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THERMAL BEHAVIOUR OF HIGH α-CELLULOSE PULP FROM FAST GROWING PLANT SPECIES AND ITS ACETYLATION PRODUCT

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ABSTRACT

High α-cellulose pulp has been extracted from a fast growing plant material, namely *Leucaena leucocephala*. Acetylated products from this α-cellulose and from commercially available α-cellulose were prepared by a homogeneous acetylation procedure. The acetylated products were characterized using IR, ^{1}H NMR and ^{13}C NMR techniques, and their molecular weights were determined. The thermal decomposition of the α-celluloses and their acetylated products were studied using thermogravimetric and differential thermal analysis techniques in the range of room temperature to 600 °C. Two major decomposition steps were identified, and the relative thermal stabilities of the α-celluloses and the acetylated products were assessed. The kinetic parameters for both the decomposition steps identified were estimated by four well known methods. IR spectra of the decomposed residue obtained after heating the cellulose at 200 and 450 °C were also examined, to obtain an understanding of the decomposition pathway.

INTRODUCTION

With the growing shortage of conventional cellulosic raw materials [1] such as soft wood, hard wood and bamboo for pulp-, paper- and cellulose-based industries, attention has been focused during the last three decades or so on the identification and generation of alternative fibre crops which could not only serve as a source of raw material for the pulp and paper industries, but also feed the raw material needs of cellulose-based industries. Fast growing plants have been identified as a cheap source of cellulosic raw material, and as such many annual and perennial plants have been cultivated in different parts of the world, and their suitability for pulp- and paper-making studied [2–6]. However, few studies have been performed relating to the production of high α-cellulose pulp for use in cellulose conversion industries [7,8].

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The highly purified cellulose commonly known as α- or dissolving cellulose finds applications in many chemical and paper-making end uses, and the pulp needs to meet certain rigid specifications [9–11]. Thus, every cellulosic raw material intended for the production of α-cellulose pulp must be examined individually to ascertain its suitability for the purpose. We have therefore made an extensive study of the extraction of high α-cellulose pulp from a fast growing plant, *Leucaena leucocephala*, which grows luxuriantly in India under ideal conditions of soil fertility and irrigation.

For some end uses, cellulose and many of its derivatives have to possess heat-resistant properties. Thermogravimetric studies can help us to understand the mechanisms of thermal degradation of the substances, and their behaviour at different temperature ranges. The combustion of cellulose and its esters, in vacuo, in air or in inert atmosphere, has been studied extensively by many workers [12–23], and the kinetics of the thermal degradation of cellulose has been explained.

The present study was undertaken to investigate the thermal behaviour of α-cellulose extracted from the above-mentioned fast growing biomass material, and its acetylated product. For comparison, the thermal behaviour of a commercially available rayon grade pulp and its acetylated product (prepared under identical conditions) was also studied, by differential thermal analysis and thermogravimetry. Kinetic parameters were calculated according to the methods of Coats and Redfern [24], Horowitz and Metzger [25], Broido [26] and Freeman and Carroll [27].

EXPERIMENTAL

Preparation of cellulose and its acetylated products

α-Cellulose was extracted from the stem portion of a 5 year old plant. The wood chips were water-prehydrolysed at 160 °C for 3 h and then sulphate-cooked at 163 ± 2 °C for 3 h with 18% total chemicals ($NaOH : Na_2S = 3:1$). The unbleached pulp obtained was bleached by a multi-stage bleaching sequence with intermediate distilled-water washings. The bleached pulp or α-cellulose pulp thus obtained contained 94.04% α-cellulose and 0.090% ash [28]. The study used this high α-cellulose pulp from *L. leucocephala*, hereafter termed ‘cellulose A’, and a commercial rayon grade pulp (M/S Harihar Polyfibers, India) containing 95.5% α-cellulose and 0.050% ash, hereafter termed ‘cellulose B’. Further samples of cellulose A and B were dissolved in appropriate amounts of paraformaldehyde and dimethyl sulphoxide (DMSO) mixture, and used for homogeneous acetylation with acetic anhydride in the presence of pyridine [29]. The acetyl content of 1 h acetylation products of cellulose A and B were determined [30], and found to be 45.501 and 45.727%, respectively.

Thermal analysis

Differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out using a Shimadzu Thermal Analyser 30. The weights of the samples of cellulose and the acetylated products were in the ranges 7.18–14.86 and 12.48–14.26 mg, respectively. α-Alumina was used as reference material, and the temperature ranged from 30 to 600 ° C at heating rates of 5, 10 and 20 ° C min^{-1} for celluloses A and B, and 10 ° C min^{-1} for the acetylated products in static air atmosphere.

IR studies

IR spectra were recorded in a Perkin-Elmer Model 580 B spectrometer using the KBr disk technique. The charred samples of cellulose were prepared by heating in a furnace in air. The samples were introduced into the furnace at the desired temperature, and the residue was cooled and then transferred to a desiccator.

RESULTS AND DISCUSSION

Analysis and characterization of the celluloses and acetylated products

The α-cellulose pulp extracted from *L. leucocephala* compared well with the commercially available rayon grade pulp. The α-cellulose and ash contents of celluloses A and B were determined by TAPPI standard methods [31,32]. The acetylated products of A and B were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy and their molecular weights were determined by GPC. The IR spectra of the 1 h acetylated product showed sharp peaks at 1740 cm^{-1}, indicating the presence of carbonyl groups. The ^{1}H NMR spectra of the acetylated product of A exhibited peaks at 2.08 δ (CH_3CO–), 3.3 δ (–C–H), 4.1 δ (–CH_2OAC), 4.6 δ (–CH–) and 5.2 δ (–O–CH_2–O), indicating the formation of cellulose acetylated product. In addition, the ^{13}C NMR spectra of the acetylated product gave peaks at 22 and 170 ppm, which can be assigned to two carbon atoms of the CO– and CH_3COO– groups. The acetylated product from cellulose B exhibited similar characteristics. The details of this study have been reported elsewhere [33].

Thermogravimetric analysis

The thermal curves (TG, DTG and DTA) for the α-celluloses and their acetylated products are shown in Figs. 1, 2, 3 and 4. For the cellulose samples, thermal curves are shown at three heating rates, i.e. 5, 10 and 20 ° C

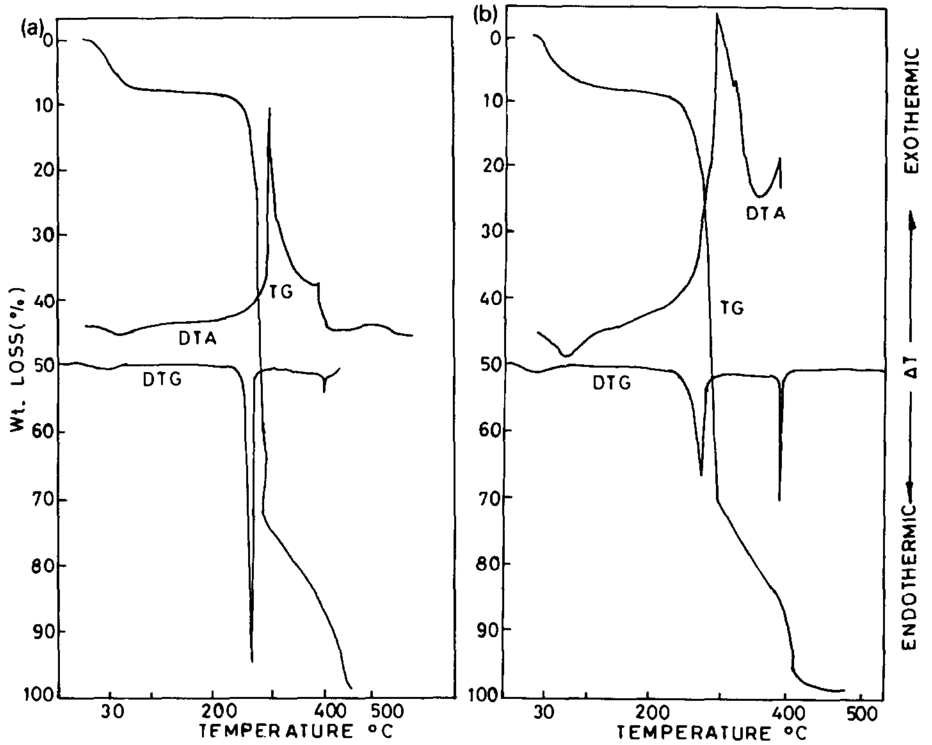

Fig. 1. DTA, TG and DTG curves at heating rate of 5 °C min^{-1}: (a) cellulose A, (b) cellulose B.

min^{-1}. For the cellulose acetylated products, which are of secondary importance in our study, curves are shown only for the heating rate 10 °C min^{-1}. The thermal analysis data are summarized in Table 1.

The DTA curves for celluloses A and B are almost identical in nature, and show an endotherm loop owing to the evaporation of moisture up to a temperature of around 80 °C. In the DTA curve for heating at 5 °C min^{-1} this endotherm is very wide with low intensity, and extends up to a temperature of around 170–180 °C. Evidently, this is a very slow process. At about 180 °C, the exothermic effect starts, and maxima occur at 280 and 285 °C for celluloses A and B, respectively, corresponding to the TG active decomposition range (Table 2), for both the samples. It may be noted that the DTA maxima increase with increased heating rate. A second exothermic peak occurs at 390 °C in the case of cellulose A, and at 410 °C in the case of cellulose B, which may be due to oxidation or carbonization of the degraded fragments of the pyrolytic products. Narrow DTA peaks of cellulose at low heating rate and rapid loss of weight as evidenced by the TG curves indicate fast propagation and carbonization. Complete decomposition of organic matter in the second exothermic process may be the reason for the low char

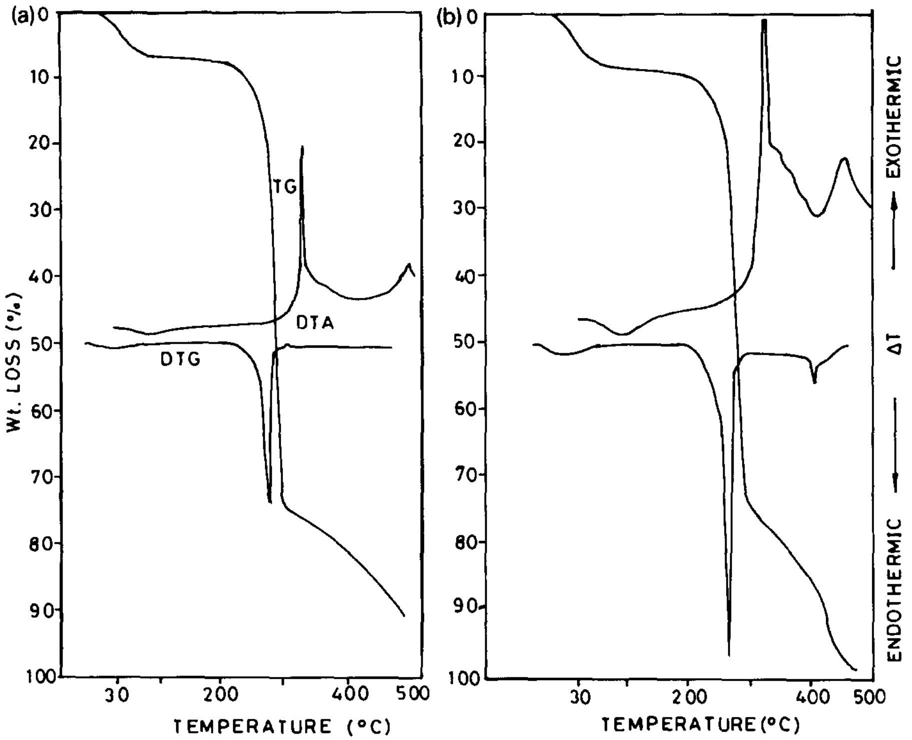

Fig. 2. DTA, TG and DTG curves at heating rate of 10 °C min^{-1}: (a) cellulose A, (b) cellulose B.

yield in the case of cellulose at heating rates of 5 and 10 °C min^{-1}. However, the char yield is an order of magnitude higher at 20 °C min^{-1}.

The DTA curves for the cellulose acetylated products show no endothermic peak below 100 °C, indicating absence of moisture. The decomposition process occurs via an endothermic process between 290 and 350 °C, with DTA peak temperatures of 310 and 320 °C for the products of celluloses A and B, respectively; and a relatively slow exothermic process between 390 and 490 °C, with DTA peak temperatures of 445 and 465 °C. The endothermic process should represent melting and rapid degradation of the fragments of the cellulose, and breakage of acetyl bonds. The exothermic process may be attributed to slow oxidation and evaporation or carbonization of the degraded fragments of the decomposed products. The low char yield, of the order of 2.2% by weight at around 600 °C in the case of both the celluloses, A and B, indicates complete but slow oxidation of the organic matter.

The dynamic TG and DTG curves show a major mass loss step, with maxima at around 280 and 285 °C for celluloses A and B, respectively. Table 2 shows the initial, maximum and final temperatures of active decomposition, represented as T_1, T_2 and T_3, respectively. It may be inferred

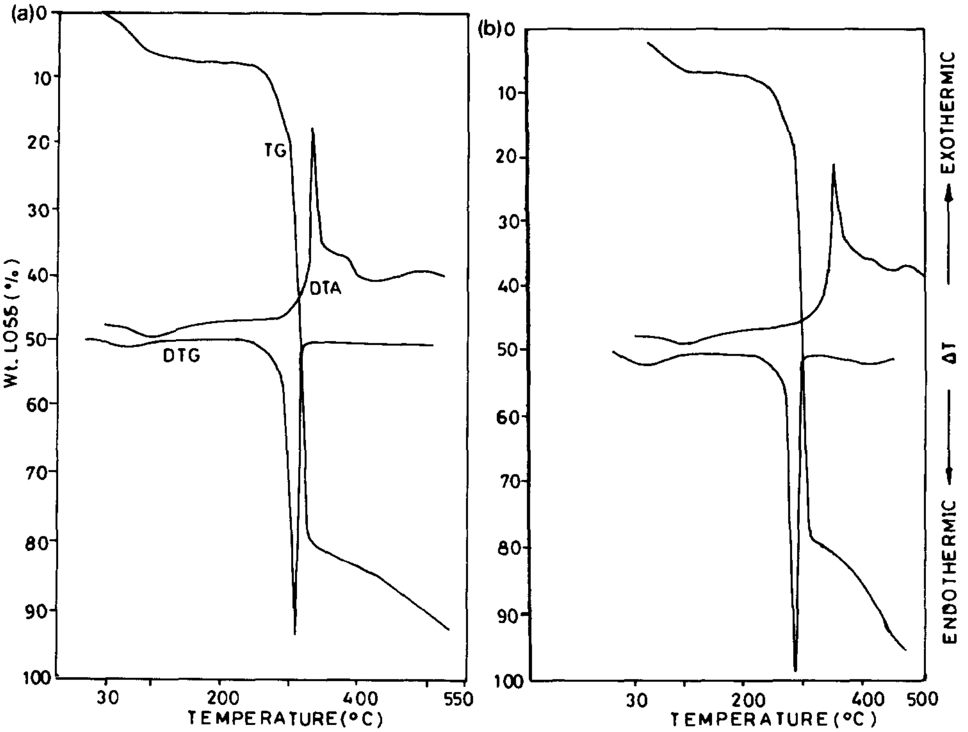

Fig. 3. DTA, TG and DTG curves at heating rate of 20 °C min^{-1}: (a) cellulose A, (b) cellulose B.

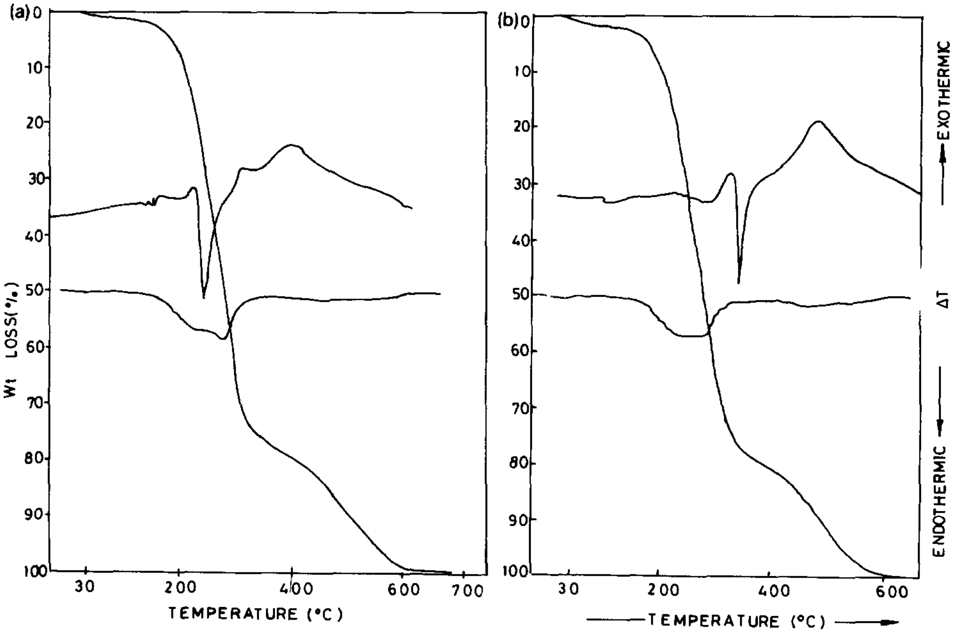

Fig. 4. DTA, TG and DTG at heating rate of 10 °C min^{-1}: (a) cellulose acetylated product A, (b) cellulose acetylated product B.

TABLE 1

Thermal analysis data for the celluloses and acetylated products

Sample	DTG peak temperature (°C) at heating rate of								
	5 °C min^{-1}			10 °C min^{-1}			20 °C min^{-1}		
	I	II	III	I	II	III	I	II	III
Cellulose A	–	265 (endo)	380 (exo)	–	280 (endo)	385 (exo)	–	280 (endo)	400 (exo)
Cellulose B	–	270 (endo)	390 (exo)	–	275 (endo)	–	–	295 (endo)	–
Acetylated product A	–	–	–	–	250 (endo, broad)	440 (exo, broad)	–	–	–
Acetylated product B	–	–	–	–	260 (endo, broad)	450 (exo, broad)	–	–	–

Sample	DTA peak temperature (°C) at heating rate of									% weight loss at 5 °C min^{-1}		
	5 °C min^{-1}			10 °C min^{-1}			20 °C min^{-1}					
	I	II	III	I	II	III	I	II	III	I	II	III
Cellulose A	–	285 (endo)	400 (exo)	–	290 (exo)	420 (exo)	–	300 (exo)	420 (exo, broad	–	68.50 (170–330)	21.00 (330–450)
Cellulose B	–	290 (exo)	420 (exo)	–	302 (exo)	440 (exo)	–	310 (exo)	470 (exo, broad)	–	69.00 (170–330)	20 00 (330–450)
Acetylated product A	–	–	–	–	310 (endo)	445 (exo, broad)	–	–	–	–	74.00 (120–340)	23.00 (340–600)
Acetylated product B	–	–	–	–	320 (endo)	465 (exo, broad)	–	–	–	–	74.50 (120–340)	22.00 (340–600)

Key: I, II, III, pre-, second and third stages; temperature ranges in °C.

TABLE 2

Dynamic thermogravimetry data for the celluloses and acetylated products

Sample	Heating rate (°C min^{-1})	Temperature of active decomposition		
		T_1	T_2	T_3
Cellulose A	5	240	280	390
	10	260	300	450
	20	265	300	–
Cellulose B	5	245	285	410
	10	260	300	–
	20	270	310	–
Acetylated product A	10	185	330	580
Acetylated product B	10	185	325	590

that three main degradation steps, namely initiation, propagation and carbonization, as suggested by Chatterjee and Conrad [12], are predominant for the celluloses studied in this work. The typical curvature in the TG curve

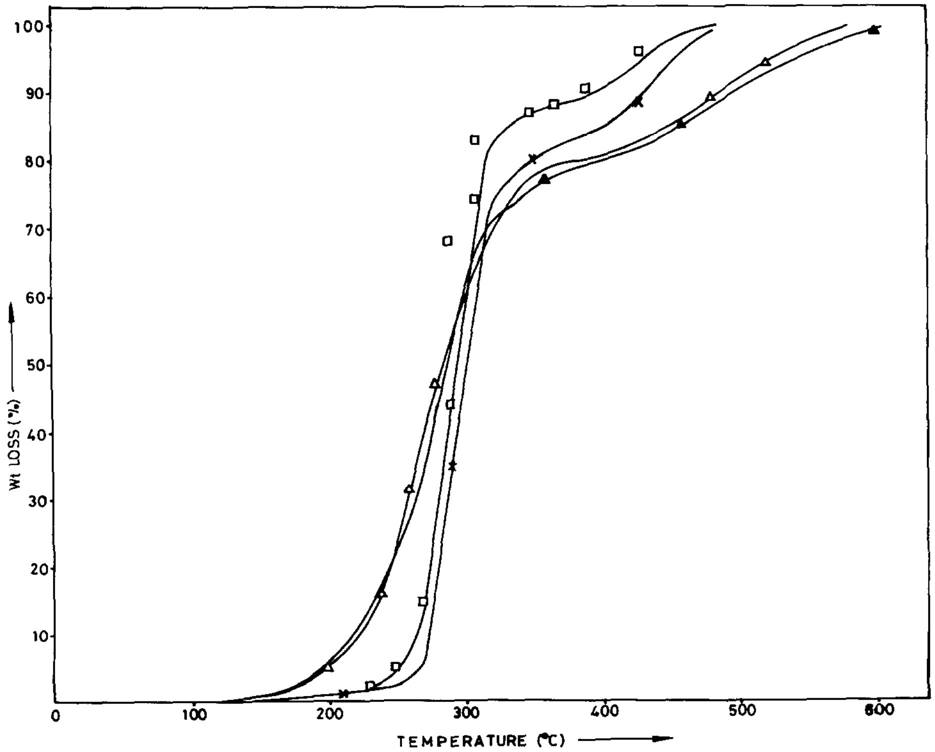

Fig. 5. Thermograms of celluloses and acetylated products at heating rate 10 °C min^{-1}: × acetylated product A, □ acetylated product B, △ cellulose A, ▲ cellulose B.

observed between T_2 and T_3, which may be attributed to the fast formation and evaporation of pyrolytic products at these temperatures, indicates that the decomposition of the celluloses studied here is a more complex process than that which has been described in previous reports of cellulose studies.

In the case of the acetylated products, the initial temperature T_1 at which the main decomposition reaction starts is much lower than temperatures observed for the celluloses. The typical maximum at around 330 °C for cellulose acetylated product is representative of cellulose diacetate, as reported elsewhere [22]. Careful study of Tables 1 and 2 and the thermograms in Fig. 5 clearly shows that the thermal stability of the acetylated products as a whole is lower as compared to cellulose in the temperature zone below around 300 °C. Considering the cellulose alone, it is worth mentioning in the context of the present study that the cellulose A extracted from the fast growing plant species is comparable to cellulose B as regards thermal stability.

Kinetic parameters

Various authors have analysed the kinetic parameters using a number of different methods [12–23]. Values of E_a and A have been found to vary widely, depending on the source of the raw material and the method of analysis.

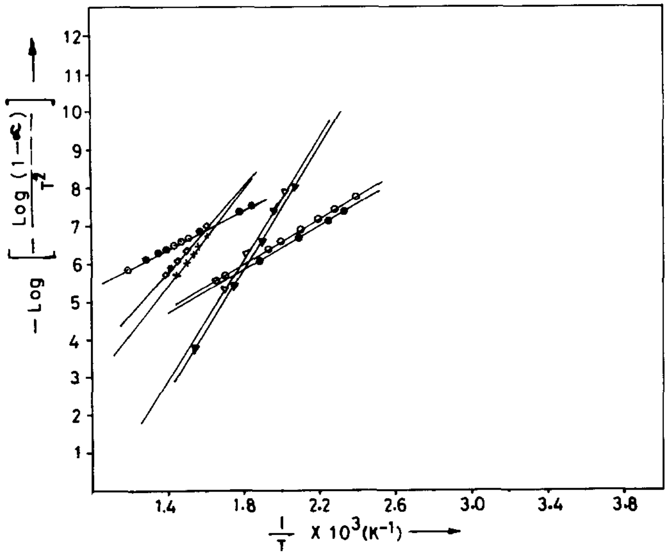

Fig. 6. Plots of $-\log[-\log(1-\alpha)/T^2]$ vs. $1/T \times 10^3$ using the Coats and Redfern equation, where α is the fraction decomposed at temperature T: △ ▲ celluloses A and B in temperature range 443–603 K, × □ celluloses A and B in temperature range 603–703 K, ○ ● acetylated products A and B in temperature range 393–613 K, ⊙ ⊗ acetylated products A and B in temperature range 613–873 K.

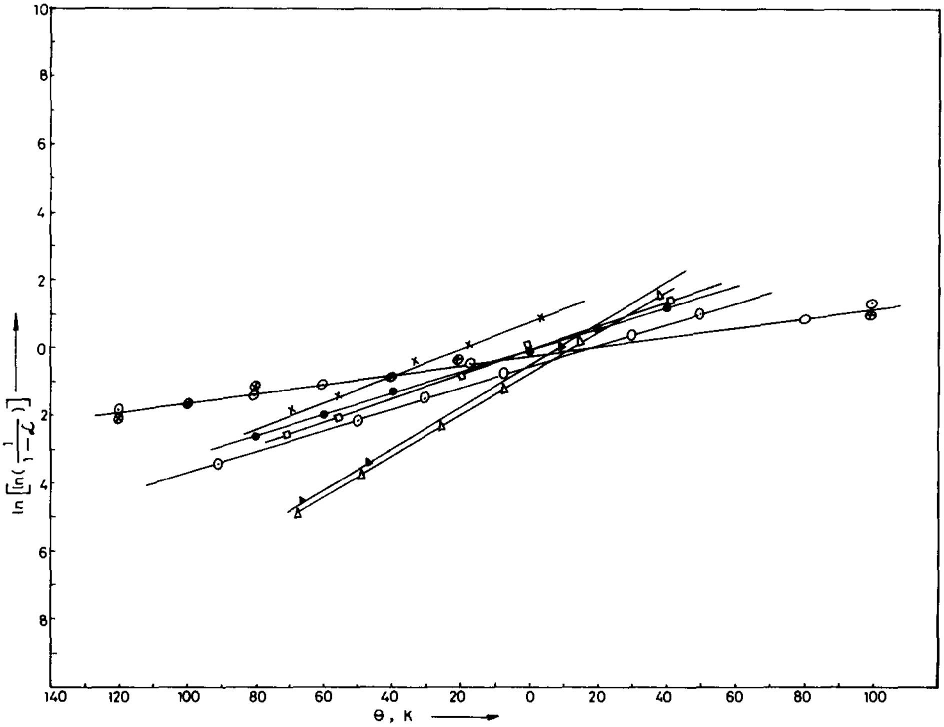

Fig. 7. Plots of $\ln[\ln(1/1-\alpha)]$ vs. θ using the Horowitz and Metzger equation, where α is the fraction decomposed at temperature T, $\theta = T - T_S$, and T_S is the inflection temperature: △ ▲ celluloses A and B in temperature range 443–603 K, × □ celluloses A and B in temperature range 603–703 K, ○ ● acetylated products A and B in temperature range 393–613 K, ○ ⊗ acetylated products A and B in temperature range 613–873 K.

In the present work, kinetic parameters were evaluated by four methods for different steps identified by thermal curves on the assumption of a first order process. The characteristic plots of the deterministic parameters for the Coats and Redfern, Horowitz and Metzger, Broido, and Freeman and Carroll methods are shown in Figs. 6–9. Table 3 shows the activation energies E_a and frequency factors A, along with values of the correlation coefficient r of the linear regression. The pre-stage in the low temperature region has been excluded from this discussion, since the actual decomposition process corresponds to stages II and III only. From Table 3 it is evident that the correlation coefficient for the linear regression of decomposition and temperature functions obtained using the Coats and Redfern method is the highest. The finding is reasonable, and substantiates the reported first order decomposition process for cellulose [12] with activation energy close to the values obtained in this study.

The values of activation energy and frequency factor for the cellulose acetylated products are lower than those obtained for the celluloses. The Coats and Redfern technique gives the lowest value of E_a, i.e. 54.20 kJ

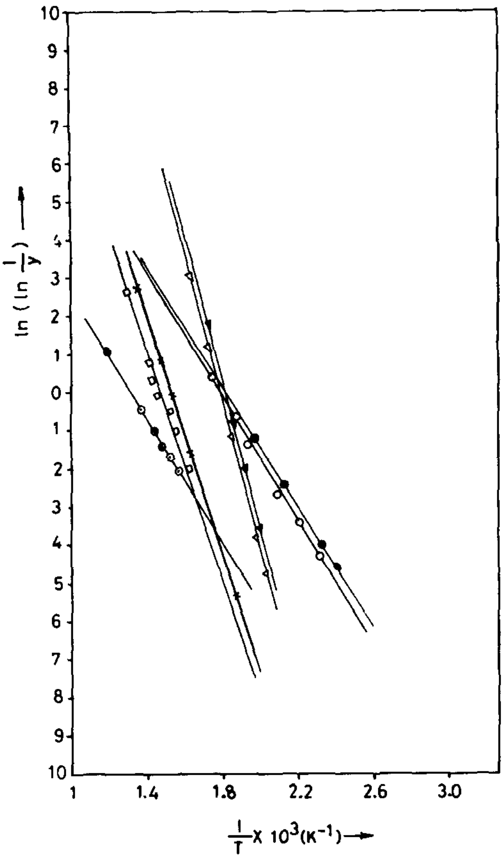

Fig. 8. Plots of $\ln(\ln(1/Y))$ vs. $1/T \times 10^3$ using the Broido equation, where Y is the fraction weight not yet decomposed at temperature T: △ ▲ celluloses A and B in temperature range 443–603 K, × □ celluloses A and B in temperature range 603–703 K, ○ ● acetylated products A and B in temperature range 393–613 K, ⊙ ⊗ acetylated products A and B in temperature range 613–873 K.

mol^{-1} for the temperature range 120–340 °C, and 22.00 kJ mol^{-1} for the temperature range 340–600 °C. The value of E_a calculated by considering the entire range of decomposition is found to be 38.00 kJ mol^{-1}, which is comparable to that reported in the literature [12,14]. However, the correlation coefficient for linear regression of the data is fairly poor, i.e. 0.89. The above values of E_a and A for the celluloses and acetylated products obtained by the Coats and Redfern method are quite reasonable.

IR spectra of pyrolysis products

The nature of the pyrolysis products of celluloses A and B, subjected to pyrolysis at temperatures of 200 and 450 °C, were studied using IR spectroscopy. At 200 °C, the spectra of the char showed evidence of dehydration

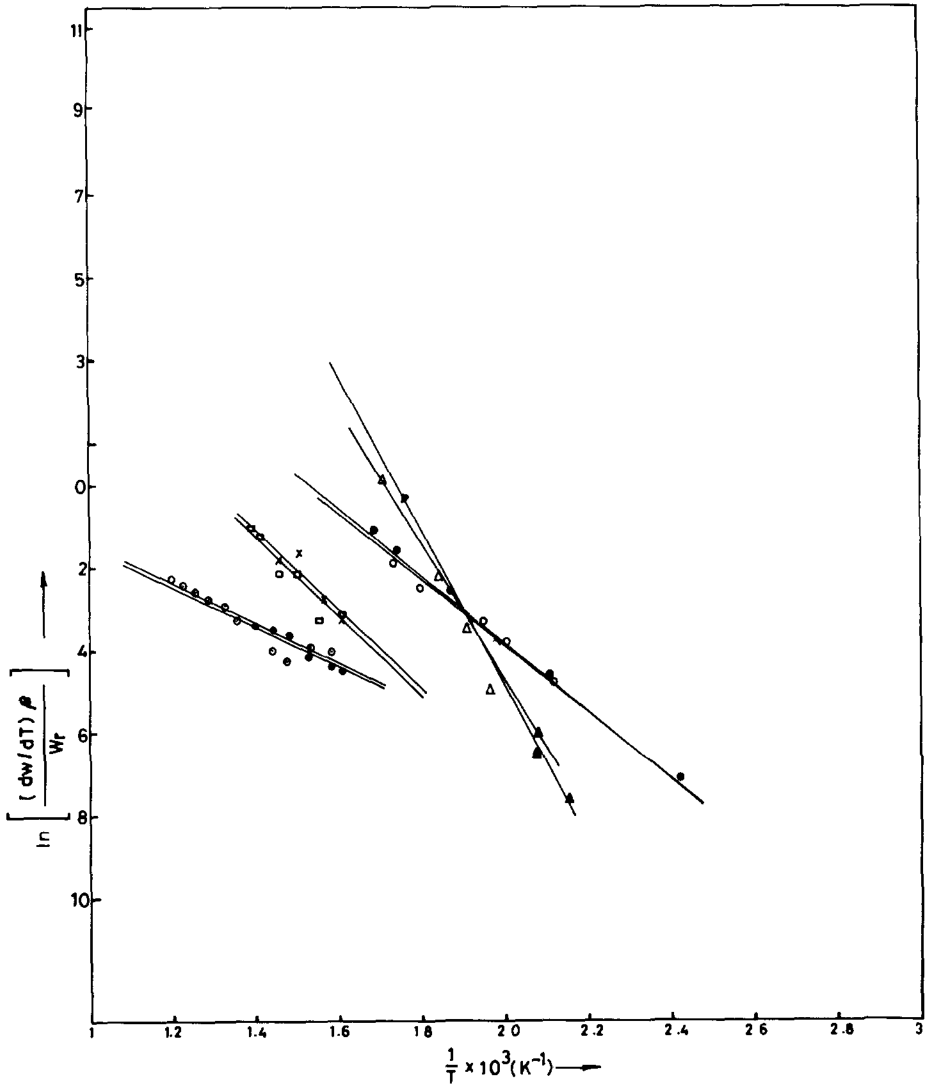

Fig. 9. Plots of $\ln[(dw/dT)\beta/W_r]$ vs. $1/T \times 10^3$ using the Freeman and Carroll equation, where $W_r = W_f - W$, W_f is the total weight decomposed, W the weight decomposed at temperature T, and β the heating rate: △ ▲ celluloses A and B in temperature range 443–603 K, × □ celluloses A and B in temperature range 603–703 K, ○ ● acetylated products A and B in temperature range 393–613 K, ⊙ ⊗ acetylated products A and B in temperature range 613–873 K.

(Fig. 10, curves c and d) compared to the original samples (curves a and b). The $-CH_2$ skeletal vibrations of the original cellulose samples at bands 1170–1140 cm^{-1} disappeared when the samples were heated to 200 °C. Again at 200 °C, absorption due to C=O stretching occurs at 1730 cm^{-1}, 1650–1645 cm^{-1}, indicating partial skeletal rearrangements. It may be noted that degradation of cellulose in the presence of air at high temperatures

TABLE 3

Kinetic parameters for the decomposition of the celluloses and acetylated products

Method	Material	Stage II			Stage III		
		E_a (kJ mol^{-1})	A (s^{-1})	r	E_a (kJ mol^{-1})	A (s^{-1})	r
Coats and Redfern	Cellulose A	154.16	5.83×10^{4}	0.989	130.15	39.10	0.988
	Cellulose B	154.20	1.19×10^{5}	0.987	112.63	8.5	0.979
	Acetylated product A	54.22	3.28	0.978	21.9	60.8	0.989
	Acetylated product B	54.20	4.82	0.985	22.0	60.8	0.989
Horowitz and Metzger	Cellulose A	154.46	–	0.985	146.90	–	0.985
	Cellulose B	153.10	–	0.986	139.36	–	0.985
	Acetylated product A	79.63	–	0.965	65.54	–	0.979
	Acetylated product B	81.00	–	0.968	65.54	–	0.979
Broido	Cellulose A	166.27	1.689×10^{6}	0.975	131.46	7.49×10^{2}	0.972
	Cellulose B	166.27	1.689×10^{6}	0.975	146.65	2.74×10^{2}	0.973
	Acetylated product A	69.50	81.92	0.965	69.63	1.1378	0.967
	Acetylated product B	81.00	81.00	0.963	69.60	1.1300	0.957
Freeman and Carroll	Cellulose A	137.46	1.33×10^{5}	0.967	82.00	13.46	0.968
	Cellulose B	158.47	8.9×10^{5}	0.967	82.00	16.44	0.972
	Acetylated product A	67.81	63.43	0.975	41.00	0.31	0.978
	Acetylated product B	68.00	81.45	0.967	41.00	0.24	0.975

might lead to the formation of small ring and acyclic compounds containing the $-CH_2-O-$ group [34]. The presence of the band at 1500–1435 cm^{-1} (curves e and f) may be attributed to the scissoring vibration δ_s CH_2, which is due to the groups $-CH_2-O-$ (acyclic) and $-CH_2-O-$ (small ring) between 1470–1435 and 1500–1470 cm^{-1}, respectively.

CONCLUSIONS

(1) The α-cellulose obtained from the fast growing plant species exhibits physico-chemical properties identical to those of α-cellulose available commercially. The physico-chemical characteristics of the acetylated products of the two types of cellulose are also identical in nature.

(2) The thermal decomposition of the α-celluloses and their acetylated products in air proceeds in two steps.

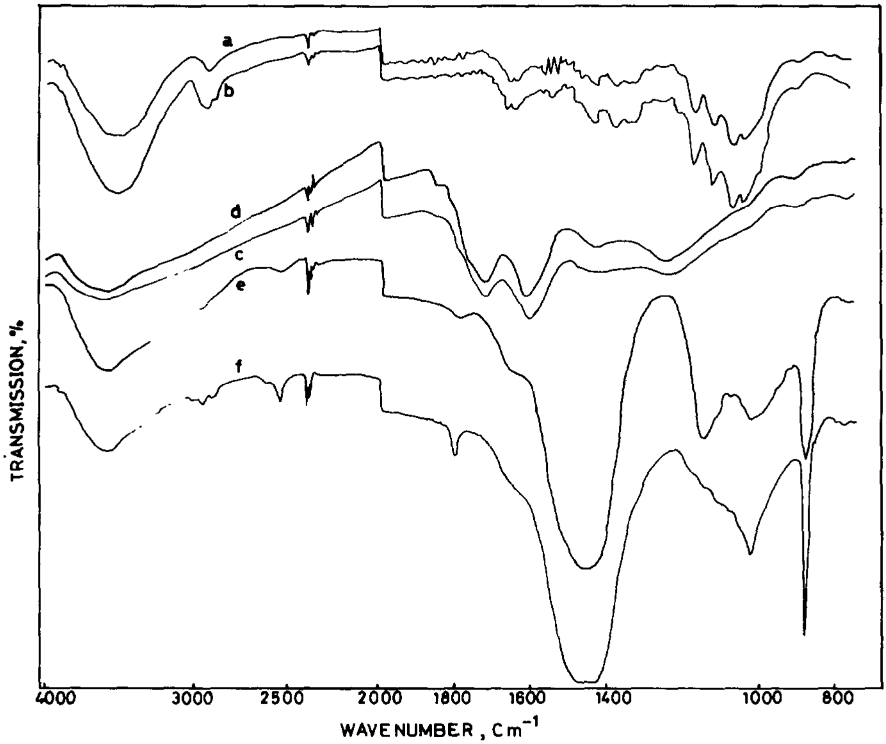

Fig. 10. IR spectra: (a) cellulose A, (b) cellulose B, (c) and (d) celluloses A and B at 200 °C, (e) and (f) celluloses A and B at 450 °C.

(3) The thermal stability of the cellulose extracted from the fast growing species is comparable to that of commercially available α-cellulose; and the acetylated products of the two types of cellulose prepared under identical conditions exhibit identical thermal stability.

(4) In general, the thermal stability of both the α-celluloses is better than that of their acetylated products at temperatures below 300 °C. The reverse is true for temperatures above 300 °C.

(5) The kinetic parameters E_a and A estimated by the Coats and Redfern technique for both the celluloses and their acetylated products were found to be more reasonable than those estimated by other methods, in view of the high correlation coefficient obtained for the regression analysis of the defining functions.

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