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 C\textsubscript{6} 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.

Keywords: cellulose thermal decomposition, competitive thermokinetics, dynamical model, char formation, fire-retarding treatments. PACS 82.40.Py 89.90

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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. In designing more efficient and effective fire-retardants for cellulose — and, more generally, in the pre-emptive control of cellulose combustion — it is thus 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 the following two key aspects of the known chemistry and thermokinetics: (1) involvement of water in promoting char formation, and (2) reaction enthalpy feedback to promote volatilization.

A great many thermogravimetry (TG) and differential scanning calorimetry (DSC) experiments, complemented by qualitative and quantitative product analysis, have affirmed that cellulose thermal decomposition is largely a competitive process [1, 2, 3, 4, 5, 6, 7]. In the big picture that has taken shape from these results and from associated modelling studies (for example, see [8, 9, 10, 11, 12, 13] and the reviews in [14] and [15]) 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 [16, 17, 18], 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 [19], on the basis of which a dynamical model was built up 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, which nevertheless contains the important rate processes in cellulose thermal decomposition: competitive temperature-dependent reaction rates, reaction enthalpy feedback, and heat losses.
2 Basic chemistry and phenomenology of cellulose decomposition

The chemistry of the primary competitive reactions is illustrated in Fig 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 in the figure) is rapidly cyclized to a levoglucozan end (B in the figure), with the -OH group on C₆ of the unit as nucleophile. Thermolysis at the next glycosidic linkage of this fragment releases the volatile levoglucozan. When water is present it can compete as a nucleophile for the positively charged centre on A to produce a reactive reducing end (C in the figure). 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 [20] led to the suggestion that the water produced in thermal dehydration reactions feeds back to hydrolyse the unreacted cellulose. In [21] and [22] 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 [17] and [23].

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 have been investigated by Gray [24] and others [25, 26, 27, 28, 29]. 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 water can increase the temperature of thermally decomposing cellulose. To guide our thinking on this, we need to put together three pieces of information:

1. 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 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.

2. Estimates of the magnitude of the reaction enthalpies vary, but there is agreement that the charring process is highly exothermal whereas volatilization is endothermic, at the very least to the extent of the enthalpy of vaporization of levoglucosan (see for example [21, 30, 31, 32, 33]).

3. As described in [19], 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 Fig 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:

\[
A \quad \xrightarrow{R_w} \quad W + Y \quad (1)
\]
\[
A + W \quad \xrightarrow{k_1(T)} \quad Y + \Delta \quad (2)
\]
\[
A + \Delta \quad \xrightarrow{k_2(T)} \quad Z. \quad (3)
\]

This may be viewed as a model for the thermal decomposition of cellulose, with A, W, Y, Z, and \( \Delta \) representing the substrate, water, dehydrated product or char, volatiles, and heat respectively. Although a gross simplification of the real process, it nevertheless contains the important overall characteristics of temperature-dependent reaction rates, reactive heat generation/consumption, and feedback of W. Making the reasonable approximations that (1) 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, (2) A is drawn from an “infinite pool”, and (3) 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:

\[
\frac{dw}{d\tau} = -e^{-1/u}w + r - fw \quad (4)
\]
\[
\frac{dz}{d\tau} = \nu e^{-\mu/u} - fz \quad (5)
\]
\[
\bar{C} \frac{du}{d\tau} = e^{-1/u}w - \alpha \nu e^{-\mu/u} + \ell (u_a - u). \quad (6)
\]

The dimensionless groups and the quantities from which they are comprised are explained in the Appendix. Briefly, \( w \) is the concentration of reactant water, \( z \) is the concentration of volatile product, \( u \) is 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 \( \ell \) is assumed to occur between the system and its immediate environment at constant ambient temperature \( u_a \).
Eqs 4–6 are based on a CSTR (continuous stirred tank reactor) paradigm with two temperature-dependent reaction rates. 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 [34] and [35], applications to the wet combustion problem were cited above, and their use in the stabilization of thermal runaway reactions was described in [36]. 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 endothermal reaction rate (the second term on the right-hand side of Eq. 6) can stabilize the system temperature [36]. In this system the effects of the high activation energy endothermal reaction are modified by the rate \( r \) at which water is fed into the exothermal reaction.

Some steady state solutions of Eqs 4–6, computed numerically, are shown in Fig 3, where the dependence on \( u_a \) is plotted for three values of \( r \). Limit cycles, where they exist, have also been computed and plotted as the amplitude maxima against \( u_a \). (Notes: (1) Eq. 5 uncouples from Eqs 4 and 6. (2) With an assumed activation energy \( E_1 \) of \( \sim 50 \) kJ/mol a dimensionless temperature \( u \) of \( \sim 0.1 \) corresponds to \( \sim 600 \) K.)

In (a), where the supply of reactant is limiting, the temperature rise is monotonic as \( u_a \) is increased. When consumption of \( w \) begins at \( u_a \sim 0.08 \) the rate increases due to thermal feedback, but when production of \( z \) cuts in at a higher temperature the rate levels out again.

In (b) the situation is impressively different, because the steady-state solutions change stability at two Hopf bifurcations. Here a faster rate of supply induces oscillatory behaviour over the active range of \( u_a \). It is noteworthy that, near the onset of the oscillations, the concentration of \( z \) (the flammable volatiles) and the temperature can rise dramatically at a relatively low ambient temperature. The amplitude and temperature range of the oscillations is, of course, also influenced by the rate of non-reactive heat removal \( \ell \) and the rate at which vapour phase material is removed from the system. However, it is not difficult to imagine a situation of restricted heat and mass transfer 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.
In (c) a higher rate of reactant supply induces multiple steady states, with a jump occurring at a comparatively low ambient temperature. Although the upper steady state occurs at quite low values of \( u \) and \( z \), it is unstable, and again \( u \) and \( z \) must jump to a catastrophic limit cycle. (For clarity the complete branch of limit cycles is not shown in (c), it terminates in a homoclinic orbit.) 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 (b): the temperature and volatile concentration can surge uncontrollably when the competing reaction is initially encouraged.

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) \[37\], metal carboxylates \[38\], sodium hydroxide \[32\], potassium chloride \[39\], phosphates \[40\], ammonium salts \[41\], and those studied in \[42\] and \[18\]. 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 4, 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 \[32\] it was reported that pyrolysis of cellulose became strongly exothermal when the material was treated with large amounts of charring.
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retardant. Another mechanism by which extensive charring could become dangerous was described in [43]: 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 in to 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 for cellulose. 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

Eqs 4–6 have the following dimensioned form, with the symbols mapped to quantities and dimensionless groups as defined in the accompanying table.

\[
V \frac{d c_w}{d t} = -V k_1 e^{-E_1/RT} c_w + R_w - F c_w \\
V \frac{d c_z}{d t} = V k_2 e^{-E_2/RT} - F c_z \\
V C_{av} \frac{d T}{d t} = V (-\Delta H_1)k_1 e^{-E_1/RT} c_w + V (-\Delta H_2)k_2 e^{-E_2/RT} + L (T_a - T).
\]

| Symbol | Definition | Units |
|--------|------------|-------|
| V      | volume of relevant zone | m³   |
| c_w    | concentration of water in zone | mol/m³ |
| c_z    | concentration of volatiles in zone | mol/m³ |
| t      | time | s |
| T, T_a | system temperature, ambient temperature | K |
| k_1    | pseudo first-order dehydration rate constant | s⁻¹ |
| k_2    | pseudo zeroth-order volatilization rate constant | mol/(m³s) |
| E_1    | dehydration reaction activation energy | kJ/mol |
| E_2    | volatilization reaction activation energy | kJ/mol |
| R_w    | constant rate of supply of water from reaction | mol/s |
| F      | rate of outflow of vapour-phase species | m³/s |
| C_{av} | average volumetric specific heat of reacting system | J/(m³K) |
| ΔH     | reaction enthalpy | kJ/mol |
| L      | combined heat transfer coefficient | J/(s K) |
| R      | gas constant | J/(mol K) |
| c_{ref} | a reference concentration | mol/m³ |
| w      | c_w/c_{ref} |
| z      | c_z/c_{ref} |
| u      | RT/E_1 |
| τ      | tk_1 |
| ν      | k_2/(k_1 c_{ref}) |
| μ      | E_2/E_1 |
| α      | ΔH_2/ΔH_1 |
| C      | C_{av}E_1/(c_{ref}R(-ΔH_1)) |
| r      | R_w/(V k_1 c_{ref}) |
| f      | F/(V k_1) |
| ℓ      | LE_1/(V c_{tet}k_1 R(-ΔH_1)) |
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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.
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