

THERMOGRAVIMETRIC STUDIES OF DIFFERENT CELLULOSES

MAGDI Z. SEFAIN and SAMIRA F. EL-KALYOUBI

Cellulose and Paper Department, National Research Centre, Dokki, Cairo (Egypt)

(Received 4 November 1983)

ABSTRACT

The thermal decomposition of native and mercerised Egyptian cotton linters, viscose rayon, and bagasse pulp was studied. The variation in the activation energy values was discussed on the basis of chemical composition and structural differences. The values of rate constant, k , and the enthalpy change, ΔH , were calculated using the theory of the first order reaction.

INTRODUCTION

Thermogravimetric analysis (TGA) is widely used as a tool to study the degradation of different materials, to elucidate the order of reaction, and also to estimate other kinetic parameters such as the activation energy and the rate of decomposition [1]. These values are of most importance in the investigation of the mechanism involved in the degradation of the materials [2]. Many authors have studied and discussed the quantitative and qualitative characteristics of the thermal degradation of polymers [3]. The thermal properties of cellulosic materials were investigated by Shafizadeh and Bradbury [4] and Chatterjee [5], and by many other authors.

The aim of this work is to study the effect of the structure and the chemical composition of different cellulosic samples on their thermal decomposition behaviour.

EXPERIMENTAL

Materials

Four cellulosic samples were used in this study.

(a) Native cotton linters.

(b) Mercerised cotton linters; samples were cleaned in 18% sodium hydroxide solution for 1 h at 20°C, washed with distilled water to reach

neutrality, acidified with 10% acetic acid, washed to free the sample from the acid, then air dried.

(c) Viscose rayon fibres delivered from the Esco Co. for Rayon Manufacture, Bahtem, Cairo; samples were cleaned with warm water, then with a mixture of sodium hydroxide and sodium sulphide solutions (desulphurisation), washed with water, then air dried.

(d) Bagasse pulp (paper grade) obtained from Edfu Mill for Sugar and Pulp Manufacture, Egypt; samples were bleached with 5% sodium chlorite solution at 80°C for 2 h, washed with distilled water to reach neutrality, then air dried.

The above samples were analysed for α -cellulose according to Markblatt IV/2a Zellecheming (German Association of Cellulose Chemists and Engineers), for pentosans [6], and the ash contents were calculated by ignition in a muffle furnace at 800°C for 45 min.

Thermogravimetric measurement

TG analysis was performed using an automatic thermobalance (Gebruder Netzsch, W. Germany). The furnace was programmed to increase the temperature by 2.5° min⁻¹ and the heat was continued until a constant weight was attained. From each sample, 200 mg was weighed accurately and used throughout this measurement.

RESULTS AND DISCUSSION

Chemical analysis of the samples is given in Table 1. It is clear from the table that native and mercerised cotton linters, and viscose rayon possess high α -cellulose contents, whereas bagasse pulp has a relatively low α -cellulose content, a high pentosan content, and a high ash content.

Thermogravimetric profiles of the four samples are shown in Fig. 1. The profile of each sample can be classified into three distinct areas: (a) a slight weight decrease due to the evaporation of the residual water and volatile materials below 290°C. T_1 represents the temperature at which the main reaction starts. Generally, there are no clear differences between the samples,

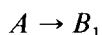
TABLE 1
Chemical composition of the experimental samples

α -Cellulose (%)	Pentosan (%)	Ash (%)	α -Cellulose (%)	Pentosan (%)	Ash (%)
<i>Native C.L.</i>			<i>Viscose rayon</i>		
99.51	—	0.080	89.55	2.31	0.10
<i>Mercerised C.L.</i>			<i>Bagasse pulp</i>		
99.58	—	0.073	76.82	21.84	0.40

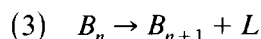
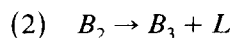
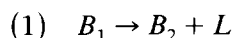
except that the bagasse sample decomposes at an earlier stage than the other three celluloses; (b) the main degradation zone, a slight curvature occurred at the end of this zone which may be attributed to the formation and evaporation of some volatile products [5], especially when the rate of heating is slow. Also this curvature starts earlier in the case of the bagasse sample: this temperature is represented as T_2 . The minimum point in this curvature, T_3 , is not fixed in the case of bagasse pulp. This may be attributed to the fast evaporation of the pyrolytic substances; and (c) the carbonisation zone at which a constant weight is obtained. T_4 represents the temperature at constant weight.

These three zones represent the main degradation steps previously suggested by Chatterjee [5], i.e., initiation, propagation and carbonisation as follows:

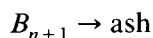
(a) Initiation



(b) Propagation



(c) Carbonisation



Where A represents the initial molecules of cellulose, B_1, B_2, \dots, B_{n+1} represent fractions of the cellulose molecules, and L represents volatile substances.

A first order reaction is usually expressed by

$$-dc/dt = kc$$

where c is the concentration of the reactant, t is the time, and k is the rate constant. If the concentration is replaced by the observed weight W_t , then

$$d(W_0 - W_t)/dt = k[W_0 - (W_0 - W_t)] = kW_t$$

Where W_0 is the original weight of the preheated sample, W_t the weight after heating for time t . Integration of the above equation gives

$$-\ln[W_0 - (W_0 - W_t)] = -\ln W_t = kt + \text{constant}$$

but at $t = 0$, $(W_0 - W_t) = 0$, hence, the constant $= -\ln W_0$, and, therefore, $\ln(W_0/W_t) = kt$. If the amount of ash at the end of the heating is considered, then

$$\ln[(W_0 - W_\infty)/(W_t - W_\infty)] = kt$$

where W_∞ is the weight at the end of heating (ash). Plots of $\ln(W_0 - W_\infty)/(W_t - W_\infty)$ against t for the experimental samples give curves that are nearly straight lines, except near the origin, as shown in Fig. 2. This indicates that the degradation of cellulose (zone b) follows a first order reaction.

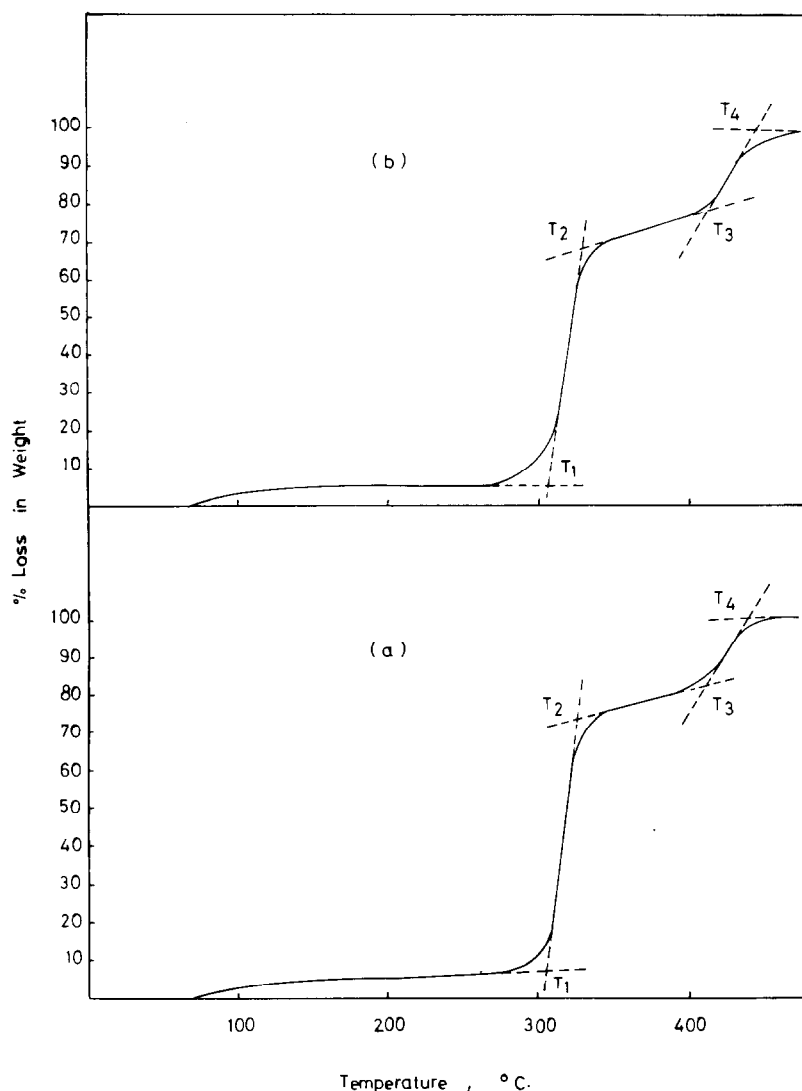


Fig. 1. Thermogravimetric profiles of the four samples studied. (a) Native cotton; (b) mercerised cotton.

Arrhenius (cf. ref. 7), stated that, since the Van't Hoff equation for the temperature coefficient of the equilibrium constant, k_c , of a reaction was

$$d \ln k_c / dT = E_a / RT^2$$

(where E_a is the activation energy and R is the gas constant) whereas the law of mass action related the equilibrium to a ratio of rate constants, i.e., $k_c = [k \text{ (forward reaction)}] / [k \text{ (backward reaction)}]$, therefore, a reasonable equation for the variation of the rate constant with the temperature is given

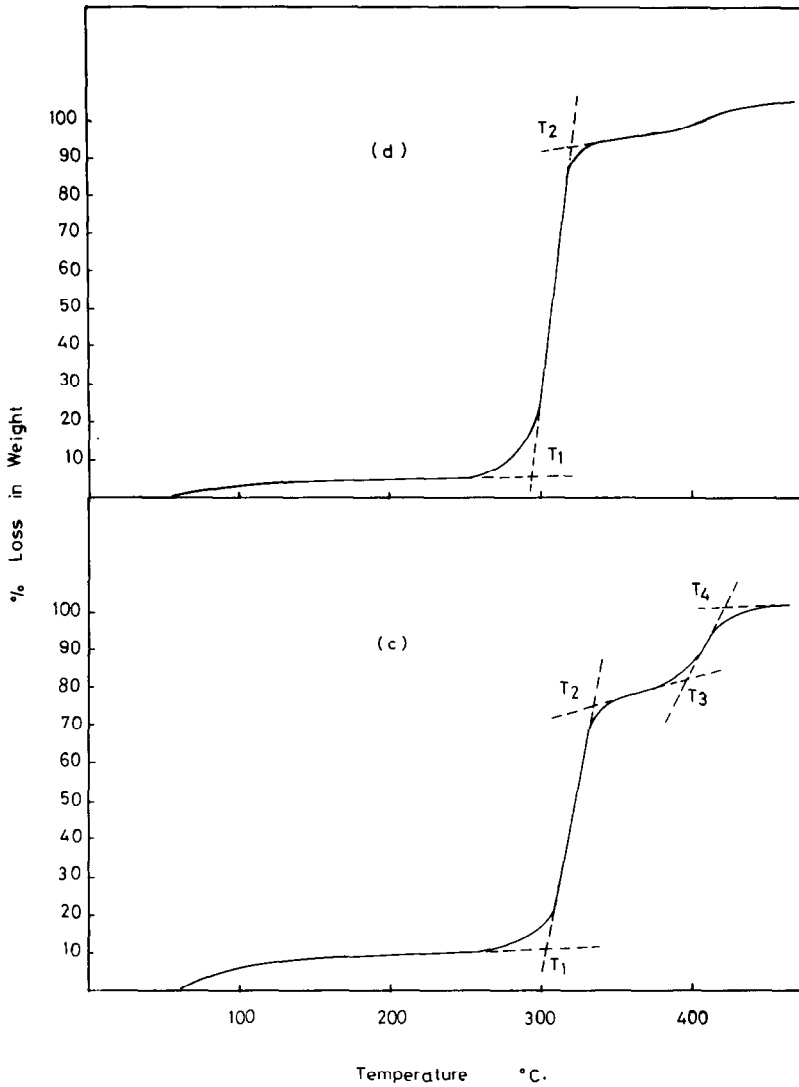


Fig. 1. (c) Viscose rayon; (d) bagasse pulp.

by

$$d \ln k / dT = E_a / RT^2$$

on integration

$$\ln k = -E_a / RT + \ln A$$

where A is a constant. Thus, a plot of $\log_{10} k$ against the reciprocal of the temperature is a straight line with a slope equal to $-E_a / 2.303 R$.

Table 2 shows the values of the activation energy, E_a , enthalpy change, ΔH , and the rate constant, k , of the experimental samples.

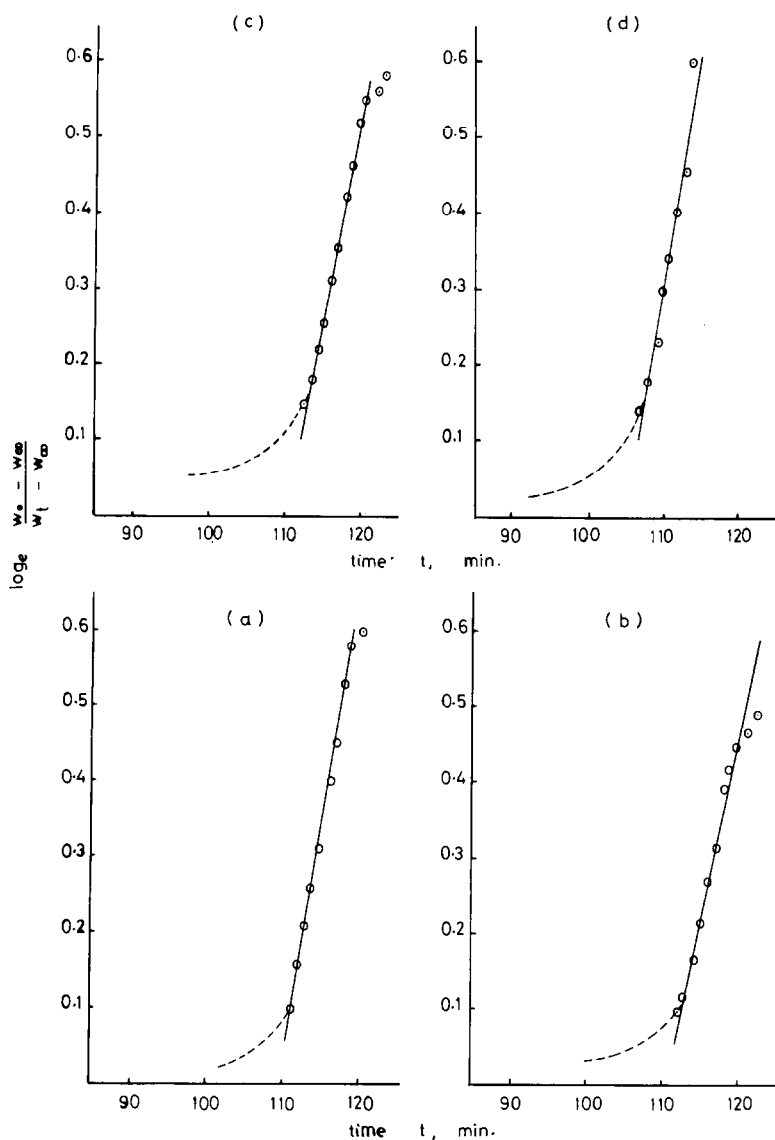


Fig. 2. Plots of $\ln [(W_0 - W_\infty)/(W_t - W_\infty)]$ against t for the four samples studied. (a) Native cotton, (b) mercerised cotton, (c) viscose rayon, (d) bagasse pulp.

TABLE 2
Values of the activation energy, enthalpy change and rate constant of the samples

	$-E_a$ (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	k (min ⁻¹)
Native C.L.	201.19	203.66	0.6289
Mercerised C.L.	96.73	99.21	0.4718
Viscose rayon	130.58	133.09	0.5736
Bagasse pulp	138.63	141.08	0.8137

It is clear from Table 2 that the activation energy values ranged between 201.19 and 96.73 kJ mol⁻¹ depending on the purity and the degree of disorder. Mercerised samples possess a low activation value, due to the disordering of the molecular chains, also due to the transformation of the unit cell to cellulose II. However, the pronounced increase in the activation energy value of the viscose rayon fibres, which possess the same unit cell, may be attributed to the effect of stretching during the manufacture of rayon (i.e., spinning which allows a better orientation of the crystallites to be attained, consequently more energy will be needed to break the chains). Bagasse pulp possesses a low activation energy, in this case the decrease may be related to several factors:

(1) A high percentage of pentosan, which decomposes more rapidly. Indeed the rate constant (*k*) of bagasse pulp was found to be high (see Table 2).

(2) The presence of some readily volatile materials. All the above activation values are within those reported in the literature [4,5,8,9]. The difference in the free energy value may be explained by the breaking of the cellulose crystallites into smaller units.

REFERENCES

- 1 H. Nishizaki, K. Yoshida and J.H. Wang, *J. Appl. Polym. Sci.*, 25 (1980) 2869.
- 2 D.W. Levi, D. Reich and I. Lee, *Polym. Eng. Sci.*, 5 (1965) 135.
- 3 D. Reich and D.W. Levi, *Macromolecular Reviews V:1 Dynamic Thermogravimetric Analysis in Polymer Degradation*, Wiley, New York, London, 1967.
- 4 F. Shafizadeh and G.W. Bradbury, *J. Appl. Polym. Sci.*, 23 (1979) 23.
- 5 P.K. Chatterjee, *J. Polym. Sci.*, 6 (1968) 3217.
- 6 G. Jayme and Sarten, *Naturwissenschaften*, 28 (1940) 822; *Biochem. Z.*, 308 (1941) 109.
- 7 S. Glasstone, *Text Book of Physical Chemistry*, Macmillan, London, 1956.
- 8 A. Pacault and G. Sauret, *C.R. Acad. Sci.*, 246 (1958) 608.
- 9 D.P.G. Fung, *Tappi*, 52 (1969) 319.