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IGNITION STUDIES ON COTTON CELLULOSE BY DTA

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ABSTRACT

Differential thermal analysis is used to investigate the spontaneous combustion of cotton cellulose in an atmosphere of flowing air. The temperature at which the onset of spontaneous ignition occurs, T_i, is determined as a function of sample mass, air flow rate and heating rate. For sample masses between 1 and 15 mg, T_i is constant although complete sample ignition occurs only for masses in excess of 8 mg where char residues fall below 5%. Air flow rates between 50 and 300 cm^3 min^{-1} do not significantly influence T_i recorded for cellulose samples having a given mass and subjected to a known heating rate, H_R. However, for heating rates ranging from 4 to 20°C min^{-1}, T_i is observed to increase according to a simple power law $T_i = 295\ H_R^{0.0579}$°C. The overall reproducibility of the technique shows $T_i = 350.5 \pm 1.5$°C when 10 mg cellulose samples are subjected to a heating rate of 20°C min^{-1} and air flowing at 200 cm^3 min^{-1}.

A simple steady-state model of pyrolysis and subsequent combustion predicts that the function ($2 \log T_i - \log H_R$) will be linearly dependent upon $1/T_i$. From the slope, an upper limit value for the activation energy of pyrolysis, E_p, is found to be 146 kJ mole^{-1}. This value compares well with measurements of E_p made by other workers using a variety of alternative methods.

INTRODUCTION

The pyrolysis, ignition and subsequent combustion of cellulose, although extensively studied, involve physical and chemical reactions of such interactive complexity that full understanding has still to be achieved.

Most workers agree that the initial heating of cellulose yields pyrolytic formation of a non-flammable residue fraction and flammable volatiles which, in the presence of oxygen, may or may not ignite, depending on whether both the relative and total volatile/oxygen concentrations are

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sufficient to produce oxidative interactions at the given temperature. Shafizadeh and Bradbury [1] have reported that the pyrolytic degradation of cellulose is not affected by the presence of oxygen which is essential for subsequent ignition.

The sustained combustion of cellulose is often seen simply as the competition of the two reactions of pyrolysis and oxidation in which the rate of energy evolution from the exothermic oxidation reaction must be sufficient to pyrolyse further cellulose and ensure a constant supply of flammable volatiles. A steady-state combustion condition will continue providing that a supply of raw materials and oxygen is maintained. However, the critical point of ignition which defines the point at which a predominantly pyrolytic mechanism transforms to one of combined pyrolysis–oxidation or steady-state combustion conditions, is the least understood process involved in the total combustion mechanism, despite extensive studies using a variety of techniques [2–7].

The procedure used to quantify the character of ignition of a polymer varies, depending on the actual ignition property under study. Limiting oxygen index (LOI) determinations for assessing the critical amount of oxygen necessary to achieve ignition or sustained steady-state combustion have been well documented [8–12]. Various methods of defining ignition temperature have been reported whereby polymeric materials are heated to a point where visual ignition is observed. The methods of heating for these studies have included both radiant heat [13–15] and heated air ignition sources [16,17] as well as numerous techniques based on piloted flame ignition [18–20].

Thermal analysis methods have been successfully used in fundamental studies of the pyrolysis and subsequent oxidation of cellulose [21–25] but these techniques have so far yielded little information concerning ignition behaviour. To date, these studies have provided only limited coherence to the understanding of the mechanisms by which ignition may be defined.

Recent work, in particular that by Dollimore and Hoath [26], provides evidence that ignition proceeds by three exothermic reactions following the initial pyrolysis of cellulose. These are the oxidation of volatiles at about 345°C, the oxidation of solid char at about 460°C, and a third oxidation occurring at approximately 500°C, which is ascribed to a char-related gas reaction.

In order to quantitatively determine ignition-related variables, the exposure of a polymeric material of known character and mass to a controlled thermal environment is essential. Furthermore, if ignition studies are to be reproducible and absolute, critical control of the gas environment surrounding the sample during heating to ignition is necessary to ensure that oxygen depletion from the immediate sample surface area is considered.

This work describes the use of differential thermal analysis (DTA) techniques to study the variables which affect the observed spontaneous ignition temperature of cotton cellulose, and extends the earlier study [27] in which the initial investigations were reported.

EXPERIMENTAL

Differential thermal analysis work was carried out using a Stanton Redcroft 671B analyser with an ambient to 500°C heating range. Control of the gas environment surrounding the sample was achieved by introducing an oxygen/nitrogen mixture of known composition, from a Stanton Redcroft FTA limiting oxygen index unit connected directly to the DTA furnace and delivered at a controlled rate. The paramagnetic oxygen sensor incorporated within the LOI apparatus recorded oxygen volume concentrations of the delivered gas to ± 1% accuracy.

The cellulose sample used for this work was a Sudanese cotton of 37 mm staple length. In order to remove the major impurities, the cotton was scoured in dilute sodium hydroxide and bleached with hydrogen peroxide to a level commensurate with commercially prepared cotton. To facilitate uniform packing of samples in the aluminium sample holders used, the fibres were reduced to 36 mesh powder in a Wiley mill. Conditioning of the samples was carried out for 24 h in an atmosphere of 65% relative humidity at 20°C prior to entering the DTA furnace. Aluminium oxide was used in all DTA runs as the reference material but no sample dilution was used as this might interfere with the flaming characteristics and affect oxygen availability with respect to the sample.

The air atmosphere surrounding samples within the furnace was from a compressed air supply subjected to a contaminating oil removal and drying pre-treatment.

Using the conditions and apparatus specified, commercially prepared cotton could be subjected to well-defined heating rates in an atmosphere of dry, oil-free air and the ensuing thermal transitions could be accurately observed.

RESULTS

The DTA scan of cotton shown in Fig. 1 for a 10 mg sample heated at 20°C min^{-1} in a static air environment shows an exothermic oxidative peak at 341°C, followed immediately by an endotherm of greater intensity at 360°C. However, under flowing air conditions, with a rate of 200 $\text{cm}^3\ \text{min}^{-1}$ through the DTA furnace, the former exothermic peak is replaced by an intense spontaneous ignition exotherm, which completely saturates the DTA instrumental differential temperature (ΔT) response and shows as a positive temperature increase on the sample temperature thermocouple output as described in Fig. 2.

Direct observation of the sample during the heating cycle confirmed that the onset of spontaneous ignition coincided with the extrapolated value, T_i, on the sample temperature recording exotherm, as shown in Fig. 2. The

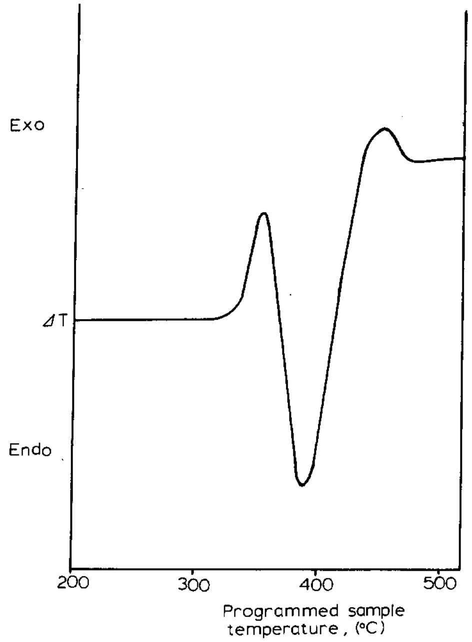

Fig. 1. DTA thermogram of a 10 mg sample of cellulose in static air.

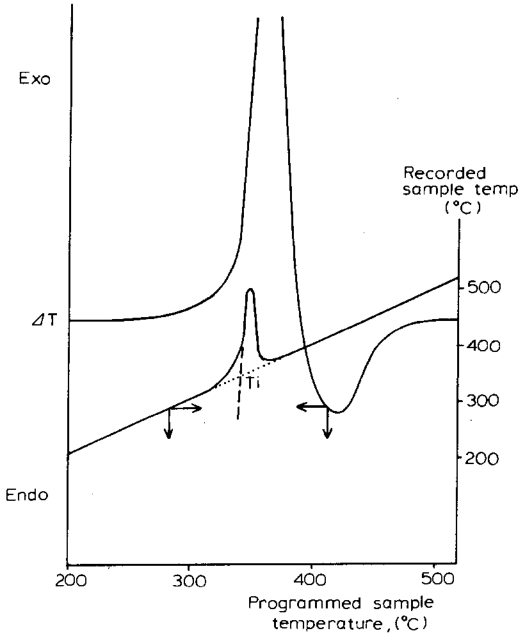

Fig. 2. Superimposed DTA thermogram and sample thermocouple response of a 10 mg sample heated in air flowing at 200 cm^3 min^{-1}.

spontaneous ignition temperature is considered to be the extrapolated point, T_i°C.

To assess the reproducibility of this extrapolated ignition temperature, thermograms for each of five 10 mg samples of cotton were produced under identical conditions of 200 cm^3 min^{-1} air flow rate and 20°C min^{-1} heating rate. The results yielded a spontaneous ignition temperature of 350.5 ± 1.5°C.

Effect of sample mass on T_i

The effect of sample mass on the spontaneous ignition temperature was evaluated within the physical restraints of the sample holder and furnace dimensions. This permitted a maximum mass of 15 mg to be analysed. A heating rate of 20°C min^{-1} was used and pre-treated compressed air constituted the gas environment at a flow rate of 200 cm^3 min^{-1}. The results shown in Table 1 of T_i for known sample masses also include the remaining residues of the sample after the thermo-oxidative transition has occurred.

No significant difference is observed in the recorded ignition temperatures, which suggests that T_i is independent of sample mass. However, the resulting residue weights after completion of the thermo-oxidative transition indicate that complete combustion of the sample does not occur for masses below 8 mg under the conditions specified. The residual char remaining after this partial ignition for sample masses < 8 mg is consumed at a higher

TABLE 1

Effect of mass of cellulose sample on the temperature of ignition, T_i, and the remaining char residues

Sample mass (mg)	T_i (°C)	Residue (%)
1	349	13.9
2	353	12.6
3	353	14.1
4	354	12.2
5	354	14.8
6	354	13.3
7	353	15.7
8	349	3.5
9	352	3.5
10	350	3.4
11	351	3.0
12	349	3.6
13	353	2.9
14	352	3.6
15	353	3.1

temperature, shown as a DTA exotherm at 480°C, in a smouldering type reaction. This high temperature oxidation of the residual char is probably the same transition reported by Dollimore and Hoath [26], who quote an exotherm at 460°C.

Effect of heating rate on T_i

The results shown in Table 2 indicate that the spontaneous ignition temperature of cotton is dependent on the rate at which the sample is heated. For each heating rate, a 10 mg sample was used under flowing air conditions and with flow rates of 50, 100, 200 and 300 cm^3 min^{-1} of dry air about the sample.

This dependence of T_i on heating rate can be described empirically [27] for heating rates, H_R, greater than 3°C min^{-1} by a simple power law of the type

$$T_i = T_i' H_R^{\alpha}$$

where T_i is the recorded spontaneous ignition temperature (°C), H_R is the rate of sample heating (°C min^{-1}), T_i' is the spontaneous ignition at $H_R = 1$°C min^{-1}, and α is a constant.

Linear regresssion of each set of log T_i and log H_R data at $H_R > 3$°C min^{-1} for each given flow rate, derived from results in Table 2, show the values of T_i' and α in Table 3. The results in Table 3 show that the power

TABLE 2

Effect of heating rate and air flow rate on the spontaneous ignition temperature, T_i, of cotton cellulose

Heating rate H_R (°C min^{-1})	Ignition behaviour at flow rate shown (cm^3 min^{-1})				
	50 cm^3 min^{-1} T_i (°C)	100 cm^3 min^{-1}		200 cm^3 min^{-1} T_i (°C)	300 cm^3 min^{-1} T_i (°C)
		T_i (°C)	Residue (%)		
20	351	350	<1	351	353
15	346	344	<1	344	344
10	340	338	<1	337	338
8	334	334	<1	331	333
6	326	326	<1	326	326
5	322	324	<1	324	322
4	320	320	<1	322	322
3	311	314	23	314	313
2	303	302	26	302	304
1	288	290	27	283	291

TABLE 3

Analysis of log T_i vs. log H_R plots at each air flow rate for 10 mg cellulose samples

Air flow rate (cm^3 min^{-1})	T_i'	α	Correlation coefficient	% Significance level
50	293.3	0.0612	0.992	0.1
100	295.9	0.0563	0.997	0.1
200	296.6	0.0551	0.993	0.1
300	294.4	0.0592	0.990	0.1
Combined results	295.0	0.0579	0.992	0.1

law relationship is independent of air flow rate, within experimental error. The combined results of log T_i vs. log H_R for air flow rates given in Table 3 are plotted in Fig. 3 and analysis of these results shows that the relation

$$T_i = 295\ H_R^{0.0579}$$

holds with high significance.

The initially reported combined results [27] showed that the relationship $T_i = 295.6\ H_R^{0.0567}$ holds for $H_R > 3$°C min^{-1} when 10 mg samples of cotton are subjected to an air flow rate of 200 cm^3 min^{-1} only. The revised relationship quoted above has greater validity because measurements have been recorded over a larger range of air flow rates. Values of T_i' at each air flow rate do not coincide with experimental values at $H_R \leqslant 3$°C min^{-1} because total sample combustion does not occur at such low heating rates, as

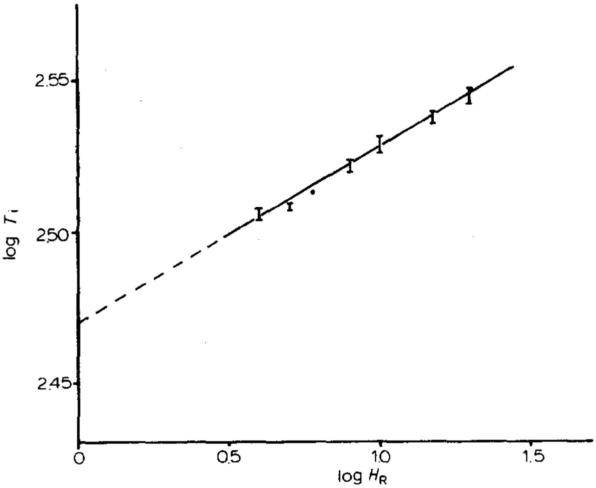

Fig. 3. Empirical logarithmic dependence of ignition temperature, T_i, on heating rate, H_R, for 10 mg cellulose samples heated under the conditions in Table 2. Vertical bars indicate the range of T_i values recorded at four air flow rates at each H_R.

indicated by the char residue results in Table 2.

If T_i is expressed as an absolute temperature, then the relation becomes

$$T_i = 566.7H_R^{0.032}$$

with a similar correlation coefficient (0.992) and significant at the 0.1% level.

Miller [2] has shown that in a real fire situation the heating rate of a polymer to ignition is in the order of 6000°C min^{-1} which, using the predictive character of the power law described, would suggest an ignition temperature for cotton cellulose in excess of 480°C. This correlates well with other values reported from combustion studies.

DISCUSSION

The results in Table 2 used to describe the above power law also fit a simple steady-state model of cellulose combustion.

Steady-state model of cellulose combustion

Consider a simple two-stage pyrolysis/oxidation reaction sequence for cellulose. The rate-determining step for flammable pyrolysis products may be considered simply as

$$(C_6H_{10}O_5)_n \xrightarrow[K_p]{\text{heat}} \text{Pyrolysis products}$$

and the subsequent oxidation of such products represented as

$$\text{Pyrolysis products} + m[O_2] \rightarrow 6n\ CO_2 + 5n\ H_2O$$

Pyrolysis products may include both volatile species such as laevoglucosan as well as solid carbonaceous char, although Chatterjee [28] and Shafizadeh and co-workers [29] consider the rate-determining pyrolysis step to be laevoglucosan formation. If C is the cellulose concentration and P the total pyrolysis product concentration at any time t, then

$$\frac{dP}{dt} = K_p \cdot C - K_{ox} \cdot P[O_2]^m \tag{1}$$

On heating cellulose in air, formation of pyrolysis products increases until the concentrations P and $[O_2]$ are sufficiently high for the oxidation stage to develop into full ignition at temperature T_i. If steady-state conditions apply with respect to P at the onset of ignition then

$$\frac{dP}{dt} = 0 = K_p \cdot C - K_{ox} \cdot P[O_2]^m$$

and

$$K_p \cdot C = K_{ox} \cdot P[O_2]^m \tag{2}$$

If $K_p = A_p e^{-E_p/RT}$ and $K_{ox} = A_{ox}^{-E_{ox}/RT}$, where A_p and A_{ox} are the Arrhenius constants and E_p and E_{ox} are activation energies for pyrolysis and oxidation, respectively, then from eqn. (2)

$$P = \frac{A_p \cdot C \cdot e^{-(E_p - E_{ox})/RT}}{A_{ox}[O_2]^m}$$

and

$$\ln P = \ln\frac{A_p}{A_{ox}} + \ln C - m \cdot \ln[O_2] - \frac{(E_p - E_{ox})}{RT} \tag{3}$$

Differentiation at constant $[O_2]$ gives

$$\frac{d\ln P}{dt} = \frac{(E_p - E_{ox})}{R} \cdot \frac{d(1/T)}{dt} - K_p \tag{4}$$

From eqn. (1) both before and during steady-state conditions have been achieved

$$\frac{d\ln P}{dt} = K_p\left(\frac{C}{P}\right) - K_{ox}[O_2]^m \tag{5}$$

and so combination of eqns. (4) and (5) gives

$$\frac{d(1/T)}{dt} = \frac{K_p(1 + C/P) - K_{ox}[O_2]^m}{-(E_p - E_{ox})/R} \tag{6}$$

which defines the influence of temperature on the steady-state condition.

If the cellulose sample is initially at temperature T_0 and is heated prior to ignition at a heating rate $dT/dt = H_R$, then between times $t = 0$ and $t = t$, the temperature of the sample rises to $T = T_0 + H_R t$ and $1/T = 1/(T_0 + H_R T)$, from which

$$\frac{d(1/T)}{dt} = -\frac{H_R}{T^2} \tag{7}$$

If after heating the sample for time t, the temperature $T = T_i$, ignition occurs, the combination of eqns. (6) and (7) gives

$$\frac{H_R}{T_i^2} = \frac{K_p(1 + C/P) - K_{ox}[O_2]^m}{(E_p - E_{ox})/R} \tag{8}$$

In this work, T_i is defined as the temperature at which the onset of ignition occurs, found from the thermal analysis trace extrapolation in Fig. 2; at this temperature, if it may be assumed that $K_{ox}[O_2]^m \ll K_p(1 + C/P)$ since $C \gg P$, then eqn. 8 reduces to

$$\frac{H_R}{T_i^2} = K_i e^{-E_p/RT_i} \tag{9}$$

where

$$K_i = \frac{A_p(1 + C/P)}{(E_p - E_{ox})/R}$$

Thus

$$2 \ln T_i - \ln H_R = \frac{E_p}{2.303R}(1/T_i) - \log K_i \tag{10}$$

Equation (10) suggests that a plot of ($2 \log T_i - \log H_R$) vs. $1/T_i$ will be linear with a slope of $E_p/2.303R$. Figure 4 shows the results in Table 2 for heating rates greater than 3°C min^{-1} and flow rates from 50 to 300 cm^3 min^{-1} plotted in accord with eqn. (10).

Linear regressional analysis of the plot in Fig. 4 shows a correlation coefficient of 0.992 at the 1% level of significance.

The slope of 7.630×10^3 K suggests an activation energy for pyrolysis, E_p of 146 kJ mole^{-1} (35 kcal mole^{-1}) for cellulose. However, this represents an upper limit because of the assumption that the effect of oxygen is negligible prior to deriving eqn. (9).

A review of published values for E_p of cotton cellulose shows a range from 67.7 kJ mole^{-1} [30] to 648 kJ mole^{-1} [31] but most workers agree on values within the limits 125–209 kJ mole^{-1} [32–37]. Madorsky et al. [32] have reported activation energies for the pyrolysis of cotton, hydrocellulose and viscose at 209, 196.5 and 205 kJ mole^{-1}, respectively, using rate of weight loss measurements whilst heating the samples under vacuum conditions.

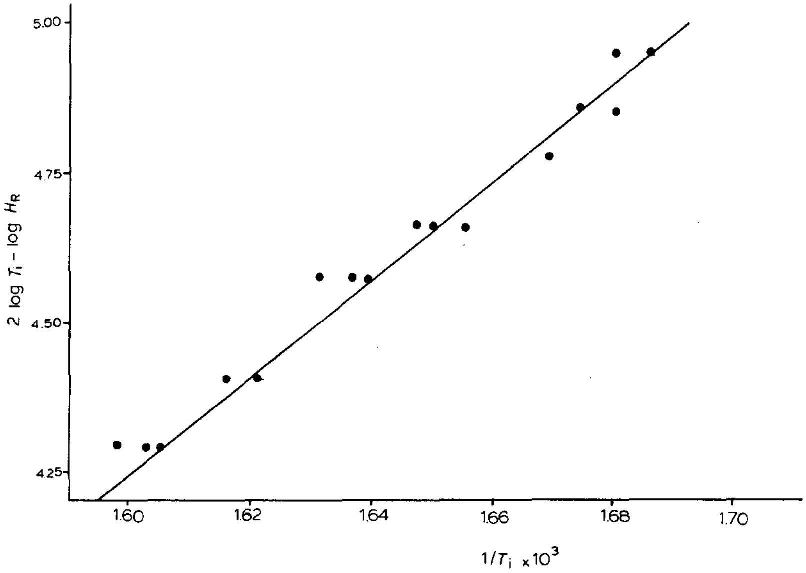

Fig. 4. Plot of ($2 \log T_i - \log H_R$) vs. $1/T_i$ for 10 mg cellulose samples heated under the conditions in Table 2. 28 data points are represented in the Fig.

McCarter [33] studied the kinetics of the pyrolysis reaction of cotton cellulose from measurements of vapour evolution rather than weight loss readings, under flowing nitrogen conditions, which resulted in an activation energy of 169.3 kJ mole^{-1}; pyrolysis was interpreted as a first order depolymerisation reaction. This correlates well with the earlier work of Chatterjee [28], who considered the rate-determining pyrolytic formation of laevoglucosan to have an activation energy of 175.6 kJ mole^{-1}. Using thermogravimetric analysis, Dollimore and Holt [34] report a value of 144 kJ mole^{-1} for the rate-determining pyrolytic step, which agrees well with E_p in this work as well as with that quoted by Fung [37] of 148 kJ mole^{-1}. It is interesting to note that Murphy [35] quotes a value of 142 kJ mole^{-1}, which represents pyrolysis of a cellulose impurity component present at 2.8%; the remaining cellulose pyrolyses with $E_p = 165$ kJ mole^{-1}.

Bradbury et al. [29] suggest that cellulose pyrolysis may be adequately described by a three-reaction kinetic model. This comprises a rapid initial activation of the cellulose followed by the slower reactions where direct volatile formation on the one hand competes with char plus gas formation on the other. Activation energies for each of these reactions have been found to be 243, 198 and 153 kJ mole^{-1}, respectively. If the respective rate constants [29] are calculated for the temperature ranges of ignition recorded in this work (283–353°C), then according to Bradbury's mechanism the production of volatiles is the favoured pyrolysis product route. If this is the rate-determining step, represented in the above steady-state mechanism, then the activation energy of volatile formation, $E_p = 146$ kJ mole^{-1} found in this work, should perhaps be compared with the value $E_p = 198$ kJ mole^{-1} of Bradbury.

Further work is being undertaken to investigate the influences that oxygen concentration and flame retardant systems have on the spontaneous ignition of cotton cellulose.

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