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Wildland Fire Combustion Dynamics

The Intersection of Combustion Chemistry and Fluid Dynamics

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1.1 Introduction

An uncontrolled high intensity wildfire is one of the most terrifying natural phenomenon anyone may have the misfortune to experience firsthand. The sheer terror generated by the immense energy released in the combustion zone of a wildfire, a terror that may recall primordial subconscious fears of the absolute uncontrolled power of Mother Nature in what may seem to be a highly chaotic and unpredictable manner, can have lasting effects upon those impacted by the fire.

The term “spread like wildfire” is part of the general vernacular of our society but even then the meaning of such a phrase is not consistent, much like the behavior of a wildfire in its nature. Meanings of this phrase include “uncontrolled,”¹ “to be or become known,”² “to spread or circulate or propagate very quickly and widely, to spread rapidly,”³ and “to quickly reach or affect a lot of people.”⁴ In all these, there is the sense of something moving rapidly and uncontrollably, yet haphazardly but incessantly.

A wildfire, then, is something considered to be uncontrollable, unpredictable, and unstoppable. Except that we know that this is not necessarily the case. Where the perception may be of a roaring inferno propagating unstoppably with immense energy and intensity, simultaneously there will be sections of the same fire quiescent and mild, hardly spreading at all. Where there may be the observation of a fire front consuming great amounts of biomass and converting it to constituent molecules and atoms to be released into the atmosphere, other sections of the same fire may barely singe the lowest layers of the vegetation. The perception of wildfire is not

¹ Cambridge Dictionary: <https://dictionary.cambridge.org/dictionary/english/spread-like-wildfire> (last accessed November 18, 2021).

² Macmillan Dictionary: www.macmillandictionary.com/dictionary/british/spread-like-wildfire (last accessed November 18, 2021).

³ The Free Dictionary: <https://idioms.thefreedictionary.com/spread+like+wildfire> (last accessed November 18, 2021).

⁴ Collins Dictionary: www.collinsdictionary.com/dictionary/english/spread-like-wildfire (last accessed November 18, 2021).

necessarily the whole story of fire and without a full and complete understanding of fire there can be no hope of ever being able to predict it or control it.

Noted French philosopher, Gaston Bachelard (1884–1962), in his work *The Psychoanalysis of Fire* (Bachelard 1938, p. 2), observed:

We are going to study a problem that no one has managed to approach objectively, one in which the initial charm of the object is so strong that it still has the power to warp the minds of the clearest thinkers and to keep bringing them back to the poetic fold in which dreams replace thought and poems conceal theorems. This problem is the psychological problem posed by our convictions about fire . . . Fire is no longer a reality for science. Fire, that striking immediate object, that object which imposes itself as a first choice ahead of many other phenomena, no longer offers any perspective for scientific investigation . . . The reason for this is that the question [what is fire?] has fallen within a zone that is only partially objective, a zone in which personal intuitions and scientific experiments are intermingled. As a matter of fact, we shall demonstrate that our intuitions of fire – more perhaps than any other phenomenon – are heavily charged with fallacies from the past. These intuitions lead us to form immediate convictions about a problem which really should be solved by strict measurement and experimentation.

It may be said that these observations remain as true today as they were when first published. Much of the operational knowledge of wildland fire in use today (be it wild or otherwise) stems from the *ad hoc* learnings gained from long experience and direct observation of fire in the landscape. For many decades this empirical font has enabled land managers and fire bosses to successfully manage fire in the landscape. But as the well of knowledge grows older and retires, as the climate and conditions in which fires burn changes, the ability to transition traditional heuristic systems into more structured and applicable paradigms quickly hits limits and intuitions and rules of thumb begin to fail, with the potential for deleterious and catastrophic outcomes. Very often, however, the admirable desire for fire and emergency managers to utilize “evidence-based” learnings for “transparent” decision making becomes adulterated by the need to urgently fill knowledge gaps or implement “novel” solutions without critical and robust analysis of the veracity of such responses. As Bachelard observed, the lack of objectivity in relation to fire at every level means that beliefs and intuitions (or worse) are quite often treated equal to (or better than) the results of strict scientific investigation.

In this chapter we will explore the intersection of two fields of study that is at the very heart of the behavior of wildland fire but for which the domains are of two completely separate scientific disciplines. These are the chemistry of biomass fuel, combustion, and heat release, and the physics of fluid dynamics and heat transfer. It is within this zone that, like Bachelard remarks, fire “is only partially objective, in which personal intuitions and scientific experiments are intermingled.” For, while the study of the problem of fire can and has traditionally been isolated

within each discipline, a complete understanding of fire cannot be achieved without the other.

The problem may be summarized in one very simple, and common, question: When starting a fire, why does blowing on the nascent embers help? As we will see, the intuitive answer of “by providing more oxygen” is not completely correct, as the preliminary reactions necessary for combustion to initiate do not involve oxygen.

We will begin by looking at the chemical composition of biomass through which wildland fires propagate, and the chemical processes and reactions by which fuels thermally degrade and react with the atmosphere to liberate heat and energy. We will then consider the processes in which these reaction pathways are influenced by the environment around the combustion zone of a fire and how the combustion zone can in turn influence the environment around it. In the nexus of the two domains we shall consider observations of fire behavior that can only be understood by joint application of each domain of knowledge.

A conceptual model of the processes involved in the propagation of a wildland fire was developed by Sullivan (2017a), who attempted to capture the key processes involved, including sources and sinks of energy and closure pathways, in the ignition, combustion, and spread of fire in wildland fuels. The key processes identified in this model may be reduced to a very simple consideration of the cycle of heating, degradation (often mistakenly called “pyrolysis”), and combustion of biomass fuel (Figure 1.1).

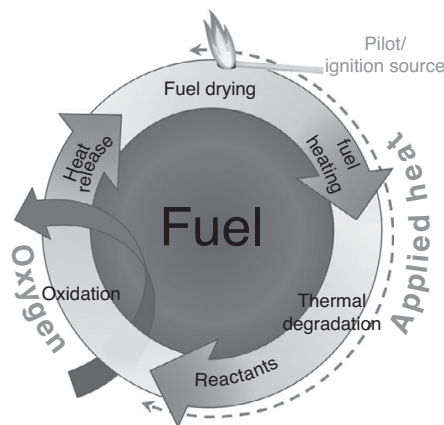


Figure 1.1 Simple conceptual model of the cycle of processes involved in the combustion and spread of wildland fire. If a fire starts with a pilot flame or ignition source and sufficient heat is applied to biomass fuel, the fuel will undergo evaporation of free moisture and dehydration that results in hydrolyzed cellulose that under continued application of heat begins to thermally degrade and produce pyrolysis and char products (reactants) which then oxidize in flaming and glowing combustion that release heat. If that heat is sufficient and localized enough, sustained spread of fire may occur.

This simplification, of what is a very complex set of chemical and physical mechanisms, identifies a closed loop inside of which the concept of sustained fire spread exists. This loop begins with the introduction of a pilot flame or ignition source to fuel which then undergoes evaporation of moisture and dehydration to produce a modified fuel structure called *activated cellulose* which physically appears very similar to the original fuel. Continued application of heat from the ignition source or pilot then begins to thermally degrade the activated cellulose which produces pyrolysis and char products (or reactants, since the reaction processes have barely begun at this point). These reactants will then energetically oxidize in the presence of air as flaming or glowing combustion, releasing heat and combustion products in the form of smoke and other emissions.

It is the stage of oxidation that the primary effect of the combustion environment comes into play, primarily in the form of oxygen in the air surrounding the combustion zone. The introduction of air – and the motion of that air – introduces turbulence (and also generates turbulence through the interaction of the energy released in combustion and the presence of the air) that affects the efficiency of the oxidation processes as well as the efficiency with which heat is transferred to adjacent fuel that enables the fire to spread. Thus, it is both the chemistry of the combustion of the fuel and also the physics of the flow of air and transfer of heat in and around the combustion zone that determines whether the resulting fire is a raging inferno or a quiescent smolder.

1.2 Combustion Chemistry

1.2.1 Chemistry of Wildland Biomass

Wildland fuel is composed of the live and dead biomass elements that make up the finer components of the vegetation. While the majority of the biomass in a wildland setting is held in the larger elements, such as tree boles, stems, and branches, these are generally too large to easily ignite and contribute meaningfully to the behavior and spread of a wildland fire (McArthur 1967; Rothermel 1972). Thus, it is the finer biomass elements, generally <6 mm in diameter, that provide the primary source of energy driving the behavior of a wildland fire front (McArthur 1967; Rothermel 1972). It is changes in the way these fuels combust (particularly in regard to efficiency of energy transfer; Anderson and Rothermel 1965) that affect the behavior and spread of the fire front.

In most wildland settings, the fine biomass fuels consist predominantly of dead fallen leaf litter, bark, twigs, shrubs, and grasses (Beall and Eickner 1970). When antecedent and prevailing weather conditions are severe, the fuel can also include larger material such as fallen branches, intermediate and overstorey tree canopies,

and even standing trees (Gould et al. 2011) but, due to their size, these generally do not contribute significantly to the dynamics of the fire front.

Live and dead biomass fuel, therefore, represents a wide range of physical structures, plant components, age, and level of accumulation and decomposition, each of which depends on the type of wildland setting and history of the land which can influence the inherent flammability of a fuel (Varner et al. 2015; Grootemaat et al. 2019). The primary constituents of biomass fuel are cellulose, hemicelluloses, and lignins, the distributions of which vary considerably across plant species and plant parts. Indicative ratios for biomass across a broad range of species and functional components (e.g. leaf, twig, stem) are 25–50% cellulose, 15–39% hemicelluloses, 12–44% lignins, and 0–33% other components (consisting of minerals, water, and extractives) (Sullivan 2017a).

Cellulose is a naturally-occurring long-chain, linear, unbranched polysaccharide ($[\text{C}_6\text{H}_{10}\text{O}_5]_n$) of β -D-glucose monomers ($\text{C}_6\text{H}_{12}\text{O}_6$) (Shafizadeh 1982; Williams 1982) in $\beta(1, 4)$ linkage (Figure 1.2). This polymer is a nonreducing carbohydrate and ranges in length from 200 to 10,000 units with molecular weights of 250,000–1,000,000 or more (Morrison and Boyd 1983, p. 1113). It is the most abundant organic material on our planet and is found in the protective walls of plant cells, particularly in stalks, stems, trunks, and all woody portions of plant tissues (O’Sullivan 1997). Cellulose is also present in bacteria, algae, fungi, and some animals, and plays a very important role in the human diet as fiber. Cellulose

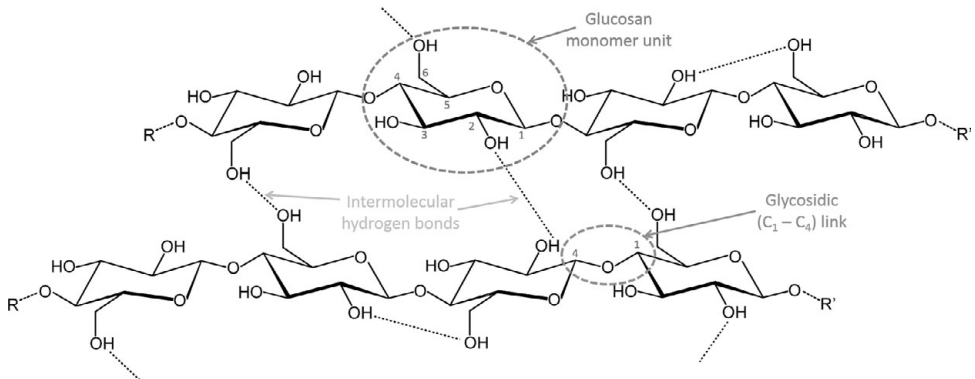


Figure 1.2 Example of the skeletal formula of a portion of two adjacent cellulose chains, indicating some of the intra- and inter-molecular hydrogen bonds (dotted lines) that may stabilize the crystalline form of cellulose. R and R' indicate continuation of the cellulose chain being reducing and nonreducing, respectively. A glucosan monomer with carbon atom numbering convention is shown by the dashed ellipse in the top chain. The glycosidic link between C₁ and C₄ of two adjacent glucosan units is shown by the dashed ellipse in the bottom chain. Reprinted with permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Current Forestry Reports (Sullivan 2017a) © 2017

is essentially the same in all types of biomass, differing only in the degree of polymerization (O'Sullivan 1997).

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 ($\beta(1, 4)$ linkage). The bond is formed through the process of condensation or dehydration between two glucosan units (i.e. a water molecule is formed and released in the joining of two D-glucose residues in this manner) as part of the larger process of photosynthesis within a plant.

The natural cellulose polymer is a straight chain with no coiling and adopts an extended rod-like morphology (O'Sullivan 1997). Parallel chains of cellulose can form hydrogen bonds in which surplus electron density on hydroxyl group oxygens is distributed to hydrogens with partial positive charge on hydroxyl groups of adjacent chains (see Figure 1.2). Multiple parallel chains may thus bond to form a crystalline structure that is very rigid and forms the basis of the microfibrils of plant cells, where bundles of up to 1,000 cellulose chains are bonded in parallel, and contribute to its high tensile strength (Jane 1956). Segments of naturally occurring cellulose can exhibit regions of both crystalline structure with ordered alignment of both inter- and intra-molecular bonds and amorphous structure in which the bonding is disordered (Broido et al. 1973) but not entirely random (O'Sullivan 1997). The ratio of crystalline to amorphous structures is in the order of 70:30, with the crystalline regions being relatively unreactive compared to those of amorphous regions (Ball et al. 1999a).

As a result of its rigid structure, cellulose is extraordinarily stable. 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. As a result, cellulosic fuels can take a long time to biologically decompose and require considerable energy to thermally degrade. Unlike starch, which has a crystalline-to-amorphous transition (i.e. breakdown of interchain hydrogen bonds) at 330–340 K in water, it takes ~ 590 K at a pressure of 25 MPa for cellulose to become amorphous in water (Deguchi et al. 2006).

Hemicelluloses are complex polysaccharides (generally copolymers of glucosan and a variety of other possible, mainly sugar, monomers) that occur in association with cellulose. Hemicelluloses generally consist of branched structures comprising 50–200 monomeric units and a few simple sugar residues, but their structures vary substantially depending on the biomass species and functional component. These polysaccharides are soluble in dilute alkaline solutions (Yaman 2004). The most abundant hemicelluloses are 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 concentrations, depending upon the species, cell type, and functional component. 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 (Yaman 2004). Lignins are the second most abundant biopolymer after cellulose and they provide rigidity and physical strength to plants (Gordobil et al. 2016).

A large variety of other elements and compounds are found in biomass fuels. These include starches (i.e. nonpolymer carbohydrates), minerals and trace elements (such as nitrogen, phosphorus, potassium, calcium, magnesium, sodium, and silica amongst others), water, and salts (Demirbaş 2004). Very minor amounts of metals, such as mercury, may also be found (Howard et al. 2019). Extractives and inorganics including terpenes (isoprene polymers) and resins (fats, fatty acids, and fatty alcohols) may also be found in fuels. After complete combustion, some of these, particularly minerals, appear as residual ash.

1.2.2 Chemistry of Wildland Fuel Combustion

Cellulose is the most widely studied substance in biomass combustion, with less focus being given to the study of the thermal degradation and combustion of hemicelluloses or lignin (Di Blasi 1998), perhaps as a result of the relative thermal instability of these compounds. Although the extrapolation of the thermal behavior of any particular individual component to describe the kinetics of a chemically complex fuel such as biomass is only an approximation (Di Blasi 1998), the properties of cellulose have been found to exert a dominating influence on the rates of thermal degradation of biomass. As a result, the detailed thermokinetics of cellulose provides the best understanding of the combustion of biomass fuels (Williams 1982). The remainder of this discussion focuses on the thermokinetic properties of cellulose; however, differences in the purity and physical properties of the cellulose, hemicellulose, and lignin in the biomass can also play an important role in the degradation process (Di Blasi 1998), with inorganic matter acting as a possible catalyst or an inhibitor of the degradation reactions.

1.2.2.1 Combustion Processes

While the word “combustion” is generally used to describe any high-temperature, self-sustaining oxidation reaction (Babrauskas 2003, p. 14), it is also used to describe the complete process in the conversion of unburnt fuel to ash and burnt residue (Luke and McArthur 1978). The combustion of biomass in wildland fire is not strictly a linear sequence of events, one in which fuels are preheated, they ignite, distilled gases combust, and then finally residual char is combusted (as portrayed, for example, in Gisborne 1948; Vines 1981; Pyne et al. 1996). Although there are several unique stages identifiable during the propagation of a flame front,

these are not necessarily sequential and can sometimes occur simultaneously or in competition with each other.

The first step in biomass combustion is heating of the fuel, often initially from a pilot source such as a direct flame or spark but also by the transfer of heat via radiation, convection, or conduction from an approaching flame front. Under continued heating, free and bound water on and in the fuel evaporates or is liberated. If sufficient heating occurs, the fuel then begins to thermally degrade and its structure changes fundamentally and irreversibly. The primary products of this thermal degradation are combustible gases (i.e. volatiles) and char. These gas and solid phase products then oxidize in air, in flaming combustion (gas phase) or glowing and smoldering combustion (solid phase).

It is often believed that a fuel must reach a specific temperature for ignition to occur. In truth, however, while the temperature of the reactants is important in determining initiation of combustion, ignition does not occur at a single fixed temperature but the reactions that may be perceived to be “ignition” become more prevalent at higher temperatures.

All chemical reactions require reactant molecules to be brought together in the correct orientation with sufficient kinetic energy to break or form bonds between or within the reactants (Morrison and Boyd 1983, p. 55). The minimum kinetic energy for a reaction to occur is called the *activation energy* and the rate at which that reaction proceeds is proportional to the concentration of the reactants and the rate of collisions between reactants that occur at or above the activation energy and in a favorable orientation, which can be expressed as the empirical relation known as the Arrhenius equation (Moore 1963, p. 273):

$$r = A \exp\left(\frac{-E_a}{RT}\right), \quad (1.1)$$

where A is a pre-exponential factor usually considered to be a constant for any particular reaction that subsumes the molecule collision and orientation factors and represents the frequency of collisions in the correct orientation (s^{-1}), E_a is the reaction activation energy (J mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the temperature of the reactants (K). This equation reveals the important role of reaction temperature in the rate constant through the exponential dependence, with a small increase in temperature resulting in a large increase in the rate constant. Values for A and E_a are generally derived from thermogravimetric analysis obtained by measuring changes in mass and overall system energy while a sample is being heated at a fixed rate under an inert atmosphere (Antal and Várhegyi 1995; Antal et al. 1998) and may be correlated (Philibert 2006).

Reaction enthalpy, ΔH_R (kJ mol^{-1}), is the change in enthalpy when a reactant forms a product following a reaction: $\Delta H_R = H_f(\text{products}) - H_f(\text{reactants})$,

where H_f is the standard state heat of formation of the reactant or product. When ΔH_R is positive, the process absorbs heat (i.e. it is endothermic) and, when it is negative, the process releases heat (exothermic).

The reactions involved in combustion of biomass fuel generally have such a relatively high activation energy and, thus, are highly temperature sensitive, that when a fuel is heated it undergoes a long incubation period during which it appears to change relatively little. When combustion finally initiates, it does so in dramatic fashion over a very small (<50 K) temperature range (Atreya 1998), giving the impression that a single ignition temperature exists.

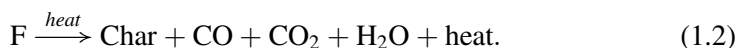
The rate of the formation and oxidation of volatiles is much faster than that of the formation and oxidation of char and thus appears to occur first in the passage of the flame front, with the char oxidation appearing to occur after the fire front has passed. In a wildland fire, all reactions can occur 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 behaviors observed in bushfires.

1.2.2.2 Thermal Degradation

Under thermal stress, cellulose undergoes thermal degradation (or thermal decomposition) reactions that commence in the range 400–500 K in which reactants that liberate the bulk of the energy during combustion are formed. In cellulose, thermal degradation occurs along two pathways: *char formation* and *volatilization*. Each of these pathways involves the fundamental modification of the underlying cellulose structure with different activation energies and promoting conditions and are fundamentally competitive in that only one or the other pathway can occur within a given section of chain. As a result, different reaction products with different enthalpies and reaction rates can be produced with each having a very different impact on overall behavior of a fire.

Char formation or *charring* occurs when cellulose fuel (F) undergoes inter- and intra-chain cross-linking and dehydration under thermal stress (Broido and Weinstein 1970; Weinstein and Broido 1970). This is more likely to occur in crystalline regions than amorphous regions (Ball et al. 1999a) and can occur via two distinct processes. Primary charring is a slow chemical conversion of a fuel that, due to a low activation energy, begins at relatively low temperatures (Eq. (1.2)). Continued heating of the fuel causes cross-linking of the carbon skeleton of the structure resulting in the elimination of water (dehydration), carbon monoxide (decarbonylation), and carbon dioxide (decarboxylation), and the formation of the desaturated anhydrous carbohydrate commonly known as char (C). In this process, the underlying morphology of the original fuel is retained as the internal structure of the substrate is maintained by the cross-linking reactions (Mok and Antal 1983).

This reaction path has an activation energy of $\simeq 110 \text{ kJ mol}^{-1}$ (Di Blasi 1993; Diebold 1994), a collision frequency of $6.7 \times 10^5 \text{ s}^{-1}$ and a reaction enthalpy of $\simeq -1$ to -2 kJ g^{-1} (Milosavljevic et al. 1996; Ball et al. 1999a).



Secondary charring occurs at a higher temperature as a result of a higher activation energy in the presence of moisture (Eq. (1.3)). It occurs in competition with the volatilization reaction pathway following thermal scission (or thermolysis) of the cellulose chain at a C_1 – C_4 glycosidic link and involves rehydration of the cellulose chain via intermolecular nucleophilic action. Here, the competitive nature of reactions means that only one or the other can occur; they cannot both occur. In this case the nucleophile that bonds to the thermolyzed carbocation at C_1 is a water molecule which may be present within the fuel substrate or the result of previous dehydration reactions occurring via primary charring (Ball et al. 1999a). The initial product is a reducing end which has “lost” the opportunity to volatilize, known as *hydrolyzed cellulose* (OH). The released hydrogen ion from the water molecule bonds to the negative ion forming a nonreducing end that can undergo no further reactions. Similar to the formation of char via the primary pathway, continued heating of the fuel causes crosslinking of the carbon skeleton of the structure with dehydration, decarbonylation, and decarboxylation desaturating the cellulose chain resulting in an anhydrous char species. While the initial glycosidic thermolysis is endothermic, the subsequent crosslinking reactions result in a net exothermicity. This reaction path has an activation energy of $\simeq 200 \text{ kJ mol}^{-1}$ (Di Blasi 1993; Diebold 1994), a collision frequency of $6.9 \times 10^{22} \text{ s}^{-1}$, and a reaction enthalpy of $\simeq -1$ to -2 kJ g^{-1} (Milosavljevic et al. 1996; Ball et al. 1999a).



While the morphology of char formed through secondary charring is often less structured than that of primary char as a result of the thermolysis of the cellulose chains, the crosslinking reactions maintain some semblance of the original fuel substrate. The degree of molecular desaturation determines the darkness of the charred fuel substrate (Coblentz 1905).

Volatilization is a reaction that occurs in competition with that of the secondary charring pathway following thermolysis and involves intramolecular nucleophilic attack of the resonance-stabilized positive center on C_1 through donation of the electron density on the C_6 hydroxyl oxygen (Ball et al. 1999b, 2004) (Eq. (1.4)). It generally occurs in conditions of low or nil moisture and comprises cyclization, depolymerization, and the release of a levoglucosan (1,6-anhydro- β -D-glucopyr-

anose or C₆H₁₀O₅) molecule via thermolysis at the next C₁–C₄ glycosidic linkage in the chain (Ball et al. 2004).



This reaction is endothermic, requiring about 300 J g⁻¹ (Ball et al. 1999a), has a collision frequency of 2.8 × 10¹⁹ s⁻¹, and an activation energy of about 240 kJ mol⁻¹ (Di Blasi 1998). Levoglucosan is a solid at ambient temperatures, often described as a “tar” (Williams 1982), but is gaseous at the temperature of thermal degradation, with a melting temperature of 455–457 K. As a result of its volatility, it is the source of a wide range of species following further thermal degradation that readily oxidize in secondary reactions, resulting in what is seen as flaming combustion. Wodley (1971) identified nearly 40 products from the thermal decomposition of levoglucosan – many of which were products of reactions between initial volatiles – including pentane, acetaldehyde, furan, furfural, in addition to 20 others previously identified, including formaldehyde and formic acid.

Thermolysis of the crystalline anhydrous cellulose tends to occur near the ends of the chains rather than at any arbitrary glycosidic link elsewhere as they are more accessible to the nucleophile (Ball et al. 1999a). This results in scission of glucose monomers, cellobiose, and short oligomers. The key morphological difference between the two competing thermal degradation pathways is that fuel that has undergone the volatilization process does not retain any of the original fuel’s structure and becomes amorphous.

The critical element involved in the combustion of biomass fuel is the competitive asymmetric chemistry between two nucleophiles competing for the positively charged carbon center on C₁ of the carbonium ion formed in thermolysis of a glycosidic bond in the cellulose chain. The nucleophiles are either a molecule of water or an -OH group on C₆ on the glucosyl-end of the cleaved chain. Hydrolyzed cellulose (OH), a reducing chain fragment with the tendency to undergo the crosslinking reactions (i.e. dehydration, decarbonylation, and decarboxylation), then results if the water molecule is successful. Under continued heating this will produce charcoal. If the -OH group is successful, a levoglucosan-end that is resilient to the crosslinking reactions and that depolymerizes to levoglucosan, known as *levoglucosan-end cellulose* (LG), will form, which will lead to the formation of other volatile products.

Broido (1976) determined from experimental weight loss data that under moderate heating cellulose undergoes an “incubation” period before branching into either the depolymerization or char formation reactions. He concluded that, although there was no weight loss during this period, the fuel underwent important changes that dictated which subsequent path would dominate under further heating

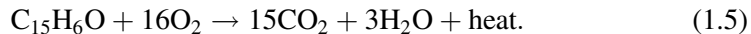
(i.e. the nucleophile competition). The product of the incubation period has been called *activated cellulose* and correlates to the formation of hydrolyzed cellulose or levoglucosan-end cellulose.

1.2.2.3 Smoldering and Glowing Combustion

Oxidation of char appears in the form of smoldering or glowing combustion and involves solid phase (fuel) and gas phase (oxidant) components reacting across the interface of the two phases. As a result, there is not a large range of intermediate pathways that can be interrupted by turbulent mixing of reactants. However, due to the many possible char species with a large range of carbon:hydrogen ratios, the possible reaction pathways can be similarly numerous.

Activation energies for char oxidation vary significantly, with higher carbon concentration species having much higher activation energies than more saturated forms. Oxidation of pure carbon requires temperatures in the order of 1,000 K, whereas more saturated species with less double bonds require 700 K (Harris 1999). While char is normally quite refractory to high temperatures, recently formed hot char can oxidize easily (Sullivan and Ball 2012).

As an example, if we assume a sample char species that has undergone some dehydration and decarboxylation (e.g. $C_{15}H_6O$), then the basic stoichiometric reaction for the solid phase oxidation would be:



This reaction can lead to a range of intermediate species such as CO or even elemental carbon if the reaction stops and oxidation is not complete, such as when reactants are cooled below the reaction's activation energy or oxygen is limited. As this reaction occurs across the interface between the solid phase and gas phase, it is possible for gas phase oxygen to be restricted or even excluded from reaching the solid phase reaction surface by the presence of reaction products such as ash which may build up during the reaction and which may form an insulating layer over the reacting surface, halting the reaction. In contrast to the oxidation of volatiles (Eq. (1.6)), it can be seen that, for this particular example char species, more than 2.5 times the amount of oxygen is required for the complete oxidation of one mole of fuel, which alludes to the sensitivity of this solid-phase oxidation reaction to the availability of oxygen for completion.

When solid phase reactions continue to completion, there remains a characteristic fine white ash combustion residue composed mainly of minerals, salts, and other inorganic components of the fuel that do not combust and which contains very little carbon (Surawski et al. 2016).

Oxidation of char is highly exothermic ($\Delta H \simeq -32 \text{ kJ g}^{-1}$), over twice that of the volatile oxidation, has a lower activation energy ($E_a \simeq 180 \text{ kJ mol}^{-1}$) but

occurs at a much slower rate ($A \simeq 1.4 \times 10^{11} \text{ s}^{-1}$) (Eghlimi et al. 1999; Branca and di Blasi 2004).

Due to the slow reaction rate of both the formation and oxidation of the char, much of the char oxidation appears to occur after the passage of the flaming front (Surawski et al. 2015) and often involves larger fuel particles, leading to the impression that glowing or smoldering combustion only occurs after flaming combustion has ceased. Much of the heat released is confined to the fuel bed, with little transported away from the combustion zone.

Solid-phase oxidation reactions of char occur in two regimes, leading to two modes of char combustion. These regimes are kinetic-controlled and diffusion-controlled reactions (Williams 1977). Kinetic-controlled reactions occur where the concentration of oxygen is not limited and the rate of reaction and heat release is strongly dependent on the temperature of the reaction. Diffusion-controlled oxidation occurs where the oxygen concentration at the reacting char surface is small compared to the ambient oxygen concentration (i.e. combustion is oxygen limited) and the rate of heat release is governed by the rate of diffusion of oxygen to the surface of the fuel.

Kinetic-controlled char oxidation leads to the char combustion mode described as “smoldering” and typically yields less complete oxidation with greater amounts of particulate or partially combusted emissions and much slower propagation rates (Ohlemiller 1985), often to the point of extinguishment (Boonmee and Quintiere 2005). Diffusion-controlled char oxidation leads to the char combustion mode described as “glowing” and generally results in more complete consumption and less particulate emissions with higher surface temperatures. Boonmee and Quintiere (2005) identified a critical temperature of 670 K that defined the two regimes; below this value smoldering would dominate, above this value glowing would dominate.

The primary difference between smoldering and glowing char combustion modes is the degree to which the underlying oxidation regime determines the completeness of the oxidation reactions. Smoldering combustion generally produces larger amounts of partially combusted particulate emissions, most often seen as smoke, where the oxidation reaction has ceased before complete oxidation of the fuel. Glowing combustion on the other hand produces few visible indicators with the exception of the dull red glow where sufficient oxygen is present at the burning fuel surface which results in complete oxidation of the char. 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 (for examples see figures in Section 1.4).

Char oxidation, whether smoldering or glowing, is the most difficult type of combustion to extinguish, particularly since water is a key ingredient in the char formation pathway, which complicates suppression efforts. Effective suppression

can require very large amounts of water (Rein 2013); as much as one to two liters of water per kilogram of burning fuel is required to stop combustion (Rein 2016).

1.2.2.4 Flaming Combustion

Oxidation of the volatilized gas-phase levoglucosan and its derivatives occurs in what we see as flaming combustion. These 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 affecting the mixing of reactants in what is known as *turbulent diffusion* (Bilger 1989). Studies of emissions of the turbulent diffusion flames from the combustion of bushfire fuel (such as those of Wodley 1971; Hurst et al. 1994; Greenberg et al. 2006) show that the number of oxidation products is considerable and often the result of many incomplete intermediate reaction paths. At its simplest, however, the stoichiometric reaction for levoglucosan oxidation can be written as:



This form of the reaction assumes that intermediate reactions are complete, but the number of pathways that such reactions can take is quite large and not all paths will result in complete combustion to carbon dioxide and water. Bowman (1975) identified 30 possible pathways for the combustion of methane (CH_4), an example of one of the many intermediates of the thermal degradation of levoglucosan. Intermediate species included CH_3 , H_2CO , HCO , CO , OH , and H_2 . Elemental carbon often forms in these reactions, particularly when combustion is incomplete, and appears as soot. It is the visible radiation from heated particles of carbon that we see as flames (Gaydon and Wolfhard 1960).

These reactions may be further complicated by the presence of other elements such as nitrogen in the atmosphere, which 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 (Gullett and Touati 2003; Lemieux et al. 2004) that can be extremely harmful, especially to firefighters (Reisen et al. 2006).

These gas-phase oxidation reactions are highly exothermic and very fast. Oxidation of levoglucosan has an activation energy of approximately 190 kJ mol^{-1} , occurs with a collision frequency of about $2.55 \times 10^{13} \text{ s}^{-1}$, and has a reaction enthalpy, ΔH , of approximately -14 kJ g^{-1} (Parker and LeVan 1989).

Turbulent diffusion oxidation occurs when the hot combustible gases from volatilization (fuel) mix diffusively with oxygen in the cooler ambient air (oxidant) in a highly turbulent environment (Bilger 1989). These react where conditions (e.g. mixing ratio, temperature) are suitable at the interface between the fuel and oxidant (Vervisch and Poinot 1998). This relatively thin interface is called the *reaction zone* and surrounds the envelope of volatile gas as it mixes and reacts with the

oxygen in the air. As a result, the oxidation reactions are often mixing-limited (that is, the oxidation reaction does not occur because the fuel and oxidant cannot be brought together in the correct stoichiometric ratio) and can result in large volumes of volatiles that separate from the reaction zone before oxidation has commenced or has completed. These gases may disperse or may subsequently burn out some height above the fire when it mixes with oxygen if it remains hot enough (Cheney and Sullivan 2008).

At any stage in the oxidation process, any reaction pathway may stop (through loss of energy or reactants) and its products advected away from the reaction zone (Sullivan 2017b). These partially combusted components form the bulk of what appears as smoke and other emissions (Andreae and Merlet 2001). The more turbulent the reaction zone, the more likely that reactants will be removed before complete combustion, hence the darker and thicker smoke from an intense section of flame front fire, as opposed to the lighter, thinner smoke from less turbulent flames.

1.3 Combustion Processes and Environmental Interactions

The foregoing material presents the current understanding of the chemical processes and pathways involved in the combustion of cellulosic biomass fuels. However, these chemical reactions do not occur in isolation or in a vacuum. By their very nature they are contained within the environment in and through which a wildland fire propagates. As a result, the conditions that define the initial and boundaries of these reactions are not constant and very often are not able to be known in great detail. Much of the knowledge thus far gathered about the thermal degradation of cellulosic biomass and subsequent oxidation of thermal degradation products comes from laboratory settings where such conditions are strictly controlled and experimental quantities are subject to negligible uncertainty. In this section we will look at how the environmental conditions in which biomass combustion occurs influences those reactions and results in what we see as wildland fire. Furthermore, the physical evidence for these processes and pathways can be found in careful observation of free-burning fires and we will investigate examples from free-burning laboratory and field scale wildland fire experiments for the evidence of such chemistry.

1.3.1 Competitive Thermokinetics

The nucleophilic competition between the volatilization pathway and the charring pathway in the thermal degradation of cellulosic biomass may be an important component of much of the apparent capricious behavior witnessed in free-burning

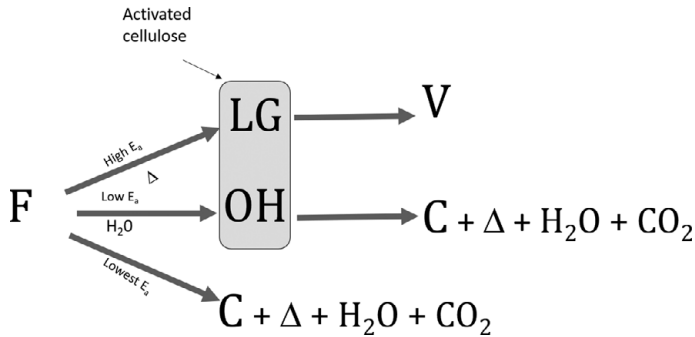


Figure 1.3 A simple schematic illustrating the macro-scale effect of the thermal degradation of cellulose fuel substrate (F) resulting in the direct formation of char at low temperatures ($F \rightarrow C$), the nucleophilic competition resulting in either levoglucosan-end cellulose (LG) and the formation of volatiles (V) through the path ($F \rightarrow LG \rightarrow V$) or hydrolyzed cellulose (OH) and the formation of char (C) at high temperatures through the path ($F \rightarrow OH \rightarrow C$). Δ indicates heat. Levoglucosan-end cellulose and hydrolyzed cellulose may be described as activated cellulose since there is no significant mass loss during this thermal degradation stage.

biomass fires, particularly the change in fire behavior around the perimeter of a fire under relatively constant conditions. The outcome of the competitive thermokinetics of this reaction is critically dependent upon thermal and chemical feedback during the reactions, which are both influenced by the macro-scale environment within which the reactions take place and influence the macro-scale fire behavior.

Figure 1.3 is a simple schematic illustrating the macro-scale effect of the thermal degradation of cellulose derived from that of Ball et al. (1999a). Thermal degradation of a fuel substrate (F) may result in the direct formation of char (C) at low temperatures. At higher temperatures thermal degradation may result in the formation of activated cellulose in the form of either levoglucosan-end cellulose (LG) or hydrolyzed cellulose (OH), depending on the outcome of the nucleophilic competition, with no significant loss of mass at this stage. Under continued heating, the levoglucosan-end will form volatiles (V), whereas hydrolyzed cellulose will form char. The exothermic char-forming reactions release heat as well as water and gases such as carbon dioxide as a result of the crosslinking reactions. In contrast, the volatile-forming reactions are endothermic with no by-products.

1.3.2 Chemical and Thermal Feedbacks

Figure 1.4 illustrates the chemical and thermal feedback involved in the thermal degradation reactions of cellulose and it is here that the complexity of the reaction

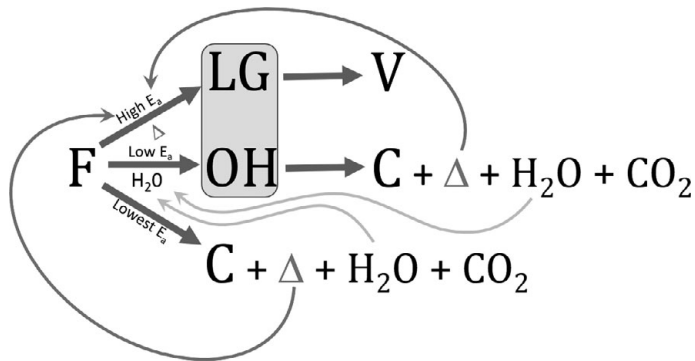


Figure 1.4 Chemical and thermal feedbacks are key features of the thermal degradation of cellulose. The nature and extent of these feedbacks will determine which thermal degradation pathway dominates. Heat released by the char formation process may drive thermal degradation into the high activation energy and endothermic volatilization pathway. Moisture released by the same process may drive thermal degradation into the low activation energy and exothermic char formation pathway.

pathways in cellulose begins to become evident. Heat released from the exothermic formation of char may feed back into the reaction to the high activation energy pathway, leading to the formation of levoglucosan-end cellulose and, subsequently, volatiles. Conversely, the release of water molecules from the dehydration process in the char formation may feed back into the reaction to the water-catalyzed lower activation energy hydrolyzed cellulose and char formation pathway. Thus, the determination of which thermal degradation pathway will dominate the thermal degradation of any particular fuel element depends on the conditions prevailing during the reaction in regard to energy available (a function of reaction temperature) and chemical catalysis.

Under combustion initiation conditions, thermal degradation may commence with char formation. If sufficient heat from this exothermic process is released it may be enough to power the reaction into the volatilization pathway. However, since the volatilization pathway is endothermic, heat will be lost from the system as soon as it begins which may push it back into a lower activation energy charring pathway. If the volatilization pathway is to continue to be maintained, an additional source of heat is required. This additional heat may be supplied by oxidation of the thermal degradation products.

Oxidation of the thermal degradation products (i.e. volatile and char) in the form of flaming and glowing/smoldering combustion introduces additional thermal and chemical feedbacks (Figure 1.5). However, these thermal and chemical elements occur in both solid and gas phase and thus their contributions to the thermal degradation processes are not as straightforward as those considered previously.

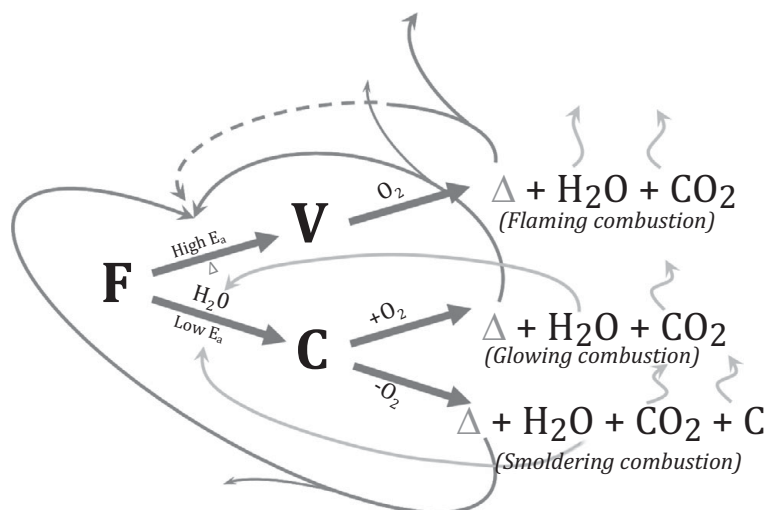


Figure 1.5 Oxidation of the cellulose thermal degradation products creates a new set of chemical and thermal feedbacks that can influence the thermal degradation pathway as well as the propagation of the combustion reactions through new fuel. Oxidation of volatiles (V) in the form of flaming combustion happens in the gas phase and so occurs well above the fuel bed, due to buoyancy, and much of the energy released is transferred outside the immediate combustion zone. In contrast, the solid phase oxidation (C) of glowing and smoldering combustion retains most of the energy in the combustion zone.

The gas phase oxidation of volatiles as flame will occur well above the fuel bed due to the buoyancy of the heated gases released during thermal degradation and, thus, the efficiency with which the heat and combustion products are transferred to the fuel bed will be greatly reduced compared to oxidation of solid phase char, which is not as exposed to such mechanisms. Indeed, this gas phase process is directly affected by the free-air stream (i.e. the wind) in and around the combustion zone and is often particularly turbulent. Similarly, the gas–solid interface reactions of the oxidation of char may also be affected by the fluid dynamics in and around the combustion zone.

However, the effect of the interaction with the free air stream in and around the combustion zone is not just in the impact on the transfer of heat from the gas phase/gas phase and gas phase/solid phase oxidation reactions to the fuel bed but also the active cooling of the fuel bed and combustion zone. The temperature of the free-air stream will be that of the ambient environment, particularly in the initiation phase of combustion, and this dramatically cooler air (compared to that of the combustion zone within the fuel bed) can act to remove heat from the thermally degrading fuel via convective cooling. Thus, the free-air stream acts to

disperse the heat and products released in the flaming combustion reactions but also to remove heat from the thermally degrading fuels.

The solid phase/gas phase oxidation of the char is likely to be less affected by the dispersal of heat and convective cooling of the wind because it is within the combustion zone for the most part and, thus, sheltered. However, given the relatively slow rate of these reactions, when the char does oxidize, the heat that is released from these reactions is likely to be at some distance from the leading edge of the combustion zone and thus not play a large role in fires spreading with the wind. At the rear of the fire, however, where the combustion zone is propagating into the wind, the char oxidation process is likely to be more open to the effects of the ambient wind, which may have a significant effect on combustion and, thus, the behavior of the fire on this segment of the perimeter.

The nature of the interaction of the ambient wind field with the combustion zone of a free-spreading fire will depend on the location of the section of the perimeter in question in relation to the direction of the wind. Sections of the fire perimeter that are open to the full influence of the ambient wind, such as the rear of a fire, will have more effective convective cooling of the combustion reactions and thus be more likely to be dominated by the charring and glowing/smoldering pathway. Sections of the perimeter that are somewhat sheltered from the effect of the ambient wind, such as the head of a fire, will have less effective convective cooling, be hotter, and be more likely to be dominated by the volatilization and flaming pathway. The flanks of a fire perimeter will alternate between both conditions as fine scale changes in wind direction alternate fire behavior at the flank between that of heading fire and backing fire.

1.4 Physical Evidence of Environmental Interactions with Combustion Processes

This penultimate section provides some interpreted physical evidence for both the combustion processes discussed in Section 1.2 as well as the interactions of these processes with the environment around them, as discussed in Section 1.3. These are sourced from studies of large-scale free-burning experimental fires as well as small-scale combustion wind tunnel experiments.

1.4.1 Fire Perimeter Propagation

The primary outcome of the environmental interactions with the chemistry of combustion, particularly for a free-spreading fire burning in uniform fuels under consistent conditions, is changes in the pathways of combustion and the resulting behavior of fire around the fire perimeter. Figure 1.6 shows a time-series of aerial

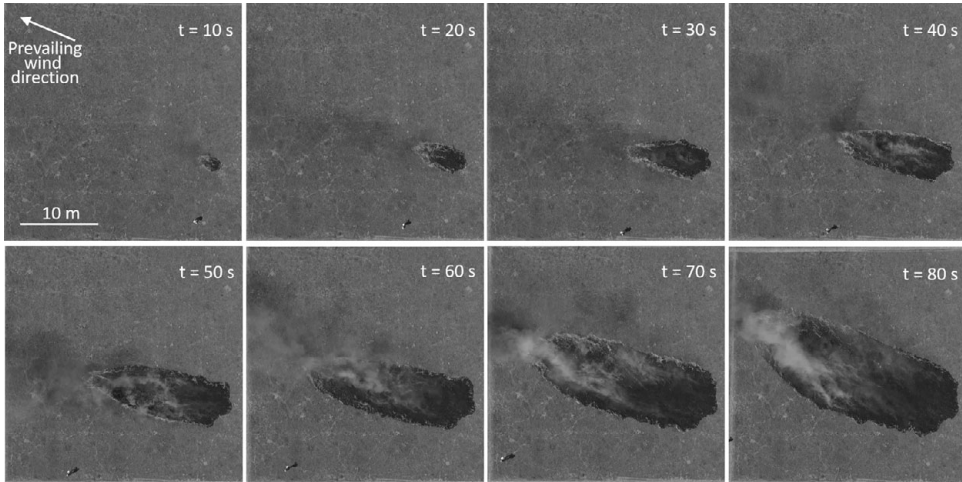


Figure 1.6 Time-series of aerial photographs of the growth of experimental fire Braidwood E14 in grass fuels ignited at a point in a 33×33 m plot, commencing 10 seconds after ignition. The growth of the fire in area, perimeter length, and forward rate of spread increases with time as the fire responds to slight changes in the direction of the wind. Conditions for experiment were: grass height 20 cm, grass curing 90%, dead fuel moisture content 7.5% (oven-dry weight), air temperature 301 K (28°C), relative humidity 30%, prevailing mean wind speed at 10 m 17.9 km h^{-1} , maximum interval rate of spread 2.16 km h^{-1} .

A black and white version of this figure will appear in some formats. For the color version, please refer to the plate section.

photographs taken from a remotely-piloted aircraft of an experimental fire burning in continuous grassy fuels after being ignited at a point (Cruz et al. 2015). From the moment of ignition, the fire exhibits nonisotropic spreading behavior determined by the direction of the wind, with the downwind sections of the fire perimeter spreading faster than those burning upwind. Despite the uniformity of the fuel, the direction of the wind imposes a difference in the combustion processes and the formation of flaming combustion. These differences then subsequently lead to a disparity in the heat release and propagation rates around the fire perimeter. The fire quickly develops the typical elliptical shape associated with free-burning fires that steadily grows in size, with slight changes in shape as it responds to minor changes in wind direction.

The rear of the fire, most open to the prevailing ambient wind, exhibits the least energetic flame and fire behavior. The head of the fire, sheltered somewhat from the ambient wind by the presence of the fire, the plume, and the burnt ground upwind of it, exhibits the most energetic flame and fire behavior. This inequality between the upwind and downwind sections of the perimeter is clearly the result of the different heat release and transfer rates, but the cause of these differences is

solely the consequence of the competition between the different thermal degradation pathways. The flank sections of the fire perimeter alternate between the behavior of heading and backing fires, depending on minute shifts in the direction of the wind (Cheney 2008).

In the latter stages of this fire, the combustion at the rear of the fire appears for all intents and purposes to have ceased, albeit for a very inconsequential level of flame that is barely, if at all, visible. However, combustion at this section of the perimeter continues and if a significant expedient change in wind direction was to occur, the section would rapidly return to full flaming combustion to become the head.

The changes in combustion dynamics around the fire perimeter appear to be driven primarily by changes in temperature in the combustion zone, driven by the strong temperature dependence of the thermal degradation reactions.

1.4.2 Char Oxidation

The presence of char in a spreading fire is not readily apparent until it undergoes oxidation, either as glowing combustion in the kinetic-controlled regime or smoldering combustion in the diffusion-controlled regime. Even then, the presence of glowing combustion is not easily visible, particularly in the daytime. It is only in comparing the residual combustion behind a spreading fire front during daylight-equivalent illumination with that of semi-darkness that the extent of glowing combustion of char becomes apparent. Figure 1.7 presents images of two free-spreading fires burning through a continuous bed of dry eucalypt forest litter in a large combustion wind tunnel (Sullivan and Matthews 2013; Mulvaney et al. 2016). In these experiments (conducted at different times with slightly different environmental conditions) dead fine fuels comprised of fallen leaves, bark, and twigs (<6 mm diameter) from a local dry eucalypt forest with a fuel load of approximately 1.2 kg m^{-2} were burnt in a constant wind of $\approx 1.5 \text{ m s}^{-1}$ flowing from right to left. Each fire was ignited from a 1,500-mm-long line at the upwind end of the 4.0 m fuel bed.

Figure 1.7(a), taken approximately 2 minutes 35 seconds after ignition, shows the head fire reaching the end of the fuel bed and the majority of the remainder of the fuel bed converted mostly to ash, evident by the predominance of a paler coloring within the darker color of combustion residue, with some residual burning in denser patches of fuel. Also present in the mostly consumed fuel bed are patches of glowing combustion, evident by the presence of red embers. Figure 1.7(b) shows a very similar scene, albeit for a different fire, but this time with the overhead lights turned off (the lower ambient light levels to which the camera self-adjusted). In this image, much more of the glowing combustion present in Figure 1.7(a) but not apparent is now clearly visible well behind the fire front. Little smoke is visible from these locations of glowing combustion.

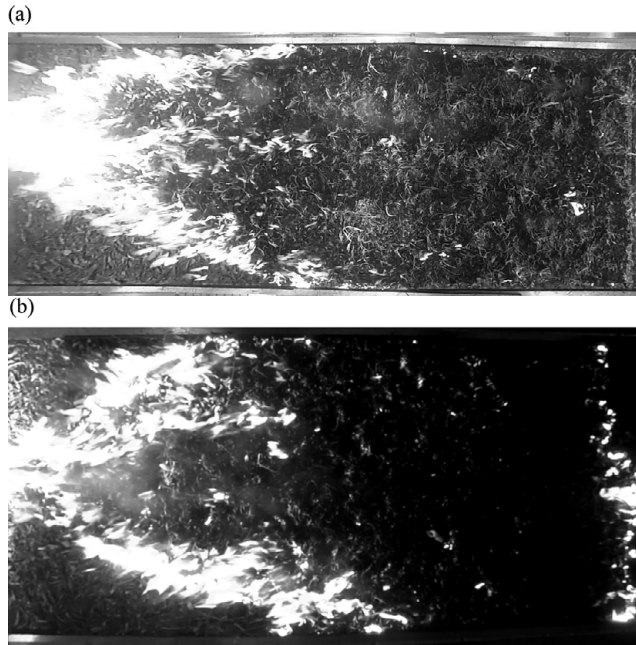


Figure 1.7 Photographs of two different experimental heading fires burning in dry eucalypt forest litter in the CSIRO Pyrotron combustion wind tunnel with wind blowing right to left. (a) Image taken 155 seconds after ignition. Most of the fuel bed has been consumed with only a small amount of residual flaming and two sources of smoldering combustion visible behind the flame front. (b) Image of another fire burning under similar conditions after the wind tunnel overhead lights have been turned off, revealing a multitude of glowing combustion behind the front. A black and white version of this figure will appear in some formats. For the color version, please refer to the plate section.

Thus, even when not apparent, there is considerable glowing combustion of char formed in or soon after the passage of the flame front. The slow rate of the solid phase oxidation means that it remains present long after the passage of the flames.

The presence of smoldering combustion is also apparent in these figures as well as those of Figure 1.6, as thin white smoke generated from residual combustion well behind the flame front. Figure 1.8 shows a time-series of aerial photographs taken from a remotely-piloted aircraft of an experimental fire burning in harvested wheat fuels after being ignited along a 33-m-long line on the upwind edge of a 50 m × 50 m plot (Cruz et al. 2020). The fire spreads energetically under a relatively strong wind with flames reaching 3–4 m in height and flames 5–10 m deep. The presence of smoldering combustion in the wake of the passage of the flame zone does not become apparent until more than 37 seconds after ignition. Prior to this there may be glowing combustion but it is not visible in the daylight nor is there any trace of visible emissions as observed in the combustion wind

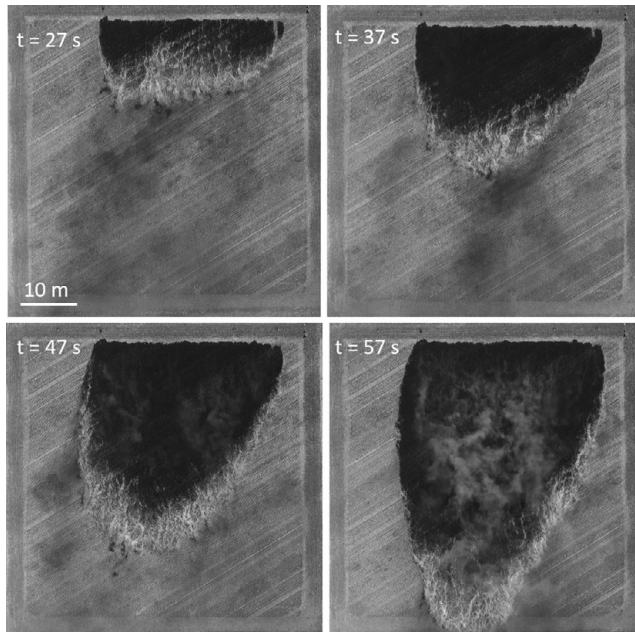


Figure 1.8 Time-series of aerial photographs of the growth of experimental fire Wallinduc WH2 in harvested wheat fuels ignited at a 33-m-long line on the up wind edge of a 50 m × 50 m plot, commencing 27 seconds after ignition. Conditions for experiment were: grass height 20 cm, grass curing 90%, dead fuel moisture content standing fuel 8.7% oven-dry weight, air temperature 303 K (30°C), relative humidity 23%, mean wind speed at 10 m 29.2 km h⁻¹, maximum interval rate of spread 5.1 km h⁻¹.

tunnel. Only after time sufficient for the glowing combustion open to the ambient wind upwind of the fire zone to transition from the kinetically-controlled regime to the diffusion-controlled regime does the presence of the char oxidation (visible as the thin white smoke again similar to that in the combustion wind tunnel) become apparent.

1.4.3 Fire Spread Mode: Heading, Backing, Flanking

While it is tempting to assign a particular thermal degradation pathway to a particular mode of fire spread (i.e. heading, backing, or flanking), the stochastic nature of the chemical processes involved does not readily allow this as both thermal degradation pathways – volatilization and charring – may occur simultaneously within the one fuel element (but not the same strand of cellulose). Additionally, as observed in the examples in Figures 1.6–1.8, the subsequent oxidation reactions of one thermal degradation product may obscure the presence

of the other. As a result, it may be simpler to use the bulk presence of a particular behavior to ascribe the dominating thermal degradation pathway. In this way, if flaming is dominant, then combustion may be described as being dominated by the volatilization pathway or, if smoldering or glowing combustion is dominant, then charring may dominate combustion. However, such a description does not convey the true nature of the combustion.

Figures 1.9–1.11 illustrate the distinct natures of the combustion of heading, flanking, and backing fires, respectively, burning in dry eucalypt litter under constant conditions of a 1.5 m s^{-1} wind in a combustion wind tunnel. Figure 1.9 shows a time series of a heading fire propagating with the wind at a speed of about 80 m h^{-1} . Figure 1.10 shows a time series of a flanking fire propagating parallel to the wind at a speed of about 6 m h^{-1} . Figure 1.11 shows a time series of a backing fire propagating against the wind at a speed of about 5 m h^{-1} . The nature of the changes in the combustion chemistry resulting from the nonisotropic forcing of the thermal degradation kinetics is clearly apparent, with the heading fire producing much more energetic flames.

The flanking and backing fires have flames of similar dimension and spread rate, with the flames of the flank fire being less uniform and spreading slightly faster than those of the backing fire. The oxidation of charred fuel formed in the

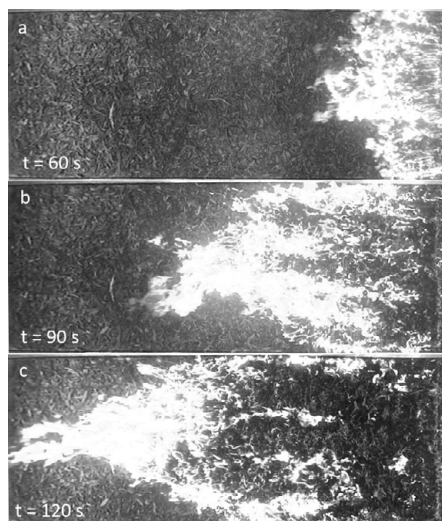


Figure 1.9 Time-series of plan-view photographs of the growth of an experimental heading fire burning in dry eucalypt litter in a 1.5 m s^{-1} wind and moisture content of 7–8% oven dry weight. The fire was ignited from a 1.5-meter line on the upwind edge of a 4-meter fuel bed. Average rate of spread was 80 m h^{-1} . Air flow is from right to left: (a) 60 seconds after ignition, (b) 90 seconds after ignition, (c) 120 seconds after ignition.

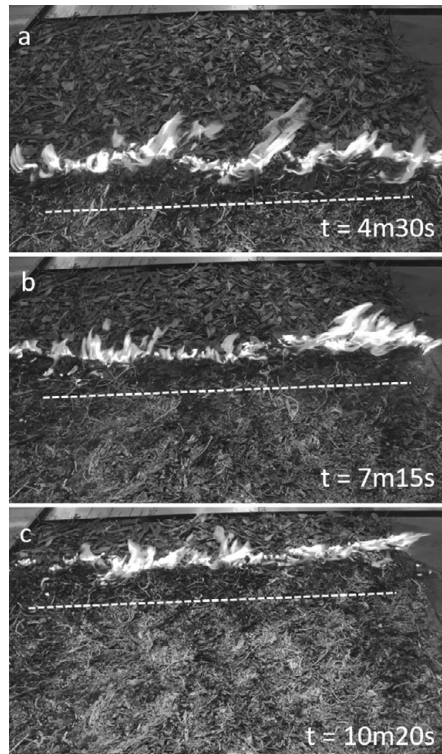


Figure 1.10 Time-series of oblique view photographs of the growth of an experimental flank fire burning in dry eucalypt litter in a 1.5 m s^{-1} wind and moisture content of 7–8% oven dry weight. The fire was ignited from a 1.5 meter-line on the parallel edge of a 1.5-meter fuel bed and had a mean spread rate of 6 m h^{-1} from bottom to top. Air flow is from left to right: (a) 4 minutes 30 seconds after ignition, (b) 7 minutes 15 seconds after ignition, (c) 10 minutes 20 seconds after ignition. The white dashed line roughly indicates the divide between the char zone undergoing oxidation and the ash zone that has completed oxidation. A black and white version of this figure will appear in some formats. For the color version, please refer to the plate section.

flame zone is recognizable in the progression of the zone of charred fuel immediately behind the flame zone immediately followed by a zone of white ash, delineated in Figure 1.10 by a dashed white line. The presence of such a zone of charred fuel is not so apparent in the images of the backing fire, possibly due to the obscuring of it by the flames leaning over the burnt fuel and also by the much slower rate of progression of the flame front, giving the false impression that fuels are converted directly to char.

While distinct differences in the behavior and spread can be seen in each fire spread mode, the impact on the residual ash is less obvious. Figure 1.12 shows images of the fuel bed taken after the completion of each type of fire. No

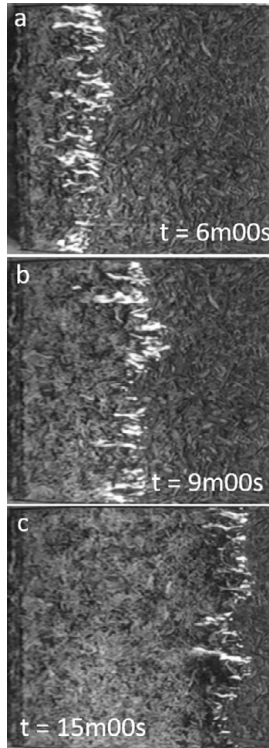


Figure 1.11 Time-series of plan-view photographs of the growth of an experimental backing fire burning in dry eucalypt litter in a 1.5 m s^{-1} wind and moisture content of 6–7% oven dry weight. The fire was ignited from a 1.5-meter line on the downwind edge of a 2-meter fuel bed and had a mean spread rate of 5 m h^{-1} . Air flow is from right to left, spread is left to right: (a) 6 minutes after ignition, (b) 9 minutes after ignition, (c) 15 minutes after ignition.

discernable difference can be easily detected between the fire spread modes illustrated here. This is primarily because, after combustion is completed, either flaming or glowing/smoldering oxidation, all fuels are generally equally consumed regardless of spread mode. This may not be the case where conditions are more marginal or the combustion process is incomplete. The fact that a char zone is visible in the flank fire spread, between the flame zone and ash zone, suggests that if the residual glowing/smoldering combustion was interrupted in some way, then the char zone would remain.

1.4.4 Emissions

It has been generally accepted (Andreae and Merlet 2001; Andreae 2019) that smoldering combustion is associated with emissions of CO and flaming

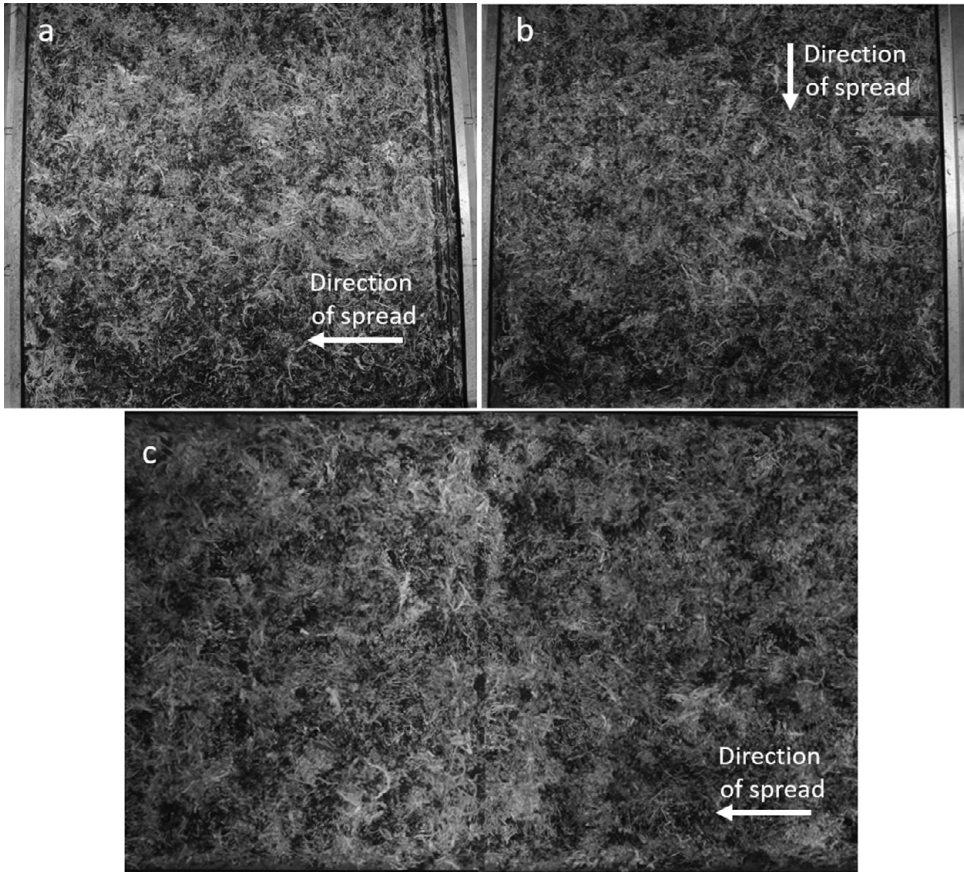


Figure 1.12 Plan views of the dry eucalypt litter ash beds after burning in a combustion wind tunnel by different fire spread modes: (a) flanking fire, (b) backing fire, (c) heading fire.

combustion is associated with emissions of CO_2 . And, since smoldering combustion is generally associated with low intensity fires such as backing fires and flaming combustion is generally associated with heading fires, then backing fires should, by inference, produce more CO than heading fires, and heading fires should produce more CO_2 than backing fires. However, the lack of distinct difference in ash observed in Figure 1.12 is also mirrored by analysis of emissions factors for carbon species (i.e. CO_2 , CO, and CH_4) by fire spread mode, as shown in Figure 1.13 and reported by Surawski et al. (2015).

It can be seen that heading fires produce both more CO_2 and more CO than flanking or backing fires. Backing and flanking fires produce roughly similar amounts of these emissions. In contrast, heading fires produce significantly less carbon residue than either flanking or backing fires, a result of the consumption of

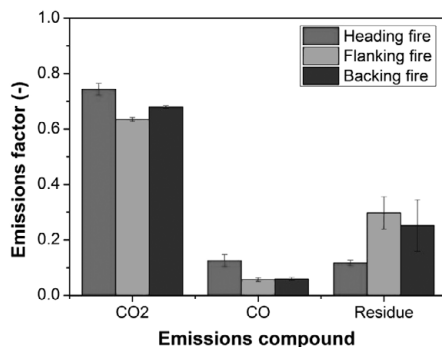


Figure 1.13 Carbon emissions factors, CO₂ and CO, and burnt carbon residue (g kg⁻¹ fuel consumed) for different fire spread modes. Source: Surawski et al. (2015)

more biomass more generally in oxidation reactions as well as a greater tendency to continue combustion through to completion. While the flashy flames of a head fire suggest all combustion is driven by the production of volatiles, it is clear that the increased temperatures associated with such spread also result in increased reaction rates for production of char. The rapid propagation of the flame zone of most head fires leaves most of the slower oxidation of the char to happen well behind the flame zone and thus exposed to the cooler ambient air flowing over the previously burnt ground, as seen in Figures 1.8 and 1.9. This then results in the char oxidizing in the kinetically controlled regime, producing more CO.

In contrast, the formation of both the volatile and char in flanking and backing fires is much reduced due to the relatively cooler combustion environment and the exposure to ambient-temperature wind resulting in lower temperatures in the combustion zone and thus lower reaction rates, leaving a greater proportion of the original fuel as not fully combusted in the form of pyrogenic carbon (Surawski et al. 2020). The subsequent oxidation as both flaming and smoldering or glowing combustion also tends to be more confined, less exposed to cooling ambient conditions, and thus more complete.

1.5 Concluding Remarks

We have seen that both the chemistry of biomass fuel and the nature of its combustion through thermal degradation and oxidation reactions is quite complex. The competitive thermodynamics of the thermal degradation reactions as a direct consequence of the nucleophilic competition between the volatilization pathway and the charring pathway as well as differences in the activation energies and enthalpies of these pathways, the high level of sensitivity of the rates of these

reactions to reactant temperature, and differences in the magnitudes and locations of heat released during oxidation explain much of the apparent capriciousness of biomass combustion.

The interaction of this complex set of competing and interacting reactions with the often-changing environment around a fire, particularly that of the ambient wind, results in a highly dynamic combustion situation peculiar to fires burning in the open.

It is the interaction of these factors that help explain many of the observed behaviors of free-burning wildland fires such as the shape of a fire's perimeter, the change in behavior around that perimeter with respect to the direction of the wind, the influence the wind has on the behavior and spread of a fire, and the importance of the different combustion pathways in sustaining spread, particularly under marginal conditions.

It is also the interaction of these factors that help explain our initial question as to why blowing on the embers of a fire when it is being lit helps. As we have seen, the actual initiating reactions are anaerobic and so blowing does not critically supply oxygen. Blowing acts to cool the incipient reactions sufficiently to drive the reaction into the charring pathway. This pathway, being exothermic, generates more heat (and, yes, some oxidation of the char as glowing combustion) which, when the blowing stops, is hopefully enough to push the reaction process into the endothermic volatilization pathway and subsequent flaming combustion.

If the blowing is too vigorous it can cool the degrading fuel too much and stop the thermal degradation reactions. If the blowing is not vigorous enough or stops too early, the transition of the reactions to volatilization will remove too much heat from the system and act to stop that thermal degradation pathway.

If we return to our initial diagram of combustion and sustained spread (Figure 1.1), we can see that it is not sophisticated enough to capture this fundamental aspect of biomass combustion, particularly for understanding the behavior and spread of free-burning fires in wildland fuels. Figure 1.14 is an attempt to revise this diagram to include these aspects but still be relatively simple.

In this revised conceptual model, fuel still undergoes drying from an ignition or pilot source. Under continued application of this heat, the fuel thermally degrades, either into hydrolyzed cellulose under the exothermic, lower activation energy reaction pathway, or into levoglucosan-end via the endothermic, higher activation energy pathway. If sufficient heat is created in the hydrolyzed cellulose pathway, the reaction may be pushed toward the endothermic pathway. Continued heating results in either char from the hydrolyzed cellulose or volatilization of the levoglucosan-end cellulose. Again, if enough heat is generated from the charring pathway, the thermokinetics may be driven into the levoglucosan-end and volatilization pathway. Conversely, if too much heat is lost from the volatilization

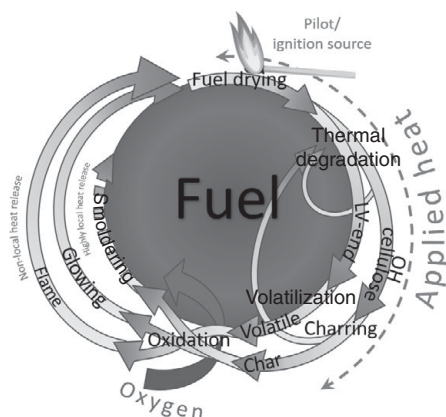


Figure 1.14 A revised version of the conceptual model presented in Figure 1.1 with the distance from the center of the circle indicating the magnitude of enthalpy. In this conceptual model, the fundamental competitive thermokinetics between the formation of levoglucosan-end cellulose (LV-end) and hydrolyzed cellulose (OH cellulose) during thermal degradation drives volatilization and the formation of volatile and charring and the formation of char, respectively. Heat formed in the production of hydrolyzed cellulose or char may be sufficient to drive the reaction toward the endothermic volatilization pathway. These thermal degradation products may then undergo oxidation in the form of flame in the case of volatile (which as a gas–gas reaction is open to turbulent mixing) and glowing or smoldering combustion in the case of char. The heat released by glowing or smoldering is highly localized within the fuel bed, while that released by flame may be some distance from the fuel bed.

A black and white version of this figure will appear in some formats. For the color version, please refer to the plate section.

pathway, the thermokinetics may be driven back into the hydrolyzed cellulose pathway, or thermal degradation may cease completely.

The thermal degradation products may then oxidize in the presence of oxygen, liberating much more heat into the system. In the case of volatiles, this is a gas–gas reaction and thus open to turbulent mixing, which may promote or inhibit oxidation. This heat is generally released well away from the fuel bed where the volatile was formed and increases the amount of adjacent fuel exposed to heating and thus the rate of spread of the fire. In the case of char, oxidation follows either the kinetic-controlled regime in which the char oxidizes in smoldering combustion or the diffusion-controlled regime in which the char oxidizes in glowing combustion. The amount of heat released in the former is much less than the latter and little of it may result in heating of adjacent fuels. In either case, the rate of propagation of a fire edge is much slower than that of flaming combustion.

Understanding the factors that determine the amount of heat released and rate at which it is transferred to adjacent fuel in order to predict the speed at which a fire

may propagate is the primary objective of wildland fire behavior science and necessarily involves a broad range of disciplines, including radiant and convective heat transfer, fluid dynamics, and meteorology, many of which are covered in other chapters of this textbook.

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