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Preservation of D-glucose-oligosaccharides in cellulose chars

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ABSTRACT

Microcrystalline cellulose was charred anaerobically at atmospheric pressure and at different temperatures ranging from 190 to 390°C. Temperature-resolved, in-source-filament pyrolysis, ammonia chemical ionisation mass spectrometry (Py-CIMS) of these chars shows ion series of ammonium adduct ions of anhydro-oligosaccharides. These anhydro-oligosaccharides were identified by high-performance liquid chromatography (HPLC) of derivatised, off-line, Curie-point-pyrolysis condensates as β-(1 → 4)-linked glucose oligosaccharides with an 1,6-anhydrosugar terminal at the reducing end. These anhydro-glucooligosaccharides were observed in chars even after 2.5 h heating at 270°C. The relative amount of preserved glucose in the chars was determined by acid hydrolysis. Coexistence of two solid phases: (i) residual crystalline cellulose and (ii) a condensed thermostable phase was observed in chars derived from cellulose by heating at 250, 270, and 290°C. It is believed that the formation of this new condensed phase is initiated in the thermally induced, amorphous domains of cellulose. No ether-bonded products of inter- and intra-chain crosslinking reactions were detected in the acid hydrolysates of the chars.

INTRODUCTION

Analytical pyrolysis techniques were used previously for chemical characterisation of charred food residues obtained from prehistoric pottery[1]. Well preserved lipids, fatty acids, and characteristic markers for proteins and polysaccharides have been detected. The process or mechanism whereby these biomolecules are preserved is not known, but they appear to be included and grafted on chars from polysaccharides. Such polysaccharides as amylose and cellulose are present in foods in large amounts and are thought to be the major char-forming component. Cellulose has been chosen as a model in this study because it's structure is well defined; it can be obtained in a relatively pure form; it bears a structural resemblance to amylose and many details of the pyrolysis of cellulose are known[2–13]. The conditions used for preparation of our experimental chars were chosen so that

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the results could be extrapolated to conditions of cooking and baking in prehistoric times[14]. Under the assumption that the actual charring at the bottom of the cooking vessel is an anhydrous, anoxic process, the dry cellulose sample is exposed to a range of high temperatures for a period of several hours under a continuous flow of nitrogen.

The pyrolysis products from cellulose can be divided in gaseous fractions, tar, and a solid charred residue. Rapid heating of cellulose to temperatures $> 300°C$ starts a thermally induced sequence of reactions such as transglycosylation, elimination, fission, and disproportionation[15]. These reactions provide complex mixtures of lower-molecular-weight products depending on the conditions used (pressure, size of sample, amount of inorganic additives), which escape from the heated zone as the tar and gaseous fractions.

In comparison to these tar and volatile fractions, considerably less research has been performed on the solid charred residue. At low temperatures from 250–300°C, cellulose pyrolyses slowly to give ultimately mainly char and gases with very little tarry product[15]. Shafizadeh[15] has shown that sustained heating of cellulose for several hours under nitrogen at temperatures in the range 150–190°C causes a reduction in the degree of polymerisation (dp), the elimination of water, the formation of carbonyl, carboxyl and hydroperoxide groups, and the evolution of carbon monoxide and carbon dioxide, leaving a charred residue[16]. To account for the ultimate formation of char, it seems necessary to consider crosslinking reactions between cellulose chains. Kilzer and Broido[16] have shown that a cellulose sample, first kept for a day at ca. 250°C, forms about three times as much char at subsequent heating to 400°C as a similar sample heated directly to 400°C. The phenomenon is explained by proposing intra- or inter-chain dehydration and crosslinking reactions.

FTIR studies of the solid residues from the vacuum pyrolysis of cellulose have shown that the char is slowly transformed from a cellulose structure to a solid with little or no pyranose character but with alkenic and carbonyl bonds[17]. The FTIR spectrum of a char (final temperature of 325°C), prepared with a slow heating rate (2°C/min), shows a decrease in absorptions assigned to hydrogen-bonded OH group stretching and a broad absorbance assigned to pyranose ring C–C and C–O stretching. The authors explain these phenomena as a small chemical change, i.e., elimination of water, which severely influences the subsequent pyrolytic depolymerisation of cellulose. The FTIR spectrum of cellulose, heated to the same constant final temperature of 325°C with a higher heating rate (16°C/min), shows dominant absorbances assigned to C=C, C=O, and C–C bonds which is interpreted at a loss of pyranose structural elements and a loss of glycosidic bonds in the char.

In this paper the primary charring conditions were chosen such that the time interval of heating was shorter than those used by other authors[18,19] over a similar temperature range. The primary heating of the cellulose was carried out under atmospheric pressure to enhance the formation of char with respect to gaseous and tar products. Structural components from these chars were released by analytical

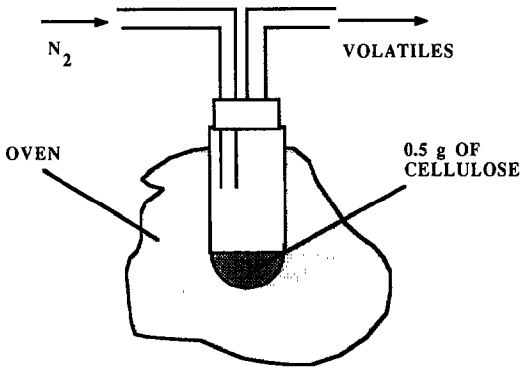

Fig. 1. Preparation of the experimental cellulose chars.

pyrolysis and by acid hydrolysis methods. Py-ammonia-CIMS (ref 20) and off-line, Curie-point-pyrolysis combined with benzoylation and HPLC (ref 21) were used to investigate the decay of the polysaccharide structural components as a function of char preparation temperature. Acid hydrolysis was used to determine the amounts of acid-labile bonds and the amount of glucose remaining in the char. The hydrolysates were perbenzoylated and analyzed by HPLC with the aim of detecting ether-linked oligomers.

EXPERIMENTAL

Preparation of chars.—The charring experiments were set-up as follows (Fig. 1). Microcrystalline cellulose (Cellulose microcrystalline, Avicel, for TLC, Merck, Germany, ca. 0.5 g) was placed in a glass tube with a sinter and continuously flushed with N_2 during the whole reaction period at a flow rate of 80 mL/min. The tube was inserted in a pre-heated oven. The tube with the sample was weighed before and after the heating in order to calculate the percentage weight loss. The heating time for all samples was 2.5 h. The temperatures used for preparation of the primary chars were 190, 220, 250, 270, 290, 310, 350, and 390°C; sample codes are denoted char 190, char 220, etc. Gases and volatiles were vented.

Mass spectrometry.—The mass spectrometer used was a Jeol DX-303 double-focusing mass spectrometer equipped with a Jeol DCI unit, and the Jeol DA-5000 data system. The sample was deposited on a platinum/rhodium filament of the DCI probe which was inserted directly into the ion source of the mass spectrometer. The platinum wire was heated resistively (at a rate of 13.5°C/min to 800°C) and the released pyrolysis products were ionised under positive NH_3 chemical ionisation conditions. The accelerating voltage was 2.2 kV, the scan speed was 1 s/decade and the dynamic resolution was set at 1500. The mass range was set m/z 60–1000 and the NH_3 pressure in the ion source was 20 Pa. Untreated microcrystalline cellulose and samples from char 190 to char 310 were measured 5 times each. The overall spectral differences within the mass spectra were analysed by

multivariate analysis, using the FOMpyroMAP which is based on the ARTHUR (1978 version) package (Infomertrix, Seattle, WA). The expansion of this package with linear discriminant analysis (d.a.) have been described by Hoogerbrugge et al.[22]. The dissimilarity between the categories (groups of multiplicate spectra) is expressed in discriminant functions and scores, which are represented graphically by reconstructed mass spectra and score plots.

Off-line, Curie-point-pyrolysis of pre-treated cellulose samples.—An off-line, Curie-point-pyrolysis device was used as described by Lomax et al.[20]. From a suspension in water, samples of cellulose pre-heated at 250 and 270°C, respectively, for 2.5 h, were applied onto a ferromagnetic wire with a Curie-point temperature of 510°C. Thirty six wires were prepared, 12 for each sample, dried in vacuo and placed in glass liners. The pyrolysis device was flushed twice with Ar to provide an anoxic environment and subsequently evacuated to a pressure of 10^{-2} mbar. The pyrolysis was accomplished in 4 s. Under these conditions, a condensate formed on the wall of the glass liners surrounding the wire. The combined pyrolysis condensates from all the tubes for each sample were dissolved in ca. 100 μL of deionised water (1.2 mL in total), resulting in a yellow solution.

Derivatisation of samples.—(*i*) Hydrolysis of chars: A 5-mg amount of char was placed in a 10-mL tube with a screw top and of 12 M H_2SO_4 (0.5 mL) was added. The tube was flushed with N_2 and the sample was incubated at room temperature for 3 h. The acid was subsequently diluted to 1 M and the sample was further hydrolysed overnight at 100°C. Some samples still contained a solid residue which was then filtered through a glass filter and washed with deionised water. The residue was dried over P_2O_5 in a vacuum desiccator at 50°C overnight and weighed.

The acid, in the liquid hydrolysate, was partially neutralised (pH 0.9–1.2) by slow addition under rapid stirring of 0.18 M $Ba(OH)_2$ (40 mL). This was sufficient to neutralise and precipitate ca. 85% of the H_2SO_4 as $BaSO_4$. The neutralisation was completed by adding 1.6–1.8 g $BaCO_3$. The precipitated and remaining $BaCO_3$ were removed by centrifugation (15 min, 7000 rpm). The supernatants were collected, the volumes were decreased to 1/3 by evaporating on a rotary evaporator. The density of the solvent was then changed by adding MeCN (0.3 mL for every mL of water) in order to facilitate the precipitation. After 10 mins, the centrifugation was repeated. The supernatants were collected and evaporated to dryness on a rotary evaporator. The concentration of glucose was determined in the hydrolysates as described below and part of the hydrolysate was benzoylated and analysed by HPLC.

(*ii*) Benzoylation of hydrolysed material and off-line Curie-point pyrolysis condensates: for benzoylation, a reagent containing 5% 4-dimethylaminopyridine and 10% of benzoic Bz_2O anhydride in pyridine was prepared. In a conical glass vial with a screw top, the yellow aqueous solution of the pyrolysis condensates (or hydrolysed sample) was evaporated to dryness under a stream of N_2 and dried over P_2O_5 in a vacuum desiccator oven (50°C). The reagent (3 mL) was added to each

sample and the vial was flushed with N_2. The mixture was heated at 40°C for 30 min and kept overnight at room temperature with stirring. Following benzoylation, the sample was applied to a C_{18} solid-phase extraction column (J.T. Baker Inc.). The column was washed with aq 10% pyridine (3 mL) and with deionised water (3 mL). After drying the column, the benzoylated samples were eluted with MeCN (4 mL). The samples were dried under a stream of N_2 and redissolved in MeCN (0.5 mL) for HPLC analysis.

Determination of D-*glucose.*—The amount of glucose in the hydrolysates was determined, with the D-glucose UV-method test from Mannheim Boehringer (cat. No. 716251), based on the enzymatic transformation of D-glucose into D-glucose-6-phosphate and 6-phospho-D-gluconate. During the latter reaction, NADPH is formed and was analysed with a spectrophotometer. The amount of NADPH formed in this reaction is stoichiometrically equivalent to the amount of D-glucose. The increase of NADPH was measured as an increase in absorbance at 340 nm[23].

HPLC.—The HPLC equipment consisted of a CM 4000 gradient pump, an A1000 auto injector (Rheodyne Model 7126 fitted with a 20-μL loop), and an SM 4000 variable wavelength UV/VIS detector (LDC/Milton Roy). A LiChroCART system with a 250 × 4 mm RP-18 column (5-μm spherical particles) from Merck was used. The detector was connected to a Nelson analytical 760 series interface, and the data were processed on an Olivetti M28 personal computer. The column was eluted at a flow of 1 mL/min with 1:3 water–MeCN for 5 min, and then with a linear gradient to pure MeCN over 15 min, and a further 6 min at the final composition. The benzoylated compounds were detected at their maximum absorbance (230 nm).

RESULTS

An important feature of the experimental set-up is the open system. At high temperatures the flow of N_2 removes the tars and other volatiles from the reaction

TABLE I

Temperatures, percentage weight loss, and colour of the primary chars [a]

Temperature (°C)	Weight loss (%)	Colour	Hydrolysed material (wt% of char)
Cellulose [b]		white	100
190	8	yellow	100
220	10	brownish	90
250	20	brown	40
270	40	brown	35
290	60	black	8
310	65	black	3
350	75	black	<1
390	90	black	<1

[a] The heating time for all char preparations was 2.5 h. [b] Untreated cellulose.

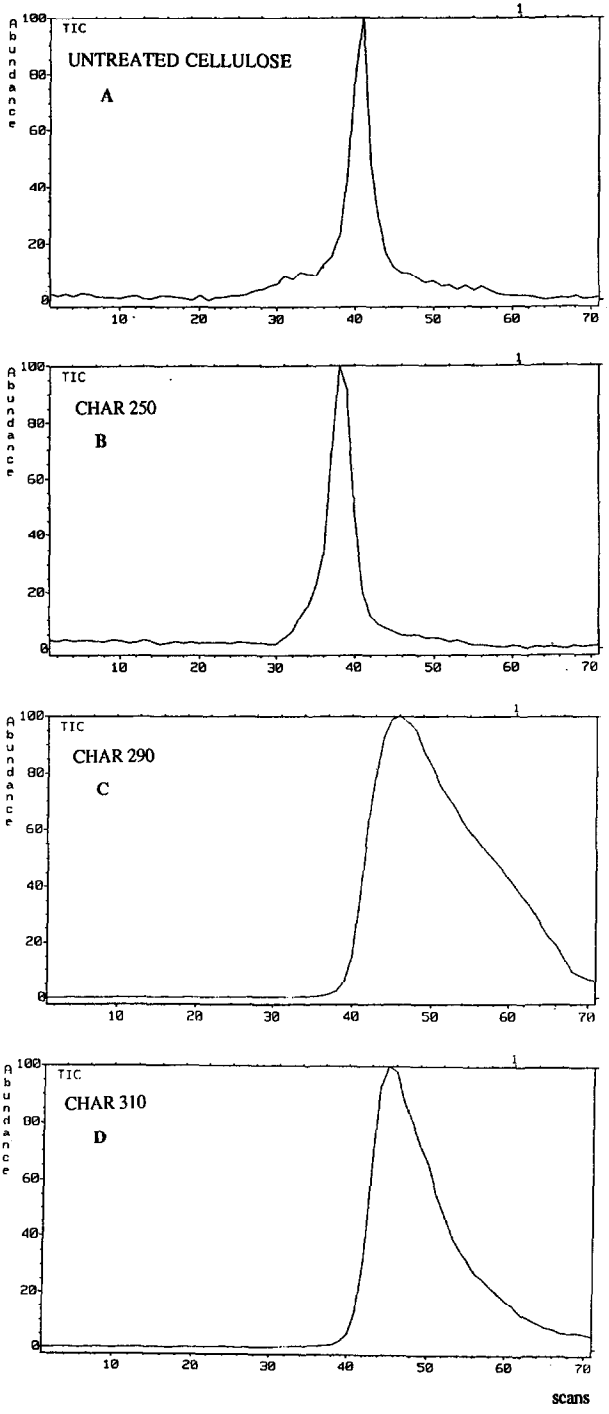

Fig. 2. Total ion current (TIC) from Py-CI (ammonia)MS measurements of selected char samples. (a) Untreated cellulose, (b) char 250, (c) char 290, and (d) Char 310.

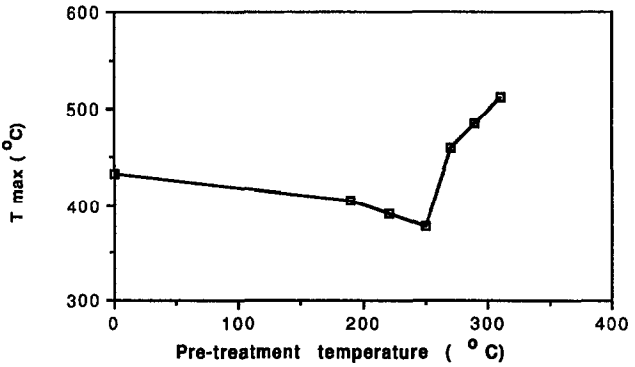

Fig. 3. The effect of pre-heating temperature on the maximum dissociation temperature (T_{max}) of the analytical pyrolysis.

zone. The constant flow of N_2 provides not only an anaerobic environment, but as it was not pre-heated, it also caused some cooling of the sample. In combination with the relatively large amount of sample used, this resulted in slow heating rates. At temperatures of 190 and 220°C, a clear liquid condensed in the cooler parts of the outlet tube. This condensate was not further analysed, but it is assumed that only water escaped from the reaction zone at these temperatures and pressures[5]. At temperatures greater than 220°C, brown tar formation was observed in the outlet tube. These tars were not further analysed.

The colour of the chars changes from light brown to black as the heating temperature increases. The weight loss data in Table I show the strongest volatilisation of cellulose taking place in the temperature range 250–290°C. The weight loss at 190 and 220°C is mainly due to loss of water (crystallization as well as resulting from chemical changes) because the drying of cellulose at 50°C over P_2O_5 in a vacuum dessicator gives a weight loss of 5%. The chars obtained above 310°C contain very small amounts of acid-hydrolysable material.

TABLE II

D-Glucose content, desorption profile width, and main mass spectrum peaks of the char samples prepared at different temperatures [a]

Sample	D-Glucose recovery (mg/mg char)	Desorption profile width [b]	Main peaks in the mass spectra (m/z) (relative intensities)							
			97	111	128	144	161	163	175	180
Cellulose [c]	0.810	5	1	2	5	14	1	1	1	100
Char 190	0.904	5	1	1	2	9	1	1	1	100
Char 220	0.641	7	1	1	5	5	1	1	1	100
Char 250	0.599	7	1	1	2	5	1	1	1	100
Char 270	0.131	13	1	2	3	5	1	1	1	100
Char 290	0.025	22	29	58	90	100	35	44	36	93
Char 310	0.005	18	60	68	80	50	97	98	100	70

[a] The samples were heated for 2.5 h at the given temperature, i.e., char 190 was heated at 190°C, etc. [b] In scans. [c] Untreated cellulose.

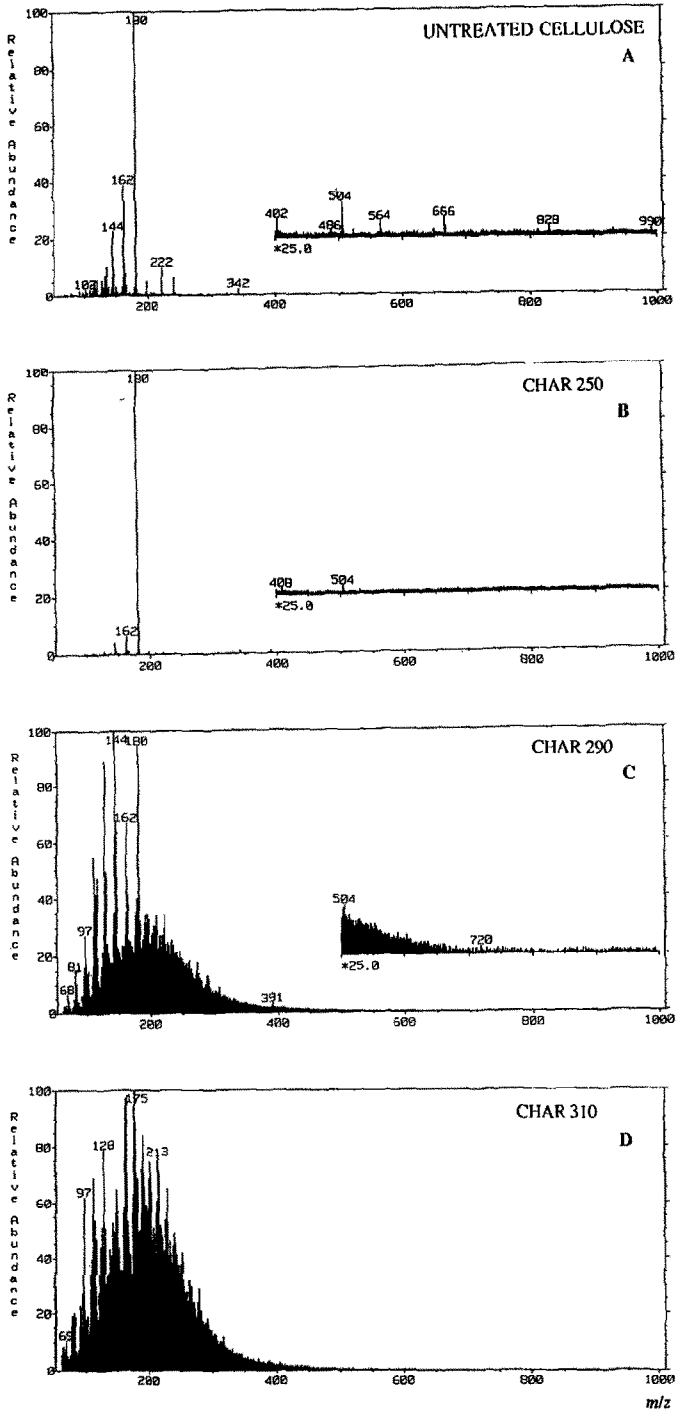

Fig. 4. Pyrolysis-CI (ammonia) mass spectra of selected char samples. (A) Untreated cellulose, (B) char 250, (C) char 290, and (D) char 310

Temperature-resolved pyrolysis-ammonia CIMS.—Fig. 2 presents the TIC (total ion current) data for cellulose, char 250, char 290, and 310 from Py-CIMS experiments. Cellulose and char 250 show a very sharp pyrolysis-product distribution with temperature with a marked shift in the T_{max} of the char 250 towards lower values by 4 scans, corresponding to ca. 60°C. The samples from char 290 and 310 show a different shape of the TIC. The maximum dissociation temperature shifted towards higher values and the desorption profile is much broader on the high temperature side. Fig. 3 and Table II show the T_{max} and the width of the pyrolysis product TICs of all samples. Above a temperature of char preparation of 250°C, the decrease of the T_{max} values changes into an increase.

The change in chemical composition which accompanies these phenomena is expressed in the mass spectra of Fig. 4, and in Table II, which lists mass peak

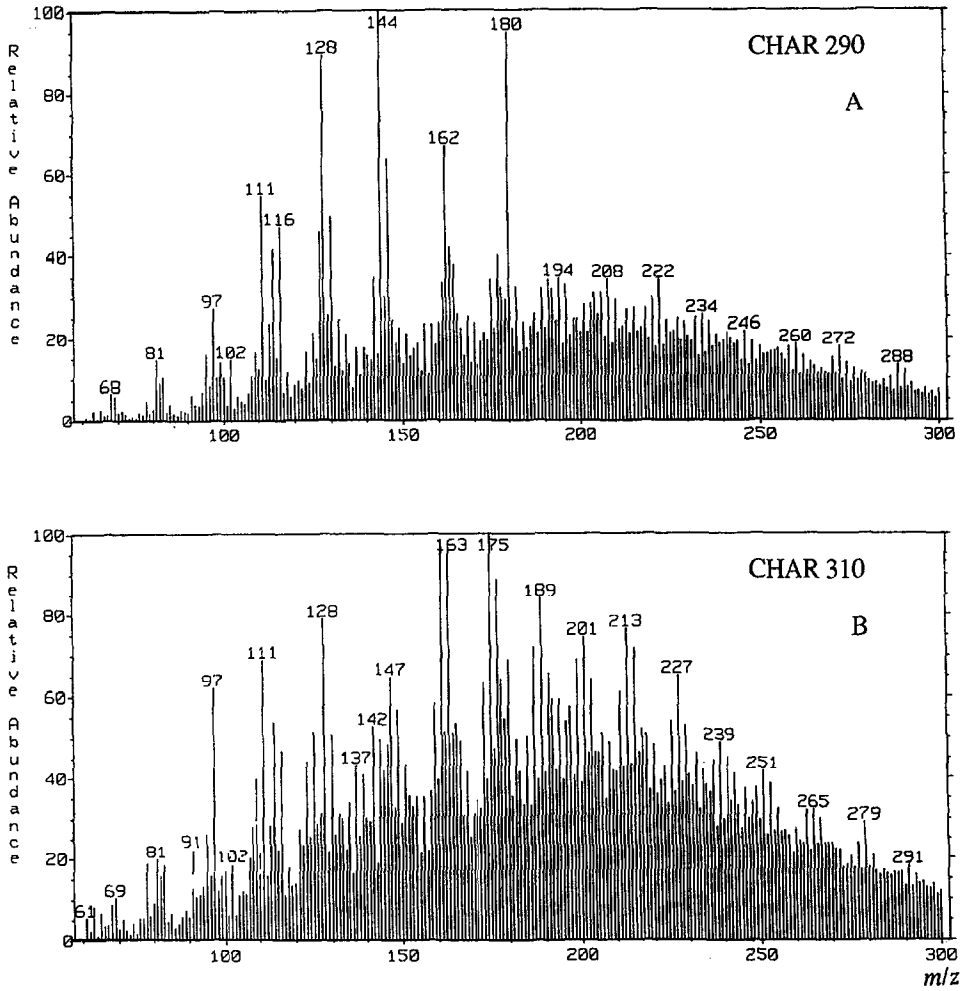

Fig. 5. Pyrolysis-CI (ammonia) mass spectra of (A) char 290 and (B) char 310.

intensities of a number of key components. With soft ionisation techniques, such as ammonia CI, the polymer characteristics of native cellulose are represented in the spectra by the series of ions m/z 180, 342, 504, 666, and 828 (ref 24). In the spectrum of native cellulose, this series is known to represent the higher homologues of cellobiosan, a 1,6-anhydro-cellobiose[25]. Oligosaccharides with the same molecular weight are well preserved in the chars, even after heating for 2.5 h at 270°C. In the spectrum of this sample, m/z 504, representing the ammonia adduct of the anhydro trimer, is still present. With heating at higher temperatures the chemical changes in the chars are also reflected in their CIMS spectra. The ion series representing oligomers have diminished and new compounds emerge in the mass range m/z 60–300. The mass spectra show an increase in m/z 128 and 111, $[M + NH_4]^+$ and $[M + H]^+$, respectively, both corresponding to compounds with a molecular weight of 110 (Fig. 5). Pyrolysis products with this parent ion have been identified in these chars as 2-ethyl-5-methylfuran, 2-(1-propyl)furan, 2-acetylfuran, and 5-methyl-2-furaldehyde[26]. Chars prepared at higher temperatures show mass spectra with very few even ions and many odd ions, which indicate a shift from the

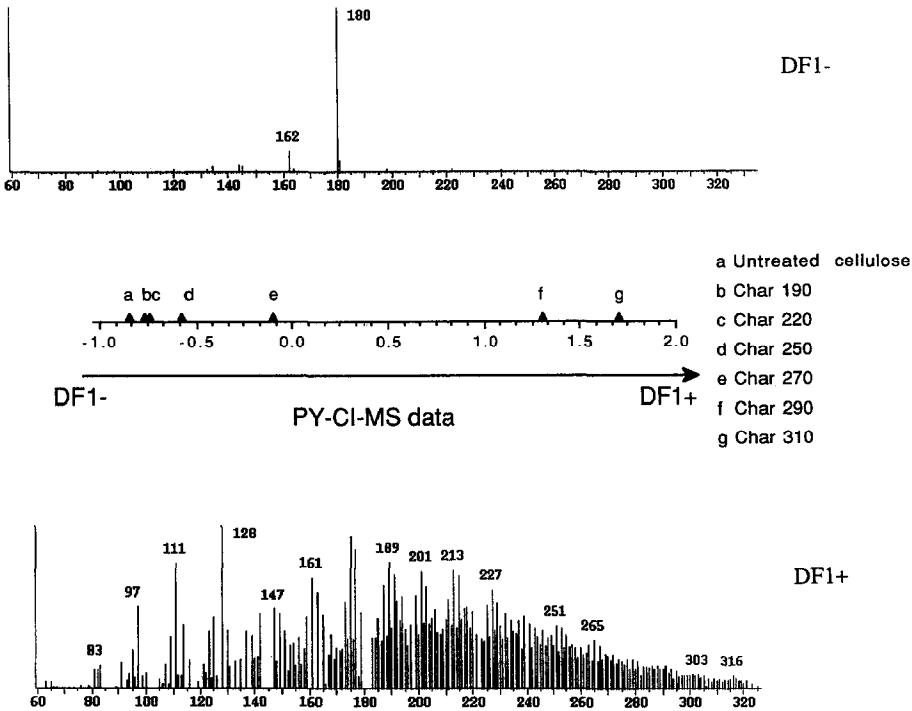

Fig. 6. Discriminant plot [discriminant function $1(DF_1)$] of 7 cellulose chars. The euclidian distance between two sample points represents the relative difference in chemical composition. DF_{1+}, Spectral characteristics indicative of the charred cellulose DF_{1-}, Spectral characteristics indicative of the uncharred cellulose microcrystalline cellulose (a), char 190 (b), char 220 (c), char 250 (d), char 270 (e), char 290 (f), and char 310 (g).

ammonia adduct to protonated quasimolecular ions[27] (see Fig. 5b). The mass increments change from 18 mass units (differences in H_2O) to a series with 14 mass units (CH_2). This can be observed in the MS of Fig. 5a by a relatively higher intensity of m/z 111, 128, and 144 compared to m/z 180 and 162. For char 290, the most abundant peak in the spectrum is m/z 144, representing the ammonia adduct for compounds with a molecular weight of 126. Several compounds with this molecular weight, e.g., levoglucosenone and dimethylpyranones, have been identified in the pyrolysates of microcrystalline cellulose[25].

The mass spectrum of Fig. 5b shows a different pattern. It is interesting that the ion at m/z 180 [M + 18], corresponding to levoglucosan or another anhydro sugar isomer, is still present (65%), even after heating cellulose to these temperatures. From m/z 147, one can observe groups of 3 peaks with a mass difference within the groups of 2, and between the groups of 14 mass units corresponding with a homologous series of condensed aromatic compounds[14].

The Py-CIMS spectra of char 190 to 310 were analysed by factor-discriminant analysis[22]. Multivariate discriminant analysis shows that 64% of the inner/outer variance is described by the first discriminant function, which describes the progressive charring of the samples as a function of pretreatment temperature. Lower priority D functions describe less than 3% of the variance and are ignored. Negative scores in the plot of Fig. 6 correspond to characteristic mass peaks of cellulose (see the D_1^- reconstructed mass spectrum). The positive scores of the first-discriminant function plot represent the "char". Many of these peaks are dominant mass peaks in the spectrum given in Fig. 5b.

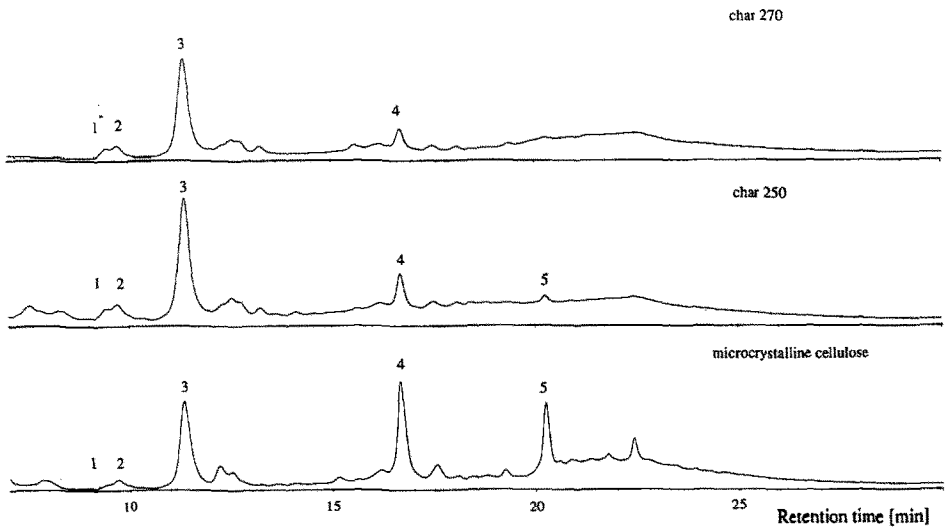

Fig. 7. HPLC plots of *O*-perbenzoylated off-line Curie point-pyrolysis condensates. (1,2), D-Glucose, (3) anhydrocellobiose, (4) anhydrocellotriose, and (5) anhydrocellotetraose.

HPLC of off-line, Curie-point pyrolysates.—Fig. 7 shows HPLC chromatograms of *O*-perbenzoylated, Curie-point condensates of char 250 and char 270. The retention times of the peaks in the oligomer region (t_R from 11 to 25 min) are identical with those of the oligomers from untreated microcrystalline cellulose identified previously, and correspond to anhydrocellobiose (peak 3), anhydrocellotriose (peak 4), and anhydrocellotetraose (peak 5)[20,21,25]. Oligomers with different linkage are present, for example after peak No. 3, but the amounts are insignificant. Since these peaks are also present in the off-line pyrolysate of the untreated cellulose sample, they were not considered specific for the chars.

Acid hydrolysis of the charred material.—The amount of hydrolysable material was determined by acid hydrolysis of the chars. The amount of acid-labile bonds strongly decreases from samples above the pre-heating temperature of 250°C. Table II presents the glucose concentration in the hydrolysate expressed as mg of D-glucose per mg of char. The increased apparent recovery in the char 190 sample may be caused by water adsorbed to the native cellulose sample thus increasing the weight, and by a predepolymerisation which facilitates the hydrolysis process. D-Glucose recovery from the char is very high, up to a charring temperature of 250°C, and decreases sharply at higher temperature. It is noteworthy that glucose is still present, even in char 310. A solid black residue remains after the hydrolysis of chars made at the higher temperatures (Table I). Water solutions of char 190, 220, 250, and 270 have a light-brown colour. The hydrolysates were further analysed as their *O*-perbenzoyl derivatives by HPLC to check for ether-linked oligomers.

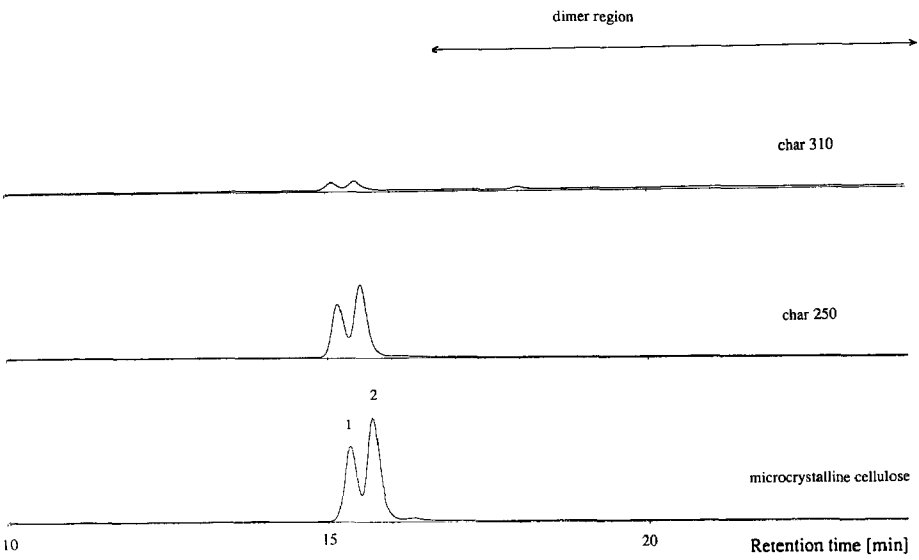

Fig. 8. HPLC plots of *O*-perbenzoylated char hydrolysates. (1 and 2), α,β-D-Glucose pentabenzoates.

HPLC of O-perbenzoylated hydrolysates.—The chromatograms of the *O*-perbenzoylated hydrolysates from the chars in Fig. 8 contain only two overlapping peaks in the sugar region, which are also present in *O*-perbenzoylated hydrolysate from native cellulose. These peaks represent α- and β-D-glucose pentabenzoate. D-Glucose was even detected in the hydrolysate of the char obtained after heating cellulose for 2.5 h at 310°C. The absence of significant peaks in the dimer area of the chromatograms (t_R 16–25 min) shows that no oligoglucans are present in the hydrolysates (Fig. 8). Comparison of Fig. 7 with Fig. 8 shows a difference in retention time for D-glucose of 7 min which is caused by the use of a new column of the same type and by a slightly different ratio of MeCN-to-water. The small peak with t_R 8 mins in the chromatogram of perbenzoylated hydrolysate char 310 was also present in the blank and is due to contamination with the benzoylation reagents.

DISCUSSION

It has already been established[13,20] that cellulose pyrolysis proceeds through three competing reaction pathways: (*i*) transglycosylation leading to one of the main pyrolysis products (levoglucosan) and oligomers having a 1,6-anhydroglucose unit at the reducing end, (*ii*) retro-aldolisation, yielding 2-hydroxyacetaldehyde and oligomers containing ring-cleavage fragments, and (*iii*) elimination reactions leading to anhydrohexoses and pyranones. Characteristic pyrolysis products of cellulose are also observed in our experiments, as may be seen from the Py-CIMS data of native cellulose and chars derived from cellulose at temperatures up to 290°C. This implies that, even in chars which have been exposed to high temperatures for a relatively long period of time, domains exist with intact linear (1 → 4)-β-D-glucan chains.

Possibly, a coexistence of two phases occurs in some of the chars, the first being residual crystalline cellulose, and the second one a new, thermostable phase consisting of aromatic compounds. Based on the results of the factor discriminant analysis of the Py-CIMS data we conclude that chars 190, 220, and 250 contain mostly crystalline cellulose and that chars 270, 290, and 310 are composed mostly from the thermostable, condensed phase. Chars 250 to 290 appear to contain both.

Thermogravimetric curves of cotton cellulose, of different degrees of crystallinity, show major differences in their decomposition processes[28]. Cotton with a high degree of crystallinity is thermally stable up to temperatures of 280°C. Major weight loss for this type of samples occurs in the temperature range 280–380°C. In cotton having a low degree of crystallinity, weight loss occurs already at 100°C and proceeds steadily until 500°C. In our experiments, a shift in T_{max} towards lower values is observed in the temperature resolved Py-CIMS data of chars 190, 220, and 250. This can be explained by a lowering in the degree of polymerisation as well as by a lowering in the degree of crystallinity due to the heating process. It is assumed that, under the batch conditions in our experiments, slow heating up to

250°C would result in a cellulose having a larger fraction of disordered and amorphous structural domains.

We postulate that the second, thermostable phase which dominates the char composition beginning at char 270 is formed in the thermally induced, amorphous domains of cellulose. There is most likely a great difference in the types of pyrolysis reactions involved in the thermal decomposition of amorphous and crystalline celluloses[28]. Probably, elimination and retro-aldolisation reactions, leading to a higher char yield, predominate over the transglycosylation pathway in amorphous cellulose. Crystalline centers are the source of the main product of transglycosylation reactions, namely, levoglucosan[29].

The conversion of crystalline to amorphous cellulose is slow, and chars 190, 220, and 250 retain some of their crystalline centers and hence the polymer structure of cellulose. Supporting evidence for this is the Py-CIMS data, which are interpreted as evidence for preservation of polysaccharide chains in these chars. The off-line, Curie-point-pyrolysis and hydrolysis results confirm this interpretation. It is striking, that relatively large amounts of D-glucose can be recovered by hydrolysis of chars 250, 270, and 290. However, this method cannot distinguish between D-glucose preserved in the chars as glucans and D-glucose released on acid hydrolysis from levoglucosan.

The coexistence of the two solid phases, namely the preserved residual crystalline cellulose and the condensed thermostable phase formed from cellulose that has been rendered amorphous, is observed in chars 250, 270, and 290. The minimum temperature required for the formation of the new thermostable phase in detectable amounts under our conditions is 250°C, as shown in our previous work[14]. The Py-EIMS spectrum of the acid hydrolysis residue from the char 250 sample showed that the aromatic polymers are being formed at these temperatures.

Kilzer and Broido[16] suggested the formation of inter- or intra-chain ether linkages between D-glucose units still linked in a polymer or oligomer by a glycosidic bond. However, such ether oligomers could not be detected in the hydrolysis data, nor are they evident from the Py-(ammonia) CIMS data. Further details about the char composition are being acquired by NMR, FTIR, and Py-GLC–MS to identify the structural components in the newly formed thermostable phase[26].

CONCLUSIONS

Preservation of the polysaccharide characteristics of cellulose in the crystalline domains is observed in cellulose chars up to the relatively high temperature of 270°C. At the same time, formation of a new condensed char phase was detected at a temperature of 250°C. We postulate that the char formation initiates in the thermally induced disordered and amorphous domains of cellulose. The coexistence of two solid phases, (*i*) residual crystalline cellulose and (*ii*) a condensed

thermostable phase, was observed in chars derived from cellulose by heating at 250, 270, and 290°C. No ether bonded products of inter- and intra-chain crosslinking reactions, as suggested earlier by Kilzer and Broido[17], were detected in our experiments.

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