

Inside the Inferno: Fundamental Processes of Wildland Fire Behaviour

Part 1: Combustion Chemistry and Heat Release

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Abstract

Purpose of Review This two-part series of articles summarises our current understanding of the fundamental processes involved in the combustion and spread of wildland fire and their interactions, and highlights the knowledge gaps that limit our ability to predict the seeming capricious behaviour of wildland fires. This first article details the fundamental chemistry involved in the thermal degradation of cellulosic biomass (vegetation), the release of combustible products from such fuel and their subsequent oxidation and release of energy in the form of heat.

Recent Findings A fundamental source of much of the complexity of the behaviour of a wildland fire can be traced to the highly temperature sensitive chemistry involved in the thermal degradation of cellulosic biomass fuels. Nucleophilic competition in the thermal degradation reactions between the endothermic volatilisation pathway that leads to gas phase flaming combustion and the exothermic charring pathway that leads to solid phase glowing interacts with the environment around a fire to sustain ongoing ignition, transition from glowing to flaming combustion and respond to changes in prevailing wind and moisture conditions to influence fire behaviour.

Summary The behaviour of a wildland fire is the result of the interactions of a number of fundamental processes governing the combustion and release of energy from vegetative fuels, the transfer of that heat to adjacent fuels and their subsequent ignition. The interacting chemical and physical processes

occur across a range of spatial and temporal scales and result in fire behaviour that often is thought to be unpredictable but is not fundamentally so. Gaps in our knowledge that limit our ability to predict the behaviour of wildland fires are highlighted.

Keywords Competitive · Thermokinetics · Chemical reactions · Enthalpy · Bushfire · Wildfire

Introduction

A fully involved and actively spreading wildland fire (or bushfire as it is known in some parts of the world) is one of the most terrifying natural phenomena that anyone might have the misfortune to encounter. To be caught in a high-intensity wildfire (a wildland fire burning out of control) is to witness a true inferno on Earth—conditions hot enough to melt metal, heat fluxes that can literally vaporise vegetation and smoke plumes so dense they turn day into night.

Most wildland fires are relatively mild and often self-extinguish when they run out of fuel or the weather abates. However, when a fire outbreak coincides with hot strong winds and continuous dry and flammable vegetation across the countryside, it has the potential to develop into a broad-ranging and fast-moving conflagration that is essentially uncontrollable until there is a substantial change in the prevailing conditions—thus the phrase ‘to spread like wildfire’. Such a high intensity fire can release a tremendous amount of energy over very large areas and sometimes over a very short period [1–5].

Understanding the factors that influence the behaviour and spread of a wildland fire is essential to predicting how fast and in which direction it will move. Reliable predictions of the future location and time of arrival of a fire front are critical

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to support operational decision making, particularly developing successful plans for controlling or suppressing it and for identifying who or what is most at threat to ensure the safety of both firefighters and the general public [6]. A number of approaches have been developed to carry out such predictions, ranging from simple rules of thumb through to process-based, computationally intense, numerical models of fire behaviour [7, 8]. No single approach satisfactorily provides all the necessary information under all situations in the time required [9]. However, our efforts to understand this phenomenon are improving the reliability of predictions, resulting in safer and more effective firefighters and enabling better prepared and safer communities to live in fire-prone landscapes [10].

The study of wildland fire behaviour is also driven by a more fundamental need to understand the complex world around us. Wildland fire is a critical process in many ecosystems around the world [11–16] and plays a pivotal role in the global carbon cycle [17–21]. Understanding the chemical and physical processes involved in wildland fuel combustion is also necessary for determining the impact of wildland fire on atmospheric processes and global climate [22, 23] as well as air quality and human health [16, 24, 25]. This knowledge of the factors that determine the behaviour and spread of wildland fire is also essential for quantifying and mitigating the impact of wildfire on structures and life safety [26–30].

Figure 1 is a conceptual model of the self-sustained propagation of a wildland fire. This framework, based on a simplified understanding of fire, serves to identify key processes

(identified in *italics*) between state variables (identified in *roman*) and their linkages and acts as a road map for this two-part review series. Fuel is heated (initially from an external source such as a match) until combustion reactions initiate. Combustion reactions release products such as carbon dioxide, water and partially combusted reactants in the form of smoke and other emissions as well as heat. The heat is transferred to adjacent fuel which then increases in temperature until ignition occurs and initiates further combustion reactions and the cycle repeats. Burning residue, such as embers, sparks and firebrands, can also act to transfer heat if physically transported to adjacent fuel. If the cycle is broken at any point, combustion reactions will cease and the fire will stop spreading.

Thus, the propagation of a fire through wildland fuel may be divided into two parts. Broadly, these are:

1. The combustion of the fuel with the release of heat and products
2. The transfer of that heat to adjacent fuel and the subsequent heating to combustion which sustains fire spread

In this first article, the focus is the former, highlighted in the grey diamond in Fig. 1, specifically the chemical reactions of thermal degradation of cellulosic biomass fuels and subsequent gas and solid phase oxidation reactions of the degradation products. The focus of the second article [31] is the latter, the physical transfer of the heat liberated by combustion and the transport of burning solid fuel to adjacent fuels.

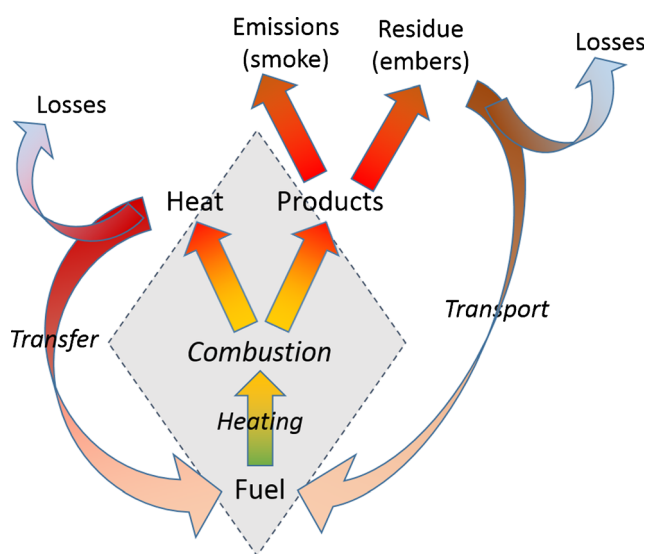


Fig. 1 A conceptual model of the self-sustained propagation of a wildland fire, which also serves as a road map for this series of review articles. Combustion reactions generate heat and chemical products that are transferred to adjacent fuel and heats them until they ignite in a continuing reaction. The transfer and transport of this heat are not efficient and result in losses out of the system. Key processes are identified in *italics*, state variables in *roman*. Breaking the cycle at any point will cause a fire to cease. This first part of the review is focused on the combustion processes (grey diamond)

The Fundamentals of Wildland Fire

What is a Wildland Fire?

In the context of this review, a wildland fire may be defined as:

‘a complex combination of highly chaotic chemical reactions and physical processes that continually and freely propagate through spatially-variable biomass fuels across variable terrain influenced by spatially and temporally varying atmospheric conditions.’

The exposure of a fire to factors that vary greatly in space and time such as the live and dead vegetative fuels, terrain and weather immediately identifies significant sources of uncertainty in attempting to predict the spread of that fire. The inherent dependency of many of the chemical reactions and physical processes upon initial conditions identifies further sources of uncertainty and error [32]. Can details of such specificity and variation be known at the spatial and temporal scales that are important to determining the behaviour of a

wildland fire? Much of the seemingly capricious behaviour of a wildland fire is the direct result of the broad range of scales over which the processes involved in the combustion of biomass fuels and the transfer of the liberated heat occur and interact (Table 1) and our inability to know precisely the conditions in which the fire is burning [10].

But the apparent unpredictable nature of a wildland fire is also a result of the nature of the fuels in which that wildland fire burns. An important source of the complexity of the behaviour of a wildland fire may reside in the fuel through which it burns—a combination of the broad range of chemical and physical structures present in the mix of live and dead vegetation that are wildland fuels and the chemistry of combustion that is unique to cellulosic biomass fuels (and which does not appear in any other type of combustion).

Processes and Scales

Chemical reactions and the release or uptake of energy occurs on the scale of molecules. The transport of that energy occurs on scales ranging from millimetres up to kilometres. Table 1, derived from Sullivan [7], summarises the main biological, physical and chemical components and processes involved in wildland fire behaviour and the temporal and spatial scales over which they occur. The interaction of these processes over such a wide range of scales renders the prediction of fire

Table 1 The major biological, physical and chemical components and processes occurring in a surface-fuel-dominated wildland fire and the order of the temporal and spatial (vertical and horizontal) scales over which they can occur. Source: modified from [7]

Type	Time scale (s)	Vertical scale (m)	Horizontal scale (m)
Components			
Fuel particles	—	0.001–0.01	0.001–0.01
Fuel complex	—	1–10	1–100
Fuel condition	—	0.1–1	0.01–1
Wind	1–1000	1–100	0.1–1000
Air temperature	100–10,000	1–100	100–1000
Relative humidity	100–10,000	1–100	100–1000
Topography	—	1–1000	1–1000
Flames	0.01–10	0.1–10	0.1–1
Plume	1–10,000	1–10,000	1–100
Processes			
Chemical reactions	10^{-20} –0.01	10^{-4} –0.01	10^{-4} –0.01
Radiation	10^{-9} –10	0.1–100	0.1–100
Conduction	0.01–1	0.01–10	0.01–10
Convection	1–100	0.1–100	0.1–10
Turbulence	0.1–1000	0.01–100	0.01–1000
Spotting	0.1–1000	1–1000	0.1–10,000

behaviour a continuous and not easily resolved challenge to science [33].

Chemistry of Combustion

While a basic understanding of the processes of combustion of biomass fuels in general has been available since the beginning of the industrial revolution, it took some time before it began to inform research into bushfire behaviour. Gisborne [34] summarised the fundamentals of wildland fire behaviour for the time (the 1940s), in which the process of combustion was identified as a single chemical reaction involving the oxidation of fuel that released heat. The prerequisites for this reaction were fuel heated to its ignition temperature and a supply of oxygen.

Byram's [35] seminal work of forest fuel combustion provided much of the basis for the current operational understanding of wildland fire behaviour and the operational prediction systems in use today. However, while the current texts of the field (e.g. [36–40]) have to some extent expanded upon the knowledge of combustion in wildland fuels, much of the current state of operational knowledge is still based on that of Byram and has not incorporated the advances that have been made subsequently. This section summarises the current understanding of the chemistry of combustion of cellulosic fuels which has largely been developed for industrial energy conversion via biomass burning. As a result, much of this understanding has come from controlled laboratory investigation of the combustion of cellulose and is only now beginning to be applied in the study of free-moving wildland fire behaviour [41••].

Biomass Chemical Composition

Wildland fuel is composed of live and dead biomass and the specific type depends on the predominant vegetation. In most circumstances, this consists primarily of fallen leaf litter, twigs and bark as well as standing grasses and shrubs [42]. Under some fire weather conditions, fuels can also include fallen logs, tree canopies and dead standing trees [43] as well as organic terrain [44, 45]. These additional fuel elements generally do not contribute to the dynamics of the fire front and may require more severe fire weather conditions to initiate combustion. The fuel represents a range of physical structures, chemical components, age and level of accumulation and decomposition, depending on the type and history of the land and biomass, all of which influence the inherent flammability of a fuel [46, 47].

Fuel is a critical component of a wildland fire—without fuel there can be no fire. The type of fuel, primarily through its chemical composition but also its ability to absorb heat, can play a significant role in influencing the thermal degradation

and combustion attributes of a fuel. These attributes are commonly combined into the general descriptor of fuel ‘flammability’ [48]. However, these attributes do not change significantly over time within a particular fuel element. Finer fuels are more flammable than coarser fuels, and it is generally accepted that it is the combustion of live fuels less than 3 mm in diameter [49] and dead fuels less than 6 mm diameter [50] that contribute the bulk of the energy released in a fire front [51].

The primary constituent of biomass is cellulose, $(C_6O_5H_{10})_n$. Cellulose is an n -component polymer of a glucosan monomer, $C_6O_6H_{12}$ [52•, 53••], and is a non-reducing carbohydrate [54, p.1112]. Glucosan, or D-glucose, is a variant of glucose, the primary source of energy of all living organisms. Cellulose is the most abundant organic material on the Earth [55] and is present in bacteria, algae, fungi and some animals and is the primary component of all plants.

Cellulose is a linear, unbranched polysaccharide of D-glucose monomers in $\beta(1,4)$ linkage (Fig. 2), ranging in length from 200 to 10,000 units [55] with molecular weights 250,000–1,000,000 or more [54, p. 1113]. Here, the D- prefix refers to one of two configurations, around the chiral centre of carbon-5 (C-5), of which only the D- variant (also known as dextrose) is biologically active. The $\beta(1,4)$ refers to the configuration of the covalent link between adjacent glucose units, called a glycosidic bond. There are two possible geometries around C-1 of the pyranose (or 5-membered) ring: in the β anomer the hydroxyl group on C-1 sits on the opposite side of the ring to that on C-2; in the α anomer it is on the same side. The glycosidic bond in cellulose is between C-1 of one β -D-glucose residue and the hydroxyl group on C-4 of the next unit. The bond is formed through the process of condensation or dehydration between two glucosan units (i.e. a water molecule is produced in the joining of two D-glucose residues in this manner).

Unlike starch, a similar polysaccharide used by plants to store excess glucose (which utilises an $\alpha(1-4)$ bond), the natural cellulose polymer is a straight chain with no coiling and adopts an extended rod-like morphology that can take on two polymorphs [55]. Parallel chains of cellulose can form hydrogen bonds—non-covalent linkages—in which surplus electron density on hydroxyl group oxygens is distributed to hydrogens with partial positive charge on hydroxyl groups of adjacent chains (Fig. 2). Multiple parallel chains thus bonded form a crystalline structure with two possible alignments, depending on the arrangement of the C-6 hydroxyl group, forming cellulose I α and cellulose I β ¹ [57]. This crystalline structure is very rigid and forms the basis of the microfibrils of plant cells, where bundles of up to 1000 cellulose chains are bonded in parallel, and contribute to its high tensile strength [58]. Segments of naturally occurring cellulose can exhibit

regions of both crystalline structure with ordered alignment of both inter- and intramolecular bonds and amorphous structure in which the bonding is disordered [59] but not entirely random [55]. Cellulose is basically the same in all types of biomass, differing only in the degree of polymerisation (i.e. the number of monomer units per polymer) [55].

As a result of this structure, cellulose is an extraordinarily stable polysaccharide: it is insoluble in water, relatively resistant to acid and base hydrolysis, and inaccessible to all hydrolytic enzymes except those from a few biological sources. This means that cellulosic fuels can take a long time to biologically degrade (i.e. decompose) and require considerable energy to thermally degrade. In contrast to starch, which has a crystalline-to-amorphous transition (i.e. breakdown of inter-chain hydrogen bonds) at 333–343 K in water, it takes 593 K and 25 MPa for cellulose to become amorphous in water [60].

Other major chemical components of biomass fuel include hemicelluloses and lignins, the distribution of which vary considerably across plant species and plant part (see Table 2).

Hemicelluloses are complex polysaccharides (generally copolymers of glucosan and a variety of other possible, mainly sugar, monomers) that occur in association with cellulose. Unlike cellulose, hemicelluloses generally consist of branched structures consisting of 50–200 monomeric units and a few simple sugar residues and are soluble in dilute alkaline solutions [64]. The structures vary substantially depending on the biomass species and functional component. The most abundant hemicellulose is xylans which are found in cell walls and made from monomers of xylose, a pentose sugar.

Lignins are highly branched aromatic polymers consisting of phenylpropane monomers in varying amounts, depending upon the species, cell type and plant part. As with hemicelluloses, they are generally found in cell walls, especially in woody species, and are often bound with cellulose to form a lignocellulose complex [64]. Lignins are the second most abundant biopolymer after cellulose and they provide rigidity and physical strength to plants [65].

A large variety of other elements and compounds are found in biomass fuels. These include starches (i.e., non-polymer carbohydrates), minerals and trace elements (such as N, P, K, Ca, Mg, Na and silica), water and salts [63]. Extractives and inorganics including terpenes—isoprene polymers—and resins—fats, fatty acids and fatty alcohols—are typically found in live fuels but may also be found in dead fuels. After combustion, some of these, particularly minerals, appear as ash.

Combustion Reactions

Cellulose is the most widely studied substance in biomass combustion. By comparison, few studies have been carried out on the thermal degradation and combustion of hemicelluloses or lignin [66], due perhaps to the relative thermal

¹ Man-made celluloses are known as celluloses II and III.

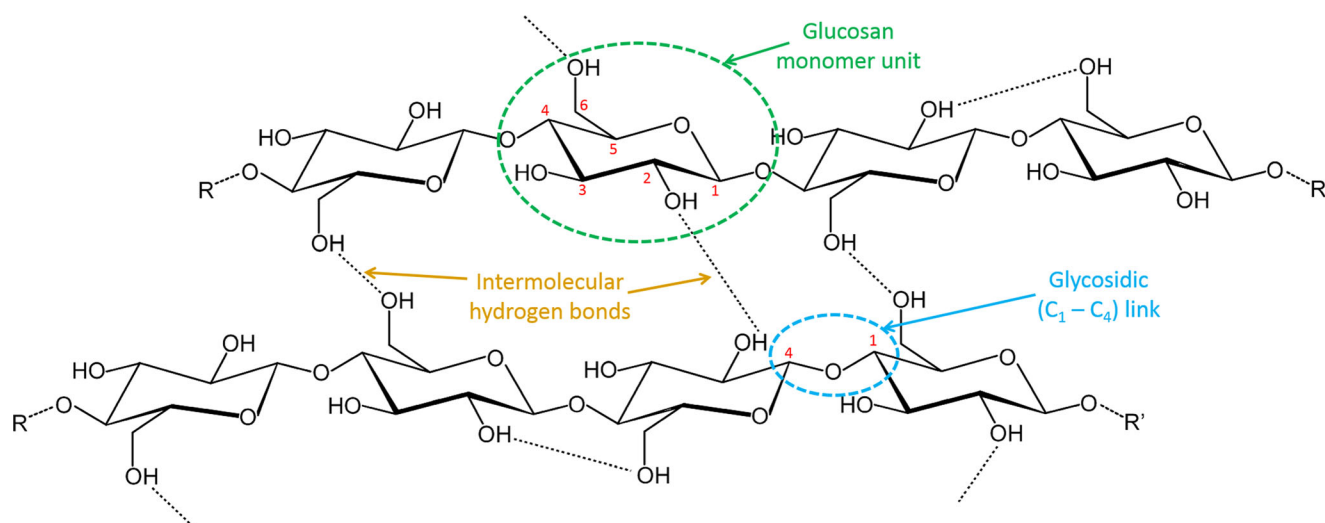


Fig. 2 Skeletal formula of a portion of two adjacent cellulose chains, indicating some of the intra- and intermolecular hydrogen bonds (*dashed lines*) that may stabilise the crystalline form of cellulose. R and R' indicate continuation of the cellulose chain. A glucosan monomer with

carbon atom numbering convention is highlighted in *green*. The glycosidic link between C₁ and C₄ of two adjacent glucosan units is highlighted in *blue*. Modified from [56]

instability of these compounds. Yang et al. [67] found that the primary mass reducing reactions in hemicelluloses occurred between 493 and 588 K, whereas those for cellulose occurred between 588 and 673 K and lignin over a much broader range of 433 to 1173 K. More recent studies of thermal degradation

of hemicellulose include that of Shen et al. [68] who found two main stages of mass loss in xylan-based hemicelluloses, a low temperature stage (around 538 K) associated with thermal cracking of the hemicellulose chain and a high temperature stage associated with char combustion. Gordobil et al. [65]

Table 2 Approximate analysis of some biomass species taken from Shafizadeh [52•], Mok and Antal [61] and Demirbaş [62, 63]. Source: modified from [41••] with permission from Elsevier

Sample	Cellulose (%)	Hemicelluloses (%)	Lignins (%)	Other ^a (%)
Shafizadeh [52•]				
Softwood	41.0	24.0	27.8	7.2
Hardwood	39.0	35.0	19.5	6.5
Wheat straw	39.9	28.2	16.7	15.2
Rice straw	30.2	24.5	11.9	33.4
Bagasse	38.1	38.5	20.2	3.2
Mok and Antal [61]				
<i>Eucalyptus saligna</i>	45	15	25	15
<i>Eucalyptus gummiifera</i>	38	16	37	9
Sweet sorghum	36	18	16	30
Sugar cane bagasse	36	17	17	30
<i>Populus deltoides</i>	39	21	26	14
Demirbaş [62, 63]				
Softwood (av.)	45.8	24.4	28.0	1.7
Hardwood (av.)	45.2	31.3	21.7	2.7
Wood bark	24.8	29.8	43.8	1.6
Wheat straw	28.8	39.1	18.6	13.5
Tobacco stalk	42.4	28.2	27.0	2.4
Tobacco leaf	36.3	34.4	12.1	17.2
Spruce wood	50.8	21.2	27.5	0.5
Beech wood	45.8	31.8	21.9	0.4
Ailanthus wood	46.7	26.6	26.2	0.5

^a Other can consist of organic compounds such as starch or inorganic material such as salts, minerals, water and extractives

found the mass loss stage of the thermal degradation of wood-derived lignins to commence around 573 K, mainly associated with cleavage of the ether linkages among the aromatic units.

While the degradation of a chemically complex fuel may be generally considered to be the sum of the contribution of its main components [69], the extrapolation of the thermal behaviour of an individual component to describe the kinetics of fuels such as biomass is only a rough approximation [66]. The presence of inorganic matter in the biomass structure can act as a catalyst or an inhibitor for the degradation of cellulose; differences in the purity and physical properties of cellulose, hemicelluloses and lignin also play an important role in the degradation process [66].

However, the properties of cellulose have been found to exert a dominating influence on the rates of degradation of biomass subjected to heat and, as a result, it is the detailed thermokinetics of cellulose that provides the best understanding of the combustion of this natural substance [53••]. The remainder of this discussion is thus focussed on the thermokinetic properties of cellulose.

Combustion Processes

The term ‘combustion’ is generally used to describe a high-temperature, self-sustaining oxidation reaction [70•, p. 14]; however, it is equally applicable to the description of the complete process in the conversion of unburnt fuel to ash and residue [71]. The mechanisms involved in this process are not fully understood but it is thought to be a free radical chain reaction that is extremely exothermic, yet requires a very high temperature (i.e. >550 K) for its initiation [54, p. 115].

The combustion of biomass in a wildland fire is not strictly a linear sequence of events as portrayed by Byram and others (e.g. [34, 38, 72])—e.g., preheating, ignition, combustion of distilled gases and then combustion of residual char. While there are several unique stages identifiable during the propagation of a flame front, these are not necessarily sequential, as assumed in many models of combustion (e.g. [73–77]), and can occur simultaneously in many instances, a function of the individual rates of the chemical reactions, or even in competition with each other.

The first step in biomass combustion is heating of the fuel, usually by the transfer of heat via radiation, convection or conduction from an approaching flame front but possibly also a pilot source such as a direct flame or spark. The fuel undergoes *drying*, in which free and bound water on and in the fuel begins to evaporate (but is not necessarily completely evaporated [78]). *Thermal degradation* is the initial chemical reaction in combustion in which the fuel changes its structure fundamentally through a series of reactions that includes dehydration (the formal chemical reaction rather than the commonly held notion of simply drying out) and depolymerisation, of which there is a range of pathways.

The primary products of thermal degradation are combustible gases (i.e. volatiles) via *volatilisation* and char via *charring*. Secondary reactions of these gas and solid phase products, primarily oxidation in air, can then occur. *Gas phase oxidation* of volatiles results in what we see as flaming combustion. *Solid phase oxidation* of char results in what is seen as glowing or smouldering combustion.

While both forms of oxidation can and do occur simultaneously to varying degrees, the reaction rate of the former is much faster than the latter, resulting in the apparent delay of the char oxidation after the fire front has passed. All reactions can occur simultaneously and some reactions occur at the expense of others (i.e., they are competitive). It is the dynamic nature of these reactions that can result in the complex larger scale behaviours observed in wildland fires.

Reaction Rates

Chemical reactions occur when reactant molecules are brought together in the correct orientation with sufficient kinetic energy to break or form bonds between or within the reactants [54, p. 55]. The minimum energy required for a reaction to occur is called the activation energy, E_a . The rate at which a reaction occurs is proportional to the concentration of the reactant and is expressed quantitatively as [79, p. 254]:

$$-\frac{dc}{dt} = r[c], \quad (1)$$

where c is the reactant concentration, dt is time interval and r is the reaction rate constant. According to the transition state theory [80], r is related to the total number of collisions that occur per second, the fraction of collisions that occur per second at or above E_a (i.e. effective collisions) and the fraction of effective collisions that occur in a favourable orientation. Thus, the reaction rate constant comprises three factors:

$$r \propto \text{collision factor} \times \text{energy factor} \times \text{orientation factor}. \quad (2)$$

The theoretical expression for r has the same form as that observed empirically for many reactions and is known as the Arrhenius Law [79, p. 273]:

$$r = A \exp\left(-E_a/RT\right), \quad (3)$$

where A is a pre-exponential factor that subsumes the collision and orientation factors, R is the universal gas constant (8.314472 J K⁻¹ mol⁻¹) and T is the absolute temperature of the reactants (K). The energy factor, $\exp(-E_a/RT)$ (derived from the Boltzmann velocity distribution of the molecules), reveals the critical role of temperature in the rate constant through the exponential dependence—a small increase in temperature results in a large increase in the rate constant. The pre-exponential factor, A , is also dependent on temperature,

but this dependence is proportional to \sqrt{T} and so is much weaker than the exponential dependence of the energy factor that A is usually considered to be a constant.

Reaction enthalpy, ΔH (kJ mol⁻¹), is the change in enthalpy when a reactant forms product following a reaction: $\Delta H = H_f(\text{products}) - H_f(\text{reactants})$, where H_f is the standard state heat of formation of reactant or product. When ΔH_R is positive, the process absorbs heat and is said to be endothermic. When ΔH_R is negative, the process releases heat and is said to be exothermic.

Values for A and E_a are generally derived from a thermogravimetric analysis curve, obtained by heating a sample at a fixed rate under an inert (e.g. nitrogen) atmosphere and measuring changes in mass and overall system energy [81•, 82]. See the “[Thermal degradation \(solid phase\) reactions](#)” section for an example of this analysis.

Reaction Rate Temperature Sensitivity

The study of the rate and productivity, transport, transfer and conversion of energy in a system is called thermokinetics [83, 84] and reveals a great deal about the temperature dependence of chemical reactions. The exponential dependence of the Arrhenius reaction rate constant on temperature is critical to the onset of ignition or thermal runaway in an exothermic system of reactions. In such a system, the rate of heating is exponential with temperature and the rate of heat losses is linear (or a relatively weak power law) in temperature.

As an example, the enthalpy balance of a single reactant undergoing first order conversion can be given (e.g. [85]) as:

$$V\bar{C} \frac{dT}{dt} = -\Delta H V c A \exp(-E_a/RT) - L(T - T_a), \quad (4)$$

where V is volume of a given system (m³), \bar{C} is the weighted volumetric specific heat (J m⁻³ K⁻¹), T is the system temperature (K), c is the concentration of the reactant, L is the linear heat loss coefficient (J s⁻¹ K⁻¹) and T_a is the temperature of the surroundings.

If this enthalpy balance is expressed in terms of dimensionless quantities, where $x = c/c_0$ (c_0 is the concentration of reactant at time $t = 0$), $\Theta = RT/E_a$, $\tau = tA$, $l = LE_a/(-\Delta H V c_0 A)$ and $C = (\bar{C}E_a/Rc_0\Delta H)$, we have:

$$C \frac{d\tau}{dt} = x \exp\left(-1/\Theta\right) - l(\Theta - \Theta_a), \quad (5)$$

where the first term on the right represents the heat production rate while the second term represents the heat loss rate. If a heuristic assumption of an infinite supply of reactant (i.e. a fixed heat production rate, $x = 1$) is made, the exponential rate has no free parameters and the effect of thermokinetics can be shown graphically (Fig. 3). With a moderate heat loss coefficient value, $l = 0.3$, (Fig. 3a), three intersections or steady

states occur where the production of heat is equal to the linear loss of heat. At P1, there is little to no reactant conversion. As system temperature, Θ , increases, the heat loss rate continues to increase but the heat production begins to increase more rapidly. At P2, the heat production rate exceeds the heat loss rate and thermal runaway or ignition is inevitable. The third intersection point (P3) is the point at which thermal quenching of the reaction occurs when the rate of increase of the heat production begins to decrease and is exceeded by the heat loss rate (however, this point cannot be reached unless the system temperature has already passed the point of no return and ignited). In reality, the system would generally have consumed all the fuel before this occurs (i.e. the heat production rate would reach a maximum and then decrease as the fuel is depleted).

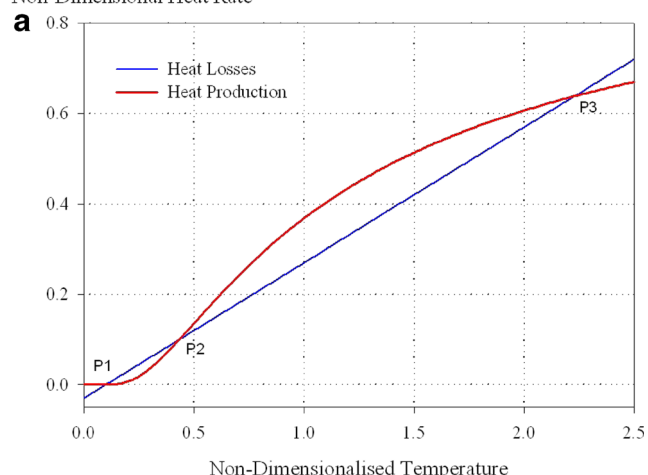
At a lower heat loss coefficient, $l = 0.2$, (Fig. 3b), the onset of thermal runaway occurs at a lower temperature and will not be subject to thermal quenching until much higher temperatures. As the heat loss rate becomes even less efficient, a point of tangency is reached below which there is no possibility of cooling the reaction and ignition is assured. At a higher heat loss coefficient, $l = 0.4$, (Fig. 3c), the onset of thermal runaway and ignition is only marginal and under even higher loss coefficients ignition will not occur at all.

A common assumption in wildland fire combustion literature is existence of a specific ‘ignition temperature’ for a particular fuel, implying that below this temperature nothing happens, and immediately above this temperature, everything happens (e.g. [86]). The assumption can be explained using a dynamical systems understanding [87] but essentially relies on two key attributes of the combustion of biomass fuels: the combustion reactions having a high activation energy and therefore being so temperature sensitive that the reaction occurs dramatically over effectively a very small temperature range, and a long incubation period during which the fuel undergoes heating with relatively little change [88–91]. However, even a temperature-dependent reaction such as the evaporation of water clearly does not only happen at the boiling point of water, as anyone who has observed a rain puddle drying out will attest; the evaporation process occurs at temperatures much lower than that of boiling, albeit much slower. Thus, the combustion reactions could occur at temperatures less than the ‘ignition’ temperature, albeit at very slow rates.

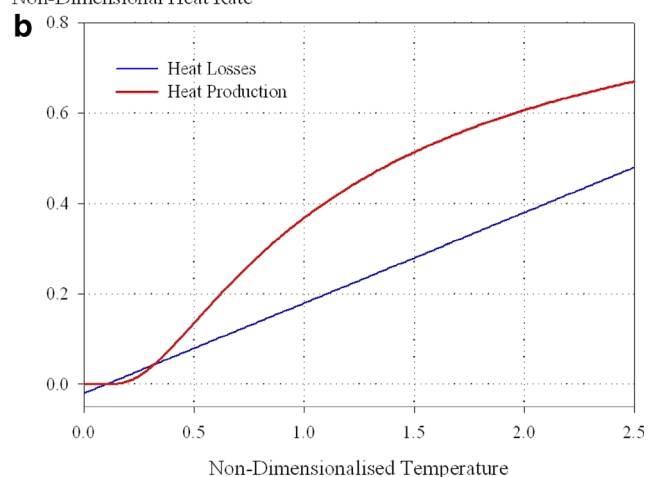
Thermal Degradation (Solid Phase) Reactions

When cellulose is heated, it undergoes a solid phase reaction called thermal degradation (also known as thermal decomposition, thermolysis or thermal scission). Cellulose can undergo two competing forms of degradation reaction: *volatilisation* or *pyrolysis* and *charring* [92•, 93•]. The term *pyrolysis* is often used formally to describe high temperature thermal degradation in the absence of oxygen [70•, p. 18].

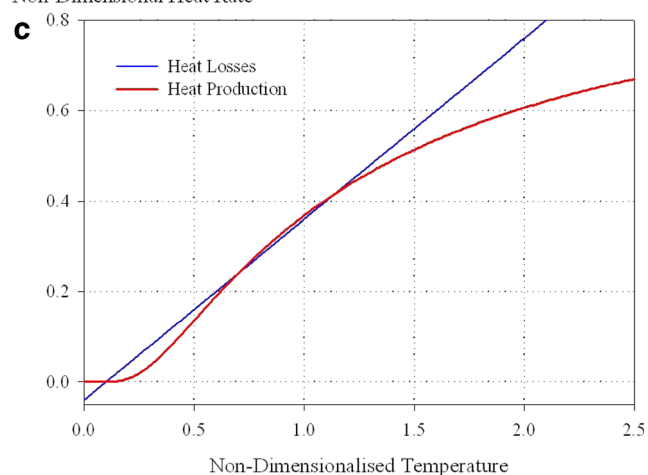
Non-Dimensional Heat Rate



Non-Dimensional Heat Rate



Non-Dimensional Heat Rate



While each of these reactions involves the depolymerisation of the cellulose, each has a different activation energy and promoting conditions, resulting in different products and heat release and therefore have very different impacts on

Fig. 3 Non-dimensional heat loss rate and heat production rate plotted against non-dimensional temperature showing the exponential temperature dependence of the heat reaction release rate (red line) and typically linear heat loss rate (blue line). **a** With moderate loss coefficient, three intersections (marked *P1*, *P2* and *P3*) occur, indicating where the heat loss rate equals the heat production rate. Between *P2* and *P3*, the heat generation rate exceeds that of heat loss and ignition is inevitable. **b** With a lower loss coefficient, the onset of thermal runaway occurs at a lower temperature and over the range here does not cease. **c** With a higher loss coefficient, ignition is marginal. From [56]

overall fire behaviour. Volatilisation involves intramolecular nucleophilic² attack of the resonance-stabilised positive centre on C-1 through donation of the electron density on the C-6 hydroxyl oxygen [94]. Charring involves rehydration via intermolecular nucleophilic action in the presence of moisture. Subsequent heating results in reactions that lead to the formation of char.

Volatilisation generally occurs in conditions of low or zero moisture and involves thermolysis of glycosidic linkages, cyclisation and the release of the highly volatile species levoglucosan (1,6-anhydro- β -D-glucopyranose or $C_6H_{10}O_5$) via thermolysis at the next linkage in the chain [94]. This reaction is *endothermic* (requiring about 300 J g^{-1} [85]) and has a relatively high activation energy (about 240 kJ mol^{-1} [66]). Levoglucosan is gaseous at the temperature of thermal degradation (≈ 400 – 600 K) but is a solid at ambient temperatures and is described as a ‘tar’ [53••]. It is the source of a wide range of species following further thermal degradation that readily oxidise in secondary reactions, resulting in what is seen as flaming combustion. Wodley [95] identified nearly 40 products from the thermal decomposition of levoglucosan—many of which were products of reactions between initial volatiles—including pentane, acetaldehyde, furan and furfural, and noted other workers identified 20 more, including formaldehyde and formic acid.

Char formation, on the other hand, occurs when thermal degradation happens in the presence of moisture or low rates of heating. In this competing reaction pathway, the nucleophile that bonds to the thermolysed carbo-cation at C-1 is a water molecule. The initial product is a reducing end which has ‘lost’ the opportunity to volatilise. This product is known as hydrolysed cellulose. The released hydrogen ion from the water molecule bonds to the negative ion forming a non-reducing end that can undergo no further reactions. Further heating of the hydrolysed cellulose causes the elimination of water (dehydration), carbon monoxide (decarbonylation) and carbon dioxide (decarboxylation) resulting in cross-linking of the carbon skeleton of the structure and the formation of the desaturated anhydrous carbohydrate commonly known as char (also activated cellulose, particularly early on in the process when there is relatively little desaturation). While the

² From the Greek, literally ‘nucleus loving’.

initial glycosidic thermolysis is endothermic, the subsequent decarboxylation, decarbonylation and dehydration reactions result in a net exothermicity. This reaction path has a relatively low activation energy ($E_a \approx 110\text{--}200 \text{ kJ mol}^{-1}$ [96, 97]) and a reaction enthalpy of $\Delta H \approx -1\text{--}2 \text{ kJ g}^{-1}$ [85, 98].

For detailed descriptions of the chemical processes involved in the thermal degradation of cellulosic biomass, see reviews such as [41••, 81••, 82, 90, 99, 100].

The desaturation of the anhydrous cellulose to charcoal species is visually apparent by a shrinkage in the substrate and a change in its colour. The colour change is similar to that of the browning of cooking food, a result of the glycosidic reaction between reducing sugars and free amino groups in proteins [101] and first described by Maillard in 1912. Saturated hydrocarbon compounds absorb light only in the ultraviolet [102, p. 330] and so appear white in the visible spectrum. As the number of carbon-carbon double bonds in the compound increases through dehydration, decarbonylation or decarboxylation, the electronic absorption spectrum broadens and shifts toward the infra-red into the visible [103, 104]. This results in the absorption of more visible spectrum light and a darkening of the substrate. This can proceed until only carbon black remains. The discoloration process is also evident in the yellowing and weakening of acidic paper through acid hydrolysis [105], which is essentially the same process as charring only much slower.

The key morphological difference between the two competing thermal degradation pathways is that fuel that has undergone the charring process retains the morphology of the original substrate [106]—i.e. one can still discern the form of the virgin fuel in the char. The cross-linking reactions that occur during charring act to retain the original shape of the fuel. Fuel that has undergone volatilisation does not retain any of the original fuel's structure and becomes amorphous.

Figure 4 shows a stylised thermogravimetric analysis for cellulose that illustrates the changes in mass of a sample under a fixed heating rate of about 10 K/min. Combustion reactions do not begin to make much impact on the overall mass of the sample until the sample temperature exceeds 550 K. At this point, initial thermal degradation reactions involving conversion of cellulose to activated or hydrolysed cellulose (precursors for the charring pathway) do not change the mass much. It is only when the thermolysis reactions occur, leading to the release of products such as levoglucosan under volatilisation and water and carbon dioxide under dehydration and decarboxylation, that the mass begins to decrease significantly. As the volatilisation and charring reactions are occurring in competition, it is very difficult to determine the primary cause of mass loss in cellulose from thermogravimetric analysis without a good understanding of the processes involved [107].

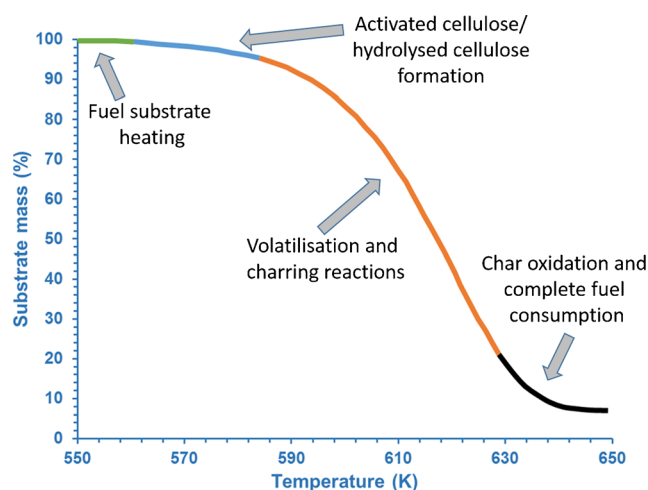
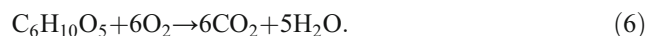


Fig. 4 Stylised thermogravimetric analysis for cellulose that illustrates the changes in mass of a sample under a fixed heating rate of about 10 K/min. Initial thermal degradation reactions involving conversion of cellulose to activated cellulose or hydrolysed cellulose do not commence until about 560 K. Significant mass loss does not occur until the thermolysis reactions and charring reactions begin to dominate between 580 and 620 K

Gas Phase Oxidation Reactions (Flaming)

The most apparent reaction involved in the combustion of biomass is the oxidation of the thermal degradation products. It is these reactions in the gas phase (involving levoglucosan and its decomposition products) and solid phase (involving char) that result in what we describe as ‘fire’—the release of heat, light and the appearance of flame. While much of the study of combustion in wildland fire research has concentrated on the transfer of heat from flames to adjacent unburnt fuel, understanding the source of the energy in flames is critical to correctly determining the rate and magnitude of the transfer of this energy.

Gas phase oxidation of the volatilised levoglucosan and its derivative products appears as flame. The oxidation reactions are highly complex and disordered due to both the chemistry involved and the susceptibility of the reactions to turbulence in the oxidant and fuel flows. Studies of emissions from combustion of wildland fuel (such as [95, 108, 109]) show that the number of oxidation products is quite considerable and often the result of many intermediate reactions. The simplest stoichiometric reaction for levoglucosan oxidation is:



However, this reaction assumes that intermediate reactions, consisting primarily of oxidation reactions of derivative products (produced through sequential thermal degradation), are complete (and also assumes that intermediate reactions can be expressed in terms of only initial and final products). But the number of pathways that such reactions can take is quite large, and not all paths will result in completion to carbon dioxide and water.

As an example of a gas phase hydrocarbon oxidation reaction, Bowman [110] identifies a minimum of 30 possible pathways for the combustion of methane (CH_4), one of the many possible intermediates of the thermal degradation of levoglucosan, to H_2O and CO_2 . Intermediate species included CH_3 , H_2CO , HCO , CO , OH and H_2 . Additionally, elemental carbon can form and be present as soot and which also acts to provide the source of visible radiation from the flame volume. This reaction is further complicated by reactions with nitrogen present in the atmosphere that can lead to the formation of a variety of nitrogen oxide (NO_x) species as well as toxins such as dioxins and polycyclic aromatic hydrocarbons [111, 112] that can be extremely harmful, especially to firefighters [113].

As the hot volatile gases released during thermal degradation must mix with oxygen for oxidation to occur, the resultant flames are known as *diffusion* flames [114]. The interface between the volatile gas and the oxidant forms a relatively thin zone where the oxidation reaction takes place and which is what we see as flame (see discussion of flame structure in the section on radiant heat transfer in the second part of this series). Due to the highly turbulent nature of the mixing of the reactants, the flames are more precisely known as *turbulent diffusion* flames [115]. Often, the reactants do not mix fast enough for the oxidation reactions to occur at the correct stoichiometric ratio and thus can be mixing-limited. This can result in incomplete oxidation, and large amounts of partially combusted reactant [116]. Mixing-limited combustion can also result in large volumes of volatiles that separate from the fire front and burn out some height above the fire [117, 118].

At any stage in the oxidation process, any reaction pathway may stop (through loss of energy or reactants) and its products be advected away from the reaction zone. These partially combusted components form the bulk of what appears as smoke. While turbulence can act to increase the mixing of reactants and thus combustion efficiency, the increased reaction rates and release of energy within the reaction zone can lead to reaction components being removed from the reaction zone before complete oxidation, hence the darker and thicker the smoke from a head fire where reaction rates are higher, as opposed to the lighter, thinner smoke from flames where combustion is more complete. See the next paper in the series for more discussion of turbulent diffusion flames.

These oxidation reactions are highly exothermic and very fast. Oxidation of levoglucosan requires an activation energy, E_a , of approximately 190 kJ mol^{-1} and occurs at a reaction rate constant of about $2.55 \times 10^{13} \text{ s}^{-1}$ and has a reaction enthalpy, ΔH , of approximately -14 kJ g^{-1} [119].

Solid Phase Oxidation Reactions (Smouldering or Glowing)

Oxidation of char in the form of smouldering or glowing combustion is generally a simpler reaction (see Eq. 7) than that of the gas phase oxidation of volatiles as there are not the

intermediate pathways that can be interrupted by turbulent mixing of reactants. However, due to the large range of possible species that are called char with a large range carbon/hydrogen ratios, the range of possible reactions can be similarly numerous [120].

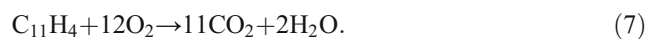
Solid phase oxidation reactions can occur in two different regimes, diffusion-controlled or kinetic-controlled [121]. The former occurs where the oxygen concentration is small compared to the ambient oxygen concentration and the rate of heat release is controlled by the rate of diffusion of oxygen to the char surface (i.e. oxygen limited). The latter occurs where the concentration of oxygen at the fuel level is the same as the ambient level. The rate of heat release in this regime depends strongly on the burning temperature.

Diffusion-controlled char oxidation may be described as ‘smouldering’ combustion and typically yields less complete oxidation with greater amounts of particulate or partially combusted emissions and much slower propagation rates [122•], often to the point of extinguishment [123].

Kinetic-controlled char oxidation may be described as ‘glowing’ combustion and generally results in more complete consumption and less particulate emissions with higher surface temperatures. Boonmee and Quintiere [123] identified a critical temperature of 670 K that defined the two regimes. Rein [124] argues that glowing combustion cannot be considered part of smouldering; however, as they are essentially the same chemically, the difference may be a matter of semantics.

Activation energies for oxidation of char varies significantly, with higher carbon concentration species having much higher activation energies for oxidation than more saturated forms. Oxidation of pure carbon requires temperatures in the order of 1000 K, whereas more saturated species require in the order of 700 K [125]. While char is normally quite refractory to high temperatures, recently formed hot char can oxidise easily [41••].

For the purpose of illustration, if we assume a sample char species that has undergone some dehydration and decarboxylation (i.e. C_{11}H_4), then the basic stoichiometric reaction for the solid phase oxidation would be:



This reaction, too, can lead to a range of intermediate species that can remain if the reaction stops for any reason, such as if reactants are cooled below the reaction’s activation energy. It is also possible for oxygen in the air to be excluded from the reaction surface by the presence of solid phase reaction products such as ash or combustion residue which can build up and form an insulating layer over the reacting surface, resulting in cessation of the reaction. Generally, however, solid phase reactions will continue to completion. When it does, there is a characteristic fine white ash residue composed mainly of minerals, salts and other inorganic components of the fuel that do not combust.

Oxidation of char is highly exothermic ($\Delta H \approx -32 \text{ kJ g}^{-1}$), over twice that of the volatile oxidation, but it has a lower activation energy ($E_a \approx 180 \text{ kJ mol}^{-1}$) and occurs at a much slower rate ($A \approx 1.4 \times 10^{11} \text{ s}^{-1}$) [126, 127].

Due to the slow reaction rate, much of the char oxidation occurs after the passage of the flaming front [128] and often involves larger fuel particles, perhaps leading to the impression that glowing combustion only occurs after flaming combustion. As the oxidation reactions take place on the solid fuel surface, much of the heat released is confined to the fuel bed. It is this aspect, along with the high reaction enthalpy of char oxidation, that is exploited for industrial and domestic use. Smouldering is the primary combustion mechanism of the largest and longest burning fires on the planet—predominantly in natural deposits of peat and coal [129]. It is the most difficult type of combustion to extinguish and suppression can require very large volumes of water [124], as much as one to two litres of water per kilogramme of burning fuel [129]. The fact that water is a key ingredient in the char formation pathway further complicates suppression.

As mentioned above, the primary difference between the two modes of solid phase oxidation is the production of larger

amounts of particulate emissions, seen as smoke, in smouldering combustion. Glowing combustion on the other hand produces few visible indicators with the exception of the dull red glow. However, in daylight, this regime is not easily detected with the naked eye, being saturated by other light sources such as the sun or flames. This is illustrated in Fig. 5 where two images taken 3 s apart in a combustion wind tunnel [130] experiment show the extent of glowing combustion that often is not visible.

Figure 5a, taken 242 s after ignition of a fire in dry eucalypt forest litter and 124 s after most flaming combustion has ceased, shows a fuel bed converted mostly to ash with some residual burning on the flanks. Figure 5b, taken 245 s after ignition, shows the same scene after the overhead lights in the wind tunnel had been turned off and the camera self-adjusted to the lower ambient light levels. In this image, the extensive glowing combustion that was present in Fig. 5b but not apparent is now clearly visible. No smoke is visible from these glowing combustion sources. Predominantly, it is this combustion regime that ultimately consumes the remaining fuels in an experiment if combustion is sustained.

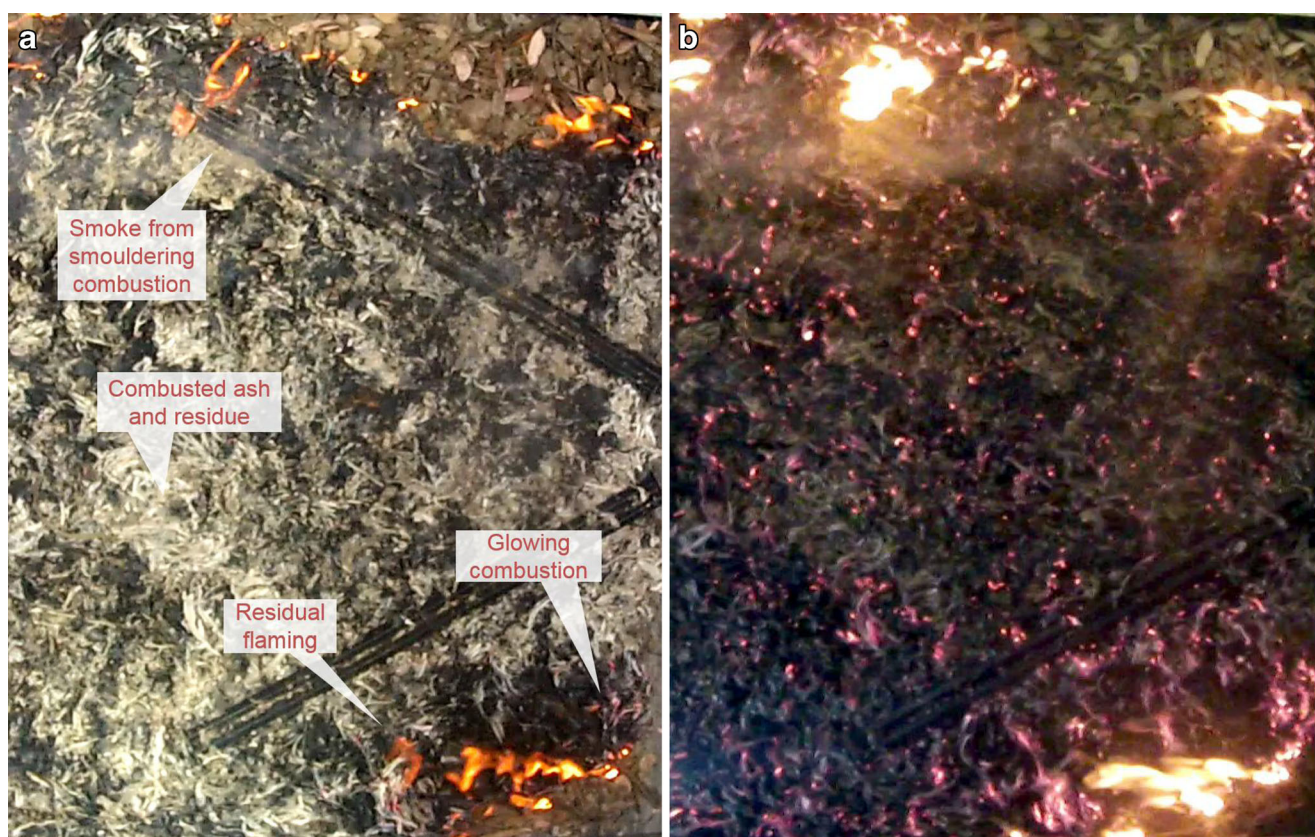


Fig. 5 Images taken after completion of experimental fire #64 in the CSIRO Pyrotron, 6 May 2016. In this experiment, dry eucalypt forest litter at 1.2 kg m^{-2} was burnt at a moisture content of 4.8% oven-dry weight in a constant wind of 1 m s^{-1} flowing from right to left. **a** Image taken 4:02 min after ignition and 2:04 min after most flaming combustion

has ceased. Most of the fuel bed has been consumed with only a small amount of residual flaming and two sources of smouldering combustion visible. **b** Image 3 s later after the wind tunnel overhead lights had been turned off revealing the multitude of glowing combustion present in **a** but not apparent

Discussion

While the role of nucleophilic competition in the thermal degradation of cellulosic biomass fuel has long been studied in industrial applications, it has not been applied to the investigation of the behaviour of wildland fires. The highly variable conditions in which wildland fires occur (weather, fuel and topography) have meant that attempts to understand the behaviour of wildland fires have focussed on more readily measurable aspects. However, it is apparent from observation of experimental fires in natural fuels that much of the phenomenological aspects of wildland fires may be explained by the fundamental processes involved in the initial competitive thermal degradation and the action of combustion of cellulosic fuels as described above.

The competitive thermal degradation of cellulose results in two possible pathways, known as the Broido-Shafizadeh model, which are controlled by thermal and chemical feedbacks (Fig. 6). This model is characterised by a high activation energy volatilisation ($S \rightarrow V$) pathway that is slightly endothermic and a low activation energy charring pathway ($S \rightarrow C$) that is exothermic.

If heating rates are low and/or moisture is present, the charring pathway dominates at the expense of the volatilisation pathway due to its lower activation energy. This pathway is exothermic and builds heat in the fuel substrate where it can further enhance thermal degradation. If sufficient heat to exceed the activation energy of the volatilisation pathway is released (or additional heat is added from outside), then volatilisation will dominate over charring. However, since the volatilisation pathway is endothermic, it takes heat out of the system, which may revert to charring.

Thus, the physical transfer of heat from exothermic reactions in the fuel substrate plays a significant role, along with the chemical reaction kinetics, in determining the pathway of the thermal degradation of the fuel processes [131]. However, the thermal degradation process is only part of the evolution of the combustion of a fuel. Each of the products of cellulosic degradation can oxidise in secondary reactions, creating additional thermal and chemical feedbacks (Fig. 7).

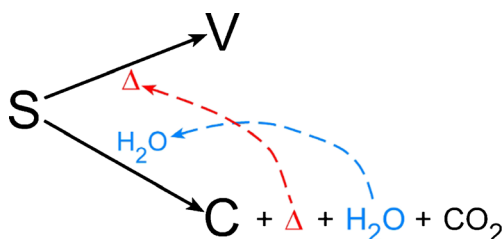


Fig. 6 Schematic of the competing paths possible in the thermal degradation of cellulose substrate (S). Volatilisation into levoglucosan (V) in the absence of moisture is endothermic. Char formation (C) occurs at a lower activation energy in the presence of moisture and is exothermic forming water. Chemical and thermal feedback paths (*dashed lines*) can encourage either volatilisation or charring. After [66, 85], modified from [56]

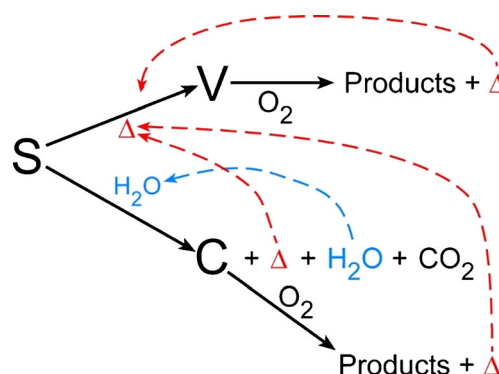


Fig. 7 Chemical and thermal feedback paths (*dashed lines*) from both thermal degradation and subsequent oxidation of released products (levoglucosan and char) can lead to self-supporting reactions. Modified from [56]

If oxidation of fresh char (as smouldering or glowing combustion) occurs, then sufficient additional heat might be absorbed by the system that will, if conditions are suitable, shift the system to the volatilisation pathway. This may result in a transition to flaming combustion if sufficient heat is available to ignite the volatile gases. If the subsequent combustion of the levoglucosan and its degradation products releases enough energy that is absorbed by the fuel substrate, then this process becomes self-supporting. However, if the volatiles are not ignited or the heat released in flaming combustion is transported away from the reactants by advection (e.g. wind), then the char formation path again becomes dominant. The chemical and thermal feedbacks between the two competing pathways and their secondary reactions in the thermal degradation of cellulose have been studied numerically and shown to exhibit oscillating behaviour until either thermal runaway occurs and fuel is completely consumed or the thermal degradation reactions cease [94].

The mechanism behind the transition to flaming combustion from smouldering combustion has long been a puzzle for researchers (e.g. [122••]). The competitive thermokinetics described above provides a robust explanation for this phenomena as well as answering the question as to why blowing air on embers helps to start a fire. Understanding the different mechanisms involved in the combustion of biomass also allows us to understand the different gas and solid phase emissions, in particular those that play a role in influencing global greenhouse gas emissions from landscape burning [128, 132–134]. The formation of char, and incompletely oxidised char in particular, may play a significant role in understanding the global carbon cycle [135, 136].

In the case of a wildland fire, where the flame zone is moving through the fuel, the thermal degradation processes occur continuously as the leading edge of the combustion zone moves into unburnt fuel. And, of course, the processes occur all around the perimeter of the fire where the local conditions can vary quite markedly.

Analysis of post-fire ash deposits has shown that the composition of the ash varies with the behaviour, particularly the intensity, of the fire [137–139]. Figure 8 shows a sequence of images showing the development of the ash distribution of an experimental fire in grassland fuels [140]. This fire was lit from a point and underwent several phases of spread, laying down a fine white ash when the flames were low, and laying down a black ash when the fire behaviour lifted and began to spread forward consistently.

The deposition of the white ash during the period of low flame concurs with the proposition that domination of non-flaming combustion is associated with the formation of char and its subsequent near complete consumption by glowing or smouldering. When flames are tall, the thermal degradation is dominated by volatilisation, resulting in much greater volume of volatiles and thus flame, leaving an amorphous residue that appears as black ash or soot due to rapid incomplete combustion. Measurements made in controlled experiments in the field and the laboratory confirm that the intensity of a fire and its mode of combustion (i.e. heading or backing fire) affects the amount and composition of partially combusted residue [128, 141].

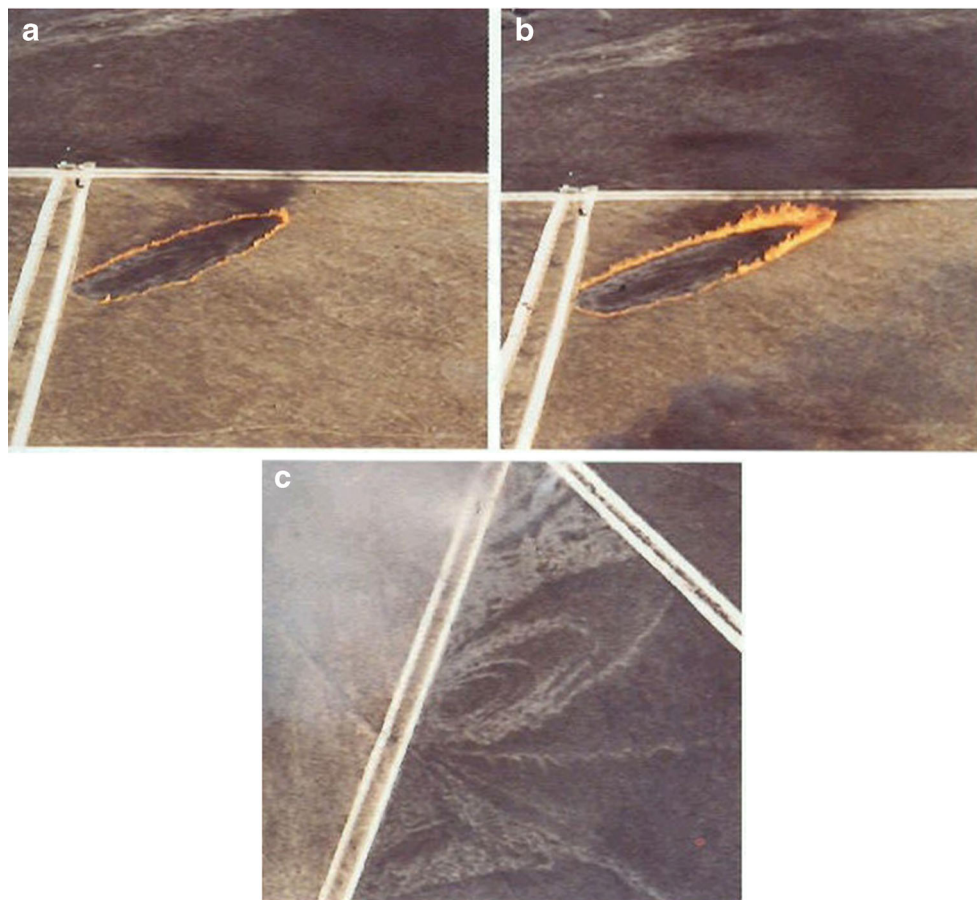
Wind is widely recognised as having a critical role in determining the broadscale behaviour of a wildland fire (where

and how fast it moves, the angle of the flames, etc.) (e.g. [3, 142, 143]. Therefore, wind must play a critical role in the finer scale combustion process. Unfortunately, wind (or advection more generally) has not been considered in the industrial biomass burning research that has formed the basis of much of our knowledge of the combustion thermokinetics of biomass fuels. In the controlled conditions of most industrial burners, air flow is very strictly managed and thus the variation of the air is not seen to play an important role in combustion dynamics.

However, in a wildland fire, the wind is the most important variable determining the behaviour and rate of spread of the fire [8]. Just how the wind explicitly affects the chemistry of combustion has not yet been adequately explored and its precise role remains unclear. Preliminary numerical investigations suggest that wind may play a dual role in the combustion processes of a free-burning fire [56].

The thermal degradation reactions are highly temperature sensitive. Changes in the temperature of the system of reactants will greatly vary the types and rates of reactions. Ambient wind, being in the order of 200–300 K cooler than the initial thermal degradation temperatures, must play a significant role in the combustion kinetics of biomass fuel. Ambient temperature wind blowing directly on the

Fig. 8 Sequence of oblique aerial photographs of an experimental fire burning in *Eriachne burkitti* showing the development of alternating white and dark ash patterns throughout the life of the fire. This fire was lit from a point and went through some of the following phases: **a** 3.1 min after ignition, a lull dominates the spread and flames are low and flame depth thin. **b** 3.6 min after ignition, the fire spreads as a heading fire with tall flames and lengthened flame depth. **c** Final ash patterns left after the fire has burned out. (Reproduced from Cheney and Sullivan (2008) [141], with permission from CSIRO Publishing)



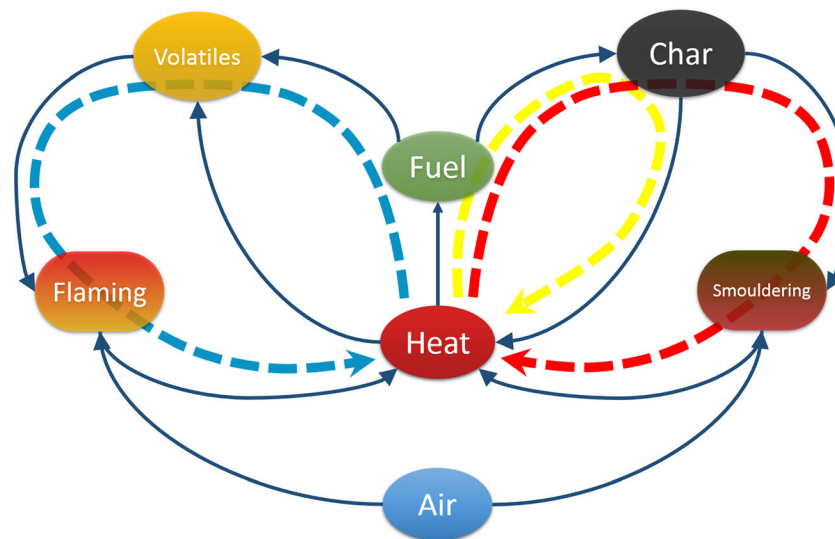


Fig. 9 A more advanced conceptual model that captures the effects of the competitive thermokinetics inherent in the combustion of cellulosic fuels. *Arrows* indicate direction of flows. The low activation energy, exothermic pathway of char formation occurs in competition with the higher activation, endothermic pathway of volatile formation. Oxidation of volatiles and char provide the bulk of the heat released during combustion and create three different feedback paths that lead to

sustained combustion. The heat generated by the formation of char is retained in the fuel substrate (*yellow pathway*) and in conjunction with the oxidation of char (*red pathway*) provides the mechanism by which a fuel can transition to flaming combustion. In most instances, it is the oxidation of volatiles (*blue pathway*) that drives the spread of a wildland fire. However, it is the char pathways that enable a biomass fire to sustain combustion under marginal conditions

combusting fuel substrate could significantly reduce the temperature of the fuel bed, driving the system initially away from the endothermic volatilisation pathway toward the lower activation energy charring pathway.

At the same time, the thermal feedbacks from the oxidation reactions of volatiles and char (see Fig. 7) are also exposed to the wind and thus may not reach the fuel bed. In particular, the flaming combustion products resulting from the rapid exothermic oxidation of the gas phase volatiles are extremely hot and thus buoyant and generally convected away from the fuel, further reducing the impact of the considerable heat being released on the thermally degrading fuel. As a result, it is possible that the endothermic reaction of volatilisation and subsequent loss of heat from the combustion zone could drive the thermal degradation reaction toward charring.

Similarly, the precise role of large amounts of moisture in the fuel substrate (as would be found in live fuels) is not precisely known. Numerical investigations [144] suggest that the presence of moisture delays the volatilisation process, decreases overall temperatures, and that considerable moisture remains in the fuel during ignition.

Conclusions

This article is the first of two reviewing the fundamental chemical and physical mechanisms involved in the behaviour of a wildland fire and focused on the chemistry involved in the thermal degradation of vegetative fuels and the subsequent

oxidation reactions of the degradation products. We started with a simple conceptual model (see Fig. 1) that identified in broad terms the key processes and their linkages. However, the unique chemistry of cellulose, the primary constituent of biomass fuels, leads to two competing pathways when thermally degrading, each of which significantly affects the broad scale behaviour of a free-moving fire spreading through vegetation.

Under high heating rates, volatilisation is an endothermic reaction that releases gas phase volatiles which can readily oxidise in air producing flames. Under lower heating rates and in the presence of moisture, charring is a highly exothermic reaction that produces a solid-phase char that when it oxidises appears as glowing or smouldering combustion. Figure 9 summarises these behaviours in a more advanced conceptual model.

The amounts, rates and locations of the heat released by the oxidation of the products of the two competing thermal degradation pathways are significantly different and explain much of the apparent capricious behaviour of wildland fire. The heat generated by the formation of char is retained in the fuel substrate (*yellow pathway* in Fig. 9) where it can act to increase reaction rates, particularly under conditions that are marginal for volatile formation. The subsequent oxidation of char (*red pathway*) is also retained in the fuel bed and together with the exothermic char formation process, provides the mechanism by which a fuel can transition to flaming combustion if the heating is sufficient to overcome the higher activation energy requirements of the endothermic volatile formation.

Oxidation of the volatiles (blue pathway), being in the gas phase, releases energy that has the potential to heat more fuel than that released from the oxidation of the solid phase char and thus be the source of energy that drives the self-sustaining spread of a fire. This heat flux also influences the speed of ignition and speed of propagation of the flame zone.

However, the efficiency of this reaction is highly dependent upon the turbulent mixing of the hot volatiles with the oxygen in the air. Turbulent mixing, along with other heat transfer processes, also influences the efficiency of the transfer of energy from this combustion to adjacent fuels and thus the sustained spread of a fire.

The second and final part of this series [31] discusses the mechanisms such as advection, radiation and mass transfer by which the heat and energy generated in combustion are transferred to adjacent fuels.

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Compliance with Ethical Standards

Conflict of Interest The author declares no conflicts of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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- Of major importance

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