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*Research Paper (National Research Council of Canada. Division of Building
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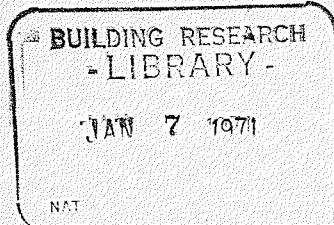
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THERMAL DECOMPOSITION PRODUCTS OF CELLULOSE

BY

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44783

REPRINT FROM
JOURNAL OF APPLIED POLYMER SCIENCE
VOL. 14, 1970
P. 2003 - 2013

RESEARCH PAPER NO. 463
OF THE
DIVISION OF BUILDING RESEARCH

OTTAWA

PRICE 25 CENTS

DECEMBER 1970

NRCC 11730

LES PRODUITS DE LA DECOMPOSITION THERMIQUE
DE LA CELLULOSE

SOMMAIRE

La cellulose, ignifugée ou non, peut être décomposée thermiquement sous vacuum et les produits analysés quantitativement par chromatographie en phase vapeur. Un produit non-identifié à l'indice de retenue 2270 (entre 5-methyl furfural et 5-hydroxymethyl furfural), α - et β - d - glucose et un groupe de "dimères" inconnus à date ont été trouvés au cours de cette étude. L'identification de ce produit non-identifié devrait aider les recherches sur la décomposition thermique de la cellulose et accroître les connaissances sur l'ignifugation.



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Thermal Decomposition Products of Cellulose

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Synopsis

Untreated and flame-retardant-treated cellulose were thermally decomposed under vacuum and the products were quantitatively analyzed by gas chromatography. An unidentified product at a retention index of 2270 (between 5-methylfurfural and 5-hydroxymethylfurfural), α - and β -D-glucose, and a group of "dimers" that have not been reported previously were found in this study. The identification of this unknown product should assist in studies on the thermal decomposition of cellulose and further the understanding of the mechanism of flame retardancy.

INTRODUCTION

Studies on the thermal decomposition of cellulose have attracted a great deal of attention over the years because this polymer is the main constituent of wool and cotton. Efforts have been made to elucidate the mechanism of thermal decomposition of cellulose for possible applications to practical problems such as that of finding new flame-retardant treatments. The authors are engaged in studies on the chemical aspects of fire and are interested in the mechanisms by which flame retardants alter the thermal decomposition of polymers. In the present investigation on flame retardancy, cellulose treated with various inorganic salts was examined.

Knowledge of the pyrolysis products is necessary for understanding the mechanism of thermal decomposition of untreated and flame-retardant-treated cellulose. Recent advances that have been made on the determination of these products of cellulose have been largely due to developments in gas chromatography. Schwenker and Beck¹ pyrolyzed cotton by heating it to 370°C in an atmosphere of air or nitrogen, and identified about 30 products from methane to 5-hydroxymethylfurfural. Kato and Komorita² used pyrolysis gas chromatography to study the effect of crystallinity of cellulose on the formation of volatile compounds. They pyrolyzed microcrystalline and tobacco celluloses at temperatures ranging from 200° to 500°C in a stream of helium and quantitatively determined the yields of acetaldehyde, furfural, and 5-hydroxymethylfurfural. Byrne, Gardiner, and Holmes³ pyrolyzed pure and flame-retardant-treated cotton under vacuum and analyzed the major products by extending the analysis to larger compounds. They determined the amount of levoglucosan in the

tar fraction at temperatures ranging from 350° to 500°C and discussed the mechanisms of pyrolytic reactions.

Experimental data on pyrolysis products of cellulose treated with flame retardants are very limited. Parks et al.⁴ studied the effect of about 50 different treatments on the amounts of char, carbon monoxide, and carbon dioxide produced. Berkowitz-Mattuck and Noguchi⁵ decomposed APO-THPC-treated cotton and identified light gases, water vapor, and organic compounds each containing three to six carbon atoms. They found no fundamental qualitative difference in the pyrolysis mechanism for the treated and untreated cloth. Golova et al.⁶ decomposed cellulose treated with 17 different inorganic salts and determined the yield of levoglucosan. Byrne et al.³ decomposed cotton treated with borax-boric acid and some commercially available flame retardants and determined the yield of condensates, tar, char, and levoglucosan.

In this study cellulose was pyrolyzed under vacuum at various temperatures ranging from 320° to 520°C and the products from light gases to the components of tar fraction were analyzed quantitatively. The decomposition products of cellulose treated with various inorganic compounds were also analyzed.

EXPERIMENTAL

Materials

Whatman No. 40 filter paper was used as the cellulose sample in this study. The ash content was 0.018%. The cellulose was treated with various compounds by dipping it into aqueous solutions of selected concentrations so that the desired weight of salt would be retained on the sample. The samples were wiped free of excess solution prior to drying under vacuum. Specimens used in the pyrolysis experiments retained about 1% by weight of the salts when dried.

Thermal Decomposition

The pyrolysis apparatus was similar to that used in a previous study.⁷ A sample weighing about 1.6 g was placed in a Pyrex tube connected to a liquid nitrogen trap and a vacuum pump. After the system was evacuated to 1×10^{-4} mm Hg, the vacuum line to the pump was closed and the sample was heated at one of the preselected temperatures, 320, 370, 420, 470, or 520°C, for 20 min. The Pyrex tube was positioned at about 5 degrees from the horizontal in order to allow some of the tar fraction to flow out of the hot zone and thus to reduce secondary decomposition. The volatile fraction in the liquid nitrogen trap was transferred to a gas-sampling bottle of known volume by removing the liquid nitrogen, and the weight of the remaining liquid fraction in the trap was determined. The residue and the tar in the pyrolysis tube were washed with water, and the solid was separated from the water extract by filtering. Both portions were dried and weighed.

TABLE I
Gas-Chromatographic Conditions

Condi- tion no.	Column	Stationary phase	Carrier gas	Detector	Temp, °C
1	Support-coated open tubular, 100 ft, 0.02 in. i.d.	diethylene glycol succinate	helium, 10 psi	flame ionization	30-180
2	Support-coated open tubular, 100 ft, 0.02 in. i.d.	silicone rubber SE-30	helium, 10 psi	flame ionization	150-250
3	Support-coated open tubular, 100 ft, 0.02 in. i.d.	didecyl phthalate	helium, 10 psi	flame ionization	70-140
4	Support-coated open tubular, 100 ft, 0.02 in. i.d.	polyphenyl ether SO-138	helium, 10 psi	flame ionization	30-200
5	Support-coated open tubular, 100 ft, 0.02 in. i.d.	glycerol	helium, 10 psi	flame ionization	30-120
6	Packed 2 m, 1/4 in. o.d.	molecular sieve 5A	helium, 20 psi	thermal conductivity	25
7	Packed 2 m, 1/4 in. o.d.	silica gel	helium, 20 psi	thermal conductivity	80

Analysis

Most components in the gaseous and liquid fractions were determined by the usual methods of gas chromatography. The liquid fraction from the trap was analyzed further for carbohydrates by dehydration with anhydrous sodium sulfate followed by trimethylsilylation.⁸ The water extract was also analyzed for carbohydrates. The gas-chromatographic conditions that were used are presented in Table I.

Most of the products were identified by comparing the retention times with those of known compounds using three or more different chromatographic conditions. They were quantitatively analyzed by applying approximate substance correction factors to the areas under each peak.⁹ For the trimethylsilylated products to which known amounts of glycerin had been added as an internal standard, the areas under the peaks were compared to those of glycerin.

RESULTS AND DISCUSSION

The thermal decomposition products of cellulose at a pyrolysis temperature of 370°C are presented in Figure 1, where the quantitative data are represented by line charts and are plotted against retention index using *n*-alkanes as standards. The experimental data on water, carbon monoxide, and carbon dioxide are not shown.

Products containing —OH groups were trimethylsilylated and analyzed. Corresponding with the results of other investigations, levoglucosan was found to be by far the most abundant organic product. Other major products included 5-hydroxymethylfurfural, 1,6-anhydro- β -D-glucofuranose, α - and β -D-glucose, and an unidentified product at a retention index of 2270. The presence of α -D-glucose is due to mutarotation¹¹; α/β equilibrium would be reached in less than 10 min at pyrolysis temperatures used in this study. Levoglucosan and 1,6-anhydro- β -D-glucofuranose and the two glucoses found in the products will be referred to as "monomers" in this paper. Five peaks were found in the 2700 region of the retention index scale. These peaks were probably due to either disaccharides or "dimers" of anhydroglucose. The authors believe that they were due to the latter, because the disaccharides having pyranose rings that were formed during the pyrolysis of glucose had retention indices of about 2800 under the same gas-chromatographic conditions.

The dimers and α - and β -D-glucose and the unidentified compound at a retention index of 2270 have not been reported previously in the literature.

The quantitative data on the thermal decomposition products of cellulose at various pyrolysis temperatures are presented in Table II and the same data are plotted in Figure 2. At 320°C, a large portion of the cellulose sample remained undecomposed, as is shown by the large amount of residue. The smaller fragments such as the hydrocarbons (of which methane and ethane were the main components) and furan and 2-methylfuran increased with increase in pyrolysis temperature. The high yield

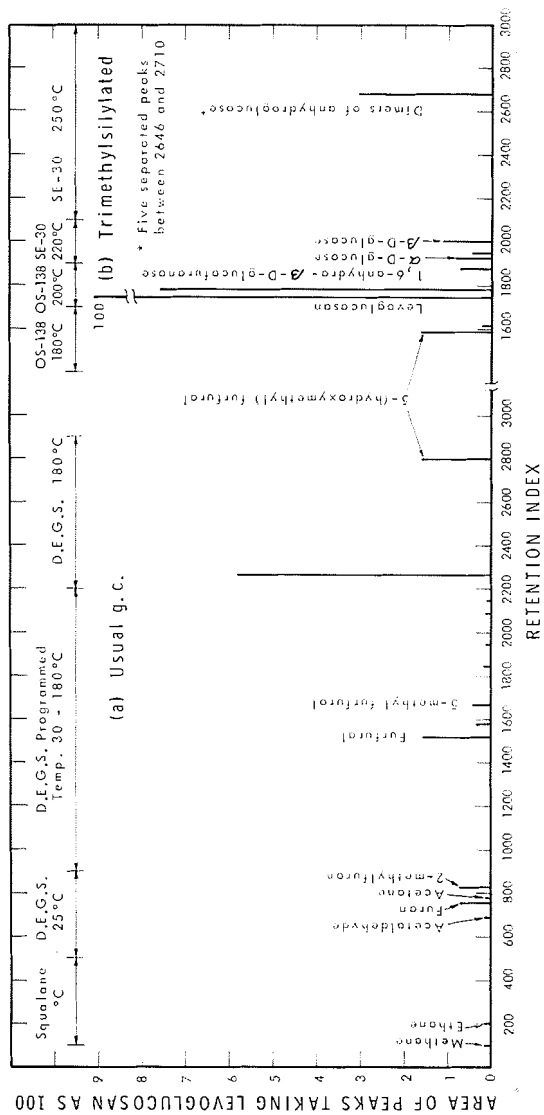


Fig. 1. Gas-chromatographic analysis of the thermal decomposition products of cellulose.

TABLE II
Thermal Decomposition Products of Cellulose^a

Products	Yield, wt-%				
	320°C	370°C	420°C	470°C	520°C
Hydrocarbons	—	0.001	0.04	0.05	0.3
Furan	0.03	0.04	0.03	0.04	0.04
2-Methylfuran	0.02	0.04	0.03	0.05	0.05
Furfural	0.06	0.11	0.10	0.10	0.08
5-Methylfurfural	0.007	0.02	0.02	0.02	0.02
Unknown (R.I. 2270) ^b	0.12	0.3	0.17	0.06	0.08
5-Hydroxymethylfurfural ^b	0.01	0.09	0.09	0.05	0.08
Levogluconan ^b	3.8	10.1	20.2	21.6	18.2
1,6-Anhydro- β -D-glucofuranose ^b	0.2	0.7	2.5	2.4	2.2
α -D-Glucose ^b	0.03	0.09	0.2	0.2	0.2
β -D-Glucose ^b	0.04	0.1	0.2	0.3	0.3
Dimers of anhydroglucose ^b	0.2	0.3	0.5	0.7	0.4
Unanalyzed tar ^b	5.9	6.5	1.9	14.7	7.0
Carbon monoxide	0.5	1.4	1.5	1.7	2.6
Carbon dioxide	1.5	3.3	2.8	2.5	2.9
Water	9.3	24.8	26.6	18.7	20.7
Char	67.8	24.8	17.5	14.4	12.8
Total	89.5	72.7	74.4	77.6	68.0

^a Figures in columns are weight percentages of sample at indicated pyrolysis temperatures.

^b Tar fraction.

of hydrocarbons at 520°C suggests that greater secondary decomposition occurred at this high temperature.

The yield of furfural was only about 0.1% and that of acetaldehyde was negligible in these experiments. Kato and Komorita² found larger amounts of the two products: 0.2% to 4.4% furfural and 0.01% to 4.7% acetaldehyde. The higher pressures that were used in their pyrolysis gas chromatography studies probably account for the greater fragmentation. The amounts of levogluconan found in the present study were smaller than those found by Byrne and co-workers.³ In their study the maximum yield of levogluconan (44%) occurred when cellulose was pyrolyzed at 456°C for 6 min. In the present study the larger sample size and the longer duration of pyrolysis probably accounts for the smaller maximum yield (22%).

The quantitative data on the pyrolysis products of cellulose treated with inorganic compounds are presented in Table III. The presence of inorganic compounds decreased the yield of tar fraction and increased that of char; this result corresponds with the findings of previous workers. The yield of organic pyrolysis products was lower, but that of carbon monoxide and dioxide and water vapor was higher. In general, char formation increased with an increase in the effectiveness of flame retardants. The decrease in the yield of levogluconan and other organic pyrolysis products is very drastic when an inorganic salt is added to cellulose even

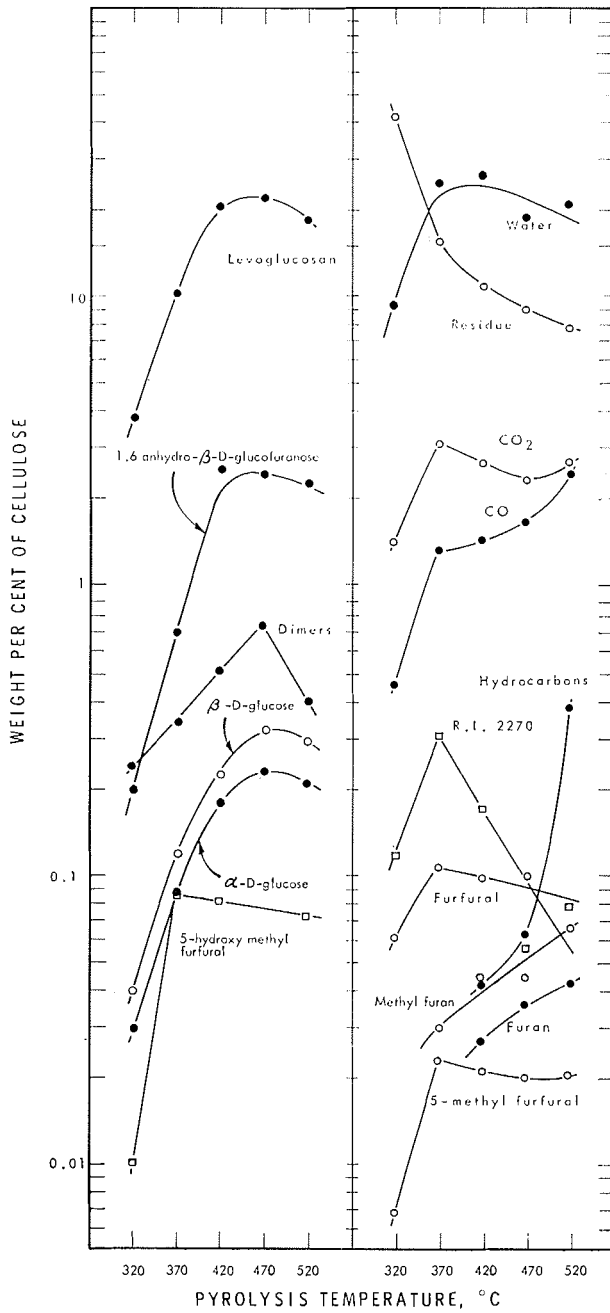


Fig. 2. Decomposition products of cellulose at various temperatures.

TABLE III
Thermal Decomposition Products of Cellulose in the Presence of Inorganic Compounds at 320°C

Products	H ₃ PO ₄	NH ₄ H ₂ P ₄ PO ₄	KH ₂ PO ₄	K ₂ HPO ₄	Na ₂ B ₄ O ₇	KBr	KCl	CaCl ₂	ZnCl ₂	KHCO ₃	K ₂ CO ₃
Hydrocarbons	—	—	—	—	—	—	—	—	—	—	—
Furan	0.03	—	—	—	—	0.02	0.03	—	—	—	—
2-Methylfuran	0.04	0.12	0.2	0.07	0.04	0.03	0.13	0.06	0.07	0.2	0.2
Furfural	0.3	0.2	0.3	0.03	0.16	0.09	0.2	0.1	0.4	0.02	0.02
5-Methylfurfural	0.04	0.04	0.10	0.01	0.03	0.04	0.08	0.02	0.04	0.003	0.005
Unknown (R.I. 1771) ^a	—	—	—	—	—	—	—	—	—	—	0.08
Unknown (R.I. 2270) ^b	1.26	0.83	0.21	—	0.02	0.3	—	0.02	0.2	—	—
Levoglucozan ^b	0.03	0.8	0.9	0.2	0.02	0.3	0.3	0.13	0.3	0.01	0.01
Unanalyzed tar	1.5	1.4	1.9	0.6	1.5	5.2	1.9	3.0	5.7	0.7	1.1
Carbon monoxide	1.7	1.6	1.7	5.4	1.8	1.1	2.5	1.7	1.4	7.7	7.3
Carbon dioxide	1.5	3.8	4.8	4.9	3.8	6.5	7.8	4.9	3.4	6.3	6.4
Water	37.1	32.9	18.8	21.9	17.9	36.5	28.8	17.6	30.1	17.9	19.4
Char	51.4	46.9	48.5	61.0	66.4	43.9	50.9	52.1	45.8	50.9	49.3
Total	96.9	86.3	77.4	94.1	91.7	94.0	92.6	79.6	87.4	83.8	83.8

^a Figures in columns are weight percentages of sample.

^b Tar fraction.

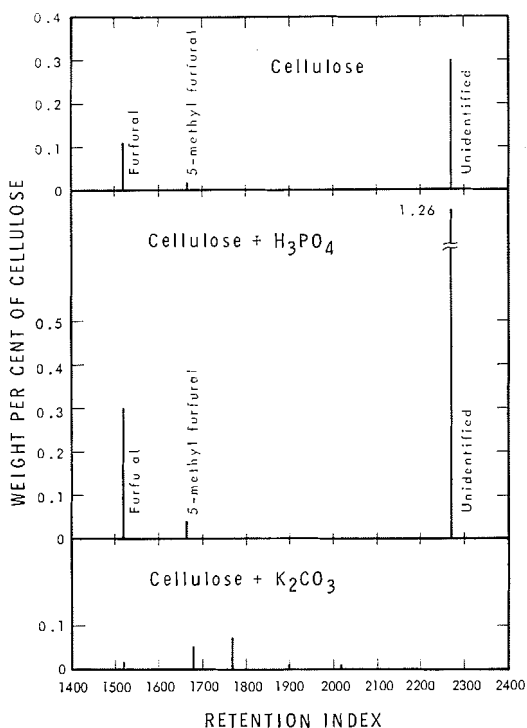


Fig. 3. Effect of acid and alkali on the pyrolysis products.

though the inorganic salt is an ineffective flame retardant. The increase in carbon monoxide and carbon dioxide was most pronounced with alkali salts.

Lipska and Wodley¹¹ reported that 2% treatment of KHCO_3 had little effect on the quality of the degradation products of cellulose having molecular weights below about 110, although it does change their relative concentrations. This finding is in agreement with the results obtained with all the treatments examined in the present study. Products having molecular weights greater than 110, however, differed significantly between treated and untreated cellulose in both their quality and quantity.

Typical examples showing the effect of acid and alkali on the pyrolysis products of cellulose in the retention index range of 1400 to 2300 are shown in Figure 3. The presence of acid increased the yield of the unidentified product with the retention index of 2270 tenfold as compared to untreated cellulose, with the result that it became the most abundant organic pyrolysis product. The presence of alkali decreased the yield of this unknown product and formed some new products. Inorganic compounds used in treating cellulose can be classified as acid type or alkali type from the pattern of the chromatograms. On this basis, pure cellulose follows acid-type decomposition.

The presence of glucose in the products is interesting. Several investigators, e.g., Irvine and Oldham,¹² have suggested that glucose might be an intermediate product in the formation of levoglucosan from cellulose. This possibility was rejected by Golova et al.¹³ because the pyrolysis of cellulose yielded 37% levoglucosan while that of glucose yielded only 6% under the same conditions. The possibility that glucose might be an intermediate decomposition product of cellulose, providing one of the routes for the formation of volatile products, has, however, not been discounted.

The water extract from the tar fraction contained most of the monomers of cellulose. It also contained dimers, suggesting that a series of trimers, tetramers, etc., were the main constituents of the tar fraction.

CONCLUSIONS

The thermal decomposition products of cellulose under vacuum at temperatures between 320° and 520°C were quantitatively analyzed by gas chromatography. An unidentified product at a retention index of 2270 (between 5-methylfurfural and 5-hydroxymethylfurfural), α - and β -D-glucose and a group of dimers that were found in this study have not been reported by previous investigators. The main decomposition products were large organic fragments such as the monomers (levoglucosan and 1,6-anhydro- β -D-glucopyranose), dimers, an unidentified product at a retention index of 2270, water, carbon monoxide, and carbon dioxide. Many carbonyl compounds, organic acids, and hydrocarbons reported by other investigators were found in smaller amounts. The authors believe that these minor products are largely due to secondary decomposition.

The unidentified peak at a retention index of 2270 is probably a primary product because its yield was greatest at the lower pyrolysis temperatures. The identification of this product should assist in studies on the mechanism of thermal decomposition of cellulose. Also, it should further the understanding of the mechanism of flame retardancy. The acidity (or alkalinity) of treatment results in significant changes in the yield of this unidentified product.

This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

The authors wish to thank Mr. J. Boulanger for assistance in the conduct of experiments.

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Received March 30, 1970

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