1

Wildland Fire Combustion Dynamics

The Intersection of Combustion Chemistry and Fluid Dynamics

ANDREW L. SULLIVAN

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 unstoppable 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

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.](image-url)
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 \textit{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 (\([C_6H_{10}O_5]_n\) of \(\beta\)-D-glucose monomers (\(C_6H_{12}O_6\)) (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

![Cellulose structure](image.png)

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 \(C_1\) and \(C_2\) 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 (β(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):

$$r = A \exp\left(\frac{-E_a}{R T}\right),$$

(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 J K$^{-1}$ 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, $\Delta H_R$ (kJ mol$^{-1}$), is the change in enthalpy when a reactant forms a product following a reaction: $\Delta H_R = H_f(products) - H_f(reactants)$,
where $H_f$ is the standard state heat of formation of the reactant or product. When $\Delta H_R$ 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 $\approx 110 \text{ kJ mol}^{-1}$ (Di Blasi 1993; Diebold 1994), a collision frequency of $6.7 \times 10^5 \text{ s}^{-1}$ and a reaction enthalpy of $\approx -1$ to $-2 \text{ kJ g}^{-1}$ (Milosavljevic et al. 1996; Ball et al. 1999a).

$$\text{F} \rightarrow \text{heat} \rightarrow \text{Char} + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{heat}. \quad (1.2)$$

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 $\text{C}_1$–$\text{C}_4$ 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 $\text{C}_1$ 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, decarboxylation, 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 $\approx 200 \text{ kJ mol}^{-1}$ (Di Blasi 1993; Diebold 1994), a collision frequency of $6.9 \times 10^{22} \text{ s}^{-1}$, and a reaction enthalpy of $\approx -1$ to $-2 \text{ kJ g}^{-1}$ (Milosavljevic et al. 1996; Ball et al. 1999a).

$$\text{F} + \text{H}_2\text{O} \rightarrow \text{heat} \rightarrow \text{OH} \rightarrow \text{heat} \rightarrow \text{Char} + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{heat}. \quad (1.3)$$

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 $\text{C}_1$ through donation of the electron density on the $\text{C}_6$ 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-