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The assessment of fire hazards, tenability and human evacuation behaviour for fire safety engineering design
Erasmus Mundus Programme

Yields of toxic products from TS19700 tube furnace and validation against large-scale test data

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Application of data

- The 19700 tube furnace is a method for measuring the yields of key toxic gases and particulates under defined combustion conditions expressed as a function of fire type and equivalence ratio for flaming fires
- A database of product yields has been produced for which expressions have been fitted to enable yields to be calculated as function of equivalence ratio for input to full-scale fire calculation models
- The toxic gas yields from a range of materials in the tube furnace have been validated against large-scale compartment fire tests over a wide range of combustion conditions

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ISO Requirements and Purser Furnace Characteristics

- Within ISO fire conditions have been defined in terms of temperature, oxygen supply (fuel/air ratio), CO_2/CO ratio and flaming behaviour
- The BS7990 (ISO TS 19700) furnace enables a range of decomposition condition to be set by controlling fuel injection rate, primary (combustion) air supply and furnace temperature
- Decomposition conditions can be identified in terms of CO_2/CO ratio, oxygen concentrations, fuel/air ratio and flaming behaviour

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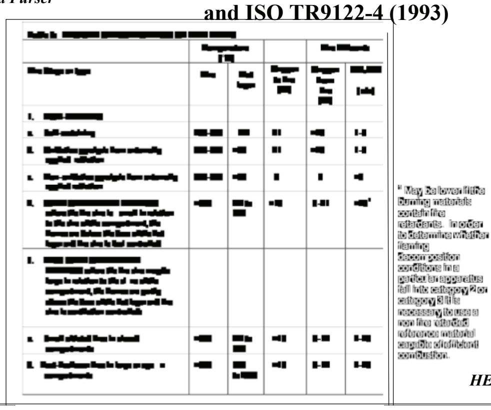
Fire Classification-BS7899-2(1999) and ISO TR9122-4 (1993)



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Yields in Flaming fires

The main interest is the range of yields occurring in flaming compartment fires under different combustion conditions ranging from early well-ventilated to pre- and post-flashover vitiated fires

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Toxic product yields in fires

Depend upon three major parameters:

1. **Elemental composition of material**
   - **Mass % C,H,O,N,P,Cl,Br,F,S,inert fillers**
2. **Organic composition of material**
   - **Aliphatic or aromatic**
   - **Char forming or decomposing into gas phase**
   - **Detailed structure, isocyanates etc**
3. **Decomposition conditions in fire**
   - **Flaming/non-flaming, ventilation, temperature**

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Main variables determining toxic product yields for any particular material

- Flaming or non-flaming decomposition
- For flaming decomposition the fuel/air (equivalence ratio)
- To a lesser extent, the oxygen concentration and compartment temperature
- Fuel composition

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The Equivalence Ratio ϕ

For well-ventilated fires, $\phi < 1$,

For fuel-rich (vitiated) combustion, $\phi > 1$

Further factors affecting yields of CO and other products:
- Oxygen concentration
- Temperature
- Fire retardants

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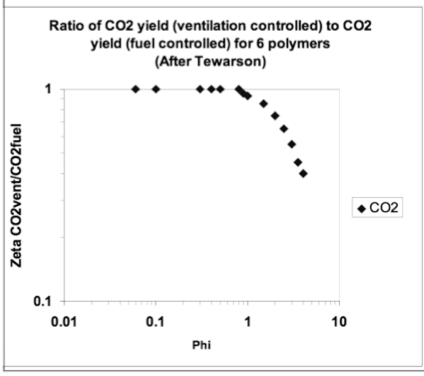
CO_2 yield and equivalence ratio

Effect of ϕ on CO_2 yield



- Under well ventilated conditions almost all fuel carbon is oxidised to CO_2
- Above phi=1 the yield decreases
- Data from Tewarson using ASTM E2058 fire propation apparatus

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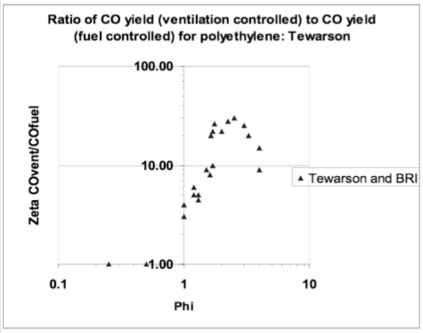
CO yield and equivalence ratio

Effect of ϕ on CO yield



- CO yield is low under well-ventilated conditions
- Above phi=1 the yield increases steeply
- Data from Tewarson using ASTM E2058 fire propation apparatus

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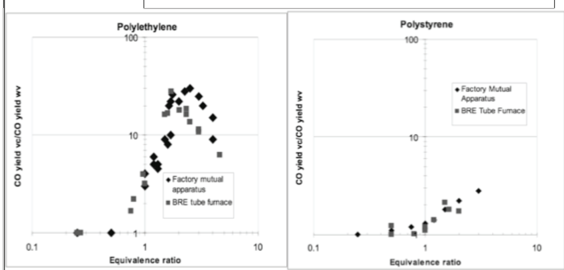
Effect of ϕ on CO yield (Tewarson – BRE comparison)



In early tube furnace experiments we found a good agreement between the ASTM E2058 and ISO TS19700 results expressed as a function of phi confirming that a fundamental (apparatus independent) property was being measured

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Effect of ϕ on CO yield (Tewarson, compartment fires BRE tube furnace comparison)

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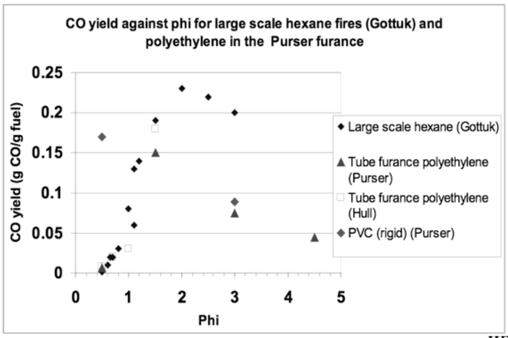
Effect of φ on CO yield (compartment fires – BRE tube comparison)



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Relationship between phi and product yields for 15 materials and large-scale validation for flaming fires

Early studies have demonstrated that for flaming fires the tube furnace:

- Measures the relationship between phi and product yields
- Provides very similar results to the Factory Mutual and BRI apparatus in relation to phi – suggesting that the results are apparatus independent and measuring relatively fundamental phenomena
- Gives a reasonably good agreement with large and full-scale fires – providing some validation of the method against full-scale data

Detailed study on a range of 15 common polymeric materials:

- Relationship with phi for flaming conditions
- Effects of temperature, oxygen concentration and fire retardants
- Validation against large scale fires for selected materials

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Derived and measured parameters

- **Mass charge concentration (mg/l)**
- **Mass loss concentration (mg/l)**
- **Effective heat of combustion (MJ/kg)**
- **Combustion efficiency**
- **phi**
- **CO_2/CO ratio (Volume ratio)**
- **Oxygen consumed (g/g)**
- **Mass loss / oxygen ratio (g/g)**
- **Smoke yield (SEA) (g/g)**
- **CO, CO_2, HCN, HCl, HBr, NO, NOx, SO_2, PO_4 yields (g/g)**
- **Acrolein, formadehyde yield individual GC-MS organics (g/g)**
- **Total carbon as organic carbon (using secondary furnace) (g/g)**

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Tube furnace combustion conditions

- Furnace temperature 650ºC (700ºC for PIR and MDF-FR) some additional experiments at 850ºC)
- **Constant flaming combustion**
- Most runs in air, but some in 10% or 12% oxygen using air/nitrogen mixtures

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Equivalence ratio measurements

- Nominal equivalence ratio from stoichiometric oxygen demand for complete combustion of fuel: 0.5-2.5 in separate runs
- Actual equivalence ratio achieved calculated from total oxygen consumed in the secondary furnace (phi meter) plus that required for oxidation of soot.

$$\phi = \frac{O_2 \text{ required } \%}{O_2 \text{ supplied } \%}$$

For materials undergoing complete combustion nominal and actual phi very similar, for char formers the actual phi was lower than nominal due to formation of carbon-rich char (close to nominal values assuming char 100% carbon)

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Large-scale validation experiments

- ISO 9705 room: MDF board or PIR aluminium-faced panels, and cribs of the same material used as radiation source in corner designed to give standard HRR (equivalent to propane flame)
- Half-scale ISO room corridor rig: MDF or PIR as cribs
- Conditions varied from well-ventilated to vitiated by varying door panel opening to obtain different global equivalence ratios
- Aimed to obtain a period of near steady-state burning during which effluent samples were taken from the upper layer for composition and equivalence ratio measurements
- For ISO room samples taken near ceiling before doorway, for half-scale rig near ceiling at back of room away from doorway (and in corridor).

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Two ways to report and compare yields

- Mass yield = mass of product (e.g. CO)/fuel mass loss (g/g)
- Mass recovery fraction = mass yield normalized in terms of carbon content (or nitrogen content) of fuel
- For CO this would be the mass of carbon released as CO as a fraction of the total carbon mass loss
- Mass yield = recovery fraction x carbon content of fuel mass loss (g)
- Recovery fractions therefore represent normalised yields showing the extent to which conversion to CO is independent of polymer composition or not

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Materials tested in the tube furnace

Material	% Fr components
PMMA	
Polyethylene (low density)	
Polystyrene	
Polyamide 6	N 12.4
Polyacrylonitrile	N 25
PVC (100%)	Cl 56.7
Medium Density Fibreboard (MDF)	N 3.7 Cl 0.62
Wood (Pinus sylvestris)	
Plywood	
Polyisocyanurate (rigid PIR foam) – FR	N 6.2 Cl 2.53
CMHR polyurethane flexible foam – FR ("blue foam")	N 8.2 Cl 2.5
Acrylic/wool/polyester fabric "boucle"	N12.9 Cl 0.3 Br 0.5 S 0.94
Acrylic/wool/polyester fabric "boucle" back coated	N10.8 Cl 0.95 Br 6.1 S 0.76
Acrylic/cotton/polyester fabric "velour"	N 12.0
Acrylic/cotton/polyester fabric "velour" back coated	N 7.3 Br 8.2

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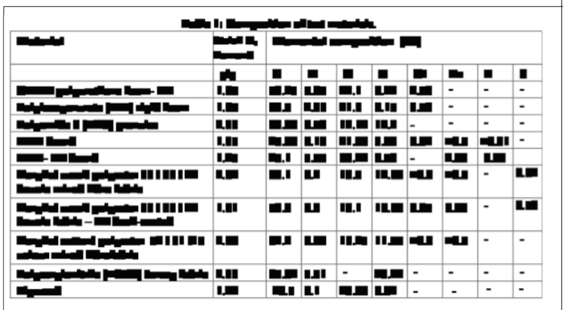
Nitrogen-containing materials tested in the tube furnace



Elemental composition obtained: from elemental composition, analysis following bomb calorimetry or 900°C well-ventilated tube furnace runs

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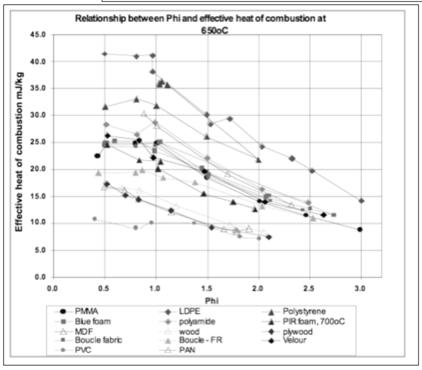
Yields versus equivalence ratios – BRE tube furnace



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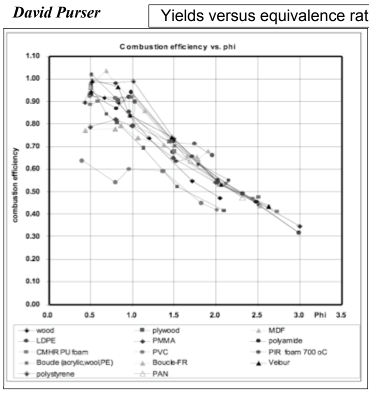
Yields versus equivalence ratios – BRE tube furnace



- Most materials had combustion efficiencies of 0.90-1.0 (phi = 0.5), some decreasing to 80-90% (phi = 1)

(aliphatics, cellulosics n-containing)

- Aromatic (polystrene) max 0.8
- FR-boucle fabric max 0.8
- PVC max 0.6
- Linear decreases above phi = 1 measured at 0.55 at phi = 2

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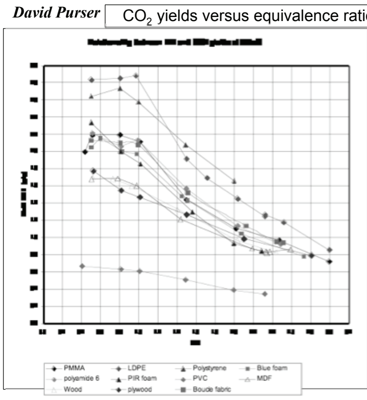
CO_2 yields versus equivalence ratios – BRE tube furnace



- CO_2 yields similar to heat of combustion

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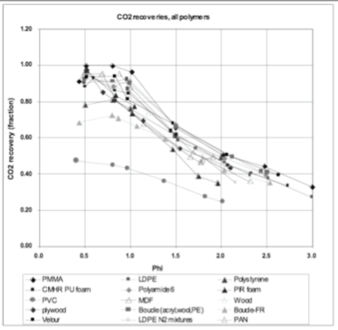
CO_2 yields versus equivalence ratios – BRE tube furnace



CO_2 recovery (fuel carbon mass loss as CO_2) similar to combustion efficiency

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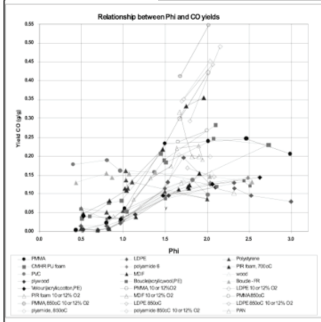
CO yields versus equivalence ratios – BRE tube furnace



- For materials leaving no residue phi was calculated from the stoichiometric oxygen demand of the whole material
- For char formers the char was considered as 100% carbon and unavailable as fuel for phi calculation
- Most materials have low CO yields (< 0.05 g/g mass loss) for phi <1 (unless heavily FR)
- Phi > 1 sigmoid with a plateau ~ phi = 1.75-2.0
- Materials fell into groups:
- High max yields up to 0.55 g/g : PMMA, Polyamide
- Low max yields up to 0.14 g/g : cellulosics
- Heavily halide FR materials (PVC, Boucle-FR) – almost constant yield across range
- Effects of oxygen: for a given phi lower CO yields in air than in 10-12% O_2/N_2 mixtures
- Effects of temperature: at 850ºC somewhat higher CO yields in some cases

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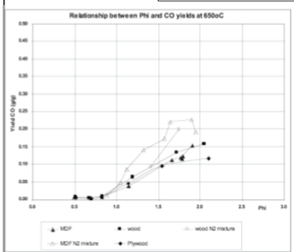
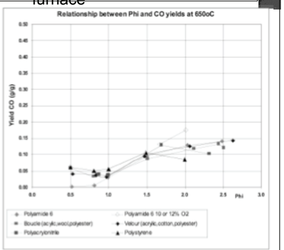
CO yields versus equivalence ratios – BRE tube furnace





- For some materials including cellulosics, aromatics and some other polymers the maximum CO yield was quite low, at 650ºC, with a maximum around 0.15 g/g
- When 10-12% O_2 air / N_2 mixtures were used instead of 21% O_2 air, the maximum CO yields was increased to around 0.2 g/g

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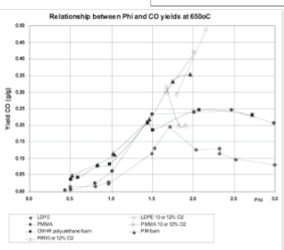
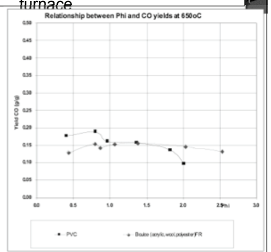
CO yields versus equivalence ratios – BRE tube furnace





- For other materials including LDPE, PMMA, PIR and CMHR PU foam, the maximum CO yields were in air were higher at around 0.2-0.25 g/g mass loss.
- For LDPE and PMMA the maximum yields were increased to 0.42-0.5 g/g using air/N_2 mixtures, and even more at 850ºC
- For PVC and the heavily FR-backcoated Boucle fabric, the yield was more or less constant at ~ 0.15 g/g throughout the phi range

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Why do the CO yields vary between different materials?

CO *yields* may be useful to compare products but in order to understand the chemistry it is necessary to normalise the data for different materials

Differences in CO yield may be due to:

- Differences in carbon content – normalise yields in terms of carbon recovery as CO
- Char formation – express normalised yields in terms of total gas phase carbon
- Differences in reaction chemistry – can then be compared for the normalised data
- Attempts have also been made to derive algebraic expressions (using the Weibull distribution) for use with engineering calculations

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Normalized Yields

- Due to the variation in yields between different materials it is necessary to use different functions for the relationship between phi and yield for each individual material
- For engineering calculations it would be useful if the variation could be reduced to one or a few generic curves
- The main variable is nitrogen content – so plotted the normalised yields (recovery fractions (mass of fuel nitrogen released as nitrogen in HCN)
- Derived Weibull functions for generic sets of materials

[illegible]

This function gives a good fit to the sigmoid relationships between phi and recovery fraction

[illegible]

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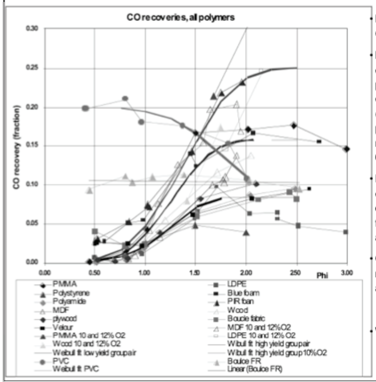
Fuel carbon recoveries as CO versus equivalence ratios – BRE tube furnace



- Now can be classified into 3 groups for CO yield.
- Low group: polymers containing only carbon and hydrogen: polystyrene and polyethylene, and some polymers containing some oxygen and nitrogen (boucle and velour fabrics, polyacrylonitrile and polyamide) – maximum recovery fraction around 0.08
- High group: oxygen-containing cellulosics (wood, plywood, MDF) and organic polymers PMMA, PU and PIR foams – maximum recovery fraction in air 0.16 and 0.25 with air/N_2 mixtures
- Quasi-constant group (fire retarded materials) – recoveries between 0.1 and 0.2
- Weibull curves fitted to groups

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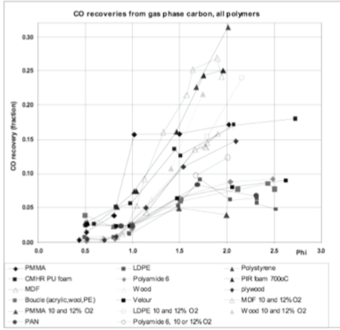
Fuel carbon gas phase recoveries as CO versus equivalence ratios – BRE tube furnace



Similar to the previous slide, but the recovery fraction for cellulosic materials is increased (due to compensation for carbon locked in the char

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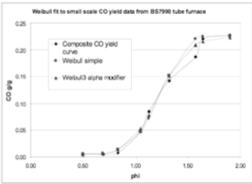
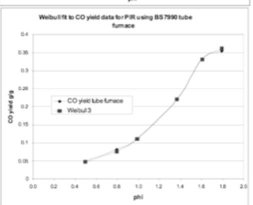
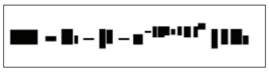
Use of Weibull function to obtain predictive curves for CO yield of individual polymers versus equivalence ratios





Weibull expression for MDF:



Where:

CO = CO yield g/g (or CO recovery fraction)

$\alpha = 7$

$\beta = 19.5$

Φ = Equivalence ratio

$k_1 = 0.004$

$k_2 = 15$

$k_3 = 4.5$

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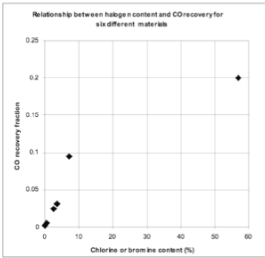
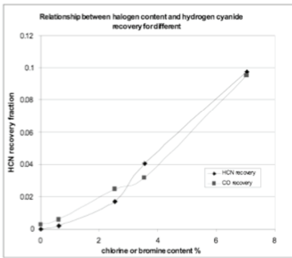
Effect of halogen content on CO yields under well-ventilated flaming conditions – BRE tube furnace





Relationship between halogen content and recoveries of hydrogen cyanide and carbon monoxide from a five different materials (PMMA, MDF, PU foam, PIR foam and Boucle FR fabric) under well-ventilated conditions (phi < 1)

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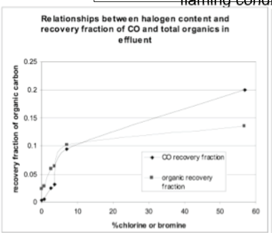
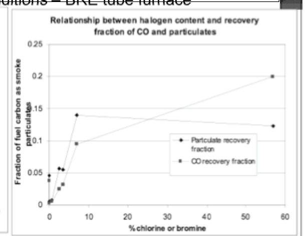
Effect of halogen content on CO yields under well-ventilated flaming conditions – BRE tube furnace





Relationship between halogen content and recoveries of total organic carbon compounds and carbon monoxide from a six different materials (PMMA, MDF, PU foam, PIR foam, Boucle FR fabric and PVC under well-ventilated conditions (phi < 1)

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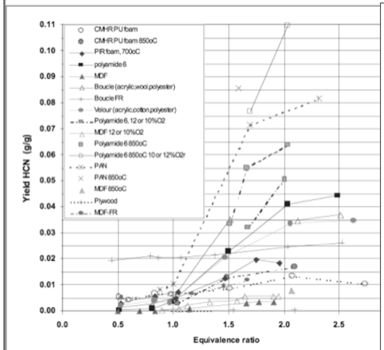
HCN yields versus equivalence ratios – ISO tube furnace



- HCN yields show a sigmoid relationship with phi as does CO, with low yields at low phi values, increasing steeply when phi >1.
- Under vitiated combustion conditions at 650ºC wide range from 0.00035 g/g MDF to 0.78 g/g PAN
- Yields of some sensitive to temperature and/or oxygen concentration (highest of all PA6 850ºC 10% Oxygen: 0.11 g/g)
- Variation due to:
  - Differences in nitrogen content
  - Differences in conversion efficiency of fuel N to HCN
  - For some materials increased yields at higher temperatures or in 10% or 12% oxygen
- Yield curve flat for fire retarded materials

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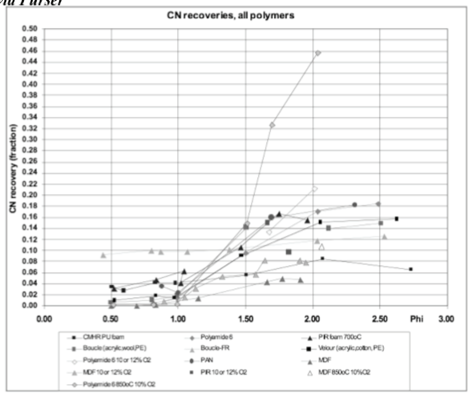
HCN recovery fractions



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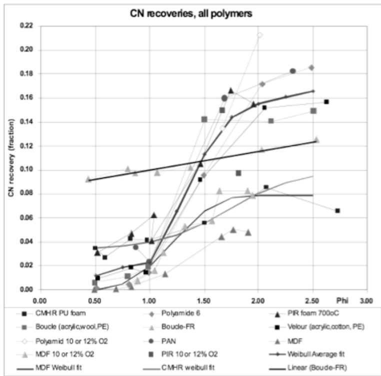
Recoveries of HCN versus equivalence ratios – BRE tube furnace



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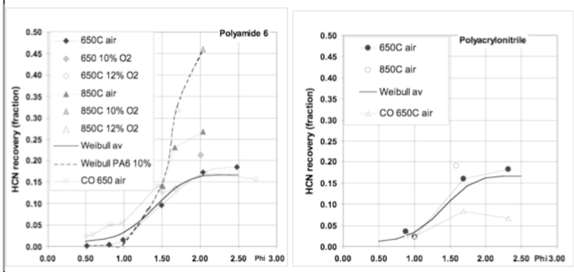
HCN recovery fractions



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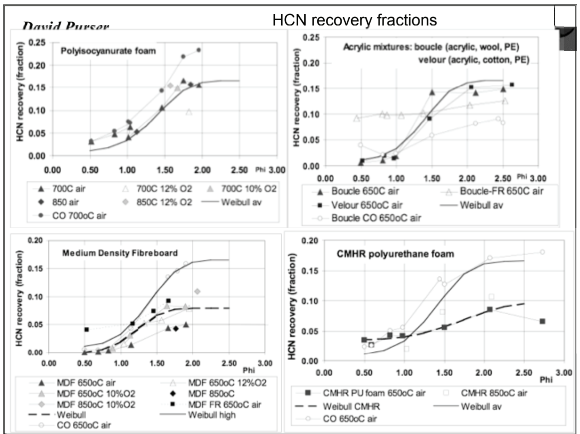
HCN recovery fractions



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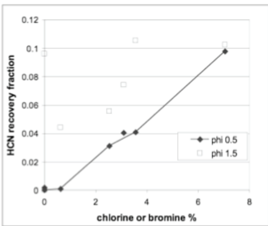
HCN recovery fractions in relation to halogen content



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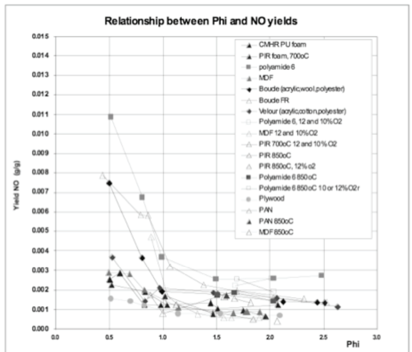
Phi and NO yields versus equivalence ratios – BRE tube furnace



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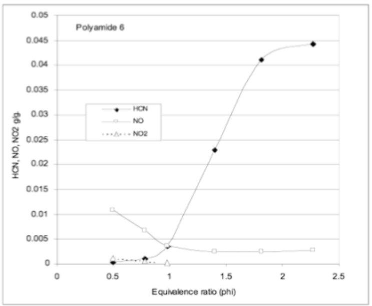
David Purser Yields of nitrogen-containing products from polyamide



Relationship between equivalence ratio and yields of NO, NO_2 and HCN under flaming combustion conditions at 650°C in air measured in the steady state tube furnace

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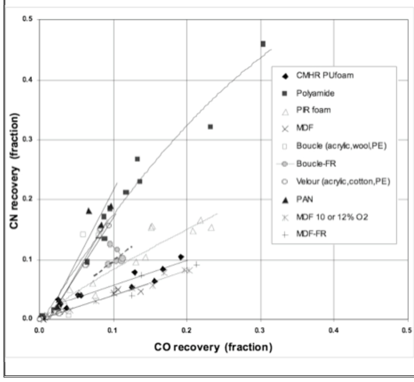
David Purser Conversion of fuel nitrogen to HCN compared to conversion of fuel carbon to CO – ISO 19700 tube furnace



In fire tests and fire models, CO is measured but HCN seldom.

If CO and HCN recoveries are similar then HCN recovery can be estimated from CO recovery

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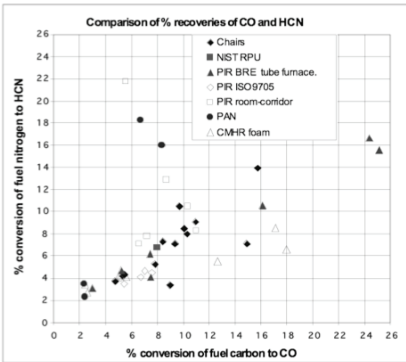
David Purser Conversion of fuel nitrogen to HCN compared to conversion of fuel carbon to CO – ISO 19700 tube furnace and large-scale fires



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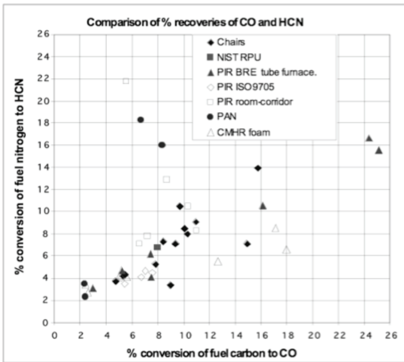

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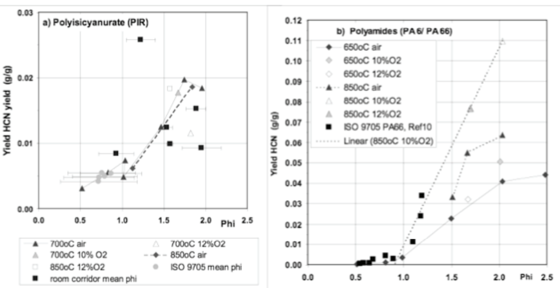
David Purser Comparison of HCN yields in large-scale fires and ISO 19700 tube furnace for polyisocyanurate foam and polyamide 6



large-scale PA data from Blomqvist and Lonnermark using polyamide 66

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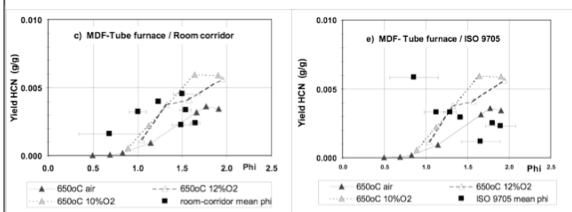
David Purser Comparison of HCN yields in large-scale fires and ISO 19700 tube furnace for polyisocyanurate foam and polyamide 6



Room corridor cribs only so fuel conditions well-defined

ISO 9705 room crib and wall linings so different combustion conditions in different parts of the room

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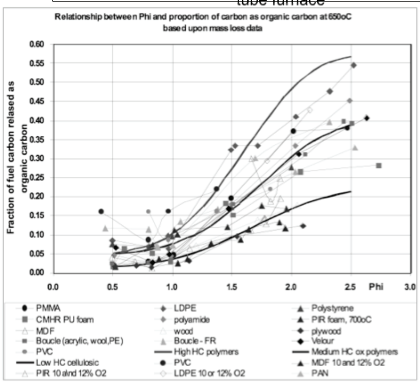
Organic carbon recovery versus equivalence ratios – BRE tube furnace



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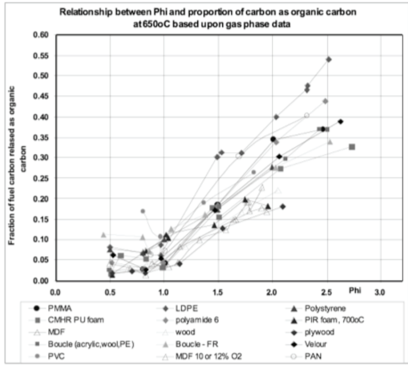
Organic carbon recovery versus equivalence ratios – BRE tube furnace



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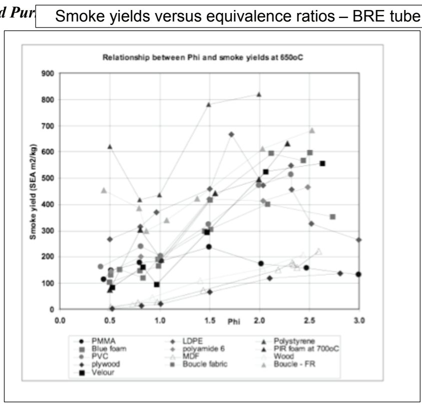
Smoke yields versus equivalence ratios – BRE tube furnace



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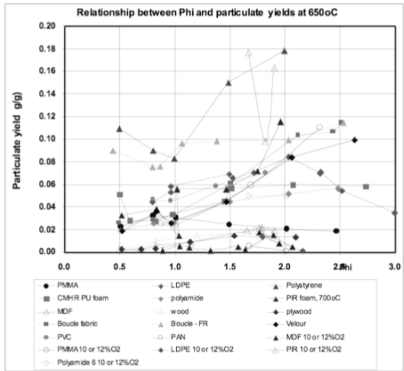
Particulate yields versus equivalence ratios – BRE tube furnace



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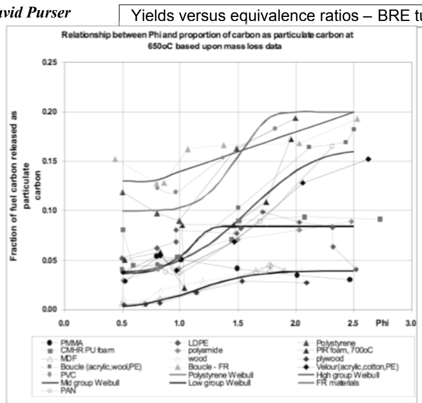
Yields versus equivalence ratios – BRE tube furnace



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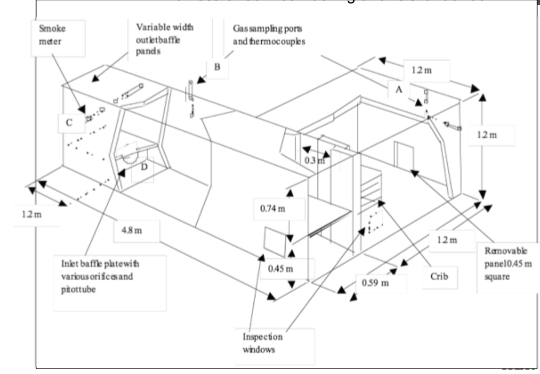
Large-scale validations against BRE tube furnace – half scale room corridor rig and ISO 9705 room



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Large-scale validations against BRE tube furnace – half scale room corridor rig and ISO 9705 room

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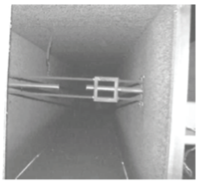
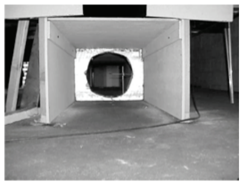
Large-scale validations against BRE tube furnace – half scale room corridor rig and ISO 9705 room





Upper section of corridor showing smoke meter and lower part showing inlet baffle with pitot

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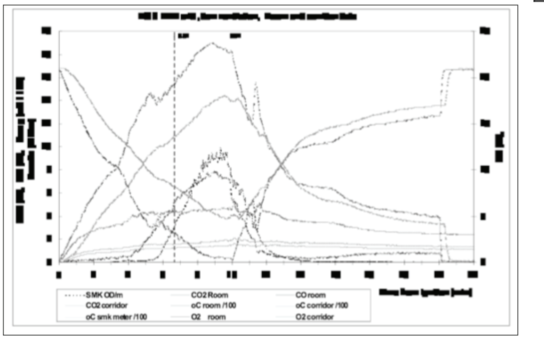
Room-corridor experiment – MDF crib



Room corridor test 3, MDF crib, 5.0 cm ventilation, Sample period: 6.67 – 9.67 min

Phi: min = 1.59, max = 1.70

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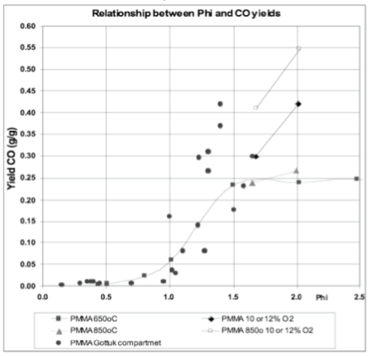
Yields versus equivalence ratios – BRE tube furnace



Comparison of CO yields (g/g) for PMMA obtained from the BRE tube-furnace apparatus in Gottuk's compartment fires

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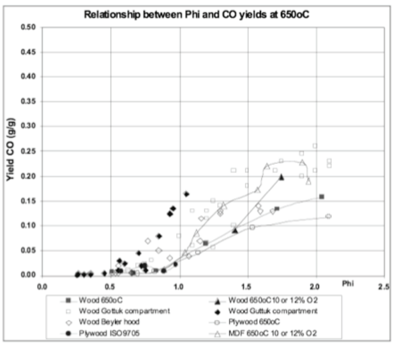
Yields versus equivalence ratios – BRE tube furnace



Comparison of CO yields (g/g) for wood and plywood obtained from the BRE tube-furnace apparatus, in Beyler hood experiments, Gottuk compartment fires and in the ISO 9705 room at BRE

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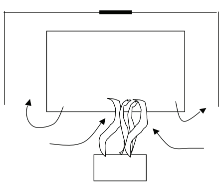
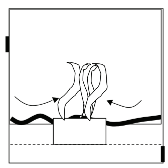
Yields versus equivalence ratios – BRE tube furnace





Beyler hood experiments, Gottuk compartment fires

Similar results have since been obtained by Marlair using the Factory Mutual apparatus

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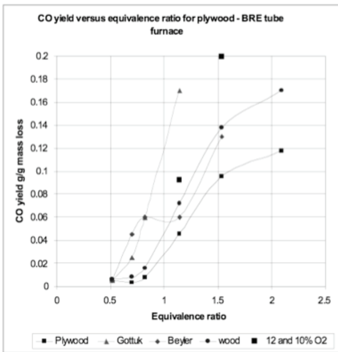
Effect of ϕ on CO yield



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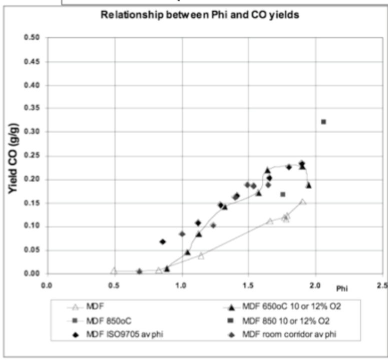
Yields versus equivalence ratios – BRE tube furnace



Comparison of CO yields (g/g) for MDF obtained from the BRE tube-furnace apparatus, in the ISO 9705 room and in the half-scale room corridor apparatus at BRE

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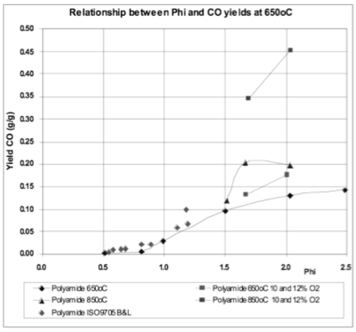
Yields versus equivalence ratios – BRE tube furnace



Comparison of CO yields (g/g) for Polyamide obtained from the BRE tube-furnace apparatus and in the ISO 9705 room by Blomqvist and Lonnermark

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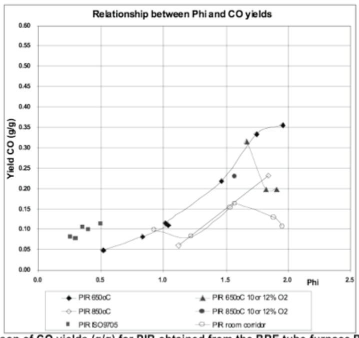
Yields versus equivalence ratios – BRE tube furnace



Comparison of CO yields (g/g) for PIR obtained from the BRE tube-furnace BRE apparatus, in the ISO 9705 room at BRE and in the and in the half-scale room corridor apparatus at BRE

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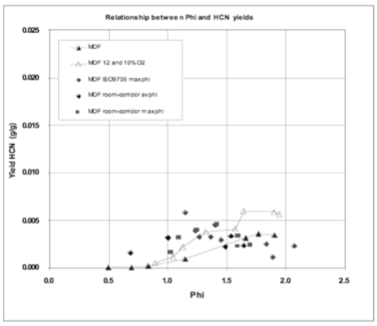
Yields versus equivalence ratios – BRE tube furnace



Comparison of HCN yields (g/g) for MDF obtained from the BRE tube-furnace apparatus, in the ISO 9705 room and in the half-scale room corridor apparatus at BRE

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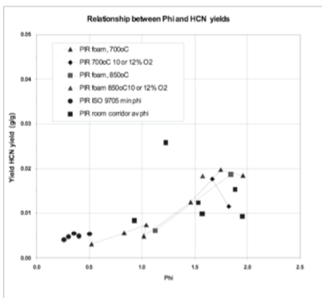
Yields versus equivalence ratios – BRE tube furnace



Comparison of HCN yields (g/g) for PIR obtained from the BRE tube-furnace apparatus, in the ISO 9705 room and in the half-scale room corridor apparatus at BRE

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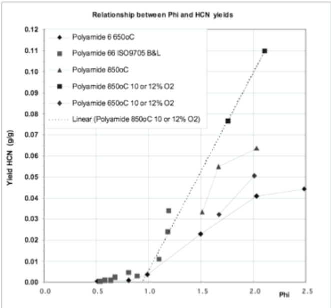
David Purser **Yields versus equivalence ratios – BRE tube furnace**



Comparison of HCN yields (g/g) for Polyamide obtained from the BRE tube-furnace apparatus in the ISO 9705 room by Blomqvist and Lonnermark

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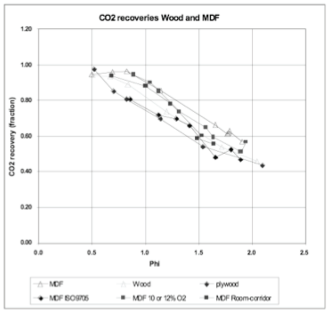
David Purser **Yields versus equivalence ratios – BRE tube furnace**



Comparison of CO_2 recovery fraction from PIR obtained from the BRE tube-furnace apparatus, in the ISO 9705 room and in the half-scale room corridor apparatus at BRE.

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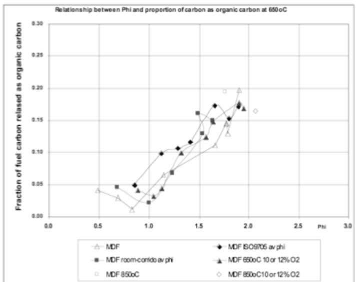
David Purser **Yields versus equivalence ratios – BRE tube furnace**



Comparison of carbon recovery as organic carbon for MDF obtained from the BRE tube-furnace apparatus, in the ISO 9705 room and in the half-scale room corridor apparatus at BRE.

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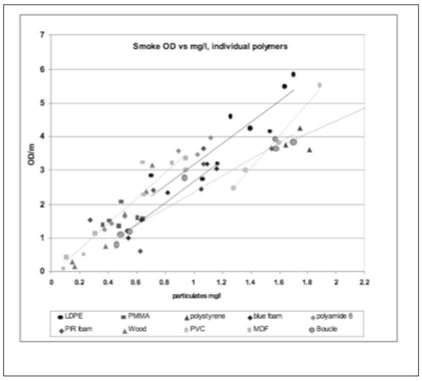
David Purser Yields versus equivalence ratios – BRE tube furnace



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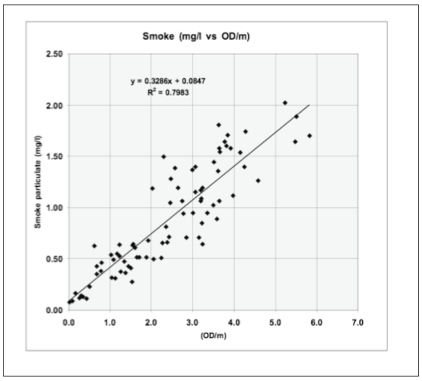
David Purser Yields versus equivalence ratios – BRE tube furnace



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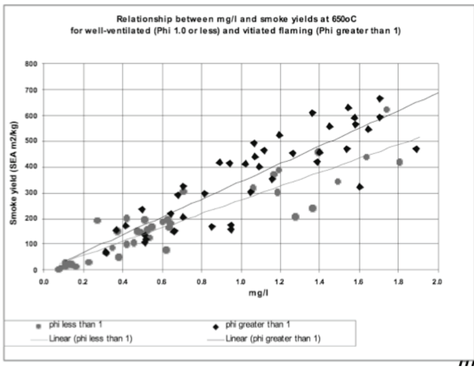
David Purser Yields versus equivalence ratios – BRE tube furnace



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Using ϕ and CO yield to model hazard in a full scale fire

- A full scale fire is estimated as a medium growth rate t^2 fire
- The fire is in an enclosed room (2.44 x 3 x 2.44 m) with a 1 m x 0.3 m vent at floor level
- The fire growth heat release rate and upper zone filling rate are modelled using C-fast
- The mass loss rate is calculated from the heat release rate
- The CO yield is taken from the tube furnace experiments as:

well ventilated	0.007	CO	2.54	g/g fuel mass loss
vitiated	0.149	CO	1.57	

The FED for incapacitation from CO and CO_2 is calculated

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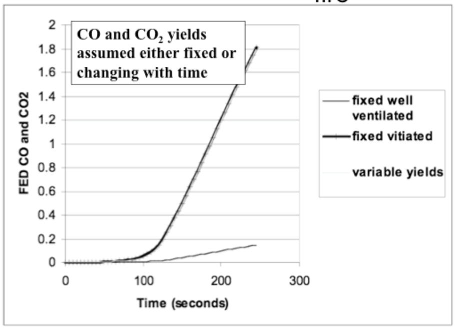
Using ϕ and CO yield to model hazard in a full scale fire



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Using ϕ and CO yield to model hazard in a full scale fire

- This fire was assumed to be a polyethylene fire, what difference (with respect to CO and CO_2 hazard would it have made if it had been a PVC fire?
- Under well ventilated conditions, the yield of CO from PVC was 0.166g/g which is 24 x the yield from PE, the toxic potency is therefore greater
- Under vitiated conditions the yield of CO from PE was 0.149 g/g which is close to that of PE
- Since the modelling shows only the vitiated yields determine the time to incapacitation, it would have made no difference if PVC had been used and grew at the same rate. In practice the PVC fire would grow more slowly, giving a longer time to asphyxiation.

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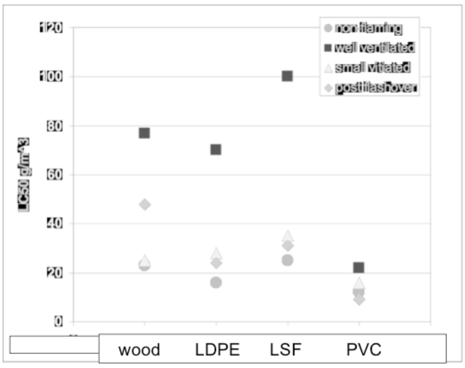
Summary of toxic potency estimations



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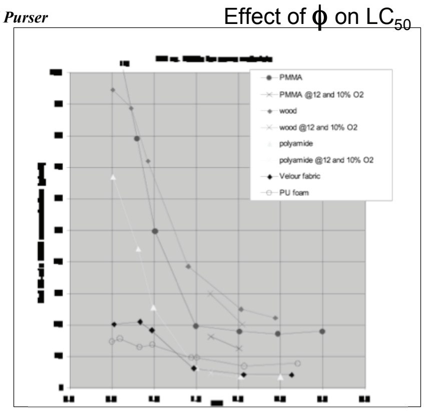
Effect of ϕ on LC_{50}



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Conclusions

- The BS7990 tube furnace provides a versatile method for measuring toxic product yields over the full range of fire conditions
- For flaming fires the yields from individual materials are very dependent upon fuel/air ratios (phi) and to a lesser extent on oxygen concentrations and temperature
- Fire retardants, especially halides also have a large effect on toxic product yields
- For flaming fires, yields expressed as a function of equivalence ratio appear to be apparatus independent and correlate well with those obtained from other test methods and large-scale fires
- Functions can be derived for the prediction of toxic product yields against phi for application to FSE calculations

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