Fire Toxicity – the burning issue?

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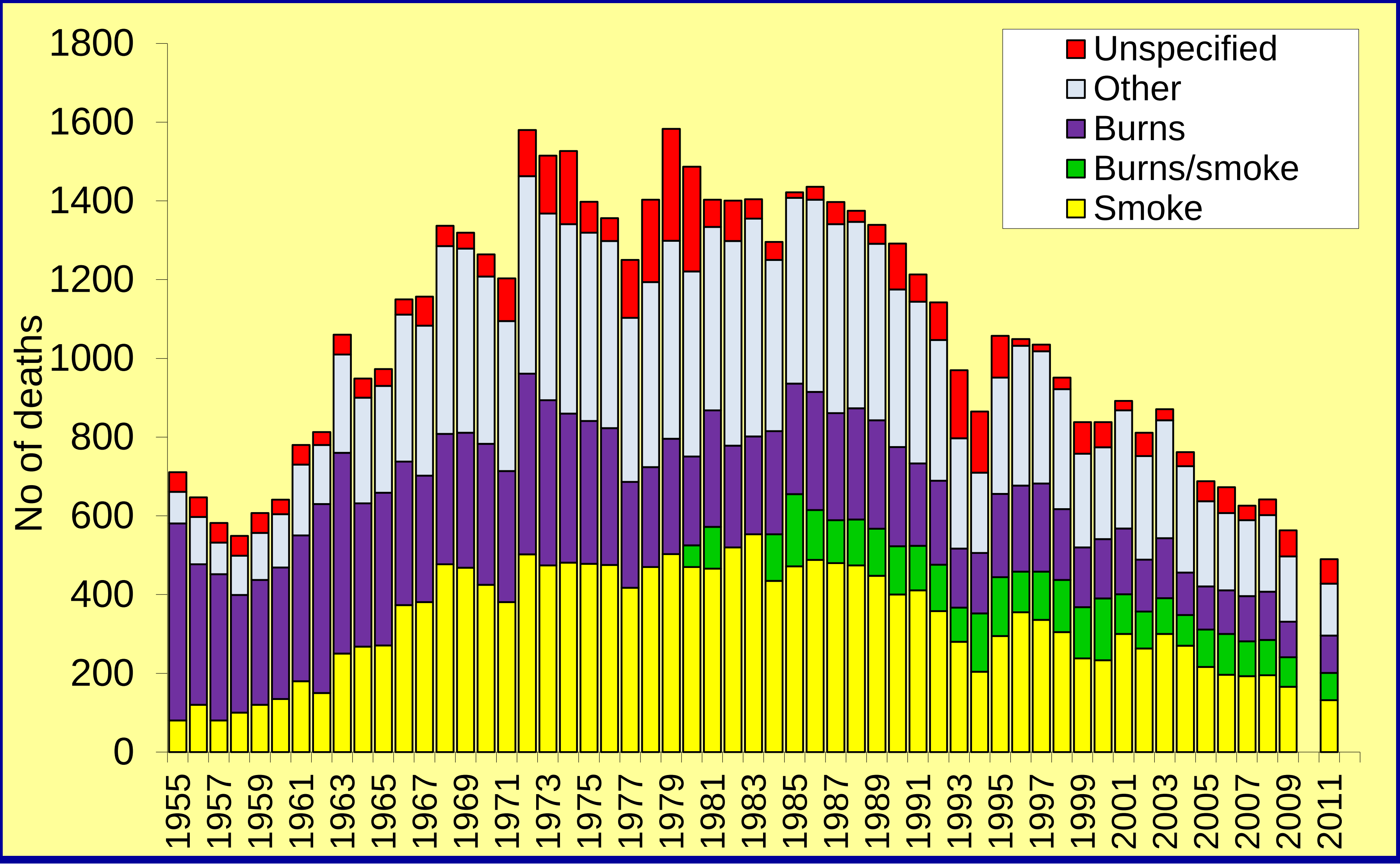
Fire Toxicity

- Most fire deaths are caused by inhalation of toxic gases, and the proportion is increasing
- Gas phase flame retardants increase the yield of major toxicants such as CO and HCN, and increase yields of hydrocarbon irritants and smoke.

UK Fire Deaths (1955-2011)



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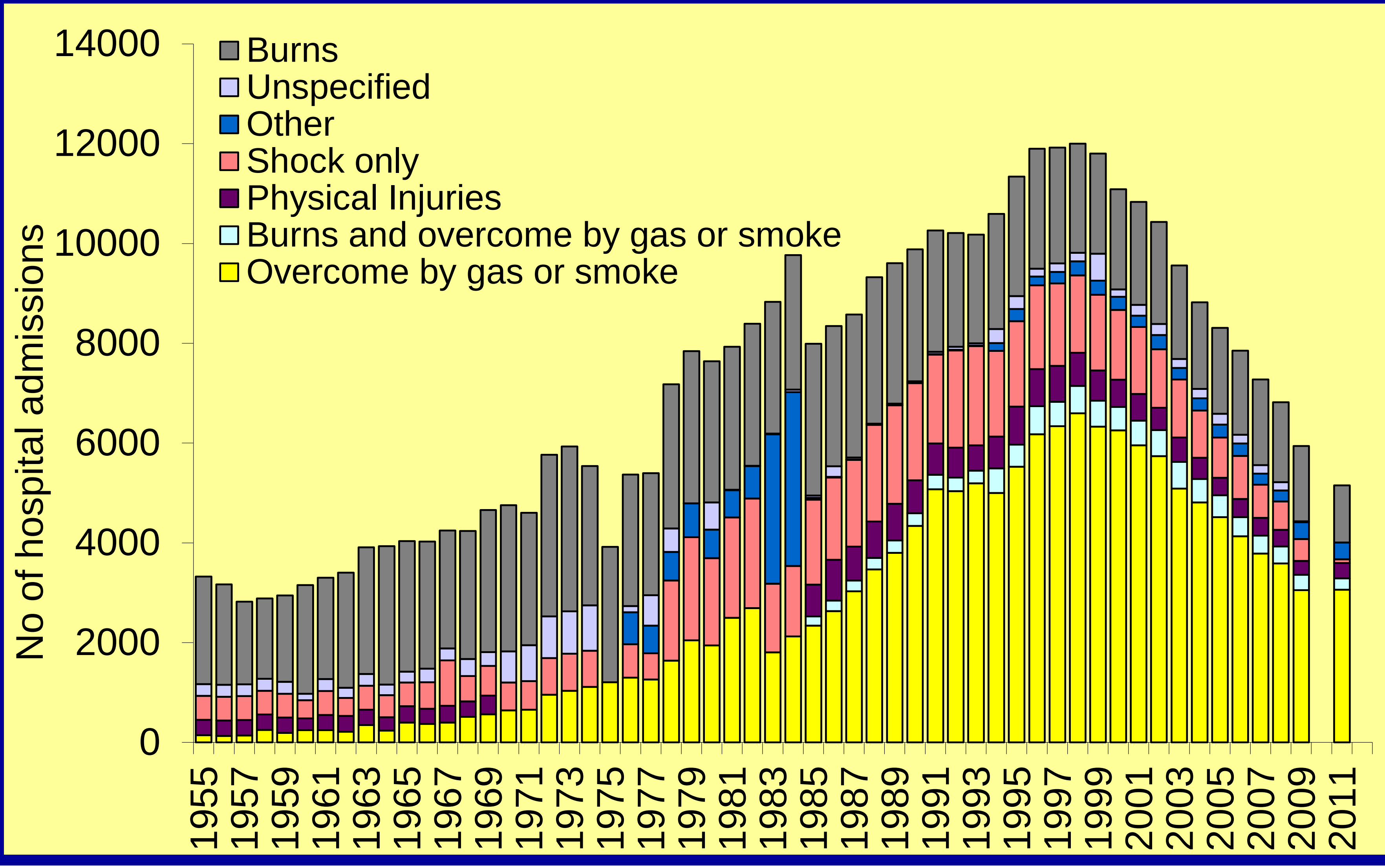
UK Fire Injuries (1955-2011)



Regulatory Requirements for fire toxicity – why do we need to measure it?

- Buildings
  - Included in remit for construction products directive (EU)
  - Mandatory in Japan and China, partially regulated in Poland and Russia, with some regulation in France and Germany
  - Necessary for calculation of ASET for performance based design
  - Acidity classification for cables in EU
- Mass Transport
  - Air transport
  - Shipping
  - Rail
  - Road vehicles – none!
- Performance based design offers an alternative to meeting each regulatory requirement.
  - Provided the available safe escape time (ASET), before the escape route becomes blocked by smoke, heat or toxic gases, is greater than the required safe escape time (RSET) then any construction materials etc may be used. Fire safety then relies on valid modelling of appropriate fire scenarios.
  - Need to know yield and toxic potency of each component of the fire effluent and use ISO 13571 to predict toxicity.

Stages of Fire Growth and their Toxicological Significance

Fire Stage	Smouldering	Well-ventilated flaming	Small under-ventilated	Post-flashover
Toxicity	High	Low	High	High
Volume of effluent	Very small	Small	Large	Very large
Toxicological significance				

Tests that only replicate well-ventilated conditions should not be used for assessment of fire toxicity!

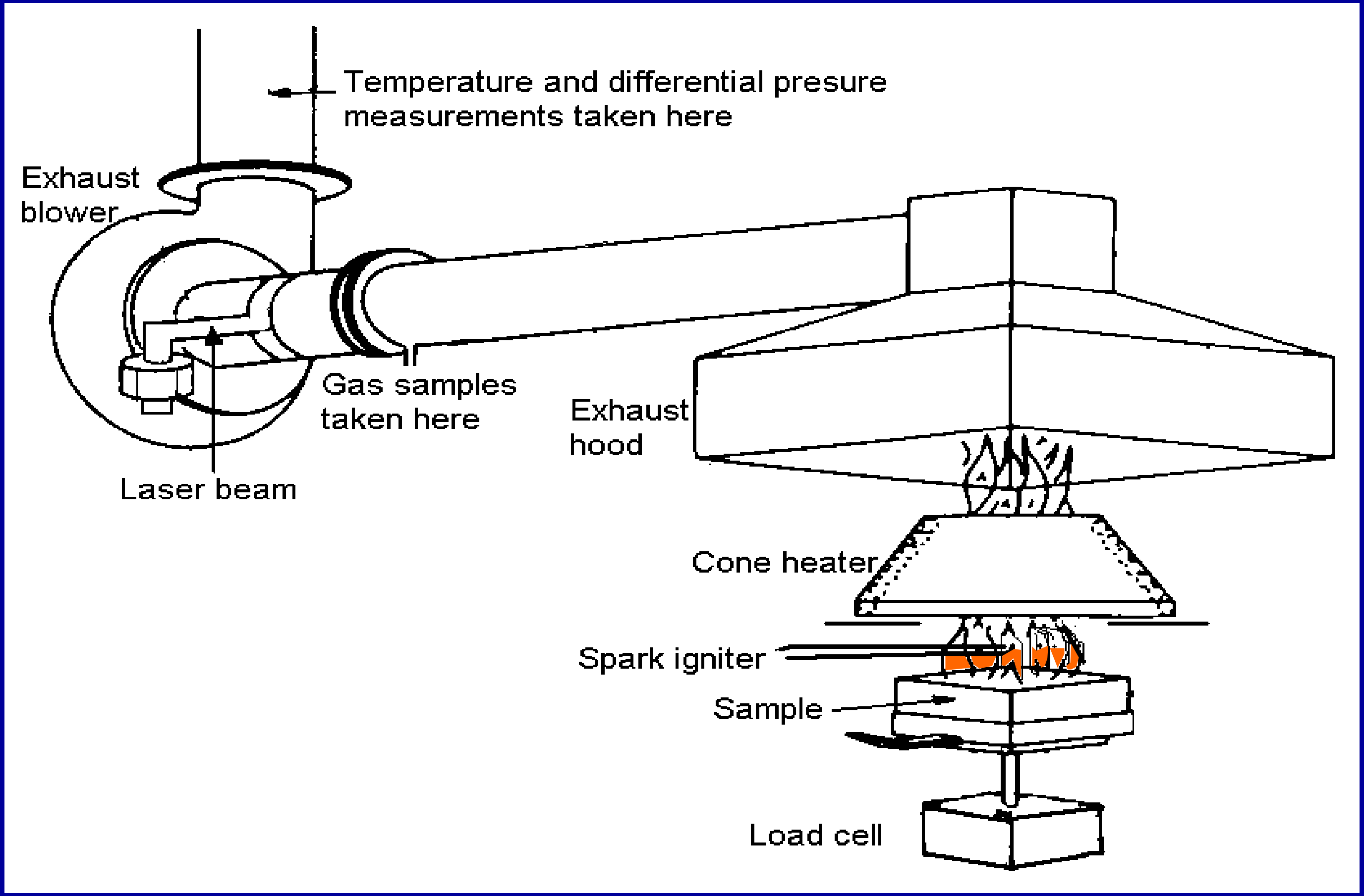
Standard methods for toxicity assessment

3 general approaches:

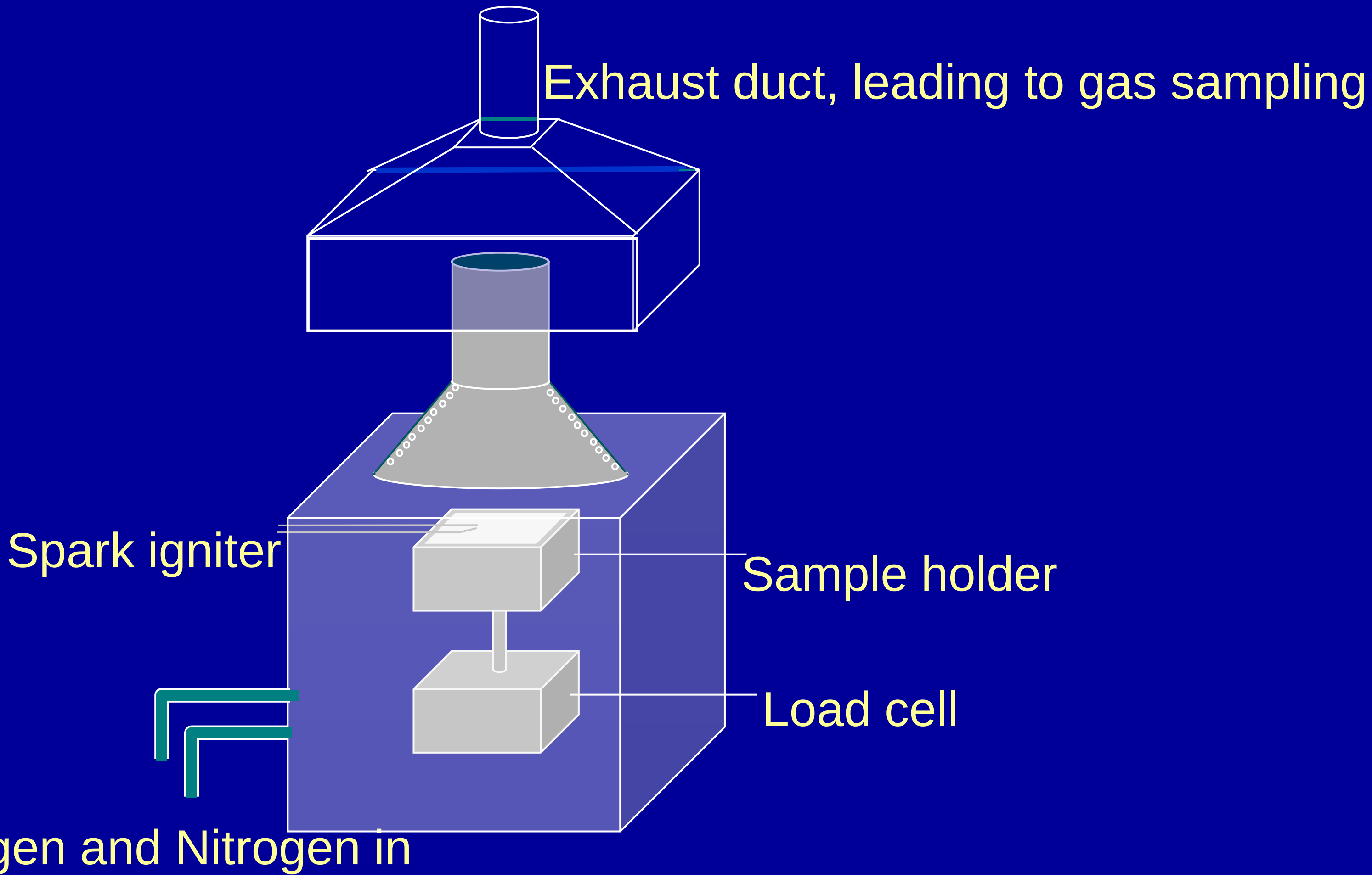
- Well-ventilated (e.g. Cone calorimeter, controlled atmosphere cone calorimeter)
- Closed box tests (e.g. NBS Smoke Box)
- Tube furnaces (e.g. NFX 70-100, Purser furnace, Fire Propagation Apparatus)

T R Hull and K T Paul, *Bench-Scale Assessment of Combustion Toxicity – A Critical Analysis of Current Protocols* Fire Safety Journal, 42, 340-365 (2007).

Cone Calorimeter (well-ventilated)



The Controlled Atmosphere Cone Calorimeter



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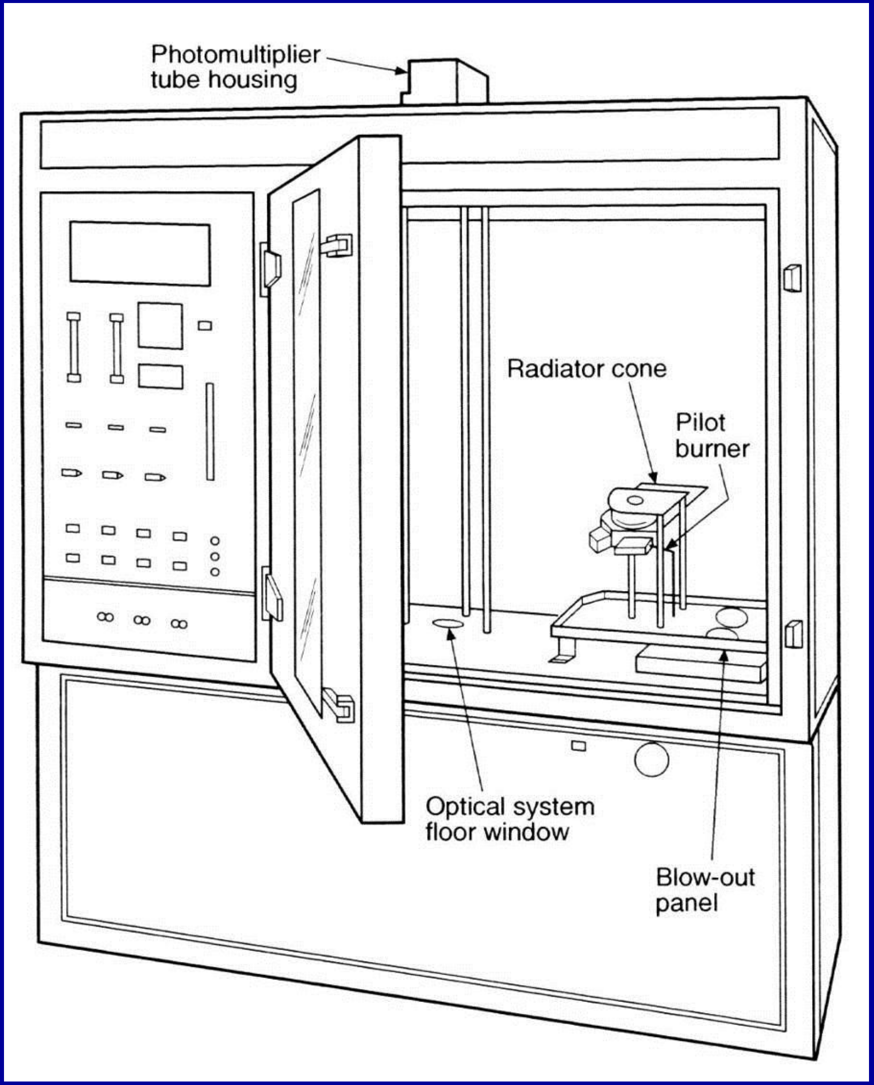
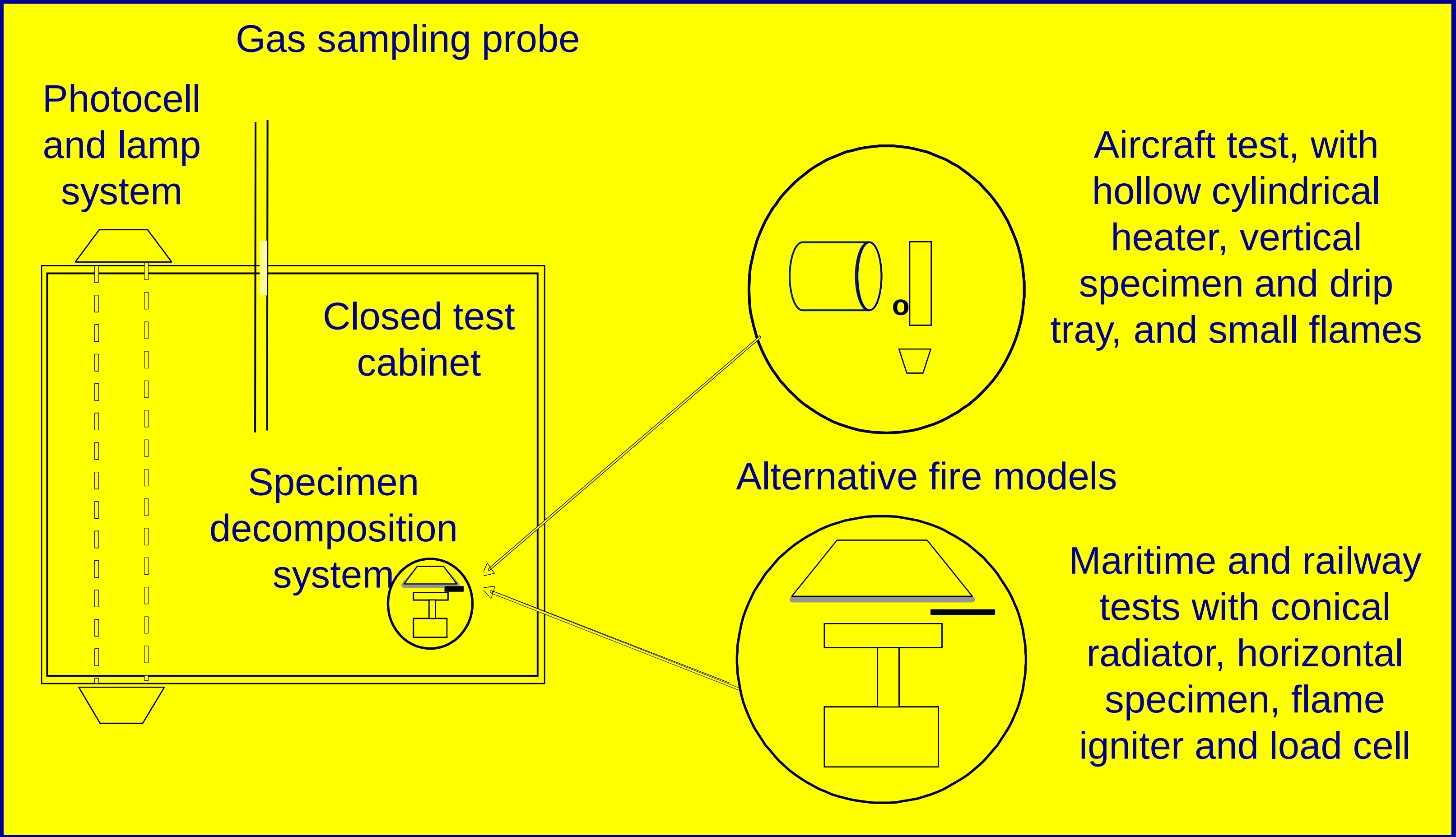
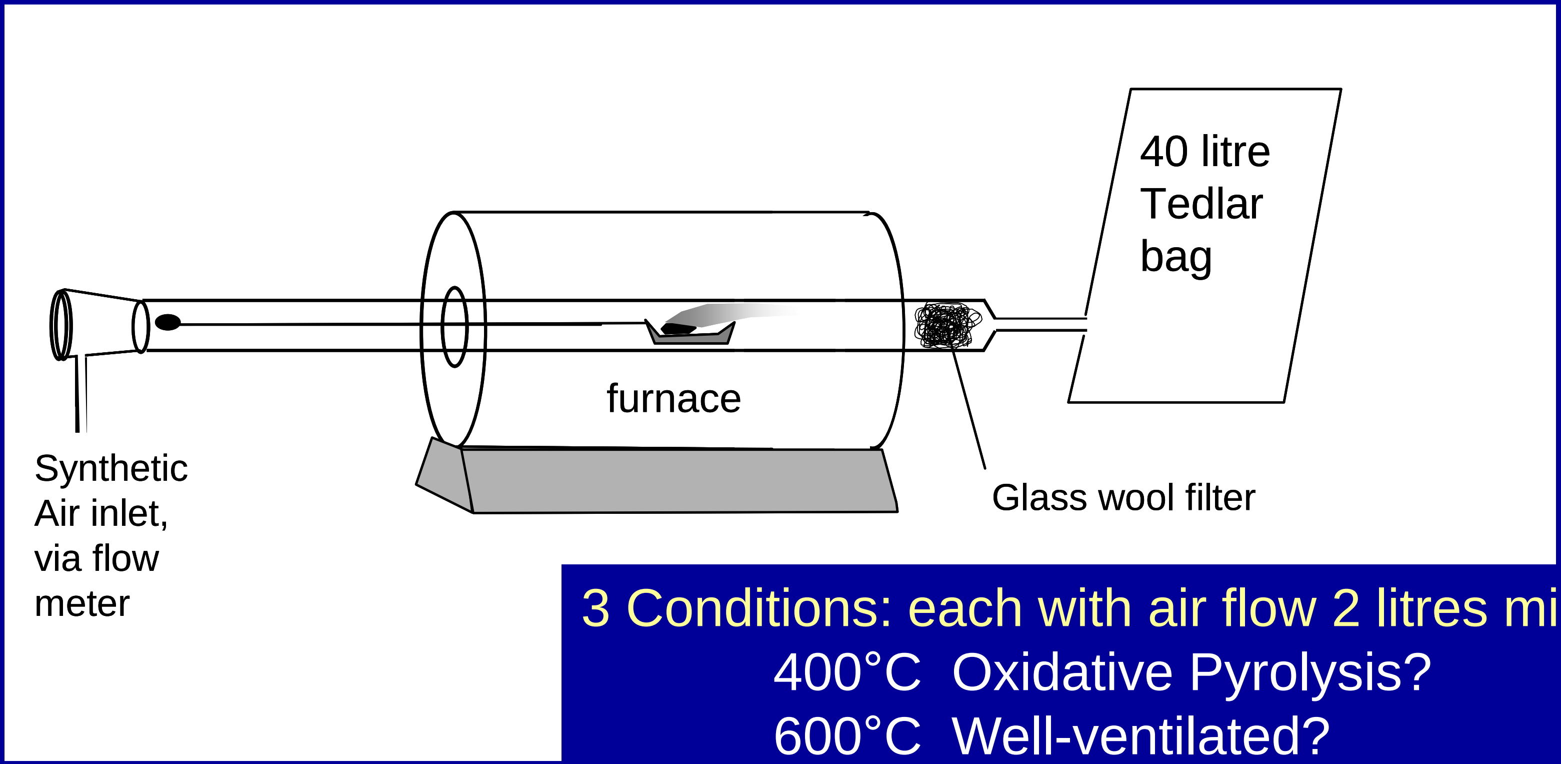
NBS Smoke Chamber (closed box)



Details of fire models



The NF X 70-100 Apparatus (simple tube furnace)



3 Conditions: each with air flow 2 litres min^{-1}

400°C Oxidative Pyrolysis?
600°C Well-ventilated?
800°C Under-ventilated?

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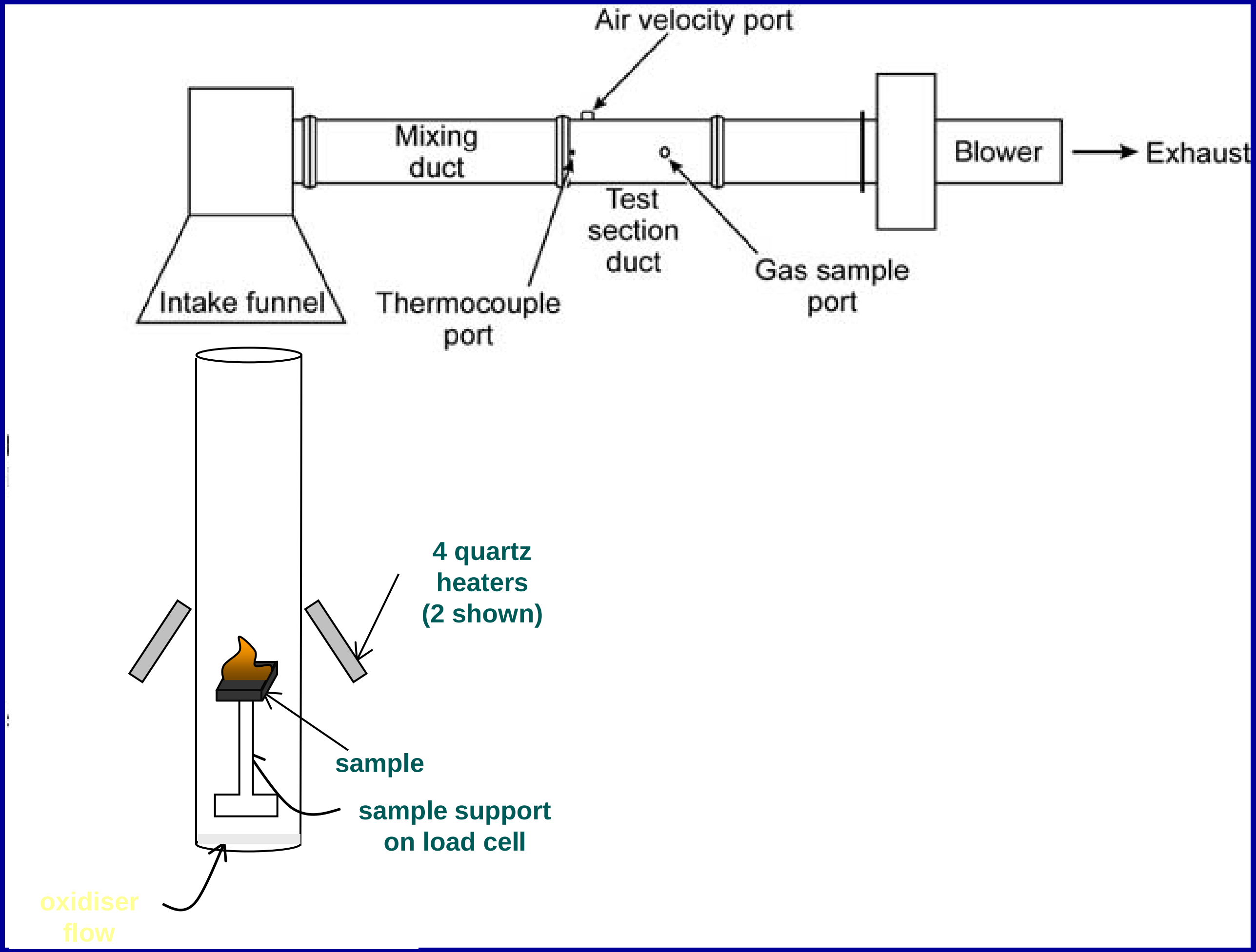
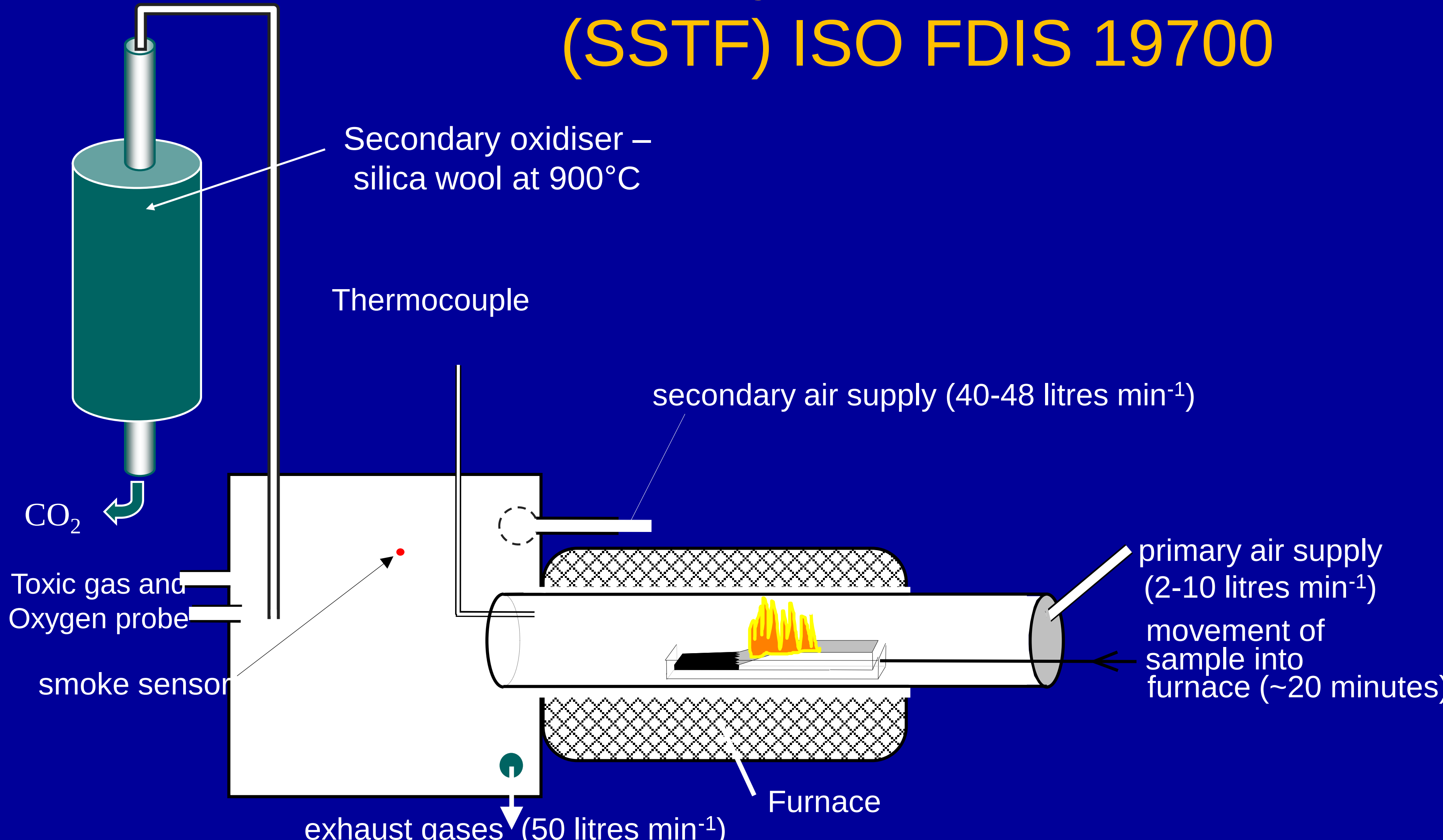
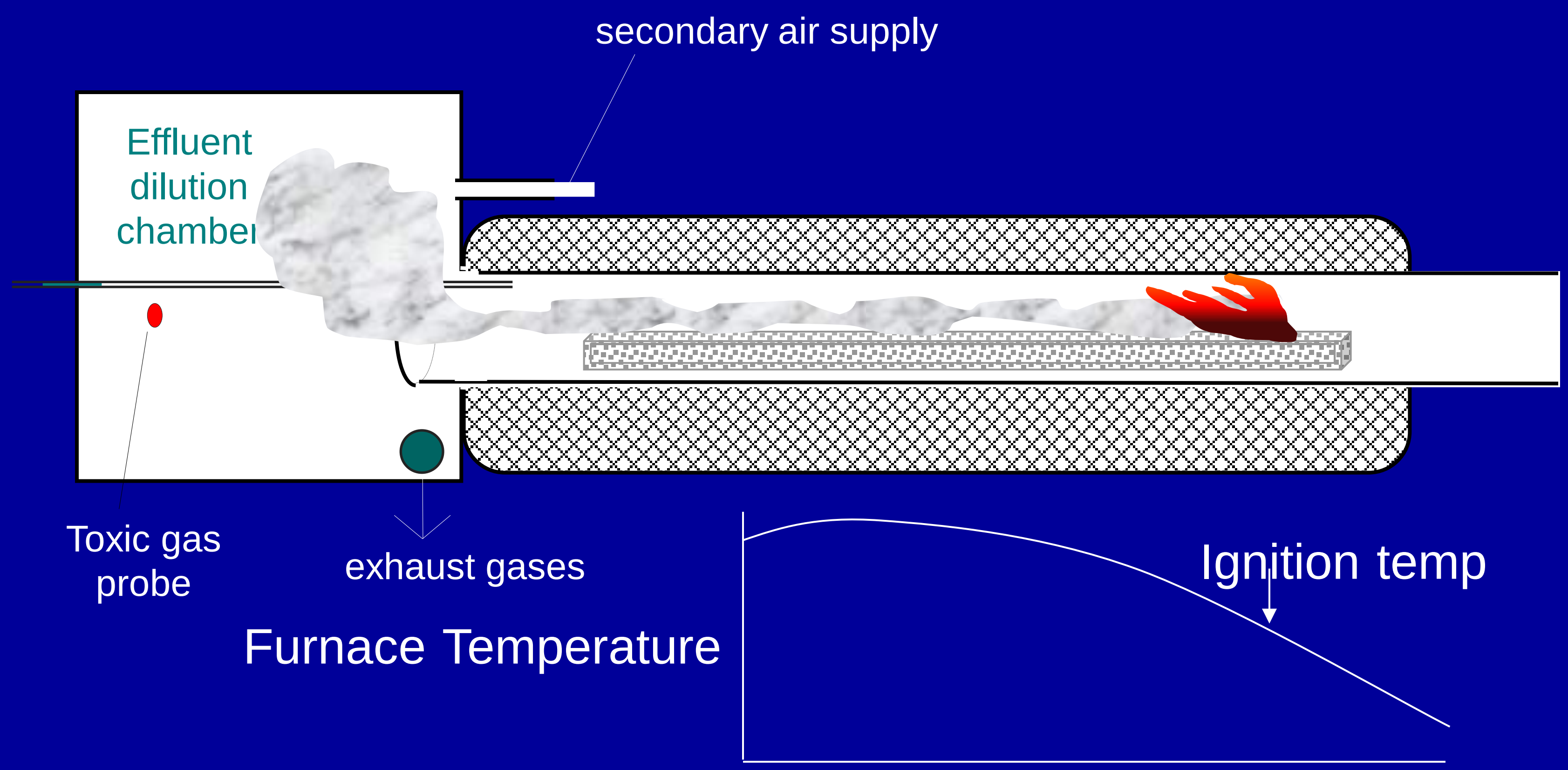
The Fire Propagation Apparatus



The Steady State Tube Furnace (SSTF) ISO FDIS 19700



Steady state burning in the Purser Furnace



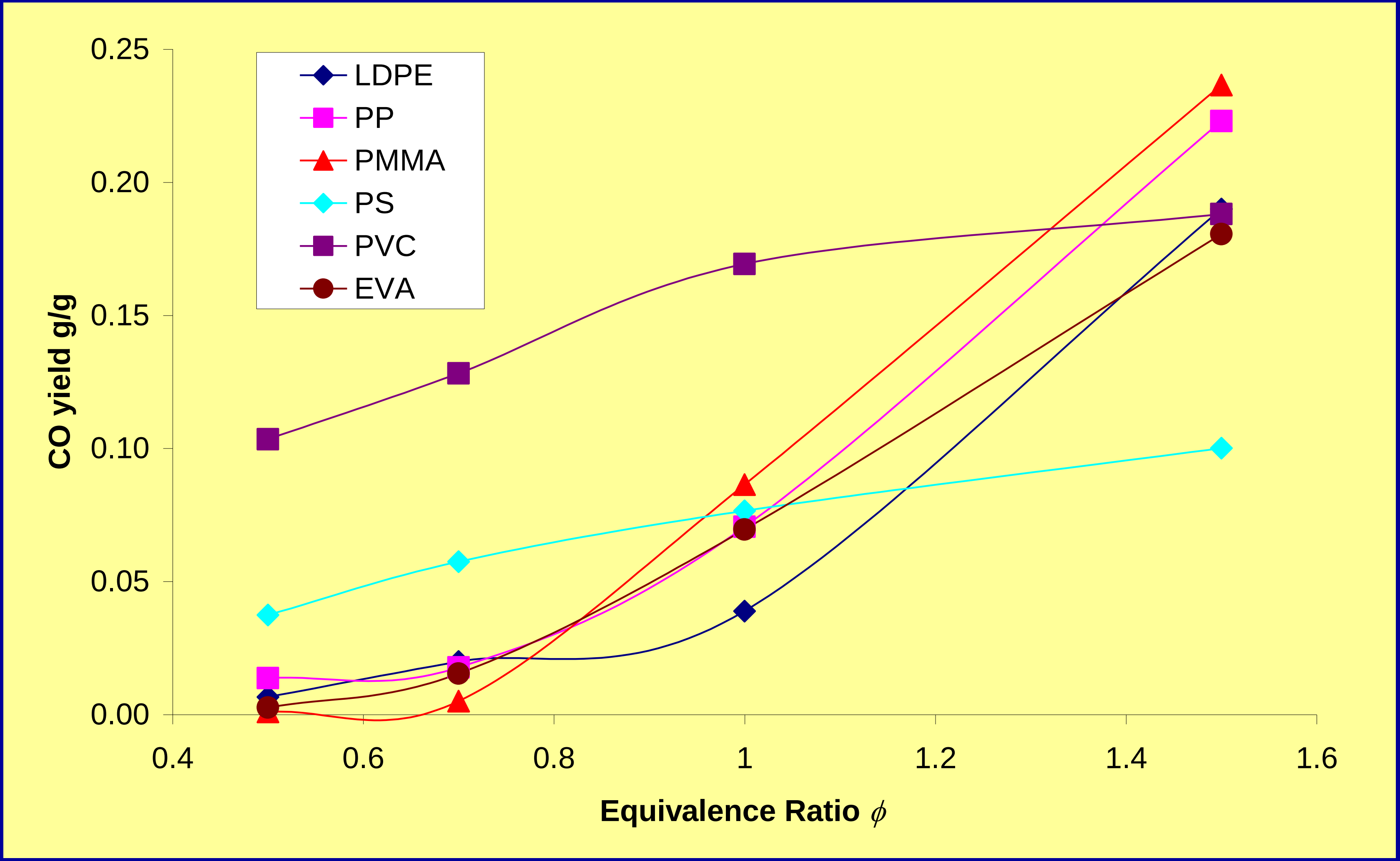
The Equivalence Ratio ϕ

This is used to define the fire condition

$$\phi = \frac{\text{Actual Fuel/Air Ratio}}{\text{Stoichiometric Fuel/Air Ratio}}$$

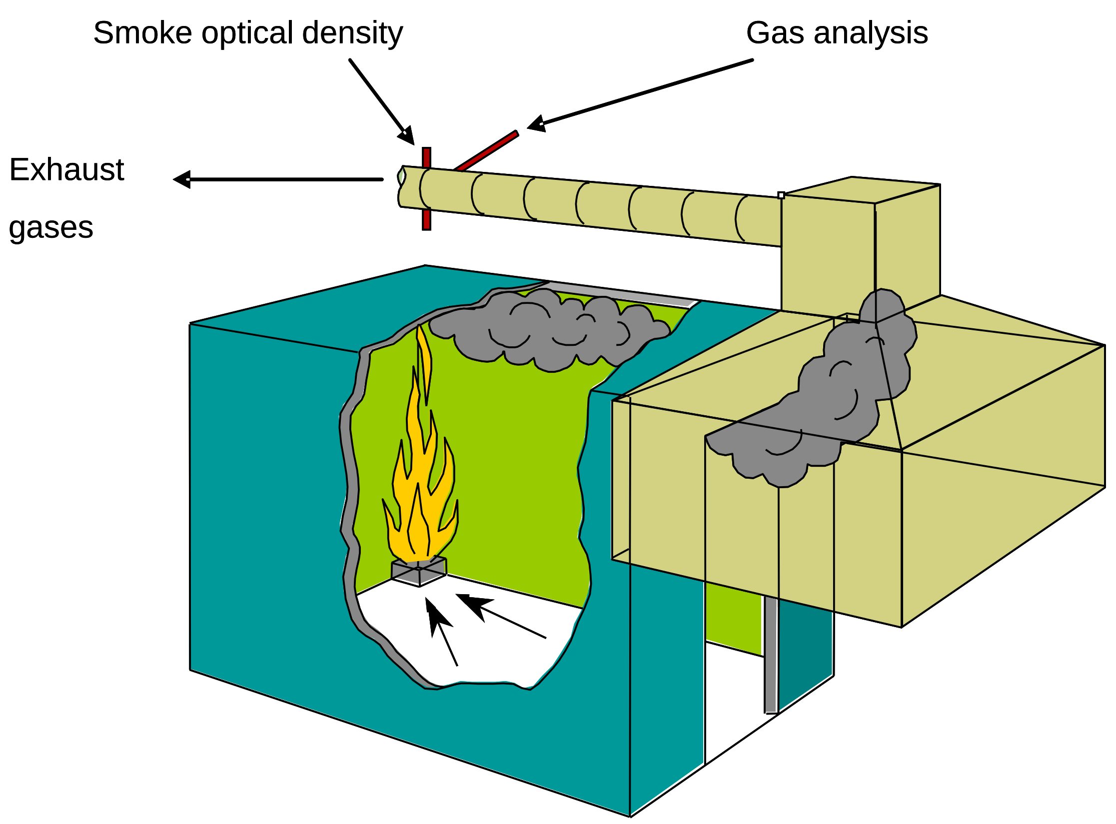
- For "stoichiometric" combustion to CO_2 and water, (or the O_2 requirement at 900°C) $\phi = 1$.
- For well-ventilated fires, $\phi = 0.5$
- For fuel-rich (vitiated) combustion, $\phi = 2$.

CO yield from steady state tube furnace

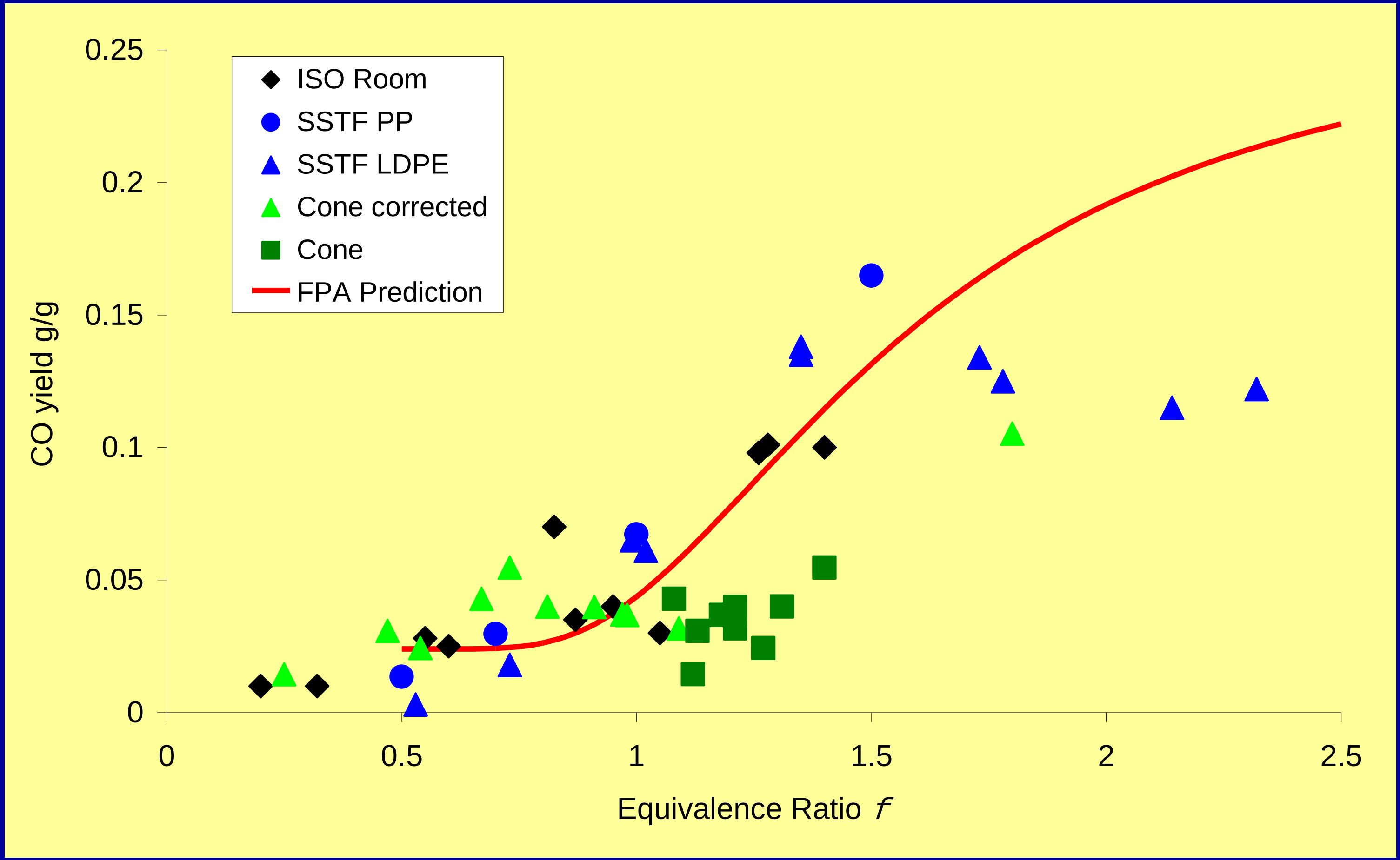


T R Hull, J M Carman and D A Purser, *Prediction of CO evolution from small-scale polymer fires*. Polymer International **49,** 1259, (2000).

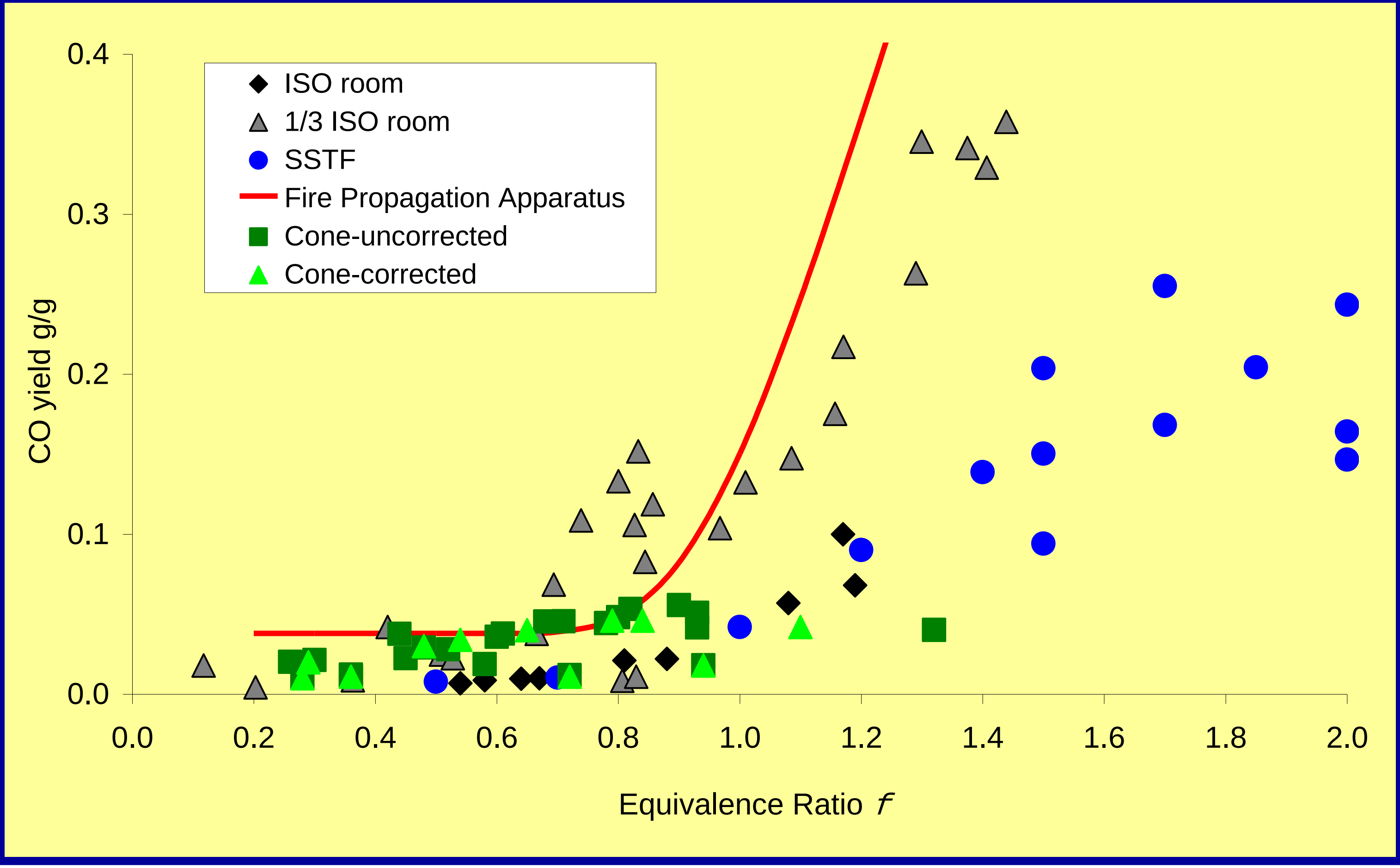
Comparison of bench-scale and large scale toxicity - ISO 9705 room



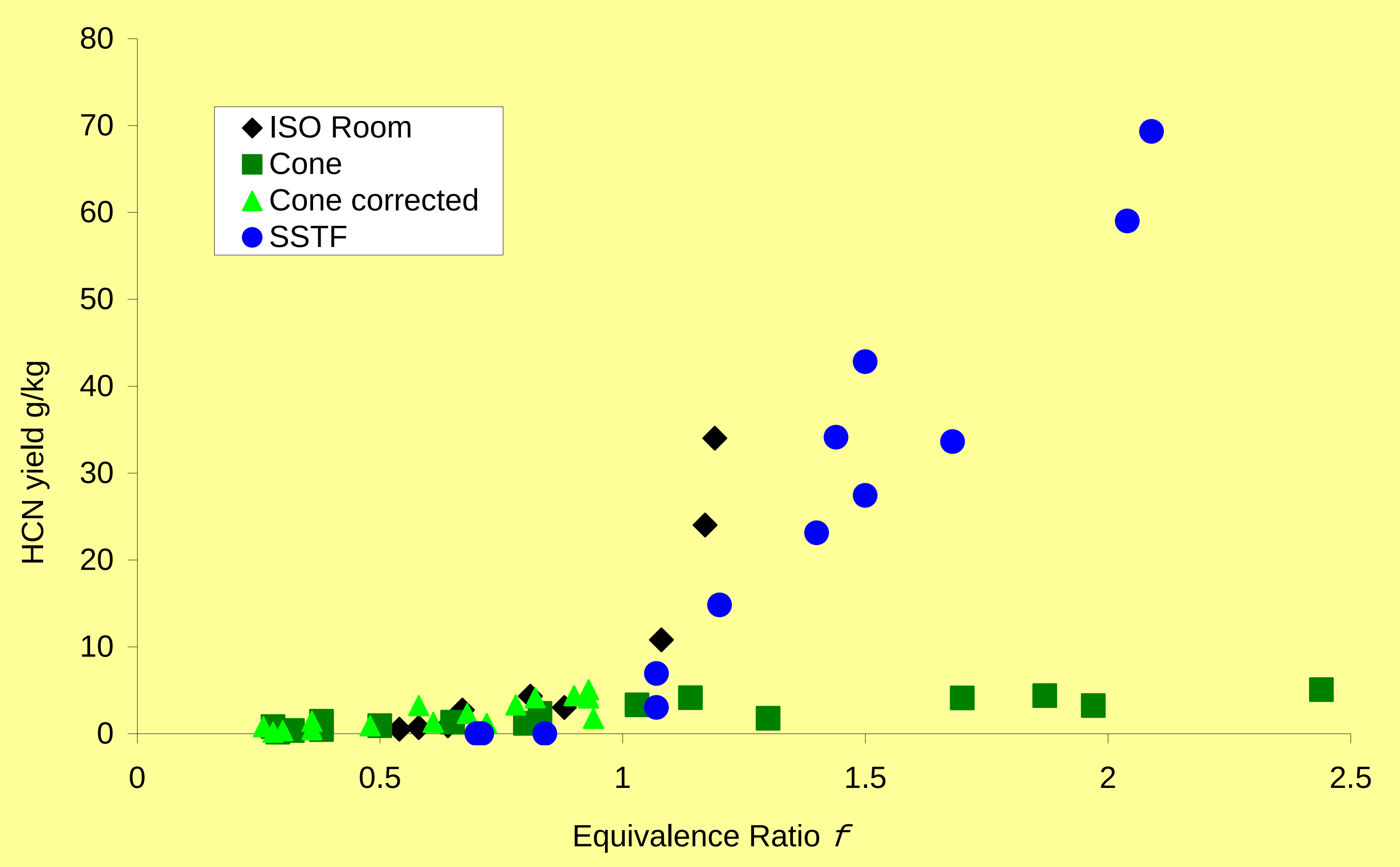
Comparison of Bench and Large-scales for CO yield from PP



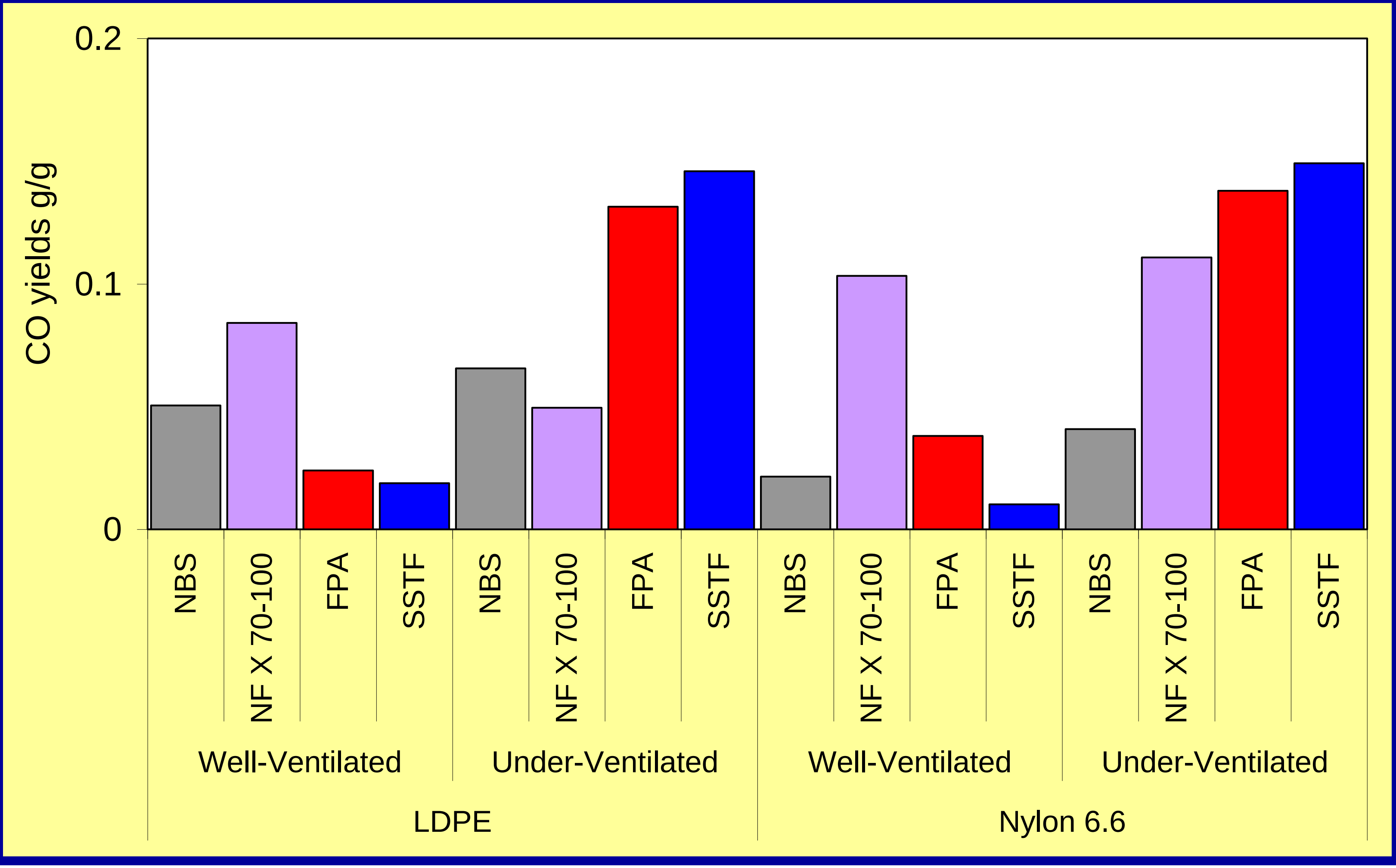
Comparison of Bench and Large-scales for CO yield from PA 6.6



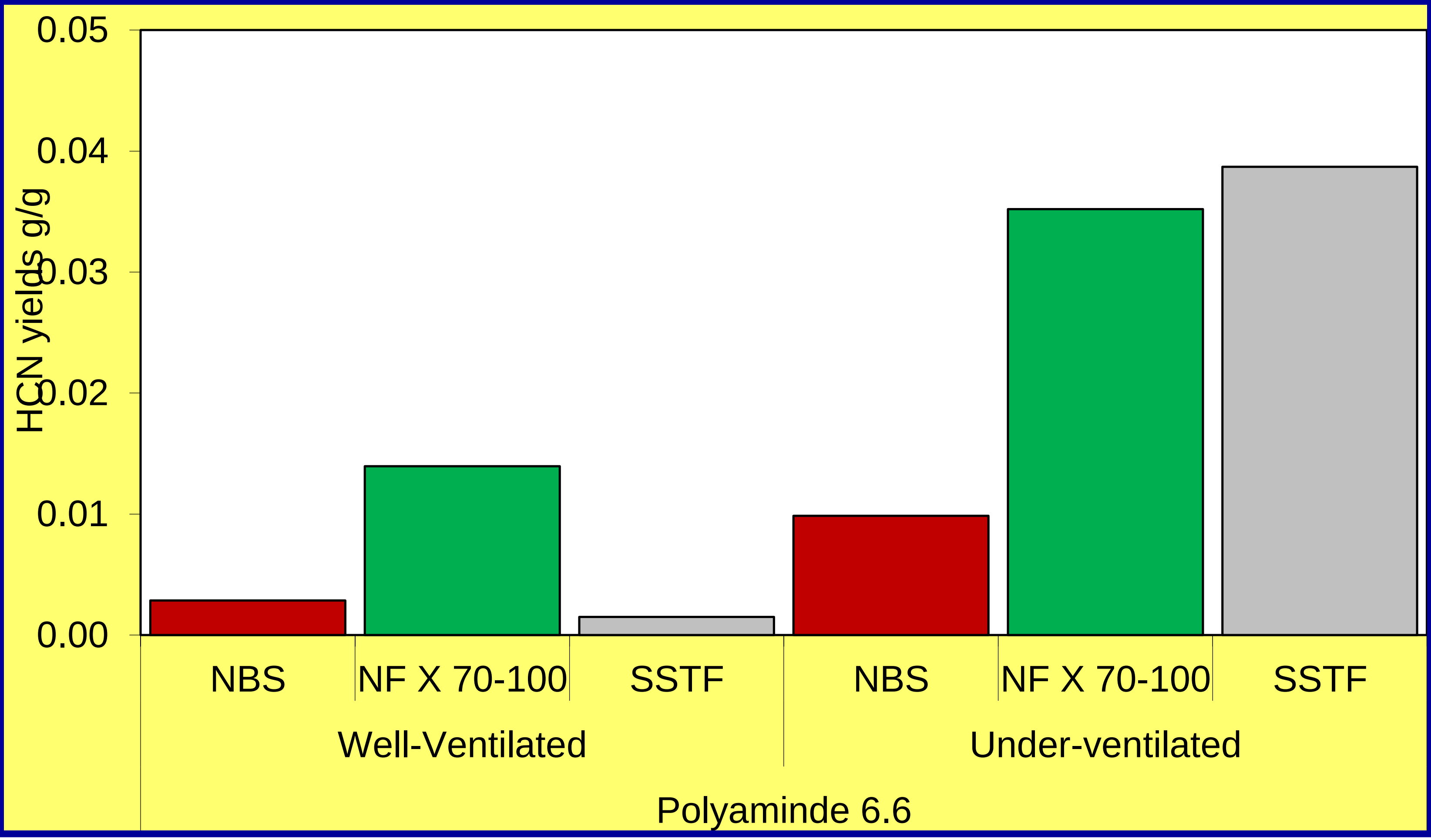
Comparison of Bench and Large-scales for HCN yield from PA 6.6



Comparison of CO yields for PP and PA 6.6 for steady burning methods with Smoke Chamber and NFX test



Comparison of HCN yields from PA 6.6 for steady burning methods with Smoke Chamber and NFX test



Can the smoke chamber replicate underventilated burning?

- So far Smoke chamber only replicates well ventilated yields.
- Increasing the fuel load in a fixed volume of air (the box!) should force underventilated combustion.
- The smoke chamber standard (ISO 5659) states that “the test results are only valid for the thickness tested”

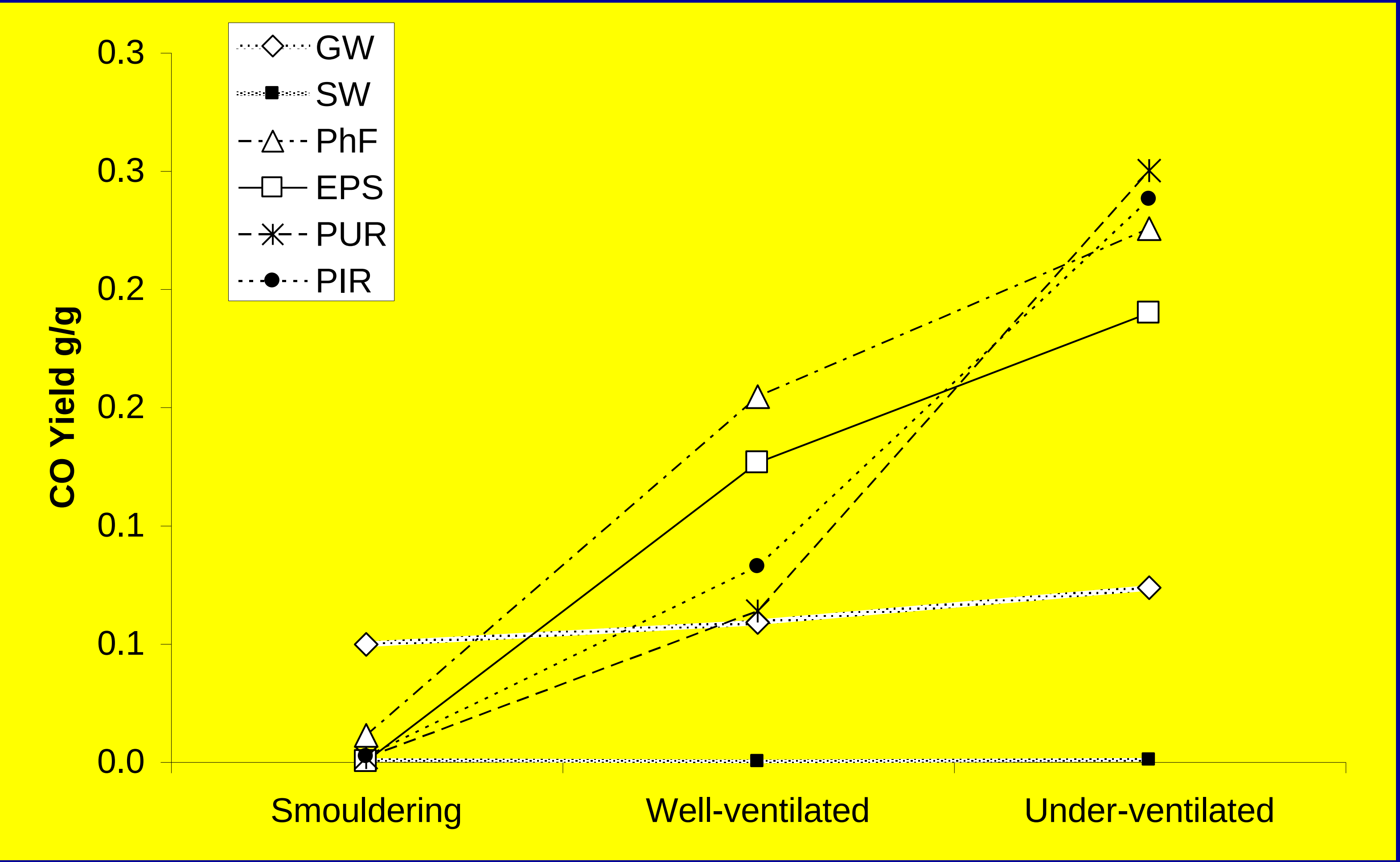
Attempt to replicate under-ventilated burning of PE in the smoke chamber

Thickness /mm	Predicted for 100% mass loss			Actual			O_2 at peak smoke %
	ϕ	Fire condition	CO yield (g/g)	mass loss %	ϕ	CO yield (g/g)	
5	0.61	well-v	0.02	95.7	0.54	0.07	12
10	1.22	under-v	0.08	57.6	0.67	0.04	12.8
15	1.83	under-v	0.17	30.4	0.54	0.04	14.4

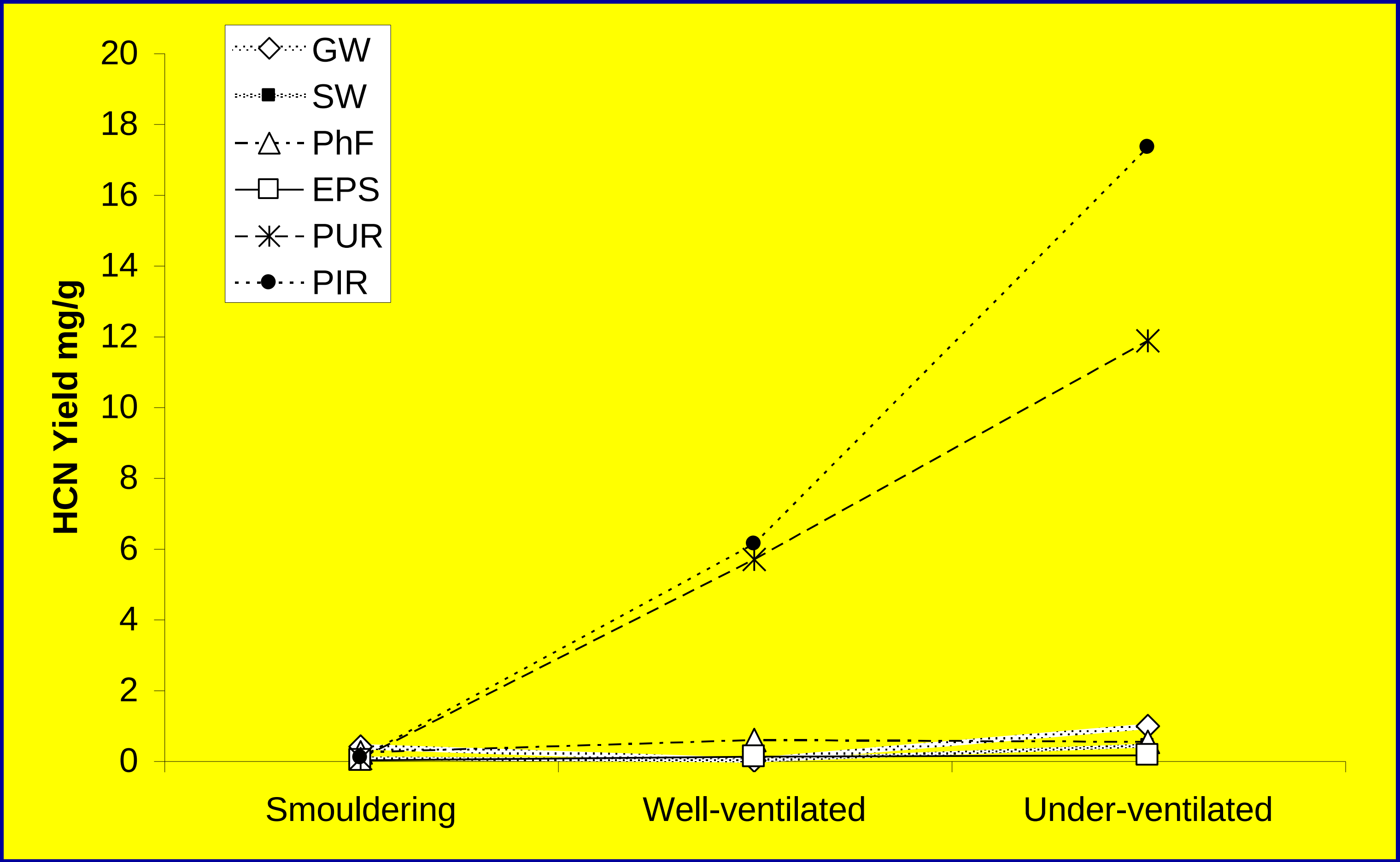
Types of Insulation

Insulation	Density range kg m^{-3}	Thermal Conductivity range W $m^{-1}K^{-1}$	Reaction to Fire Euroclass
Glass wool (GW)	13 - 100	0.030 - 0.045	A1 – A2
Stone wool (SW)	30 - 180	0.033 - 0.045	A1 – A2
Extruded polystyrene (XPS)	20 - 80	0.025 - 0.035	E – F
Expanded polystyrene (EPS)	18 - 50	0.029 - 0.041	E – F
Phenolic (PhF)	30 - 40	0.029 - 0.041	B – C
Polyurethane (PUR)	30 - 80	0.029 - 0.041	D – E
Polyisocyanurate (PIR)	30 - 80	0.023 - 0.041	C - D

CO yields from Insulation Materials



HCN yields from Insulation Materials



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Estimation of fire toxicity

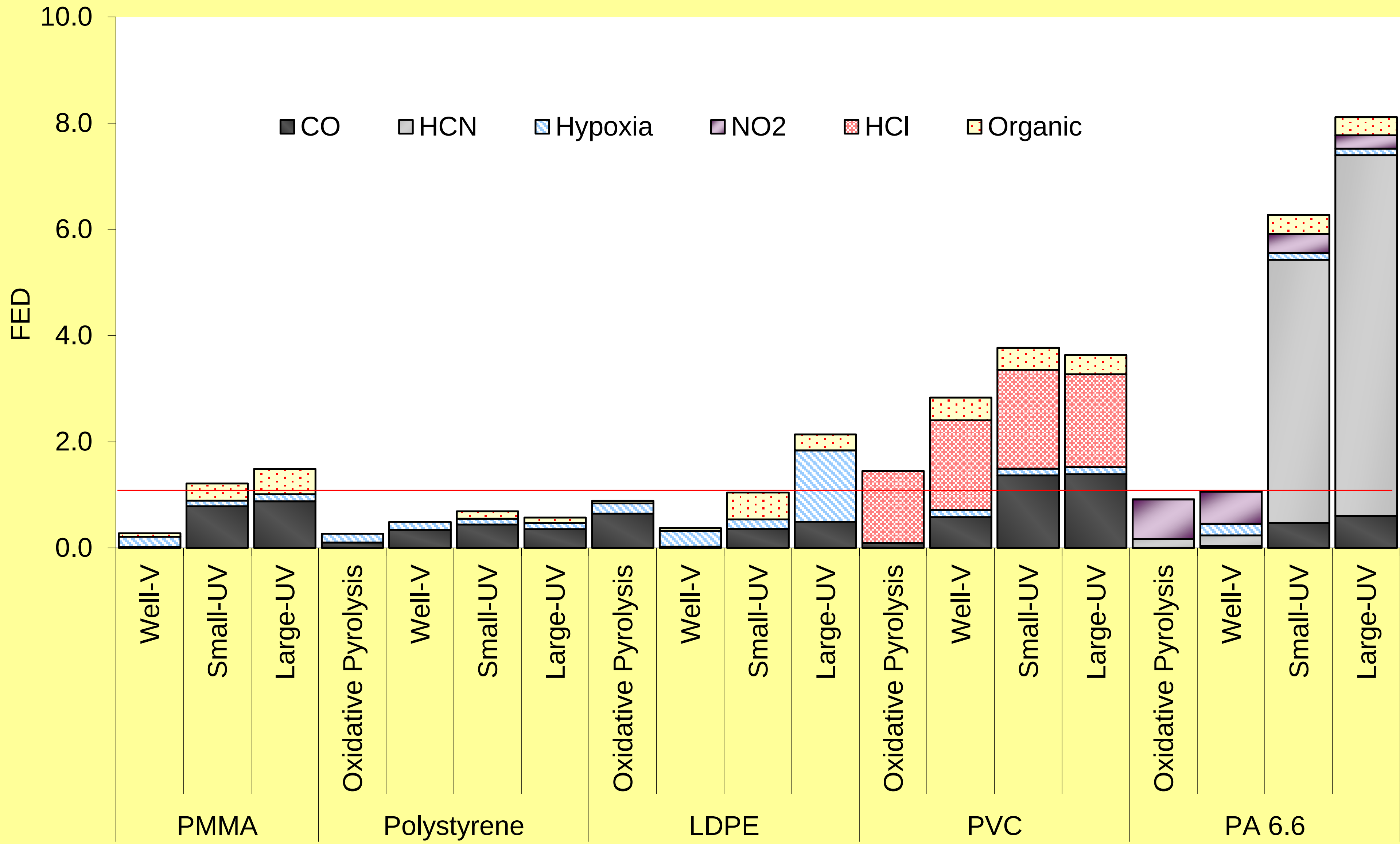
FED - the fraction of a lethal dose (for 50% of the population)
When FED = 1 then 50% of the exposed population will die.

$$\mathrm{FED} = \left\{ \frac{[\mathrm{CO}]}{\mathrm{LC}_{50,\mathrm{CO}}} + \frac{[\mathrm{HCN}]}{\mathrm{LC}_{50,\mathrm{HCN}}} + \frac{[\mathrm{HCl}]}{\mathrm{LC}_{50,\mathrm{HCl}}} + \frac{[\mathrm{NO}_2]}{\mathrm{LC}_{50,\mathrm{NO}_2}} + \ldots. + organics \right\} \times \mathrm{V}_{\mathrm{CO}_2} + \mathrm{A} + \frac{21 - [\mathrm{O}_2]}{21 - 5.4}$$

$$\mathrm{V}_{\mathrm{CO}_2} = 1 + \frac{\exp(0.14[\mathrm{CO}_2]) - 1}{2}$$

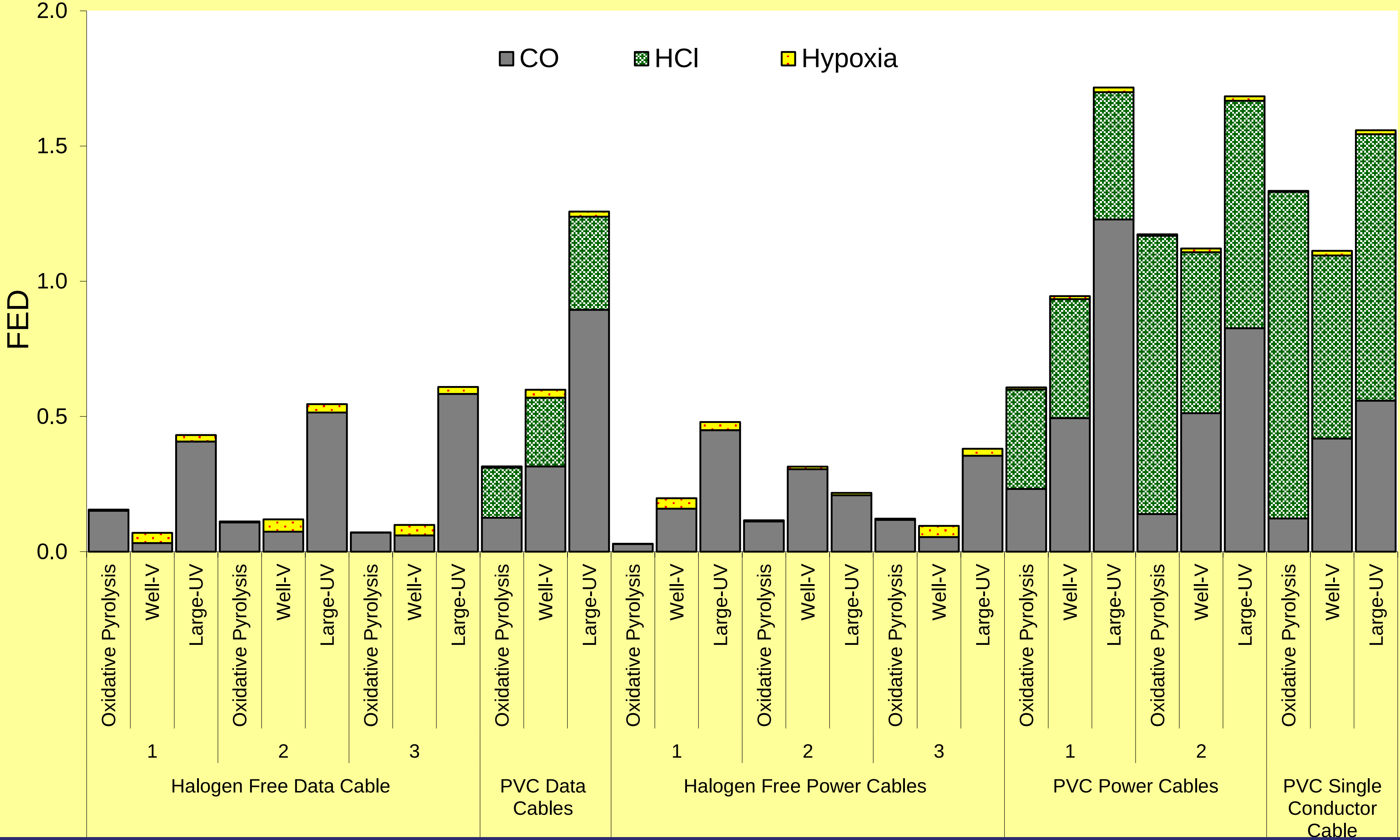
A is an acidosis factor equal to $[\mathrm{CO}_2] \times 0.05$.

Fire toxicity of Common Polymers at 20 g/m^3 loading



Hull, T.R., Stec, A.A., Lebek, K., Price, D.Factors affecting the combustion toxicity of polymeric materials(2007) Polymer Degradation and Stability, 92 (12), pp. 2239-2246

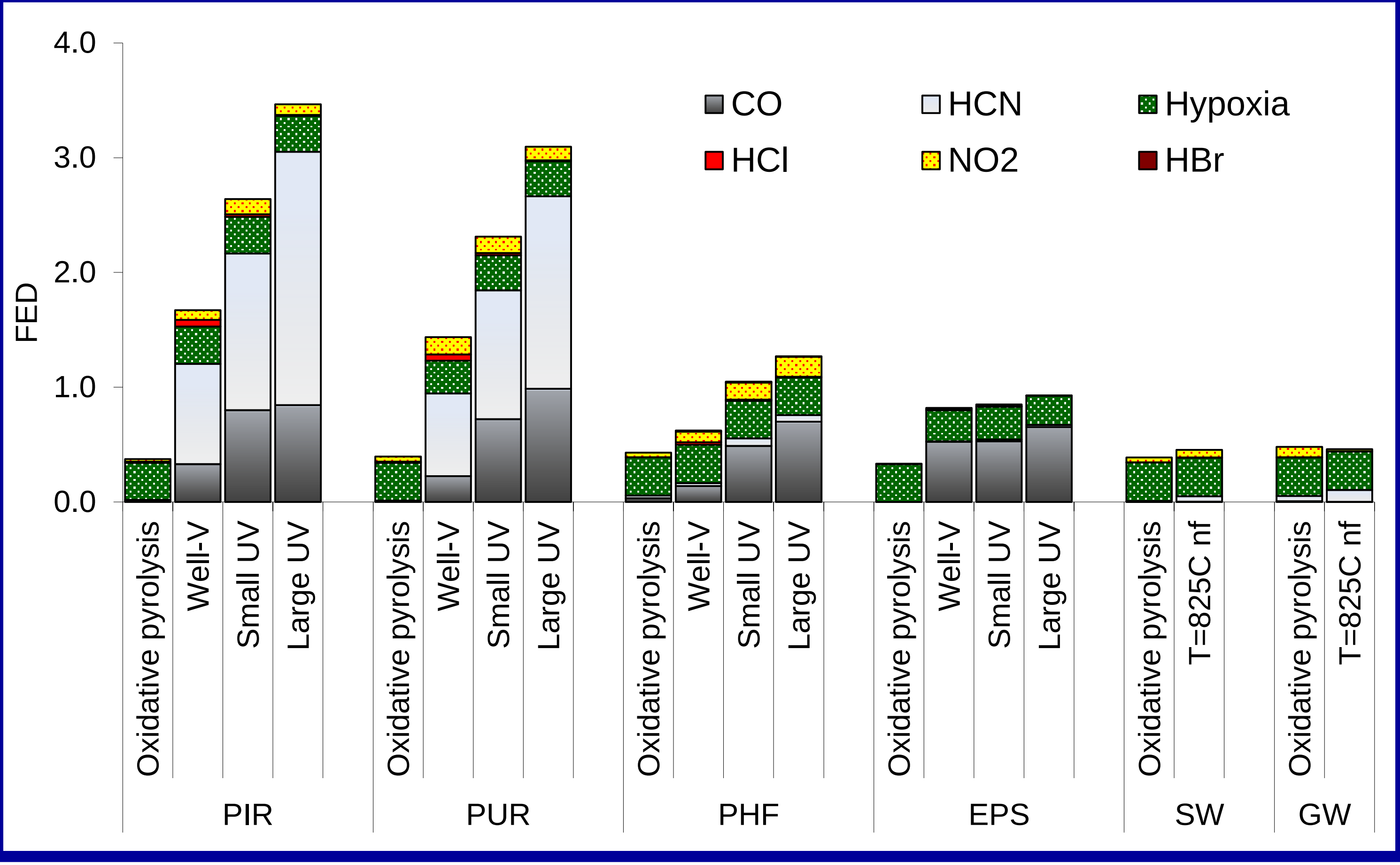
Electric Cables at 20 g/m^3 loading



T.R. Hull, T Richard Hull, Krzysztof Lebek, and James E Robinson, *Acidity, toxicity and European cable regulation,* Transactions of the International Wire and Cable Symposium (Trans IWCS) 2006

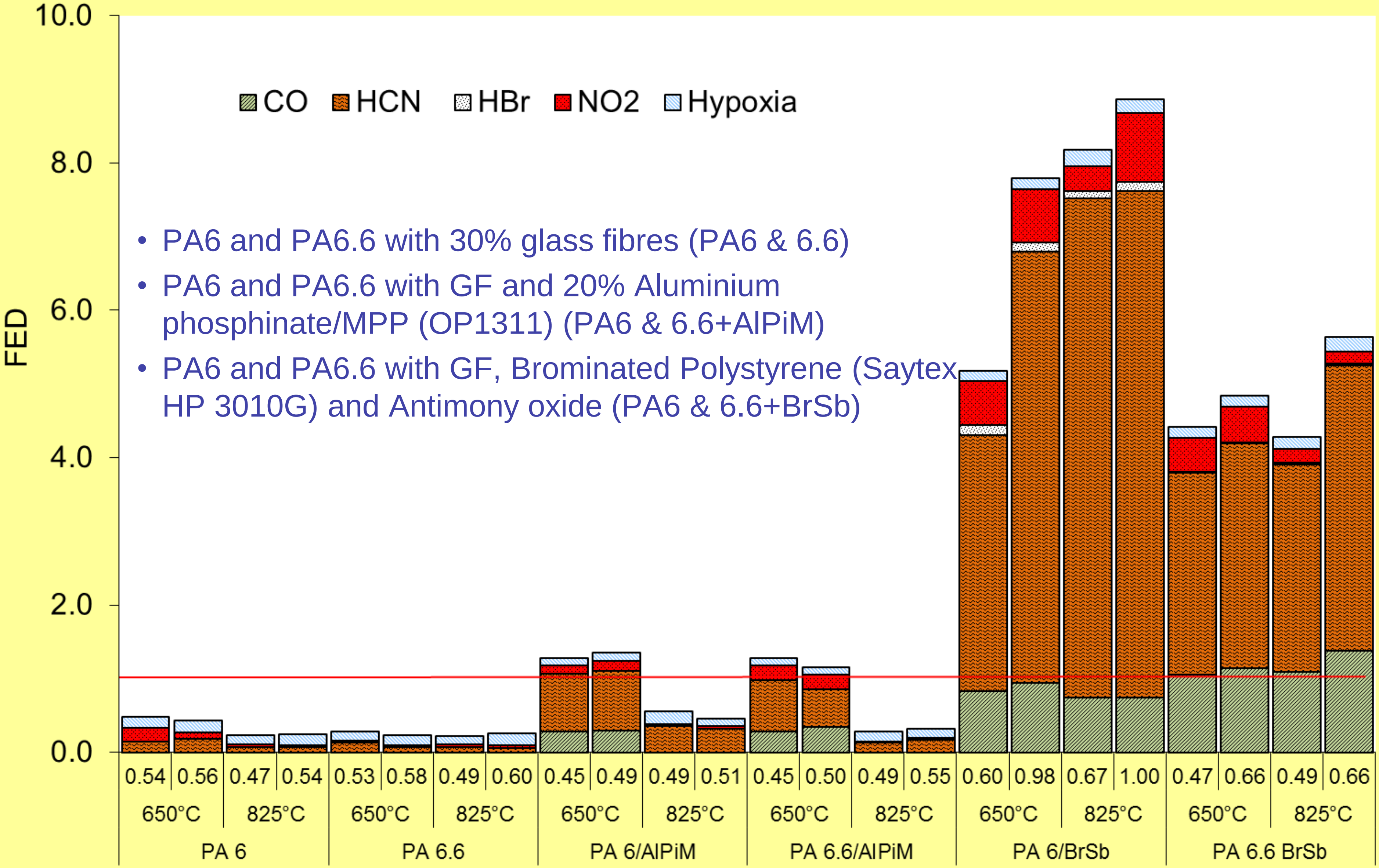
The fire toxicity of six insulation materials (20 g/m^3)

Polyisocyanurate Foam (PIR)
Polyurethane Foam (PUR)
Expanded Polystyrene Foam (EPS),
Phenolic Foam (PhF)
Stone Wool (SW)
Glass Wool (GW)



A.A. Stec and T.R. Hull, *Assessment of The Fire Toxicity of Building Insulation Materials*, Energy and Buildings, 43, pp. 498-506, 2011

Effect of Fire Retardants on Polyamides (20 g/m³)

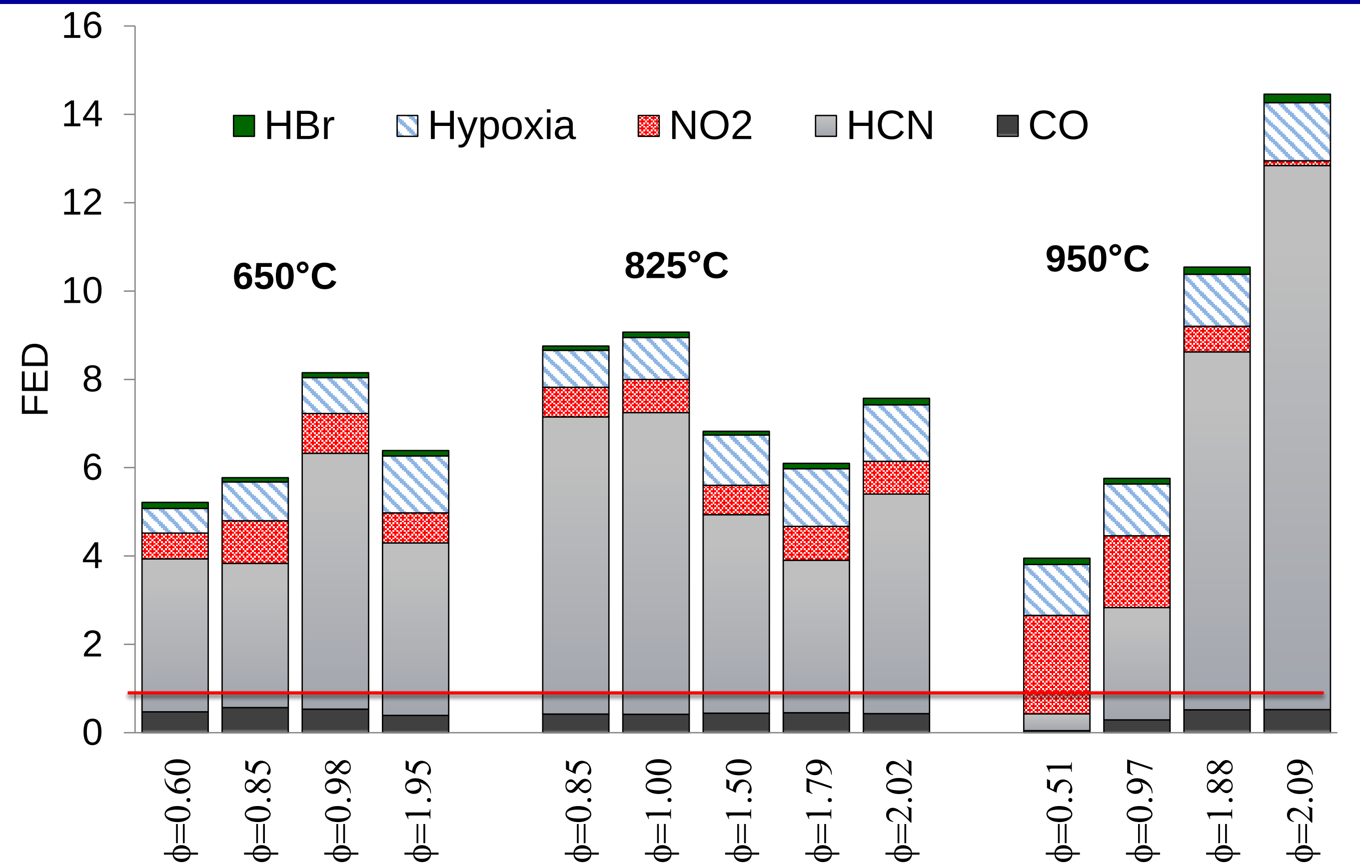


- PA6 and PA6.6 with 30% glass fibres (PA6 & 6.6)
- PA6 and PA6.6 with GF and 20% Aluminium phosphinate/MPP (OP1311) (PA6 & 6.6+AlPiM)
- PA6 and PA6.6 with GF, Brominated Polystyrene (Saytex HP 3010G) and Antimony oxide (PA6 & 6.6+BrSb)

Molyneux, S., Stec, A.A., and Hull, T.R., Polymer Degradation and Stability In Press Sept 2013
http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.013

Effect of Brominated Flame Retardants (20 g/m^3)

- 44% Polyamide 6.6 (Ultramid A27) + 30% Glass fibres (Vetrotex EC 10 983) + 20% Brominated polystyrene (Saytex HP 3010G) + 6% Antimony Trioxide (as masterbatch in PA 6, Campine 2617)



This shows that the flame inhibition of halogens is effective at 650 and 825°C, but not at 950°C. Unlike CO, which reaches a plateau, the HCN yield rises continuously with under-ventilation

Conclusions

- Fire toxicity is the biggest cause of death and injury in fires, but the most widely ignored by regulators!
- Fire toxicity is highly dependent on conditions, and harder to replicate on a bench scale.
- Most methods of assessment of fire toxicity are not fit for purpose!
- Material chemistry can dramatically affect fire toxicity.

Questions?

COST MP1105 FLARETEX

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