Combustion science for (and) Fire science - 1

- Combustion? Fire? – Commonalities and Differences
- Fire triangle – components – fuel, oxidizer and chemistry – chemical thermodynamics and chemical dynamics (rate)
- Gaseous (g), liquid (l) and solid (s) fuels – what gives you heat finally?
- What are fuels, oxidizers anyway? O/F ratio? Heats?
- Steps in fire – ignition, incipient fire, propagation, flash back, full fire, rollover, extinguishment – at different environmental conditions – wind, ambient temperature, pressure, humidity,
- Are fuels only fuels? oxidizer only oxidizer? What about reactive substances having fuel and oxidizer elements in the molecule.
- Species, heat of formation, oxidant-fuel ratio for combustion, stoichiometry, fuel richness, reaction pathways– heat of combustion?, flame temperature? product gases composition?
- Premixed and diffusion flames in laboratory and practical situations

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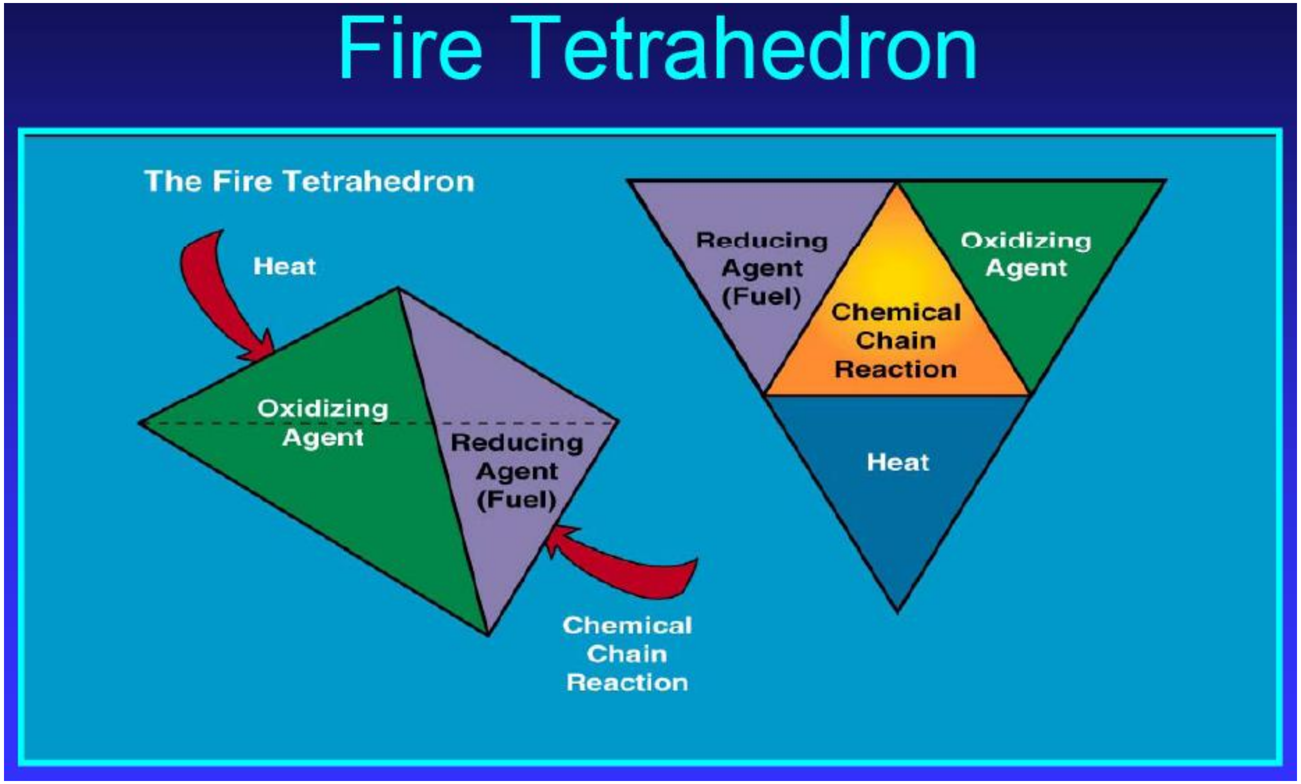
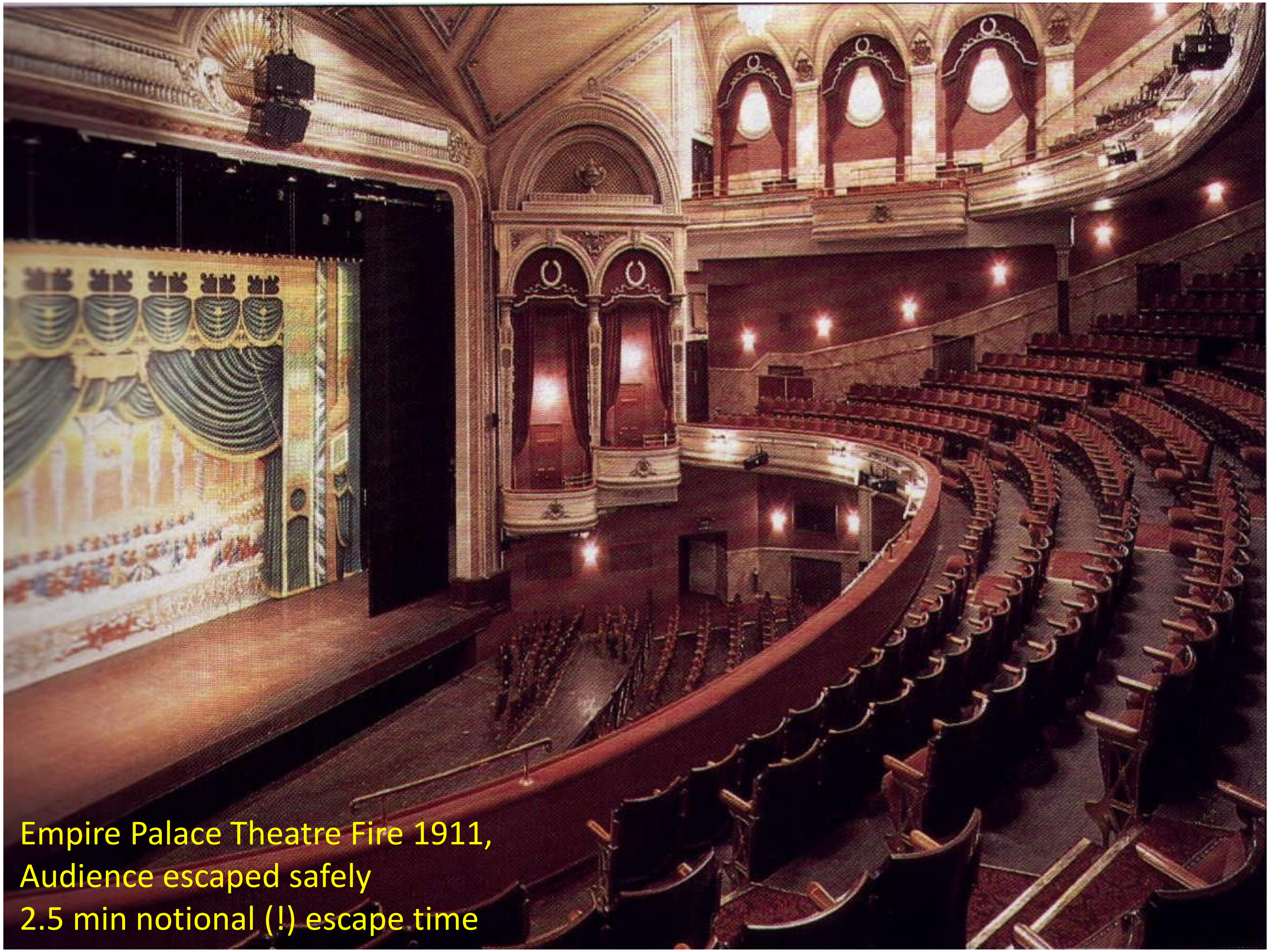
Combustion? Fire? – Commonalities and Differences



Combustion and fires require the "fire tetrahedron" to understand and explain. Combustion occurs in controlled way occurs more frequently (fortunately) than unwanted and uncontrolled combustion process. Combustion in controlled way is managed with enough or slightly more oxidant (most usually oxygen in air, but with others as well)

Uncontrolled combustion may start with enough oxidant but reaches its full size with much reduced oxidant. These have larger fraction of incomplete combustion products (toxic most of the time) and an appearance that is very bright and perhaps **sooty**.



Empire Palace Theatre Fire 1911,
Audience escaped safely
2.5 min notional (!) escape time

Example of what I consider ill-designed theatre. I spent three hours in Lincoln theatre at Manhattan, NYC - same design. Enormous fire load and dangerous balcony. Solid and some liquid fuels too. I was positively scared of spending more time in the most congested arrangement!

Gaseous (g), liquid (l) and solid (s) fuels – what gives you heat finally?

- Fuel will achieve a reaction rate with oxygen sufficient to produce a flame only when it is in the gaseous state.
- Liquid burns when temperature high enough to vaporize it (flash point to provide flash fire and fire point to establish the fire) – in droplet form or in the form of a pool.
- Solid must be hot enough to decompose into gaseous products (pyrolysis)
- Thus flame appears only when gases react with oxidizer exothermically.
- Gaseous fuels are: natural gas (mostly methane), LPG and propane and other liquid fuels storage and transport that are both liquid to start with and gas later (problem of BLEVE, see later), hydrogen in laboratories and industries.
- Liquid fuels – hydrocarbons like gasoline, diesel, n-heptane, and alcohols, ammonia and other reactive liquids like nitroglycerine and explosive mixtures.
- Solid fuels like a range of plastics in semi-solid and finished form, wood products, vehicular tires, reactive substances like ammonium nitrate (for fertilizer industry), propellants and explosives like nitrocellulose, etc
- Oxidizers are oxygen in air (23 % w), liquid oxygen, oxides of nitrogen like nitrogen tetroxide, hydrogen peroxide, Ammonium perchlorate solid
- Stoichiometrically balanced compounds like RDX, HMX, PETN, etc
- Both oxidizer and fuel elements are present in many compounds.

What are fuels, oxidizers anyway?. O/F?, heat?

- Chemically, an oxidizer is defined as one which acquires electrons and fuel as the one which can donate electrons. Fuel reduces and oxidizer oxidizes.

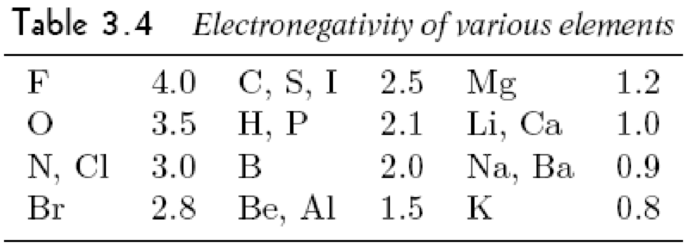


Table 3.4 *Electronegativity of various elements*

F	4.0	C, S, I	2.5	Mg	1.2
O	3.5	H, P	2.1	Li, Ca	1.0
N, Cl	3.0	B	2.0	Na, Ba	0.9
Br	2.8	Be, Al	1.5	K	0.8

- The table of electro-negativity reveals it all. *F* is the most powerful oxidizing element and K is the most powerful fuel. In F_2O_3, O is the “fuel”
- Generally, oxygen is the largest oxidizing element that we need to be concerned with. Carbon(C) and hydrogen (H) are the largest fuel elements.
- Fuel and oxidizers will react at correct “stoichiometry” to produce stable products of combustion:

  $H_2 + 0.5\ O_2 \rightarrow H_2O$; $C + O_2 \rightarrow CO_2$; $CH_4 + 2O_2 + 2(79/21)\ N_2 \rightarrow CO_2 + 2\ H_2O + 2(79/21)\ N_2$

  H_2O and CO_2 are the stable products of combustion at ambient conditions and N_2 is inert.
- Nitrogen (N) is usually non-reactive. It is however, reactive at high temperatures (~ 2500 K+). N_2O_4 is an oxidizer (it goes to $2NO_2$). Hydrogen peroxide (H_2O_2) is an oxidizer (for it goes to H_2O and 0.5 O_2). AP(NH_4ClO_4) is an oxidizer for it releases 35 % O_2 and some Cl_2 that acts also as oxidiser (to give HCl). AP is used as the prominent rocket oxidizer.
- RDX [$C_3H_6N3(NO_2)_3$] is fuel rich to 20 %, HMX [$C_4H_8N_4(NO_2)_4$] is also 20 % fuel rich. NC is 12.5% fuel rich and NG is 4 % oxidizer rich. Both these are rocket oxidizer and explosive compounds.
- Those that have less than 25 % oxidizer or fuel rich are called stoichiometrically balanced.
- Explosions can result from high temperature and pressure rise in a container with exothermic reactions. Explosives are heat or friction sensitive compounds that react in milliseconds to high temperature gaseous products leading to very high pressure rise and shock waves.

O/F

H2 (1 mole) + 0.5 O2 (0.5 mole) $\longrightarrow$ H_2O (1 mole)

2 g + 16 g $\longrightarrow$ 18 g

(O/F by moles is 0.5 and O/F by mass is 16/2 = 8)

C (1 mole) + O2 (1 mole) $\longrightarrow$ CO_2 (1 mole)

12 g + 32 g $\longrightarrow$ 44 g (O/F moles is 1; O/F mass = 32/12 = 2.67

CH_4 (1 mole) + $2O_2$ (2 moles) + 2(79/21) N_2 (7.52 moles)

$\longrightarrow$ CO_2 (1 mole) + 2 H_2O (2 moles) + 2(79/21) N_2 (7.62 moles)

16 G + 64 g + 210.6 g $\longrightarrow$ 44 g + 36 g + 210.6 g

(Molar air-to-fuel ratio is 9.52 and mass air-to-fuel ratio is (64 + 210.6)/16 = 17.1

Summary: There is no molar balance. This means there is no volume conservation. However mass is conserved. This is the fundamental principle of natural changes.

Combustion does not always occur in stoichiometry particularly when fuel and oxidizer are premixed in specific proportions. They can be fuel rich or fuel lean. This is decided by equivalence ratio (er or ϕ) $\phi = (\text{fuel:air})/(\text{fuel:air})_{\text{stocihiometry}}$

Thus if ϕ < 1, the mixture if fuel lean and ϕ > 1, it is fuel rich.

Heats of reaction and combustion

- Chemical reactions that are exothermic are of importance here. All the hydrocarbons and oxygenated fuels (like alcohols , wood or reactive species).
- Different species are at different states of enthalpy. These are called the heats of formation. When reactions occur the reactants go to products by reducing the net enthalpy. This net change of heat is called the heat of reaction. The negative of this is the heat of combustion and this is always positive – heat is released to raise the temperature of products. The heats of formation are determined so that the heats of combustion are correctly obtained.
- With the table of heats of formation for various species and by treating the chemical equation as an algebraic equation, one can sum up the heats of formation with associated coefficients (called stoichiometric coefficients) to get the heats of combustion.

Reaction pathways, equilibrium, composition and flame temperature

- Chemical reactions do not go along the simplest pathways discussed earlier. In reality such a pathway has a large hump of enthalpy in between the reactants and the products. This hump is called activation energy.
- Only those molecules that have high random kinetic energy, higher than the mean collide with several other molecules and produce several species including the final products.
- Under certain conditions of mixture leanness, the products at flame temperatures lower than the maximum possible, the largest fraction will be the stable products.
- Near stoichiometry and under fuel rich conditions, many intermediate products like CO, OH, O, H, HO_2 are all produced in various proportions.
- Under very fuel rich conditions many gas phase pyrolysis products that are produced because broken fuel fragments get only other broken fuel fragments to react largely. These are aldehydes, poly-aromatic hydrocarbons (PAH) some of which are carsinogenic.
- At high temperatures, depending on the residence times for the reaction in a flowing fluid, the reactions go close to chemical equilibrium. What this means is that the forward and the reverse reaction rates are nearly equal to each other. Under these conditions the chemical times are much smaller than flow times.

Reaction pathways, equilibrium, composition and flame temperature

- The equilibrium conditions that is a limit close to which the system will reside are valid near lean and stoichiometric conditions and mildly rich conditions (for all $\phi < 1.1$ or so).
- For very rich conditions, the rates of reaction control the generation of the products. In these cases, the flow dynamics will strongly affect the composition. This implies that geometry of the flow as well whether flow conditions are laminar and turbulent will matter. Determining the actual composition in such cases calls for invoking larger chemistry information in a FDS like calculation.
- However, under equilibrium conditions, one needs the balance of chemical elements and equilibrium relations to compute the composition. This is done by using advanced codes called CEC 71 etc.
- The determination of the composition depends on the initial composition (like one mole of H_2 with one mole of O_2 or half mole of O_2, etc). It also depends on the temperature and pressure at which you are seeking the composition. For instance one can ask what the composition of propane-air mixture at an equivalence ratio of 0.9,say at a temperature of 1500 K or 2000 K or whatever you choose to set.
- If this temperature is higher than the adiabatic flame temperature (the ideal temperature that is obtained with no heat losses or other entropic losses like friction etc), further decomposition will occur absorbing the energy to back to adiabatic conditions.
- By hunting for that flame temperature that preserves the enthalpy including the heats of formation of initial reactants, one gets the adiabatic flame temperature. The calculation process is also affected by pressure since increased pressure opposes decomposition (it also opposes evaporation in heated liquids)
- Thus one gets the composition and flame temperature of any given reactant set.

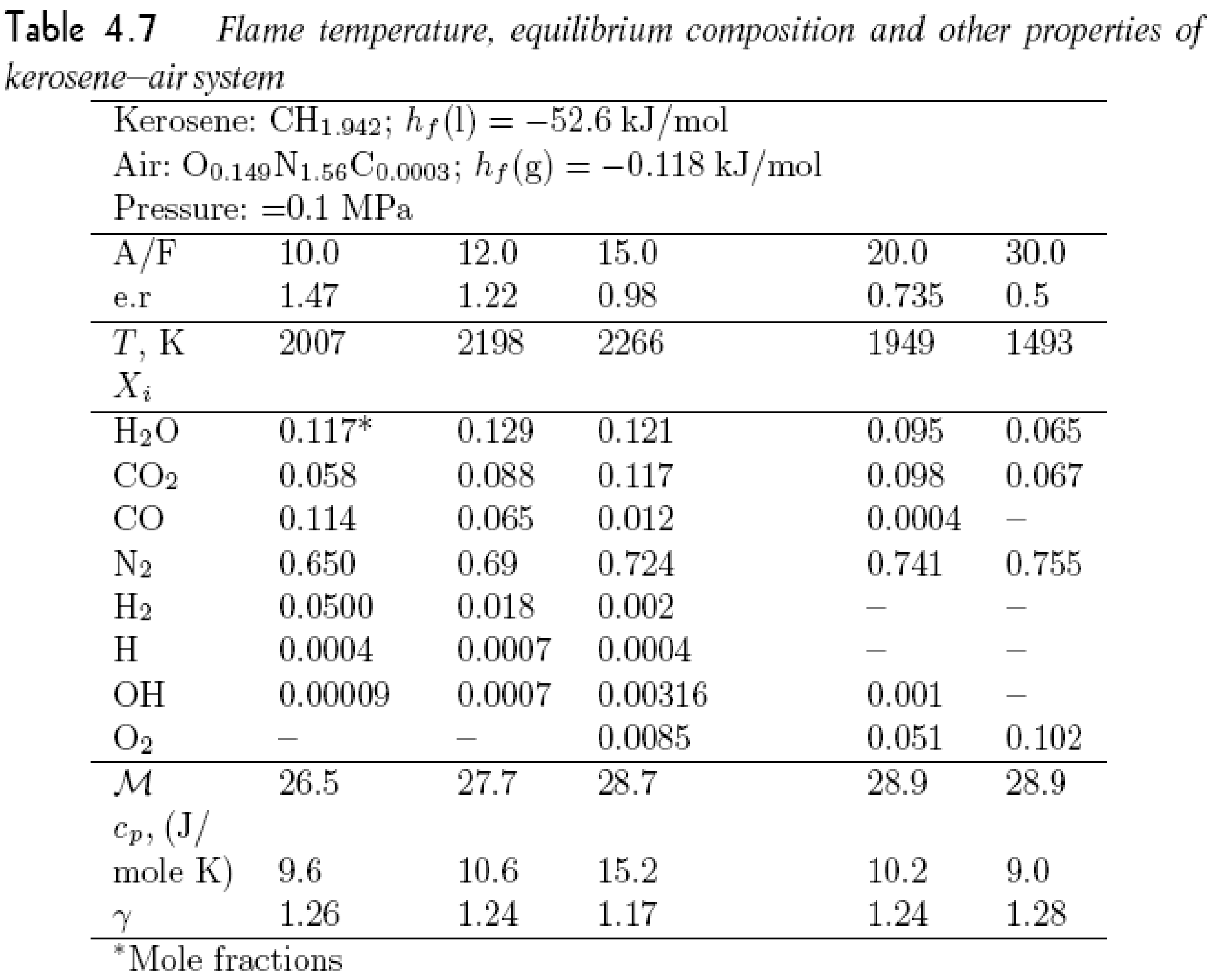


Table 4.7 *Flame temperature, equilibrium composition and other properties of kerosene–air system*

Kerosene: $CH_{1.942}$; $h_f(\mathrm{l}) = -52.6$ kJ/mol
Air: $O_{0.149}N_{1.56}C_{0.0003}$; $h_f(\mathrm{g}) = -0.118$ kJ/mol
Pressure: =0.1 MPa

A/F	10.0	12.0	15.0	20.0	30.0
e.r	1.47	1.22	0.98	0.735	0.5
T, K	2007	2198	2266	1949	1493
X_i					
H_2O	0.117*	0.129	0.121	0.095	0.065
CO_2	0.058	0.088	0.117	0.098	0.067
CO	0.114	0.065	0.012	0.0004	–
N_2	0.650	0.69	0.724	0.741	0.755
H_2	0.0500	0.018	0.002	–	–
H	0.0004	0.0007	0.0004	–	–
OH	0.00009	0.0007	0.00316	0.001	–
O_2	–	–	0.0085	0.051	0.102
$\mathcal{M}$	26.5	27.7	28.7	28.9	28.9
c_p, (J/mole K)	9.6	10.6	15.2	10.2	9.0
γ	1.26	1.24	1.17	1.24	1.28

*Mole fractions

Note: Left to right the mixture is becoming leaner. Little of radicals and CO seen as we move towards lean conditions

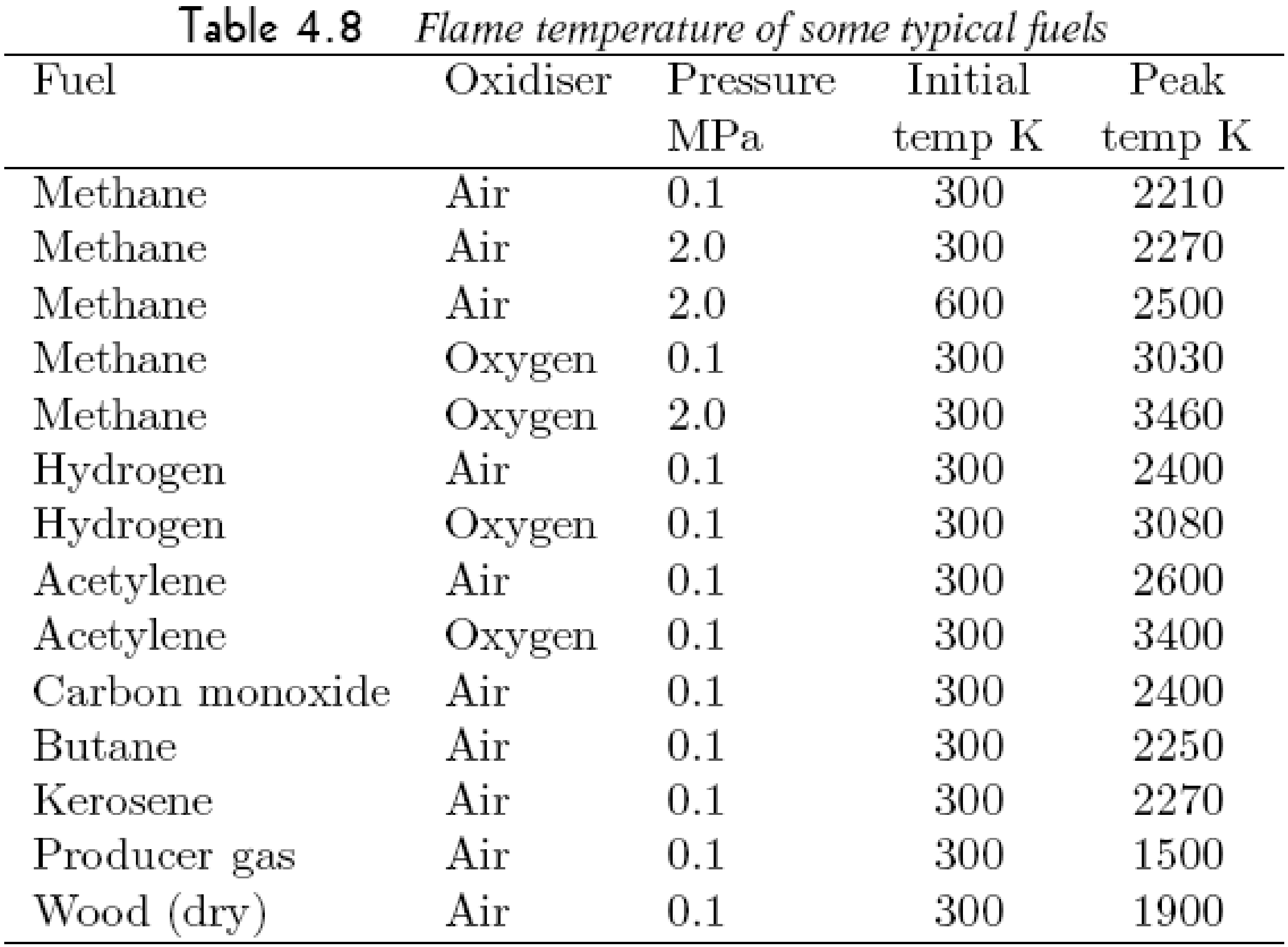
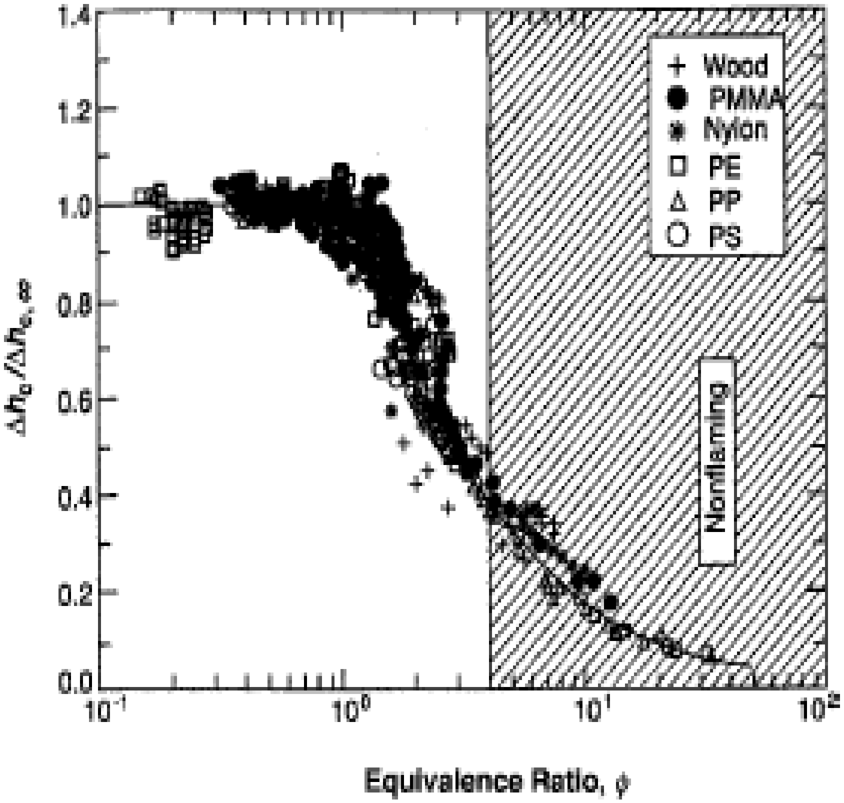


Table 4.8 *Flame temperature of some typical fuels*

Fuel	Oxidiser	Pressure MPa	Initial temp K	Peak temp K
Methane	Air	0.1	300	2210
Methane	Air	2.0	300	2270
Methane	Air	2.0	600	2500
Methane	Oxygen	0.1	300	3030
Methane	Oxygen	2.0	300	3460
Hydrogen	Air	0.1	300	2400
Hydrogen	Oxygen	0.1	300	3080
Acetylene	Air	0.1	300	2600
Acetylene	Oxygen	0.1	300	3400
Carbon monoxide	Air	0.1	300	2400
Butane	Air	0.1	300	2250
Kerosene	Air	0.1	300	2270
Producer gas	Air	0.1	300	1500
Wood (dry)	Air	0.1	300	1900

Note: Most stoichiometric hydrocarbon-air and hydrogen-air mixtures have flame temperatures of 2200 to 2300 K. H_2-O_2 has very high flame temperature


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
$\Delta h_c / \Delta h_{c,\infty}$
10^{-1}
10^{0}
10^{1}
10^{2}
Equivalence Ratio, ϕ
+ Wood
● PMMA
✱ Nylon
□ PE
△ PP
○ PS
Nonflaming

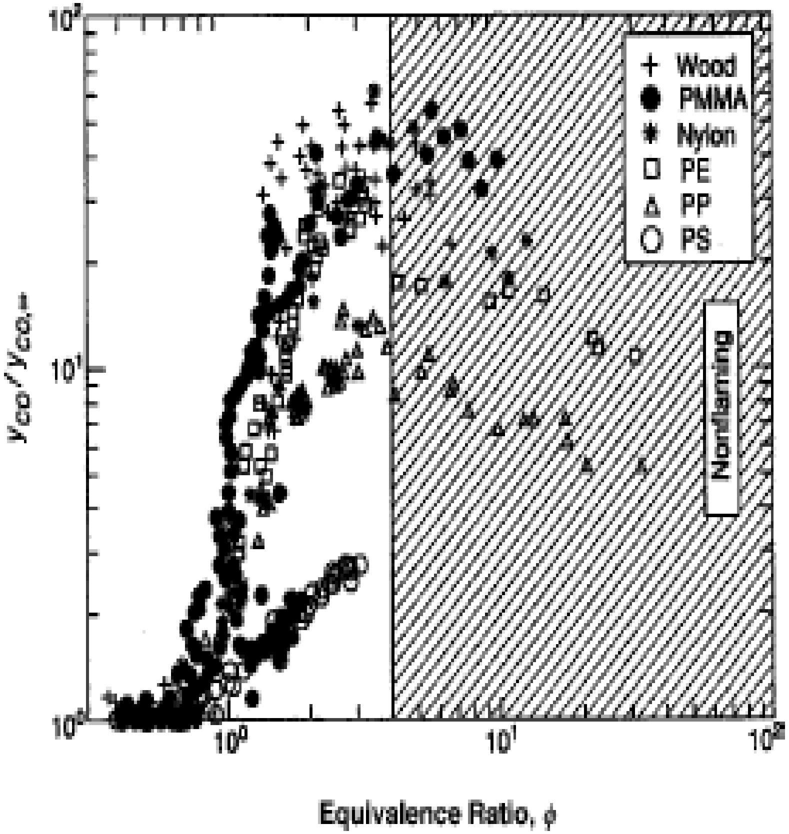
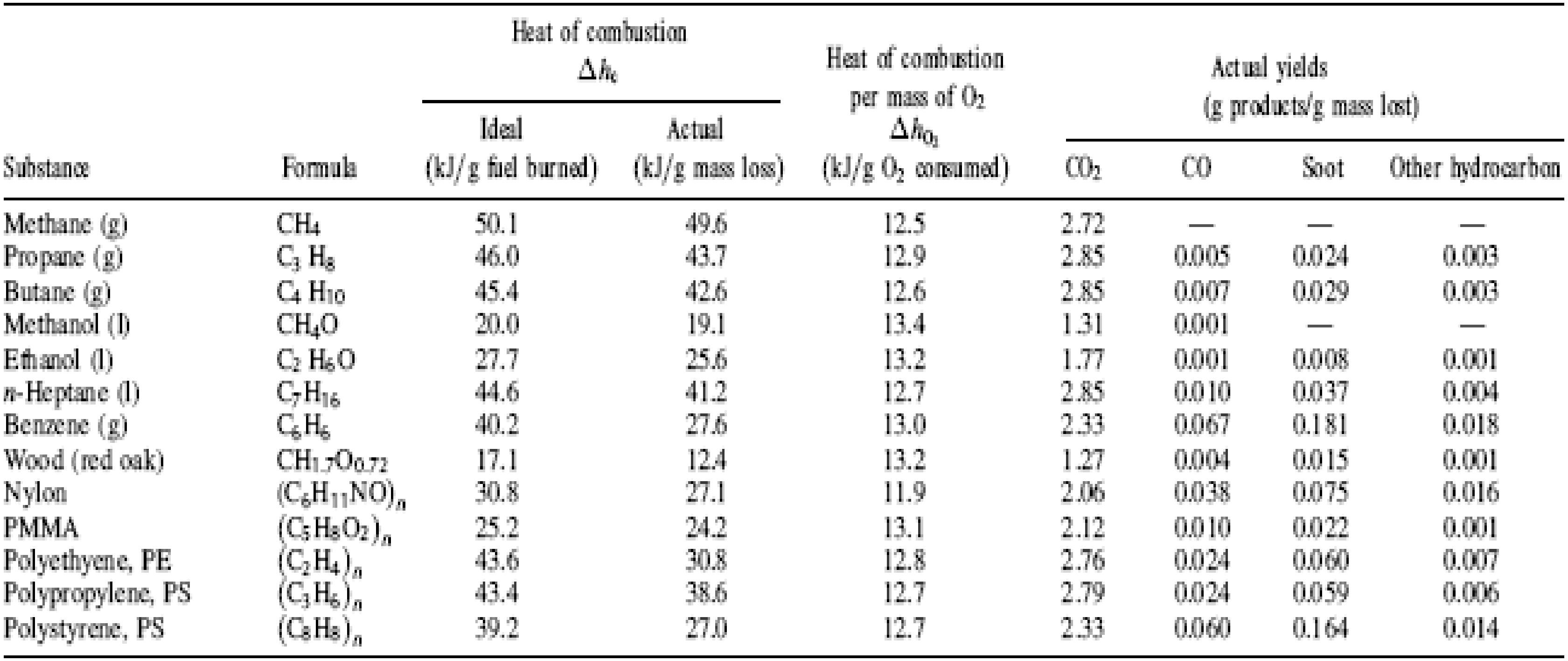

10^{2}
10^{1}
10^{0}
$y_{CO} / y_{CO,\infty}$
10^{0}
10^{1}
10^{2}
Equivalence Ratio, ϕ
+ Wood
● PMMA
✱ Nylon
□ PE
△ PP
○ PS
Nonflaming

Table 2.3 Products of combustion in fire with sufficient air (abstracted from Tewarson [3])



Substance	Formula	Heat of combustion Δh_c Ideal (kJ/g fuel burned)	Heat of combustion Δh_c Actual (kJ/g mass loss)	Heat of combustion per mass of O_2 Δh_{O_2} (kJ/g O_2 consumed)	Actual yields (g products/g mass lost) CO_2	CO	Soot	Other hydrocarbon
Methane (g)	CH_4	50.1	49.6	12.5	2.72	—	—	—
Propane (g)	C_3H_8	46.0	43.7	12.9	2.85	0.005	0.024	0.003
Butane (g)	C_4H_{10}	45.4	42.6	12.6	2.85	0.007	0.029	0.003
Methanol (l)	CH_4O	20.0	19.1	13.4	1.31	0.001	—	—
Ethanol (l)	C_2H_6O	27.7	25.6	13.2	1.77	0.001	0.008	0.001
n-Heptane (l)	C_7H_{16}	44.6	41.2	12.7	2.85	0.010	0.037	0.004
Benzene (g)	C_6H_6	40.2	27.6	13.0	2.33	0.067	0.181	0.018
Wood (red oak)	$CH_{1.7}O_{0.72}$	17.1	12.4	13.2	1.27	0.004	0.015	0.001
Nylon	$(C_6H_{11}NO)_n$	30.8	27.1	11.9	2.06	0.038	0.075	0.016
PMMA	$(C_5H_8O_2)_n$	25.2	24.2	13.1	2.12	0.010	0.022	0.001
Polyethyene, PE	$(C_2H_4)_n$	43.6	30.8	12.8	2.76	0.024	0.060	0.007
Polypropylene, PS	$(C_3H_6)_n$	43.4	38.6	12.7	2.79	0.024	0.059	0.006
Polystyrene, PS	$(C_8H_8)_n$	39.2	27.0	12.7	2.33	0.060	0.164	0.014

Thus the net enthalpy called the heat of combustion comes down wherever and whenever the fraction of incomplete products increases. When you compute the heat produced per unit mass of oxygen participating in the combustion reaction, its is about the same – 12.5 to 13. This information is used in an apparatus known as ***Cone calorimeter*** a standard apparatus to characterize the behavior in fires under different intensities and to measure the heats of combustion.

What about reaction rates?

The next aspect to address is the reaction rate. Gaseous reactions occur because of energetic collisions. These are true of heterogeneous reactions as well, though more complex. They are represented by Arrhenius law as

$$\dot{w}_f''' = A_f Y_f^{n_1} Y_0^{n_2} p^n e^{-E/RT}$$

where the Y_i's are mass fractions and p the pressure and T, the temperature and $\dot{w}_f'''$ is the reaction rate is in terms of kg/m^{3}s;

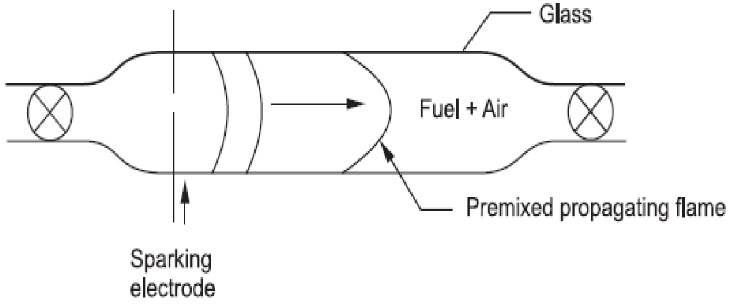
$\dot{w}_f'''/\rho$ (1/s), where ρ is the density of the gaseous mixture. This quantity represents the inverse of reaction time. Reaction time, $\tau_{ch} = \rho / \dot{w}_f'''$

Steps in a Fire

Ignition, Incipient fire, Propagation, flash over, Full fire, Extinguishment – at different environmental conditions – wind, ambient temperature, pressure, humidity

We first deal with propagation of flames in premixed gas mixtures since these can be directly related to reactivity of the fuel- oxidant mixture. If the oxidant is fixed (say air), then this means we get the reactivity of the fuel gas.

Premixed flames



$$S_u \simeq \sqrt{(k/c_p)A_f}\frac{RT_{in}}{p}p^{n/2}e^{-E/2RT_f} \simeq p^{(n/2)-1}e^{-E/RT_f},$$

$$S_T/S_u = d_t/d_l = \sqrt{(0.01Re)} = 0.1Re^{1/2}$$

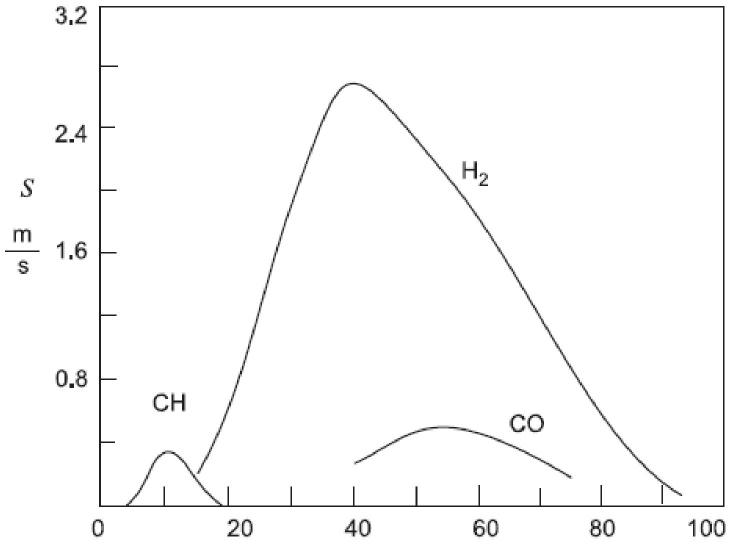
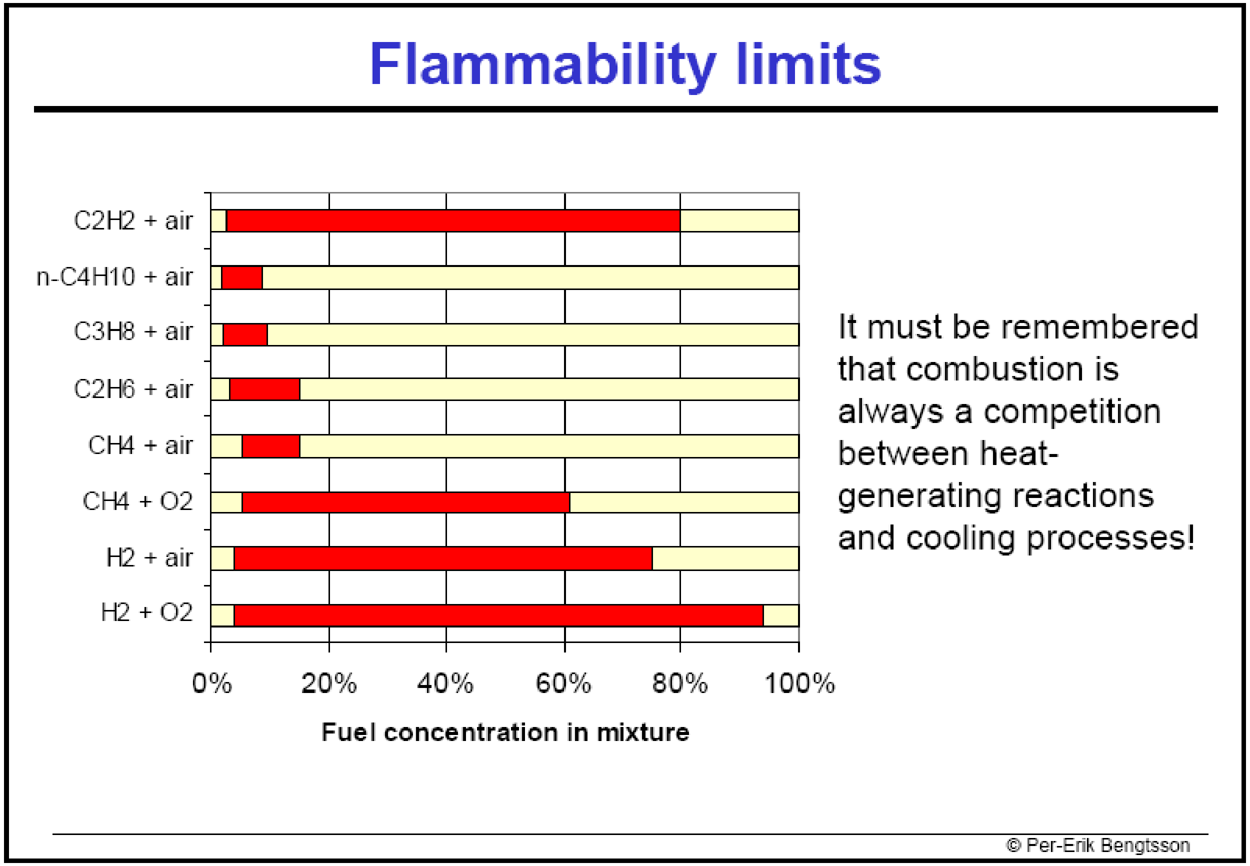


Figure 6.2*Flame speed of fuel–air mixtures*

Comments: The flame speed at stoichiometry obeys a simple relationship with reaction rate. In fact it is proportional to the square root of the reaction rate. Turbulent flame speeds are related to Reynolds number as above.

There are upper and lower limits for flame propagation.– rich and lower. Adiabatic flame temperature also drops towards the limits. It is about 1000 K at the limits. Rich flames saturate at about 1200 to 1400 K due to energy absorption in sooting and PAH, etc.

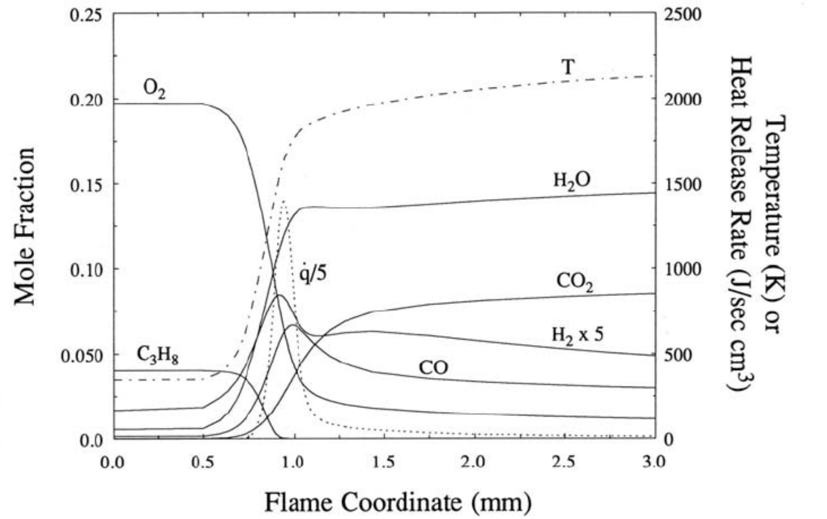


Flammability limits

It must be remembered that combustion is always a competition between heat-generating reactions and cooling processes!

Flammability limits are observed because the flames grow very weak towards the Limits and the propagation cannot keep with the minimum heat losses in any system. If heat losses are more the flames will propagate at lower speeds. Even the stoichiometric flame will refuse to propagate through a tube of small diameter. This is called quench distance for the mixture.

Concentrations profiles across reaction zone (1)



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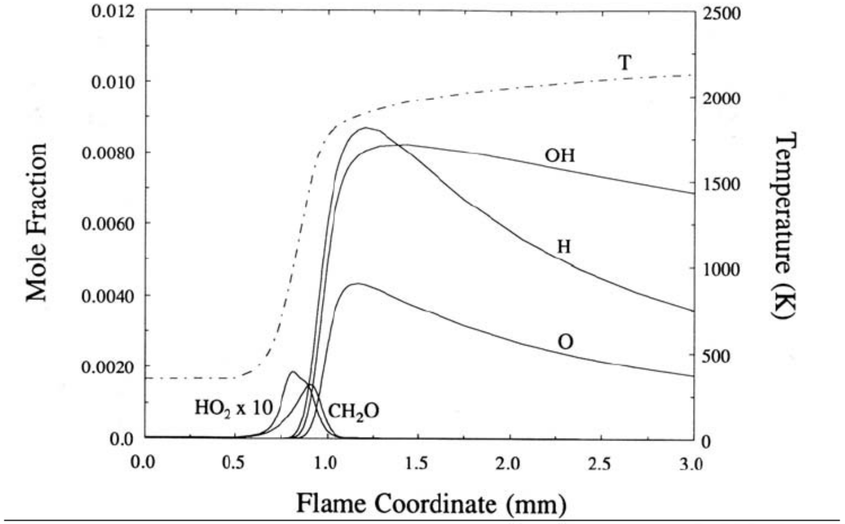
Concentrations across the reaction zone (2)



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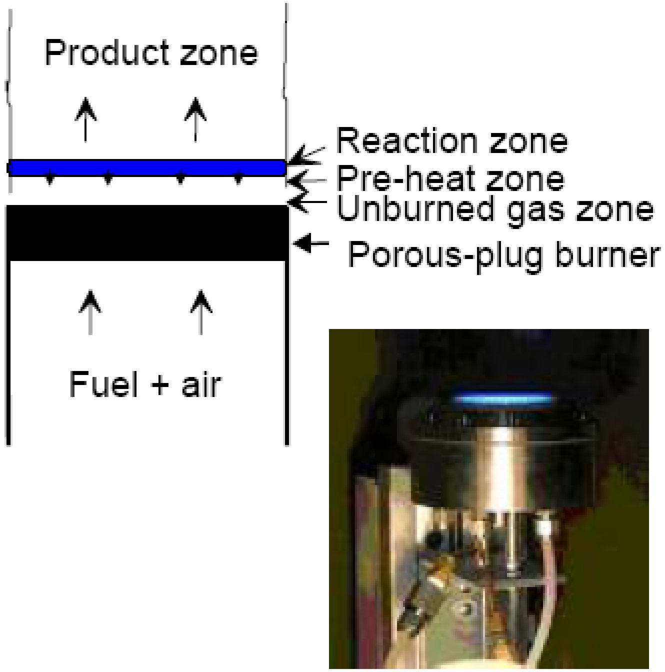
Note: There are several species seen through the laminar premixed flame. There are several radicals and ions that are also present in the flame. The flame thickness, δ_f if measured as significant heat release zone, is about 0.4 mm in this case. The thickness behaves as $\rho_u S_u \delta_f = (k/cp)$, mean gas density x flame speed x flame thickness ~ constant. Thus faster flames are thinner. The presence of ions and radicals makes the flame electrically conducting.

Premixed flames - Diffusion flames

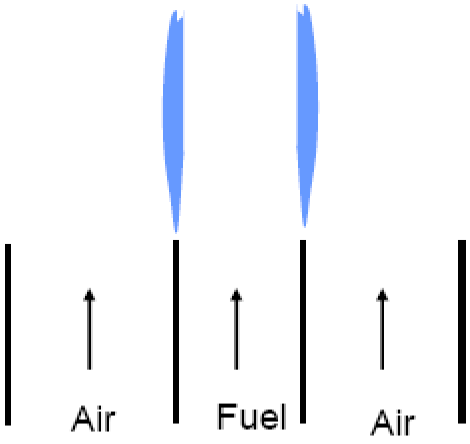
Premixed flames

Fuel and air is mixed before combustion

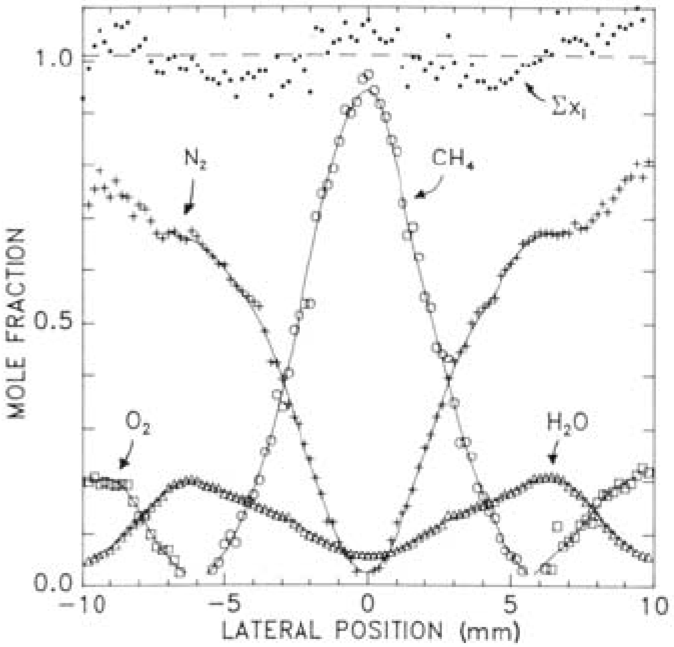


Nonpremixed flames (Diffusion flames)

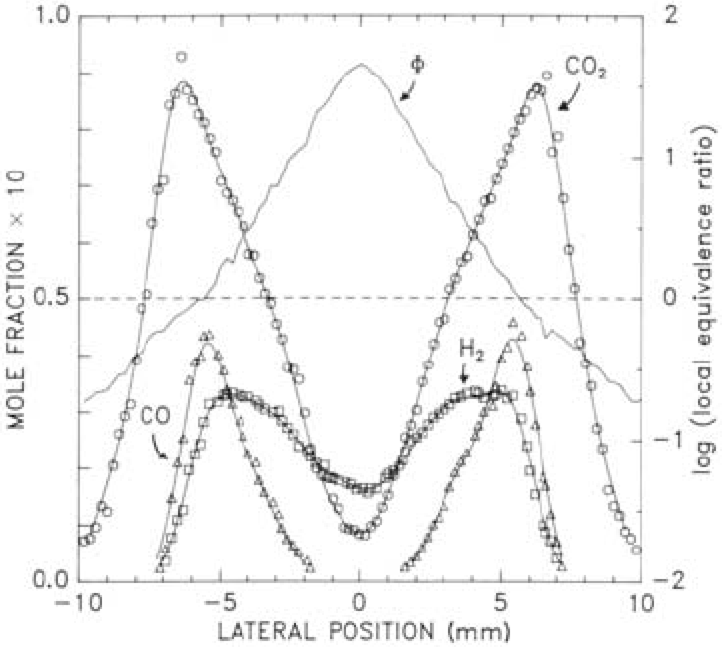
Fuel and air burn when they meet



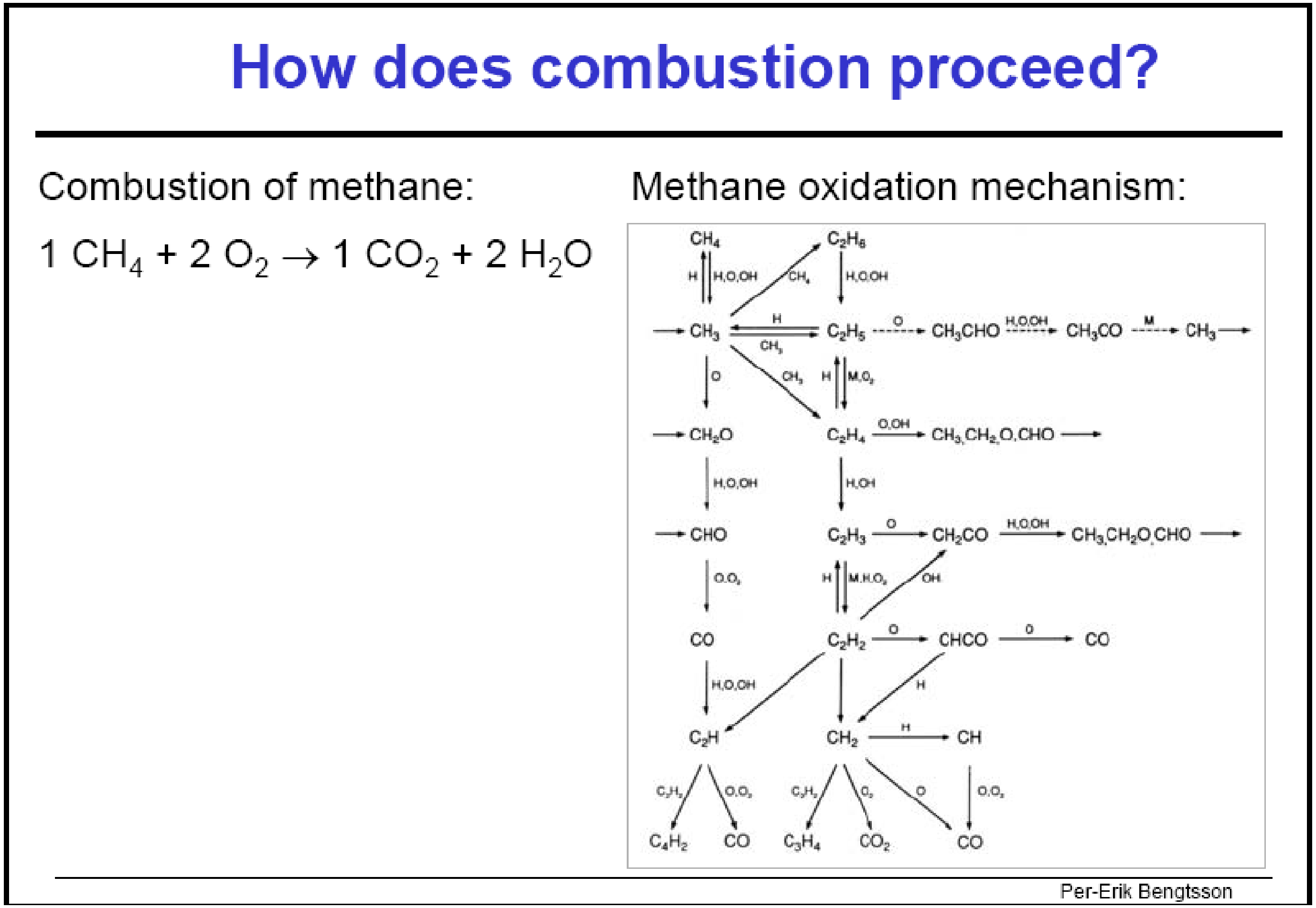
Concentration distributions in diffusion flames



The figure illustrates the concentration distribution of major species in a diffusion flame on methane and air.



The figure illustrates the concentration distribution of additional species in a diffusion flame on methane and air.



How does combustion proceed?

Combustion of methane:

$$1\ CH_4 + 2\ O_2 \rightarrow 1\ CO_2 + 2\ H_2O$$

Methane oxidation mechanism:

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Notes: The combustion chemistry at a fundamental level is the same for premixed and diffusion flames. In diffusion flames, diffusion is the rate limiting step.
Hence for computing burn rates, chemistry does not play a major role. In fact, the assumption that when the fuel and oxidizer mix, reaction instantaneously occurs is a standard procedure for computing diffusion limited flames. If however, one wants the detailed species profile one needs to take into account the chemistry

Premixed flames

Example: Spark-Ignition Engine

- Gaseous fuel and oxidizer are mixed on a molecular level prior to combustion
- Hydrocarbon/air flames have burning velocities around 0.5 m/s

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Nonpremixed flames (Diffusion flames)

Example: Diesel Engine

- Fuel and oxidizer are introduced separately and mix during combustion
- Energy release rate limited by mixing process
- Reaction zone between oxidant and fuel zone

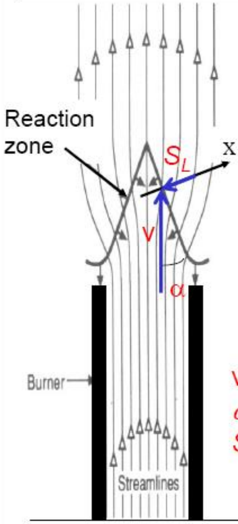
Laminar flames

- **Premixed**
  - e.g. Bunsen flame
  - Rather low flame velocity
- **Nonpremixed (Diffusion)**
  - e.g. candle flame
  - Fuel: wax, Oxidizer: air
  - Reaction zone between wax vapors and air

Photo: Per-Erik Bengtsson

Photo: Per-Erik Bengtsson

Bunsen flame structure



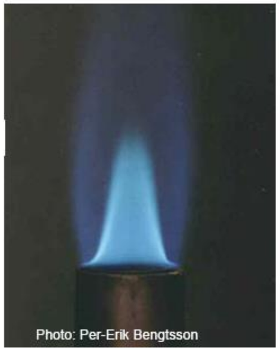


Photo: Per-Erik Bengtsson

v cold flow velocity

α half the cone angle

S_L laminar flame speed

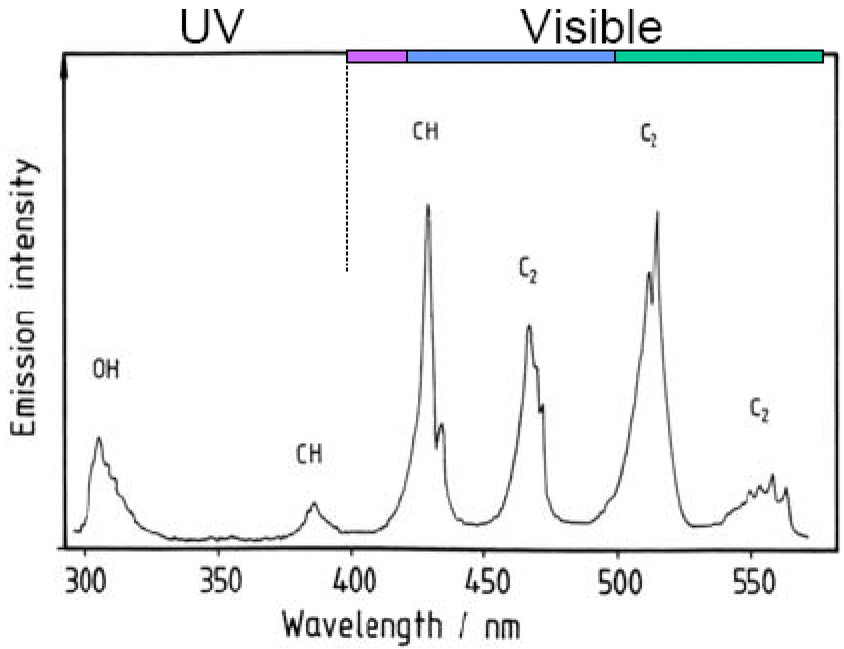
(the velocity of a reaction zone orthogonal to its surface)

The flame is stationary, thus the following relation is valid:

$S_L = v \sin\alpha$

S_L is a property of a fuel/oxidant mixture at certain T and p, and it is around 0.5 m/s for hydrocarbon/air mixtures.

The blue-green emission from flames



The blue-green emission from the reaction zone has its origin in radicals that have been produced in an excited electronic state from chemical reactions, so-called chemi-luminescence.

CH contributes in the blue spectral region, and C_2 contributes in the blue and green spectral regions.

More on diffusion flames

Fuel and oxidizer need to mix before combustion. This process of mixing in laminar diffusion flames is by molecular diffusion. In turbulent flames it is by turbulent mixing process. The rate of mixing is to be compared with the rate of reaction. Alternately, it can also be expressed In terms of the ratio of mixing time to reaction time. This ratio is called the Damkohler number = τ_f/τ_{ch}. Fundamental studies use this number and basic estimates of this number are made to assess whether the process is mixing controlled or reaction controlled. Typically in vigorous flames – either laminar or turbulent as in fires, this number is large implying they are mixing controlled. Reaction occurs very fast when mixing is completed.

It is only when flames are close to extinction chemistry acquires importance. These concepts are extremely important in modeling. The basis of fire dynamics simulator (FDS) is the use of this idea. The mixing time in the case of turbulent flows is calculated by the solution of the conservation equations including mass, momentum, energy and species. Roughly stated, it is the ratio of a fine eddy length scale to the mean local speed.

Smoke Point

Smoke point is a characteristic of diffusion flames used in estimating the radiant heat transfer From sooty flames. It is the luminous length of a laminar diffusion flame at the point of incipient sooting. Smoke points occur because an increase in fuel flow rate increases soot formation and residence time, but there is a smaller increase in soot oxidation time. Laminar smoke points are the most widely used measure of a fuel's sooting propensity in diffusion flames. Radiant energy from the combustion products has the strongest influence on heat transfer and can offer insight to the effects on surroundings. This effect can be related to the fuel's smoke point. Laminar smoke points are such good indicators that most aviation fuel sold worldwide is required to have a smoke point of 25 mm or longer.

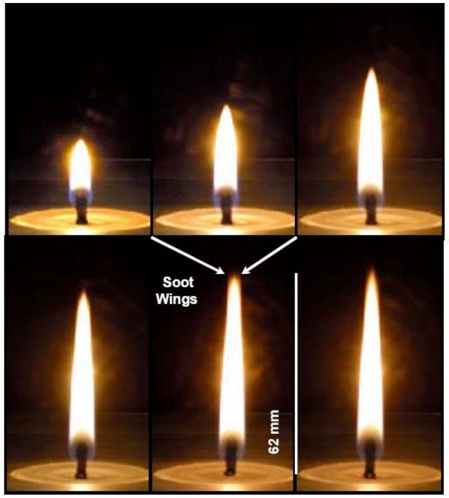


Figure 4.1. Color images of a paraffin candle flame growth to the laminar smoke point. Luminous length is 62 mm and the wick diameter is 2.7 mm.

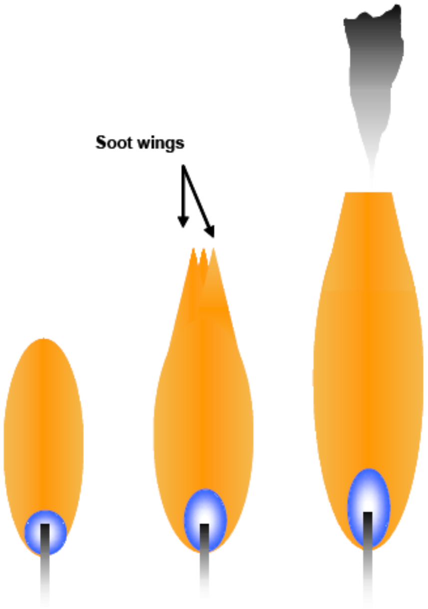
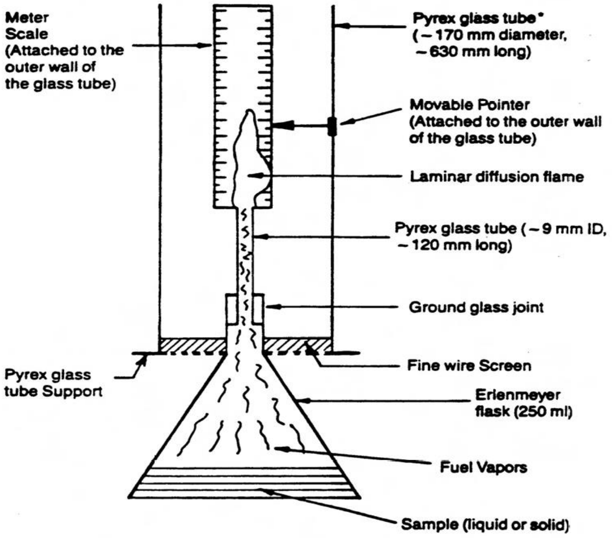


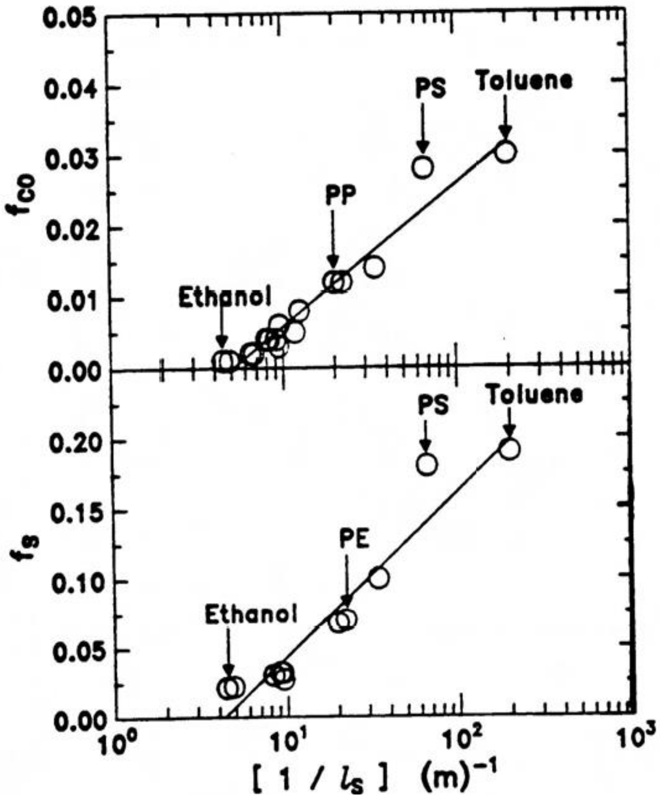
Figure 3.2: Illustration of smoke point for a laminar candle flame.

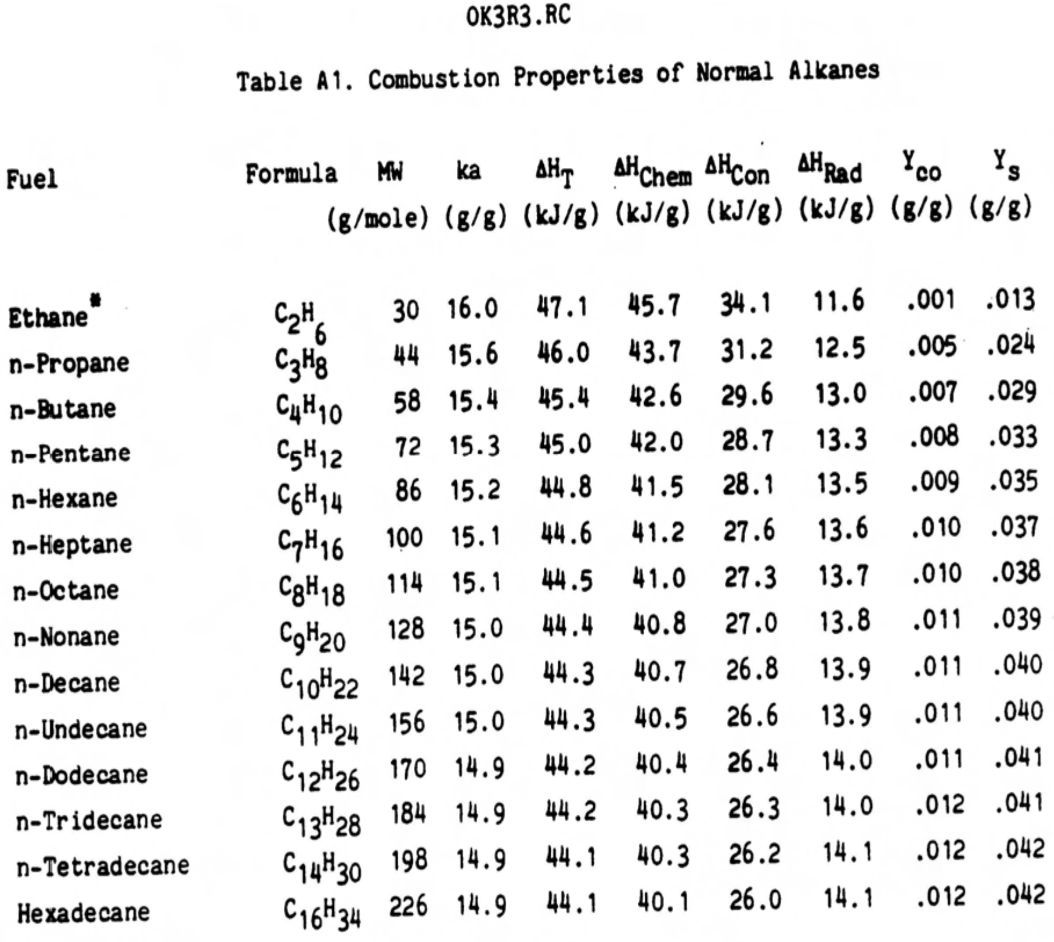


*or double very fine wire mesh cylinder (~190 mm diameter and ~460 mm long)

Figure 1. Smoke Point Apparatus for Liquids and Solids.

From Tewarson, NIST, GCR 88 -555, 1988, Ys = soot yield. l_s = smoke point height. f_s, f_{CO} efficiency of generation of soot and CO





OK3R3.RC

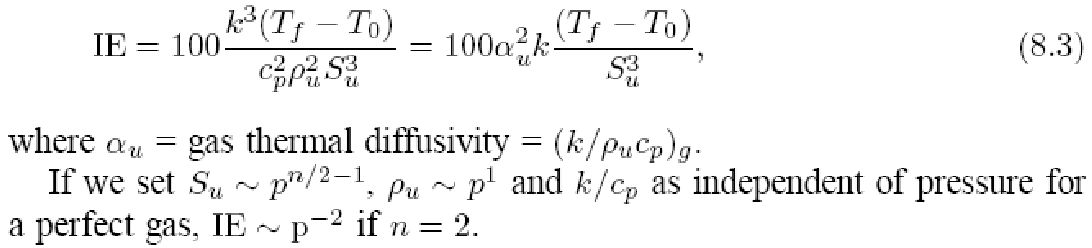
Table A1. Combustion Properties of Normal Alkanes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Ethane*	C_2H_6	30	16.0	47.1	45.7	34.1	11.6	.001	.013
n-Propane	C_3H_8	44	15.6	46.0	43.7	31.2	12.5	.005	.024
n-Butane	C_4H_{10}	58	15.4	45.4	42.6	29.6	13.0	.007	.029
n-Pentane	C_5H_{12}	72	15.3	45.0	42.0	28.7	13.3	.008	.033
n-Hexane	C_6H_{14}	86	15.2	44.8	41.5	28.1	13.5	.009	.035
n-Heptane	C_7H_{16}	100	15.1	44.6	41.2	27.6	13.6	.010	.037
n-Octane	C_8H_{18}	114	15.1	44.5	41.0	27.3	13.7	.010	.038
n-Nonane	C_9H_{20}	128	15.0	44.4	40.8	27.0	13.8	.011	.039
n-Decane	$C_{10}H_{22}$	142	15.0	44.3	40.7	26.8	13.9	.011	.040
n-Undecane	$C_{11}H_{24}$	156	15.0	44.3	40.5	26.6	13.9	.011	.040
n-Dodecane	$C_{12}H_{26}$	170	14.9	44.2	40.4	26.4	14.0	.011	.041
n-Tridecane	$C_{13}H_{28}$	184	14.9	44.2	40.3	26.3	14.0	.012	.041
n-Tetradecane	$C_{14}H_{30}$	198	14.9	44.1	40.3	26.2	14.1	.012	.042
Hexadecane	$C_{16}H_{34}$	226	14.9	44.1	40.1	26.0	14.1	.012	.042

Radiation fraction (%) = 41.6 – 0.9 (Smoke point height in cms); Convection and incomplete combustion compose of the rest. For data, see p.104 of Principles of fire protection chemistry and physics, **Raymond Friedman.**

Ignition

Ignition of gaseous fuels occurs through an electrical spark of a small flame that deposits heat and reactive species into a zone of the order of flame thickness.



$$\mathrm{IE} = 100\frac{k^3(T_f - T_0)}{c_p^2\rho_u^2 S_u^3} = 100\alpha_u^2 k\frac{(T_f - T_0)}{S_u^3}, \tag{8.3}$$

where α_u = gas thermal diffusivity = $(k/\rho_u c_p)_g$.

If we set $S_u \sim p^{n/2-1}$, $\rho_u \sim p^1$ and k/c_p as independent of pressure for a perfect gas, $\mathrm{IE} \sim \mathrm{p}^{-2}$ if $n = 2$.

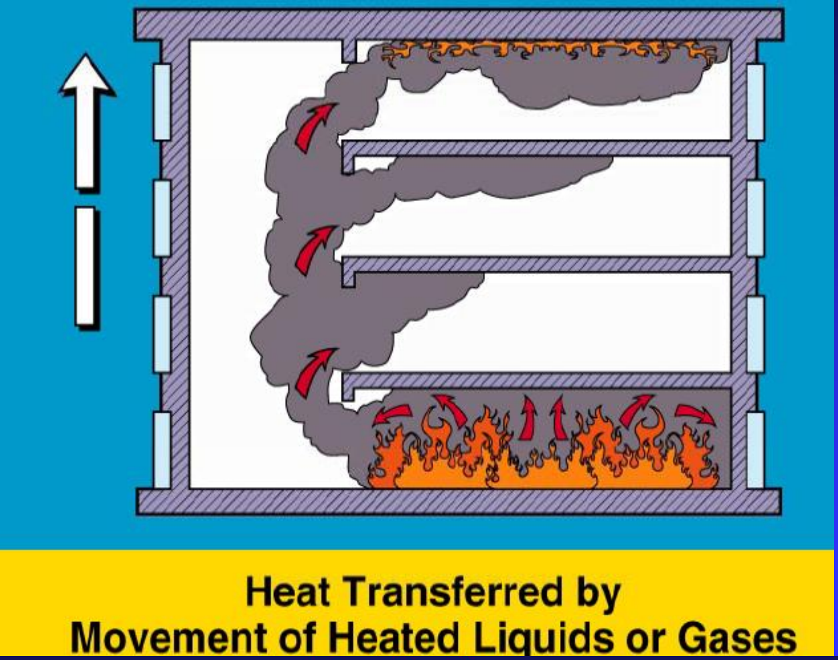
Thus as the pressure decreases, the ignition energy becomes larger by a factor p^{-2}. This is a steep dependence on pressure. Let us look at some typical values for vapors of kerosene or natural gas in air, viz. k = .04W/mK, Tf –T0 = 2000 K, cp = 1.3kJ/kg K, Su = 0.4 m/s, _u _ 1.2 kg/m3. These values lead to an ignition energy of 0.11 mJ. Igniting gases in quiscent atmosphere requires little energy.

If there is flow of gases, the heat likely to be carried away by convection has to be accounted for. In this case, the energy for ignition when the mixture is in the flammability regime goes up by a factor 50 to 100 depending on the speed of the stream. There ia also an upper limit beyond which the flame cannot be sustained. This is called the Extinction speed.

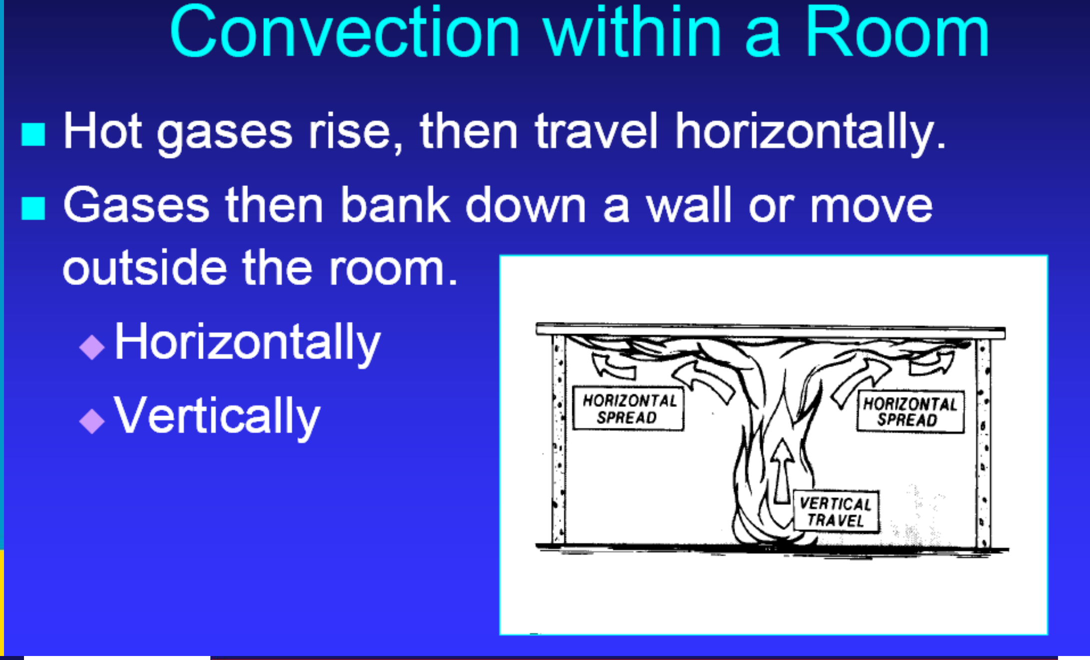
Ignition of liquid pools.

They are associated with a flash point and a fire point. They depend on the vaporization Characteristics of liquids. The minimum liquid temperature at which a flame is seen at the spark is called the flashpoint. Fire point is the Liquid temperature at which any ignition process creates a steady flame.

Heat transfer processes

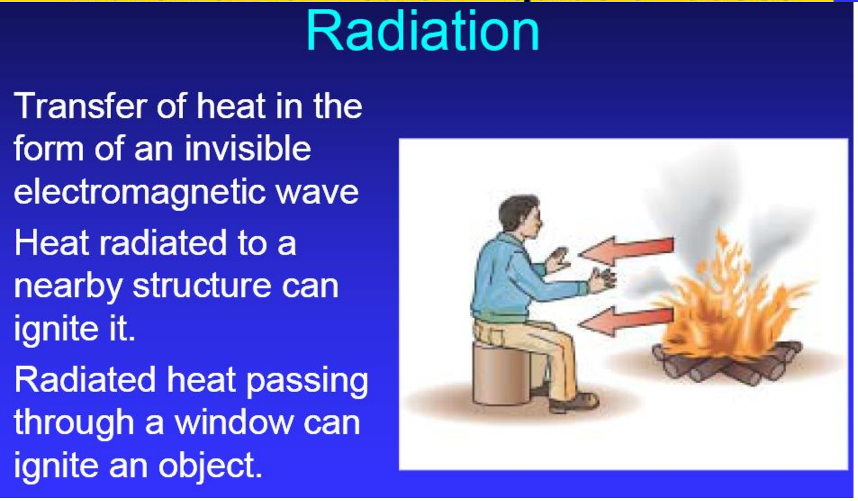


Heat Transferred by Movement of Heated Liquids or Gases



Convection within a Room

- Hot gases rise, then travel horizontally.
- Gases then bank down a wall or move outside the room.
  - Horizontally
  - Vertically

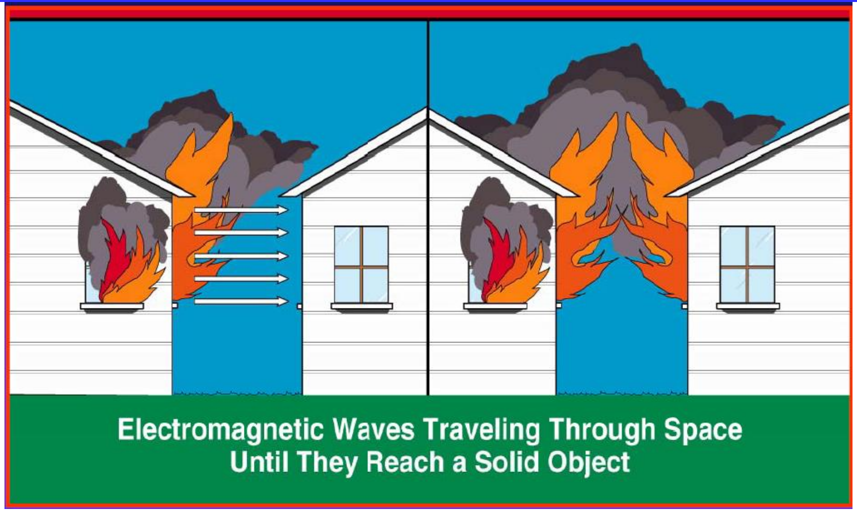


Radiation

Transfer of heat in the form of an invisible electromagnetic wave

Heat radiated to a nearby structure can ignite it.

Radiated heat passing through a window can ignite an object.



Electromagnetic Waves Traveling Through Space Until They Reach a Solid Object

The heat transfer mechanisms in fires as well a in any other situations are conduction, convection and radiation. While conduction and convection mechanisms are similar to other non-combusting but hot gas flow situations, radiation in fires acquires a special significance since the gas composition affects it significantly. The presence of soot particles enhances the radiation. Also, the size of the fire controls it.

Pool Fire burn rates

Pool fire burn rate – cm/ min

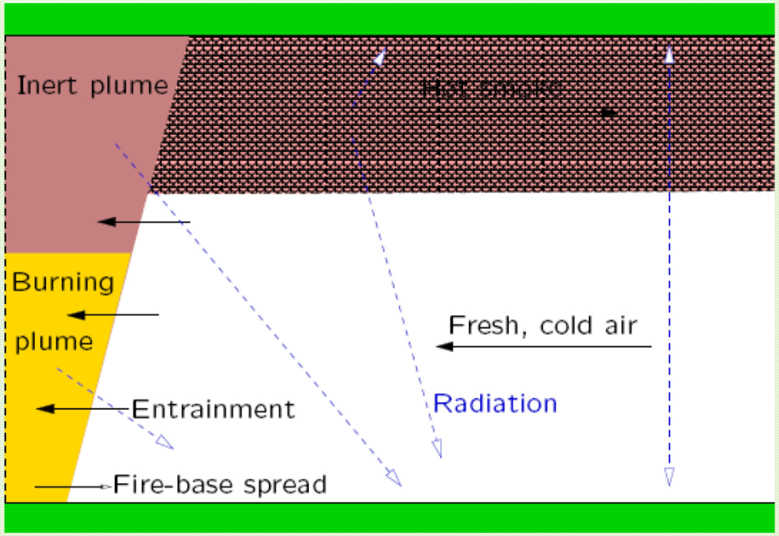
See p. 119 for pool fire data with density and latent heat. For large pool fires, experimental data shows $\dot{r}$ (*cm/min*) = *160/$\rho_l L$*, the denominator being a product of density of the liquid and its latent heat of vaporization The product in terms of *cm^3/J*. This can be easily derived by recognizing the heat balance at the surface recognizing that the principal heat transfer mode to the surface of the pool is radiation. The radiation temperature of the soot laden flame does not vary a whole lot. One estimates the radiant flux as follows. The flame emissivity is obtained from

$$\epsilon_f \approx 1 - e^{-\kappa D}$$

where κ is called the extinction coefficient and D, the flame size. Large size flames (because of large pool sizes). For large pool fires ε_f is about 0.6 to 0.8. The radiant flux is then $\varepsilon_f \sigma (T_f^4 - T_s^4)$ where σ = radiation constant = 5.678×10^{-8} W/m^2K^4. If we simply take the heat balance to be accurate to first order we can write $\rho_l L\dot{r} = \varepsilon_f \sigma T_f^4$, we get $\dot{r} = \varepsilon_f \sigma T_f^4/\rho_l L$. T_f itself is about 1000 to 1100 K for sooty flames. Thus if we put these together we get

$\dot{r}$ = (0.6 to 0.8) x 5.678×10^{-8} x (1 to 1.8) x 10^{12} W/m^2 /[(750 to 900) kg/m^3 x (100 to 200) kJ/kg.

This leads to $\dot{r}$ of 0.25 to 0.5 cm/min in the range in which experimental data are. Thus this simple analysis gives the results.



Whether inside the flame/fire or outside, heat balance occurs because of convection – radiation - re-radiation - gasification with solid/liquid fuels

$$\dot{m}''_{\mathrm{F}} L = k\left(\frac{\mathrm{d}T}{\mathrm{d}y}\right)_{y=0} + \dot{q}''_{\mathrm{f,r}} + \dot{q}''_{\mathrm{e}} - \sigma(T_{\mathrm{v}}^4 - T_{\infty}^4)$$

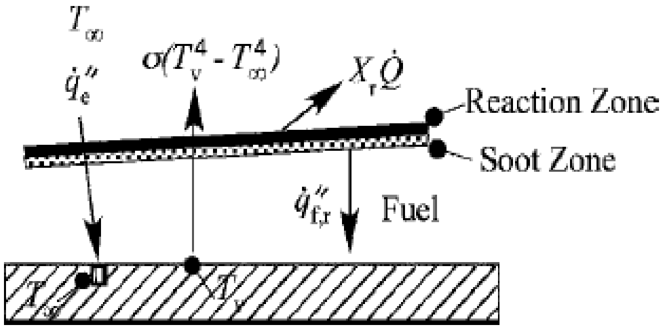
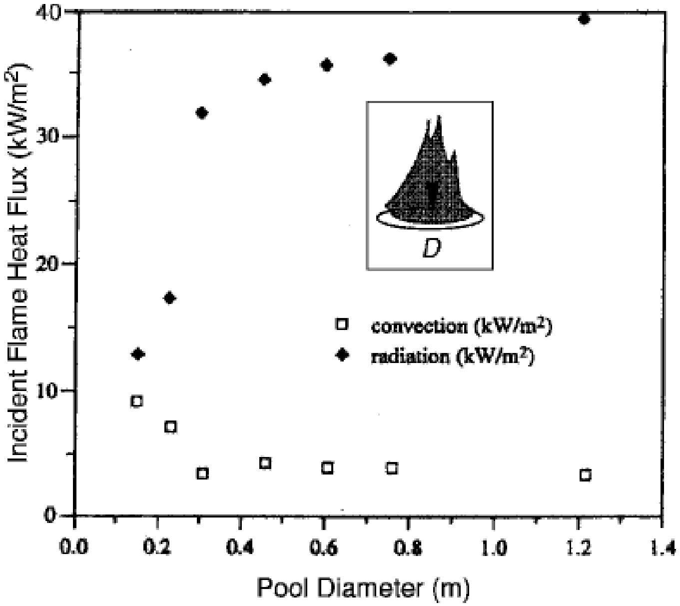


Figure 9.12 Radiative heat transfer in burning



Feature	POM	PMMA	PP	PS
Flame base, m	0.305 square	0.305 x 0.31	0.305 square	0.305 square
Base area, m^2	0.093	0.095	0.093	0.093
Mass burn flux, g/m^2s	6.5	10.5	8.5	14.5
$A/F]_{stoich}$ -	4.6	8.3	14.8	13.0
Surface temp, °C	312	385	479	438
Heat of Combustion, MJ/kg	15.5	24.9	43.4	39.8
Heat of phase change, MJ/kg	2.43	1.61	2.03	1.76
Transfer No, B -	1.23	1.57	1.16	1.44
Combustion completeness, %	100	85	87	57
Radiation fraction, %	15	34	38	35
Theoretical. Heat release, kW	9.3	24.8	34.3	53.7
…rate kW/m^2	100	222	321	329
Convective heat flux, kW/m^2	17.5	7.6	6.8	2.9
Radiative heat flux, kW/m^2	5.0	20.1	28.7	37.2
Surface re-radiation, kW/m^2	6.7	10.7	18.2	14.6
Gasification flux, kW/m^2	15.8	17.0	17.3	25.5
Flame radiation temp, K	1400	1400	1350	1190

Poly oxymethlyene (POM) through Polymethyl methacrylate (PMMA), Poly Propylene (PP) to Polystyrene (PS) **A/F increases, Radiation fraction, sooting tendency Increase.**

Effective radiation temperature decreases… From De Ris, Comb symp, 1978

Spontaneous Ignition

Spontaneous ignition implies ignition of a set of materials with internal heating due to internal Exothermic reactions. Factors that can contribute to the spontaneous ignition of solids are many: (a) bulk size: contributes to the storage of energy and interior temperature rise; (b) porosity: contributes to the diffusion of air to promote oxidation and metabolic energy release of biological organisms; (c) moisture: contributes to the growth of bacteria and other micro-organisms; (d) contamination: additives, such as unsaturated oils, can promote exothermicity; (e) process defects: storage of heated materials, insufficient additives (such as antioxidants in synthetic polymers) or terminating a process before its chemical reactions are completed.

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(k\frac{\mathrm{d}T}{\mathrm{d}x}\right) + (A\Delta h_c)\mathrm{e}^{-E/(RT)} = 0$$

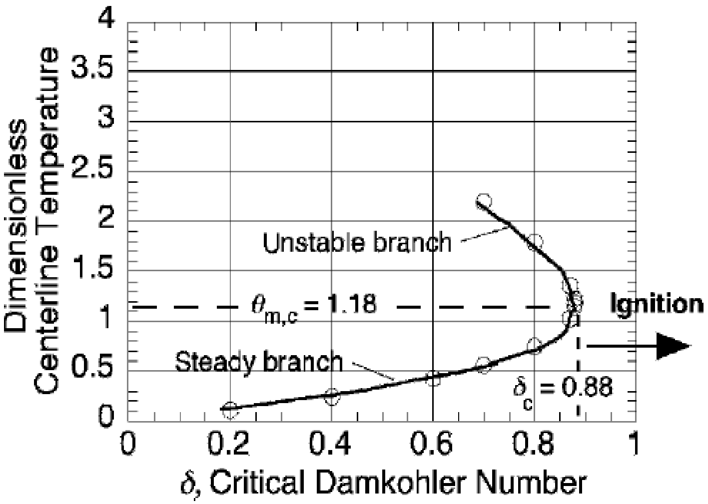
$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\xi^2} + \delta \mathrm{e}^{\theta} = 0 \qquad (5.11)$$

with $\mathrm{d}\theta/\mathrm{d}\xi = 0$ at $\xi = 0$ and $\mathrm{d}\theta/\mathrm{d}\xi + Bi\ \theta = 0$ at $\xi = 1$. The dimensionless parameters are:

$$\boxed{\theta = \left(\frac{T - T_\infty}{T_\infty}\right)\frac{E}{RT_\infty}}$$

(a) the Damkohler number, δ:

$$\boxed{\delta = \left(\frac{E}{RT_\infty}\right)\left[\frac{r_o^2 (A\Delta h_c)\mathrm{e}^{-E/(RT_\infty)}}{kT_\infty}\right]} \qquad (5.12)$$



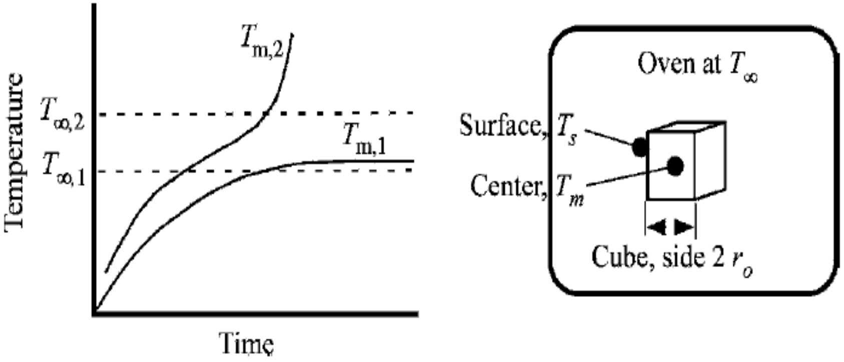


Figure 5.2 Solution for a slab at a constant surface temperature

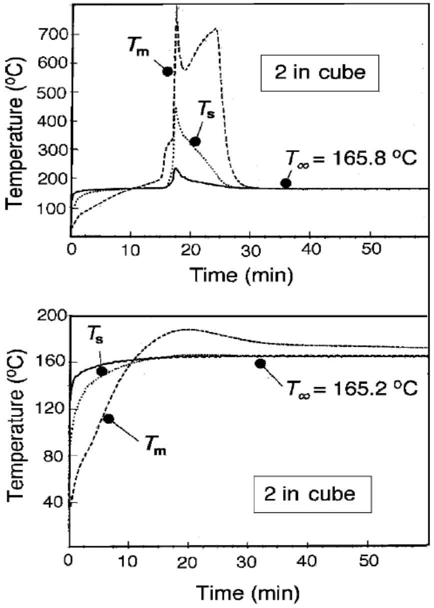
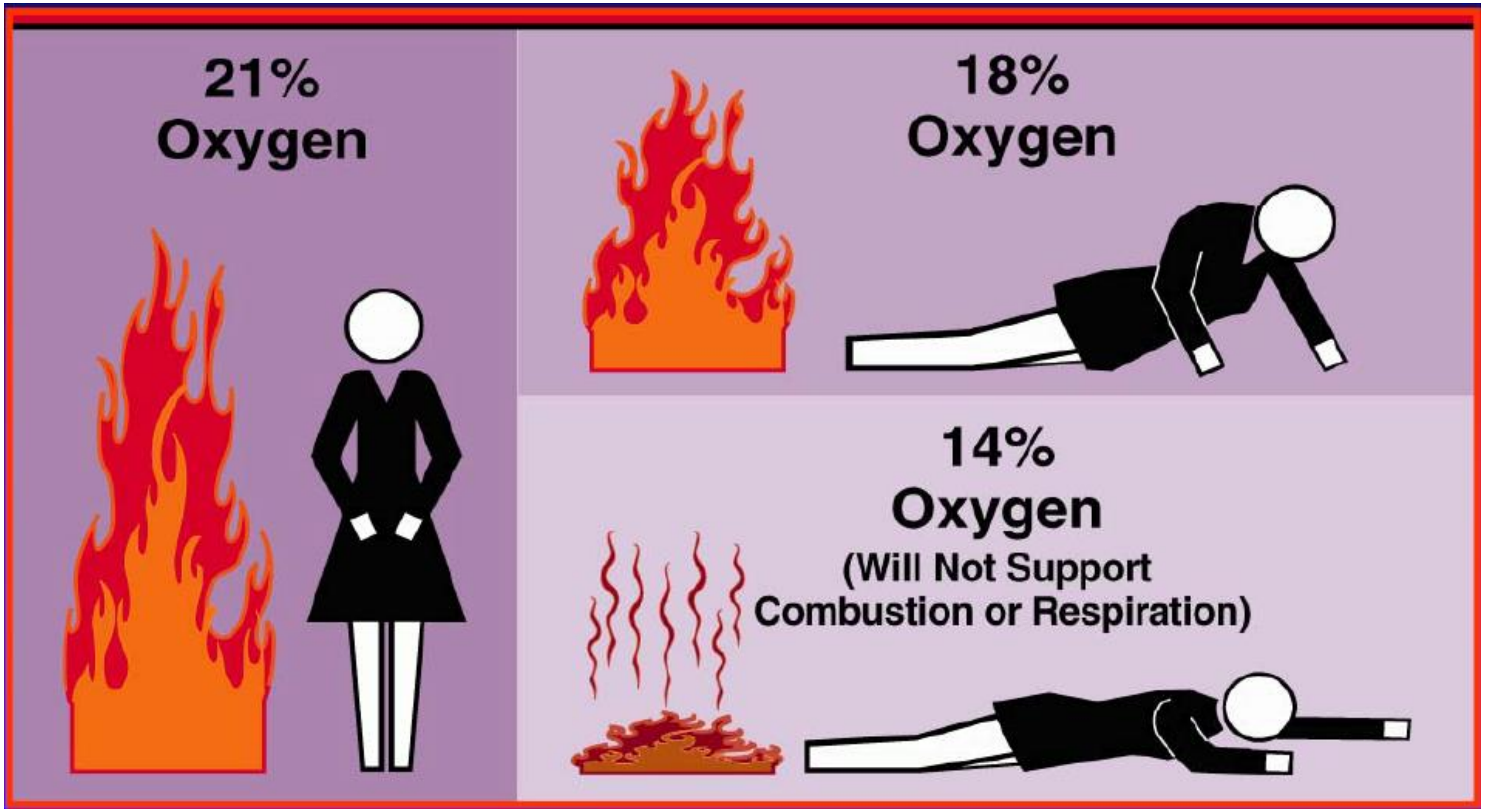


Table 5.3 Critical oven temperatures for cubes of sawdust with and without oil (from Bowes [1])

Cube size $2r_o$ (mm)	Oil content (%)	Ignition temperature (°C)
25.4	0	212
25.4	11.1	208
51	0	185
51	11.1	167
76	0	173
76	11.1	146
152	0	152[a]
152	11.1	116
303	0	135
303	11.1	99
910	0	109[a]
910	11.1	65

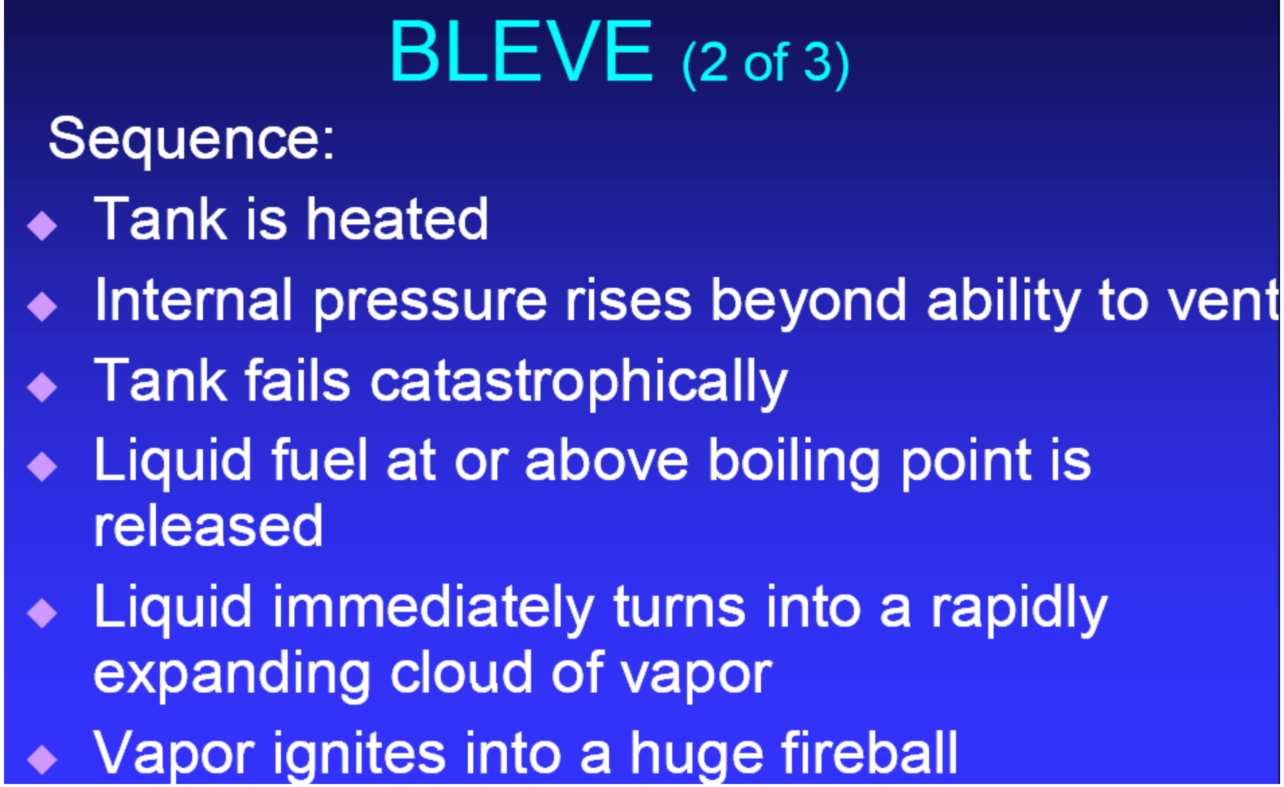
[a] Calculated.

The above problem has significant implications and there have been many cases of miscarriage of justice in accusation of arson when natural causes have resulted in the damages – material and human.


21% Oxygen
18% Oxygen
14% Oxygen
(Will Not Support Combustion or Respiration)

BLEVE (1 of 3)

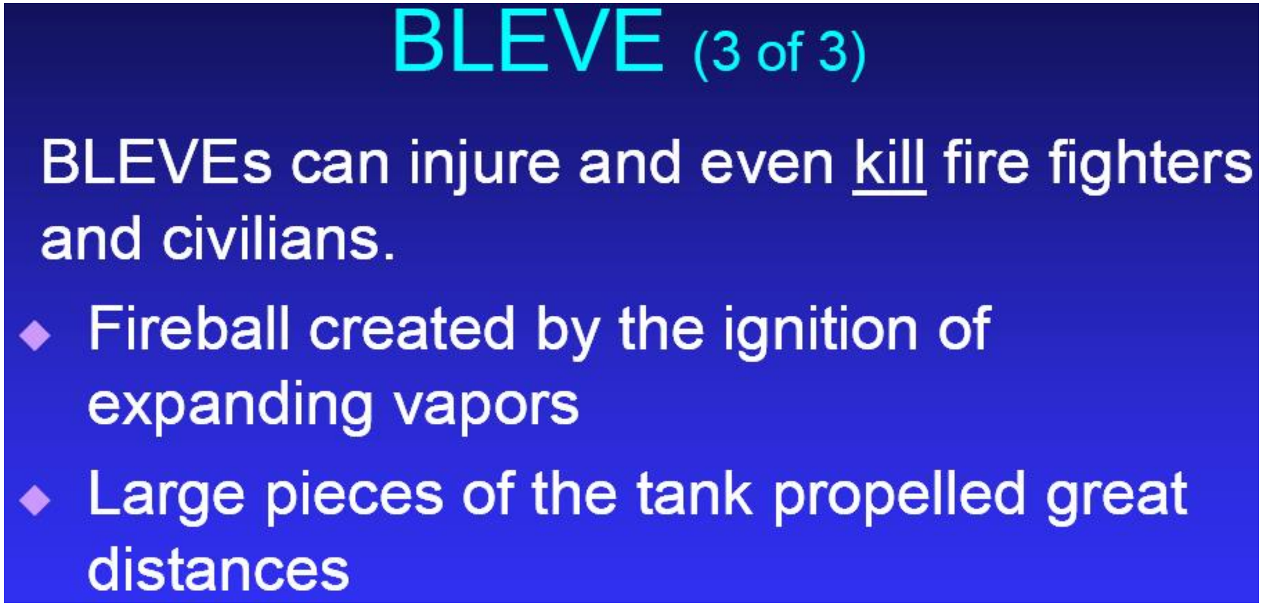
- Boiling Liquid, Expanding Vapor Explosion
- Occurs when a tank storing liquid fuel under pressure is heated excessively



BLEVE (2 of 3)

Sequence:

- Tank is heated
- Internal pressure rises beyond ability to vent
- Tank fails catastrophically
- Liquid fuel at or above boiling point is released
- Liquid immediately turns into a rapidly expanding cloud of vapor
- Vapor ignites into a huge fireball

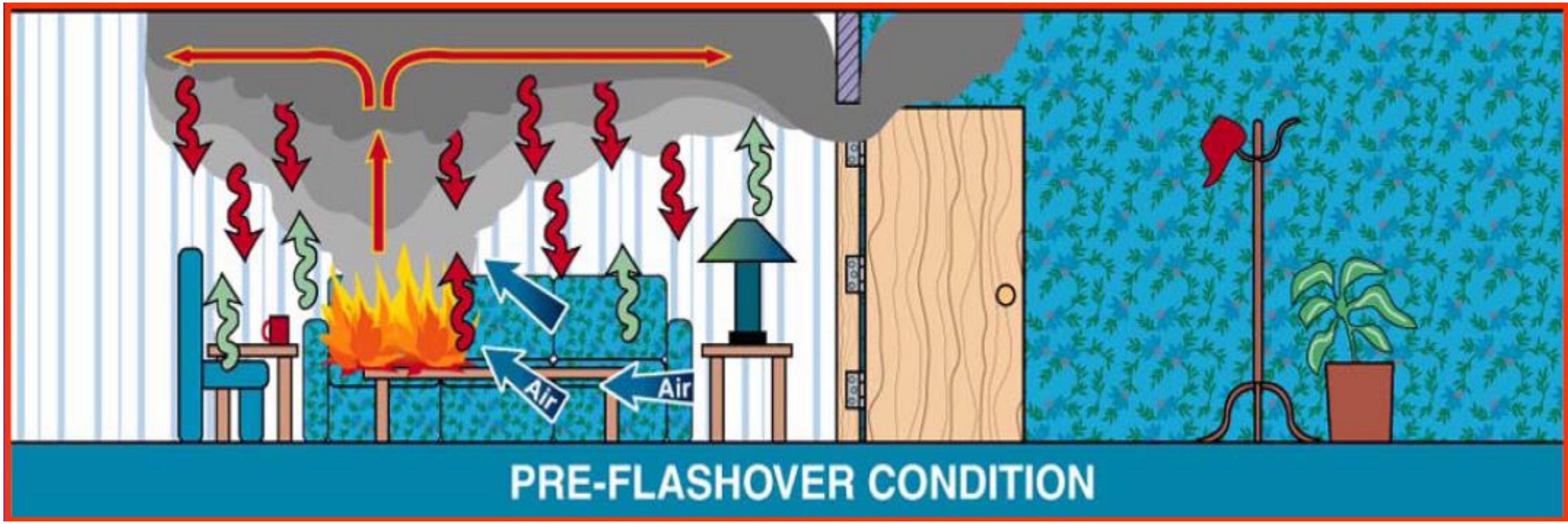


BLEVE (3 of 3)

BLEVEs can injure and even kill fire fighters and civilians.

- Fireball created by the ignition of expanding vapors
- Large pieces of the tank propelled great distances

Flashover in room fires



The third phase of fire development

Transition point between growth phase and fully developed phase

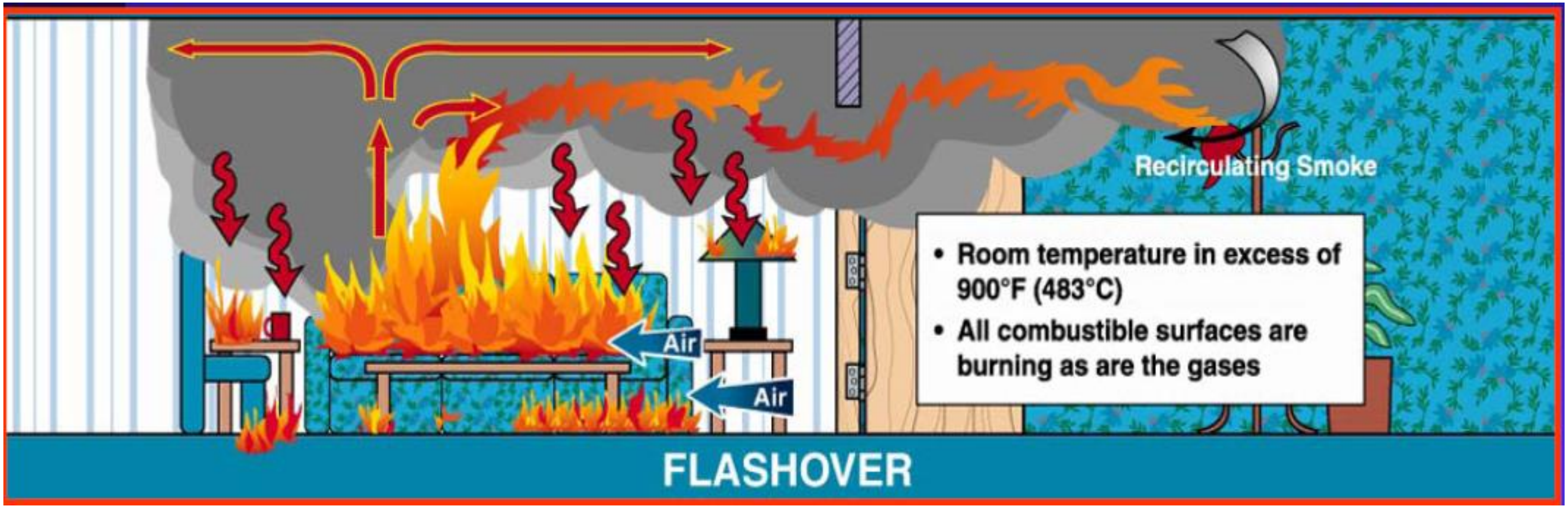
All combustible materials in a room ignite at once.

Flashover

Super-heated fire gases have heated nearby unburned combustibles liberating flammable fire gases

When the temperature reaches the ignition point of another substance in the room, a new chain reaction combustion site occurs and additional heat is added beyond the initial source of the fire

Flashover is not instantaneous but occurs rapidly

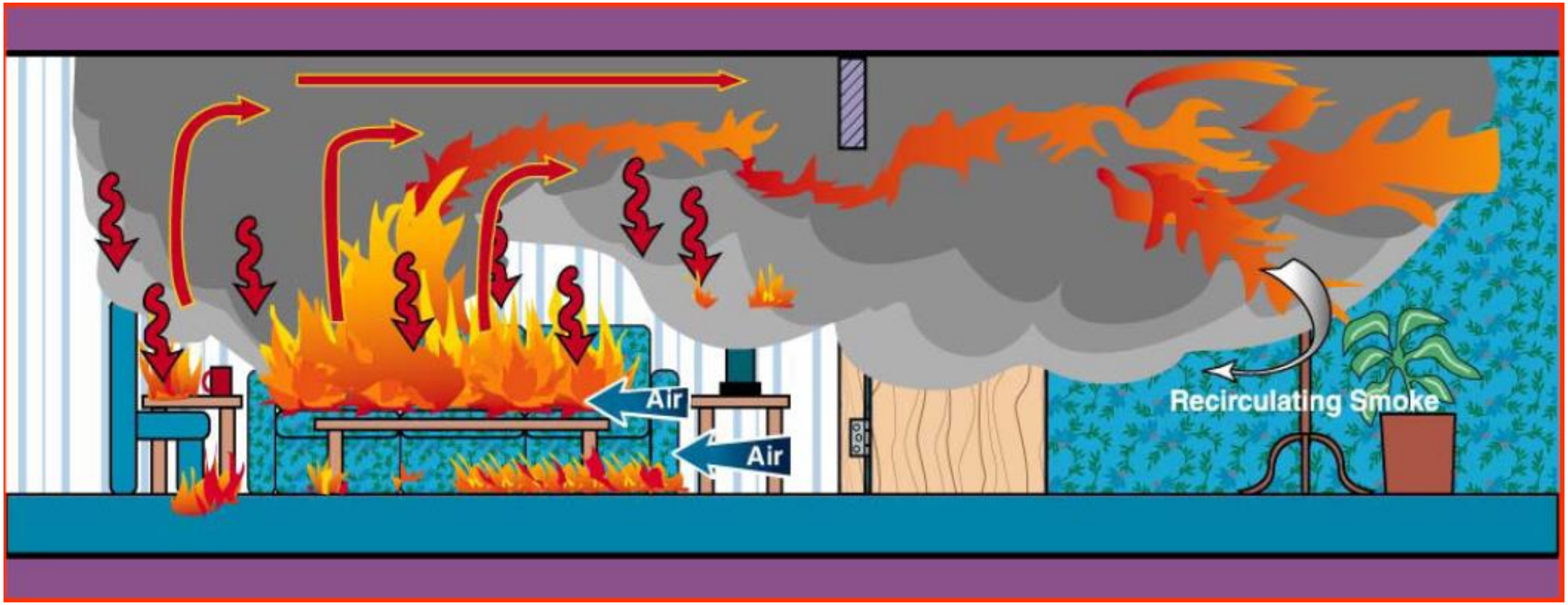


- Room temperature in excess of 900°F (483°C)
- All combustible surfaces are burning as are the gases

Fully Developed Phase

Fourth phase of fire development.

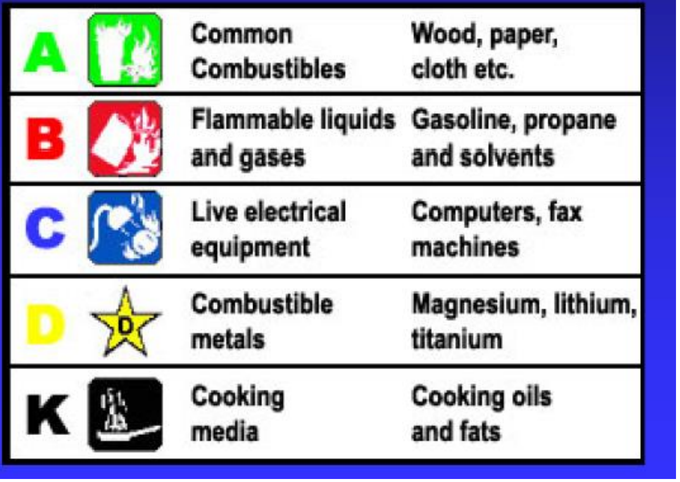
All combustible materials in the room are burning.



Classes of Fire (2 of 2)

Five classes of fires:

- Class A
- Class B
- Class C
- Class D
- Class K



A		Common Combustibles	Wood, paper, cloth etc.
B		Flammable liquids and gases	Gasoline, propane and solvents
C		Live electrical equipment	Computers, fax machines
D		Combustible metals	Magnesium, lithium, titanium
K		Cooking media	Cooking oils and fats

Class A

Fuel: Ordinary solid combustibles

- Wood
- Paper
- Cloth

A Common Combustibles

Extinguishing agents:

- Water (cools the fuel)

Class B

Fuel: Flammable or combustible liquids

- Gasoline
- Kerosene
- Oils

B Flammable liquids and gases

Extinguishing agents:

- Foam or carbon dioxide
- Dry chemicals

Class C

Fuel: Energized electrical equipment

- Underlying fuel is often Class A or Class B
- Special classification required due to electrical hazards

C Live electrical equipment

Extinguishing agents:

- Carbon dioxide
- Use of water is not advised.
  - Be sure to shut off power before using water.

Class D

Fuel: Burning metals

- Potassium
- Lithium
- Magnesium

D Combustible metals

Extinguishing agents:

- Special salt-based powders or dry sand
- Do NOT use water.

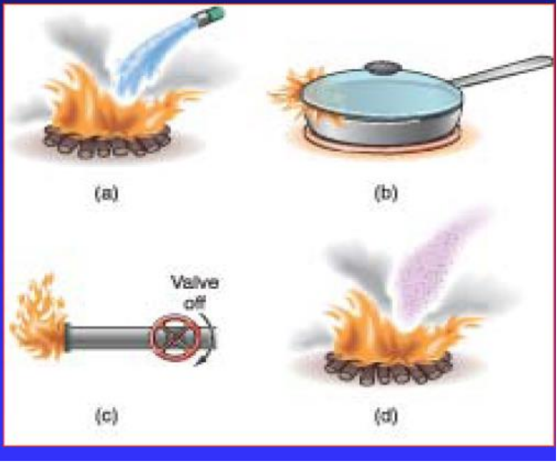
Methods of Extinguishment

Cool the burning material.

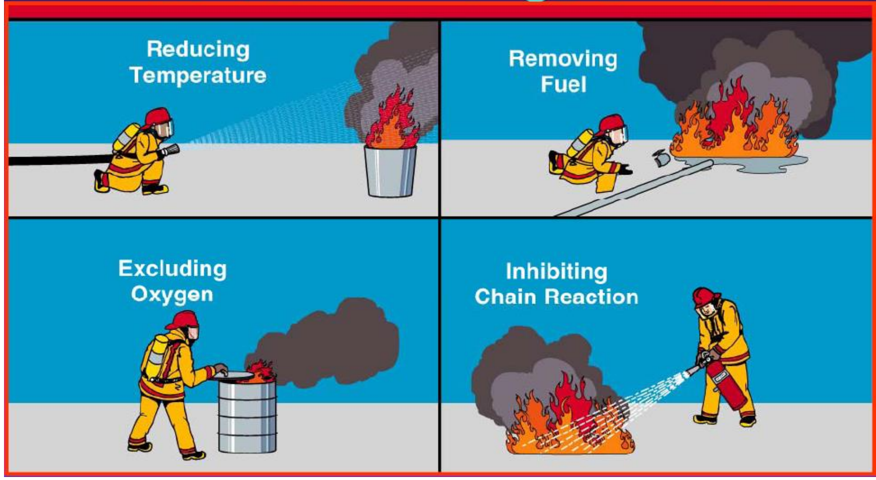
Exclude oxygen.

Remove fuel.

Break the chemical reaction.



Methods of Extinguishment



Water Use

- Class A fires
- Class B fires
  - Certain instances
- Class D fires
  - Very limited

CO₂ Use

Class A fires

- Limited instances

Class B fires

Class C fires