Thermogravimetric Analysis of Cellulose: Effect of the Molecular Weight on Thermal Decomposition

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Synopsis

Cellulose fractions of different molecular weights were subjected to dynamic thermogravimetric analysis in a nitrogen atmosphere. From the experimental data, activation energies and reaction orders were obtained following the Freeman–Carroll and Broido methods. The thermal stabilities of the samples were estimated taking into account the values of T_i, T_{max}, and E_a. The results show that thermal stability increases as the molecular weight increases. It was also found that the cellulose pyrolisis process cannot be described as having a single value of E_a over the entire pyrolisis range. The dependence of E_a on molecular weight is also discussed.

INTRODUCTION

Over the years, an extensive experimentation on pyrolitic degradation of cellulose has been made, because of the practical importance of the phenomenon of flame resistance.[1] Previous investigations on cellulose pyrolisis have been carried out by a wide variety of techniques[2-5] and methods[6-11] of analysis. Despite the extensive research on the subject, the exact mechanism and kinetics of the process remain unclear.

It is known that the fine estructure, i.e., crystallinity, crystalline size, orientation, degree of polymerization, and packing density affect the pyrolisis kinetics of cellulose.[8,12-15] Despite the importance that the study of fine structure can have on the knowledge of the pyrolisis of cellulose, there have been few reports on the subject.

As far as molecular weight is concerned, Madorsky et al. reported that rayon decomposes faster than cotton and suggests that the differences might be due to the low degree of polymerization of rayon.[16,17] Basch and Lewin[15] found the degree of polymerization as one of the parameters having influence on the pyrolisis rate of cellulose.

The present study has been undertaken to examine the thermal stability of several fractions of different molecular weight obtained from cellulose pulp by studying the corresponding thermograms obtained by means of a thermogravimetric analyzer and calculating various thermal parameters, taking also into account the influence of the crystallinity of the samples.

EXPERIMENTAL

Purified and bleached bisulfite pulp of eucalyptus was fractionated by the method described elsewhere.[18] The pulp was dissolved in cadoxen[19] to give a

TABLE I
Molecular Weight, Initiation Temperature, DTG Maxima, Crystallinity Index
and Char Yield of Fractions of Purified Cellulose Pulp

Fraction	$\overline{M}_n \times 10^{-3}$	T_i (°C)	T_{max} (°C)	X-ray crystallinity index	Char yields at 973 K (wt %)
F-1	201	210	340	39	2.5
F-2	173	190	335	37	3.0
F-3	157	185	335	21	5.0
F-4	146	175	335	26	2.8
F-5	123	165	330	23	2.0
F-6	103	150	300	15	6.2
F-7	66	—	297/317	—	5.3

concentration of 1.2% (w/v). The fractionation was carried out under nitrogen atmosphere at 25°C. The mixture water/propanol (1:3) was used as nonsolvent. Ten fractions were isolated. The last three were neglected because they were too small for the analysis. The fractions were washed with methanol, acetone, and benzene successively. Then, they were dried under vacuum at 40°C until constant weight, and kept in hermetically sealed containers until use.

The molecular weights of the fractions were measured by capillary viscometry in aqueous cadoxen solution[20] at 25°C. The average molecular weights were calculated using the relationship:

$$[\eta] = 5.23 \times 10^{-5}(\overline{M}_n)^{0.93}$$

which was established previously.[20] The results are shown in Table I.

The thermogravimetric analysis was carried out by means of a Dupont 951 thermobalance attached to a DuPont 990 module. In order to compare the thermal stability of the samples, all of them were handled under identical conditions. The nitrogen flow rate was kept constant at 30 mL/min. The heating rate was 5°C/min.

X-ray diffraction measurements were carried out in a Phillips Geiger-counter X-ray diffractometer. The diagrams were recorded at room temperature in the 2θ range between 4 and 40°C, using Ni filtered Cukα radiation. The "crystallinity index" was calculated by the empirical method of Nelson and O'Connor.[21]

RESULTS AND DISCUSSION

Dynamic thermogravimetric curves for the cellulose pulp fractions F-1–F-5 were similar to those reported in the literature,[6,7,11,22] as can be seen in Figure 1 for the F-1 sample. The initial small weight loss, which occurs at temperatures below 100°C and constituting about 5–8% of the total weight loss, was attributed to the evaporation of retained moisture from the cellulose.[6,7,11,22] This initial weight loss is followed by a plateau region before the onset of the major weight loss, which shows an acceleratory period, after which the weight
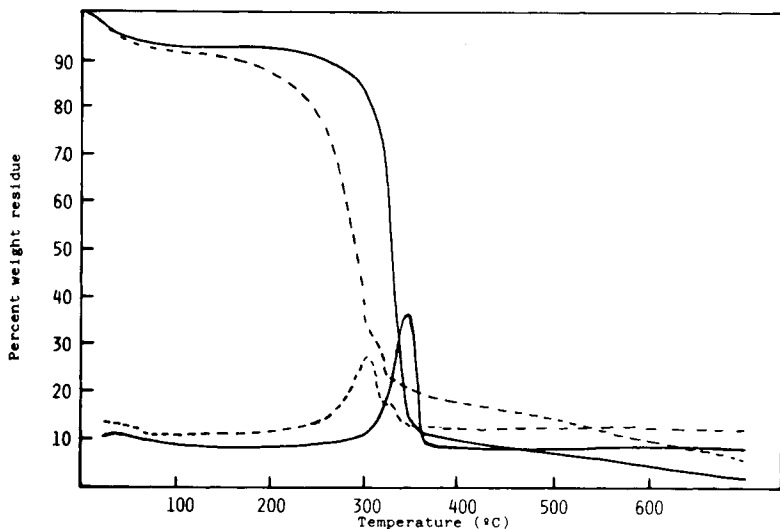
Fig. 1. Thermogravimetric curves of cellulose fractions with $\overline{M}_n$ = 201,000 (—) and $\overline{M}_n$ = 66,000 (– – –), in nitrogen.

loss rate is almost constant. Finally, there was a very slow approach to constant weight. For the F-6 and F-7 fractions, after the major event has taken place, a third event begins, and the rate of weight loss is not constant as it is shown in Figure 1 for F-7.

The initial rapid but small weight loss, attributed to the loss of retained moisture, was neglected. The initial decomposition temperature T_i was taken at the point in which the thermogravimetric curve deviates from the horizontal line. In Table I, we can see that T_i decreases, as the molecular weight decreases. For the F-7 fraction, we have not determined T_i because of the absence of a true horizontal plateau for this fraction.

From the derivative TG curves, T_{max} values were determined as those temperatures at which the rate of decomposition reaches its maximum value. T_{max} values are also shown in Table I. The second value of T_{max} for F-7 corresponds to the third event found for this fraction. For F-6, this event appears in the derivative curve as a shoulder and, therefore, it is not possible to give a precise value of T_{max}. The residual weight of each sample at 700°C and the crystallinity index are also shown in Table I. The crystallinity index of F-7 has not been determined because the amount of the sample was too small to perform the measurement.

According to the T_i and T_{max} values, the lower the molecular weight, the more readily degradable the species are. On the other hand, as the molecular weight decreases, the percentage of crystallinity decreases, except for F-3, which showed an abnormally low value. We have no explanation for this phenomenon at present. The results mentioned above are in good agreement with those in the literature, as it has been reported that the crystallinity has a stabilizing effect on the thermal decomposition of cellulose.[14,15,23]

The kinetics of pyrolisis of the samples was examined by the differential method of Freeman and Carroll[24] and by the integral method of Broido.[25]
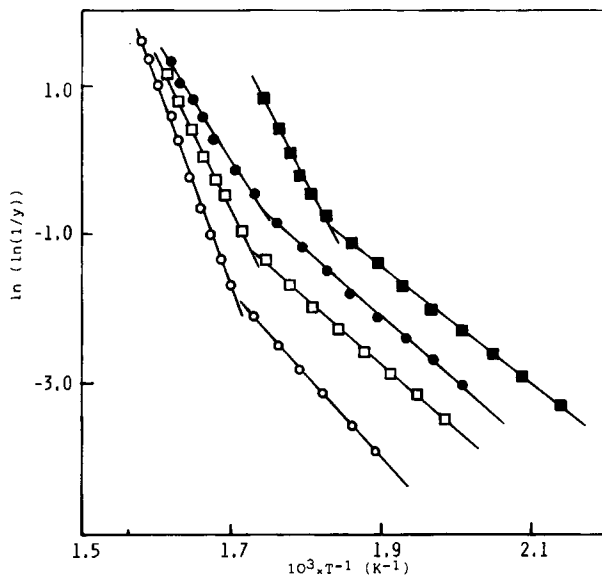
Fig. 2. Plots of $\ln[\ln(1/y)]$ vs. $10^3 \times T^{-1}$ (K^{-1}) using Broido equation for fractions with $10^{-3} \times \overline{M}_n$: 201 (○), 157 (□), 123 (●) and 66 (■) for the main stage of pyrolisis.
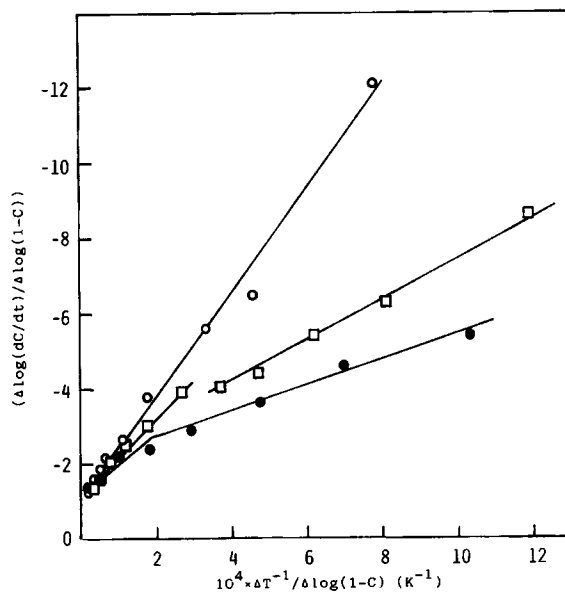

Fig. 3. Plots of $[\Delta \log(dC/dt)/\Delta \log(1 - C)]$ vs. $[10^4 \times \Delta(1/T)/\Delta \log(1 - C)]$ (K^{-1}) using the Freeman and Carroll equation for fractions with $10^{-3} \times \overline{M}_n$: 201 (○), 157 (□), and 123 (●) for the main stage of pyrolisis.

The first method uses the equation:

$$\frac{\Delta \log(dC/dt)}{\Delta \log(1-C)} = n - \frac{E_a \Delta(1/T)}{2.3R\Delta \log(1-C)} \tag{1}$$

where the conversion C is defined as $C = (w_0 - w)/(w_0 - w_\infty)$, w_0 and w_∞ being the initial and final weights, and w the weight at any time. T is the absolute temperature recorded on the thermogram and R is the gas constant. E_a is the activation energy and n is the reaction order.

The equation of Broido is

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{R}\frac{1}{T} + \text{const} \tag{2}$$

where y is defined by the relationship $y = (w - w_\infty)/(w_0 - w_\infty)$. The other parameters present in the equation have the meaning mentioned above.

From the Broido method, plots of $\ln(\ln 1/y)$ vs. $1/T$ [eq. (2)] for the principal stage of the pyrolisis process are given in Figure 2.

Using the Freeman–Carroll method, the values of $[\Delta \log(dC/dt]/\Delta \log(1 - C)$ were plotted against $\Delta(1/T)/\Delta \log(1 - C)$, as is shown in Figure 3 for the principal stage of pyrolisis of fractions with $\overline{M}_n$ equal to 201,000, 157,000, and 123,000 as an example.

The values of E_a and n obtained from eqs. (1) and (2) as well as the conversion and temperature ranges in which the parameters were calculated are summarized in Table II. The E_a and n values were evaluated by using the least squares method.

According to the Freeman–Carroll method, a pseudo-first-order reaction took place during most of the pyrolisis process for F-1 and F-2. The data points corresponding to a conversion range lower than that showed in Table II have not been considered because the differential method magnifies the possible small errors in the initial stage, where the weight loss is small. F-3–F-5 fractions exhibit an initial stage of pyrolisis with a pseudo-zero reaction order and a final stage with a pseudo first order. Generally, the conversion range which follows a zero order becomes wider as the molecular weight decreases, while the conversion range for the first-order stage becomes narrower.

As has been mentioned above, the F-6 and F-7 fractions have thermogravimetric curves with a third event, but, in this work, we have only studied the major event, which is controlled in almost all the conversion range by pseudo-zero-order kinetics. There are a few points which do not follow a zero-order reaction, but their number is not enough for a precise calculation.

The activation energies calculated by this method decrease considerably with the decreasing molecular weight when the kinetics are of pseudo first order. On the contrary, there is not a clear tendency when the kinetics are of pseudo zero order, and the variations exhibited are not significant.

Using the Broido method, two stages of decomposition were encountered for all the fractions in the major event. The activation energies for the first step, corresponding to the lower temperatures of decomposition, show little varia-

TABLE II
Activation Energies and Reaction Orders Using Different Methods for the Pyrolisis Main Stage of Fractions of Purified Cellulose Pulp

| Fraction	Freeman–Carroll method				Broido method		
	Temperature range (°C)	C	E_a (kcal/mol)	n	Temperature range (°C)	y	E_a (kcal/mol)
F-1	—	—	—	—	250–305	0.98–0.88	22.0
	310–355	0.14–0.98	61.8	0.90	310–360	0.86–0.07	54.2
F-2	—	—	—	—	225–305	0.98–0.83	15.2
	310–355	0.21–0.98	56.2	0.75	310–360	0.79–0.01	49.4
F-3	295–315	0.20–0.39	24.3	0.03	225–305	0.97–0.72	17.5
	315–355	0.39–0.99	50.3	0.92	310–355	0.67–0.01	45.3
F-4	207–305	0.13–0.30	18.6	0.00	225–305	0.97–0.71	17.8
	305–345	0.30–0.98	46.2	0.85	310–350	0.66–0.02	43.6
F-5	270–310	0.17–0.53	17.0	0.08	225–305	0.95–0.54	17.8
	320–350	0.67–0.98	35.4	0.69	310–350	0.47–0.02	32.5
F-6	245–290	0.15–0.69	22.7	0.09	200–270	0.96–0.69	16.0
	—	—	—	—	275–300	0.64–0.20	31.9
F-7	225–295	0.10–0.78	22.9	0.00	190–270	0.97–0.67	15.2
	—	—	—	—	275–300	0.62–0.10	39.0
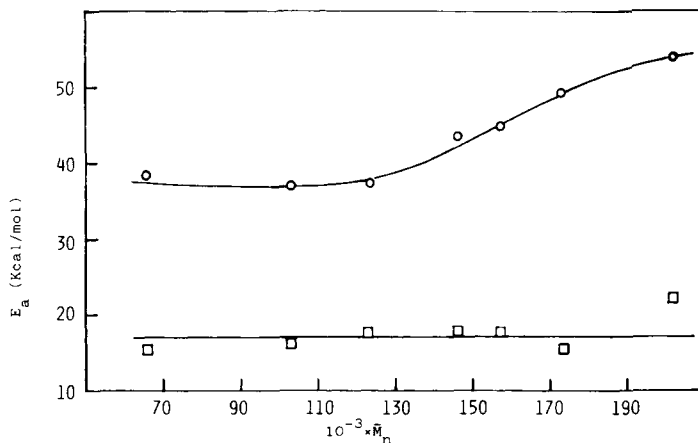
Fig. 4. E_a (kcal/mol) vs. $\overline{M}_n$, for E_a calculated following the Freeman–Carroll method. First (□) and second (○) steps of the major weight loss.

tion with molecular weight, whereas for the second step they decrease generally with decreasing molecular weight, and are higher than those found for the first step.

When one compares the values of E_a calculated by both analytical methods, it can be seen that activation energies obtained by the Freeman–Carroll method for the first order reaction are a little higher than those obtained for the latter step by the Broido method. Nevertheless, a relative agreement was obtained between the values calculated by both methods. A similar behavior to that mentioned above is shown when the activation energies for zero order reaction (Freeman–Carroll method) are compared with those obtained from the Broido method for the lower temperature range. Nevertheless, in this latter case, it should be noted that the Broido method assumes kinetics of first
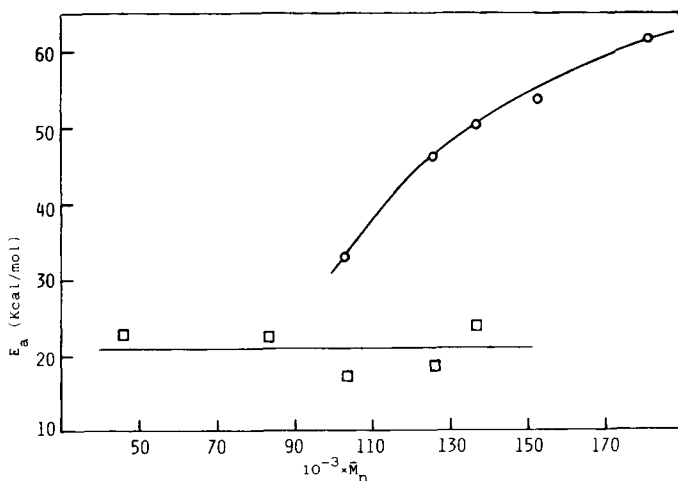

Fig. 5. E_a (kcal/mol) vs. $\overline{M}_n$, for E_a calculated following the Broido method. First (□) and second (○) steps of the major weight loss.

TABLE III
Activation Energies for Thermal Decomposition of Cellulosic Materials

Sample	Techniques and atmosphere[a]	Temperature range (°C)	E_a (kcal/mol)	Reference
Cotton cellulose	I-TGA-vacuum	275–305	50	16
Bleached linen	Evolved gas analysis	100–250	39.4	2
Chromatographic paper	D-TGA-N$_2$	240–310	33.1–35.2	3
		310–360	53.1–55.7	
Cellulose	Fluidized bed	250–300	46	4
Cotton cellulose	I-TGA-He	270–310	33	8
Cotton cellulose	D-TGA-N$_2$	290–395	48.8	26
Filter paper	D-TGA-vacuum	300–350	53.5	27
Bleached wood pulp	D-TGA-vacuum	300–361	46	28
Microcrystalline cellulose	D-TGA-vacuum	285–320	60	28
		320–360	39	
Filter paper	D-TGA-N$_2$	250–280	36.2	29
		285–320	45.4	
Filter paper	Evolved gas analysis	300–450	40.5	30
Cotton cellulose	Evolved gas analysis	300–450	40.5	30
Microcrystalline cellulose	Evolved gas analysis	300–450	40.5	30
Cellulose chromatographic	I-TGA-N$_2$	260–285	34.5	6
Cellulose fibers and fabrics	D-TGA-vacuum	250–400	29.6–61.2	14
Cell. chromatographic powder	D-TGA-N$_2$	284–337	59.5	7
	D-TGA-air	290–360	82.3	
Cotton cellulose	I-TGA-N$_2$	275–325	37	31
	I-TGA-air	275–325	17	
Cellulose	D-TGA-air	250–300	29.9	32
		300–350	60.6; 62.7	

[a] I = isothermal conditions of decomposition; D = dynamic conditions of decomposition.

order. This contradiction may perhaps be attributed to the fact that the Broido method is not sensitive to the reaction order at the early portion of the plot (relative to lower temperatures).[25]

The E_a values obtained by means of the Freeman–Carroll and Broido methods are represented against molecular weight in Figures 4 and 5, respectively.

Different values of the activation energy are reported in the literature depending upon the technique used, the source of cellulose, and the analytical method employed (Table III). If we compare our results with those found by other authors who have used the same analytical methods as we have used, we find that Tang and Neill,[3] using the Freeman–Carroll method, reported that cellulose decomposes in two stages. The first one followed a zero-order reaction with an activation energy of 33.1–35.2 kcal/mol, while the second stage obeyed a first-order kinetics with an activation energy of 53.1–55.7 kcal/mol. The E_a values for the second stage are in good agreement with those found in this work for the high molecular weight fractions.

Kaur et al.,[32] employing the Freeman–Carroll method, found that E_a is 62.7 kcal/mol in the temperature range 300–350°C. This E_a value is almost the same as that given in the present work for the highest molecular weight fractions. The same authors obtained by means of the Broido method, E_a values of 29.9 and 60.6 kcal/mol in the temperature ranges 250–300 and 300–350°C, respectively. Both E_a values are a little higher than those found in our work using the same method.

The fact that our activation energy values for the first stage do not change much with molecular weight suggests that the number of free chain ends has not an appreciable effect on the thermal decomposition. This behavior agrees with the generally accepted proposition in the sense that a first stage which involves dehydratation, partially due to thermal crosslinking, and simultaneously random chain cleavage of the less ordered regions (LOR) takes place.[2,8,14,16,33] The conversion range for this first stage is wider, the lower the molecular weight, as we mentioned above. This may be understood taking into account that a lower molecular weight implies a greater percentage of LOR, as it is confirmed by the X-ray data.

The activation energies for the second stage take different values for the different fractions. Such behavior cannot be directly related to the molecular weight, as a random chain cleavage has taken place previously. Several authors[14,23] suggest that in this second stage the decomposition of cellulose crystallites occurs. Thus, different factors related to the size and structure of the crystallites could also affect the values obtained.

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