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THE PREPARATION AND EXAMINATION OF PARTIALLY COMBUSTED CELLULOSE CHARS

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ABSTRACT

Partially combusted samples of cellulose, removed at different stages of decomposition from several thermogravimetric experiments, have been subjected to elemental analysis and IR spectroscopy. The values of maximum temperature and final mass loss for each sample have been obtained from the thermogravimetric curves. These data have been combined with values for the percentage of carbon, hydrogen and oxygen and plotted as the decline in the percentage of each of these elements with temperature. Infrared spectra of the chars have been obtained by the KBr disc technique; the mass of sample mixed in the disc was in proportion to the thermogravimetric value of the mass of sample remaining. It is shown that few changes occur to the combustion residue below 260°C. Above this temperature there is a steady increase in unsaturated groups. Under the conditions of the experiment, hydrogen and oxygen are lost in a ratio close to 2 : 1. Up to 333°C the original carbohydrate structure is retained; samples obtained from above this temperature have spectra dominated by C=C and C=O bonds.

INTRODUCTION

The majority of cellulose degradation studies indicate that at high (greater than 250°C) temperatures the preferred decomposition path is via levoglucosan (1,6 anhydro β-D-glucopyranose) but that at low temperatures char formation and the evolution of water vapour and the oxides of carbon are more likely — especially in an oxidising atmosphere [1].

Higgins [2] noted a change in the formula of (originally) cellulose from $C_{3.6}H_{6.5}O_{3.1}$ to $C_{5.0}H_{3.0}O_{2.3}$ after heating in air at 250°C for 24 h. The progressive development of carbonyl groups and the simultaneous diminution of carbohydrate hydroxyl concentration were demonstrated by IR spectroscopy; the changes in elementary composition, spectra and colour were attributed to the development of an aliphatic unsaturated cyclic structure.

Elemental analysis, X-ray and IR techniques were applied to the carbonaceous residues of the isothermal pyrolysis of cellulose by Tang and Bacon [3]. Each sample was heated in argon at a different temperature for 12 h. At 200°C a char of formula $C_6H_{9.69}O_{4.79}$ was produced, at 400°C the formula of the char was $C_6H_{2.95}O_{0.614}$ and at 600°C the formula had changed to $C_6H_{1.36}O_{0.283}$. The IR analysis showed rapid changes in the spectrum above

240° C with the band corresponding to C=O stretching becoming the dominant peak at 280° C. Above 400° C the C=O band became very weak and the C=C band at 1613 cm^{-1} dominated the spectrum. In contrast to Higgins [2], Tang and Bacon [3] postulate the formation of aromatic ring systems at temperatures above 400° C.

It appears that increasing the heating rate results in a diminished char yield. Flash photolysis has been shown [4] to give a low char yield but a heating rate of 20° C per day up to 1500° C gave a high (32%) char yield [5]. Isothermal experiments in a nitrogen atmosphere at both 1.5 mm Hg and atmospheric pressure have shown a halving of char yield at low pressure [6]. Since the char can be formed both directly from cellulose and indirectly via levoglucosan, this diminution in yield can be explained by the increased volatility of levoglucosan at low pressures; the levoglucosan therefore escapes from the hot zone before it can decompose to form char.

The effect of the degree of crystallinity was investigated by Weinstein and Broido [7]. The cellulose was heated isothermally under vacuum at 260° C and samples were removed periodically and analysed for mass loss and crystallinity index. A second batch of samples was treated with concentrated ammonia to destroy all crystallinity and then subjected to the same isothermal treatment. The crystallinity of the second batch of samples was largely regained during the 40 min heating from room temperature to 260° C. Char yield after 24 h was virtually identical for the crystalline and (originally) non-crystalline samples.

EXPERIMENTAL

Materials

The cellulose used to prepare the chars was Whatman CC31 [1]. In order to correlate the char analysis with the thermal analysis of cellulose reported previously [1], a thermobalance was used to prepare the samples. Seven separate TG experiments were performed on the cellulose, but each experiment was suddenly terminated at a progressively higher temperature and

TABLE 1

Percentage mass and temperature data of cellulose and degraded cellulose samples

Sample designation	Max. temp. (°C)	% Mass loss	% Mass remaining
Cellulose		0	100
A	259	3.7	96.3
B	301	8.1	91.9
C	318	18.4	81.6
D	325	32.6	67.4
E	333	45.0	55.0
F	341	47.1	32.9
G	403	75.0	25.0

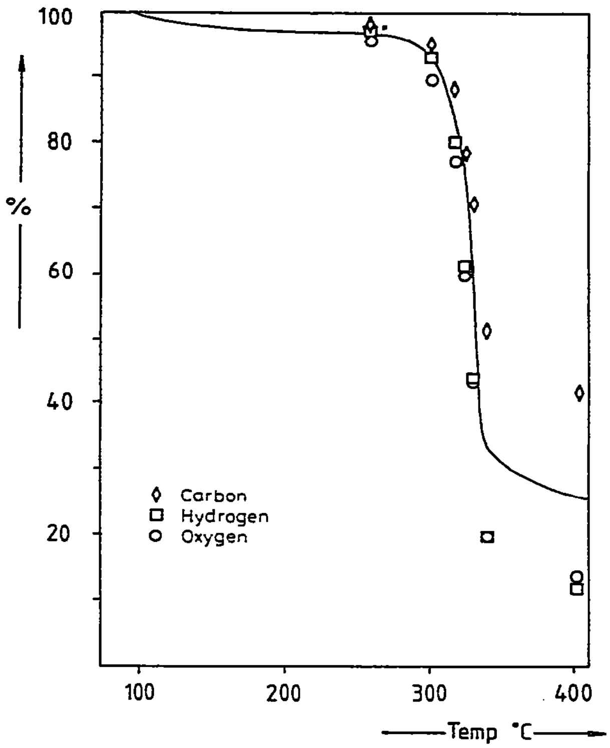

Fig. 1. TG combined with elemental analysis for cellulose in air.

the sample remaining was retained in each case. The TG runs were performed in the normal way until, at the required sample temperature, the furnace was raised from around the sample, which cooled to room temperature within 10 min. The sample designations and corresponding masses and temperatures are listed in Table 1. A check on the TG data showed that identical curves had been obtained in all the experiments and a typical plot is illustrated in Fig. 1.

Equipment

A Stanton TR1 thermobalance was chosen for the char preparation because of its large sample capacity. The sample temperature was measured by a Pt/Pt—Rh thermocouple situated immediately below the sample crucible. The experimental conditions were: heating rate, 4°C min^{-1}; atmosphere, static air; sample mass, 1 g; nickel crucible.

The instruments used to obtain the IR spectra and the elemental analyses were both made by Perkin-Elmer, models 521 and 240, respectively.

RESULTS

Elemental analysis

The % carbon and hydrogen were determined directly and the % oxygen was calculated by difference. Table 2 lists the elemental analysis results as

TABLE 2

Elemental analysis data

Sample	Carbon			Hydrogen			Oxygen			Formula based on C6
	Analysis result (%)	As % of original sample	As % of original carbon	Analysis result (%)	As % of original sample	As % of original hydrogen	% by difference	As % of original sample	As % of original oxygen	
Cellulose	44.40	44.40	100	6.25	6.25	100	49.35	49.35	100	$C_6H_{10.1}O_{5.0}$
A	44.86	43.20	97.30	6.33	6.10	97.6	48.81	47.00	95.24	$C_6H_{10.1}O_{4.9}$
B	45.76	42.05	94.71	6.29	5.78	92.5	47.95	44.07	89.30	$C_6H_{9.8}O_{4.7}$
C	47.64	38.87	87.55	6.08	4.96	79.4	46.28	37.76	76.51	$C_6H_{9.1}O_{4.4}$
D	51.12	34.45	77.59	5.63	3.79	60.6	43.25	29.15	59.07	$C_6H_{7.9}O_{3.8}$
E	56.45	31.04	69.91	4.98	2.74	43.8	38.57	21.21	42.98	$C_6H_{6.3}O_{3.1}$
F	67.96	22.36	50.36	3.43	1.19	19.0	28.61	9.41	19.07	$C_6H_{3.6}O_{1.9}$
G	71.89	17.97	40.47	2.76	0.069	11.0	25.35	6.33	12.83	$C_6H_{2.7}O_{1.6}$

percentages for each element. These figures were then multiplied by the corresponding TG figures for the % mass remaining (Table 1) to obtain the elemental analyses as percentages of the original sample (Table 2), each of these latter figures was then expressed as a % of the corresponding elemental figure for the cellulose (Table 2). By plotting these "% of original" values against the corresponding temperatures, results similar to TG plots were obtained for each element. These are illustrated in Fig. 1.

If the continued existence, throughout the degradation process, of a six-carbon skeleton is assumed — an assumption supported by the following IR results — then the formulae of the chars can be calculated directly from their elemental analyses (Table 2). A comparison between the formulae shows that the ratio of hydrogen to oxygen is approximately 2 : 1 throughout the process; however, a more detailed check indicates that during the decomposition from cellulose to char B the oxygen is lost more rapidly than the hydrogen but that in subsequent decomposition the converse is increasingly true. Although it is almost certain that each formula represents the average formula of a range of chars, it is possible that the end of the rapid reaction and the commencement of the slower reaction (shown at ~340°C by the TG curves in Fig. 1) corresponds to the formation and subsequent decomposition of a single intermediate. Using the formula of the subsequent sample F as a reference it can be suggested that if a single intermediate exists at this point, then its formula is $C_6H_4O_2$.

Infrared spectroscopy

The probable assignments for the IR adsorption spectra of cellulose and thermally degraded celluloses have already been made by Higgins [2]. The technique employed in our study for obtaining the spectra involved the dispersion of the samples in discs of potassium bromide. A feature of the disc preparation was that the mass of sample mixed with KBr was deliberately made in proportion to the final TG value of that sample (Table 3). Thus a comparison between the same bonds in the spectra of the different samples should show a diminution in absorbance due to groups which have been

TABLE 3

Sample masses used for IR studies

Sample	% Sample remaining (from TG)	Sample mass for IR studies (mg)
Cellulose	100	2.0
A	96.3	1.9
B	91.9	1.8
C	81.6	1.6
D	67.4	1.4
E	55.0	1.1
F	32.9	0.7
G	25.0	0.5

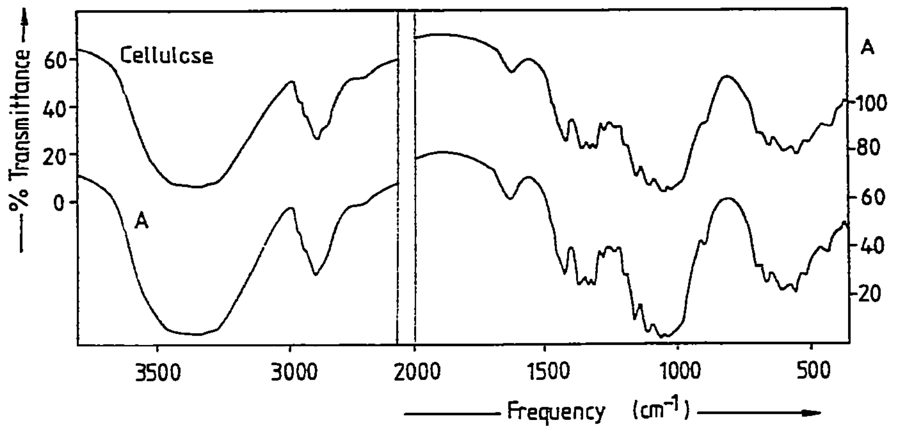

Fig. 2. Infrared spectra of cellulose and partially combusted char A.

affected by the decomposition process, and equal intensities for bands from groups which have remained untouched by the pyrolysis.

The spectrum obtained for the original cellulose (Fig. 2) agrees well with those of Higgins [2], Zhbankov [8] and Tang and Bacon [3]. Sample A (Fig. 2) taken to 259°C produced a similar result to cellulose, but sample B (Fig. 3) showed the emergence of a band at 1720 cm^{-1}, assigned by Higgins to carbonyl stretching, but few other changes except for a slight general decrease in absorption intensity. The spectra of samples C and D illustrate the growth of the C=O band (1720 cm^{-1}) and also that of a band at 1620 cm^{-1} which could be assigned either to C=C vibration or to O—H stretching of adsorbed water; however, the growth of this band in subsequent samples suggests that its cause is C=C vibration.

Sample E, removed from the thermobalance at 333°C still gave a carbohydrate type of spectrum (Fig. 4) although the bands at 1620 cm^{-1} and 1720 cm^{-1} had become very pronounced. Between sample E and sample F (341°C) rapid changes apparently occurred. Sample F produced a spectrum (Fig. 5) quite unlike the original cellulose, the newly-dominant C=O and C=C bands having shifted to 1710 cm^{-1} and 1600 cm^{-1}. The spectrum of

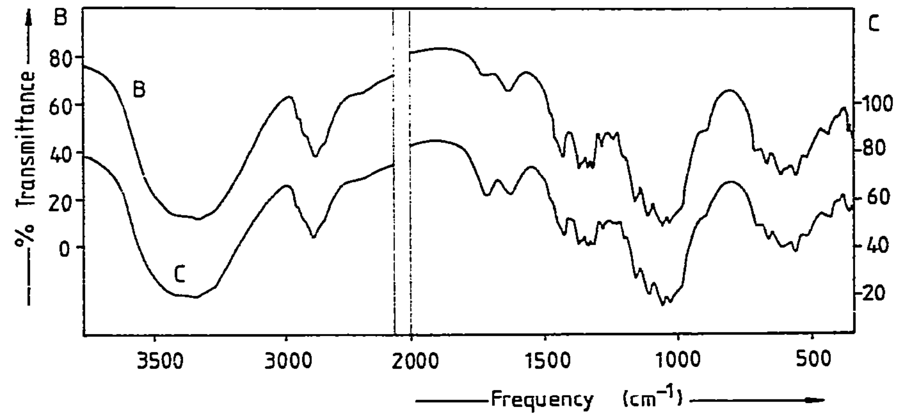

Fig. 3. Infrared spectra of partially combusted chars B and C.

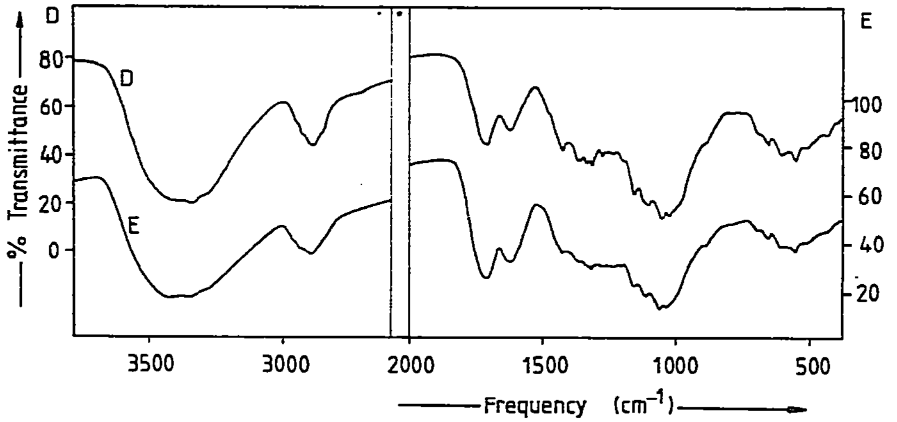

Fig. 4. Infrared spectra of partially combusted chars D and E.

sample G (Fig. 5) removed at 403°C shows little further change relative to the previous spectrum.

The results indicate that, up to 333°C, the basic carbohydrate structure was retained although there was an increasing proportion of carbonyl groups and unsaturated carbon—carbon bonds. Zhbankov [8] has recorded the IR spectra of a wide range of cellulose derivatives and a comparison between his spectra and those obtained here show some similar results. Many of the oxidation products of cellulose (prepared chemically) analysed by Zhbankov — for example monocarboxycellulose and dialdehydocellulose — show the 1720 cm^{-1} C=O peak superimposed on a cellulose spectrum, and give broadly similar results to the char samples. In particular char D and dicarboxycellulose (resulting from oxidation of the hydroxyls at C2 and C3) produce very similar spectra. The IR spectrum, obtained by Zhbankov for levoglucosan, is completely different from those discussed so far; it appears that at no stage of the decomposition is any significant amount of levoglucosan present in the solid phase.

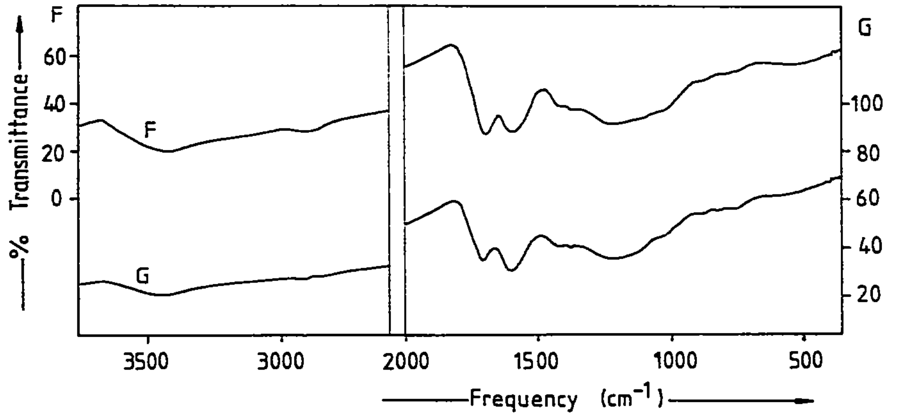

Fig. 5. Infrared spectra of partially combusted chars F and G.

DISCUSSION

Between ambient temperature and 260°C very few changes to the cellulose have been detected. The mass loss is small but it does involve a diminution of carbon as well as hydrogen and oxygen contents. Depolymerisation would not be detected by these experiments and it is postulated that this process is accompanied by some decomposition which is responsible for the carbon loss.

Infrared spectroscopy has shown a steady increase in unsaturated groups (C=C and C=O) between 260 and 330°C. The experimental results indicate the presence of two main processes at this stage.

(i) Dehydration, producing unsaturated bonds and loss of hydrogen and oxygen in the proportion 2 : 1. This reaction is largely responsible for the changes in char composition and the consequent IR spectra. This reaction is more likely to occur in the amorphous regions of the cellulose.

(ii) Formation and simultaneous evolution and combustion of levoglucosan. It should be recalled that the absence of levoglucosan from the chars has been established; this implies that it is evolved immediately after its formation. Levoglucosan has been shown to evaporate at 200°C at atmospheric pressure [9]. Levoglucosan formation results in a major mass loss and evolution of volatiles; its combustion is primarily responsible for a DTA exotherm at around 350°C [1].

These two processes may be consecutive, competitive or components of a single reaction. It is generally accepted that char production and levoglucosan production are quite separate processes since varying the experimental conditions can cause either process to be favoured. The possible schemes are therefore either competitive or consecutive (Fig. 6). It is, however, also believed that the decomposition of cellulose into levoglucosan does not involve an unsaturated intermediate. It would appear therefore that reactions (i) and (ii), as postulated above, are largely competitive. Reaction (i) will result in the loss of hydrogen and oxygen in the ratio 2 : 1, and reaction (ii)

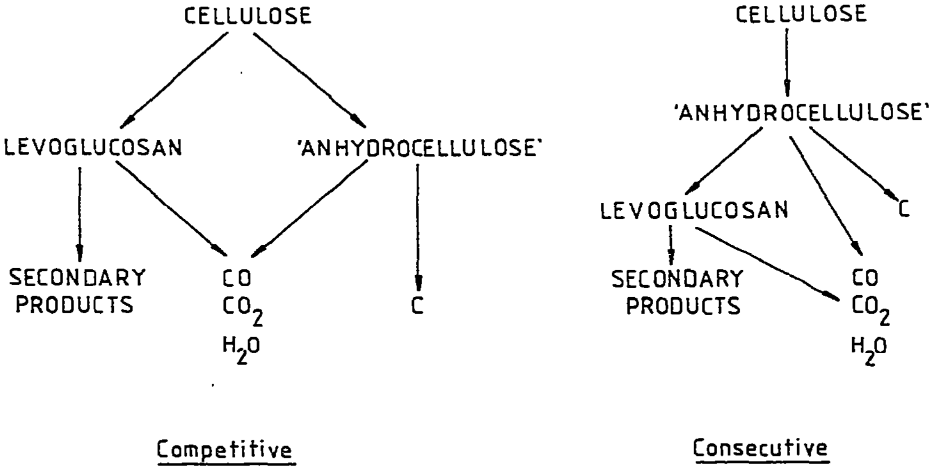

Fig. 6. Schemes for the formation of levoglucosan and "anhydrocellulose".

TABLE 4

Elemental mass loss data

Stage of decomposition	Temp. range (°C)	Carbon loss as % of original sample	Hydrogen loss as % of original sample	Oxygen loss as % of original sample	Formula of evolved material based on O_5	"% Reaction" based on C6		Ave. rate % per °C
						(i)	(ii)	
Cellulose—A	Ambient—259	1.20	0.15	2.35	$C_{3.4}H_5O_5$			0.01
A—B	259—301	1.15	0.32	2.93	$C_{2.6}H_{8.7}O_5$			0.10
B—C	301—318	3.18	0.82	6.31	$C_{3.4}H_{10.4}O_5$	44	56	0.61
C—D	318—325	4.42	1.17	8.61	$C_{3.4}H_{10.9}O_5$	44	56	2.03
D—E	325—333	3.41	1.05	7.94	$C_{2.9}H_{10.6}O_5$	52	48	1.55
E—F	333—341	8.68	1.55	11.80	$C_{4.9}H_{10.5}O_5$	18	82	2.76
F—G	341—403	4.39	0.50	3.08	$C_{9.5}H_{13}O_5$			0.13

will cause a loss of carbon, hydrogen and oxygen in the proportion 6 : 10 : 5. If these are the two main reactions then the proportion of hydrogen to oxygen in the chars will always be approximately 2 : 1; our elemental analysis results confirm this hypothesis.

Table 2 shows elemental analysis and thermogravimetric data for the material remaining after partial combustion of cellulose. A similar table can be constructed for the evolved gases and vapours, using the same original data. Table 4 shows the "mass loss" of each element, for each of the seven experimental stages of the decomposition (e.g. from cellulose to char A is the first stage), as a % of the original sample. From these figures the average formula of the evolved material has been calculated for each stage. If the previous argument regarding two processes is true, then the formulae of the lost material should be $C_{<6}H_{10}O_5$ for all except the later stages when relatively more carbon will be lost.

The argument is supported by the results, except for the earlier stages up to 301°C. It can be suggested that an additional precursor reaction at the lower temperatures (probably depolymerisation) causes evolution of oxidised species such as carbon monoxide and carbon dioxide. From the deviation of the carbon from C_6, in the formulae of evolved material, the proportion of the extent of reaction (i) to reaction (ii) can be calculated and expressed as a percentage (the "% reaction" in Table 4). The figures indicate that the proportion of the reactions to each other is not constant — confirming the "competitive" hypothesis — and that levoglucosan formation is favoured at higher temperatures. A comparison of the "% reaction" values with the figures for the average rate of each stage (Table 4) suggests that these processes occur rapidly.

The obvious flaw in the presentation of this simplified model is the possibility of other significant reactions. Thermal analysis results indicate that char combustion commences at about 365°C; this reaction is probably responsible for the increased rate of carbon loss between 341 and 403°C (Table 4) but it may also affect the previous stage, causing the apparent increase in reaction (ii). Infrared spectroscopy has shown that the original carbohydrate structure is retained up to 333°C but that rapid changes occur between samples E and F as the carbohydrate structure is destroyed. The rate of the reaction becomes relatively slow in its final stages which consist of the formation and combustion of carbonaceous material. The process is complete when no more char remains.

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