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KINETICS OF THERMAL DECOMPOSITION OF CELLULOSE. PART II. TEMPERATURE DIFFERENCES BETWEEN GAS AND SOLID AT HIGH HEATING RATES

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ABSTRACT

The use of high heating rates when studying the thermal decomposition kinetics of cellulose gives rise to a gap between the solid temperature and the thermogravimetric system temperature. A model is proposed which accounts for this temperature gap and permits the calculation of the actual solid temperature. The results for various heating rates are fitted using the same kinetic equation.

INTRODUCTION

The use of dynamic thermogravimetric methods to study the thermal decomposition kinetics of cellulose has several advantages over the isothermal approach. One of these advantages is the possibility of obtaining results at higher temperatures.

Various methods of data analysis have been proposed to determine the kinetic parameters from TGA curves obtained by a variety of procedures [1–6]. These methods are based on the applicability of the Arrhenius equation after accounting for diffusion effects.

In a previous paper [7] Bilbao et al. used TGA techniques to study the kinetics of cellulose pyrolysis in a nitrogen atmosphere. Their results indicate that the dynamic experiments performed at a low heating rate ($\beta = 1.25\,^\circ C\ min^{-1}$) provide kinetic data up to a temperature of 330 °C. However, for the same temperature, the values of the kinetic coefficient decrease as the heating rate is increased. This does not seem reasonable considering the known mechanisms of pyrolysis of cellulose materials. Therefore, an explanation was proposed based on the difference between the true temperature T of the solid and the temperature T_f measured for the system (thermobalance oven).

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The present work proposes a model to account for this temperature gap. The model permits the calculation of T as a function of T_f, and hence the value of the kinetic coefficient corresponding to the actual temperature of the solid.

MODEL DEVELOPMENT

The model proposed assumes the variation in the solid temperature T to have two causes: heat transferred by convection from the system at a temperature T_f and heat absorbed or released in the solid by decomposition and/or evaporation processes. These assumptions were similar to those used by Lede [8].

According to the assumptions stated, for a time interval $\mathrm{d}t$ in which there is a weight loss $\mathrm{d}W$ it follows that

$$WC_p\,\mathrm{d}T = hS(T_f - T)\,\mathrm{d}t + (-\Delta H_r)(-\mathrm{d}W) \tag{1}$$

This equation has been solved considering various temperature (or time) intervals, defined from the analysis of the TGA curves obtained. An example of these curves is shown in Fig. 1.

Four temperature intervals have been considered.

(a) $T_f < T_{f1}$: the solid temperature increases without weight loss.

(b) $T_{f1} < T_f < T_{f2}$: a slight weight loss can be observed (between 1 and 4 wt.% of the original sample). This is mainly due to the loss of moisture, as well as the evolution of CO and CO_2 in the first stages of cellulose decomposition.

(c) $T_{f2} < T_f < T_{f3}$: no significant weight loss is observed.

(d) $T_f > T_{f3}$: the main weight loss takes place in this interval.

Equation (1) has been applied to the various intervals after appropriate simplifications.

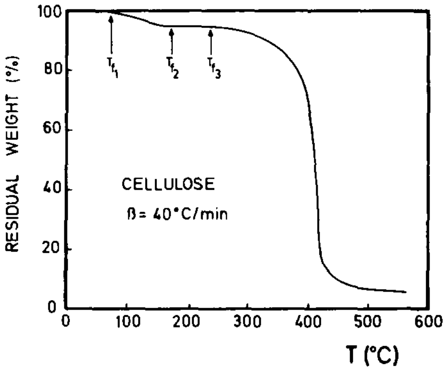

Fig. 1. Temperature intervals observed in the decomposition of cellulose.

(a) $T_f < T_{f1}$. For this interval, $dW = 0$, $W = W_0$. Then eqn. (1) becomes

$$W_0 C_p \, dT = hS(T_f - T) \, dt \tag{2}$$

where

$$T_f = T_0 + \beta t \tag{3}$$

The values of C_p, h and S can be considered to be constants. Thus

$$\frac{dT}{dt} = B(T_f - T) \tag{4}$$

where

$$B = hS/C_p W_0 \tag{5}$$

Integration of eqn. (4) gives the temperature of the solid as a function of time for this temperature interval

$$T = T_f - (\beta/B)(1 - e^{-Bt}) \tag{6}$$

At the end of the interval

$$T_1 = T_{f1} - (\beta/B)(1 - e^{-Bt_1}) \tag{7}$$

According to eqn. (7), the temperature difference between solid and system at the end of the first interval increases as the heating rate is increased. This effect is mitigated to some extent by the fact that t_1 decreases with increasing β, and hence the value $(1 - e^{-Bt_1})$.

(b) $T_{f1} < T_f < T_{f2}$. In this temperature interval a slight (less than 5%) weight loss is observed as a result of the loss of water and of small amounts of CO and CO_2.

Equation (1) has been applied to this interval with the following assumptions. Firstly, the sample weight is approximately constant; thus in the heat accumulation term we can consider $W \approx W_0$. Secondly, C_p and ΔH_{r1} are taken as constant throughout the interval. Thirdly, a linear relationship has been assumed for weight change with time in the term corresponding to heat absorbed or released.

With these assumptions, and bearing in mind that $W = W_0(1 - X)$, eqn. (1) becomes

$$dT/dt = B(T_f - T) - D \tag{8}$$

where

$$D = -\frac{(-\Delta H_{r1})}{C_p}\frac{dX}{dt} = \frac{(-\Delta H_{r1})}{C_p}\frac{H}{100(t_2 - t_1)} \tag{9}$$

t_1 and t_2 being the times for $T_f = T_{f1}$ and $T_f = T_{f2}$, respectively; H represents the solid weight fraction lost at $T < 150\,^\circ C$. Integration of eqn. (8) with the initial conditions $t = t_1$, $T = T_1$ yields

$$T = T_0 + \beta t - \frac{\beta}{B}(1 - e^{-Bt}) - \frac{D}{B}(1 - e^{-B(t - t_1)}) \tag{10}$$

Applying this equation to the end of the second interval and taking into account eqn. (3), the following expression is obtained

$$T_2 = T_{f2} - \frac{\beta}{B}(1 - e^{-Bt_2}) - \frac{D}{B}(1 - e^{-B(t_2-t_1)}) \tag{11}$$

According to eqn. (11), the temperature gap between the solid sample and the oven at the end of the second interval depends mainly on two factors. Firstly, the heating rate β is important. An increase in the value of β gives rise to a higher temperature gap, in the same way as pointed out above for T_1 and T_{f1}. Secondly, the value of D in eqn. (9) depends on the percentage weight loss H at $T \leqslant 150\,^\circ\mathrm{C}$. An increase in the value of H produces an increase in D, and thus, according to eqn. (11), a higher temperature gap is obtained. This effect is more pronounced for higher values of β, since the value of $(t_2 - t_1)$ is lower, and therefore D increases for a given H. This last effect is somewhat compensated since when $(t_2 - t_1)$ decreases, the value of $(1 - e^{-B(t_2-t_1)})$ in eqn. (11) also decreases.

(c) $T_{f2} < T_f < T_{f3}$. The calculation of the solid sample temperature is based on the fact that no noticeable weight loss is observed for this interval. Therefore, eqn. (1) can be simplified to give eqn. (2). With the same assumptions as in section (a) above, eqn. (4) can be obtained. Integration of this equation with the initial conditions $t = t_2$, $T = T_2$ yields

$$T = T_0 + \beta t - \frac{\beta}{B}(1 - e^{-Bt}) - \frac{D}{B}\, e^{-Bt}(e^{Bt_2} - e^{Bt_1}) \tag{12}$$

This equation can be applied at the end of the interval, considering also eqn. (3). Then

$$T_3 = T_{f3} - \frac{\beta}{B}(1 - e^{-Bt_3}) - \frac{D}{B}\, e^{-Bt_3}(e^{Bt_2} - e^{Bt_1}) \tag{13}$$

According to this equation, the temperature difference between T_3 and T_{f3} depends on the same factors mentioned for T_2 and T_{f2}; in other words, for a given β, the temperature gap increases when increasing H, while for a given H the temperature gap increases when increasing β.

(d) $T_f > T_{f3}$. In this interval, a significant weight loss, given by $W = W_0(1 - X)$, can be observed. Equation (1) can now be written as

$$W_0(1 - X)C_p\frac{dT}{dt} = hS(T_f - T) + (-\Delta H_{r2})W_0\frac{dX}{dt} \tag{14}$$

where ΔH_{r2} is the heat of reaction for this interval. Rearranging

$$\frac{dT}{dt} = \frac{B}{1 - X}(T_f - T) + \frac{(-\Delta H_{r2})}{C_p}\,\frac{1}{1 - X}\,\frac{dX}{dt} \tag{15}$$

This equation can be solved by numerical methods, using the initial conditions $t = t_3$, $T = T_3$.

According to eqn. (15), the temperature difference between the oven and the solid sample during the "true" pyrolysis period depends on two factors.

Firstly, the temperature difference at the start of the pyrolysis process ($T_{f3} - T_3$), which in turn depends on the factors mentioned in section (c) above, is a major factor. Secondly, the heat of reaction of the pyrolysis process, ΔH_{r2}, whose effect becomes more pronounced as β is increased, is also involved. The effect of the heat of reaction can be very different, depending on whether the reaction is endothermic or exothermic. In the first case it will give rise to a higher temperature gap, while in the second, the temperatures will be closer with respect to the initial difference $T_{f3} - T_3$.

RESULTS

Knowledge of the "true" solid temperature for a given set of T_f, β and H values requires the previous determination of B and ΔH_{r1}. These parameters can be calculated using eqns. (7), (11) and (13) with the appropriate values of T_{f1}, T_{f2} and T_{f3} for each experiment. The following assumptions have been made for the purposes of calculation. Firstly, the solid sample temperatures (T_1, T_2 and T_3) which mark the boundaries of the intervals obtained in the TGA curves do not depend on the values of β and H. Secondly, when very low heating rates are employed ($\beta = 1.25\,^\circ\text{C min}^{-1}$), there is no temperature gap between the solid sample and the oven: thus $T_1 = T_{f1}$, $T_2 = T_{f2}$, $T_3 = T_{f3}$.

Table 1 shows the values of T_{f1}, T_{f2}, T_{f3} and t_1, t_2, t_3 obtained experimentally for various heating rates. It may be observed that the values shown follow trends similar to those predicted by eqns. (7), (11) and (13), i.e.: T_{f1} increases as the heating rate increases; for a given β, T_{f2} increases as H increases; T_{f3} increases as β and H increase.

TABLE 1

Experimental values of T_{f1}, T_{f2}, and T_{f3} for various β and H

β ($^\circ$C min^{-1})	H (%)	T_{f1} ($^\circ$C)	t_1 (min)	T_{f2} ($^\circ$C)	t_2 (min)	T_{f3} ($^\circ$C)	t_3 (min)
80	3.87	87	0.55	210	2.18	279	3.05
80	1.43	81	0.50	178	1.78	265	2.87
40	3.85	77	1.05	174	3.47	239	4.75
40	1.06	75	1.00	157	3.05	230	4.87
20	3.19	64	1.45	142	5.35	225	8.55
20	1.13	63	1.40	135	5.00	206	15.0
10	2.26	58	2.30	126	9.10	204	16.0
10	1.47	55	2.00	123	8.80	195	16.0
5	4.70	53	3.60	120	17.0	190	31.0
2.5	2.28	52	6.80	115	32.0	188	61.3
1.25	2.80	51	12.8	110	60.0	185	120
1.25	4.00	51	12.8	111	60.8	185	120
1.25	5.20	51	12.8	111	60.8	185	120

Calculation of B

The value of the parameter B has been obtained from eqn. (7), using the appropriate values of T_{f1} and t_1 for each β. Table 1 shows that when the heating rate is decreased, T_{f1} decreases until it reaches the constant value of 51°C corresponding to $\beta = 1.25\,°\mathrm{C\ min^{-1}}$, $T_1 = T_{f1}$. The average value obtained for B was 1 min^{-1}.

Calculation of $\Delta \mathrm{H}_{r1}$

From eqns. (11) and (13) it may be derived that

$$\Delta H_{r1} = \frac{-BC_p(t_2 - t_1)100(T_3 - T_{f3} + (\beta/B)(1 - e^{-Bt_3}))}{H\,e^{-Bt_3}(e^{Bt_2} - e^{Bt_1})} \tag{16}$$

The determination of T_3 has been carried out using the same procedure as for T_1, since T_{f3} is considered to be very close to T_3 when the heating rate is $1.25\,°\mathrm{C\ min^{-1}}$. Thus, according to Table 1, T_3 has been taken to be 185°C. The average value of ΔH_{r1} found was close to 540 cal g^{-1}, which confirms that the slight weight loss observed in the second temperature interval is mainly due to the evaporation of water from the solid sample.

Calculation of the true solid temperature

When different heating rates or values of H are involved, the determination of the intrinsic kinetics of the process requires the previous calculation of the temperature gap between oven and solid sample. To this end, T is determined as a function of T_f, β and H. The calculation is carried out according to the following procedure.

(i) The solid temperature is assumed to be equal to the temperature measured for the system ($T = T_f$) when the heating rate is set to $1.25\,°\mathrm{C\ min^{-1}}$. This permits the calculation of the boundaries of the true temperature of the solid for each interval T_1, T_2, T_3.

(ii) For heating rates higher than $1.25\,°\mathrm{C\ min^{-1}}$, eqns. (3) and (7) can be used together with the values of T_1 and B to calculate t_1 and T_{f1} for a given value of β.

(iii) The values of t_2 and T_{f2} can be calculated from eqns. (3), (9) and (11) together with the values calculated for T_2, t_1, B and ΔH_{r1}.

(iv) Using the parameters calculated above, t_3 and T_{f3} can be obtained from eqns. (3) and (13). Thus, these four steps enable us to calculate the relationship between T and T_f for the first three intervals.

(v) Equation (15) has been solved by numerical methods to determine the temperature gap between solid sample and oven for the temperature interval $T_f > T_{f3}$. In eqn. (15), ΔH_{r2} is a variable with a very strong influence.

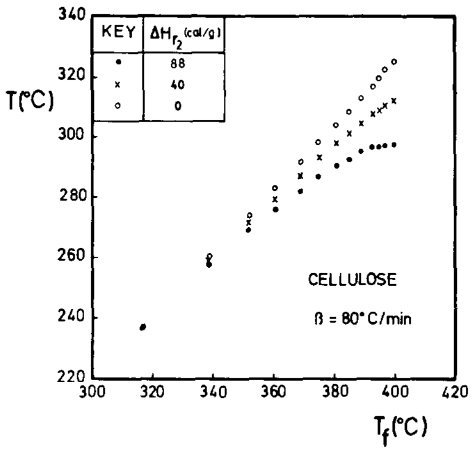

Fig. 2. Differences between T and T_f for various values of ΔH_{r2}.

A number of authors [9–11] agree regarding their classification of the thermal decomposition of cellulose in the temperature range studied in this work as an endothermic process with values for ΔH_{r2} of between 0 and 88 cal g^{-1}.

A study has been carried out of the influence of the heat of reaction between these limits on the function $T = f(T_f)$. For instance, Fig. 2 shows that for $T_f < 400\,^\circ C$, an increase in the endothermic heat of reaction gives rise to a slightly higher temperature difference. Given the high degree of scattering in the values of ΔH_{r2} reported in the literature, correction of temperatures for the fourth interval has been carried out here assuming $\Delta H_{r2} = 0$. Figure 3 shows T as a function of T_f for $\Delta H_{r2} = 0$ and various

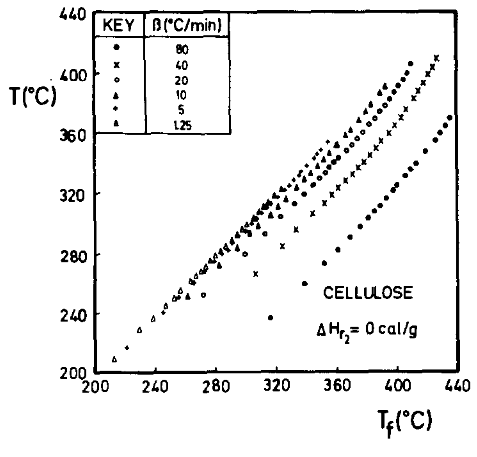

Fig. 3. Differences between T and T_f for various heating rates.

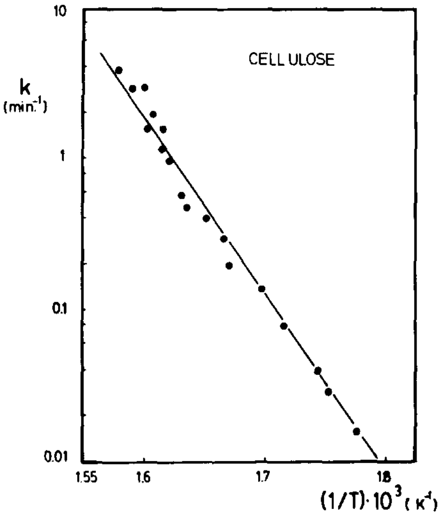

Fig. 4. Values of k for dynamic experiments in which the temperature has been corrected.

values of β. From the figure it is clear that the difference $T_f - T$ can be taken as constant throughout the interval.

From the values of $T = f(T_f)$ in the first three intervals and assuming that for a given heating rate $(T_f - T)$ is constant in the fourth interval, the temperature corrections can be carried out. Thus the value of the true solid temperature has been determined for each temperature of the system. This in turn allows the calculation of the kinetic constant corresponding to the temperature of the solid. Figure 4 shows the plot of k vs. $1/T$ obtained from the experiments. The results are fitted by the same straight line, which correspond to the equation

$$k(\mathrm{min}^{-1}) = 9.5 \times 10^{18}\ \mathrm{e}^{-53800/RT} \tag{17}$$

This expression is similar to the one obtained [7] with $\beta = 1.25\,^\circ\mathrm{C\ min}^{-1}$.

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