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Isothermal Pyrolysis of Cellulose: Kinetics and Gas Chromatographic Mass Spectrometric Analysis of the Degradation Products

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Synopsis

Untreated and fire-retardant-treated white α-cellulose samples were isothermally pyrolyzed in a fluidized bath in a nitrogen environment at 298–360°C. Results were reported in terms of volatilization (based on weight loss–time measurements) and the degradation products (based on gas chromatographic–mass spectrometric analysis). The findings on untreated cellulose indicate that: (*1*) pyrolysis occurs in three distinct phases in the temperature range 276–360°C; (*2*) there is a single activation energy of 42 kcal/mole over this temperature range; (*3*) the initial rapid weight loss is not due to the desorption of water, but primarily to decomposition of the cellulose molecules; (*4*) there is little difference in either the quality or relative quantity of the volatiles generated during the three different phases of pyrolysis. The findings on treated cellulose show that the fire retardant, $KHCO_3$, does not markedly change the types of degradation products having molecular weights below about 110, although it does change their relative concentrations. Furthermore, the rate of product generation and the quantity of residual char are increased.

INTRODUCTION

Spontaneous ignition of cellulose can take place around 325°C, while the temperature of a burning cellulosic material exceeds 400°C. The rate of production of the pyrolysis products versus temperature and the type of products produced at each temperature need to be known in order to understand the ignition, burning rate, and rate of fire spread in cellulosic materials. Furthermore, an understanding of the effects of fire retardants on the mechanism of decomposition of cellulose and the type of pyrolysis products formed is needed in order to develop more effective fire retardants with less detrimental side effects.

Past investigations on the isothermal degradation of cellulose in the temperature range 250–300°C indicate that between 275°C and 300°C there are three phases of pyrolysis.[1,2] First there is a region of very rapid weight loss, followed by a region in which the rate of weight loss is constant, and finally there is a region in which the weight drops exponentially to a constant residual char. However, very few data are available at higher temperatures which are of primary concern in fire studies.[3–6]

The present work provides a detailed kinetic study of the pyrolytic process in untreated and treated cellulose at temperatures between 300 and 360°C. An analysis of the volatile products is given for each of the three pyrolysis phases.

The scope includes (a) measurements of the weight loss for untreated cellulose pyrolyzed in a N_2 fluidized sand bath at 315, 335, 350, and 360°C to determine the effect of temperature on the basic degradation process of cellulose and on the activation energy, (b) measurements of the weight loss for treated cellulose pyrolyzed at 300°C in order to determine the detailed effect of fire retardants on the rate of degradation in each of the three stages, (c) analysis, by means of a gas chromatograph–mass spectrometer (GC-MS) combination instrument, of the products resulting from the pyrolysis of untreated cellulose in the fluidized bath during each of the three states of pyrolysis, (d) measurements on the volatile pyrolysis products of untreated cellulose isothermally generated in and analyzed by a time-of-flight mass spectrometer in order to obtain detailed information about the rates of formation of a limited number of individual volatile pyrolysis products at any instantaneous time or period of time, and (e) analysis, by means of the GC-MS combination instrument, of the degradation products of treated cellulose in order to determine the effect of a fire-retardant treatment on the type of the degradation components formed during pyrolysis.

EQUIPMENT AND PROCEDURE

Kinetics

As in previous work[7] the present nitrogen fluidized bath was designed to meet the following requirements: (1) rapid and uniform heating of the samples to the controlled temperatures; (2) uniformity of temperature throughout the pyrolysis chamber; (3) constancy of temperature to within 0.2°C over prolonged time intervals; (4) continuous removal of volatile products and rapid recovery of solid residue. In addition to meeting these requirements it was built for extending the temperature range of the previous chamber from 300°C to 400°C and for intermittent sampling of the volatile degradation products for gas chromatographic analysis.

The arrangement of the pyrolysis unit, which consists of the loading chamber and reaction chamber, is shown in Figure 1. The sample loading chamber is separated from the reaction chamber by a retractable double-seal plug; thus all of the volatiles reach the sampling system. The reaction chamber contains 60–85 mesh thoroughly cleaned Monterey sand, which is fluidized by preheated, 99.997% pure nitrogen. It is brought to the desired temperature by the Aerograph oven and maintained within 0.1°C by the trimmer heater. The cellulose samples are raised to the pyrolysis temperature in 15 sec and are kept isothermal within ±0.12°C throughout the length of all the runs.

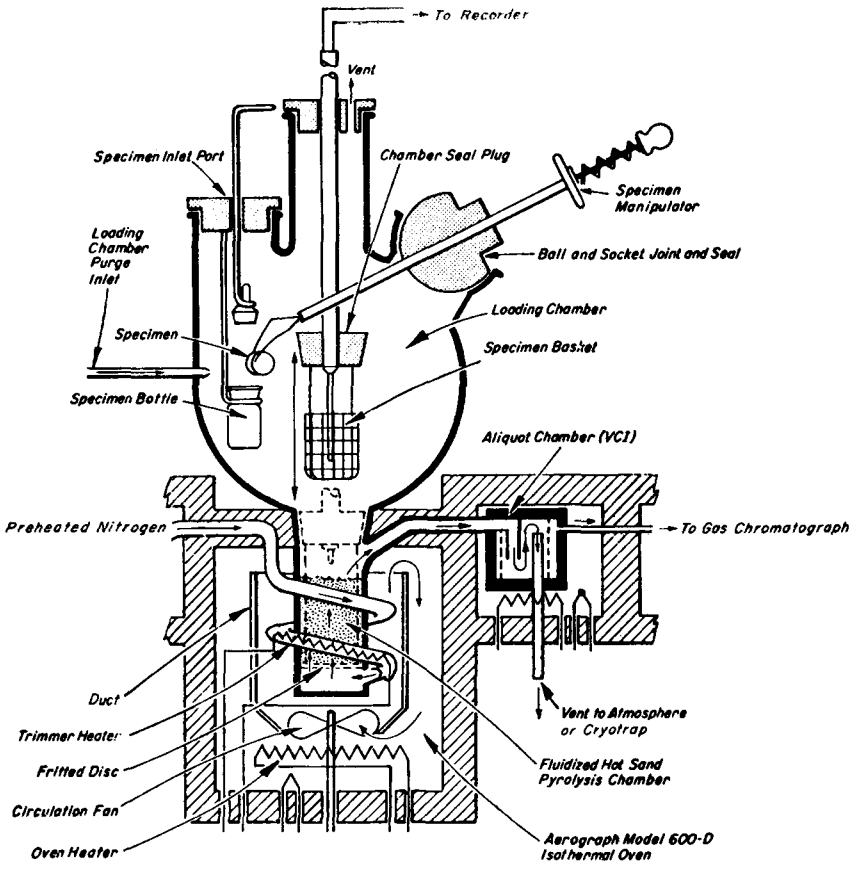

Fig. 1. Apparatus for the study of isothermal degradation of cellulosic materials.

Disks (2.0 cm in diameter) of untreated white α-cellulose were cut from cellulose sheets 0.030-in. thick. The treated samples were prepared by soaking in either a $KHCO_3$ or a $NH_4H_2PO_4$ solution, pressing to remove excess liquid, and drying to constant weight in a vacuum oven at 25°C (the samples retained 2% by weight of the salts when dried). Both treated and untreated samples were then evacuated for 30 minutes, dried to a constant weight in nitrogen in the presence of phosphorus pentoxide, transferred in covered, tared weighing bottles to the loading chamber and then inserted into the reaction chamber. The procedure for the weight loss determination was described earlier.[1]

The technique for generating pyrolysis products directly in the mass spectrometer used a wire-wound heater, controlled electronically to maintain a constant temperature. The rate of formation of each gaseous species was measured as a function of time by periodically recording the mass spectra of the evolved gases.

Analysis

Two approaches were used in introducing the degradation products (generated in the fluidized bath) into the gas chromatograph (GC): (1) utilization of a specially designed gas chromatograph inlet system;[10] (2) cryogenic trapping of pyrolysis products with subsequent syringe injection. This analysis pertains only to the degradation products with molecular weights below 110 and does not include tar and char.

In the first method, the volatile degradation products were sampled intermittently and allowed to collect in prechilled traps. These were partially filled with Chromasorb T 40-60 mesh and Poropak Q 80-100 mesh, respectively, and served to concentrate the nitrogen diluted products as well as to separate them into two gross groups: (1) the heavier organic products and (2) the fixed gases (defined here as CO, CO_2, and the lighter hydrocarbons). After collection, the nonadsorbed nitrogen was removed from the traps by a forepump, the traps were heated to 200°C for 3 min, and the products were distilled into the evacuated, liquid-nitrogen chilled, 5.0-cc sample loops. The loops were isolated, then heated, and the products were swept with helium into two parallel chromatography columns. A 10-ft × 0.25-in. o.d. stainless steel liquid partition column for the heavier organic components was packed with Carbowax-20M on Chromasorb T and a 6.5-ft × 0.25-in. o.d. solid adsorption column for the fixed gases and lighter hydrocarbons was packed with either Poropak Q 80-100 mesh or silica gel. By using a helium flow rate of 40 cc/min, the liquid partition column was ballistically temperature-programmed from 90°C to 220°C in 35 min. The solid adsorption column was run at ambient temperature with a helium flow rate of 30 cc/min.

Separate collections by the second method were also made during the three regions of pyrolysis. The volatiles were collected in a liquid-nitrogen cold trap and manually injected at room temperature into the analytical column. This method cannot be successfully employed in analyzing the fixed gases and lower molecular weight organics because of their high vapor pressure at this temperature. On the other hand, this approach seems to be a simpler, more effective technique for the introduction of organics, in the boiling point range 20–220°C, onto the analytical column.

In the past, a qualitative identification of complex mixtures has been obtained, for the most part, by the technique of retention times. Unfortunately it is very difficult to reproduce the experimental conditions necessary for this method to be valid; therefore this method of identification is very tedious and may yield ambiguous results especially if the composition of the mixture is completely unknown. Mass spectrometry, on the other hand, offers a unique characterization of individual molecules. Mixtures are difficult to analyze with a mass spectrometer because each species is split into fragments and so each mass peak may contain fragments from many different species. If a gas chromatograph could be used to separate the different species, then all the mass peaks belonging to a particular unknown species could be referred to the reference mass spectral tables

for identification. In the present work, a Bendix time-of-flight mass spectrometer in conjunction with a gas chromatograph has provided the primary means of effluent identification.

Two techniques have been successfully used for the introduction of gas chromatographic effluents into the mass spectrometer: (1) utilization of a trap packed with column material to collect individual compounds separated by the gas chromatograph for introduction, one at a time, into the mass spectrometer, (2) direct continuous introduction of the gas chromatographic effluent into the ion source of the mass spectrometer.

In the first technique,[12] 4-in. sections of small-diameter glass tubing are loosely packed with about 1-in. of 5% Carbowax on Chromasorb. Each gas chromatographic peak is collected by attaching a packed tube after the thermal conductivity detector. After a given GC peak is collected, the column packing is placed into a small volume probe which fits into the mass spectrometer. The air in this small volume is pumped out and the packing opened up to the ion source. Then the mass spectrum of the vaporized sample is recorded. It should be noted that this technique is quite straightforward for samples having boiling points in the range 100–200°C. Below this temperature range, cooling for both trapping of effluents and their subsequent introduction into the mass spectrometer must be employed, and above this temperature range, another less volatile packing material is necessary.

The second technique,[13] using a helium separator of the type used by Watson and Biemann, has been found the most effective. This method has the following advantages: (1) information about the composition of any GC peak, whether a single compound or a mixture, may be obtained by scanning different portions of the peak; (2) the disadvantages of effluent trapping, such as inefficient condensation of small, volatile samples, and contamination of the sample before introduction into the mass spectrometer are eliminated; (3) mass spectra can be obtained in about one-tenth the time taken to use a method such as effluent trapping.

As shown in Figure 2, the helium separator is simply a 20 cm long fritted glass tube (Corning Glassware, Corning, New York) with constrictions at both ends and a means of pumping the central section. The separator link (1) reduces the pressure from atmospheric at the outlet of the gas chromatograph to about 10^{-6} mm Hg in the ion source of the mass spectrometer, and (2) concentrates the sample entering the mass spectrometer.

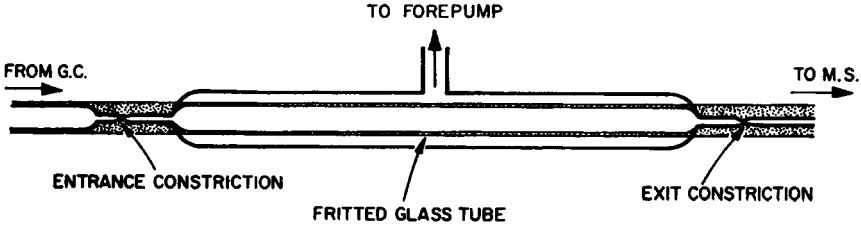

Fig. 2. Helium separator.

Pressure reduction and sensitivity are controlled by the size of the constrictions, while concentration of the sample occurs when the carrier gas, having a lower molecular weight than the sample effluent, is pumped from the system at a higher rate than the sample. A trial-and-error method was used to make the inlet and outlet constrictions. The effectiveness of the constrictions was tested by placing the inlet of the separator at atmospheric pressure and pumping on the central section and outlet with a forepump and a getter-ion pump respectively. When the pressure at the outlet was reduced to about 10^{-6} mm Hg, the size of the constrictions was assumed to be reasonable.

Since effluent concentration in the ion source changes with time, fast scanning is necessary to provide accurate mass spectra. Due to the somewhat slow scanning rate of the mass spectrometer, the number of scans per GC peak is limited and a concentration correction may be necessary in the case of sharper GC peaks. A Visacorder (Honeywell 1508) records total ion current simultaneously with mass spectra. For identification purposes both 70 and 15 eV spectra are taken. The entire mass spectrometer/gas chromatographic system is represented by Figure 3.

Reference tables of mass spectra[14,15] were used to identify the condensables. Fixed gases on the other hand were identified by measuring their retention times on the Poropak and silica gel columns. Furthermore retention time provided a secondary means of identification in the case of the higher molecular weight organics.

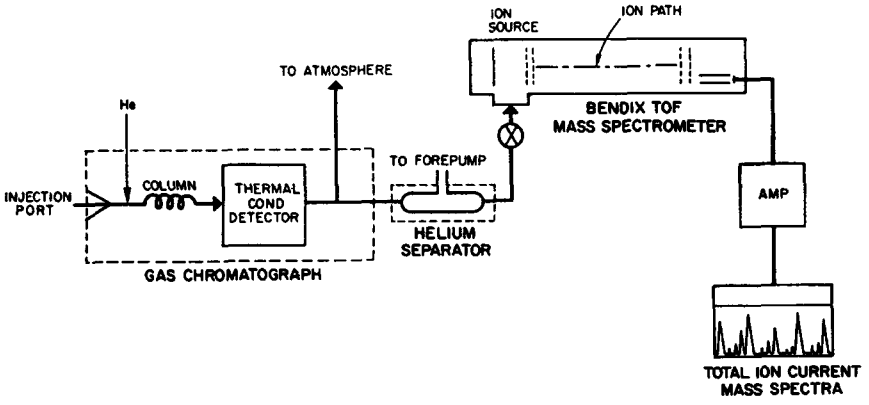

Fig. 3. Schematic diagram of gas chromatograph/mass spectrometer combination instrument.

RESULTS AND DISCUSSION

Kinetics

The conditions and results of the weight loss experiments are summarized in Table I. The percentages of the residual components are based on the weight of the original dry cellulose samples.

TABLE I. Pyrolysis of α-Cellulose in Nitrogen

Temp, °C	Sample description	Duration, min	Dry weight of original sample, g	Weight of pyrolyzed sample, g	Residual weight of pyrolyzed sample, %
298[a]	Untreated white α-cellulose, 0.030-in. thick	5.0	0.1868	0.1742	93.23
		15.0	0.1805	0.1631	90.36
		30.0	0.1892	0.1558	82.35
		60.0	0.1814	0.1196	65.93
		120.0	0.1834	0.0743	40.52
		180.0	0.1849	0.0510	27.59
		360.0	0.1880	0.0340	18.09
298	2% $KHCO_3$-treated white α-cellulose, 0.030 in. thick	0.5	0.1900	0.1535	80.79
		1.0	0.1730	0.0922	46.85
		4.0	0.1890	0.0880	46.57
		7.0	0.1829	0.0840	45.93
		10.0	0.1875	0.0822	43.84
		20.0	0.1907	0.0833	43.69
		35.0	0.1909	0.0823	43.11
		60.0	0.1899	0.0810	42.66
300	2% $KHCO_3$-treated white α-cellulose, 0.030-in. thick	0.5	0.1934	0.1757	90.85
		1.0	0.1870	0.1621	86.69
		2.0	0.1919	0.1589	82.80
		4.0	0.1897	0.1448	76.33
		5.0	0.1954	0.1419	72.62
		6.5	0.1906	0.1301	68.26
		8.0	0.1919	0.1170	60.96
		10.0	0.1883	0.1003	53.26
		14.0	0.1934	0.0972	45.00
		20.0	0.1891	0.0730	38.60
		21.0	0.2015	0.0766	38.01
		40.0	0.1867	0.0671	35.94
		60.0	0.1843	0.0650	35.27
315	Untreated white α-cellulose, 0.030 in. thick	0.5	0.1825	0.1781	97.58
		2.0	0.1872	0.1734	92.62
		4.0	0.1824	0.1622	88.92
		7.0	0.1850	0.1519	82.11
		10.5	0.1775	0.1345	75.77
		15.0	0.1823	0.1234	67.69
		22.0	0.1753	0.0992	56.58
		30.0	0.1811	0.0770	42.52
		40.0	0.1829	0.0505	27.61
335	Untreated white α-cellulose, 0.030 in. thick	0.5	0.1829	0.1724	94.25
		2.0	0.1811	0.1543	85.20
		4.0	0.1825	0.1288	70.57
		6.0	0.1810	0.1090	60.22
		7.0	0.1777	0.0988	55.59
		8.0	0.1850	0.0959	51.83
		10.0	0.1846	0.0784	42.47
		14.0	0.1872	0.0449	24.00
360	Untreated white α-cellulose 0.030 in. thick	0.5	0.1796	0.1545	86.03
		1.0	0.1700	0.1261	74.18
		1.5	0.1823	0.1174	64.39
		2.0	0.1796	0.0903	50.28
		4.0	0.1749	0.0378	21.61

[a] Data for the untreated samples at 298°C from Lipska and Parker.[1]

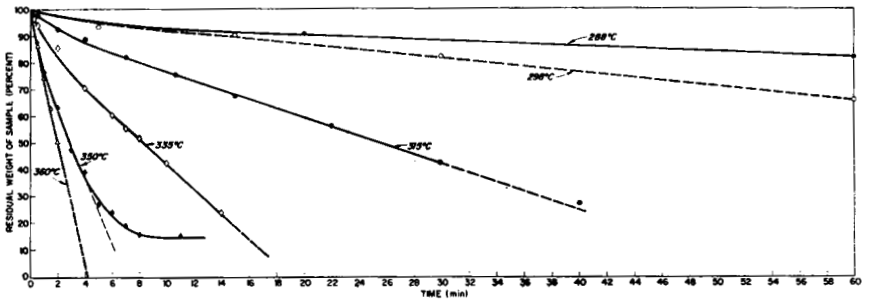

Fig. 4. Residual weight of untreated white α-cellulose pyrolyzed in nitrogen in the temperature range 288–360°C. Data taken at 288 and 298°C taken from Lipska and Parker.[1]

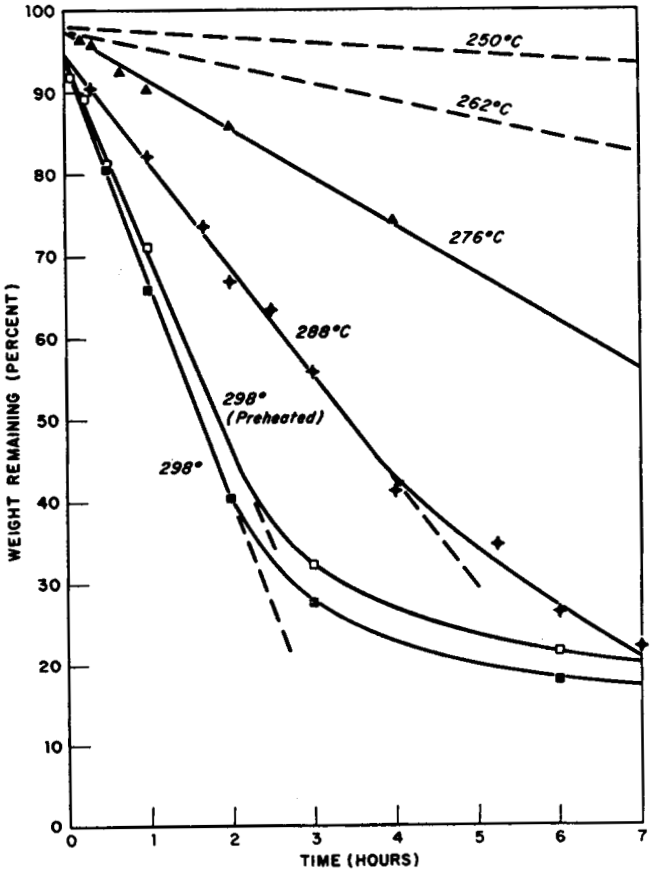

Fig. 5. Residual weight of untreated white α-cellulose pyrolyzed in nitrogen in the temperature range 250–298°C as reported by Lipska and Parker.[1]

Figure 4 shows the residual weight of the untreated samples as a function of time for all the temperatures used in this work. For comparison's sake, weight loss data for the untreated cellulose pyrolyzed between 250 and 298°C by Lipska and Parker,[1] are also included as shown in Figures 4 and 5. Similarities in the overall degradation pattern for the untreated cellulose between 275°C and 360°C indicates the same mode of decomposition. The ratio of the rate of weight loss in the initial region versus that in the linear region decreases with increasing temperature up to 350°C, i.e., the ratio goes from 4.0 at 288°C to 1.1 at 350°C. At 360°C the ratio has fallen to unity so that the initial region is no longer distinguishable from the linear region.

A detailed analysis of the rates of formation of the decomposition products of α-cellulose has been made by isothermally pyrolyzing a sample in the vicinity of 300°C directly in the mass spectrometer. The rates of formation of several individual mass peaks versus time of pyrolysis are shown in Figure 6. It should be stressed again that mixtures are difficult to analyze with a mass spectrometer because each species is split into fragments and so each mass peak may contain fragments from many different species. The masses plotted are those which most readily correlate with a given species, i.e., those for which a single species contributes to the mass peak.

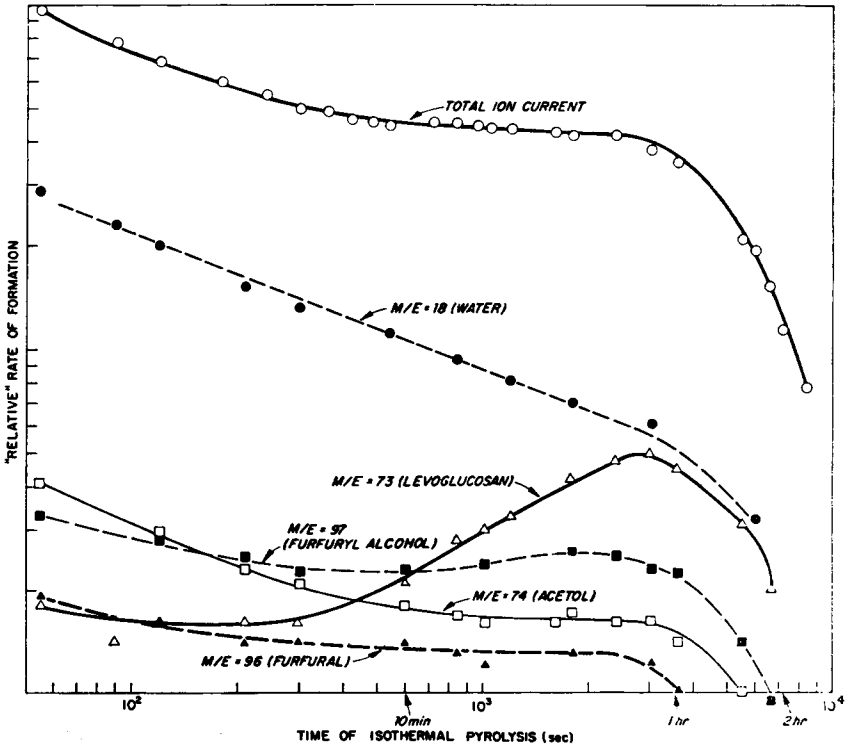

Fig. 6. Rates of formation of five individual mass peaks vs. time of pyrolysis at 298°C.

For a complete analysis of the mass spectral data, a knowledge of all the kinds of decomposition products generated in this manner is necessary. It should be noted that total ion current, the best available measure of "weight loss" from the existing data, is qualitatively similar to the weight loss data reported above. The total ion current curve of Figure 6 shows three distinct regions: an initial region of high decomposition rate which decreases with time, a region of constant decomposition rate, and a final region of decreasing decomposition rate. The rate of decomposition in the initial region is about twice that of the linear region, supporting previous

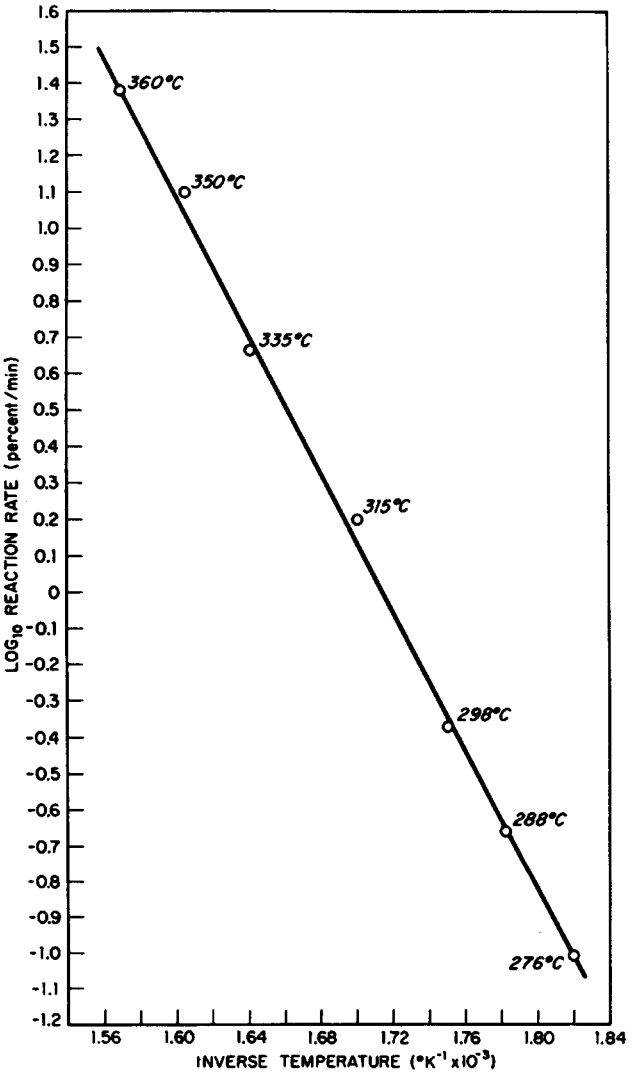

Fig. 7. Activation energy of the thermal degradation of untreated cellulose based on zero-order weight loss rates obtained from the linear region of pyrolysis.

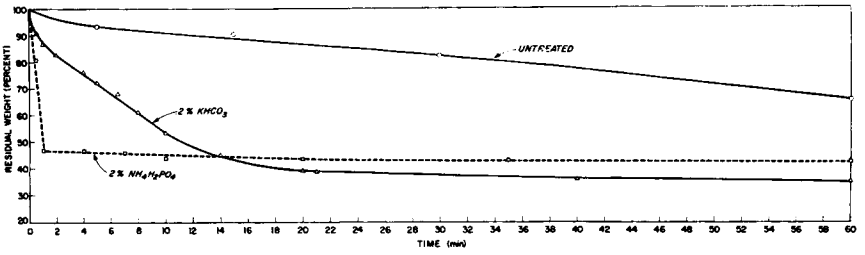

Fig. 8. Comparison of residual weights of untreated and treated white α-cellulose samples pyrolyzed in nitrogen at 300°C.

work.[11] Water and levoglucosan follow routes quite different from the majority of species shown in Figure 6; water decreases while levoglucosan increases with time in the linear region.

Figure 7 is an Arrhenius plot of the rate of weight loss in the zero-order region of untreated cellulose between 275 and 360°C. These data show that the activation energy of 42 kcal/mole is constant from 275°C up to at least 360°C.

Figure 8 shows the weight remaining as a function of time at 300°C for untreated, 2% $NH_4H_2PO_4$-treated, and 2% $KHCO_3$-treated white α-cellulose samples. The isothermal degradation of 2% $NH_4H_2PO_4$-treated cellulose is so rapid at 300°C that a detailed kinetic study was not performed. Since it is important to compare the behavior of treated with untreated cellulose at the same temperature, the effect of a slower-acting retardant, specifically $KHCO_3$, on the rate of degradation and the type of product generation was investigated at 300°C. The general shape of the weight loss curve for the 2% $KHCO_3$-treated sample is the same as that observed for the untreated samples at this temperature; the rate of volatilization in the linear region was 3.0%/min for the treated samples as opposed to 0.43%/min for the same region for the untreated samples. The active pyrolysis of the 2% $KHCO_3$-treated cellulose was completed in 20 min, leaving a residual weight of 35%, whereas the active pyrolysis of the untreated sample was completed in 3 hr, yielding a residual weight of 18%. The observed increase in the rate of volatilization and the marked increase in the final char residue tend to support the findings of Tang and Neil.[16] The results of their thermogravimetric analysis (TGA) show that the treatment of cellulose by 2% $KHCO_3$ lowered the threshold temperature for active pyrolysis from 270 to 230°C and increased the final char yield from 14% to 34% as measured at 360°C.

Analysis

Figures 9 and 10 show typical linear region chromatograms obtained from the pyrolysis of treated and untreated cellulose, respectively. The pyrolysis temperatures were so chosen that both the rates of degradation of the treated and untreated samples were comparable and that sufficient

TABLE II
Qualitative and Relative Quantitative Analysis of the Degradation Products[a]

Peak	Compounds Identified	Identification[b] GC	MS	Relative quantitative analysis[c] Treated samples Initial	Linear	Char	Untreated samples Initial	Linear	Char	Literature reference
	CO_2	P	P	+++	+++	+++	+++	+++	+++	9
1	Fixed Gases CO	P	NI	−	−	Trace	Trace	Trace	−	9
	CH_4	P	NI	−	−	Trace	Trace	Trace	−	9
	C_2H_6	P	NI	−	−	Trace	Trace	−	−	9
2	Acetaldehyde	P	P	Trace	++	++	+	++	++	2,7,8,9
3	Furan	P	P	Trace	+	+	Trace	+	+	8
4	Acetone	P	P	Trace	++	+	+++	+++	+++	2,7,8,9
5	2-Methylfuran	P	P	−	+	Trace	++	Trace	−	
9	2,3-Butanedione	P	P	Trace	++	+	+	+	+	
10	Water	P	P			Very strong				2,7,8,9
13	Acetol	P	P	+++	+++	+++	+++	+++		
14	Methyl Formate +	NI	T	++	++	++	++	++	++	
16	Furfural +	P	P	++	+	++	+++	+++	+++	2,7,8
18	2,2,3-Pentanedione	NI	T	−	−	Trace	−	Trace	−	
19	Propanoic acid	NI	T	−	+	+	−	Trace	+	
20	Unidentified	NI	P	Trace	+	Trace	++	++	++	
22	5-Methyl-2-Furfuraldehyde	NI	P	−	−	−	−	+	+	2
24	Furfuryl alcohol	P	P	++	++	+	++	++	++	
25	Butyrolactone	P	P	++	++	+	−	Trace	+	
28	Cyclohexanone	NI	T	+	++	+++	−	++	++	
29	Tiglaldehyde	NI	T	−	+	++	−	+	+	

[a] Untreated white α-cellulose was pyrolyzed at 315°C and treated white α-cellulose was pyrolyzed at 300°C.

[b] P = positive identification; T = tentative identification, NI = not identified.

[c] Acetol used as a standard for relative quantitative analysis with the following notation in order of decreasing concentration: very strong, +++, ++, +. A nondetectable concentration is indicated by (−).

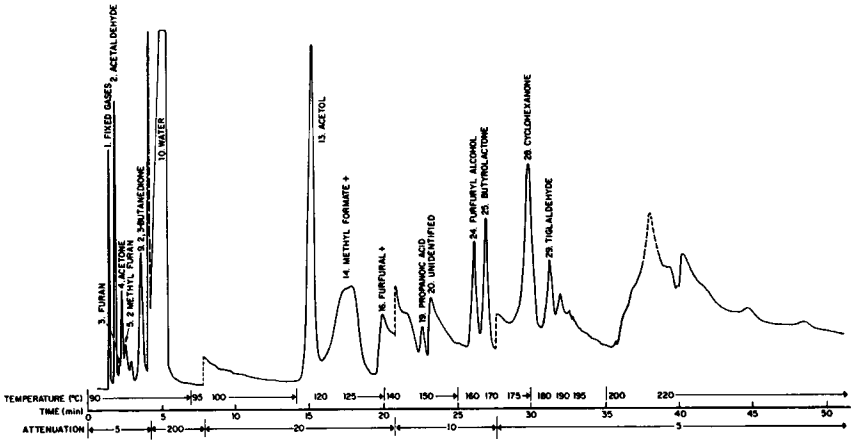

Fig. 9. Linear region chromatogram of the degradation products of treated white α-cellulose pyrolyzed at 300°C.

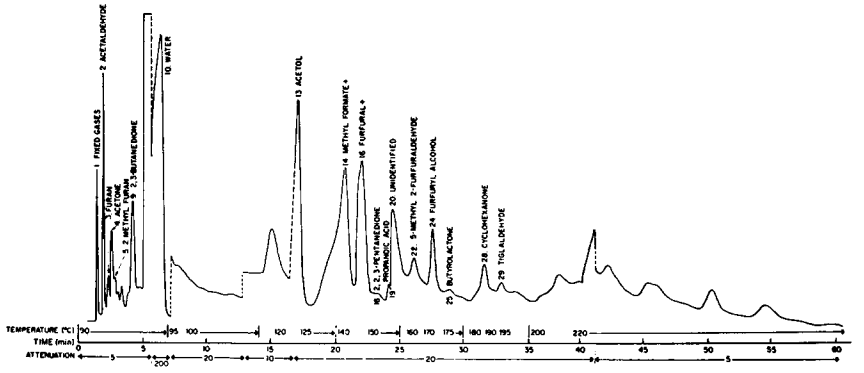

Fig. 10. Linear region chromatogram of the degradation products of untreated white α-cellulose pyrolyzed at 315°C.

quantities of the degradation products could be collected in each distinct stage of pyrolysis. In most cases peaks were qualitatively identified by mass spectral analysis. Figure 11 depicts the mass spectrum obtained for peak 13. In this instance the signal-to-noise ratio was about 80, making identification quite easy. In all the chromatograms, the relative quantitative identification is based on acetol as the standard. A total of 36 peaks is indicated, of which 17 are identified. The gas chromatographic data on the untreated and 2% $KHCO_3$-treated cellulose are summarized in Table II. Comparison of the three phases of pyrolysis in terms of types and relative amounts of components indicates that water is a predominant peak in all the regions of both the treated and untreated samples. Since other major components are generated during the initial pyrolysis phase, the initial rapid weight loss is not due entirely to desorption of surface water, but also to the decomposition of the cellulose molecules.

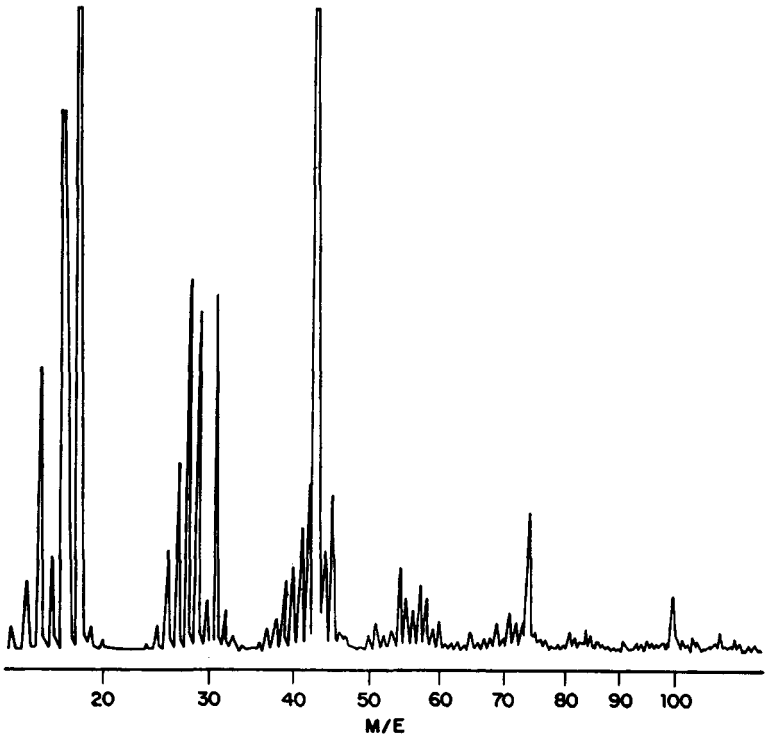

Fig. 11. Mass spectrum of GC peak 13.

In terms of gross changes, there seems to be little difference in either the quality or relative quantity of the compounds generated in the three regions of pyrolysis.

The results of Table II indicate that 2% $KHCO_3$ treatment has little effect on the quality of the degradation products of cellulose of molecular weights below about 110. The quantity of water and CO_2 relative to that of the other components, and the rate of product generation are markedly increased in the treated samples. Furthermore the relative concentration of furfural and 5-methyl-2-furfuraldehyde appears to be greater in the untreated than in the treated samples. Butyrolactone seems to be more prevalent in the treated than in the untreated samples.

CONCLUSIONS

Weight loss measurements of white α-cellulose pyrolyzed at 315, 335, and 350°C revealed three distinct phases of pyrolysis which correlate with those previously reported for the temperature range of 276–298°C.[1]

A single activation energy of 42 kcal/mole was found for the decomposition of cellulose in the 276–360°C range.

The 2% $KHCO_3$ treatment of white α-cellulose at 300°C increased the rate of volatilization sevenfold and the residual char from 18% of the original weight for the untreated sample to 35% for the treated samples.

There is little difference in either the quality or relative quantity of volatiles generated during the three different phases of pyrolysis.

The fire retardant, $KHCO_3$, does not markedly change the types of degradation products having molecular weights below about 110, although it does change their relative concentrations; the quantity of water and CO_2 relative to that of the other components, and the rate of product generation are markedly increased in the treated samples.

The initial rapid weight loss in both the treated and untreated samples is not due to desorption of water, but primarily to decomposition of the cellulose molecules.

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