An Introduction to FIRE DYNAMICS

Third Edition

Dougal Drysdale

WILEY

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To my family –
Jude
David, Misol and Manow
Andrew, Catriona, Izzy and Alex
and Peter

Contents

About the Author

Dougal Drysdale graduated with a degree in Chemistry from the University of Edinburgh in 1962. He gained a PhD in gas phase combustion from Cambridge University (UK) and after two years' postdoctoral work at the University of Toronto, moved to the University of Leeds to work with the gas kinetics group in the Department of Physical Chemistry. He joined the newly formed Department of Fire Engineering at the University of Edinburgh in 1974 and helped develop the first postgraduate degree programme in Fire Engineering under the leadership of Professor David Rasbash. He was invited to teach Fire Dynamics during the spring semester of 1982 at the Centre for Firesafety Studies, Worcester Polytechnic Institute, MA. The notes from this course formed the first draft of the first edition of *An Introduction to Fire Dynamics*, which was published in 1985.

His research interests include various aspects of fire dynamics, including ignition and the fire growth characteristics of combustible materials, compartment fire dynamics and smoke production in fires. He was a member of the Editorial Board for the third and fourth editions of the SFPE *Handbook of Fire Protection Engineering* and was Chairman of the International Association of Fire Safety Science (IAFSS) from 2002–2005. From 1989–2009 he acted as editor of *Fire Safety Journal*, the leading scientific journal in the field. He has been involved in a number of major public inquiries, including the King's Cross Underground Station fire (London, 1987), the Piper Alpha Platform explosion and fire (North Sea, 1988) and the Garley Building fire (Hong Kong, 1996). More recently, he was a member of the Major Incident Investigation Board which was set up following the explosions and fires at the Buncefield Oil Storage and Transfer Depot (Hemel Hempstead, England, 11 December 2005). He is a Fellow of the Royal Society of Edinburgh, the Institution of Fire Engineers and the Society of Fire Protection Engineers. His awards include: 'Man of the Year' (1983), the Arthur B. Guise Medal (1995) and the D. Peter Lund Award (2009) of the Society of Fire Protection Engineers, the Kawagoe Medal of the International Association for Fire Safety Science (2002), the Rasbash Medal of the Institution of Fire Engineers (2004) and the Sjolin Award of FORUM, the Association of International Directors of Fire Research (2005).

He is married to Judy and has three sons and three grandchildren, all living in Edinburgh. His interests are music, hillwalking, curling and coarse golf.

Preface to the Second Edition

The thirteen years that have elapsed between the appearance of the first and second editions of *Introduction to Fire Dynamics* have seen sweeping changes in the subject and, more significantly, in its application. Fire Engineering – now more commonly referred to as Fire Safety Engineering – was identified in the original preface as ‘a relatively new discipline’, and of course it still is. However, it is beginning to grow in stature as Fire Safety Engineers around the world begin to apply their skills to complex issues that defy solution by the old ‘prescriptive’ approach to fire safety. This has been reflected by the concurrent development in many countries of new Codes and Regulations, written in such a way as to permit and promote engineered solutions to fire safety problems. The multi-storey atrium and the modern airport terminal building are but two examples where a modern approach to fire safety has been essential.

Preparing a second edition has been somewhat of a nightmare. I have often said that if the first edition had not been completed in late 1984 it might never have been finished. The increased pace of research in the early 1980s was paralleled by the increasing availability of computers and associated peripherals. The first edition was prepared on a typewriter – a device in which the keyboard is directly connected to the printer. Graphs were plotted by hand. In 1984 I was rapidly being overtaken by the wave of new information, so much so that the first edition was out of date by the time it appeared.

In 1984, the International Association for Fire Safety Science – an organisation which has now held five highly successful international symposia – was still to be launched, and the ‘Interflam’ series of conferences was just beginning to make an impression on the international scene. The vigour of fire research in the decade after 1985 can be judged by examining the contents of the meetings that took place during this period. The scene has been transformed: the resulting exchange of ideas and information has established fire science as the foundation of the new engineering discipline. This has been largely due to the efforts of the luminaries of the fire research community, including in particular Dr. Philip Thomas, the late Prof. Kunio Kawagoe, Prof. T. Akita, Prof. Jim Quintiere and my own mentor, the late Prof. David Rasbash. They perceived the need for organisations such as the IAFSS, and created the circumstances in which they could grow and flourish.

A second edition has been due for over 10 years, but seemed an impossible goal. Fortunately, my friends and colleagues at Worcester Polytechnic Institute came to the rescue. They took the initiative and put me in purdah for four weeks at WPI, with strict instructions to ‘get on with it’. Funding for the period was provided by a consortium, consisting of the SFPE Educational Trust, the NFPA, Factory Mutual Research Corporation, Custer Powell Associates, and the Centre for Firesafety Studies at WPI. I am grateful to them all for making it possible, and to Don and Mickey Nelson for making me feel so welcome in their home. Numerous individuals on and off campus helped me to get things together. There was always someone on hand to locate a paper, plot a graph, discuss a problem, or share a coffee. I am grateful to David Lucht, Bob Fitzgerald, Jonathan Barnett, Bob Zalosh and Nick Dembsey for their help. I am indebted to many other individuals who kindly gave their time to respond to questions and comment on sections of the manuscript. In particular, I would like to thank (alphabetically) Paula Beever, Craig Beyler, John Brenton, Geoff Cox, Carlos Fernandez-Pello, George Grant, Bjorn Karlsson, Esko Mikkola, John Rockett and Asif Usmani. Each undertook to review one or more chapters: their feedback was invaluable. Having said this, the responsibility for any errors of fact or omission is mine and mine alone.

It is a sad fact that I managed to carry out over 50% of the revision in four weeks at WPI, but have taken a further two years to complete the task. I would like to thank my colleagues in the Department of Civil and Environmental Engineering for their support and tolerance during this project. This was particularly true of my secretary, Alison Stirling, who displayed amazing *sang-froid* at moments of panic. However, the person to whom I am most indebted is my wife Judy who has displayed boundless patience, tolerance and understanding. Without her support over the years, neither edition would ever have been completed. She finally pulled the pin from the grenade this time, by organising a ‘Deadline Party’ to which a very large number of friends and colleagues were invited. Missing this deadline was not an option (sorry, John Wiley). It was a great party!

Preface to the Third Edition

'The thirteen years that have elapsed between the second and third editions of *Introduction to Fire Dynamics* have seen sweeping changes in the subject and, more significantly, in its application.' I admit with some embarrassment that this sentence is virtually identical to the one that opens the preface to the second edition. The number 13 bothers me, not simply because of its association with bad luck, but because 13 years is a long time and it could be argued that enough new research had been published for a new edition to have been compiled by 2005. However, a textbook on Fire Dynamics cannot be a literature review – it should be limited to information and data that are deemed to be well-founded by the fire community. The evolution of research results into accepted knowledge takes time, requiring not only the initial peer-review process but also scrutiny by way of further research and application. The practice of Fire Safety Engineering is based on such knowledge but has been in existence as a recognized professional engineering discipline for a remarkably short period of time. Although it was being developed from the mid-1970s onwards by Margaret Law and others, it was not until c. 1990 that it was pulled into the mainstream with the introduction of regulations permitting the use of performance-based fire safety engineering design. At this time, the underpinning 'fire science' was at a relatively early stage in its development and research into many aspects of fire dynamics was still active.

Indeed, Fire Safety Engineering is very close to its research roots. It is significant that the *Handbook of Fire Protection Engineering*, originally published by the Society of Fire Protection Engineers in 1988, is now in its 4th edition (2008). Its chapters cover all aspects of fire safety engineering, but those that deal with the scientific and engineering fundamentals are *de facto* review articles. The practitioner – and indeed the fire safety engineering student – should be alert to the fact that he/she is working in a field that is still developing and that it is necessary to remain aware of current research activities. Consequently, this book should be regarded as a snapshot of where we are at the end of the first decade of the 21st century.

Compared to the first two editions, the third has been prepared under very different circumstances. On the previous occasions, I had the luxury of working on early drafts while at the Centre for Fire Safety Studies at Worcester Polytechnic Institute, away from the usual demands of academic life at Edinburgh University. The third edition has been written at Edinburgh University, but after retirement. I have been very fortunate to have been immersed in a very active fire research group, the BRE Centre for Fire Safety Engineering, led by José Torero. This has been a source of both inspiration and distraction. With so many new colleagues, I have had a unique opportunity to discuss the contents of the book and develop some new areas that were missing from the second edition. However, I have taken care not to change the style of the text, nor to create a tome which might be seen as an attempt to be a literature review. The first edition was close to being such, but the field has developed so rapidly during the last 25 years that such an approach would have been impossible, even if desirable. I am aware that there are some topics that deserve more emphasis and that some recent research has not been included, but I take full responsibility for the decisions regarding the content. I would welcome comments regarding the content as these would be helpful in planning for a fourth edition. Whether or not I will be the author, time (and John Wiley & Sons) will tell!

I owe a huge debt of gratitude to a large number of people for helping me at various stages along the way. In particular, I would like to thank (in alphabetical order) Cecilia Abecassis-Empis, Ron Alpert, Craig Beyler, Luke Bisby, Ricky Carvel, Carlos Fernandez-Pello, Rory Hadden, Martin Gillie, Richard Hull, Tom Lennon, Agustin Majdalani, Jim Quintiere, Guillermo Rein, Pedro Reszka, Martin Shipp, Albert Simeoni, Mike Spearpoint, Anna Stec, Jose Torero and Stephen Welch. I can only apologize if I have missed anyone from the list. In the prefaces to previous editions I acknowledged many others who helped and inspired me at the relevant periods of time. Their contributions are part of this text and although their names are not included here, their roles should not be forgotten. However, I would like to acknowledge two individuals by name: my original mentor, the late David Rasbash who was responsible for establishing the first postgraduate degree programme in Fire Engineering at Edinburgh University, and Philip Thomas who has made so many outstanding contributions to the field and continues to be a source of inspiration. Finally, I wish to thank my wife Judy and our family for their unfailing support over the years and tolerating my highly erratic working practices.

List of Symbols and Abbreviations

a	Absorptivity
A	Arrhenius factor (Chapter 1)
A_f	Fuel bed area (m^2)
A_t	Total internal surface area of a compartment, including ventilation openings (m^2) (Chapter 10)
A_T	Internal surface area of walls and ceiling, excluding ventilation openings (m^2) (Chapter 10)
A_w	Area of ventilation opening (window or door) (m^2)
b	Plume radius (m) (Section 4.3.1)
b	Conserved variable (Equations (5.20) and (5.21))
b	Stick thickness (m) – applies to Figure 5.20 only
b	$\sqrt{k\rho c}$ $\mathrm{J/m^2 \cdot s^{1/2} \cdot K}$ (Table 10.3 only)
B	Spalding’s mass transfer number (Equation (5.22))
B	Width of ventilation opening (m) (Chapter 10)
Bi	Biot number (hL/k)(−) (k is the thermal conductivity of the solid)
c_p	Thermal capacity at constant pressure (J/kg·K) or (J/mol·K)
C	Concentration (Chapter 4)
C	Constant (Equations (7.9) and (7.10))
C_d	Discharge coefficient (−) (Chapters 9 and 10)
C_st	Stoichiometric concentration (Table 3.1)
d_b	The required depth of clear air above floor level (m) (Chapter 11)
d_q	Quenching distance (mm)
D	Pipe diameter (m) (Sections 2.3 and 3.3)
D	Pool or fire diameter (m) (Chapters 4 and 5)
D	Depth of compartment (Section 10.3.1)
D	Optical density (decibels) (Chapter 11)
D_m	Specific optical density ($(\mathrm{b/m}) \cdot \mathrm{m^3/m^2}$) (Equation (11.5))
D_0	Smoke potential ($(\mathrm{db/m}) \cdot \mathrm{m^3/g}$) (Equation (11.6))
$\mathcal{D}$	Diffusion coefficient ($\mathrm{m^2/s}$)
E	Total emissive power of a surface ($\mathrm{kW/m^2}$) (Equation (2.4))
E	Constant (Equation (1.14))

E_A	Activation energy (J/mole)
f	Fraction of heat of combustion transferred from flame to surface (Equation (6.16))
f_{ex}	Excess fuel factor (Equation (10.22))
F	Constant (Equation (1.14))
F	Integrated configuration factor ('finite-to-finite area' configuration factor) (Section 2.4.1)
Fo	Fourier number $(\alpha t/L^2)(-)$
g	Gravitational acceleration constant (9.81 m/s^2)
Gr	Grashof number $(gl^3 \Delta\rho/\rho\nu^2)$ $(-)$
h	Convective heat transfer coefficient ($kW/m^2 \cdot K$)
h_c	Height of roof vent above floor (m) (Chapter 11)
h_0	Height to neutral plane (m) (Figure 10.4)
h_f	Height above neutral plane (m) (Figure 10.4)
h_k	Effective heat transfer coefficient ($kW/m^2 \cdot K$) (Equation (9.6))
H	Height of ventilation opening (m) (Chapter 10)
h	Planck's constant (Equation (2.52))
I	Intensity of radiation (Equations (2.56), and (2.79), and Section (10.2))
I	Intensity of light (Equation (11.2))
k	Thermal conductivity ($kW/m \cdot K$)
k'	Rate coefficient (Equation (1.1))
κ	Boltzmann's constant (Equations (2.52) and (2.54))
K	'Effective emission coefficient' (m^{-1}) (Equations (2.83), (5.12), (10.27))
l	Flame height or length (m) (Chapter 4)
l	Preheat length (m) (Section 7.2.3)
L	Thickness, or half-thickness (m) as defined locally (Section 2.2)
L	Mean beam length (m) (Section 2.4.2)
L	Lower flammability limit (Chapter 3)
L	Pathlength (m) (Section 11.1)
L_v	Latent heat of evaporation or gasification (J/g)
$\dot{m}$	Rate of mass loss (g/s)
M	Mass of air (kg)
M_f	Mass of fuel (kg)
M_w	Molecular weight
n	An integer
n	Number of moles (Chapter 1)
n_A, n_B	Molar concentration (Equation (1.16))
Nu	Nusselt number $(hL/k)(-)$ (k is the thermal conductivity of the fluid)
O	Opening factor, $A_w H^{1/2}/A_t$ ($m^{1/2}$) (Table 10.3 only)
p	Partial pressure (mm Hg, or atm, as defined locally)
p^o	Equilibrium vapour pressure (mm Hg)
P	Pressure (atm)
P_f	Perimeter of fire (m) (Section 11.2)
Pr	Prandtl number $(\nu/\alpha)(-)$

q_{f}	Fire load (Equation (10.40)) (MJ)
Q	Rate of heat transfer (W or kW)
$\dot{Q}_c$	Rate of heat release (W or kW)
$\dot{Q}_{\mathrm{conv}}$	Rate of convective heat release from a flame
$\dot{Q}_c'''$	Rate of heat production per unit volume (kW/m^3) (Equation (2.13))
$\dot{Q}^*$	Dimensionless heat release rate (−) (Equation (4.3))
r	Radial distance (m) (Equations (2.58), (4.49))
r	Stoichiometric ratio (fuel/air) (Chapters 1 and 10)
r_{c}	Height of roof vent above virtual source of the fire (m) (Section 11.2)
r_0	Characteristic dimension (m) (Chapters 6 and 8)
R	Ideal gas constant (Table 1.9) (Chapters 1, 6 and 8)
R	Radius of burner mouth (m) (Section 4.1)
R	Regression rate, or burning rate (Section 5.1.1)
Re	Reynolds number (ux/ν)(−) (Table 4.4)
S	Surface area (Equation (6.2))
S	Rate of transfer of 'sensible heat', defined in Equation (6.18)
t	Time (seconds, unless otherwise specified)
t*	Γt(hours) (Table 10.3 only)
t_{e}	Escape time (Chapters 9 and 11)
t_{u}	Time to achieve untenable conditions (Chapters 9 and 11)
T	Temperature (°C or K)
u	Flow velocity (m/s)
u^*	Dimensionless windspeed (Section 4.3.4)
U	Upper flammability limit (Chapter 3)
v	Linear velocity or flowrate (m/s)
V	Volume (m^3) (Chapters 1, 2 and 6)
V	Flame spread rate (Chapter 7)
W	Width of compartment (m)
W	Mass loss by volatilization (g) (Section 11.1)
x	Distance (Δx = thickness) (m)
$x_{\mathrm{A}}, x_{\mathrm{B}}$	Mole fractions
y	Distance (m)
Y	Mass fraction
z	Distance (m) (e.g., height in fire plume)

Greek symbols

α	Thermal diffusivity ($k/\rho c$) (m^2/s)
α'	Entrainment constant (Section 4.3.1)
$\alpha_{\mathrm{A}}, \alpha_{\mathrm{B}}$	Activity (Equation (1.17))
β	Coefficient of expansion (Equations (1.12) and (2.41))
β	Cooling modulus (−) (Equation (6.26))
γ	Energy modulus (−) (Equation (6.30))
$\gamma_{\mathrm{A}}, \gamma_{\mathrm{B}}$	Activity coefficients (Equation (1.17))

γ_i, γ_u	Pettersson's heat transfer coefficient (kW/m^{2}K) (Equations (10.33) and (10.35))
Γ	$[O/b]^2/(0.04/1160)^2$ (−) (Table 10.3 only)
δ_cr	Critical value of Frank-Kamanetskii's δ (Equation (6.13))
δ_h	Thickness of hydrodynamic boundary layer (m) (Section 2.3)
δ_θ	Thickness of thermal boundary layer (m) (Section 2.3)
ΔH	Change in enthalpy (kJ/mol)
ΔH_c	Heat of combustion (kJ/mol or kJ/g)
ΔH_f	Heat of formation (kJ/mol)
ΔU	Change in internal energy (kJ/mol)
ε	Emissivity
ξ	Dummy variable (Equation (2.23))
θ	Temperature difference (e.g., $T - T_\infty$)
θ	Dimensionless temperature (Chapter 8)
θ	Angle (Equation (2.56), Section 4.3.4 and 7.1)
κ	Absorption coefficient
κ	Constant (Equation (6.9))
λ	Wavelength (μm)
λ_n	Roots of Equation (2.19)
μ	Absolute or dynamic viscosity (Pa·s or N·s/m^2)
η_{O_2}	Mole fraction of oxygen (Equations (1.24) and (5.30))
ν	Kinematic viscosity (μ/ρ) (m^2/s)
ρ	Density (kg/m^3)
σ	Stefan–Boltzmann constant (5.67×10^{-8} W/m^2·K^4)
τ	Slab thickness (m) (Equation (2.21) and Section 6.3.1)
τ'	Length of induction period (s)
ϕ	Configuration factor (Section 2.4.1)
ϕ	Equivalence ratio (Equation 1.29, Section 9.2.1)
χ	Factor expressing combustion efficiency (Chapters 1 and 5)
χ	$\dot{m}_\mathrm{air}/A_\mathrm{w}H^{1/2}$ (Chapter 10)
χ_R	Fraction of heat of combustion lost by radiation (−)

Subscripts

a	Ambient
b	Black body (radiation)
c	Cold (Chapter 2)
c	Convective (with f) (Chapter 6)
C	Combustion
cr	Critical
d	Duration (of burning) (Equation (10.39))
e, E	External
f	Fuel

F	Flame
FO	Flashover
g	Gas
h	Hot
ig	Ignition or firepoint
l	Liquid (Chapter 5)
L	Loss by gas replacement (Equation (10.23)))
m	Mean
max	Maximum
n	Normal to a surface (as in Equation 2.56)
o	Initial value or ambient value
o	Centreline value (buoyant plume (Chapter 4))
ox	Oxygen
p	Constant pressure
p	Pyrolysis (Chapter 7)
pl	Plate (Equation (8.1.3))
R	Radiative
s	Surface
u	Unburnt gas
W	Wall (Equation (10.23))
x	In the x-direction
∞	Final value

Superscripts

$\cdot$	Signifies rate of change as in $\dot{m}$
$\cdot$	Indicates that a chemical species is a free radical (e.g., H, the hydrogen atom) (Chapter 1)
$'$	Single prime (signifies 'per unit width') (Chapter 4)
$''$	Double prime (signifies 'per unit area')
$'''$	Triple prime (signifies 'per unit volume')

List of acronyms and abbreviations

ASET	Available Safe Egress Time
ASTM	American Society for Testing and Materials
BRE	Building Research Establishment (Garston, Watford, UK)
BSI	British Standards Institution
CEN	Comité Européen de Normalisation
CFAST	Consolidated model of Fire And Smoke Transport
CFD	Computational Fluid Dynamics
CIB	Conceil Internationale du Bâtiment
CSTB	Centre Scientifique et Technique du Bâtiment (France)
DIN	Deutsches Institut für Normung

ECSC	European Coal and Steel Community
FDS	Fire Dynamics Simulator (developed at NIST)
FMRC	Factory Mutual Research Corporation (Norwood, MA, USA). Now FMGlobal
FPA	Fire Protection Association
*FRS	Fire Research Station (now part of BRE, see above)
FTA	Flammability Testing Apparatus (developed at FMGlobal)
*IAFSS	International Association for Fire Safety Science
ISO	International Organization for Standardization
LFL	Lower Flammability Limit
NBS	National Bureau of Standards (now NIST)
NFPA	National Fire Protection Association (1 Batterymarch Park, Quincy, MA, USA)
NIST	National Institute for Standards and Technology (Building and Fire Research Laboratory, Gaithersburg, MD, USA)
RSET	Required Safe Egress Time
SBI	Single Burning Item
SFPE	Society of Fire Protection Engineers (Bethesda, MD, USA)
UFL	Upper Flammability Limit

*Frequent references are made in this text to the Fire Research Notes (from FRS) and the proceedings of the triennial IAFSS symposia. These are available on the IAFSS website http://www.iafss.org. Note that the Proceedings of the Symposia are now referred to as individual volumes of “Fire Safety Science”.

1

Fire Science and Combustion

As a process, fire can take many forms, all of which involve chemical reactions between combustible species and oxygen from the air. Properly harnessed, it provides great benefit as a source of power and heat to meet our industrial and domestic needs, but, unchecked, it can cause untold material damage and human suffering. In the United Kingdom alone, direct losses probably exceed £2 billion (2010 prices), while over 400 people die each year in fires. According to the UK Fire Statistics (Department for Communities and Local Government, 2009), there were 443 fatalities in 2007, continuing a downward trend from over 1000 in 1979. In real terms, the direct fire losses may not have increased significantly over the past two decades, but this holding action has been bought by a substantial increase in other associated costs, namely improving the technical capability of the Fire Service and the adoption of more sophisticated fire protection systems.[1]

Further major advances in combating unwanted fire are unlikely to be achieved simply by continued application of the traditional methods. What is required is a more fundamental approach that can be applied at the design stage rather than tacitly relying on fire incidents to draw attention to inherent fire hazards. Such an approach requires a detailed understanding of fire behaviour from an engineering standpoint. For this reason, it may be said that a study of fire dynamics is as essential to the fire protection engineer as the study of chemistry is to the chemical engineer.

It will be emphasized at various places within this text that although ‘fire’ is a manifestation of a chemical reaction, the mode of burning may depend more on the physical state and distribution of the fuel, and its environment, than on its chemical nature. Two simple examples may be quoted: a log of wood is difficult to ignite, but thin sticks can be ignited easily and will burn fiercely if piled together; a layer of coal dust will burn relatively slowly, but may cause an explosion if dispersed and ignited as a dust cloud. While these are perhaps extreme examples, they illustrate the complexity of fire behaviour in that their understanding requires knowledge not only of chemistry but also of many subjects normally associated with the engineering disciplines (heat transfer, fluid dynamics, etc.). Indeed, the term ‘fire dynamics’ has been chosen to describe the subject of fire

[1] The total cost associated with fire in England and Wales in 2004 was estimated to be £7.03 billion. This figure includes costs of fire protection, the Fire and Rescue Service (including response), property damage and lost business, as well as the economic costs associated with deaths and injuries and the prosecution of arsonists (Office of the Deputy Prime Minister, 2006).

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behaviour as it implies inputs from these disciplines. However, it also incorporates parts of those subjects which are normally associated with the terms ‘fire chemistry’ and ‘fire science’. Some of these are reviewed in the present chapter, although detailed coverage is impossible. It is assumed that the reader has some knowledge of elementary chemistry and physics, including thermodynamics: references to relevant texts and papers are given as appropriate.

1.1 Fuels and the Combustion Process

Most fires involve combustible solids, although in many sectors of industry, liquid and gaseous fuels are also to be found. Fires involving gases, liquids and solids will be discussed in order that a comprehensive picture of the phenomenon can be drawn. The term ‘fuel’ will be used quite freely to describe that which is burning, whatever the state of matter, or whether it is a ‘conventional’ fuel such as LPG or an item of furniture within a room. With the exception of hydrogen gas, to which reference is made in Chapter 3, all fuels that are mentioned in this text are carbon-based. Unusual fire problems that may be encountered in the chemical and nuclear industries are not discussed, although the fire dynamics will be similar if not identical. General information on problems of this type may be gleaned from the *National Fire Protection Handbook* (NFPA, 2008) and other sources (e.g., Meidl, 1970; Stull, 1977; Mannan, 2005).

1.1.1 The Nature of Fuels

The range of fuels with which we are concerned is very wide, from the simplest gaseous hydrocarbons (Table 1.1) to solids of high molecular weight and great chemical complexity, some of which occur naturally, such as cellulose, and others that are man-made (e.g., polyethylene and polyurethane) (Table 1.2). All will burn under appropriate conditions, reacting with oxygen from the air, generating combustion products and releasing heat. Thus, a stream or jet of a gaseous hydrocarbon can be ignited in air to give a flame, which is seen as the visible portion of the volume within which the oxidation process is occurring. Flame is a gas phase phenomenon and, clearly, flaming combustion of liquid and solid fuels must involve their conversion to gaseous form. For burning liquids, this process is normally simple evaporative boiling at the surface,[2] but for almost all solids, chemical decomposition or *pyrolysis* is necessary to yield products of sufficiently low molecular weight that can volatilize from the surface and enter the flame. As this requires much more energy than simple evaporation, the surface temperature of a burning solid tends to be high (typically 400°C) (Table 1.2). Exceptions to this rule are those solids which sublime on heating, i.e., pass directly from the solid to the vapour phase without chemical decomposition. There is one relevant example, hexamethylenetetramine (also known as methenamine), which in pill form is used as the ignition source in ASTM D2859-06 (American Society for Testing and Materials, 2006). It sublimes at about 263°C (Budavari, 1996).

The composition of the volatiles released from the surface of a burning solid tends to be extremely complex. This can be understood when the chemical nature of the solid is

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[2] Liquids with very high boiling points ($\geq 250^\circ$C) may undergo some chemical decomposition (e.g., cooking oil).

Table 1.1 Properties of gaseous and liquid fuels[a]

Common name[b]	Formula	Melting point (°C)	Boiling point (°C)	Density (liq) (kg/m^3)	Molecular weight
Hydrogen	H_2	−259.3	−252.8	70	2
Carbon monoxide	CO	−199	−191.5	422	28
Methane	CH_4	−182.5	−164	466	16
Ethane	C_2H_6	−183.3	−88.6	572	30
Propane	C_3H_8	−189.7	−42.1	585	44
n-Butane	n-C_4H_{10}	−138.4	−0.5	601	58
n-Pentane	n-C_5H_{12}	−130	36.1	626	72
n-Hexane	n-C_6H_{14}	−95	69.0	660	86
n-Heptane	n-C_7H_{16}	−90.6	98.4	684	100
n-Octane	n-C_8H_{18}	−56.8	125.7	703	114
iso-Octane[c]	iso-C_8H_{18}	−107.4	99.2	692	114
n-Nonane	n-C_9H_{20}	−51	150.8	718	128
n-Decane	n-$C_{10}H_{22}$	−29.7	174.1	730	142
Ethylene (ethene)	C_2H_4	−169.1	−103.7	(384)	28
Propylene (propene)	C_3H_6	−185.2	−47.4	519	42
Acetylene (ethyne)	C_2H_2	−80.4	−84	621	26
Methanol	CH_3OH	−93.9	65.0	791	32
Ethanol	C_2H_5OH	−117.3	78.5	789	46
Acetone	$(CH_3)_2CO$	−95.3	56.2	790	58
Benzene	C_6H_6	5.5	80.1	874	78

[a] Data from Lide (1993/94).

[b] It should be noted that IUPAC (International Union of Pure and Applied Chemistry) has defined a standard chemical nomenclature which is not used rigorously in this text. ‘Common names’ are used, although the IUPAC nomenclature will be given where appropriate. See, for example, ‘iso-octane’ and ‘ethylene’ in this table.

[c] 2,2,4-Trimethyl pentane.

considered. All those of significance are polymeric materials of high molecular weight, whose individual molecules consist of long ‘chains’ of repeated units which in turn are derived from simple molecules known as monomers (Billmeyer, 1971; Open University, 1973; Hall, 1981; Friedman 1989; Stevens, 1999). Of the two basic types of polymer (addition and condensation), the addition polymer is the simpler in that it is formed by direct addition of monomer units to the end of a growing polymer chain. This may be illustrated by the sequence of reactions:

$$R^\bullet + CH_2 = CH_2 \rightarrow R \cdot CH_2 \cdot CH_2^\bullet \qquad (1.R1a)$$

$$R \cdot CH_2 \cdot CH_2^\bullet + CH_2 = CH_2 \rightarrow R \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2^\bullet \qquad (1.R1b)$$

etc., where $R^\bullet$ is a free radical or atom, and $CH_2{=}CH_2$ is the monomer, ethylene. This process is known as polymerization and in this case will give polyethylene, which has the idealized structure:

$$R\!\left(\underbrace{CH_2 \cdot CH_2}_{\text{monomer unit}}\right)_{\!n}\!R'$$

Table 1.2 Properties of some solid fuels[a]

	Density (kg/m^3)	Heat capacity (kJ/kg·K)	Thermal conductivity (W/m·K)	Heat of combustion (kJ/g)	Melting point (°C)
Natural polymers					
Cellulose	V[b]	~1.3	V	16.1	chars
Thermoplastic polymers					
Polyethylene					
Low density	940	1.9	0.35	46.5	
High density	970	2.3	0.44	46.5	130–135
Polypropylene					
Isotactic	940	1.9	0.24	46.0	186
Syndiotactic				46.0	138
Polymethylmethacrylate	1190	1.42	0.19	26.2	~ 160
Polystyrene	1100	1.2	0.11	41.6	240
Polyoxymethylene	1430	1.4	0.29	15.5	181
Polyvinylchloride	1400	1.05	0.16	19.9	–
Polyacrylonitrile	1160–1180	–	–	–	317
Nylon 66	~ 1200	1.4	0.4	31.9	250–260
Thermosetting polymers					
Polyurethane foams	V	~ 1.4	V	24.4	–
Phenolic foams	V	–	V	17.9	chars
Polyisocyanurate foams	V	–	V	24.4	chars

[a] From Brandrup and Immergut (1975) and Hall (1981). Heats of combustion refer to CO_2 and H_2O as products.
[b] V = variable.

in which the monomer unit has the same complement and arrangement (although not the same chemical bonding) of atoms as the parent monomer, $CH_2{=}CH_2$: n is the number of repeated units in the chain and is known as the degree of polymerization, which may be anything from a few hundred to several tens of thousands (Billmeyer, 1971). This type of polymerization relies on the reactivity of the carbon–carbon 'double bond'. In contrast, the process of polymerization which leads to the formation of a 'condensation polymer' involves the loss of a small molecular species (normally H_2O) whenever two monomer units link together. (This is known as a condensation reaction.) Normally, two distinct monomeric species are involved, as in the production of Nylon 66 from hexamethylene diamine and adipic acid.[3] The first stage in the reaction would be:

$$\underset{\substack{\text{hexamethylene}\\\text{diamine}}}{NH_2(CH_2)_6\,NH_2} + \underset{\text{adipic acid}}{HO\cdot CO\cdot (CH_2)_4\cdot CO\cdot OH} \qquad (1.R2)$$

$$\rightarrow NH_2(CH_2)_6\,NH\cdot CO\cdot (CH_2)_4\cdot CO\cdot OH + H_2O$$

---

[3] The IUPAC systematic names of these two compounds are: diaminohexane and butane-1,4-dicarboxylic acid, respectively.

The formula of Nylon 66 may be written in the format used above for polyethylene, namely:

$$H\!\leftarrow\!\!\!\!\!-\; NH \cdot (CH_2)_6 \cdot NH \cdot CO \cdot (CH_2)_4 \cdot CO \;\!-\!\!\!\!\!\rightarrow_n OH$$

It should be noted that cellulose, the most widespread of the natural polymers occurring in all higher plants (Section 5.2.2), is a condensation polymer of the monosaccharide D-Glucose ($C_6H_{12}O_6$). The formulae for both monomer and polymer are shown in Figure 5.11.

An essential feature of any monomer is that it must contain two reactive groups, or 'centres', to enable it to combine with adjacent units to form a linear chain (Figure 1.1(a)). The length of the chain (i.e., the value of n in the above formulae) will depend on conditions existing during the polymerization process: these will be selected to produce a polymer of the desired properties. Properties may also be modified by introducing branching into the polymer 'backbone'. This may be achieved by modifying the conditions in a way that will induce branching to occur spontaneously (Figure 1.1(b)) or by introducing a small amount of a monomer which has three reactive groups (unit B in Figure 1.1(c)). This can have the effect of producing a cross-linked structure whose physical (and chemical) properties will be very different from an equivalent unbranched, or only slightly branched, structure (Stevens, 1999). As an example, consider the expanded polyurethanes. In most flexible foams the degree of cross-linking is very low, but by increasing it substantially (e.g., by increasing the proportion of trifunctional monomer, B in Figure 1.1(c)), a polyurethane suitable for rigid foams may be produced.

With respect to flammability, the yield of volatiles from the thermal decomposition of a polymer is much less for highly cross-linked structures since much of the material forms an involatile carbonaceous char, thus effectively reducing the potential supply of gaseous fuel to a flame. An example of this can be found in the phenolic resins, which on heating to a temperature in excess of 500°C may yield up to 60% char (Madorsky, 1964). The structure of a typical phenolic resin is shown in Figure 1.2. A natural polymer that exhibits a high degree of cross-linking is lignin, the 'cement' that binds the cellulose structures together in higher plants, thus imparting greater strength and rigidity to the cell walls.

Synthetic polymers may be classified into two main groups, namely thermoplastics and thermosetting resins (Table 1.2). A third group – the elastomers – may be distinguished on the basis of their rubber-like properties (Billmeyer, 1971; Hall, 1981; Stevens, 1999),

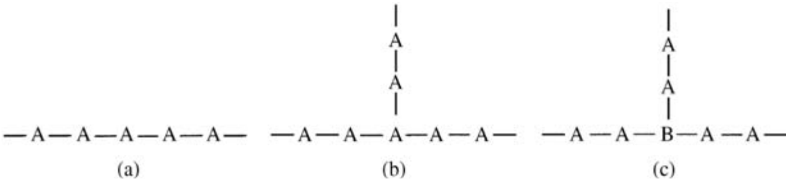

Figure 1.1 Basic structure of polymers: (a) straight chain (e.g., polymethylene, with A=CH_2); (b) branched chain, with random branch points (e.g., polyethylene, with A=CH_2–CH_2, see text); (c) branched chain, involving trifunctional centres (e.g., polyurethane foams in which the straight chains (— A— A—, etc.) correspond to a co-polymer of tolylene di-isocyanate and a polymer diol and B is a trihydric alcohol)

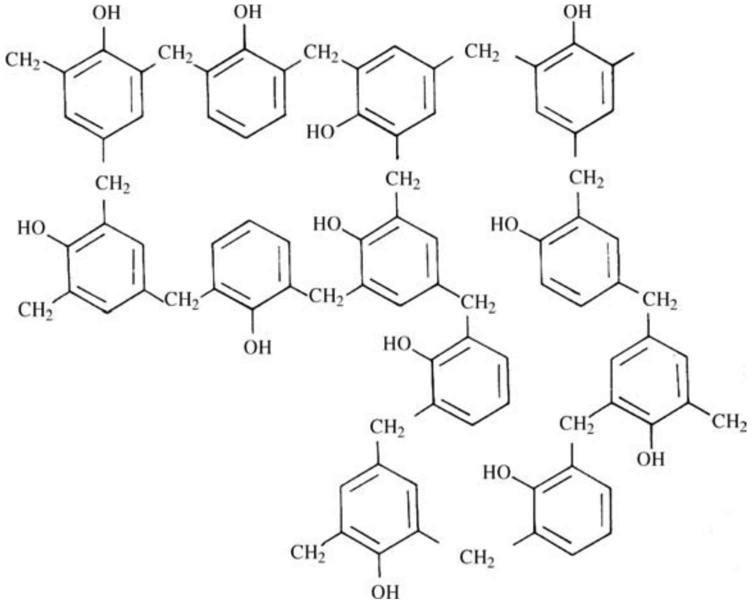

Figure 1.2 Typical cross-linked structure to be found in phenol formaldehyde resins

but will not be considered further here. From the point of view of fire behaviour, the main difference between thermoplastics and thermosetting polymers is that the latter are cross-linked structures that will not melt when heated. Instead, at a sufficiently high temperature, many decompose to give volatiles directly from the solid, leaving behind a carbonaceous residue (cf. the phenolic resins, Figure 1.2), although with polyurethanes, the initial product of decomposition is a liquid. On the other hand, the thermoplastics will soften and melt when heated, which will modify their behaviour under fire conditions. Fire spread may be enhanced by falling droplets or the spread of a burning pool of molten polymer (Section 9.2.4). This is also observed with flexible polyurethane foams, although in this case the liquid melt is a product of the decomposition process.

1.1.2 Thermal Decomposition and Stability of Polymers

The production of gaseous fuel (volatiles) from combustible solids almost invariably involves thermal decomposition, or pyrolysis, of polymer molecules at the elevated temperatures which exist at the surface (Kashiwagi, 1994; Hirschler and Morgan, 2008). Whether or not this is preceded by melting depends on the nature of the material (Figure 1.3 and Table 1.3). In general, the volatiles comprise a complex mixture of pyrolysis products, ranging from simple molecules such as hydrogen and ethylene, to species of relatively high molecular weight which are volatile only at the temperatures existing at the surface where they are formed, when their thermal energy can overcome the cohesive forces at the surface of the condensed fuel. In flaming combustion most of these will be consumed in the flame, but under other conditions (e.g., pyrolysis without combustion following exposure to an external source of heat or, for some materials,