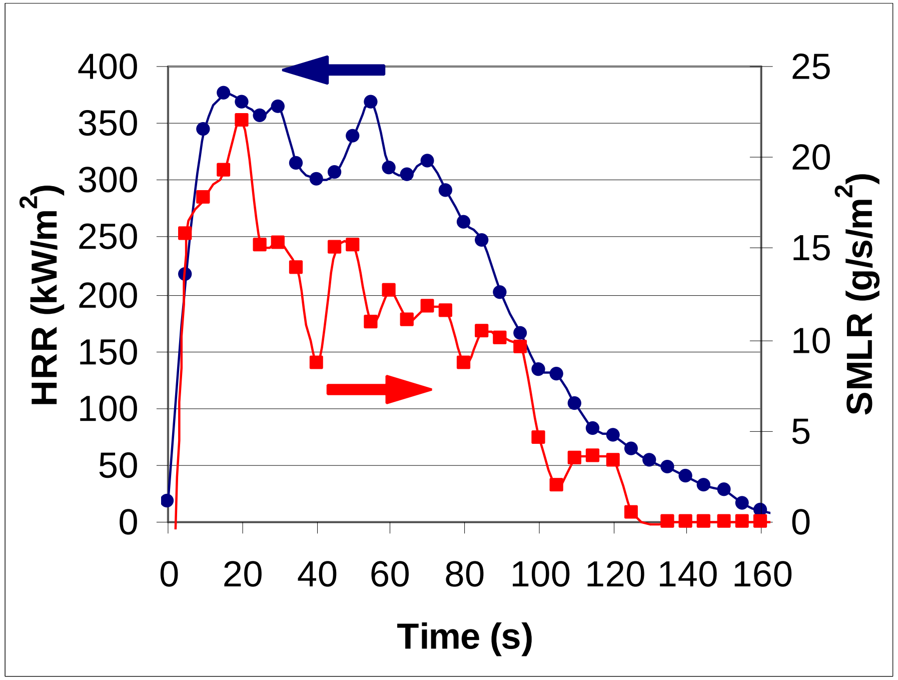
X^0_A Initial environment concentration of the species A (1)

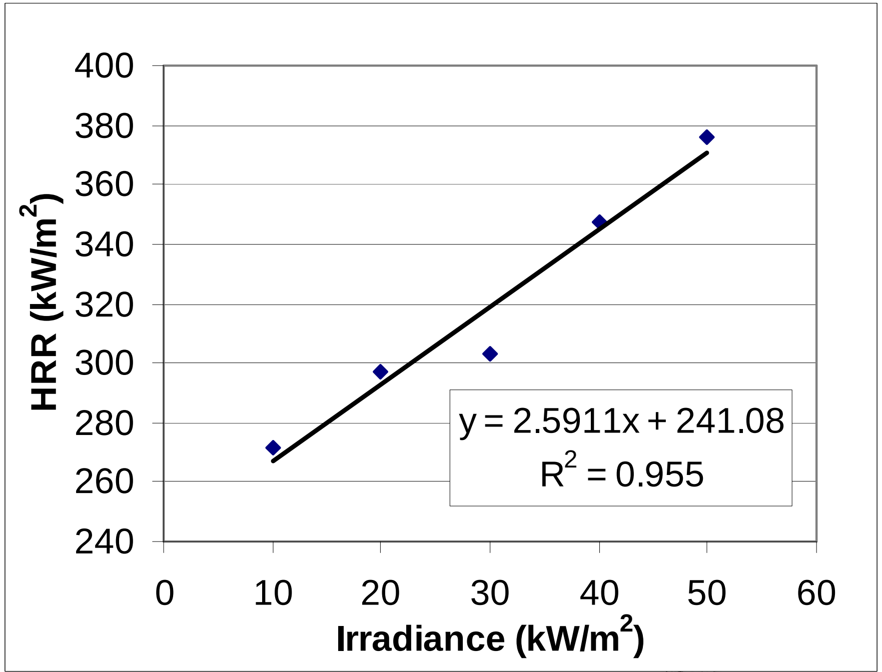
$X^a_{O_2}$ Environment oxygen mole fraction (1)

X_A Concentration of the species A at the time t (1)

$\dot{m}_e$ Exhaust duct volume flow (l/s)

$$\Phi = \frac{X^0_{O_2}\left(1 - X_{CO_2}\right) - X_{O2}\left(1 - X^0_{CO_2}\right)}{X^0_{O_2}\left(1 - X_{CO_2} - X_{O_2}\right)}$$





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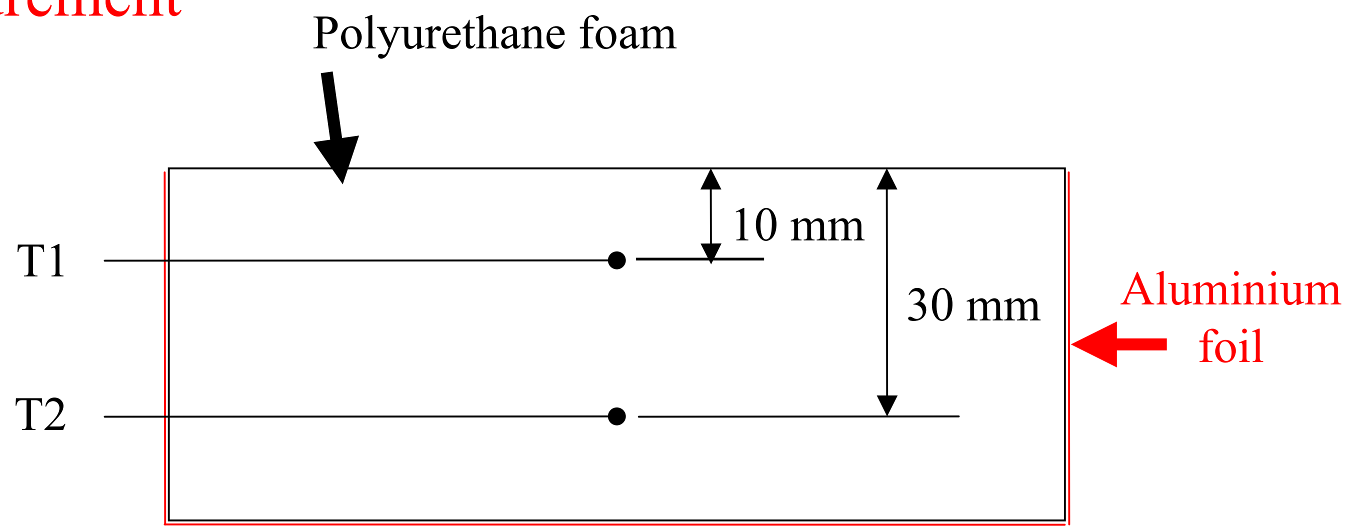
Temperature measurement

Thermocouples location - K type



Material	Density (kg m^{-3})	Conductivity (W m^{-1} K^{-1})
Polyurethane Foam	20.87	0.04
Polystyrene Foam	20	0.042
Rigid Phenolic Foam	50	0.05
Rubber	1200	0.15
Epoxy Resine	1200	0.201
Oak wood	825	0.209
PMMA	1190	0.21
Polycarbonate	1200	0.23
Polyesters	1500	0.4
LD Polyethylene	960	0.46

Source LNE data base

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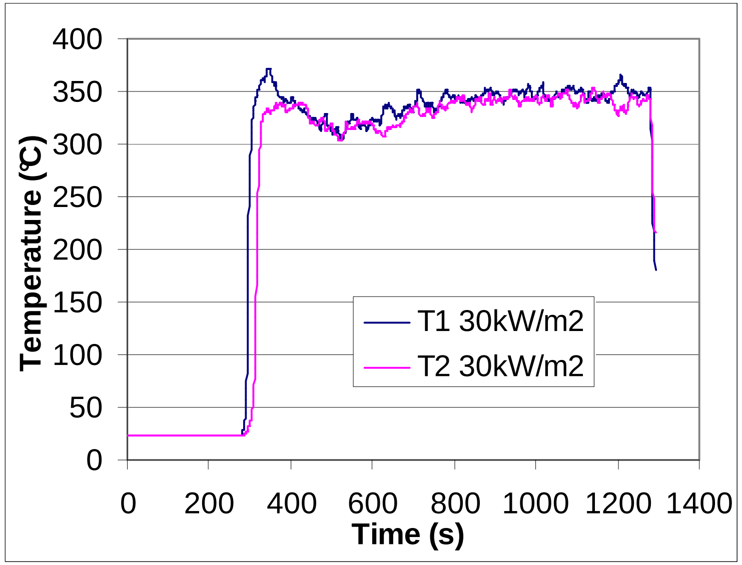
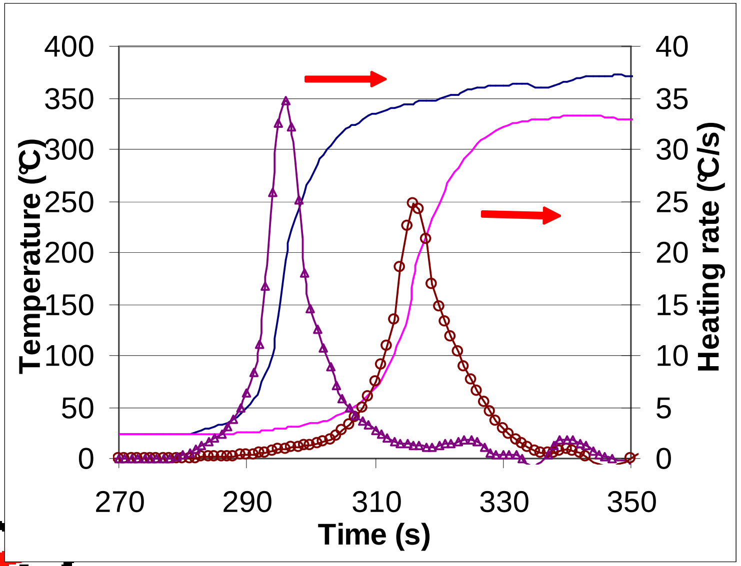
Temperature at a Heat Flux of 30 kW/m^2

Evolution of the internal temperature of sample

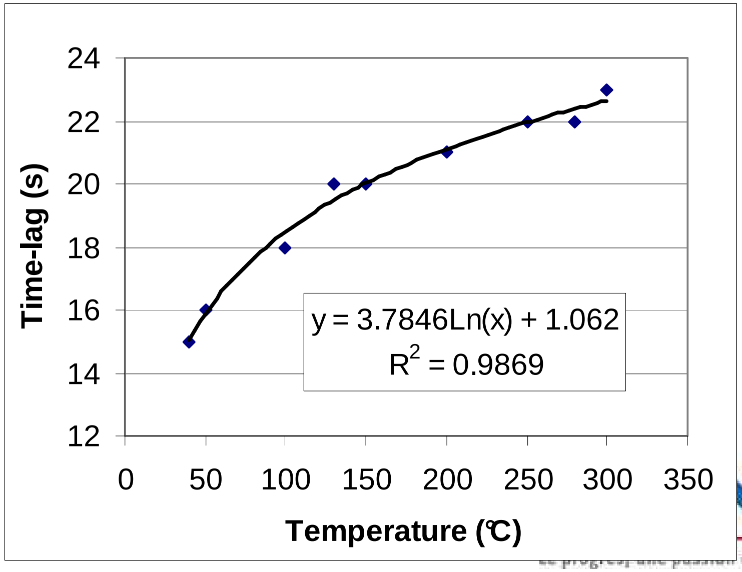


Nonflaming condition

Heating rate of the Polyurethane Foam

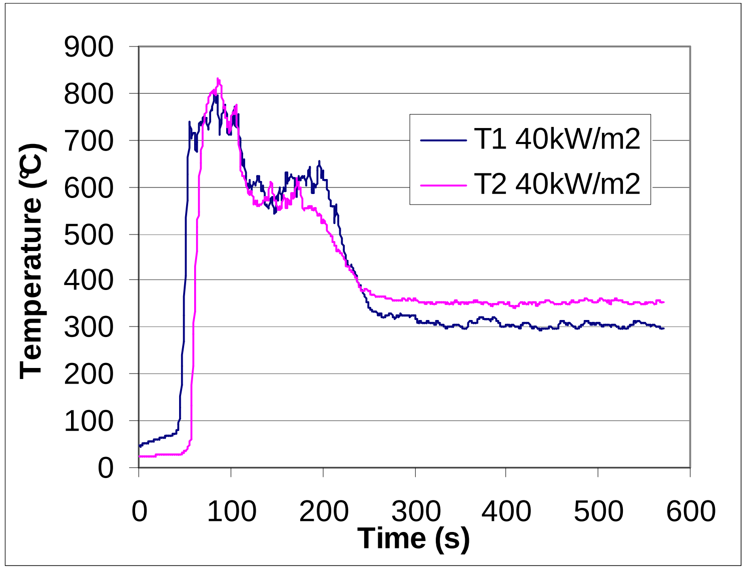


Time-lag between the thermocouples for given temperatures



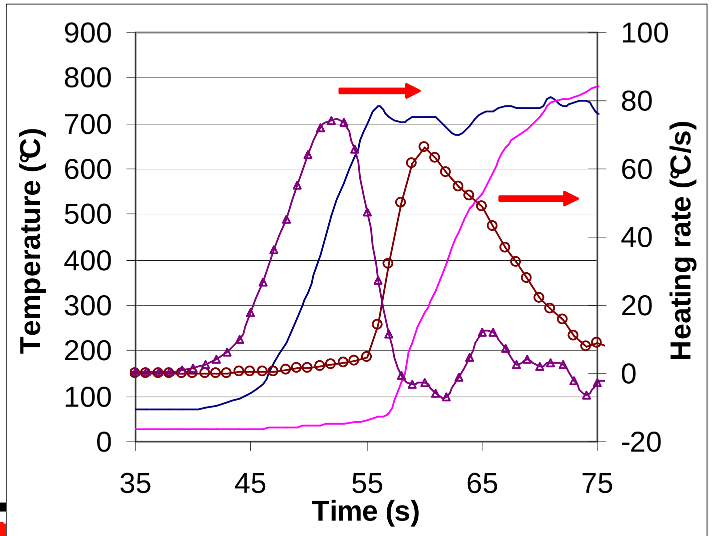
Temperature at a Heat Flux of 40 kW/m^2

Evolution of the internal temperature of the PF

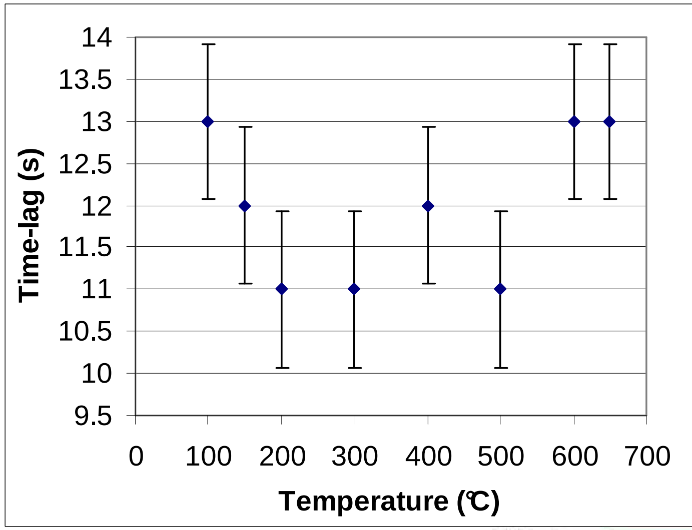


Flaming condition

Heating rate of the Polyurethane Foam

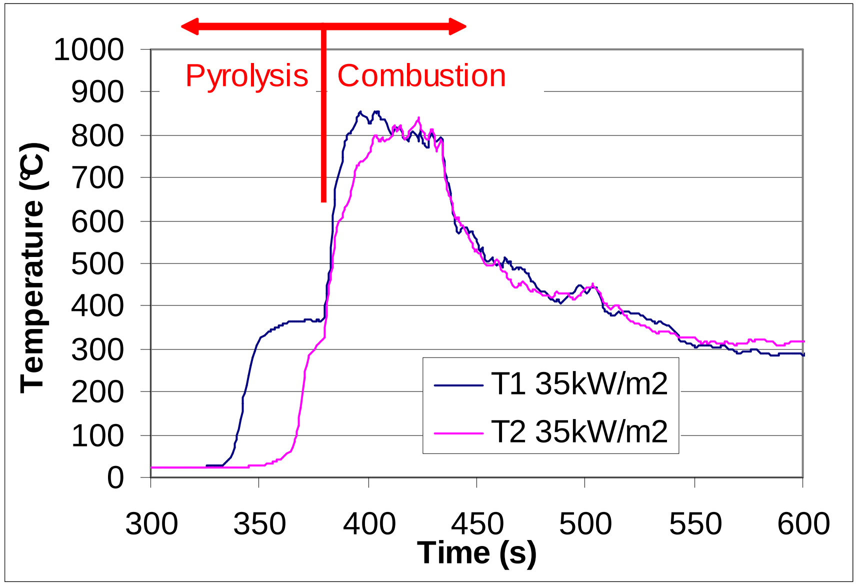


Time-lag between the thermocouples for given temperatures



Temperature at a Heat Flux of 35 kW/m²

Evolution of the internal temperature of the PF



Nonflaming to flaming condition

The ignition temperature measured = **320 °C and 350 °C**.

The **LNE Fire Data Base** (Data No. 3329) = **280 °C**.

(We do not know which was the method for determinate it).

Analysed Chemical Compounds

Gas name	**Formula**	LoD (ppm)	LoQ (ppm)	Method	Concentr. (ppm)
Carbon monoxide	**CO**	1.18	3.93	FTIR - ND	
Carbon dioxide	**CO_2**	22.64	75.47	FTIR - ND	
Nitric oxide	**NO**	2.22	7.40	FTIR	
Water	**H2O**	N/D	N/D	FTIR	
Total hydrocarbons		0.1	0.33	FID	
Sulphur dioxide	**SO_2**	1.12	3.73	FTIR	< LoD
Ammonia	**NH_3**	1.75	5.83	FTIR	< LoQ
Hydrogen chloride	**HCl**	1.54	5.13	FTIR	< LoD
Methane	**CH_4**	4.75	15.83	FTIR	< LoQ
Nitrous oxide	**N_2O**	0.53	1.77	FTIR	< LoQ
Nitrogen dioxide	**NO_2**	1.97	6.57	FTIR	< LoD
Ethylene	**C_2H_4**	21.13	70.43	FTIR	< LoQ
Acetylene	**C_2H_2**	5.28	17.60	FTIR	< LoD
Hydrogen cyanide	**HCN**	1.42	4.73	FTIR	< LoD
Formaldehyde	**$HCHO$**	N/D	N/D	FTIR	< LoD

FTIR = Fourier Transform Infrared Spectroscopy (FTIR)
FID = Flame Ionisation Detector
ND = Non Dispersive Analyser

$$LoQ = 10\sigma$$

$$LoD = 3\sigma$$

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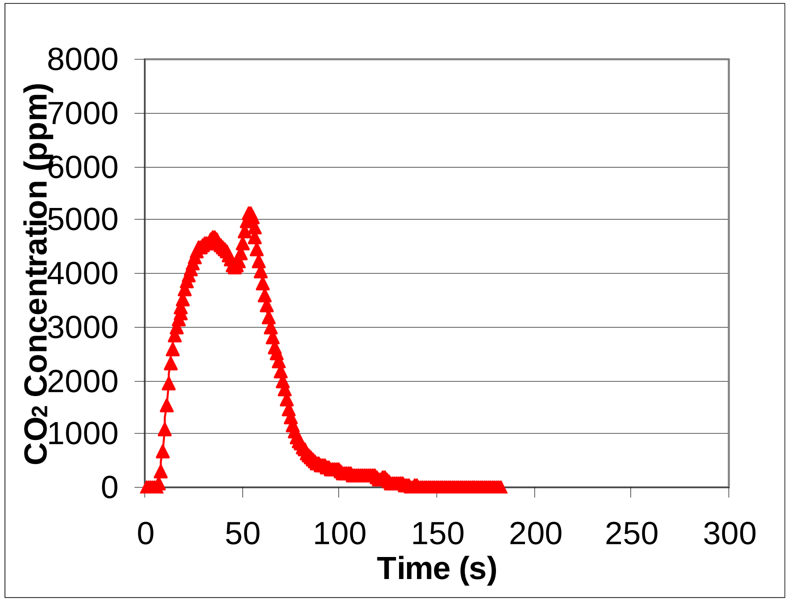
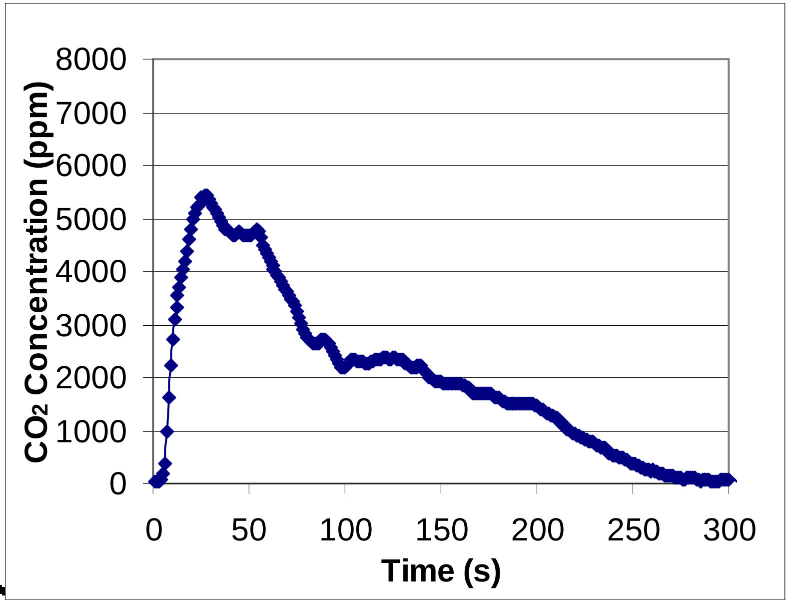
CO_2 release during PF combustion

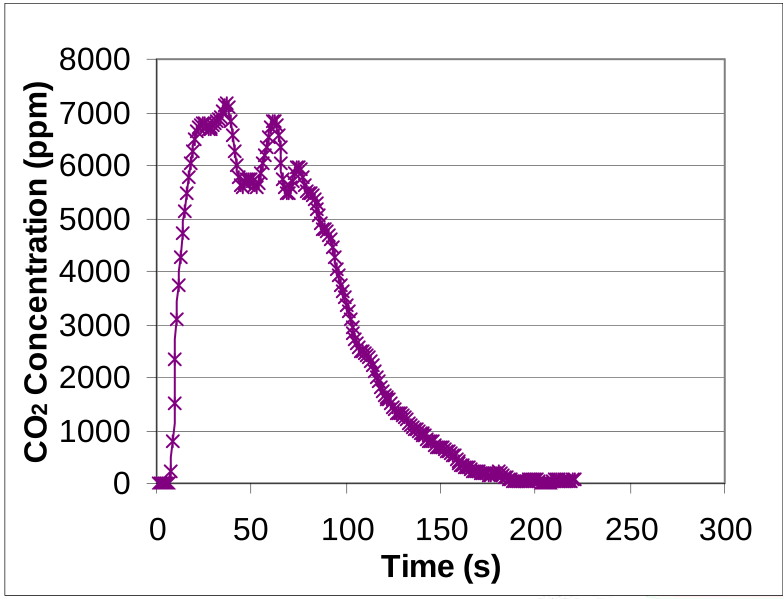
10 kW/m²



30 kW/m²

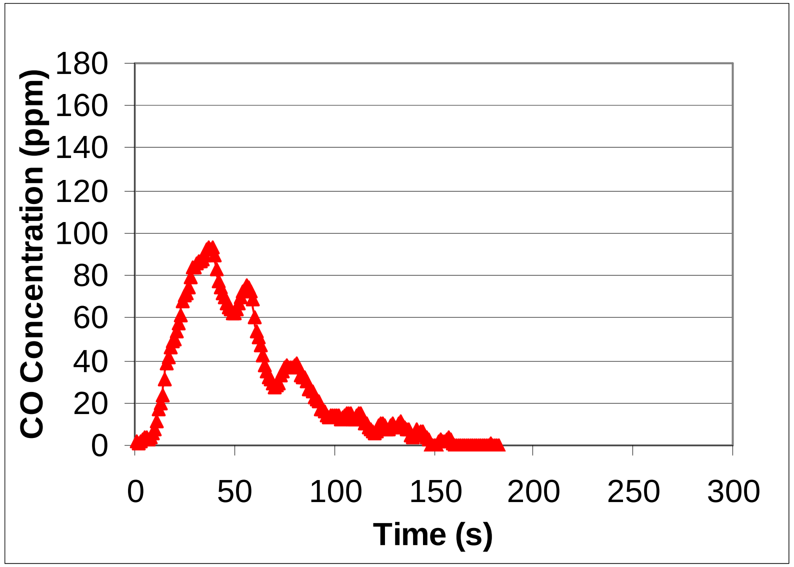


50 kW/m²

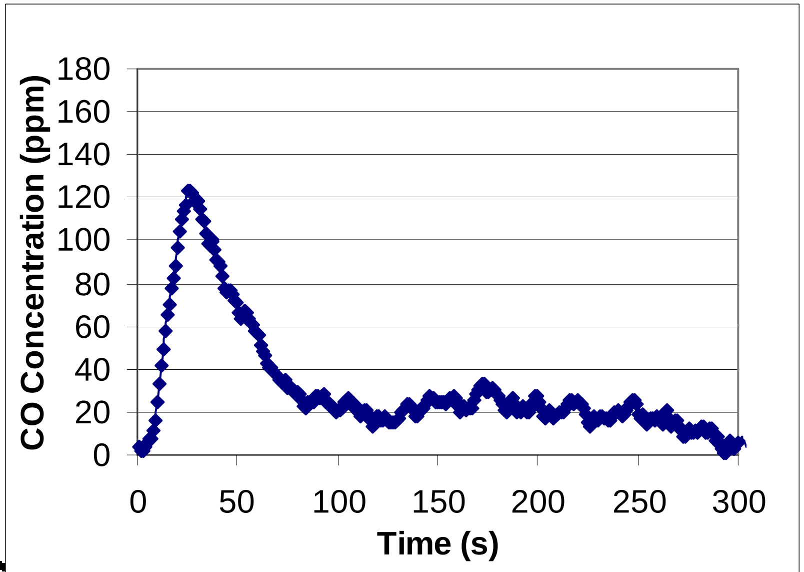


CO release during PF combustion

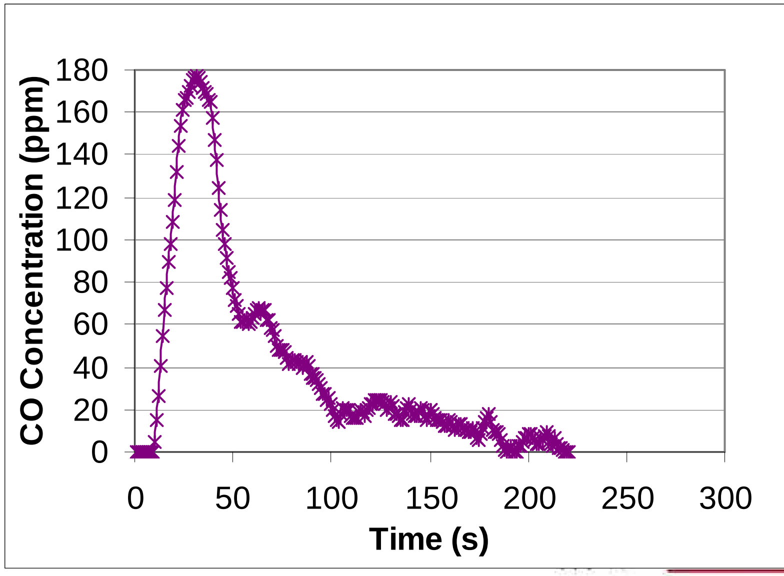
10 kW/m^2



30 kW/m^2

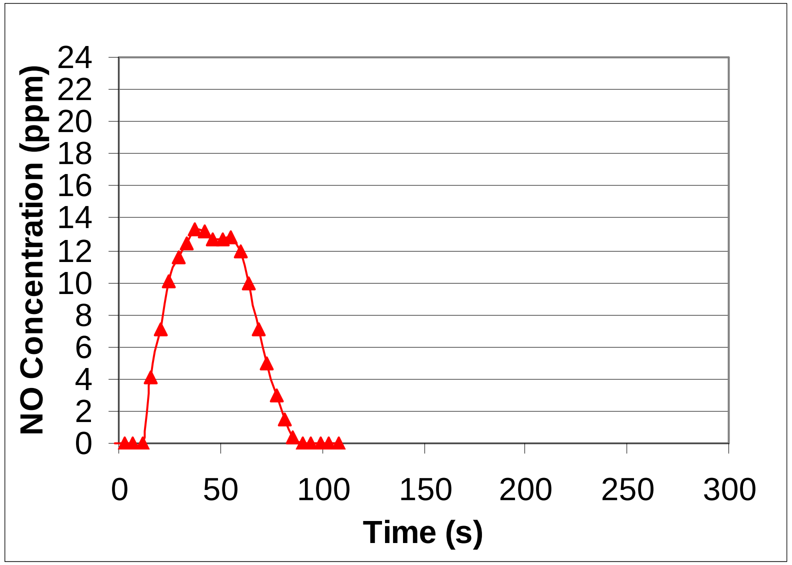


50 kW/m^2

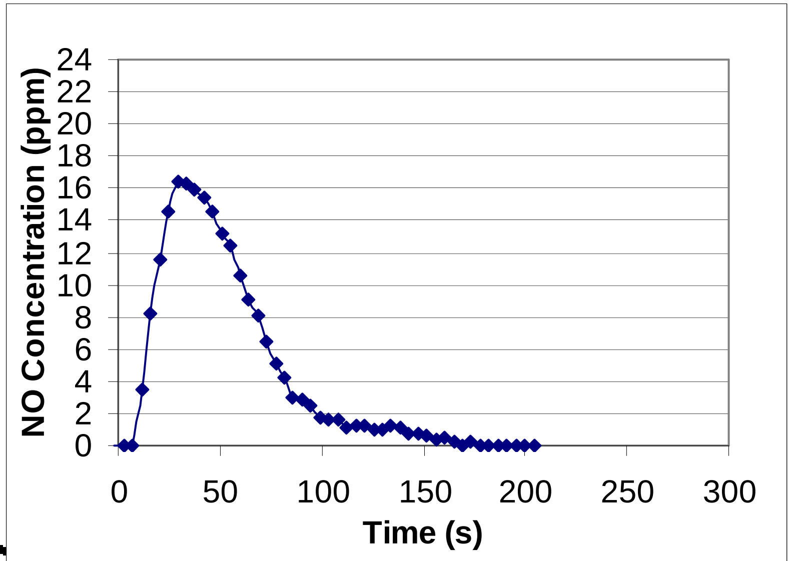


NO release during PF combustion

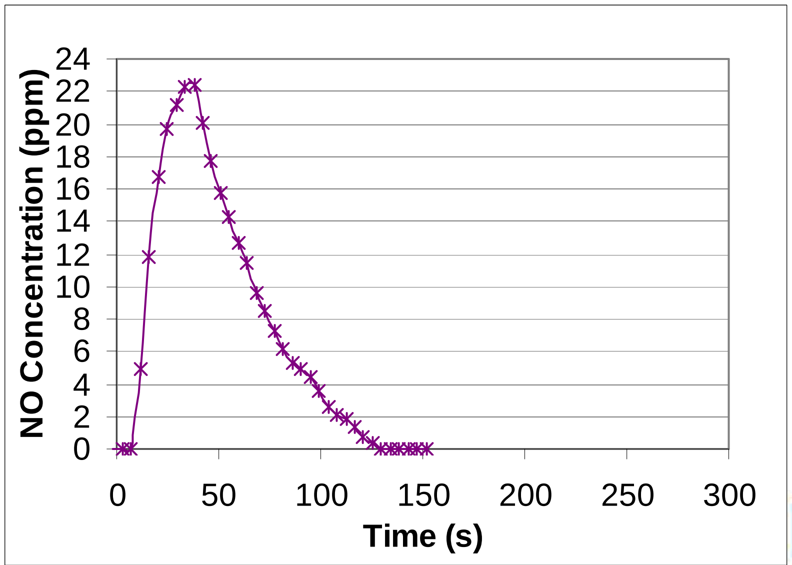
10 kW/m²



30 kW/m²



50 kW/m²



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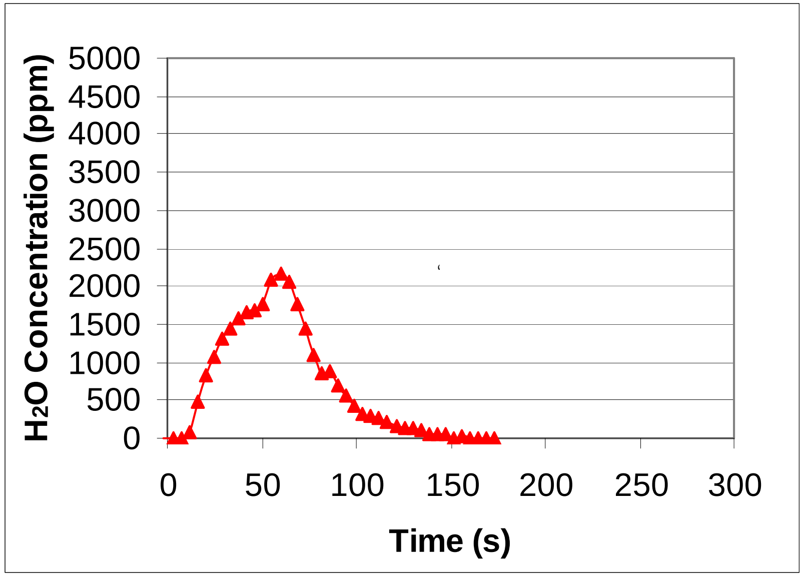
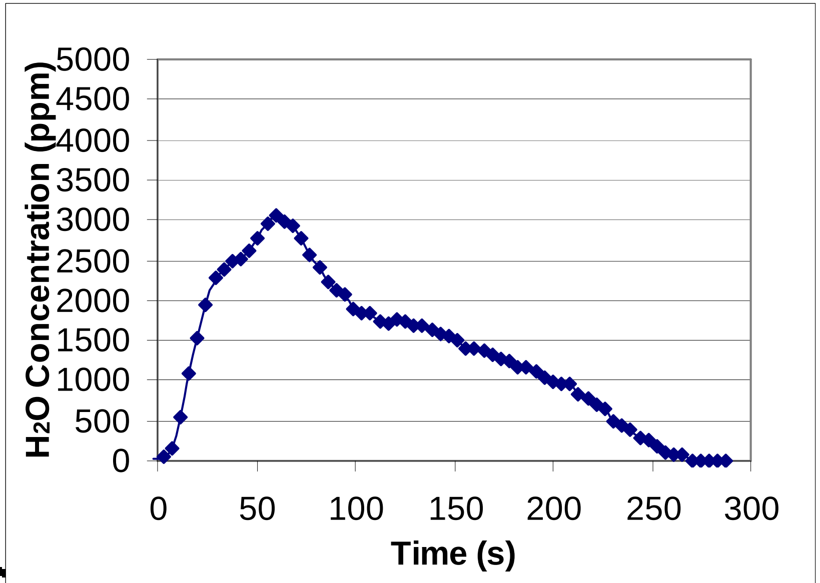
H_2O release during PF combustion

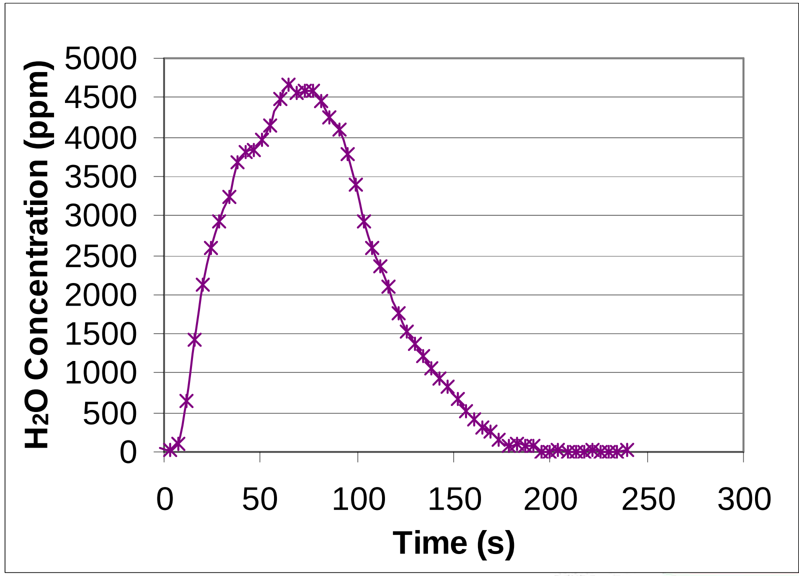
10 kW/m²



30 kW/m²



50 kW/m²



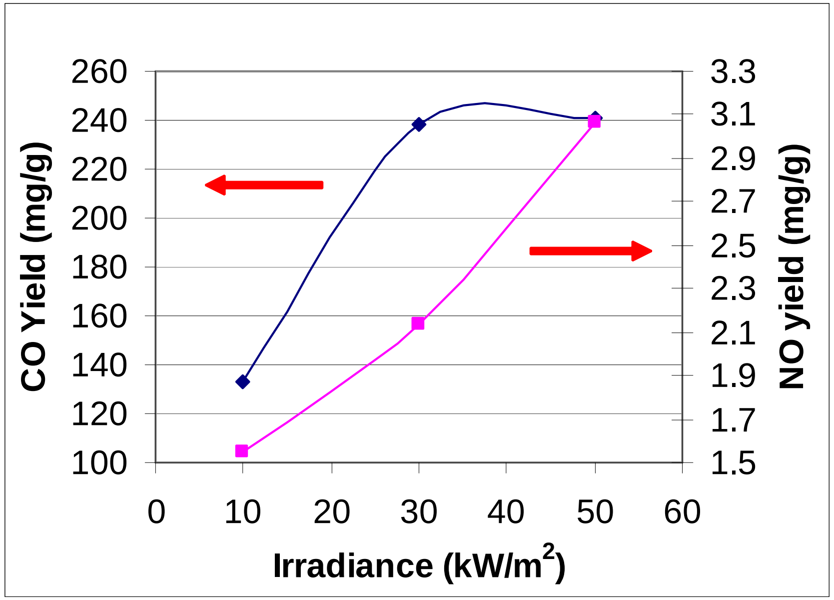
CO_2, CO, H_2O and NO yield

$$Y_b = \frac{\Delta t \cdot V \cdot MW_b / V_{mol \cdot b}}{m}\left(\frac{1}{2}x_{b,1} + \sum_{i=2}^{i=n-1} x_{b,i} + \frac{1}{2}x_{b,n}\right)$$

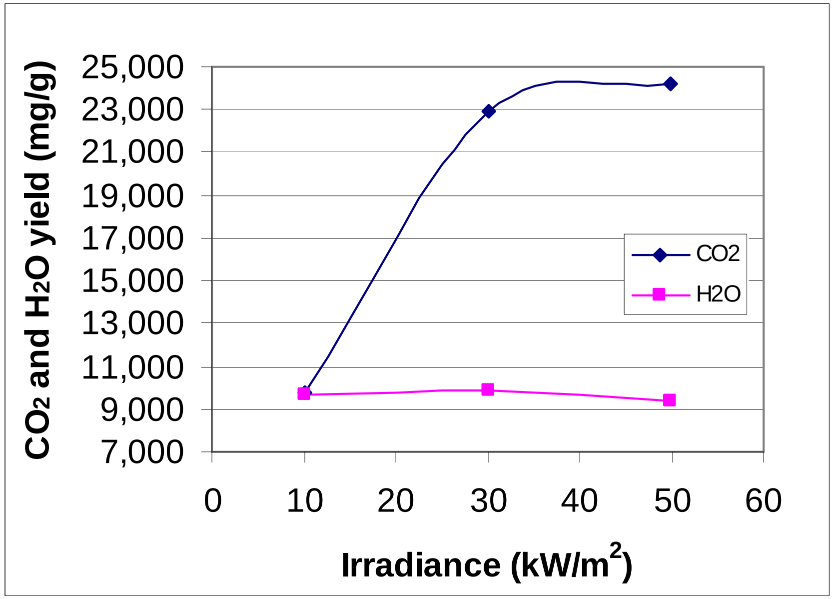
Where:

Yb	Yield of the chemical gas b (mg/g)
Δt	Time between data (s)
V	Volume flow in the cone calorimeter exhaust (l/min)
MWb	Molar mass of the gas b (g/mol)
Vmol·b	Molar volume of the gas b (l/mol)
m	Mass of the PF sample (g)
xb,i	Concentration of the gas b at the time i

CO and NO yield



CO_2 and H_2O yield



$$C_1H_{1.63}O_{0.27}N_{0.08} + 1.30O_2 \rightarrow 0.98CO_2 + 0.02CO + 0.82H_2O + 0.08NO$$

A « real » combustion equation for ventilated fires

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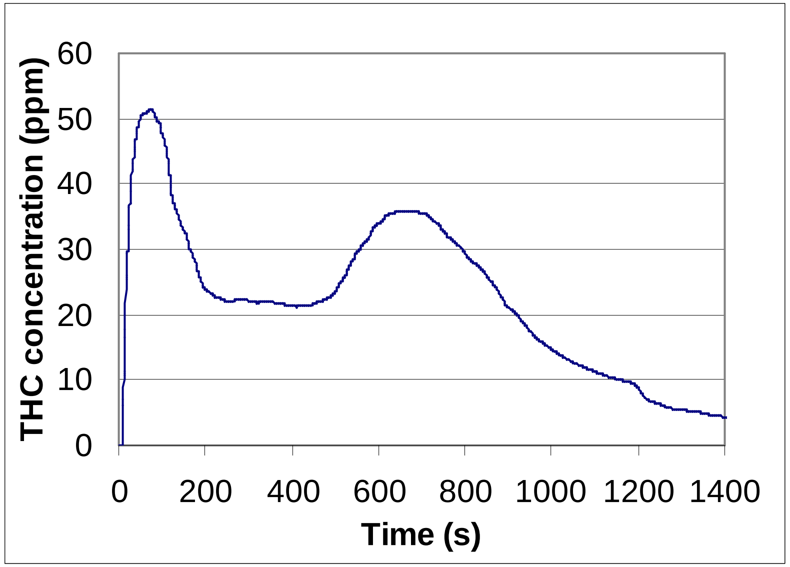
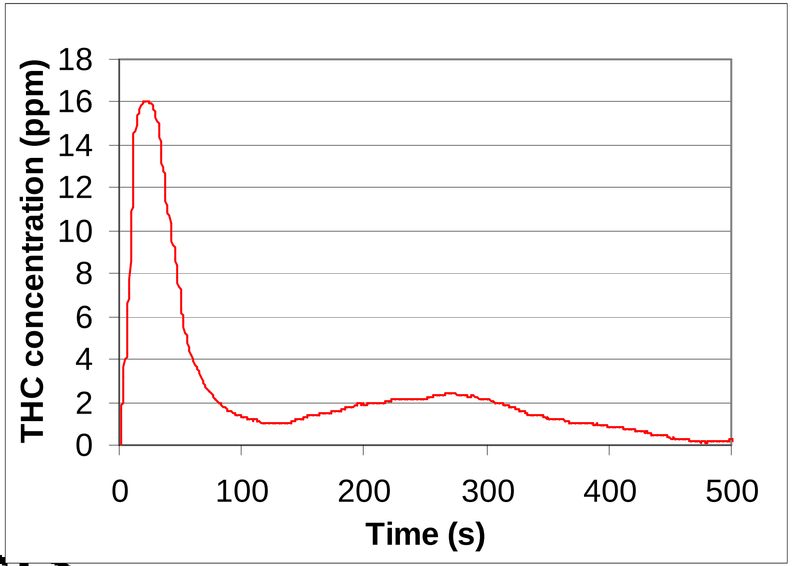
THC release during PF combustion

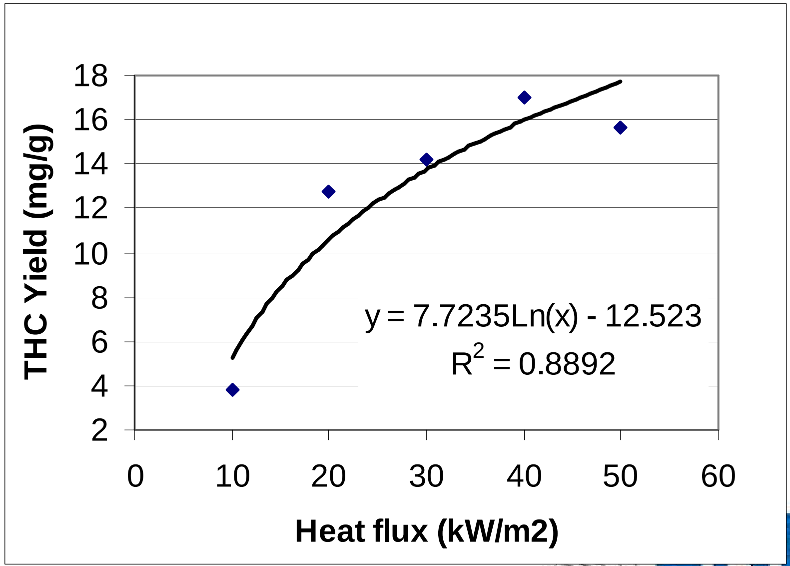
THC release in **nonflame** condition at 30 kW/m²



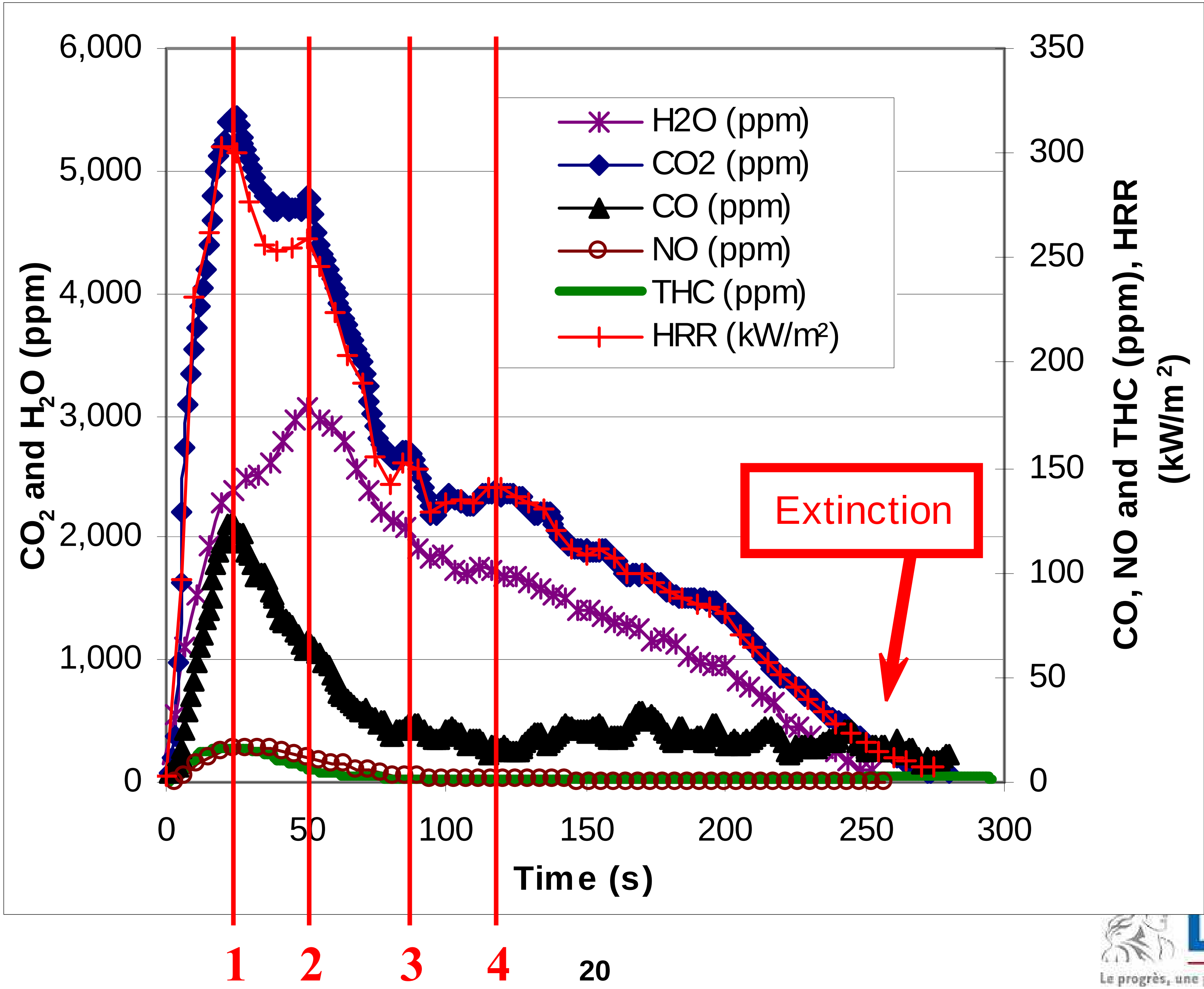
THC release in **flame** condition at 30 kW/m²



THC release in **flame** in function of heat flux



HRR and gases off during combustion at 30kW/m²



Thank you !

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Background Slides

The instruments and the measurements

INSTRUMENT	MEASUREMENT
Cone Calorimeter	Thermal properties and fire behaviour of PF
Fourier Transform Infrared Spectroscopy (FTIR)	Chemical species leaked during pyrolysis and combustion
Exhaust gas temperature measurement	Exhaust gas temperature used for molar correction of gas-off
Inner Polyurethane Foam temperature	Measurement of the inner temperature of the foam during degradation
Flame Ionisation Detection (FID)	Total hydrocarbons production
Camera	Evaluation of foam degradation

Scheme of the PhD research work

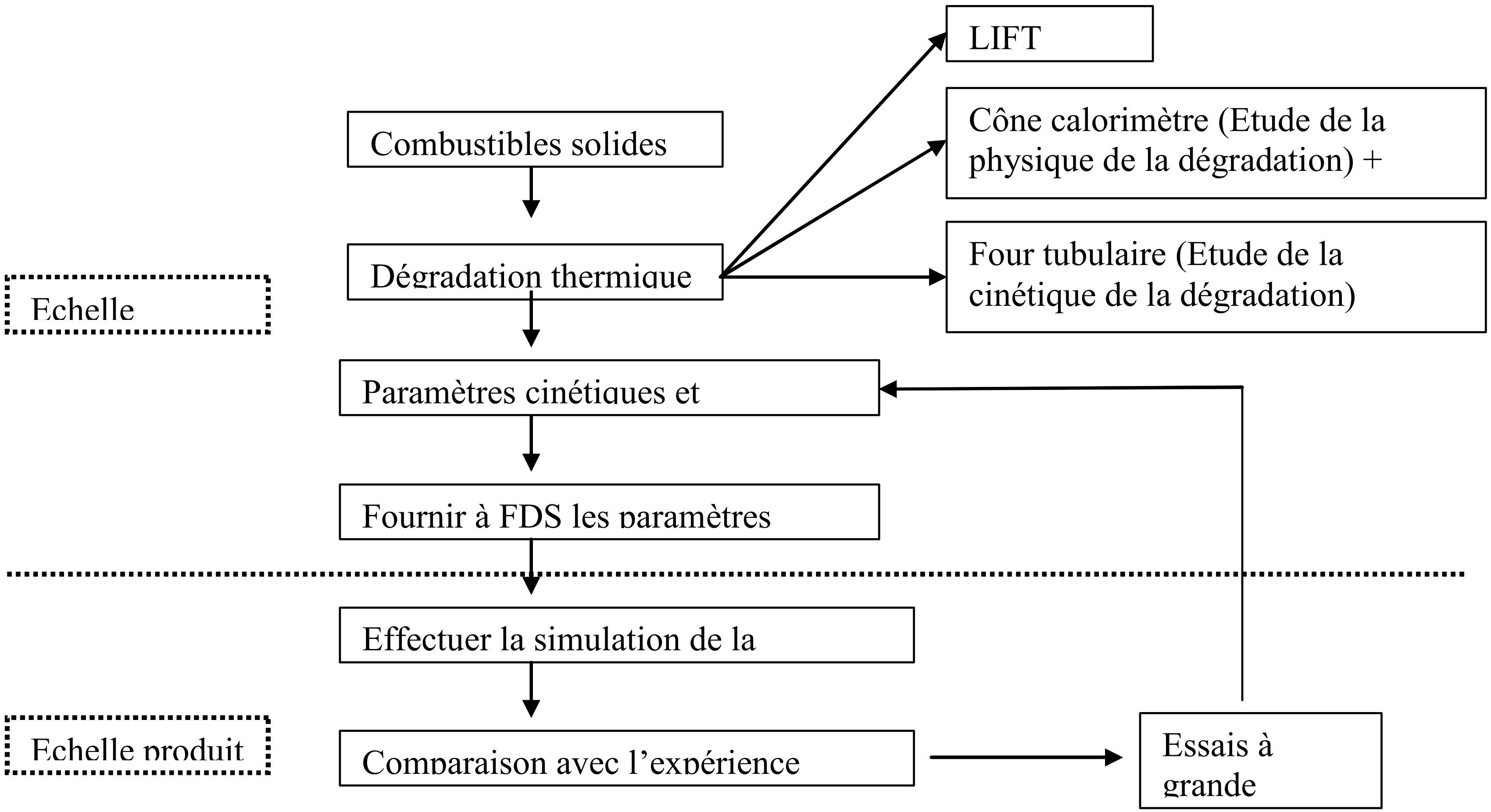

Figure 1 : schéma des études à réaliser pendant la thèse