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

Large scale fire scenarios: Fire development, fire effluent characteristics and physiological and toxic hazards

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- **Fire chemistry basics**
- **Relationships between decomposition conditions and effluent product yields: equivalence ratio concept**
- **Large scale fire scenarios**
- **Compartment fire development**
- **Fire effluent characteristics and toxic hazards**
- **Toxic fire gases: decomposition behaviour of different types of materials**
- **Effects of fire retardants**
- **Yield calculations for FSE**
- **Test methods**

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Why is fire chemistry important?

- **Fire is a chemical process, an uncontrolled exothermic (heat producing) reaction and the reaction rate depends upon the temperature**
- **This is why it is dangerous, the heat from a flame radiates back to the fuel and increases the rate of decomposition and hence the burning rate – a runaway positive feedback process**
- **This process is represented by the t^2 fire growth curves used for engineering calculations**
- **The products of the reaction are heat and the fire effluent: smoke and toxic gases that represent the fire hazard**

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Toxic fire hazards

Toxic hazard evaluation for buildings or products:

1. Time-concentration curves for major products which depends on:
- **Fire growth curve (mass loss rate of fuel [kg/s])**
  Cone calorimeter, SBI, large-scale test
- **Yields of toxic products under a range of combustion conditions (e.g. kg CO/kg material burned)**
  ISO TS19700 tube furnace, ASTM E2058 flammability apparatus

Input data into CFAST or FDS to calculate time concentration curves for different specific fire scenarios

2. Physiological effects of the products
exposure concentrations [$kg.m^{-3}$] or exposure doses [$kg.m^{-3}.min$] required to cause toxic effects in terms of :
- **concentrations or doses likely to impair escape efficiency**
- **incapacitating exposure concentrations or doses**
- **lethal exposure concentrations or doses**

Physiological FED methods in ISO 13571, Purser SFPE Handbook, BS7899-2
Combine 1 and 2 to calculate time to incapacitation.
Compare with specified acceptable tenability time for the end use scenario

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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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Effect of ϕ on CO yield (Tewarson, compartment fires ISO TS 19700 tube furnace comparison)

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Combustion mechanisms and products

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Toxic product yields in fires

- For carbon the main product of combustion is Carbon dioxide. For a well ventilated fire involving non-fire retarded materials, more than 90% of fuel carbon decomposed should be released as CO_2.
- When the fuel/air ratio increases so that combustion becomes vitiated (reduced oxygen availability), then a small % of carbon is released as CO. A small change in combustion efficiency therefore results in a big change in CO yield so that CO concentration is more variable than CO_2.
- The CO concentration is affected mainly by fuel/air ratio, but also by temperature, heating time and fire retardants
- The remainder of the decomposed carbon is in the form of partially decomposed organic products and carbonaceous soot particles (but only a few % as soot).

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Toxic product yields in fires

- The effects of fire retardants on CO formation depend on the mechanism of fire retardancy. Fire retardants acting primarily in the gas phase (free radical scavengers) such as chloride ions (e.g. in antimony halide systems) inhibit gas phase oxidation of CO providing high yields. This is also true to some extent of nitrogen and phosphorus.
- Fire retardants promoting char formation, which reduces oxidation and provides a protective char, tend to lock up some of the carbon in the char and reduce the release of oxides of carbon
- Hydrated alumina systems reduce combustion rates.

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Yields of particulates

- Smoke particles are formed by a process of dehydrogenation and ring cyclization
- Benzene is a major primary aromatic product, further condensation leads to large and large multi-ring molecules with the loss of hydrogen at each stage and ending up with plates of carbon rather like graphite
- Various acid gases and organic vapours become associated with these particles

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Toxic smoke products

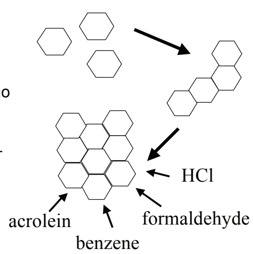
Particles:

Carbonaceous soot particles:

Organic hydrocarbon fragments undergo ring cyclization, forming aromatic ring compounds which coalesce into progressively larger molecular graphite-like plates by removal of hydrogen

Volatile toxic species including acids, organic irritants and carcinogens condense on the particles

The particles if inhaled provide a delivery system for deep lung penetration of "packets" of concentrated toxins



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Yields of organics

- Complex mixtures of a wide range of organic compounds are released from fires, particularly during non-flaming or vitiated flaming decomposition
- Depending to some extent on the composition of starting material, thermal decomposition forms a series of saturated and unsaturated aliphatic compounds, biased towards the low molecular weight end (lots of methane and ethane).
- These become partially oxidised to form aldehydes and ketones (some unsaturated), and organic acids
- Aromatic compounds form by ring cyclization including benzene, toluene, styrene, phenol etc.
- A wide range of more exotic compounds such as isocyanate derivatives, PAHs, dioxins and furans can also be formed depending upon the conditions and the materials decomposed.
- Under well-ventilated flaming conditions yields are low

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Yields of nitrogen-containing compounds

- For nitrogen in fuel materials the main product of combustion is usually N_2, at least from some materials
- Under oxidising conditions (low fuel/air ratios) some is converted to oxides of nitrogen NO and NO_2
- Most is released as NO during fires, which is relatively harmless, but over a period of minutes some is gradually oxidised to NO_2, which is a dangerous lung irritant
- Under less well ventilated conditions some is converted to hydrogen cyanide and other nitriles such as acetonitrile, acrylonitrile, propionitrile and benzonitrile
- There may also be some release of ammonia

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Yields of acidic compounds

- Hydrogen chloride is released directly from PVC by dehydrochlorination rapidly at a around 300°C. Yields may be somewhat lower from chloride in fire retardant compounds such as chlorinated phosphates. Similarly for brominated compounds
- For fluorinated compounds the main product is $COF_{2,}$ which hydrolyses to HF. Some fluorinated hydrocarbons are also releases (e.g. CF_4) and other very toxic compounds and particulates can be formed under certain conditions (see Purser)
- Phosphorus is mainly released as phosphorus pentoxide and converted to phosphoric acid, but some may be released as toxic organophosphorus compounds (TMPP)

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Main fires types and hazard scenarios

1. Non-flaming/smouldering fires
2. Early/well ventilated flaming fires
3. Ventilation controlled fires
- **pre-flashover vitiated flaming fires**
- **post-flashover vitiated flaming fires**

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Non-flaming fires

- Slow rate of decomposition so hazard takes hours to develop – two forms:
- non-flaming thermal decomposition from applied radiation
- Self-sustained smouldering of char forming materials (e.g. wood, cotton)
- High yields of irritant organic partial decomposition products, smoke particles (grey), carbon monoxide and acid gases
- Transition to rapidly growing flaming often occurs at some time, especially if ventilation increased

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Fuel controlled fires

- Flaming fires are initially fuel controlled
- Early well-ventilated fires

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Early/well ventilated flaming fires

- Flaming fires when the fire is small compared with the size of the enclosure and there is plentiful air
- Fire growth depends upon rate of fuel involvement
- Fires outside or during the early stages of fires in buildings
- Main products are heat, water and carbon dioxide, yields of smoke and toxic products low
- Fire type used for most standard tests

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Simple chemistry basics

- Flames consist of combustion gases burning in air the size of the fire depends upon the rate of formation of fuel gases generated by chemical deposition of the solid or liquid fuel or by vaporization of volatile liquids (like petrol) or by direct supply of gas (as in a propane flame)
- In most cases the fuel is generated from a specific area at the base of the fire which combines with oxygen in the air entrained into the flame
- Under open burning conditions the slope of the t^2 fire curve depends upon the ease with which volatile fuel enters the flame.
- The slowest fire growth occurs with materials with a high heat of gasification. A lot of heat is required to produce flammable vapour. E.G. a solid block of oak
- Rapid fire growth occurs when materials have a low thermal conductivity and a low heat of gasification. E.G. Polyurethane foam or expanded polystyrene. Or for volatile liquids like petrol.

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Simple chemistry basics

- Very rapid fire growth occurs when fuel vapours are mixed with air before ignition. This causes a gas explosion. The flame front spread rapidly through the gas/air mixture in a few seconds or less. When the flame front travels faster than the speed of sound a detonation occurs, as with explosives.
- In a closed compartment, the heat from a fire causes an increase in gas pressure. This drives the effluent plume, but seldom causes much of an overpressure. For gas explosions the rapid heating of the air can cause a sufficient overpressure to rupture a building. There was a problem some years ago with gas explosions caused by sudden hydrocarbon propellant release from aerosol cans, such as hair sprays or furniture sprays. In some cases in Birmingham this was sufficient to blow out the walls of buildings.
- Gas leaks followed by explosions can destroy a building, but ignition of a ruptured gas pipe during a fire only results in a flame in most cases.

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BS7974 fire growth rate curves

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Fire growth and reaction to fire properties of materials

- Early fire growth can be estimated from the generic fuel type in a room or from fire test data
- For various types of fuel loads: offices, shops, clothing stores, warehouse packaging, supermarket, children's play areas we have measured fire growth curves and the data are available on a CD rom: natural fire database
- For individual products, such as wall linings or furniture calorimetry data may be available.
- Once a fire gets to sufficient size that it interacts with the enclosure it is in, then fire modelling calculations can be performed. The most important considerations are the extent to which the fire is fuel limited or ventilation controlled.

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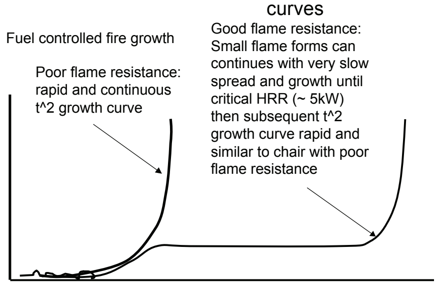
CBUF upholstered furniture fire growth rate curves



Early flames spread and fire growth can be unpredictable depending on composition and geometry of fuel. One a fire reaches a critical size, subsequent growth becomes more predictable

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Ventilation controlled fires

- Once a fire grows to a size where the ventilation is affected by the enclosure size and vents it becomes ventilation controlled
- Almost all fires in enclosures such as buildings or transport vehicles become ventilation controlled ("underventilated" or "vitiated [=*dirty*]) " within a few minutes of flaming ignitions (exception might be a fire in an atrium)
- By far the majority off injuries and deaths occur in ventilation controlled fires

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Ventilation controlled pre-flashover fires

- Vitiated flaming fires with restricted ventilation which limits fire size
- Fire often restricted to object of origin and follows early flaming
- Most common in enclosed buildings, particularly small buildings (houses, shops, offices)
- Main cause of injury and death in buildings
- High yields of smoke and toxic products including CO, HCN and irritants

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Fuel controlled fires: pre-flashover vitiated

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The Equivalence Ratio ϕ

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

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

- Like a carburettor setting: fuel-rich conditions produce CO, smoke and unburned hydrocarbons
- Fuel-lean conditions produce a cleaner burn

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Toxic product yields in fires

- As the fuel/air ratio increases the yields of CO and unburned hydrocarbons increase

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Fuel controlled fires: vented pre-flashover

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Ventilation controlled post-flashover fires

- Vitiated flaming fires similar to pre-flashover case but hotter, with more ventilation and involving much more fuel.
- All surfaces in fire enclosure burning
- Occur in large spaces or when large vents are open, e.g. Bradford stadium, Summerland, Kings Cross, Woolworths
- Very high yields of toxic products including smoke, CO, HCN and irritants. Main cause of death in major fire disasters

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Fuel controlled fires: post-flashover

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Flashover and life-safety

- Flashover occurs when the upper layer temperature away from the fire reaches temperatures exceeding 600°C such that the downwards radiation ignites fuel remote from the immediate fire
- In my experience flashover occurs only when there are large open vents or when a small enclosure opens via a vent into a large open atrium space (such as a fire in a shop unit opening into a shopping mall).
- Most enclosures in most buildings are enclosed most of the time, so in my experience most fires tend to be ventilation limited, at least during the early stages when many occupants are at risk.
- I therefore consider that small vitiated fires are a major cause of injury and death.

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Non-Flashover and life-safety

Examples:

- Enclosed domestic dwelling room fires (victim in room with door and window shut). Three sets of experiments reported here, all small fires which self extinguished without breaking windows, but produced lethal conditions. Fire death involving grandmother and granddaughter in enclosed room.
- Fire test in enclosed "charity shop" rig 432 m^3 volume self extinguished without reaching high temperatures (see later). Fires tests in lounge of enclosed house with open fire room doorway and other small external vents also self extinguished while confined to item ignited. Fire in Chesterfield department store in UK.
- Fire test in bedroom of apartment with external windows partly open and internal doors – fire remained small and confined to bed
- Wood crib fires in large enclosure with small vent remained small (Gordon Cooke FRS)

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Flashover and life-safety

Scaled up examples designed to flashover but failing to do so for some time – structural fire resistance research

- Timber frame multi-storey apartment building. Large fire load consisting of wood cribs placed in lounge of apartment. Windows and room door fully open. Even with large vent temperature only 500ºC after 21.5 minutes Fire Fighters asked to break kitchen window. Improved ventilation led to flashover at 24 minutes. Room temperature increased to 1000ºC and oxygen concentration down to zero.
- Eight storey steel framed building: whole floor open and exterior glazed. Large fire load of 100 kg cribs. Glazing had to be broken from outside by fire fighters to enable flashover. Case of woman in open plan office in New York? On radio. Died after some time but no flashover.

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0.30 1.15 2.15

3.00 3.17 3.20

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Stardust disco Dublin

Moment of flashover

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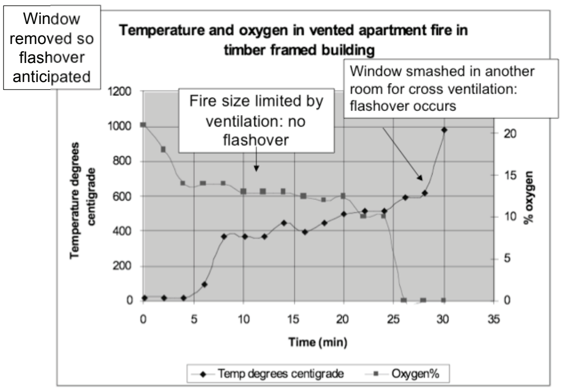

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When Flashover has occurred

Examples of flashover:

- Domestic: When occupants run around and open vents, flashover and serious destruction can occur. Wind on apartment blocks. Hove?
- Store fire: Manchester Woolworths? Woolworths and Stardust large scale tests.
- DuPont plaza hotel, MGM grand?
- Dusseldorf airport
- King's Cross subway
- Summerland, Bradford

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Differences in toxic hazard between pre- and post- flashover ventilation controlled fires

- The yields of toxic gases and chemical composition of effluents from pre and post flashover ventilation controlled fires are similar, perhaps slightly increased CO and HCN yields
- The hazard to occupants remote from the fire are greater, partly due to the larger fire and increased volume of effluents
- and partly due to the hotter fire plume and danger of fire spread beyond the enclosure of origin

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Conclusion regarding fire types and deaths

- Small early well ventilated fires can cause death by burns if victim is intimate with fire
- In most cases fires inside buildings (especially in domestic enclosures) become small vitiated fires which cause incapacitation and death due to toxic effluent exposures and heat.
- In some cases fires are supplied with air from vents and are able to grow to flashover. Occupants nearby are likely to be dead but fire may then break out to fill large spaces within building with toxic effluent and heat.
- Some lethal fires may remain in the smouldering phase and never flame, or smoulder for some time and then flame (possibly involving back-draught if vents are opened on an enclosed fire compartment

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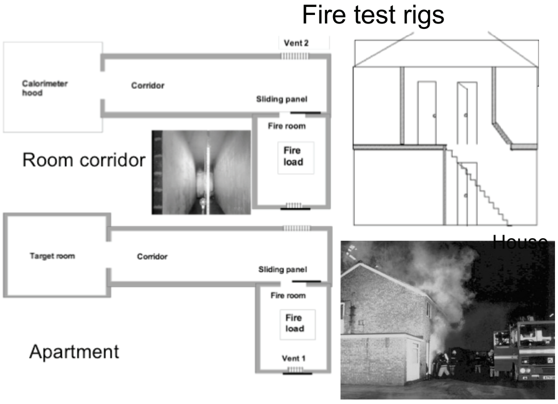
Fire test rigs



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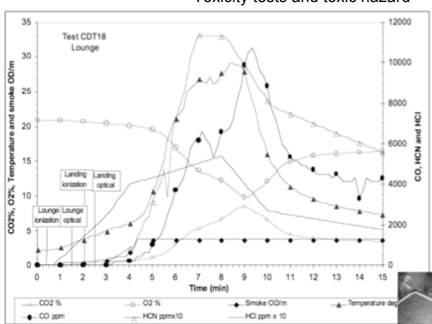
Toxicity tests and toxic hazard



Armchair: FR polyacrylonitrile covers, CM polyurethane foam burning in lounge with open doorway in enclosed house

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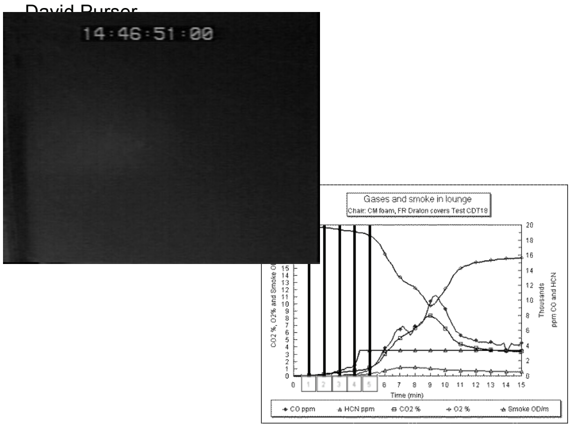

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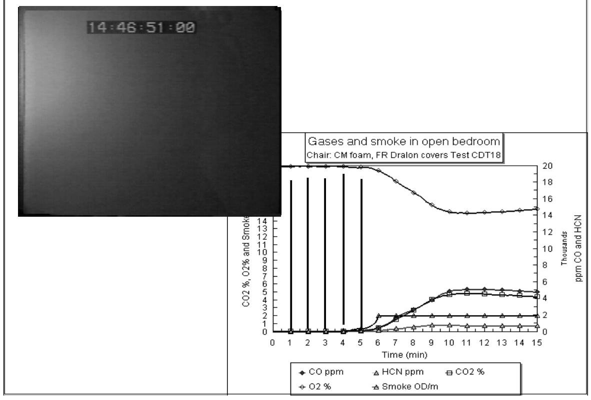

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Fully furnished house fire

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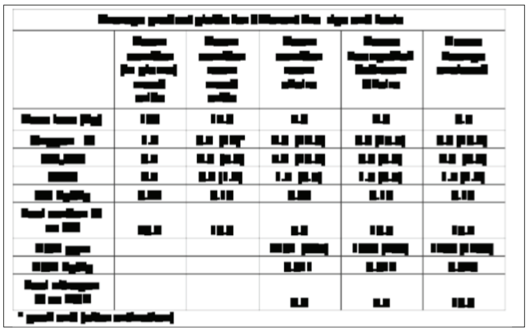
Average yields for apartment and house fire tests



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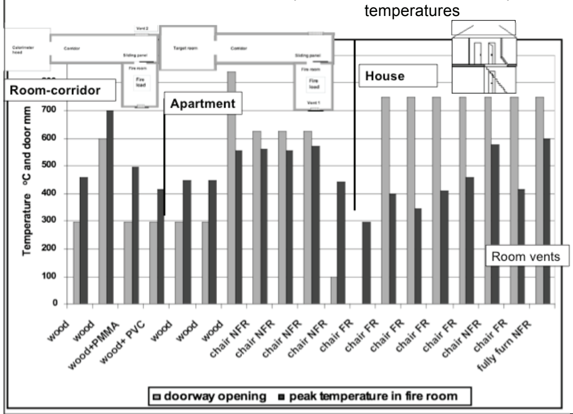
Apartment fires ventilation and peak temperatures



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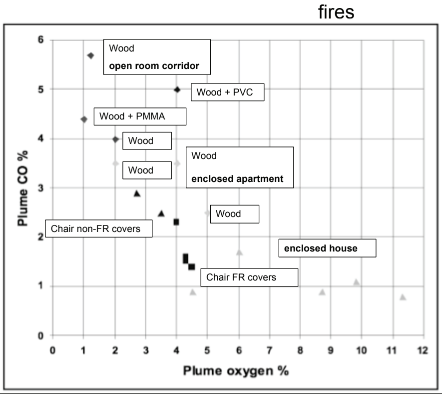
Plume CO versus plume oxygen for all fires



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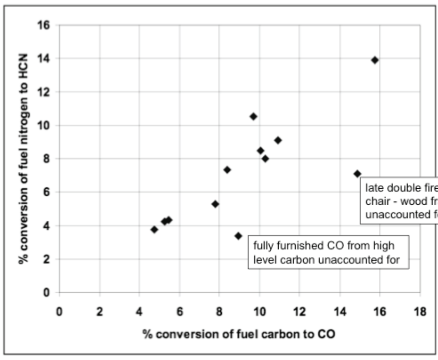
CO and HCN yields in apartment and house chair fires



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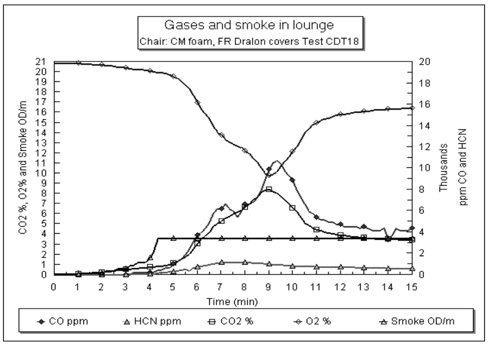
Toxic gases and smoke in fire room for an armchair fire in a house lounge (door to hall open)



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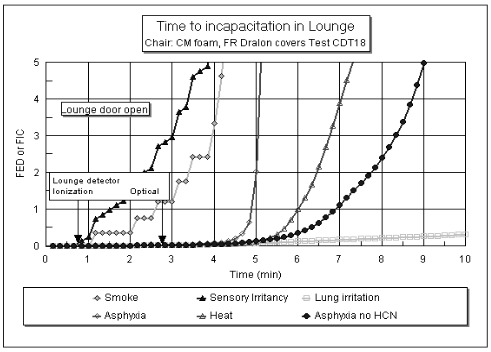
Hazards in fire room from an armchair fire in a house lounge



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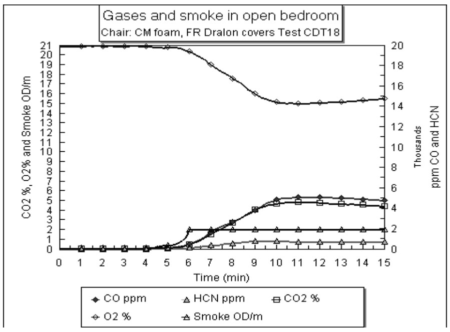
Toxic gases and smoke in open bedroom for an armchair fire in a house lounge (door to hall open)



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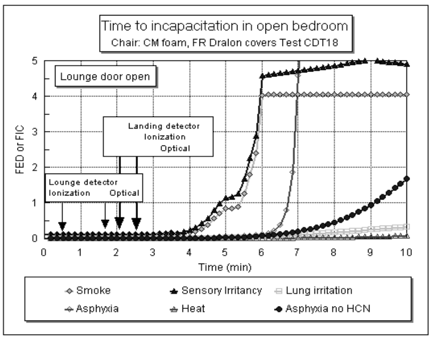
Hazards in open bedroom from an armchair fire in a house lounge



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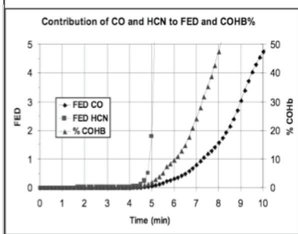
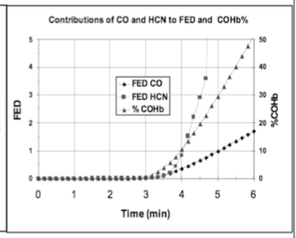
Relative contributions of CO and HCN to incapacitation FED and COHb%



Test CDT 18 lounge chair with FR acrylic covers



Test CDT 23 bedroom chair with non-FR acrylic covers, room fully furnished

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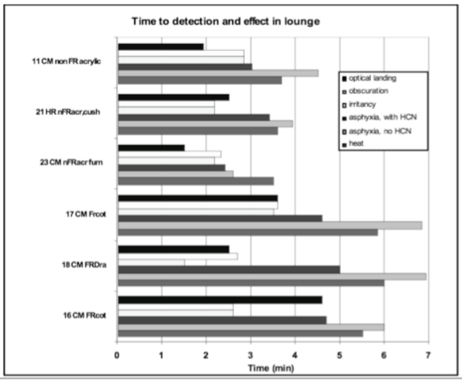
House and apartment fires - times to detection and tenability



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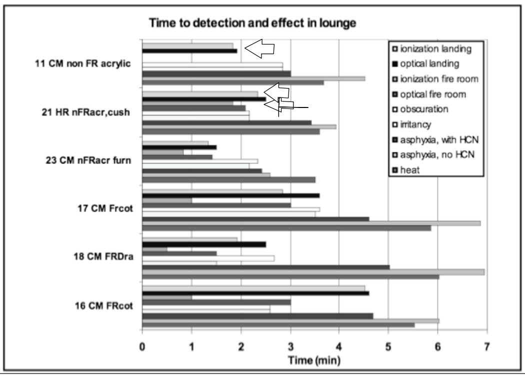
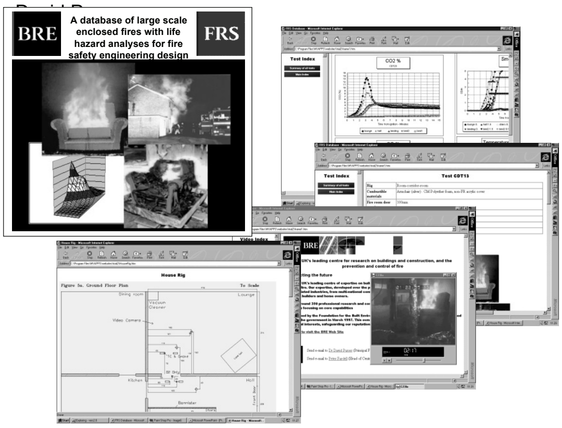
Effect of detector location





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Backdraught

- Clouds of flammable fire gases mixing rapidly with air can occur sometimes during fires. This can result in a rapid jet of fire called a backdraught
- This tend to occur when an active fire occurs in an enclosure with is or becomes enclosed. The fire is starved of oxygen so the flames die down and may extinguish (to a residual glow). The partially burned fuel is still very hot so it continues to decompose, producing flammable fire gases.
- Something happens to let fresh air into the enclosure to mix with the fuel gases. This may be a door being opened or a window failing.
- The fuel/air mixture ignites and a flame front passes rapidly through the mixture, producing a large jet of flame.

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Backdraught experiment

- Using room corridor rig a 100 kg crib was ignited in the ISO room with the room doorway to the corridor and an external door to the room open.
- The fire was therefore well ventilated and grew to a large size. The doors were suddenly closed to fully enclose the fire.
- The fire died down and ceased flaming, but contained a fuel rich atmosphere
- The door to the corridor was suddenly opened
- A fuel rich plume fed into the corridor and mixed with incoming air
- The plume ignited suddenly such that a long blast of flame was formed briefly in the corridor.

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Backdraught incident in Birmingham

- A backdraught incident occurred in Birmingham a few years ago that resulted in firefighter deaths.
- A fire occurred in an apartment at a high floor level in a tower block (near Bristol circus?)
- The fire was in a domestic lounge or bedroom on the side of the building facing the high wind. The room window and door were shut.
- The fire consumed the oxygen in the room (combustion became vitiated) and the fire died down somewhat.
- A firefighter opened the room door, whereupon the wind pressure cause the glazing to fail. The sudden mixture of air and fuel produced a backdraught jet from the room door which engulfed the firefighters.