



**FIRE PHENOMENA AND
THE EARTH SYSTEM**

An Interdisciplinary Guide to Fire Science

Edited by
CLAIRE M. BELCHER

 **WILEY-BLACKWELL**

FIRE PHENOMENA AND THE EARTH SYSTEM

DEDICATION

Joseph Priestley famously used a magnifying glass to focus the sun's rays on a small sample of mercury(II) oxide. The heating of the compound produced a gas that he observed allowed a candle to burn more brightly and in which a mouse, contained within a jar, could live four times longer than in the same quantity of 'common air'. This gas, which he termed 'dephlogisticated air', was oxygen, which breathes life both into our planet and into fire.

This book is dedicated to those, like Priestley, who dare to discover, seek the truth and push the boundaries of knowledge in order to believe.

Fire Phenomena and the Earth System

An Interdisciplinary Guide to Fire Science

Edited by

Claire M. Belcher

College of Life and Environmental Sciences, University of Exeter

 **WILEY-BLACKWELL**

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Foreword

This book sets out to act as a catalyst to bring together diverse groups of scientists with interests in fire and fire-related processes to collaborate across a wide range of disciplines. The scientists are drawn from a spectrum of disciplines, ranging from those concerned with fire in industrial and domestic settings (where imperfections in humanity's harnessing of fire exposes us to a series of hazards) to those with interests in the role of fire in natural ecosystems, now and in the past. Inter alia, a study of the involvement of fire in the history of terrestrial life in deep time, and its links with atmospheric composition and climate, will help inform the current debate on global warming and its potential impact.

The first part of the book introduces flaming and smouldering combustion and surveys some important aspects of wildland fires. In Chapter 1, Torero introduces some of the fundamentals that are relevant to our understanding of ignition and flaming combustion of solid 'fuels'. Flame being a gas-phase process, 'burning' of a combustible solid involves pyrolysis of the fuel, releasing low molecular weight flammable vapours, which mix and burn with oxygen from the air, releasing gaseous and particulate products ('smoke') that will be dispersed in the atmosphere. Biomass materials will invariably leave behind a carbonaceous residue, which may be partly consumed by heterogeneous oxidation but a significant amount may survive the fire. The fate of such material from wildfire is discussed in Chapter 8 by Doerr and Shakesby, who refer to it as 'ash',

although the term 'black carbon' is used to describe all combustion-generated carbonaceous matter, including that released into the atmosphere. Hammes and Abiven (Chapter 9) discuss a number of techniques that may be used to analyse black carbon found in the Earth system.

Biomass materials may also undergo smouldering combustion as discussed by Rein in Chapter 2. This process does not involve flame and in the present context is associated with the burning of subsurface accumulations of organic material such as peat. It is a very slow process in comparison to flaming combustion which has a high rate of generation of fire products and can lead to very high rates of fire spread. This is explored in Chapter 3 by Simeoni in a review of experimental work that has contributed to our understanding of the mechanisms of burning and fire spread. The focus has been on the development of predictive models for fire spread rate, informed by the results of experiments, which range in size from small-scale laboratory tests to full-scale burns in live vegetation. This theme is picked up and developed further by Pastor and Planas in Chapter 4. They examine in greater detail the role of the structure of the fuel bed (tree canopy, shrub, forest litter, etc.) and its characteristics (moisture content, size of individual fuel elements, etc.) in determining the fire hazard rating, a concept that is widely used in areas that are prone to wildfire. The first part concludes with an overview of the use of remote sensing of fires

from satellites by Roy *et al.* (Chapter 5). This technique can monitor the spread of large wildfires and be used to determine the extent of damage caused. Such data should allow fire spread models to be tested to greater effect as well as providing more accurate assessments to be made of the total amount of material consumed in a given fire. The latter can be used to estimate the impact of the fire on atmospheric pollution.

The second part reaches into the relationship between fire and the biosphere – all forms of terrestrial life. Davies (Chapter 6) leads off with an exploration of the ecology of fire, about which we have seen a surge of literature in recent decades. What to fire scientists is regarded as ‘fuel’ is for plant ecologists a vast range of different plant communities, with different flammabilities and with a range of different responses to fire during the course of their evolution. Many aspects of this kind of fire ecology lead into considering the time dimension of change in climate as seen in the geological record, and hence to changes in atmospheric composition through time. Midgley and Bond (Chapter 7) focus on those changes in plant structure and behaviour that enable them to survive exposure to fire – and the extreme case of certain serotinous (fire-adapted) species, where exposure to fire is a requirement for the release of seeds – and the regeneration of the plant population following fire. Above all, they explore how plants have evolved in response to fire as a recurring feature of their environment, and the kinds of changes that this selective pressure has brought about in plants. Doerr and Shakesby (Chapter 8) move on to consider the impact of fire on the physical environment, beyond just the removal of the biomass as fuel, to the effect on the hydrology and geochemistry of the soil and what lies beneath it. The physical effect of fire depends on the two related parameters of fire severity and fire intensity, which are in turn dependent on the character of the fuel involved and the temperature reached in the burning process. These in turn influence the ease with which plant colonization and succession can ensue. Some communities are well adapted to frequent occurrence of wildfires, while others are not, and take far longer to become re-established.

The impact of fire on the soil will of course be influenced by where within that range a given fire falls, and hence there is a strong element of uncertainty in predicting the physical environment’s response to a given fire episode.

The third part bears the heading ‘Fire and the Earth’s Past’. Glasspool and Scott (Chapter 10) deal with the recognition of char in ancient sediment records, which represent the occurrence of wildfire through the geological past, back over some 400 million years – indeed, for as long as land-adapted plants have generated biomass as fuel. They explore the significance of fossil charcoal as a measure of the incidence of wildfire through the course of Earth history, with its links to palaeoclimate, the character of the vegetation and the composition of the palaeoatmosphere. The study of fossil charcoal has given us a unique insight into all three of those components of time past. The last 21 000 years of the fire record of Earth history is pursued in depth by Power (Chapter 11), who sees evidence for major changes in the fire regimes through that period of drastic climate change. That interval takes us from full glacial conditions in high northern latitudes, through progressive warming as we move into the present Interglacial, and this of course impacts on the vegetation, the incidence of wildfire and eventually the involvement of humans with their exploitation of fire for cooking, heating and industrial applications. Belcher, Collinson and Scott (Chapter 12) review the whole range of phenomena linking the evolution of plant life on land with the changes in atmospheric composition that ensued. As they explain, the oxygen content of the air through that period had already been generated by photosynthesis by algae and photosynthetic bacteria from an originally carbon-dioxide-rich atmosphere at a much earlier period of Earth history. Changes that took place as terrestrial vegetation evolved from small reed-like herbs to massive forest trees included alteration of the carbon dioxide and oxygen levels, and with that, the vulnerability to wildfire. Major events in plant evolution – the rise of conifer forests, the evolutionary explosion of flowering plant diversity and their global dominance, and the eventual expansion of the grasses

and grassland ecology – all had far-reaching effects on global fire ecology. Indeed, as they explain, fire has been a significant factor in evolutionary change throughout the history of plant life on land.

The final part of the book deals with the widest dimension of fire phenomena, their role in the total Earth system. Turquet (Chapter 13) reviews a series of aspects of the atmospheric and climatic impact of fire, ranging from the medical problems ensuing from inhalation of particulate matter from smoke and volatile organic compounds, to the climatic impact of the release of CO₂. It is important to note that carbon dioxide released from wildfires has only been out of circulation for a geologically brief interlude, so that it is in effect a re-emission of a greenhouse gas. This places the CO₂ generated by wildfire in a different category from that generated by burning fossil fuels, which are introducing into the contemporary atmosphere carbon held for many millions of years in the Earth's crust. Turquet also emphasizes the impact that satellite imagery has had on fire studies, both as a means of measuring changes in atmospheric composition, and of mapping fire incidence at various scales.

The chapter by Watson and Lovelock (Chapter 14) takes us back to the first serious experimental investigation in the 1970s attempting to quantify the relationship between moisture content of the biomass, the process of ignition by electric spark, and the atmospheric oxygen level (which has clearly changed through the course of geological time). The experimental set-up was simple, and moist computer (paper) tape was used as a model of living plant material, ignited by a controlled electric spark. Although some thought this was too remote from the reality of a natural wildfire, the work was a real landmark in experimental fire ecology and it eventually stimulated others to develop systems involving natural biomass fuels and an experimental environment closer to reality. This chapter is important in revealing some of the details of those experiments that were published in only rather abbreviated form at the time.

The penultimate chapter by Lenton (Chapter 15) explores in depth the long-term relationship

between the global incidence of fire, the atmospheric oxygen level and the biological consequences of such changes in those phenomena as are revealed in the fossil record. This includes such issues as the high level of oxygen believed by some to characterize the Carboniferous period, which made possible larger insects than have ever occurred before or since. But the principal focus of this chapter is the extent to which the incidence of fire either stabilizes the oxygen level, or has the reverse effect. On this question the evidence is conflicting, and Lenton presents results based on a new model, relating oxygen levels and the feedbacks associated with the occurrence of fire.

In the final chapter, a very different aspect of fire is explored by Mašek (Chapter 16), who deals with an aspect of biomass burning that has received relatively less attention than many others. The portion of the biomass that becomes charcoal following the occurrence of wildfire is remarkably inert chemically, and at least some of it will survive transport into the drainage system, and thence into the oceans and eventual burial in deep ocean sediments. As such, this biochar represents a route that takes the carbon from atmospheric carbon dioxide (via photosynthesis of plants) and renders it out of 'circulation' at least in the (geological) short term. In other words, it constitutes a form of carbon sequestration occurring naturally, and much more cheaply, than capturing the carbon dioxide resulting from the burning of fossil fuel and seeking to sequester it by human endeavour!

The Editor should be congratulated for her foresight in identifying the need for a volume of this nature. It will, almost inevitably, reveal exciting opportunities for collaborative research between scientists currently working in very different disciplines.

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Preface

Fire is a natural process integral to the order and function of our planet. It is both friend and foe to the human race, having strongly influenced our social development and success as a species, yet it remains a serious threat to human life. Our planet is inherently flammable. Earth's forests and vegetation provide a vast source of fuel, and fires consume huge quantities of biomass in all ecosystems ranging across all biomes, from tundra to savanna and from boreal to tropical forests, where many of our ecosystems are considered fire dependent. Fires influence atmospheric carbon dioxide concentrations and may even regulate the oxygen content of our atmosphere enabling us to breathe. The unique products formed by fires interact with the carbon and nutrient balance of our planet. Some of these products (e.g. chars, soots and chemical signatures) are traceable in soils, sediments and ancient rocks and provide us with a record of Earth's past fire history. The effects of fire on both the built and the natural environment have begun to generate sustained scientific interest from a broad spectrum of scientific disciplines. It is this interest, spread across the disciplines, that has led to the conception of this book, the goal of which is to unite the disciplines within fire science towards increasing our scientific understanding of the impact of fires on the Earth system.

One challenge of this book has been to get everyone onto the same page, i.e. to explain each other's terminology and begin to communicate

better our research between our strongly interlinked areas. To this end and bearing in mind the breadth of background of both the contributors and the readers, I feel it is necessary to define what I mean by the Earth system. The concept of the 'Earth system' revolves around us considering it as a whole, where we recognize the interaction of individual processes with one another in order to produce the relative stability that allows life to thrive on our planet. This includes understanding, for example, interactions between the atmosphere and the oceans, temperature and climate, and life on land and in the oceans; and in this case how fire influences these interactions. So, whilst this book might not provide all the answers I hope that by bringing together fire scientists from all walks of the discipline, both as contributors and readers, it may move us towards gaining a better understanding of the important role that this physical force plays in maintaining our planet's relative stability.

To this end this book comprises a state-of-the-art compendium of 16 chapters contributed and peer-reviewed by experts of international standing in their field. These chapters cover four broad themes, which constitute the four parts of this book: (1) Fire Behaviour, (2) Fire and the Biosphere, (3) Fire and the Earth's Past, and finally (4) Fire and the Earth System. It was not possible to cover all disciplines that stretch across the fire sciences, therefore the focus of this book is on natural wildfires and their implications for Earth system processes. As such contributors have been

selected who are well placed to outline core research in areas focused to improve this understanding. The book does not include archaeological research and the early interactions of humans with fire nor the impact of fire on society. This is not to say that these areas are unimportant contributions to fire science but that they fall just outside the remit of this book. The book also touches relatively little on forest fire management, for which a wealth of literature, including more than adequate books, already exists. I believe that the chapters within this book provide an excellent overview of the important research areas that contribute to improving our understanding of the role of fire in the Earth system. In the paragraph below I summarize the linkages between the core research areas highlighted in the book.

Part 1 outlines the fundamentals of fire behaviour. It shows how bench- to field-scale experiments are used to monitor and understand fire behaviour in respect to the physical and chemical conditions imposed upon the fire. This part also deals with practical applications and shows how knowledge of fire behaviour is used to predict 'fire danger' for our modern ecosystems, as well as how such wildfires are monitored. Without this core knowledge we cannot begin to understand the true impact of fire on our ecosystems. Part 2 builds on these fundamentals and considers the influence of fire on the biosphere. Variations in vegetation impact upon the availability and type of fuel and lead the book to introduce the concept of fire regime. This concept draws on knowledge of combustion dynamics and known plant responses to fire. The part moves on to consider the evolutionary consequences of fire and how different plants have developed adaptations in order to survive fire. It then outlines the hydrological, geomorphological and geochemical impacts that fires have on the land surface via either direct effects or the addition of products of fire such that in this part fire begins to be firmly positioned within an Earth system context. In Part 3 the book looks at the influence of fire on the biosphere in Earth's past. It links the fossil record of fire activity, as

evidenced from fossil charcoals, to past variations in atmospheric composition, climate and evolutionary events in Earth's vegetation. It shows that fire has not only been strongly influenced by climate variations in Earth's past, but also how fire has shaped the abundant life that we see on our planet today. Finally in Part 4 the impact and relationship of fire and the Earth system are considered particularly in respect to atmospheric chemistry and composition. Over relatively short timescales it assesses the impact of fires on air quality and on the carbon cycle. Over long multi-million-year timescales it looks at the influence that variations in atmospheric oxygen have had on fire and how the prevalence of fire may feed back into regulating the oxygen content of our atmosphere. Finally we move on to consideration of future uses of the products of fire in the rapidly emerging field of biochar research, and consider how biochar might be able to provide a useful means to sequester carbon into geologically stable long-term carbon pools. As such the book captures a diversity of methods, observations and applications across different scales.

Consideration of scale is key to building an understanding of the Earth system and is therefore an important theme of this book. This compilation aims to highlight consideration of both spatial and temporal scales to those working within the fire sciences, so that each sub-discipline might explore new collaborations that better cross-cut these multitude of scales. These scales cover small to large experimental scales that are required to improve our understanding of fire. Laboratory-scale experiments allow control of conditions and increase our understanding of the chemical and physical phenomena that drive fire ignition, spread and extinction. Larger field-scale prescribed burns allow observation of real fires but allow little control over conditions. In both cases the observed phenomena can be used to develop models to describe fire behaviour. Such models might range from relatively simple cellular automata models to more complex models using computational fluid dynamics. Forest fire behaviour and risk can be modelled or predicted on the

ecosystem scale using ground-based estimates of fuel loads coupled to understanding of flammability from laboratory experiments. Such fires can be monitored using satellite remote sensing, which allows us to monitor not only known fires but also to gain insight into otherwise unnoticed fires burning in remote areas. This provides us with a picture of both the size of burned areas as well as the number of fires burning yearly on our planet today. These data can be compared with historical records of fires, which can in turn be compared to pre-industrial records of fire activity, records from pre-human times, through timescales of millions of years ago. Study across these scales can allow us to

estimate not only the human influence on fire over the ages but also the impacts that past environmental changes have had on Earth's fire activity. The study of fires over both spatial and temporal scales allows us to better understand the role that fire plays in managing the carbon and nutrient balance of our planet, its influence on the atmosphere over daily to multi-million-year timescales through to evolutionary processes. I hope that you will enjoy this journey across space and time so that we can improve our understanding of the role that fire plays within the Earth system.

Claire M. Belcher

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Firstly I wish to thank Guillermo Rein (Department of Mechanical Engineering, Imperial College London) for his drive along with mine to cross-cut boundaries within the fire sciences. Guillermo had significant input to the early conception of this book, which was born through our fruitful interdisciplinary collaborations that have linked Earth Science and Fire Safety Engineering. Guillermo has introduced me to many of the authors in this book particularly those in Part 1 (Fire Behaviour) and some of the authors in Part 2 (Fire and the Biosphere). Without such contacts these sections would not have such strength and expertise contained within them. I feel certain that this book would not exist if it were not for my collaborations with Guillermo.

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Claire M. Belcher
July 2012

Part 1

Fire Behaviour

1 An Introduction to Combustion in Organic Materials

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1.1 Introduction

Combustion is a process by which fuel and oxidizer react to produce a different set of chemical products and heat. The process is intimately linked to the nature of the fuel but also to different transport processes that define the characteristics of the combustion process. This chapter provides a brief and general description of the different processes and of commonly used nomenclature.

Discussing combustion of organic materials needs to start with simple definitions that enable the description of the main phenomena involved. Organic materials can be defined as carbon-based materials, which can be divided into natural materials and processed materials. Processed materials are those generated through some modification that alters the physical or chemical characteristics of the natural materials. Natural materials include vegetation, decomposed vegetation, coal or the large group known as hydrocarbons (oils, tars, etc.). Processed materials include timber, plastics, petrol and many other industrial products. It is important to emphasize that many inorganic materials will also combust, but these will not be discussed here.

From the combustion perspective natural or processed organic materials are no different; in both cases the combustion process can be described

as a chemical reaction that is defined by the following generic expression:



The 'fuel' being the organic material and the 'oxidizer' being oxygen extracted in most cases from air. Chemical reactions associated with combustion are exothermic, thus the products are released with a significant amount of energy. The specific energy (i.e. joules produced per kilogram of the material) tends to be extremely high when combustion processes are compared to other energy-generating mechanisms (electric batteries, fuel cells, etc.; Fernandez-Pello, 2002). Thus, combustion of organic fuels has been a preferred source of energy.

Combustion processes have been controlled for at least 100 000 years (Stahl, 1984; James, 1989) and humans have learnt to harness the energetic content of organic fuels for cooking, comfort and power. Until the industrial revolution combustion was poorly understood and was limited to controlled burning of natural fuels (i.e. coal, wood). The Industrial Revolution generated the first true understanding of combustion (Faraday, 1908), the massive use of organic fuels, and the first attempts to modify organic compounds to produce more efficient fuels (Frank, 2005).

Today, combustion of modified organic fuels represents more than 85% of the total worldwide energy production (Jacobson, 2009).

A different form of combustion is known as fire. Fire is the uncontrolled chemical oxidation of organic fuels that is generally associated with destruction. In fire, the heat of the combustion process serves to sustain the uncontrolled burning of any adjacent organic fuels. Fires occur in many forms and scales and are generally deemed as detrimental to humans, economies and the environment. Natural fires include peat, forest and underground fires (Rein, 2009) while infrastructure fires affect buildings of all natures and sizes (Torero and Rein, 2009).

To be able to discuss controlled or uncontrolled combustion of organic solids it is important to understand the fundamental underlying physical and chemical phenomena involved. The following sections will therefore present a brief discussion of combustion related processes.

1.2 The Reactive Zone

Given that combustion is an exothermic chemical reaction, it has to happen in a specific location. The location is given by the way reactants are delivered and by the local temperature. If the temperature is too low or in the absence of fuel or oxidizer combustion cannot occur, thus there are specific conditions that will sustain combustion. If adequate conditions are attained at a specific location the chemical reaction will proceed at a defined rate ($\dot{\omega}'''$; 1/seconds). The dot denotes per unit time while the triple prime per unit volume. The rate is a function of the supply of reactants and the temperature as indicated by Equation 1.2:

$$\dot{\omega}''' = AY_{\text{F}}^n Y_{\text{O}}^m e^{-E/RT} \quad (1.2)$$

Equation 1.2 is a common way to represent typical combustion reactions and is one potential form of the family of Arrhenius type equations that describe the reaction rate on the basis of kinetic theory. This expression indicates that the

presence of oxygen and fuel is necessary with them appearing through their respective concentrations (Y_{F} is the concentration of fuel while Y_{O} is the concentration of oxygen). Both terms are dimensionless. The coefficients n and m are called the reaction orders and denote the sensitivity of the rate to each of the reactants. The exponential term brings the dependency on temperature. This term shows that the reaction rate will be very small unless the temperature reaches a threshold that makes the product RT comparable to the activation energy (E). The constant R is the gas constant ($R=8.314$ J/mol K) and T is the temperature in kelvin. The product RT represents the energy accumulated in the molecules as the temperature increases; thus when the temperature reaches a certain threshold the number of collisions induced by the increase in kinetic energy results in the breakdown of the molecules and the onset of the reaction. The rate will then continue to increase as the temperature increases. The term A (1/second) is just the constant of proportionality that links the reaction rate to the parameters controlling it.

The magnitude of the activation energy (E) will define the sensitivity of the reaction rate to temperature: the larger the value of E (high activation energy) the more sensitive the reaction rate is to variations of the reactants' temperature. Combustion reactions have very high activation energies, thus are extremely sensitive to temperature.

As the molecules of reactants combust to produce products they release energy. The energy produced per unit time and volume of reactants is denoted by \dot{Q}''' (joules/m³.s) and is given by Equation 1.3:

$$\dot{Q}''' = \rho \Delta H_{\text{C}} \dot{\omega}''' \quad (1.3)$$

where ΔH_{C} is the heat of combustion or energy produced per kilogram of fuel (joules/kg_{FUEL}) while ρ is the global density of the reactants. The heat of combustion depends on the organic fuel, and typical values are tabulated in most combustion books (Glassman and Yetter, 2008). Table 1.1 lists the heat of combustion of a small group of organic materials.

Table 1.1 Representative heats of combustion (ΔH_c) of different organic materials.

Fuel	ΔH_c (MJ/kg _{FUEL})
Hydrogen	141.80
Propane	50.35
Gasoline	47.30
Paraffin	46.00
Kerosene	46.20
Coal (lignite)	15.00
Wood	15.00
Peat (dry)	15.00
PVC (Polyvinyl chloride)	17.50
PE (Polyethylene)	44.60

The energy produced is then transferred back to the products or lost to the environment. The fraction of the energy transferred to the products will define the temperature of the products and is normally referred to as the flame temperature, T_F . If the flame temperature is high enough then heat will be transferred to fresh reactants leading to a self-sustained reaction; if the temperature is too low then the reaction will have to be assisted by an external supply of energy.

Equation 1.2 shows clearly the requirements for a sustained reaction: fuel and oxidizer have to be delivered in sufficient quantities to maintain adequate concentrations, and the flame temperature has to be high enough to guarantee sufficient heat transfer to the reactants to achieve a high enough temperature that will result in a strong reaction rate. Thus, ignition requires the supply of reactants within the necessary concentrations (flammability limits) and a supply of energy to initiate the reaction and increase the reaction rate to a level where it becomes self-sustained (critical ignition energy). Extinction can be then achieved by precluding the arrival of either reactant or by enhancing heat losses so that the temperature of the flame decreases below the threshold that will enable sufficient energy production to self-sustain the reaction.

Combustion chemistry has been briefly discussed here using a simple approach; nevertheless, the complexity of this process can be significant, involving many reactions and different transport

processes (heat and mass). For a more detailed discussion the reader is directed to Glassman and Yetter (2008).

While combustion is a chemical reaction and thus the reaction rates are expressed in chemical terms, it is in many cases a process controlled by the transport of heat and mass. How fast the reactants reach the reaction zone determines the production of energy, and how fast the energy is transferred towards the reactants will determine the vigour of the reaction rate.

The simplest way to separate different forms of combustion is by specifying the mechanisms by which reactants reach the reaction zone. The first case is the premixed flame; in this case fuel and oxidizer are mixed in concentrations that are adequate for combustion to occur. Here, no mass transport is necessary and the reaction consumes the reactants as fast as the energy is transferred towards the unburnt gases. Thus the problem is dominated purely by heat transfer. The other extreme is the non-premixed flame; in this case fuel and oxidizer are separate and the energy produced is determined only by the rate at which reactants can be delivered to the flame. In this case the process is dominated purely by mass transfer, so many texts refer to non-premixed combustion as 'diffusion flames'. Premixed flames will require fuel and oxidizer to both be in the gas phase, and they are thus commonly used for burners and other controlled energy-generating processes such as engines or turbines. Non-premixed flames are typical of condensed-phase fuels (liquids or solids) where the fuel is supplied at a rate that is defined by the amount of energy delivered by the combustion reaction. This energy is what enables the phase of the fuel to change. Non-premixed combustion is typical in uncontrolled processes such as fires but can also be used in boilers, fireplaces and engines.

1.2.1 Premixed flames

Figure 1.1 shows a schematic of how a combustion reaction will propagate through a flammable mixture. The reactants (right) and products (left) are stationary and the chemical reaction ($\dot{\omega}'''$) propagates at a velocity U . The velocity is determined

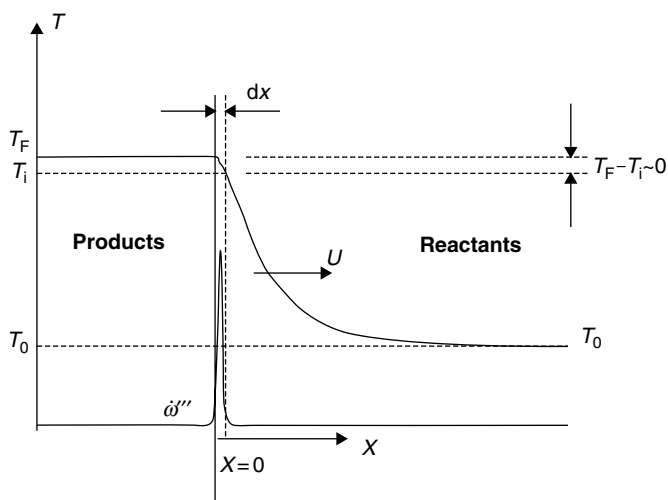


Fig. 1.1 Schematic of a propagating premixed flame.

by the transport of heat from the products at the flame temperature, T_F , to the reactants at ambient temperature (T_0). The reaction is concentrated in a very thin region (dx) (written as a differential because it is a small length) bounded by total consumption of the reactants (left) and the ignition temperature, T_i (right). As explained before, the reaction is concentrated in a thin region because combustion reactions have typically high activation energies, and thus are very sensitive to temperature. Instead, preheating can occur through a much wider region, thus it is common to assume that the ignition and flame temperatures are very similar. As the reaction propagates the hot products expand. The thermal expansion can dissipate slower than the speed of the reaction front, in which case there will be no pressure build-up and the result will be a deflagration. If the expansion is violent and the reaction (i.e. heat transfer) cannot proceed fast enough then a pressure front will develop behind the reaction resulting in an explosion or a detonation (Lewis and von Elbe, 1937).

For premixed flames the main parameter of concern is the flame propagation velocity, U . The first theoretical treatment that provided a flame propagation velocity, U , is due to Mallard and Le Châtelier, described in Le Châtelier's '*Cours de chimie industrielle*' at *École des Mines* (1897) and later formalized by Lewis and von Elbe (1937).

The flame propagation velocity is controlled mainly by heat transfer ahead of the flame. Heat transfer is influenced by the nature of the flow field (laminar vs turbulent), the thermal properties of the mixture, and radiative heat losses from the hot gases towards the environment. In Figure 1.1 the hot gases are shown at constant temperature thus heat losses are being ignored. In reality the hot gases will cool behind the flame.

1.2.2 Non-premixed flames

Figure 1.2 shows a schematic of a non-premixed flame. The fuel comes from the right with an initial concentration of $Y_{F,i}$ while the oxidizer comes from the left with an initial concentration of $Y_{O,i}$. As they approach the flame zone, dx , fuel and oxidizer are transported towards the flame where they will be consumed, while products move away from the flame diluting fuel and oxidizer. Mass transport mechanisms could be diffusion or convection, and the mass flux of reactants towards the flame dominates the reaction and energy release rates and therefore determines the flame temperature. Heat transfer from the flame, especially radiation, will also affect the flame temperature, thus ignition and extinction become a complex function of mass and heat transfer to and from the flame.

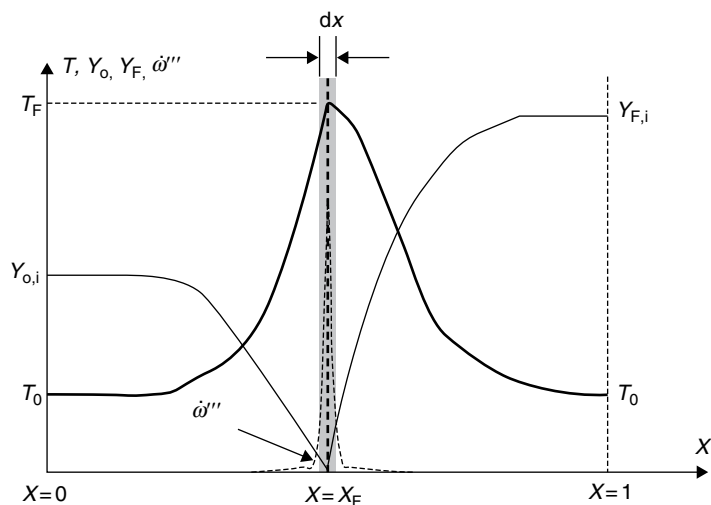


Fig. 1.2 Schematic of a non-premixed flame.

The structure and characteristics of non-premixed flames have been studied extensively, with the first theoretical description presented by Burke and Schumann (1928). The main parameter of interest is the location of the flame. To establish the location of an axisymmetric gas flame with an oxidizer co-flow, Burke and Schumann (1928) required a series of assumptions of which the most important is that the chemistry is infinitely fast and therefore all fuel and oxidizer is consumed at the flame location. As illustrated in Figure 1.2, the concentration of fuel in the oxidizer zone is zero as well as that of the oxidizer in the fuel zone. This approach was later formalized using a compounded variable (Shvab-Zel'dovich variable; Williams, 1985) that enables the solution of mass and energy transport equations through a single scalar (mixture fraction). Further studies of non-premixed flames have emphasized details of transport and chemistry; nevertheless the original mixture fraction analysis is still extensively used.

1.3 Fuel Generation

So far the discussion has concentrated on gas-phase combustion processes. In the case of premixed flames the fuel is delivered into the gas phase

and mixed to guarantee a flammable mixture. In non-premixed flames the fuel can either be delivered in the gas phase (e.g. in a Bunsen burner) or it can be generated through a phase change process from a condensed fuel. This section will discuss the latter.

Organic solids and liquids have the potential to produce gas-phase fuels that can feed premixed or non-premixed flames. The production of the gas-phase fuel is sustained by the supply of heat. When heat is delivered to a condensed fuel its temperature increases until gas-phase products start emerging (Drysdale, 1998). If the condensed fuel is a liquid (and for some solids) the gasification process does not include any chemical changes and follows basic thermodynamic laws of thermal equilibrium between phases. Given an ambient temperature and pressure, gasification will aim to attain an equilibrium partial pressure of fuel at the gas side of the fuel surface (the Clausius-Clapeyron relation), the rate at which this equilibrium condition is attained is defined by the net heat supplied for gasification and the rate at which the gas-phase fuel is removed from the surface by convection or diffusion. Detailed explanation of the gasification of liquid fuels is provided by Drysdale (1998) or the Society of Fire Protection Engineers' Handbook (SFPE, 2009).

Most organic fuels undergo chemical changes when changing phase; this process is called pyrolysis. The pyrolysis process is a chemical reaction whose rate is generally described in a similar manner as a combustion reaction. Thus Arrhenius type formulations with high activation energies (Equation 1.2) are the norm when describing pyrolysis chemistry.

The process of pyrolysis can be extremely complex and, depending on the fuel and heating characteristics, can follow distinctly different paths. These paths can be a compendium of numerous reactions, which can be sequential or compete against each other. Furthermore, the chemical pathways followed can be strongly influenced by the presence of oxygen, as indicated in Equation 1.2.

It is important to note that while degradation of some fuels will show dependency on the oxygen concentration many others will not (Hirata *et al.*, 1985; DiBlasi, 1993). In those cases m in Equation 1.2 is assumed to be zero.

The chemical pathways leading to the pyrolysis of most solid organic fuels are fundamentally incomplete inasmuch as the constants associated with the equations that will serve to quantify the rate of each reaction step are unknown. Many studies have evaluated reduced chemical mechanisms (i.e. only including the main reaction rate-limiting steps) for the pyrolysis of different solids (Horrocks *et al.*, 2000) but there is still great uncertainty on the chemical pathways, the number of steps required and the constants associated with them. Thermo-gravimetric analysis (TGA) has been used in the past to establish reduced chemical reaction mechanisms as well as the associated constants. TGA deduces the kinetic constants of chemical reactions by measuring the rate of a reaction (mass loss) as a function of the controlled heating of a fuel. The principles behind TGA studies and some applications to materials relevant to fire are presented in SFPE (2009).

Despite the generalized use of TGA data, there is increasing recognition that pyrolysis reaction pathways are sensitive to the heating rate. The correlation of mass loss with kinetic constants used to interpret TGA data requires heating rates

of the order of 1 to 20°C/min, which is generally an order of magnitude slower than heating rates typical of any combustion process. Thus, recent studies have established methodologies that use complex models together with standard test methods and advanced optimization techniques to establish reaction schemes and their associated constants (Lautenberger *et al.*, 2006). Although these procedures allow exposure of the materials to heating rates typical of combustion and obtaining of comprehensive sets of constants they have only been applied to a limited number of materials. Currently, methodologies that use combinations of optimization techniques, models and tests remain research tools and are not widely used.

Before flaming ignition can occur, fuel in the gas phase needs to be produced. Solid materials that are not susceptible to spontaneous ignition (Drysdale, 1998) will show very little evidence of chemical reactions at ambient temperatures, thus can be deemed as inert. The reaction rates associated with pyrolysis can be considered negligible and therefore the material will not follow any transformation. As the temperature increases the reaction rates increase and the solid fuel starts changing. Given the temperature distribution within the material, the rates of decomposition are a function of x , with a greater production of pyrolysates close to the surface and lesser production at depth (Figure 1.3).

Local production of fuel is not the only important variable. The gas-phase fuel produced might be the result of a combination of pyrolysis and oxidation reactions, thus its composition might include large quantities of fully oxidized compounds such as carbon dioxide (CO₂), partially oxidized gases such as carbon monoxide (CO) and other molecules that can have all levels of partial oxidation. Therefore, together with the reaction rates, the mass fraction of inert gases needs to be subtracted leaving the remaining reactive gases. As an example, Kashiwagi and Nambu (1992) studied the degradation products of cellulosic paper showing that there is a significant presence of inert gases like water vapour, fully oxidized gases like CO₂, partially oxidized products like CO, and fuel like CH₄ and H₂.

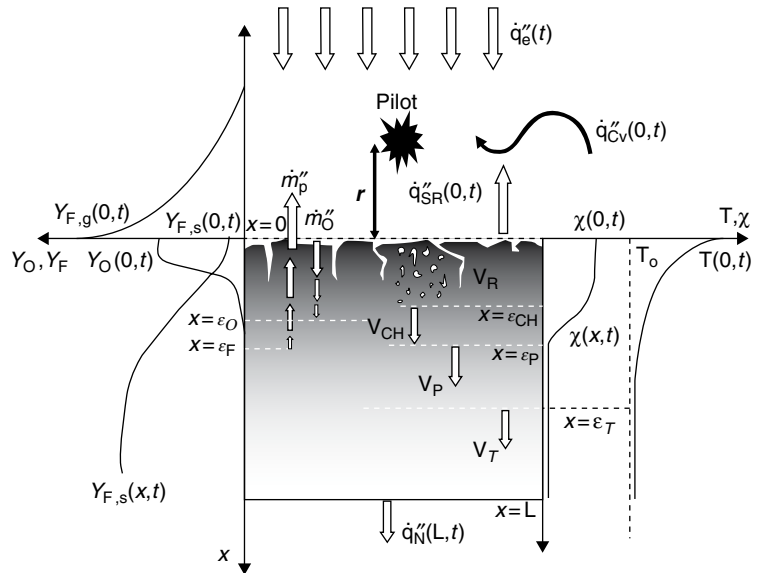


Fig. 1.3 Schematic of the different processes occurring as a material undergoes degradation prior to ignition induced by an external source of heat.

There are scant data available on the degradation products of most organic combustible materials; therefore, the mass fraction of flammable gases present in the local products of degradation will be described here by means of a single variable, $Y_{F,s}(x,t)$, which represents a global contribution of all compounds that can be further oxidized. Figure 1.3 represents $Y_{F,s}(x,t)$ as an increasing function with a minimum at the surface ($Y_{F,s}(0,t)$). This is based on the assumption that where there is a greater presence of oxygen there are greater levels of oxidation.

Oxygen can migrate inside a fuel resulting also in an in-depth distribution ($Y_{O}(x,t)$) that reaches ambient values at the surface ($Y_{O}(0,t)$). In-depth oxygen and fuel diffusion is controlled by the structure of the solid. Some materials are highly permeable and allow unrestricted transport of species in and out of the solid. For other materials oxidation will occur only very close to the surface and could be potentially neglected. The permeability of the fuel can be a function of many variables including the degradation and consumption of the material and has received very little attention in the combustion literature. In the absence of a well-defined permeability

function, here a simple variable associated with the fuel permeability ($\chi(x,t)$) will be introduced and assumed to describe in a generic manner the fraction of the fuel produced that can flow through the solid material. It has to be noted that $\chi(x,t)$ is not strictly a permeability function but a combination of permeability, porosity and any fractures within the material. The permeability according to Darcy's law is a constant of proportionality that links the pressure gradients to the flow velocity in a homogeneous material. Here the material will have a more complex and heterogeneous structure. The permeability of the fuel has been found to be critical in the development of forest fires (Bartoli *et al.*, 2011) and peat fires (Rein, 2009; see also Chapter 2).

Oxygen and fuel concentrations will be controlled by the local permeability and by production/consumption rates, and thus indirectly by the temperature distribution ($T(x,t)$). This makes it necessary to treat them independently; therefore two independent variables emerge, $\epsilon_F(t)$ and $\epsilon_O(t)$. The former represents the region where fuel is being produced while the latter represents the region where oxygen is present in relevant quantities.

If all the reactions occurring can be represented in an Arrhenius form (Equation 1.2) then the local mass production, $\dot{m}_p''(x, t)$, can be summarized into a function of the form:

$$\dot{m}_p''(x, t) = Y_{F,s}(x, t) \sum_{i=1}^{i=N} \left[A_i Y_O^{m_i}(x, t) Y_F^{n_i}(x, t) e^{-E_i/RT(x,t)} \right] \quad (1.4)$$

where the summation is not truly a sum of all the different N reaction steps but just some global combination of them that includes sequential and competitive reactions.

To obtain the total fuel production at the surface per unit area ($\dot{m}_p''(0, t)$) it is necessary to integrate Equation 1.4 across the entire depth including the permeability function described above. It is important to note that fuel produced in-depth does not have to come out, and in many cases pressure increases within the fuel structure can be observed. A common manifestation of trapped fuel is the formation of bubbles. Figure 1.4 shows a sectioned sample of plastic where bubbles generated by heating from the top can be clearly seen. The effects of permeability and pressure are combined in a complex manner to define the flow within the porous medium. This remains an unresolved problem; thus the use of a simple variable such as $\chi(x, t)$ is justified.

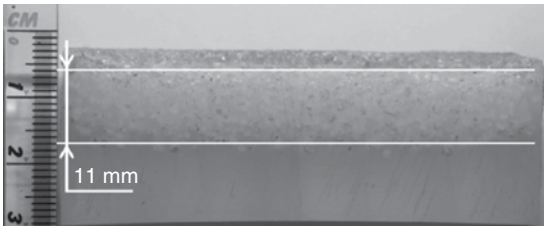


Fig. 1.4 Vertical sections of a clear plastic sample showing the bubble layer depth. The sample was exposed to a heat flux level of 20 kW/m² for 35 minutes with a conical heater. The image corresponds to a section of the sample where heat was imposed at the top. The layer between the lines is filled with bubbles while the layer below is transparent.

Once enough fuel is produced a flammable mixture can be generated in the gas phase and combustion can proceed as described in previous sections. The heat feedback from the flames will sustain the production of fuel and if enough fuel is produced then combustion will be self-sustained. If the heat does not produce enough fuel then the flame will have to be assisted by an external source of heat. The ratio of heat produced to the heat needed to sustain combustion of a condensed fuel is called the mass transfer number, or B number (Drysdale, 1998), and can be represented in its simplest form by Equation 1.5:

$$B = \frac{\dot{Q}_{\text{Feedback}}}{\dot{Q}_{\text{Pyrolysis}}} \quad (1.5)$$

Where all losses are neglected, $\dot{Q}_{\text{Feedback}}$ is the energy from the flame delivered to the fuel surface and $\dot{Q}_{\text{Pyrolysis}}$ is the energy required for the fuel to emerge in the gas phase. Theoretically, if $B > 1$ then the reaction will be self-sustained and if $B < 1$ it is necessary to deliver an external supply of heat to assist the combustion process. In combustors used for energy production it is essential that the fuel has $B > 1$ while in fires it is only necessary that one of the fuels has a $B > 1$ to support the combustion of all other fuels. In fires, it is typical that a single item such as a sofa or mattress made out of fuels that have mass transfer numbers much greater than one (e.g. polyurethane, cotton, nylon) sustains the combustion of other fuels that will naturally not burn on their own (e.g. wood, PVC). In some cases fuels that cannot sustain combustion can be induced to burn in a self-sustained manner just by placing and igniting several pieces together so that each piece delivers sufficient heat feedback to maintain the others' burning (e.g. wood burning in a fireplace). Although the concept is simple its application is very complex and it requires a detailed understanding of heat and mass transfer processes.

A common example that illustrates the importance of the B number and its complexity in the



Fig. 1.5 Burning candle. For a colour version of this figure, see Plate 1.1.

combustion of organic fuels is the candle. This example was used by Faraday in his famous Christmas lecture of 1861. Figure 1.5 shows a familiar picture of a candle where the presence of a glowing wick is clear. Solid wax will not burn in a self-sustained manner unless there is a wick. The energy feedback from the combustion of the wax is not sufficient to produce enough fuel ($B < 1$) unless a mechanism is established to enhance the recovery of the energy and compensate for the energy required for the phase change of wax from solid to gas. The wick is this mechanism. The wick allows the melted wax from the candle to move upwards (capillary forces between the liquid and the solid fibres) and spread through the wick. This enhances the surface area that receives heat from the combustion reaction and thus enhances fuel production; the larger the wick, the greater the fuel produced and the larger the flame. At some point the production of fuel will be sufficient for the flame to be sustained.

1.3.1 Heterogeneous combustion of organic fuels

While wax illustrates an extreme where surface area enhancement represents the mechanism for heat recovery that increases the mass transfer number above unity ($B > 1$), the wick also provides an illustration of a different form of combustion that occurs in the solid phase. This form of combustion is called heterogeneous combustion because fuel and oxidizer are not in the same phase. Commonly the fuel will be in the solid phase while the oxidizer will be in the gas phase. Other commonly used terms for heterogeneous combustion are glowing, smouldering, embers, etc. (Rein, 2009).

The tip of a wick is formed by a large amount of loose fibres that are no longer impregnated by fuel. In the absence of the wax, the fibres burn and the wick is consumed. The end of the tip emerges outside the flame region (Figure 1.5), thus it is directly exposed to the air. The very large surface area provided by the fibres enables fast diffusion of oxygen towards the fibres' surface resulting in exothermic oxidation of the solid fuel before it can pyrolyze and change phase. Many natural and processed materials will sustain heterogeneous combustion under the right conditions. In some cases heterogeneous combustion will coexist with gas-phase flames. Very good examples of this are organic fuel beds typical of forest fires. Figure 1.6a shows a sample of pine needles arranged in a manner so that they form a porous medium with enhanced surface area for oxygen diffusion. If air flows through the bed then heterogeneous combustion can occur within the bed. In most cases gaseous fuel will also be produced resulting in a flame (Figure 1.6b). Timber also has the potential for both forms of combustion. In the case of timber an enhancement of the external supply of heat will result in pyrolysis dominating over diffusion and homogeneous combustion (Figure 1.7a). Whereas for low heat fluxes diffusion dominates, the flame disappears and glowing remains (Figure 1.7b). It is important to note that the porous nature of the fuel retains heat therefore heterogeneous

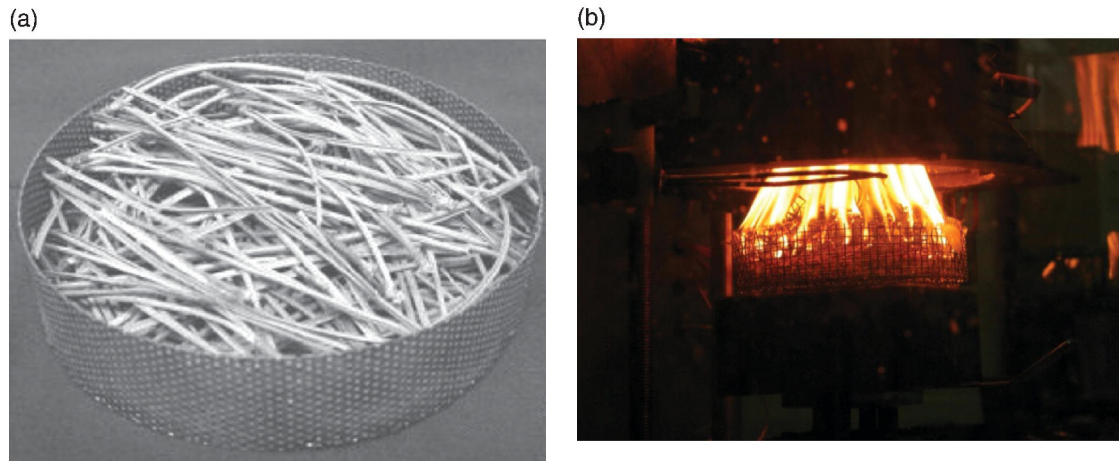


Fig. 1.6 (a) A bed of pine needles. (b) A burning bed of pine needles with homogeneous and heterogeneous combustion.

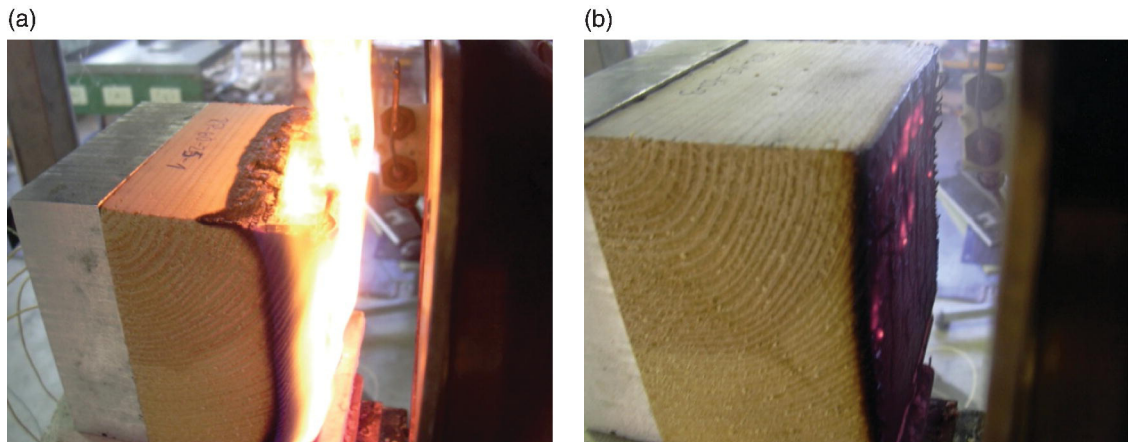


Fig. 1.7 (a) A piece of timber subject to a high heat flux resulting in flaming. (b) A piece of timber subject to a low heat flux resulting in heterogeneous combustion. For a colour version of this figure see, Plate 1.2.

combustion can occur under conditions (low heat input, low oxygen or fuel concentrations) that will not sustain flames.

1.4 Summary

The combustion of organic fuels is a chemical reaction that results in the generation of products and heat. The nature of the process is controlled

by heat and mass transfer and can result in very different forms of combustion. The different transport mechanisms provide the basis to forms of combustion that include a wide range of commonly used terms such as detonations, explosions, deflagrations, fires, glowing, embers or smouldering. The nature of the fuel, natural or processed, will also play an important role in the nature of the combustion process. The main process linked to the fuel is the transformation of