

Feedback processes in cellulose thermal decomposition: implications for fire-retarding strategies and treatments

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Abstract

A simple dynamical system that models the competitive thermokinetics and chemistry of cellulose decomposition is examined, with reference to evidence from experimental studies indicating that char formation is a low activation energy exothermal process and volatilization is a high activation energy endothermal process. The thermohydrolysis chemistry at the core of the primary competition is described. Essentially, the competition is between two nucleophiles, a molecule of water and an –OH group on C₆ of an end glucosyl cation, to form either a reducing chain fragment with the propensity to undergo the bond-forming reactions that ultimately form char, or a levoglucosan end-fragment that depolymerizes to volatile products. The results of this analysis suggest that promotion of char formation under thermal stress can actually increase the production of flammable volatiles. Thus, we would like to convey an important safety message in this paper: in some situations where heat and mass transfer is restricted in cellulosic materials, such as furnishings, insulation, and stockpiles, the use of char-promoting treatments for fire retardation may have the effect of increasing the risk of flaming combustion.

Nomenclature

V	volume of relevant zone, m ³
c_w	concentration of water in zone, mol m ⁻³
c_z	concentration of volatiles in zone, mol m ⁻³
t	time, s
T, T_a	system temperature, ambient temperature, K

k_1	pseudo-first-order reaction (2) rate constant, s^{-1}
k_2	pseudo-zeroth-order volatilization rate constant, $\text{mol}(\text{m}^3 \text{s})^{-1}$
E_1	reaction (2) activation energy, kJ mol^{-1}
E_2	volatilization reaction activation energy, kJ mol^{-1}
R_w	constant rate of supply of water from reaction (1), mol s^{-1}
F	rate of outflow of vapour-phase species, $\text{m}^3 \text{s}^{-1}$
C_{av}	average volumetric specific heat of reacting system, $\text{J}(\text{m}^3 \text{K})^{-1}$
ΔH_1	enthalpy of exothermal reaction (2), kJ mol^{-1}
ΔH_2	enthalpy of endothermal reaction (3), kJ mol^{-1}
L	combined heat transfer coefficient, $\text{J}(\text{s K})^{-1}$
R	gas constant, $\text{J}(\text{mol K})^{-1}$
c_{ref}	a reference concentration, mol m^{-3}
w	c_w/c_{ref}
z	c_z/c_{ref}
u	RT/E_1
τ	$t k_1$
ν	$k_2/(k_1 c_{\text{ref}})$
μ	E_2/E_1
α	$\Delta H_2/\Delta H_1$
\bar{C}	$C_{\text{av}} E_1/(c_{\text{ref}} R(-\Delta H_1))$
r	$R_w/(V k_1 c_{\text{ref}})$
f	$F/(V k_1)$
ℓ	$L E_1/(V c_{\text{ref}} k_1 R(-\Delta H_1))$

1. Introduction

Thermokinetic and chemical feedback processes that determine the course and outcome of cellulose thermal decomposition are of particular interest in the development of appropriate flame-inhibiting treatments of manufactured goods such as bedding, furnishings, and insulation, or stockpiled raw cellulosic material such as bagasse or hay. The fuel that ignites in the flaming combustion of cellulose substrates consists mostly of volatile, small-molecule substances that are supplied continuously by thermal degradation of the solid cellulose. Therefore, in designing more efficient and effective fire-retardants for cellulose—and, more generally, in the pre-emptive control of cellulose combustion—it is important to understand both the dynamics and the chemistry of decomposition. In this work we investigate a phenomenological model for the thermal decomposition of cellulose substrates that is based on two key aspects of the known chemistry and thermokinetics: involvement of water in promoting char formation, and reaction enthalpy feedback to promote volatilization.

A great many thermogravimetry and differential scanning calorimetry experiments, complemented by qualitative and quantitative product analysis, have affirmed that cellulose thermal decomposition is largely a competitive process [1–8]. In the broad picture that has taken shape from these results and from associated modelling studies (e.g. see [9–14] and the reviews in [15] and [16]), formation of volatiles and char are seen to be reciprocally linked to some extent.

Some details have also emerged of the chemistry involved in these competitive pathways [17–19], although a complete picture of the complex reaction network remains a major experimental challenge. What is clear though is that the involvement of water in hydrolysis

reactions is crucial in determining the rates and outcomes of the competitive pathways. A thorough survey and compilation of the known chemistry and thermokinetics of cellulose thermal decomposition was carried out in [20], on the basis of which a dynamical model was constructed that includes the role of water in the reaction chemistry. In this paper, we concentrate on the kinetic and thermal aspects of the decomposition process, emphasizing the role played by thermal feedback in regulating the decomposition pathways. We demonstrate the potential for thermal instabilities by considering the qualitative behaviour of a very simple thermokinetic model for cellulose thermal decomposition, which nevertheless expresses the important rate processes of competitive temperature-dependent reaction rates and heat losses.

2. Basic chemistry and phenomenology of cellulose decomposition

The chemistry of the primary competitive reactions is illustrated in figure 1. The initial step is believed to be heterolytic thermal scission of glycosidic linkages at random chain locations in amorphous regions of the cellulose. In a dry environment the positively charged end (*a*) is rapidly cyclized to a levoglucosan end (*b*), with the $-OH$ group on C_6 of the unit as nucleophile. Thermolysis at the next glycosidic linkage of this fragment releases the volatile levoglucosan. When water is present it can compete as a nucleophile for the positively charged centre on (*a*) to produce a reactive reducing end (*c*). It is this species which is believed to undergo the subsequent dehydration, decarboxylation, and cross-linking reactions that produce the char. (The negatively charged fragment of the thermal scission rapidly picks up a positive hydrogen ion from the $-OH$ nucleophile group or from water to form a non-reducing end (*d*). In general, non-reducing ends of carbohydrates are relatively unreactive.)

Empirical methods for producing good yields of char by heating damp wood in an oxygen-deficient atmosphere have been used for centuries. Systematic investigations of this effect using DSC experiments were carried out by Mok *et al* [4], who observed that either a high concentration of vapour products or added water increased char yield and decreased the temperature of onset of decomposition. Subsequent analysis of these data [21] led to the suggestion that the water produced in thermal dehydration reactions feeds back to hydrolyse the unreacted cellulose. In [22] and [23], evidence was also presented from pyrolysis experiments that product water accelerated the formation of char. Some investigations of the role of the hydrolysis chemistry of cellulose under thermal stress in producing this effect were reported in [18] and [24].

It is also known that covered stockpiles of cellulosic materials such as bagasse, hay, and cotton undergo spontaneous combustion much more readily when critically damp than in dry conditions. Dynamical models that reproduce qualitatively the behaviour that is typical in damp combustion of various materials have been investigated by many workers [25–30]. In these systems, which model the combustion subsequent to decomposition, critical, unstable, or oscillatory thermal behaviour can occur due to the coupling of two or more nonlinear temperature-dependent reaction rates with restricted linear heat losses.

3. Alternative pathways are thermally connected

The studies reviewed briefly in the previous section suggest the rather counter-intuitive notion that, in some circumstances, water can increase the temperature of thermally decomposing cellulose. To guide our thinking on this, we need to put together three pieces of information.

- (i) The volatilization rate is more temperature-sensitive, i.e. has higher activation energy, than the charring rate. A typical experimental result that leads to this inference was

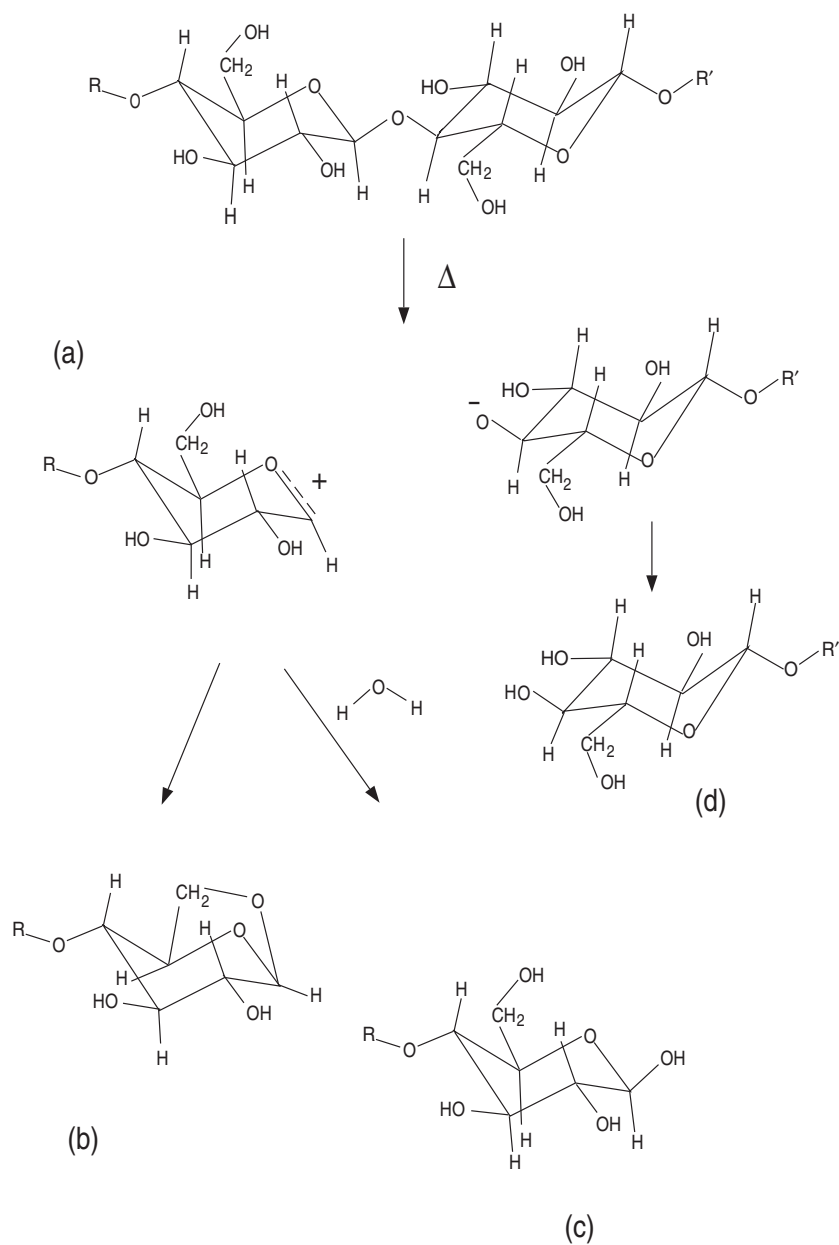


Figure 1. The carbonium ion (a) may form a levoglucosan end (b) via intramolecular nucleophilic attack, or a reducing end (c) when intercepted by a water molecule. In both cases a non-reducing end (d) is also formed.

reported in [5]. It was found that as the pyrolysis temperature of pine wood, cellulose, hemicellulose, and lignin was increased, the percentage mass of solid char decreased, while that of gas and oil (volatile or tar) products increased.

- (ii) Estimates of the magnitude of the reaction enthalpies vary, but there is agreement that the charring process is highly exothermic whereas volatilization is endothermic, at

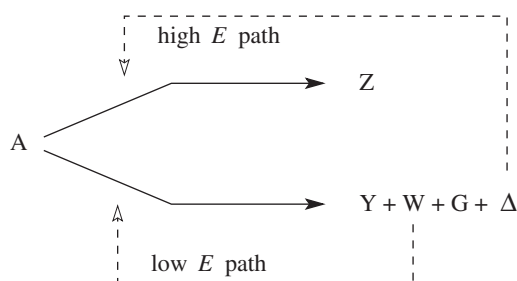


Figure 2. How chemical and thermal feedback may be involved in cellulose decomposition: A, Z, W, Y, G, and Δ stand for cellulose, volatiles such as levoglucosan, water, dehydrated product or char, gases such as CO and CO₂, and heat, respectively; E is activation energy.

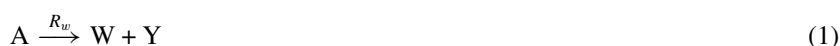
the very least to the extent of the enthalpy of vaporization of levoglucosan (see, e.g. [22, 31–34]).

- (a) As described in [20], water of dehydration can participate in hydrolysis that effectively blocks the cyclization to levoglucosan.

Putting these together we can draw the schematic diagram of the competitive decomposition shown in figure 2. As the substrate A is heated the low activation energy dehydration reactions are initiated. The water produced by this process can feed back into hydrolysis reactions that inhibit volatilization and enhance char formation. However, the charring reactions are bond-forming and heat-releasing. Under circumstances where there is no efficient linear heat sink, the alternative, high activation energy, volatilization reactions begin to take over. The heat requirement of volatilization means that it can self-damp, thus opening the reaction field again to the charring pathway. It is clear that there is potential for the system to attain a stable steady-state or limit cycle. In reality, of course, the situation is more complex—and probably more dangerous—because accumulation of hot volatiles in what is often a highly oxidizing environment is likely to lead to spontaneous flaming ignition.

4. A simple proxy for competitive thermal decomposition

To strengthen our feel for the qualitative aspects of the system described above, we will study the thermokinetics of the following simple competitive reaction scheme:



This may be viewed as a model for the thermal decomposition of cellulose, with A, W, Y, Z, and Δ representing the substrate, water, dehydrated product or char, volatiles, and heat, respectively. Although a gross simplification of the detailed chemistry of the process, it nevertheless captures the governing characteristics of temperature-dependent reaction rates, reactive heat generation/consumption, and feedback of W. Making the reasonable approximations that the rate of supply R_w of W from reaction (1) is constant (the activation energy for this reaction is believed to be very low) and thermally neutral, the substrate A is drawn from an ‘infinite pool’, and the system is spatially homogeneous with linear heat dissipation, we can write the following dynamical equations to describe the evolution of the

vapour-phase components and the temperature:

$$\frac{dw}{d\tau} = -e^{-1/u}w + r - fw \quad (4)$$

$$\frac{dz}{d\tau} = ve^{-\mu/u} - fz \quad (5)$$

$$\bar{C} \frac{du}{d\tau} = e^{-1/u}w - \alpha ve^{-\mu/u} + \ell(u_a - u). \quad (6)$$

The dimensionless groups and the quantities from which they are derived are explained in the appendix and nomenclature. Briefly, w is the concentration of reactant water, z the concentration of volatile product and u the dynamical temperature. Water is supplied by reaction (1) at a temperature-independent, thermally neutral rate r , and is removed with the vapour-phase outflow at rate f and by the hydrolysis process (2) that ultimately leads to char formation. Volatiles are produced in process (3) and are also removed in the vapour-phase outflow. Process (2) is a heat source, process (3) is a heat sink, and a linear heat exchange with rate coefficient ℓ is assumed to occur between the system and its immediate environment at constant ambient temperature u_a .

In equations (4)–(6) convective derivatives and spatial dependences have not been included because it is the intention of this work to elucidate purely the dynamical capabilities of this system where there are two competing temperature-dependent reaction rates. (Future work will investigate the influence of other factors, such as gradient-driven transport phenomena, on these dynamics.) Cellulose pyrolysis experiments under kinetically controlled conditions, designed so that heat and mass transport occur on a timescale that is not seen by the thermokinetics, have been carried out by several groups, e.g. [35–37].

Comparable dynamical models that include two or more temperature-dependent reaction rates have been analysed in the literature from several points of view: fundamental studies of the dynamical and bifurcation behaviour may be found in [38, 39], applications to the wet combustion problem were cited above, and their use in the stabilization of thermal runaway reactions was described in [40]. In all of these problems it was found that the coupling of two non-identical Arrhenius terms could give rise to steady-state and oscillatory behaviour of greater complexity than in corresponding systems with a single Arrhenius term. Concomitantly, it has been shown that an endothermic reaction rate (the second term on the right-hand side of equation (6)) can stabilize the system temperature [40]. In this system, the effects of the high activation energy endothermic reaction are modified by the rate r at which water is fed into the exothermic reaction.

Some equilibrium solutions of equations (4)–(6), computed numerically, are shown in figure 3, where the dependence on ambient temperature u_a is plotted for three values of r , the supply rate of water.

In column (a), where the supply rate r of reactant water w (from reaction (1)) is relatively low, the temperature rise is monotonic and the nonlinearity is mild. When consumption of w (due to reaction (2)) begins at $u_a \sim 0.062$ the temperature increases nonlinearly because the heat produced accelerates the reaction rates exponentially. However, the higher temperature allows the competing production of volatiles z (due to reaction (3)) to dominate, which absorbs the heat so that the temperature increase levels out.

In column (b) the situation is impressively different, because two Hopf bifurcations bracket an unstable section of the solution curve. Here, a faster supply rate r induces oscillatory behaviour over most of the active range of u_a . It is noteworthy that, even quite near the onset of the oscillations at the lower temperature Hopf bifurcation, the concentration of flammable

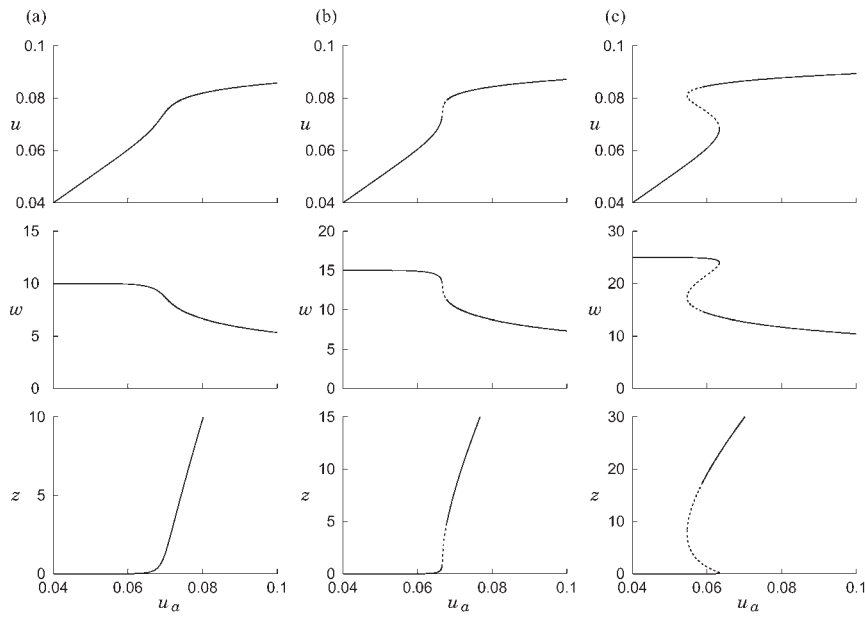


Figure 3. Equilibria of equations (4)–(6) as a function of u_a , the ambient temperature: column (a) $r = 0.0001$, column (b) $r = 0.00015$, column (c) $r = 0.00025$. Other parameters: $\mu = 1.7$, $\alpha = 0.3$, $f = 1 \times 10^{-5}$, $\ell = 0.002$, $C = 1$, $v = 1 \times 10^5$. —: stable solutions, \cdots : unstable solutions.

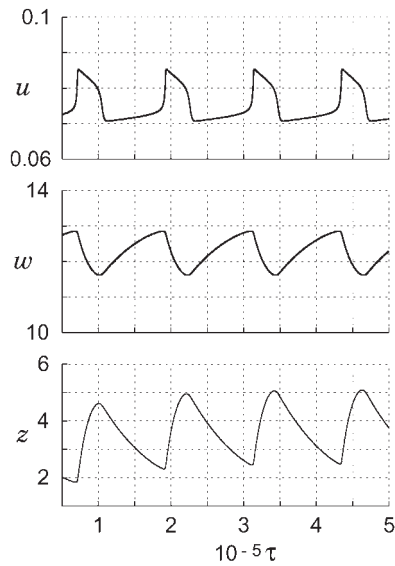


Figure 4. $u_a = 0.067$, other parameters as in figure 3(b).

volatiles z and the system temperature u can rise dramatically, as shown in the time series of figure 4.

These oscillations illustrate very well the feedback dynamics schematized in figure 2. If we consider the time series beginning at a temperature u minimum (say, at $\tau \approx 3.5 \times 10^5$) we can see that the system self-heats quite slowly while water accumulates; when the

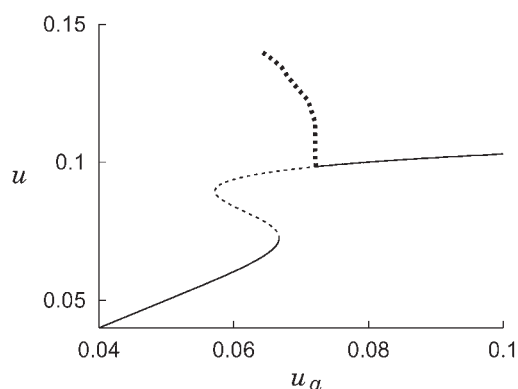


Figure 5. A jump to an oscillatory state can occur: $\ell = 0.004$, $\nu = 1 \times 10^4$, other parameters as for figure 3(c). The thick dotted line marks the maximum amplitude envelope of the branch of limit cycles that emanates from the Hopf bifurcation.

exothermal reaction starts to consume water faster than it is produced the temperature can spike dramatically. Consequently, the flammable products z of the high-temperature reaction are released rapidly. This reaction absorbs the heat, bringing the temperature down and allowing w to increase again.

The amplitude, form, and ambient temperature range of the oscillations are, of course, also influenced by other parameters of the system, such as the activation energy ratio ν , the rate coefficient of non-reactive heat removal ℓ , and the rate coefficient f for removal of vapour phase material from the system. However, it is not difficult to imagine a situation of restricted heat and mass transfer in an oxidative environment, where this sudden surge in the temperature and concentration of volatiles leads to spontaneous ignition of the volatiles, whence the system enters a new regime of flaming combustion (not considered in this work).

In figure 3(c) a higher rate of reactant supply induces folds in the solution curve, with a jump to the high temperature branch occurring at a comparatively low ambient temperature. The switch in stability on this upper curve also occurs at a Hopf bifurcation. At these parameter values the associated oscillations are of low amplitude and are not accessible directly from the jump at the lower fold bifurcation, but at parameter values which give a slightly greater mismatch in rates the situation can be quite different. In figure 5, for example, the Hopf bifurcation occurs at a higher value of u_a and the jump from the lower branch at the fold takes the system directly onto a limit cycle. The branch of limit cycles terminates at a homoclinic orbit, at which extinction may occur if the ambient temperature is sufficiently lowered. Note that in this oscillatory region of the solution curve the temperature u rises as the ambient temperature is lowered. The amplitude of the limit cycles becomes unrealistically high, due to the assumption of an infinite pool of substrate that is built into this simple model. Nevertheless, the qualitative effect is similar to that in figure 3(b): the temperature and volatile concentration can surge uncontrollably when the competing reaction of low activation energy is initially encouraged.

Qualitative and quantitative considerations. The dimensionless temperature u is defined in the appendix using E_1 , the lower activation energy. For an E_1 of $\sim 100 \text{ kJ mol}^{-1}$ a dimensionless ambient temperature u_a of ~ 0.06 corresponds to $\sim 700 \text{ K}$. This is compatible with the wide range of reported activation energies for the low temperature pathway, although a little on the low side [12, 41–43]. In this model, adjustment of the other parameters—which are imprecisely known, especially quantities such as the ratio of pre-exponential factors ν —can always yield lower or higher temperatures at critical points such as the jump in figure 3(c), or

over ‘interesting’ regions such as the limit cycle régime in figure 3(b). However, the qualitative features of the model, as illustrated in the bifurcation diagrams of figures 3 and 5, are robust, in the sense that they are not pathological, singular, or higher-order occurrences. In principle, they are therefore amenable to experimental investigation and quantification. The qualitative phenomena such as limit cycles and hysteretic jumps are manifestations of the dynamics of competing and nonlinear rate processes and thermochemical feedback that characterize cellulose thermal decomposition.

5. Discussion and conclusion

To a large extent, the development of fire-retarding treatments of and strategies for cellulosic materials has been based on the large body of experimental evidence, some of which was cited above, for the competitive nature of thermal decomposition. If char is formed at the expense of volatile fuel, then intuition suggests that we should expect to see a positive correlation between char yield and fire resistance. Many different additives to cellulosic materials have been found to enhance char-formation, e.g. chromated copper arsenate treatments (CCA) [44], metal carboxylates [45], sodium hydroxide [33], potassium chloride [46], phosphates [47], ammonium salts [48], and those studied in [49] and [19]. Some of these are used commercially.

However, from the point of view of promoting fire safety in real situations, the idea that better charring properties equate to better flame resistance is too simplistic, because of the nonlinear feedback effects on the competition between volatile and char formation described in section 4. The results of this study indicate that char-forming treatments should be used circumspectly, with proper consideration of the particular situation of potential thermal decomposition—in particular, whether heat and volatiles are removed efficiently enough to prevent the thermal feedback that promotes volatilization. Even without taking into account the detailed role of the hydrolysis chemistry described in section 2, it is clear from thermokinetic considerations alone that there is a delicate balance between the amount of char and the degree of fire resistance, because the temperature—and therefore the rate of volatile fuel formation—can increase dramatically as the exothermal charring reactions occur. In [33] it was reported that pyrolysis of cellulose became strongly exothermal when the material was treated with large amounts of charring retardant. Another mechanism by which extensive charring could become dangerous was described in [50]: since char has much higher permeability than the unreacted substrate, flammable volatiles would flow more rapidly through hot char as it forms. The volatiles may either undergo secondary exothermal charring in the existing char, heating up the system further, or ignite on contact with oxygen.

As pointed out in [6], many other factors such as rate of external heating, heat and mass diffusion, secondary chemistry, and the immediate environment can influence the decomposition process. None of these is built into the simplified, homogeneous model in section 4, which is a crude and much-reduced simplification of a complex thermokinetic system. Nevertheless, it does reflect the reality of the effects of cellulose thermal decomposition (there is nothing fine or subtle about a catastrophic spontaneous fire in a haystack, either), and it is consistent with the known important features of the process—namely, the competitive pathways, the involvement of water, and the thermokinetics. It is also not difficult to envisage other situations where dangerous self-heating could take place. It is often a statutory requirement that cellulosic materials in bedding, furnishings, and textiles in nursing homes contain fire-retardants. However, a bedding fire started by a cigarette is exactly the kind of situation we have in mind—the necessary moisture would already be present and the heat of charring cannot easily escape, thus provoking the volatilization reactions.

This study of a simple model does not pretend to be quantitatively precise. Rather, its intent is to elicit important qualitative information concerning the dynamical behaviour of a cellulosic system under thermal stress, and highlight some thermokinetic effects that could be a consideration in the design of targeted fire-retarding strategies. Further modelling studies will examine the thermokinetics in the presence of fire-retardants, and simulate cellulose decomposition behaviour in an oxidizing environment, looking at critical conditions for ignition of the volatile products and the question of whether decomposition is coupled to the flame chemistry as well as thermal feedback.

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Appendix

Equations (4)–(6) have the following dimensional form, with the symbols mapped to quantities and dimensionless groups as defined in the nomenclature.

$$V \frac{dc_w}{dt} = -Vk_1 e^{-E_1/RT} c_w + R_w - Fc_w \quad (\text{A1})$$

$$V \frac{dc_z}{dt} = Vk_2 e^{-E_2/RT} - Fc_z \quad (\text{A2})$$

$$C_{av} V \frac{dT}{dt} = V(-\Delta H_1)k_1 e^{-E_1/RT} c_w + V(-\Delta H_2)k_2 e^{-E_2/RT} + L(T_a - T). \quad (\text{A3})$$

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