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Thermal decomposition and combustion chemistry of cellulosic biomass

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ABSTRACT

Emissions from open vegetation fires contribute significantly to global atmospheric dynamics. However, the value of improved quantification of areas burned and knowledge of the composition and structure of biomass fuel is compromised in current emissions modelling and measurement by inadequate understanding of the chemistry of biomass combustion. Physical models of the behaviour of open vegetation fires also have relied on over-simplified combustion chemistry. Considerable knowledge of the thermal degradation and combustion of cellulose, the major constituent of the terrestrial biomass, exists but has yet to make an impact in the fields of atmospheric emissions monitoring and open vegetation fire behaviour modelling. This article provides an interpretive summary of the current knowledge of the chemistry and dynamics of the processes of thermal degradation and combustion of cellulosic biomass and discusses the role of these processes in determining the emissions from, and behaviour of, open fires in such fuels. The important role of competitive thermal decomposition is emphasised, as a driver and regulator of emissions and fire spread (short-term, local effects) and global carbon distributions (long-term, global effects).

1. Introduction

Knowledge of the sources, sinks and cycling of atmospheric carbon is essential for understanding impacts of greenhouse gases (GHG) on climate globally and air pollution regionally and locally. Biomass burning, both naturally occurring and anthropogenic, is an important modifier of atmospheric GHG (Seiler and Crutzen, 1979; Crutzen and Andreae, 1990). Open burning sources emit greater amounts and a wider distribution of chemical compounds, aerosols and particulates than controlled or enclosed fires (Andreae, 1991). Freely burning wildland or bushfires consume 60% of all biomass fuel, are responsible for 61% of the emissions from biomass burning (Andreae and Merlet, 2001) and, during large and catastrophic events, can inject smoke and gases into the upper atmosphere (Dirksen et al., 2009) that may persist for long periods. Accurate estimates of open vegetation fire emissions are necessary to predict GHG impacts on the atmosphere and on climate change.

Current methods for estimating emissions from biomass burning are based on simple models of fuel composition and combustion. A commonly calculated quantity is emission ratio (ER), the emitted mass of a species per mass of reference compound, usually CO_2 for flaming combustion or CO for smouldering combustion, released during combustion (Delmas et al., 1995). This was based on experimental results of Crutzen and Andreae (1990) who studied the combustion of grass in a chamber and found that CO_2, NO_x and N_2O peaked during flaming combustion and CO, CH_4 and other gases peaked during subsequent smouldering combustion. The ratio of CO_2 emission to total C in the unburned fuel is called the combustion efficiency: the higher the ratio, the more efficient the combustion is considered.

A variety of sampling techniques are employed in laboratory experiments and field measurements of biomass fire emissions (Ward and Radke, 1993). Wide variations in reported ER values have been found to correlate with the efficiency of combustion (Yokelson et al., 1996), and Ward et al. (1996) found that the variation in calculated ER values could be narrowed by considering combustion efficiency with respect to the sum of CO and CO_2 emissions (termed the modified combustion efficiency) rather than total C; however significant variation in ER remains for each type of biomass fuel.

Average values of ER are often given for particular biomass fuels in order to facilitate estimates of global emissions from burning these fuels. But the wide variations in measurements of emissions from open biomass fires raises uncertainties about their validity (Robinson, 1989). These uncertainties are compounded by a generally poor understanding of biomass combustion (Lobert and Warnatz, 1993), which tends to negate the value of improvements

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in quantification of burned areas and knowledge of the structure and chemistry of biomass fuels.

Similarly, simulating the behaviour and spread of bushfires across the landscape also requires a good understanding of biomass combustion. The behaviour of a bushfire is determined by thermochemical processes, such as reaction rates and enthalpies and chemical and thermal feedbacks, and by physical processes such as the transfer of heat to surrounding unburnt fuel and gas phase convections. The interactions of these processes and the high variability of fuel, wind and topography complicate the behaviour of the fire (Sullivan, 2009). Many physical bushfire models (e.g. Linn et al. (2002); Mell et al. (2007)) aim to simulate the interactions between flames and the atmosphere and emphasise high-fidelity modelling of the flows in the domain. However, a one-step reaction representing conversion of solid fuel to gas phase products is often employed. While this may be computationally economical it removes the potentially important chemistry of cellulosic biomass thermoconversion that may play a role in determining fire behaviour.

Functional understanding of the thermokinetics of cellulosic thermal decomposition and combustion has existed for many years (e.g. Broido (1976); Bradbury et al. (1979)), and underpins many industrial processes that use biomass fuels. These advances in biomass combustion knowledge have not yet percolated into the study of emissions from open vegetation fires or their behaviour. In this article we précis the chemistry of the key processes involved in the thermal degradation and combustion of cellulosic biomass fuel with the aim of raising awareness of the complexity of the reaction pathways inherent in this fuel, involving chemical and thermal feedbacks.

We discuss the mechanisms by which these processes may contribute to the apparent capricious nature of emissions from open fires and elucidate the central role of competitive thermal degradation in influencing emissions of biomass fires globally and in shaping the propagating fire front locally. While it may not be feasible or even necessary to incorporate all chemical reactions involved in the combustion of biomass, a thorough understanding of the chemistry will enable development of better informed models of emissions and fire behaviour, resulting in improved understanding of the global carbon cycle and improved performance of fire behaviour predictions.

2. Chemical composition of biomass fuels

The fuel for open biomass fires consists primarily of fine leaf litter, twigs, bark, small wood, grasses, and shrubs (Gould et al., 2011). Under more severe fire weather conditions it can also include other material such as fallen logs and live tree canopies that would not normally burn. Chemically the fuel is composed mainly of cellulose, hemicelluloses and lignin polymers (represented in the general biomass emissions and fire behaviour literature as an unstructured empirical carbohydrate: $(CH_2O)_n$ (Seiler and Crutzen, 1979; Andreae, 1991)). Other components include minerals, water, salts, and organics such as proteins, starches, nucleic acids, oils, and resins. In most fuels, cellulose is the major constituent (Table 1).

While each constituent will play some role in combustion, the chemistry of biomass fires is dominated by that of cellulose thermoconversion. Cellulose is the most widely studied pure substance in the fields of biomass pyrolysis and combustion and understanding of its combustion is generally mature and stable. For these reasons the remainder of this article will focus on cellulose as a model proxy for biomass in the form of "cellulosic" biomass. While some discussion is given on the combustion of hemicelluloses and lignin, few studies have been carried out on these components in isolation (Di Blasi, 1998) and these remain areas of active research. Until understanding of these processes matures, detailed knowledge of cellulosic biomass combustion is an important first step in developing a more complete understanding of biomass combustion.

Table 1
Approximate analysis of some biomass types and species (Shafizadeh, 1982; Mok et al., 1992).

Type or species	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Other[a] (%)
Shafizadeh (1982):				
Softwood	41	24	28	7
Hardwood	39	35	20	7
Wheat straw	40	28	17	15
Rice straw	30	25	12	33
Bagasse	38	39	20	3
Mok et al. (1992):				
Eucalyptus saligna	45	15	25	15
Eucalyptus gummifera	38	16	37	9
Sweet sorghum	36	18	16	30
Sugar cane bagasse	36	17	17	30
Populus deltoides	39	21	26	14

[a] Other includes organic compounds such as starch and inorganic material such as salts, minerals, and water.

2.1. Cellulose

The cellulose molecule is an unbranched polysaccharide of D-glucose[1] monomers linked in $\beta(1\rightarrow4)$ configuration. The structure of glucose is shown in Fig. 1(a) and the $\beta(1\rightarrow4)$ configured link is illustrated in Fig. 1(b). Cellulose has the empirical formula $H(C_6H_{10}O_5)_nOH$ where n is the number of monomer units, from 200 to ~10,000, with corresponding molecular weights of 32,400 to more than 1,600,000 (O'Sullivan, 1997).

The natural cellulose polymer is a straight chain with no coiling. Parallel chains of cellulose are stabilised by inter-chain and intra-chain hydrogen bonds, non-covalent linkages in which surplus electron density on hydroxyl group oxygens is distributed to hydrogens with partial positive charge on hydroxyl groups of adjacent residues. The most stable (and most probable) hydrogen bonds were observed spectroscopically by Zhbankov et al. (2002), some of which are indicated in Fig. 2. Multiple chains thus bonded yield a rigid flat structure of high tensile strength, the hydrophobic faces of which allow the structures to stack (Lindman et al., 2010), and form the basis of plant cell microfibrils. Naturally occurring cellulose can exhibit regions of crystalline structure, with ordered alignment of both inter- and intra-molecular hydrogen bonds, and amorphous structure of higher energy in which the hydrogen bonding is disordered but not entirely random (Broido et al., 1973; O'Sullivan, 1997).

Because of this structure, cellulose is an extraordinarily stable polysaccharide. Despite its capacity to form hydrogen bonds it is insoluble in water; the rigidity of the structure and the hydrophobic faces that allow transversely hydrogen-bonded chains to stack restrict the entropy of mixing so that a negative free energy change of dissolution is not achieved (i.e. dissolution in water is forbidden thermodynamically) (Lindman et al., 2010). Cellulose is relatively resistant to weak acid and base hydrolysis, and the glycosidic linkages are not readily accessible to the hydrolytic cellulase enzymes from microorganisms and fungi. This means that

[1] The D-prefix refers to the configuration around the lowest chiral carbon of a monosaccharide species, where the carbonyl carbon (C-1 of glucose) is designated as the highest. The enantiomer or mirror image of a D-species is known as the L-species. L-glucose has no biological significance.

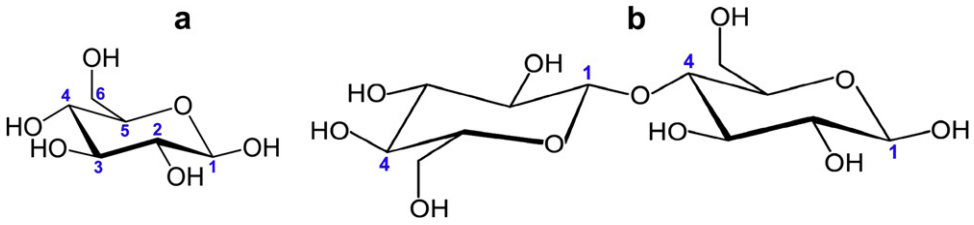

Fig. 1. (a) Structural formula of D-glucose, showing the lowest energy "chair-like" conformation of the ring. By convention the structure is drawn as shown, with a carbon atom implicit at each vertex and hydrogen atoms bonded directly to carbon not shown. Carbon atom numbering convention is shown. (b) Structural formula of 2-unit fragment of cellulose chain, known as cellobiose, showing the $\beta(1\rightarrow4)$ glycosidic bond.

cellulosic fuels on the ground can take months to years to degrade through biological action and need to be heated to well above normal ambient temperatures to degrade thermally.

2.2. Hemicelluloses, lignin and other components

Hemicelluloses are formed as copolymers of glucose and a variety of other, mainly carbohydrate, monomers. They are amorphous and have a lower degree of polymerisation than cellulose. Xylan is the main hemicellulose of hardwoods and glucomannans is the main hemicellulose of softwoods (Shafizadeh, 1982). Hemicelluloses have been shown to soften and melt under controlled heating before volatilisation commences (Fisher et al., 2002).

Lignin is a cross-linked, phenolic polymer of p-hydroxyphenyl-propanoid monomers connected by C–O and C–O–C links and may be cross-linked to hemicelluloses (Lee, 1997). It stiffens the walls of wood cells and is hydrophobic, amorphous and of high molecular weight (Shafizadeh, 1982). The phenolic groups may be substituted with methoxy groups, which modify the physical properties of the wood. Lignin is extremely resistant to chemical and enzymatic degradation and decomposes slowly over a broad temperature range (Branca et al., 2005). The methoxy groups may be readily dissociated to produce methyl radicals and ultimately methane.

Few studies have been carried out on the combustion of hemicelluloses or lignin in isolation (Di Blasi, 1998). The thermal degradation kinetics of whole biomass is considered to be the sum of the contributions of its main components (Güllü and Demirbaş, 2001), although minor components can influence the kinetics. Inorganic substances such as salts, metals, phosphates and other trace elements in the biomass can catalyse or inhibit the thermal degradation of biomass (Di Blasi, 1998; Müller-Hagedorn et al., 2003; Scarff and Westoby, 2008).

3. Biomass combustion involves three classes of chemical processes

In the context of biomass burning the term "combustion" is used loosely to describe the overall oxidative conversion of unburnt solid fuel to gases, ash and residue. Often this is represented as the single process $(CH_2O)_{n(s)} + nO_{2(g)} \rightarrow nCO_{2(g)} + nH_2O_{(g)}$ (Byram, 1959; Seiler and Crutzen, 1979; Andreae, 1991). In fact the raw solid biomass substrate does not undergo combustion directly and two distinct types of combustion typically occur.

Byram (1959, p. 64) described three distinct stages of combustion: 1) pre-ignition, in which solid fuels are heated, dried and partially volatilised, 2) flaming combustion of the vapour-phase volatiles and CO, and 3) glowing (or smouldering) combustion of some of the char residue. In reality, however, these stages of combustion do not occur uniformly or sequentially over the fuel bed, but are intrinsically linked by nonlinear chemical and thermal feedbacks.

Initially the fuel is heated by heat transfer from adjacent, already hot or burning fuel or from a pilot source such as a flame or spark, and unbound water in and on the fuel evaporates. Thermal decomposition begins to occur in the heated fuel. This is the first class or family of chemical reactions involved in biomass combustion, which we elucidate in Section 4. There are two subsets of this largely non-oxidative family of reactions: 1) primary volatilisation of the solid cellulose substrate and secondary cracking of the volatiles to gas-phase fuels, and 2) the chemical dehydrations,

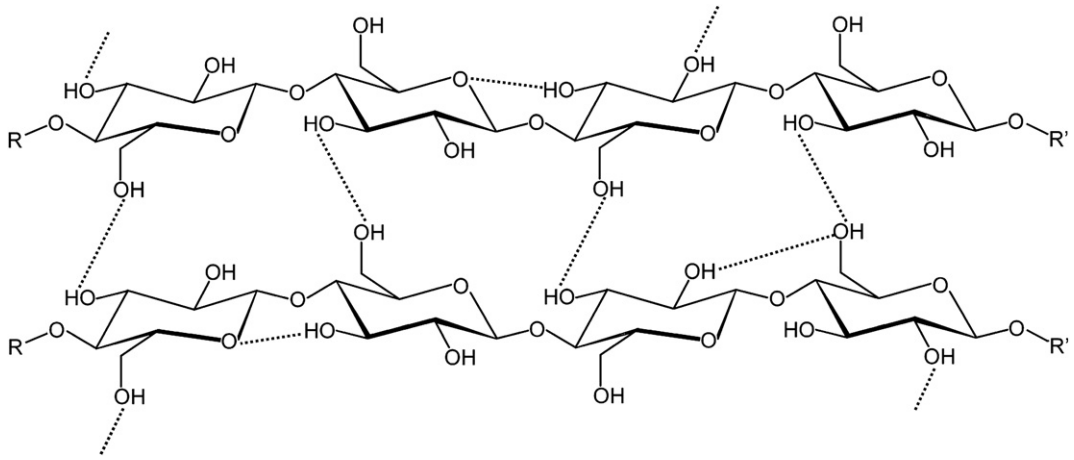

Fig. 2. A segment of neighbouring cellulose chains showing some of the intra- and inter-molecular hydrogen bonds (dotted lines) that stabilise the crystalline form of cellulose. R and R′ represent continuation of the chains.

decarbonylations, cross-linking, and aromatisation reactions that produce char and gases such as water vapour and CO.

Understanding the thermochemistry and thermokinetics that govern this family of reactions is crucial to understanding biomass emissions and fire behaviour because char formation (the product of which undergoes glowing combustion) and volatilisation (the products of which undergo flaming combustion) are reciprocally linked, or competitive, and depend on each other nonlinearly.

The second class of chemical reactions (discussed in Section 5.1) is flaming combustion. This is the oxidation in air of the hot gaseous products of volatilisation, observed as incandescent emission of visible light from excited electronic states of gaseous carbon atoms and free radical species.

The third class of chemical reactions (discussed in Section 5.2) is glowing combustion of the char, which involves heterogeneous solid-gas phase oxidation. Although char combustion is usually incomplete in biomass fires because the charred residue cools below ignition temperature, and it cannot propagate at speeds anywhere near the often furious pace of flaming combustion, it is important in fire behaviour and emissions because it can provide a reservoir of heat and involves a separate set of reactants.

4. Cellulose thermal decomposition chemistry

Most of what we know about cellulose thermal decomposition comes from experimental studies carried out under pyrolytic conditions—i.e., with exclusion of oxygen so that combustion cannot occur. As a cellulose sample is heated, trapped moisture is vaporised and heterolytic thermolysis of glycosidic bonds along the chains occurs. This reduction in the degree of polymerisation begins at around 250 °C, but in the presence of electron acceptors (which may be proton-donating acid catalysts or metal ions such as Mg^{2+}) significant thermolysis can occur at lower temperatures.

In Fig. 3 the initial thermolysis chemistry is shown for the general case where acid catalysis may occur via reversible acceptance of electrons by a proton (where, by convention, it is ignored that the free proton does not actually occur but is bound in species such as H_3O^+) from the glycosidic oxygen on the cellulose chain **A**. The electron pair forming the C-1—O′-4 bond is retained by this oxygen. The products are the carbocation **B**, which is a resonance-stabilised hybrid of two contributing structures, and the fragment **C**, which is relatively unreactive at that end. (In carbohydrate chemistry this is called the non-reducing end because, having no free or hemiacetal carbonyl group, it does not reduce Fehling's or Tollens' reagents.)

The carbocation **B** is at the heart of cellulose thermoconversion. It is a stable, relatively long-lived intermediate because electron density on the hemiacetal oxygen O-5 can be distributed to stabilise the positive carbon centre on C-1 (Ball et al., 1999). In Fig. 3 this hybrid is drawn as two structures enclosed by square brackets; this is an heuristic convention that helps us to understand a quantum mechanical object that cannot be represented by a single structure. Species **B** may undergo competing reactions to form different products. The outcome of the competition depends on the local micro-environment: if it is hot, energetic and dry, intra-molecular cyclisation is more likely, with release of levoglucosan ($C_6H_{10}O_5$) to the gas phase; in a less energetic, cooler, wetter local environment a water molecule is more likely to add to the positively charged centre, forming a hydrolysed cellulose strand that begins to char.

4.1. Volatilisation

Addition of an intra-molecular nucleophile to the resonance-stabilised positive centre on C-1 of species **B** in Fig. 3 occurs via

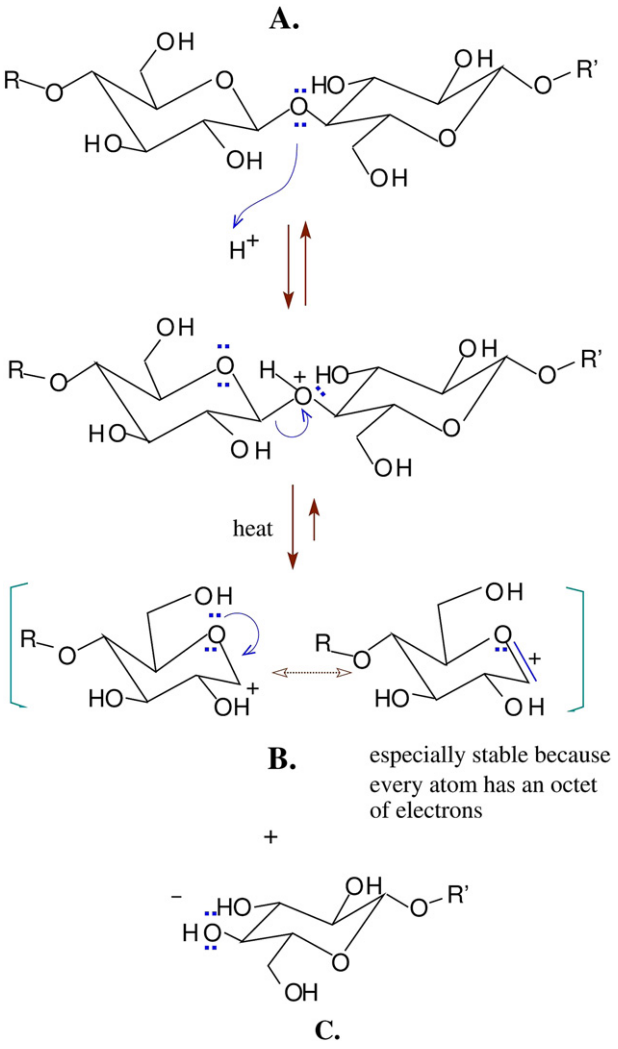

Fig. 3. Thermolysis of a cellulose chain **A** at the glycosidic C-4—C-1 bond initially produces a resonance-stabilised positively charged hybrid species **B** and a non-reducing end **C**.

donation of electron density on O-6 to form a levoglucosan end, as shown in Fig. 4. This is a particular case of transglycosylation, or substitution at C-1 by another carbohydrate moiety (Mamleev et al., 2007).

The free levoglucosan molecule is released by thermolysis at the adjacent glycosidic linkage. Mamleev et al. (2007) found that although transglycosylation can occur at any point on the chain, once the process starts at the end unit it is more likely to proceed sequentially along the chain, giving rise to the commonly used metaphor of the polymer "unzipping".

Levoglucosan is a vapour at the temperature at which volatilisation begins to occur (330—350 °C), with an estimated boiling point around 300 °C (Milosavljevic et al., 1996). (The boiling point of levoglucosan cannot be obtained directly because it tends to decompose before it boils.) At ambient temperatures it is a solid that is often called a "tar" (Williams, 1982) due to its sticky nature; the crystalline form has a melting point around 180 °C. It is the precursor to a large number of subsequent volatile decomposition species of lower molecular weight that readily oxidise in flaming combustion (see Section 5.1). Levoglucosan also forms various polymerised anhydrous products, which may undergo secondary charring (Kawamoto et al., 2003).

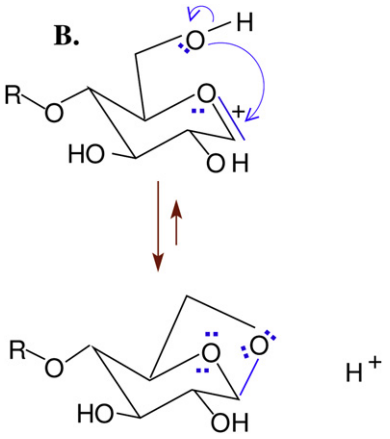

Fig. 4. Intramolecular nucleophilic addition to the positively charged centre results in cyclisation between O-6 and C-1, forming a levoglucosan end of the cellulose chain.

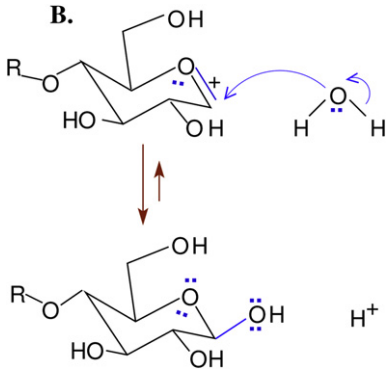

Fig. 5. Nucleophilic addition of a water molecule to the positively charged centre forms a hydrolysed cellulose fragment.

Due to its highly volatile nature, rapid decomposition to secondary volatiles, and formation of condensation products, levoglucosan is not a high yield product from the combustion of biomass under open burning conditions when compared to laboratory studies of pure cellulose. Nevertheless, the formation of levoglucosan is the primary volatilisation pathway of cellulosic thermal decomposition and occurs in sufficient concentrations that it has been used as tracer for biomass burning (Simoneit et al., 1999). Thus, while the production of levoglucosan from thermal decomposition under open burning conditions is not significant in terms of product yield, it is a key component in the elucidation of the competing thermal decomposition mechanisms.

The volatilisation of cellulose to levoglucosan is endothermic, requiring about 300 J g^{-1} of levoglucosan produced, or 48.6 kJ mol^{-1}. The reaction thermokinetics exhibits an activation energy of about 220–240 kJ mol^{-1} (Table 2). Such high activation energy reactions are extremely temperature-sensitive; cellulose volatilisation barely occurs at all below 300 °C then sets in quite suddenly and proceeds rapidly until the substrate is consumed or it is quenched.

4.2. Charring

The alternative, and competing, reaction of species **B** in Fig. 3 is hydration via nucleophilic addition of a molecule of water (which, in all but the driest of fuels, is present even under heating) to C-1 to yield hydrolysed cellulose, as shown in Fig. 5. The formation of levoglucosan is thus effectively blocked at this "wet" end. Under continued heating, the hydrolysed fragment begins to undergo the chemical dehydration, decarbonylation, decarboxylation, cross-linking and aromatisation reactions that produce solid primary char.

Chemical dehydration reactions generically occur via acid catalysis, with elimination of a molecule of water and formation of a carbon–carbon double bond. The acid may be a proton donor or an alkali metal cation such as Mg^{2+}, which is ubiquitous in biomass. In char formation a characteristic step is acid-catalysed opening of the hemiacetal ring of the hydrolysed cellulose reducing end unit to a free aldehyde group (Drysdale, 1985). The opened ring tends to undergo C-2–C-3 dehydration, the unsaturated product of which may undergo C-4–C-5 dehydration.

^{13}C NMR spectroscopic studies (Sekiguchi et al., 1983) have shown that during charring of cellulose, in addition to desaturation of the carbon skeleton by dehydration, the C-1 group disappears and new carbonyl and carboxyl groups appear that in turn disappear at higher temperatures. This suggests that the C-1 carbonyl group is lost as CO, and that remaining hydroxyl groups are oxidised to carbonyl and carboxyl groups before being lost as CO and CO_2. NMR signals for aliphatic and aromatic carbons appear and grow in intensity.

The reactions described here are undoubtedly only a few of the heterolytic reactions that are actually involved in charring. Free radical reactions are also believed to be important. However, much of the chemistry of char formation is yet to be elucidated and further research is needed before we fully understand this most ubiquitous terrestrial thermoconversion process.

The char formed under open biomass fire conditions consists of anhydrous species of indeterminate molecular weight, varying from partially unsaturated species through to highly aromatised clusters and even crystalline graphitised carbon in which all functional groups have been eliminated. For the study of biomass fires we are interested in all of the charred residue, which has an average H/C molar ratio of about 0.4. We define here for illustrative convenience a single fictitious char species that is fully dehydrated with empirical formula $C_{11}H_4$.

Charring is highly exothermic, releasing about 1–2 kJ g^{-1} (Table 2) which corresponds to 136–272 kJ mol^{-1} of our fictitious char. The activation energy of charring under pyrolytic conditions has been reported as 110–200 kJ mol^{-1} (Table 2), depending on experimental conditions, which is significantly lower than the activation energy for the competing volatilisation process. The heat produced by charring helps to maintain biomass fires because it

Table 2
Typical thermokinetic and thermochemical data for cellulose combustion.

Reaction	Activation energy (kJ mol^{-1})	Frequency factor (s^{-1})	Reaction enthalpy (kJ g^{-1})	Reference
Charring	110	6.7×10^5	−1.0[a]	Di Blasi (1993)
Volatilisation	198	3.2×10^{14}	0.3[b]	Antal and Várhegyi (1995)
Char oxidation	183	1.4×10^{11}	−33[c]	Branca and Di Blasi (2004)
Volatile oxidation	188	2.6×10^{13}	−14[d]	Parker and LeVan (1989)

[a] of char formed.
[b] of volatiles formed.
[c] of char oxidised.
[d] of volatiles oxidised.

provides a local source of heat that drives the endothermic production of the volatile fuel.

Secondary charring of condensed volatiles and of volatile cracking products also occurs during a biomass fire. The powdery particles of soot from biomass fire smoke are formed in a different manner from solid primary char, and the mechanism is currently an open research problem (Fitzpatrick et al., 2009). Pyrolysis experiments cannot investigate soot formation because, it seems, the flame environment is necessary to provide free radicals that are involved in soot initiation and particle nucleation and growth. In experimental hydrocarbon-fuelled flames, it is believed that the soot precursors are polycyclic aromatic hydrocarbons (PAH) and polyacetylenes (Rasbash and Drysdale, 1982). Various chemical schemes have been proposed for the formation of the first aromatic ring from small unsaturated molecular species or free radicals, growth and agglomeration of PAH via free radical chain processes and nucleation (or transition to solid particles) and further growth via heterogeneous surface reactions (Frenklach, 2002).

Macroscopically the different types of char may usually be distinguished by eye. The primary product of direct charring of the solid substrate often retains the shape of the original substrate (Williams, 1982) whereas secondary char from volatiles condensate is amorphous, soft and powdery.

We note that the char residue from vegetation fires is a long-term reservoir for carbon from atmospheric CO_2. This suggests that open vegetation fires may remove and sequester atmospheric carbon, since at every fire event some char is formed, and that fire is therefore an important regulator of global carbon cycles (Ball, 2008).

5. Combustion reactions

5.1. Gas phase oxidation

The simplest chemical equation for levoglucosan oxidation is

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O.$$

This stoichiometrically satisfying equation gives no hint as to the complexity of real flaming combustion of the volatiles. Studies of smoke from combustion of biomass fuel have found many different intermediates and partially oxidised products. Wodley (1971) identified nearly 40 products from the thermal decomposition of levoglucosan, many of which were products of secondary reactions between volatiles, including pentane, acetaldehyde, furan, and furfural, and noted that other workers had identified 20 additional compounds including formaldehyde and formic acid. Bowman (1975) gives a non-exhaustive list of 30 possible reaction pathways for the combustion of CH_4, one of the many products of the thermal decomposition of levoglucosan. In this case, subsequent intermediate species included CH_3, H_2CO, HCO, CO, OH and H_2. Coupling of the chemistry to the turbulent flow field adds to the complexity by limiting combustion in fuel-rich zones.

The turbulent diffusion flames of an open biomass fire have a relatively thin reaction zone between fuel and oxidant (Sullivan et al., 2003). Consequently the oxidation reactions are often mixing-limited and large volumes of volatiles may separate from the reaction zone and subsequently burn out at some height above the fire (Cheney and Sullivan, 2008) or not at all. Reaction pathways may be quenched through loss of heat or reactants and partial oxidation products may be transported away from the fire in the smoke (Gaydon and Wolfhard, 1960).

These oxidation reactions are highly exothermic and very fast. Oxidation of levoglucosan requires an activation energy of approximately 190 kJ mol^{-1} and has a reaction frequency of about 2.55×10^{13} s^{-1} (Table 2). The reaction enthalpy for complete combustion is approximately -14 kJ g^{-1} (Parker and LeVan, 1989).

5.2. Solid phase oxidation

Oxidation of char appears as glowing combustion. In air, charcoal is normally quite refractory to very high temperatures. However, freshly made hot char can oxidise quite easily. Pure carbon requires temperatures in the order of 700 °C to oxidise, whereas more saturated chars may oxidise at around 400–450 °C (Harris, 1999). In a biomass fire it is typically the hot char just behind the flaming front that undergoes glowing combustion, where rapid and selective chemisorption of oxygen onto the porous carbon surface takes place with the formation of surface oxide groups. Adsorption of oxygen onto fresh char is a highly exothermic process that delivers -486 kJ mol^{-1} at 200 °C and up to 900 kJ mol^{-1} at 450 °C, which is much larger than the standard enthalpies of formation of CO and CO_2 (-111 kJ mol^{-1} and -394 kJ mol^{-1} respectively). In an active bushfire, the indraw of air due to the convection at the flame front and the highly turbulent air flow ensures there is more than sufficient oxygen available for oxidation.

The stoichiometric reaction for complete oxidation of our fictitious char species is:

$$C_{11}H_4 + 12O_2 \rightarrow 11CO_2 + 2H_2O,$$

although CO can also be a primary product of the surface reaction. It is also possible for oxygen to be excluded from the reaction surface by the presence of ash, resulting in quenching of the reaction (Cheney and Sullivan, 2008). Char itself may insulate the fuel bed, acting as a thermal barrier. Where char combustion is completed the ash remains as a characteristic fine white residue composed of phosphates, salts, trace elements and other inorganic components of the fuel.

Char combustion is highly exothermic ($\Delta H \simeq -32\ kJ\ g^{-1}$) but has a lower activation energy ($E_a \simeq 180\ kJ\ mol^{-1}$) and occurs at a much slower rate ($A \simeq 1.4 \times 10^{11}\ s^{-1}$) (Branca and Di Blasi, 2004) than volatile combustion. Due to the slower reaction rate much of the char oxidation occurs after the passage of the fire front, giving the impression that glowing combustion occurs after flaming combustion but in fact it can occur at the same time.

6. Discussion

Although the thermoconversion chemistry of cellulosic fuel seems formidable, it may not be necessary to include all reactive steps in combustion modelling for the study of biomass emissions or bushfire behaviour. However, the modelling does need to capture the dynamics of the competition between volatilisation and charring, which determines the combustion outcomes. Incorporation of this chemistry gives self-consistency to a model, in that the amounts of char and volatile fuels formed are determined by thermokinetic and reaction enthalpy parameters. It also allows for a natural differentiation between flaming and glowing combustion.

6.1. Competitive thermal decomposition—a fundamental driver of biomass fires

Consider the thermal and chemical feedbacks at the heart of cellulose thermal decomposition, illustrated in Fig. 6 (based on a stylisation of the Broido–Shafizadeh model (Broido et al., 1973; Bradbury et al., 1979), together with the kinetic and thermochemical data in Table 2 for charring and volatilisation.

Chemical feedback of the water of chemical dehydration autocatalyses the charring path, but the heat produced promotes the

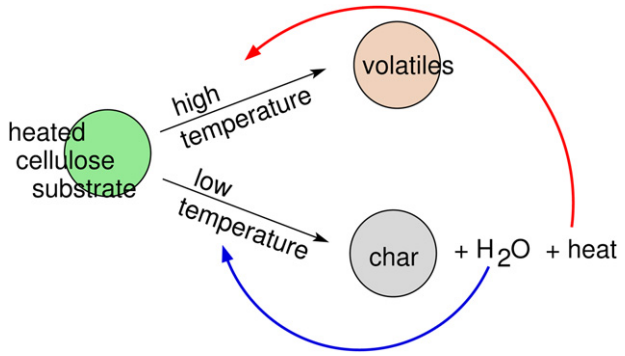

Fig. 6. Chemical feedback autocatalyses charring, but the heat produced promotes the competing volatilisation process. The chemical dehydrations have moderate activation energy and therefore set in at relatively low temperatures. But charring is highly exothermic and the hotter reaction zone allows the high activation energy volatilisation to kick in and take over—for a short time. Volatilisation is endothermic so locally it self-damps, thus switching the reaction field again to the charring path, unless subsequent flaming combustion of the volatiles provides enough heat to self-sustain.

competing volatilisation. Charring sets in at relatively low temperatures, due to the lower activation energy, but charring is highly exothermic and the hotter reaction zone allows the high activation energy volatilisation to kick in and take over. However, volatilisation is endothermic so unless there is sufficient heat available it will self-damp locally, switching the reaction field again to the charring path. It was found in Ball et al. (2004) that solutions of a dynamical model for cellulose thermal decomposition have the properties of a relaxation oscillator. The mechanism is just the competitive volatilisation and charring chemistry described in Section 4.

In the context of a bushfire moving freely through biomass fuel, this thermochemical oscillator may play an important role in fire propagation and fire front shaping. The formation of both volatiles and charcoal occurs at each point around the fire perimeter. However, the extent to which one process dominates the other is determined by total heat flux received by the fuel which may be moderated by the ambient wind. At the rear of the fire, where the reaction zone is open to the ambient wind, char formation dominates. At the head of the fire, where the reaction zone is essentially blocked from the effect of ambient wind, volatile formation dominates. The flanks of the fire alternate between heading and backing behaviours, depending on the fine scale shifts in wind direction. At the head of a fast-moving fire the heat from the flames may be advected ahead of the fuel; in this case the reservoir of heat provided by the charring reactions may serve to maintain volatilisation. At the rear of the fire charring produces heat too, but there is less heat per unit length of the interface than at the head so it can dissipate more effectively. The rear and flanks of a fire are consequently cooler with more char being formed than at the front.

6.2. Implications for emissions modelling

It has long been recognised that there are two modes of combustion in biomass fuels—flaming and smouldering (or glowing) combustion (e.g. Crutzen and Andreae (1990)). This fact has been incorporated into ER calculations by assigning different reference gases based on the predominant mode of combustion at the time of sampling in the belief that the different combustion modes produce different characteristic emissions. A deeper examination of combustion of cellulosic biomass fuels reveals that this is a gross simplification that may lead to fallacious results.

The products of thermal decomposition that undergo either flaming or smouldering combustion form in competition, resulting in one or the other modes of combustion dominating a particular particle of fuel. However both CO and CO_2 can be produced in either mode.

A freely propagating open biomass fire will exhibit both types of combustion, producing a complex mix of emissions. The head of a moving bushfire is dominated by flaming combustion with relatively tall flames whereas the back of the fire is dominated by smouldering combustion with low flames. Very intense fires often release considerable amounts of partially oxidised products as thick dark smoke from the headfire (Cheney and Sullivan, 2008). Thus, analysis of measurements of emissions from an active, high intensity bushfire assuming CO_2 as the dominant emission species may incorrectly relate the ratios of other emitted species if CO is formed in quantity. Similarly, glowing combustion from the rear of a bushfire is often very efficient, producing little smoke and fully oxidised products. Analysis of measurements of this type of fire that assumes that CO is the dominant emission species will also incorrectly relate the ratios of other emission species.

As estimates of total global mass and area burnt by biomass fires improve (Henderson et al., 2010), so too must estimates of the sources of the emissions. Areas of vegetation that are consumed by heading and backing fires can now be distinguished through remote sensing of radiative power and smoke plume observations (Smith and Wooster, 2005).

The preferential formation of char at the rear and flanks of a free moving fire or from backing fires may play an important role in sequestering carbon. Char is believed to be a long-term reservoir for carbon from atmospheric CO_2 and methane. Thus the competitive combustion of cellulosic fuels may have another important role in regulating global carbon cycles. The carbon fraction put down into long-lived char is high for cooler, slower fires that produce much char and lower for hotter, more intense fast-moving fires. The net time and spatially averaged global bias towards cool or hot fires—whether as a consequence of natural global dynamics or induced by human activity—is likely to contribute substantially to global carbon balances (Ball, 2008).

6.3. Implications for bushfire behaviour modelling

The purpose of physical models of bushfire behaviour is to predict the spread of a bushfire. In these fire spread simulations combustion is often treated as a single-step process, but this ignores the role of the primary competition between charring and volatilisation in determining fire behaviour and may predict combustion and spread outcomes that are qualitatively wrong.

Validation of these models (e.g. Mell et al. (2007)) has shown that the prediction of the location of the head of a freely moving fire in grass fuels agrees reasonably well with experimental measurements. However, these models fail to predict the progress of the remainder of the fire perimeter, where the flames and intensity are lower. One reason for this inadequacy may be the lack of treatment of the competitive chemistry of the two pathways that lead to volatilisation and flaming combustion and to char formation and glowing combustion, and the thermal and chemical feedbacks that can allow one pathway to cede to the other with little or no change in external conditions.

7. Conclusions

The chemistry of thermal degradation and combustion of cellulosic biomass involves a fundamental competition between two key reactions. These are intra-molecular and inter-molecular nucleophilic addition at the positive centre of the carbocation end of a cellulose chain that has undergone thermal scission at a glycosidic bond. If intra-molecular nucleophilic addition occurs, the end residue

undergoes cyclisation and devolatilises to levoglucosan. If intermolecular nucleophilic addition of a water molecule occurs, cyclisation is blocked. Further heating causes dehydration, decarbonylation, decarboxylation, cross-linking and aromatisation of this hydrolysed cellulose end to char. The products of volatilisation undergo flaming combustion and char undergoes glowing combustion.

These competing combustion processes produce different distributions of emissions products. The behaviour of a fire is also affected by the combustion pathway at the fire edge. Flaming combustion is predominant at the head of a fire and releases a large amount of heat very rapidly. Glowing combustion is more predominant at the rear and flanks of a fire and, being a gas–solid interface process, is fixed in location and thus provides a slow, steady, and high heat input to adjacent fuel. Turbulence, particularly in high intensity bushfires, can result in quenching of the volatile oxidation reactions, resulting in a very broad range of partially combusted emission species. CO and CO_2 can be produced from the charring process and from oxidation of both char and volatiles, confusing current methods of determining emission ratios based on the belief that CO is the result only of glowing combustion and CO_2 the result only of flaming combustion.

Thermal and chemical feedbacks between the competing pathways can allow the dominant mode of combustion to switch between flaming and glowing with little change in burning conditions but with significant impact on the local emission profile and behaviour of the fire.

This basic understanding of cellulosic biomass thermal degradation and combustion is an important step in towards a complete picture of biomass combustion. Good understanding of these processes is essential for accurate modelling of the spread of a bushfire through a vegetated landscape and estimations of emissions from biomass burning.

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