OCD Work Unit No. 2542A
[redacted]

Final Report

THE SYNERGISTIC EFFECT OF BENZHYDRYLATION-IODINATION ON THE FLAMMABILITY OF ALPHA-CELLULOSE

by

Anne E. Lipska

May 1969

Prepared for Office of Civil Defense under Contract No. DAHC20-67-C-0149
Work Unit 2542A

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NAVAL RADIOLOGICAL DEFENSE LABORATORY
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ADMINISTRATIVE INFORMATION

This report covers a portion of the work authorized by the Office of Civil Defense under Work Order Number DAHC20-67-C-0149, OCD Work Unit 2542A.

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for

Office of Civil Defense
Office of the Secretary of the Army
Washington, D. C. 20310

through

U. S. Naval Radiological Defense Laboratory
San Francisco, California 94135

May 1969

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ABSTRACT

Cellulose samples were subjected to various degrees of iodination, benzhydrylation and benzhydrylation followed by iodination. The effect of these treatments on crystallinity, rate of thermal degradation, char production and pyrolysis products was investigated. Results indicated that in general the crystallinity index varies inversely with the percent of substitution, rate of weight loss, and amount of residual char. Although the rates of weight loss of the substituted samples increased from 0.3%/min. to as high as 108%/min. depending on the type and percent of substitution, the overall weight loss pattern of the treated cellulose was similar to that of the untreated samples. Of the three types of retardants tried, iodine was the best flame retardant in that the residual char increased by a much larger factor for a given increase in rate. The addition of benzhydryl to the iodinated sample seemed to decrease rather than increase the char producing ability. All three treatments drastically reduce the number of degradation products of molecular weights lower than 150; untreated cellulose gave 59 components whereas the substituted cellulose led to five major compounds; water, acetic acid, furfural, 5 methyl-2-furfuraldehyde, and 1,5 anhydro-2, 3-doxy-β-D-pent-2-eno-furanose. Of these water and the furnose derivative were the major components.

SUMMARY OF REPORT

The Problem

In a nuclear explosion roughly one third of the energy is released as thermal radiation. The resulting exposure levels are high enough to ignite fabrics and other light weight materials inside of buildings well beyond the range of severe blast damage. These primary ignitions can result in destructive fires and, under some circumstances, could lead to the development of mass fires that could destroy whole sections of the city which would not be significantly damaged by the initial effects of the detonation. Existing fire retardants have certain shortcomings in that they reduce the heat resistance and strength of the fabrics, they add on an appreciable amount of weight to the fabrics, the non-durable fireproofing has to be renewed upon laundering and cleaning and the durable ones add too much to the cost of the material to make them widely acceptable. In order to produce more satisfactory flame retardants it is necessary to understand more about how the different classes of retardants act on the material to be protected.

The Findings

The effect of benzhydrylation, iodination, and benzhydrylation followed by iodination of white α-cellulose on the rate of thermal degradation, char build up, and degradation products was investigated. Iodination proved to be the most effective fire retardant treatment in terms of char production and rate of weight loss. The addition of the benzhydryl group to an iodinated sample decreased its retardant property in that it reduced the amount of char formed for a given rate of weight loss. All three treatments decreased the number of degradation products (molecular weights lower than 150) from 59 from the untreated cellulose to 5 major components in the treated cellulose. Of these water was the dominant component and was produced in the largest amount in samples having the combined treatments. The results of this study support the model of cellulose decomposition and flame retardant action developed in OCD work order 2531C.

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INTRODUCTION

The scope of work unit 2542 A as given in OCD Task Order No. 65-200(77), the work of which has continued under OCD Task Order No. 2540(68) is as follows: "The objectives of this work are the following; (1) To determine the most effective fire retardant for fabrics in terms of ignition protection against high energy-fluxes. (2) To determine the concentration of such a retarder required to prevent a material from being ignited by a thermal pulse from a given nuclear burst. (3) To investigate the retardation mechanisms of various types of retarder treatment from the point of view of predicting even more effective but as yet untried candidates. The first phase of the work will measure the ignition energy of alpha-cellulose as a function of retarder concentration for retarders selected from the list of fire retardant treatments recommended by the National Fire Protection Association. A more limited set of tests will be made on cotton and other household fabrics. The second phase of the work will examine different classes of treatments that might have potential value in thermal hardening. The third phase will involve the development of techniques necessary to study the retardation processes in detail. This will include development of a highly sensitive means of determining the time history of the pyrolysis products."

The third objective is followed in the work described in this paper.

Existing fire retardants have certain shortcomings. Although they retard flaming, they also reduce the heat resistance and strength of the fabrics and the treated fabrics discolor at moderately high temperatures. They also add on an appreciable amount of weight and the fireproofing has to be renewed upon laundering or cleaning. The most desirable fire treatment, of course, is one which renders the material permanently nonflammable without appreciably changing its normal physical characteristics.

Since cellulose is commonly found in fire environments, its mechanism of thermal decomposition is of fundamental interest in developing flame resistant clothing and other cellulosic materials. As many as 59 degradation products of cellulose have been found.

The two basic ways in which a retardant may act are to (1) decrease the quantity of the gases produced and (2) decrease the flammability of these gases.

The standard retardant treatments increase the amount of residual char and thus decrease the quantity and flammability of the degradation products. However, at the same time they increase the rate of thermal degradation of the material at a given temperature and thus reduce its heat resistance.

Experiments with γ - radiation from CO^{60}, on aromatically substituted cellulose indicated that there was a decreased yield of free radical sites in the aromatically substituted cellulose as compared with those in unsubstituted cellulose.[1] It has been suggested that the substitution of aromatic groups on the carbohydrates affected energy transfer particularly localization of energy. In this process, the energy from the secondary electrons could be directly absorbed by the aromatic groups, and the energy re-irradiated without localizing at a chemical bond causing decomposition or induced free radical formation.

Experiments dealing with blocking the formation of levoglucosan (one of the major constituents of tars) have been conducted in the past by esterifying the hydroxyl groups of cellulose with methanesulfonyl chloride.[2] Since levoglucosan decomposes into volatile and flammable products, the mesyloxy groups were partially replaced with halogens particularly bromine and iodine, which are very effective flame inhibitors.

The above investigations indicated that the substituted cellulose definitely deviates from its normal decomposition scheme. However, existing information does not show how the rate of pyrolysis and the amount of residual char are affected by these retardants under isothermal conditions. Furthermore, nothing is being said about the effect of the treatments on the quality of the degradation products formed during combustion.

The present work is directed towards studying the combined effects of benzhydrylation-iodination on the degradation process of white alpha cellulose. The cellulose used in this work is composed of a blend of 25% southern pine purified sulfite pulp and 75% sweetgum purified sulfate pulp. The samples are 0.07 cm thick, with a density of 0.70 g/cm^3 and molecular weight distribution of 700-4000 DP.

The scope includes; (1) Development of the most efficacious means of incorporating the benzhydryl and iodine groups into the cellulose molecule without producing undesirable side effects. (2) X-ray diffraction measurements of the treated cellulose in order to determine the extent of crystallinity change produced by the various degrees of substitution. (3) Measurements of weight loss for benzhydrylated cellulose pyrolyzed in a nitrogen fluidized sand bath at 288°C in order to determine the effect of benzhydrylation in terms of degree of substitution on the rate of degradation and the amount of residual char. (4) Measurements of the weight loss for the iodinated cellulose pyrolyzed at 288°C in order to determine the effect of iodination in terms of degree of substitution on the rate of degradation and the amount of residual char. (5) Measurements of weight loss of benzhydrylated and iodinated cellulose (of various ratios of substitution) in order to determine the most effective combination of these retardants which would produce the lowest rate of degradation and the highest residual char. (6) Analysis, by means of a gas chromatograph-mass spectrometer combination instrument, of the degradation products of the benzhydrylated, iodinated and the combined benzhydrylated-iodinated cellulose samples in order to determine the effect of the various treatments on the types of degradation products formed during combustion.

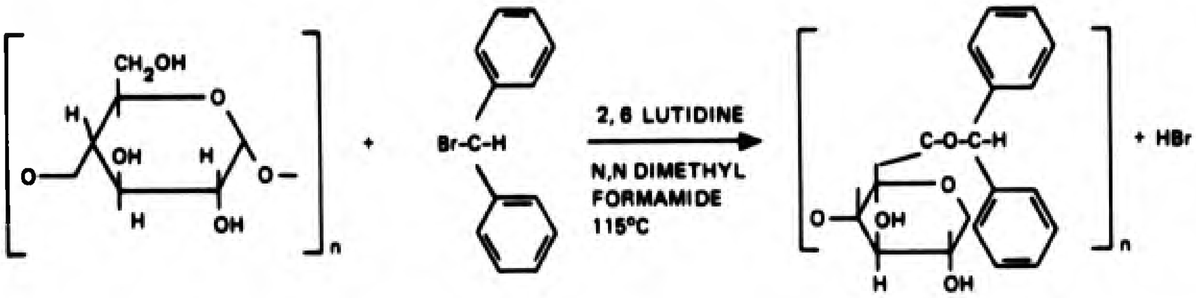
EXPERIMENTAL PROCEDURE

To facilitate substitution, white alpha cellulose disks (2.0 cm in diameter) were first soaked in 20% NaOH solution for various time intervals ranging from 10.0 seconds to 15.0 minutes. The samples were washed free of excess NaOH, soaked for 5.0 minutes in a 5.0% HAC solution and washed again with water until the wash-water was pH 5.5 as measured with a pH meter. In order to study the effect of alkaline pretreatment on the degree of substitution and the crystallinity index, at least 2.0 grams of cellulose from each pretreatment were used in each substitution. The procedure for the synthesis of the derivatives was as follows:

1. Benzhydrylation[3]

Four grams of cellulose were suspended in pyridine to remove as much of the water as possible and then washed with 2,6-lutidine. The samples were then placed in a mixture of 18.4 ml of N, N-dimethylformamide, 18.4 ml of 2,6-lutidine and 31.7 g of benzhydryl bromide. The reaction was carried out at 115°C under reflux for 20.0 minutes.

The crude samples were purified by first washing them with pyridine and then extracting the brown discoloration for 24 hours with methanol in a Soxhlet apparatus. The resulting white derivatives were washed with water, air dried and stored for subsequent studies.

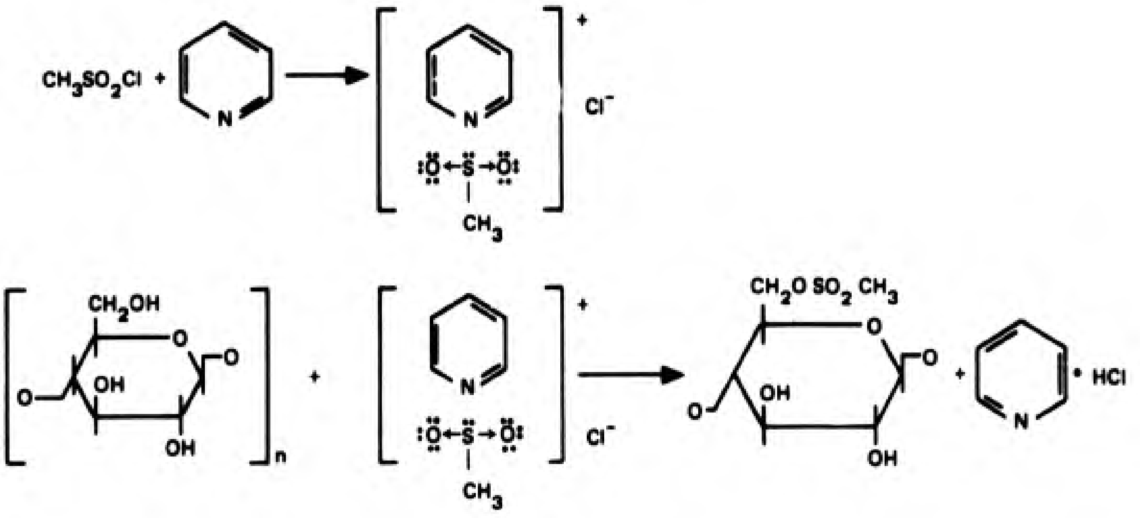


2. Iodination[3]

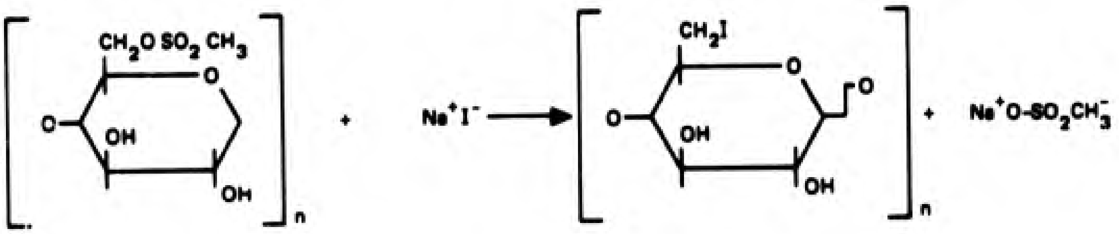
Preferential iodination of the primary hydroxyl group was attempted by replacing the primary mesyloxy group with iodine. The general procedure for mesylation was as follows:

A mixture of methanesulfonyl chloride and pyridine was prepared by carefully adding 8.5 ml of methanesulfonyl chloride to 40.0 ml of redistilled pyridine, cooled to 15°C.

After 5.0 minutes, the mixture was removed from the ice bath and was allowed to stand at room temperature until a deep amber color developed. To this mixture were added 2.0 g of pretreated and pyridine soaked cellulose. The temperature of the reactants was slowly raised to 65°C and was maintained around 65°C ± 1.0°C for 20.0 minutes by alternately placing the reaction flask in hot and cold water baths.



The mesylated cellulose was first washed with formamide and then the brown discoloration was removed by extraction with methanol in a Soxhlet apparatus for 24 hours. The resulting white derivatives were washed with water and were ready for iodination. The substitution was carried out in a 20% NaI solution in the presence of $BaCO_3$ for 5.0 hours under reflux using a heating mantle.



The derivatives were washed with water, air dried and stored for subsequent studies.

3. Benzhydrylation-iodination

In order to determine the combined effect of both treatments on the degradation rates, decomposition products and char formation, a number of alkaline pretreated samples were subjected to 20 minutes benzhydrylation, followed by 20.0 minutes mesylation and 5.0 hours iodination. The reactants' ratios and the experimental procedure were kept the same as in the individual substitutions described above. A number of measurements were performed on the substituted samples:

1. Elemental analysis

Carbon, hydrogen and oxygen analysis was performed on the samples in order to determine the percent of substitution. The results were correlated with the crystallinity indices rates of weight loss, and final char measurement.

2. X-ray diffraction

Diffractograms of substituted, alkaline soaked, and untreated cellulose were obtained with a General Electric Model XRD-3 diffractometer equipped with a copper target to produce the Cu K α radiation. Relative diffraction intensities as a function of angle were recorded on a strip chart recorder and the intensity of the peaks was measured by a G.M. counter with a scaling circuit.

3. Weight Loss Rates

The isothermal pyrolysis chamber (a nitrogen fluidized sand bath) used in the degradation studies was described earlier.[4,5] Prior to the actual pyrolysis, each sample was evacuated for 30 minutes, dried to a constant weight in nitrogen in the presence of phosphorus pentoxide, transferred in a covered, tared, weighing bottle to the loading chamber and then inserted into the reaction chamber. Since the object of this study was to determine the effect of the degree of substitution on the degradation rate and char formation, the samples were all pyrolyzed only at 288°C. This temperature was chosen because it was low enough for detailed kinetic studies and high enough to be well in the 276-350°C temperature range, where the mode of degradation follows a specific pattern. Below 276°C the scheme of degradation is different. The procedure for the weight loss determination was described earlier.[4,5]

Final char determinations on the variously substituted samples were made in an oven at 600°C. To eliminate oxygen contamination, the weighed samples were placed between two index cards and wrapped with aluminum foil. They were then pyrolyzed for 12.0 minutes and reweighed.

4. Analysis of degradation products

For a better understanding of the effect of chemical substitution on the mechanism of degradation, gas chromatographic/mass spectrometric analysis was performed on the pyrolysis products of the substituted and untreated samples. A detailed description of the analytical techniques and the findings appears in Wodley's NRDL-report.[6] Briefly, cellulose samples were rolled into cylinders and burned in air. To collect the degradation products (excluding the fixed gases and more volatile compounds) one end of the cylinders was placed in a liquid nitrogen cooled centrifuge tube and the other ignited. This method allowed the pyrolysis products to flow down the center of the cylinder and condense out on the bottom of the centrifuge tube. Aliquots of 10µl were then injected with a syringe onto a 10' by 0.25" o.d. stainless steel column packed with Carbowax-20M on Chromosorb T. The column was then ballistically temperature programmed from 90 to 220°C in 40 minutes. The helium flow rate was 60cc/min., the thermoconductivity detector oven was maintained at 225°C, and the injection port at 240°C. Identification of the gas chromatographic peaks was done with the aid of the time-of-flight mass spectrometer, which was linked to the gas chromatograph by means of the Watson-Bieman helium separator. To facilitate identification of the components, mass spectra were taken at both 15 and 70 electron volts.

RESULTS AND DISCUSSION

The effect of substitution on crystallinity, rates of degradation and char build up is summarized in Table I. For better correlation of the results, the effect of alkaline soaking on crystallinity, rate of weight loss, and final char is also included. The crystallinity indices were calculated by an empirical method based on Segal et. al.[7] In this method, the diffractogram heights above a base line at $2\theta = 19^\circ$ and 22.6° for the untreated, $2\theta = 16.0^\circ$ and 21.7° for the treated samples were used to calculate the index of crystallinity from the relationship:

$$\mathrm{Cr\ I} = \frac{\mathrm{I002} - \mathrm{Iam}}{\mathrm{I002}} \times 100$$

where CrI is the crystallinity index; I002 is the maximum intensity (in arbitrary units) of the 002 lattice diffraction, 22.6° for the untreated and 21.7° for the treated; and Iam is the intensity of diffraction in the same units for the amorphous background; in our case at $2\theta = 19^\circ$ for the untreated cellulose, and $2\theta = 16.0^\circ$ for the treated cellulose. This difference in angles is due to the different crystalline structure in the untreated and the treated material. The treatment changes the structure from cellulose I to cellulose II.

As stated earlier, alkaline pretreatment of the samples is necessary for efficient substitution. Unfortunately, such soaking leads to the transformation of the crystalline lattice as well as decrystallization of the samples which in turn increases the rate of degradation. Table I shows that the crystallinity indices of the 20% NaOH treated samples gradually decrease with the length of soaking. The index varies from 80.5 for the 10 seconds soaked samples to 75.0 for the 15.0 minutes soaked samples. Figure 1 compares a number of diffractograms of the variously treated samples with a diffractogram of an untreated sample (curve A). Alkaline treatment for as short an interval as 10 seconds changes the native crystalline pattern of $2\theta = 19.0^\circ$ and 22.6° to that of $2\theta = 16.0^\circ$ and 21.7° (curve B) which is the characteristic pattern of Cellulose II. In view of these findings, a number of samples which were soaked in 20% NaOH for 5.0 minutes were subjected to nitrogen pyrolysis at 288°C for various lengths of time. The rate of weight loss in the linear region of pyrolysis was 3 times as fast as that of the untreated sample and the final char residue remained essentially unchanged. The increased rate in the linear region suggests loosening of the macromolecular packing of the molecule by the NaOH treatment and thereby making the sample less heat resistant.

Table I

THE EFFECT OF SUBSTITUTION ON CRYSTALLINITY, RATES OF WEIGHT LOSS AND CHAR BUILD UP

Sample Description	Substitution (%)	Crystallinity Index	Angles used in calculating the crystallinity Index	Rates of Wt. loss (%/min)	Final Char (%)
Untreated sample	0	81.0	19° and 21.7°	0.3	9.23
10 sec in 20% NaOH	0	80.5	16° and 21.7°		
30 sec in 20% NaOH	0	80.0	16° and 21.7°		
75 sec in 20% NaOH	0	78.0	16° and 21.7°		
2.5 min in 20% NaOH	0	77.5	16° and 21.7°		
5.0 min in 20% NaOH	0	75.25	16° and 21.7°	1.0	9.40
10.0 min in 20% NaOH	0	75.2	16° and 21.7°		
15.0 min in 20% NaOH	0	75.0	16° and 21.7°		
10.0 sec in 20% NaOH and benzhydrylated	4.1	80.5	16° and 21.7°	14.0	16.22
30.0 sec in 20% NaOH and benzhyd.	34.0	77.0	16° and 21.7°	60.0	18.80
15.0 min in 20% NaOH and benzhyd.	6.0	82.0	16° and 21.7°	18.0	16.47
10 sec in 20% NaOH and iodinated	3.6	76.0	16° and 21.7°	7.5	23.08
75.0 sec in 20% NaOH and iodinat.	8.0	78.0	16° and 21.7°	19.0	31.29
2.5 min in 20% NaOH and iodinat.	3.0	84.0	16° and 21.7°	9.0	20.88
15.0 min in 20% NaOH and iodinat.	4.0	78.2	16° and 21.7°	15.0	22.96
10.0 sec in 20% NaOH then benzhyd. and iodinat.	27.0	Amorphous	16° and 21.7°	108	21.35
30 sec in 20% NaOH then benzhyd. and iodinat.	20.29	Amorphous	16° and 21.7°	96	19.89
2.5 min in 20% NaOH then benzhyd. and iodinat.	15.0	55.0	16° and 21.7°	8.0	26.43
15.0 min in 20% NaOH then benzhyd. and iodinat.	8.0	82.0	16° and 21.7°	6.0	22.09

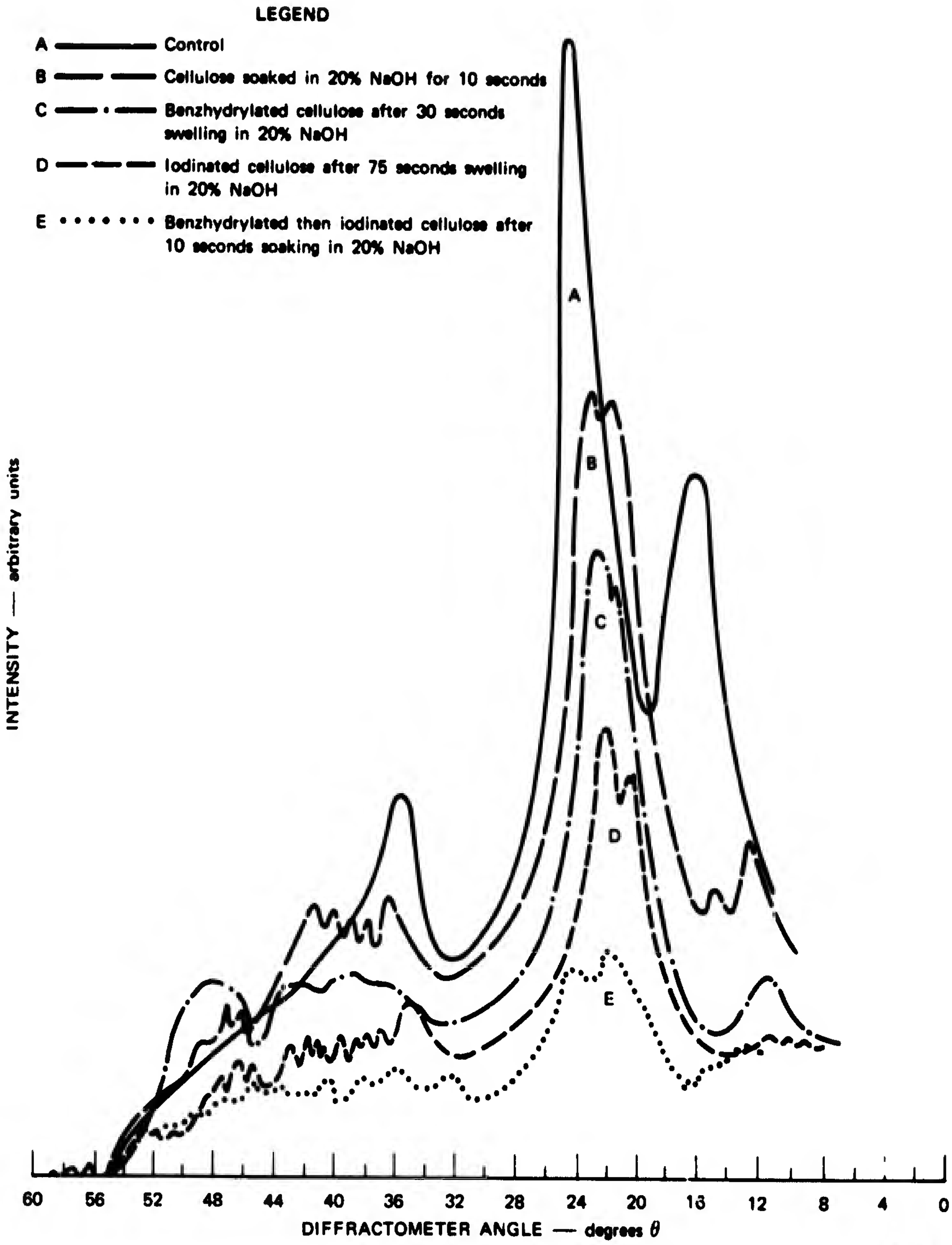


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FIGURE 1 THE EFFECT OF NaOH SOAKING AND SUBSTITUTION ON CRYSTALLINITY

An optimum soaking time of 30 seconds in 20% NaOH produces the highest degree of benzhydrylation and also the lowest crystallinity index. Although this degree of substitution is not high enough to destroy the cellulose II pattern (Fig. 1, curve C), it definitely lowers the crystallinity index. The highest percent of iodination is achieved after 75.0 seconds of soaking time in 20% NaOH which also exhibits the lowest crystallinity index (Fig. 1, curve D). Benzhydrylation followed by iodination not only lowers the crystallinity index, but at higher percent of substitution reduces the crystalline region to an essentially amorphous state (Fig. 1, curve E).

Figure 2 shows the remaining weights of benzhydrylated cellulose as a function of time and percent of substitution. The overall shape of the curves follows that observed for both the unsubstituted cellulose and samples treated with basic or acidic salts. All of the retardant treated samples display markedly increased rates of degradation and a considerable increase in the final char. Correlation of the pyrolysis results with the X-ray diffraction measurements shows that in general, the rates of degradation and amount of final char vary inversely with the crystallinity indices.

The remaining weights of the iodinated samples as a function of time and percent of substitution are shown on Figure 3. The general shape of the curves follows the same pattern as that of benzhydrylated samples. Although the rate of weight loss per percent of substitution is essentially the same for benzhydrylated and iodinated samples, the increase of char per percent of substitution for the iodinated samples is considerably greater than for the benzhydrylated samples. Thus in the series of iodinated samples a substitution of 8% leads to the highest production of char which is approximately 31%; while in the benzhydrylated series even a substitution of 34% gives only 19% of char.

Although the exact mechanism of the action of these retardants as well as basic and acidic salts on the breakdown of the cellulose molecule is as yet not fully understood, experiments with fire retardant products on treated levoglucosan indicate that the primary action of the retardant is on the levoglucosan, formed during the decomposition of cellulose rather than the cellulose molecule itself. The retardant breaks up levoglucosan into char and decreases the amount of flammable species. If the rate of decomposition of the retardant itself is faster than the char formation process, then the amount of the char produced will naturally be lower due to the depleting concentration of the retardant. This might be applicable to the benzhydryl group, whereas although scission of the iodine does occur during pyrolysis, the iodine radical can still cause the levoglucosan molecule to break down into char.

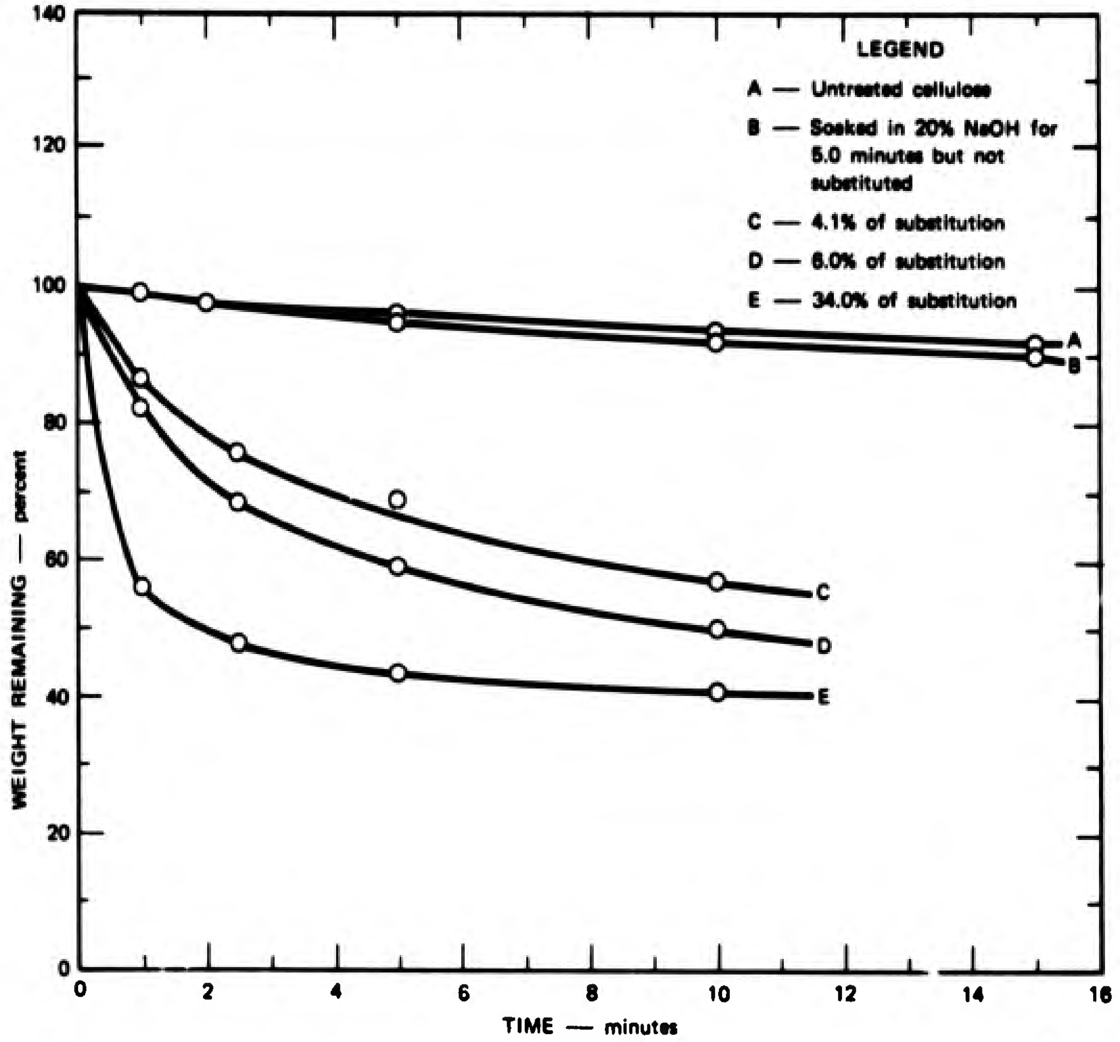

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FIGURE 2 ISOTHERMAL PYROLYSIS OF BENZHYDRYLATED WHITE α-CELLULOSE IN NITROGEN AT 288°C.

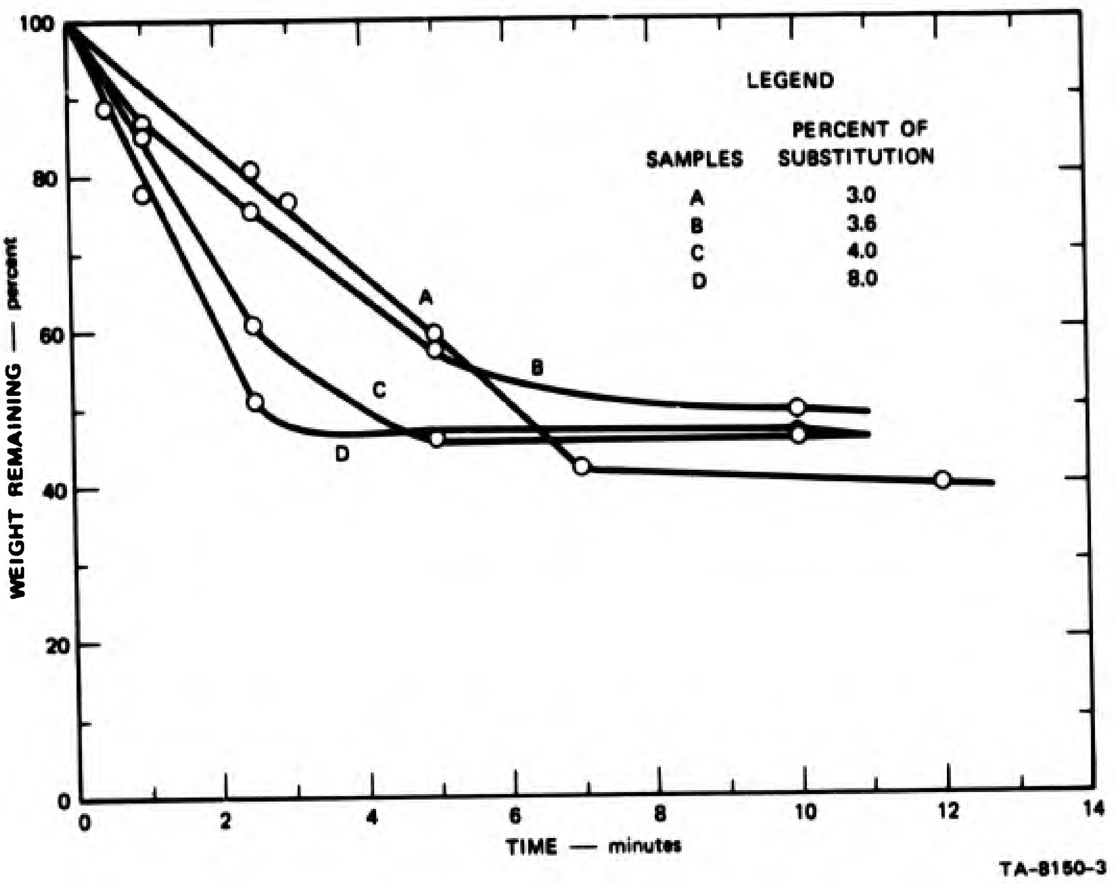


FIGURE 3 ISOTHERMAL PYROLYSIS OF IODINATED WHITE α-CELLULOSE IN NITROGEN AT 288°C

Figure 4 shows the residual weights of benzhydrylated-iodinated samples. The rate of degradation is directly proportional to the percent of substitution and crystallinity indices, which is comparable to the overall effect of the singly derivatized samples seen in Figures 2 and 3. However, the rate of degradation per percent of combined substitution in the higher substituted samples is faster than produced by sole benzhydrylation or iodination. At the same time the char produced by this combination is lower per percent of substitution than in samples subjected to either benzhydrylation or iodination.

These findings as well as those from the singly substituted derivatives point out that of the three types of treatments tried, iodination renders the most effective retardant in terms of rate of weight loss and char production. The addition of the benzhydryl to the iodinated sample seems to decrease rather than increase its char producing property.

Figures 5a-5d as taken from Wodley's report,[6] compare a chromatogram of the degradation products of untreated cellulose with chemically bonded cellulose. The percent of substitution used for the analysis was 6% benzhydrylation, 4% iodination, 5% benzhydrylation followed by 4% iodination. A typical chromatogram of the degradation products of untreated cellulose consists of 39 peaks which represents at least 59 compounds as analyzed by the time-of-flight mass spectrometer. These vary from CO and CO_2 to benzene and furan derivatives. Since no silyl derivatives were prepared for the identification of higher molecular weight components, the gas chromatographic analysis involves only compounds with molecular weights less than about 150. The degradation products of the chemically substituted compounds consist of only five prominent compounds; water, acetic acid, furfural, 5-methyl-2-furfuraldehyde and peak 31a. Of these, water is the dominant peak and appears as the largest peak in the combined benzhydrylated-iodinated samples.

Since the size of peak 31a was markedly increased in the treated cellulose as well as in treated levoglucosan, it was decided that identification of this peak was important. Therefore the compound comprising peak 31a was trapped in a cooled glass tube (4" long by 1/10" diameter) after being separated in the G.C. and was then subjected to various analyses.

Low and high resolution mass spectra indicated a possible mixture; with the main compound having a molecular weight of 98 and an empirical formula of $C_5H_6O_2$. The sample was optically inactive. Examination of the infrared spectrum led to the following tentative identification:

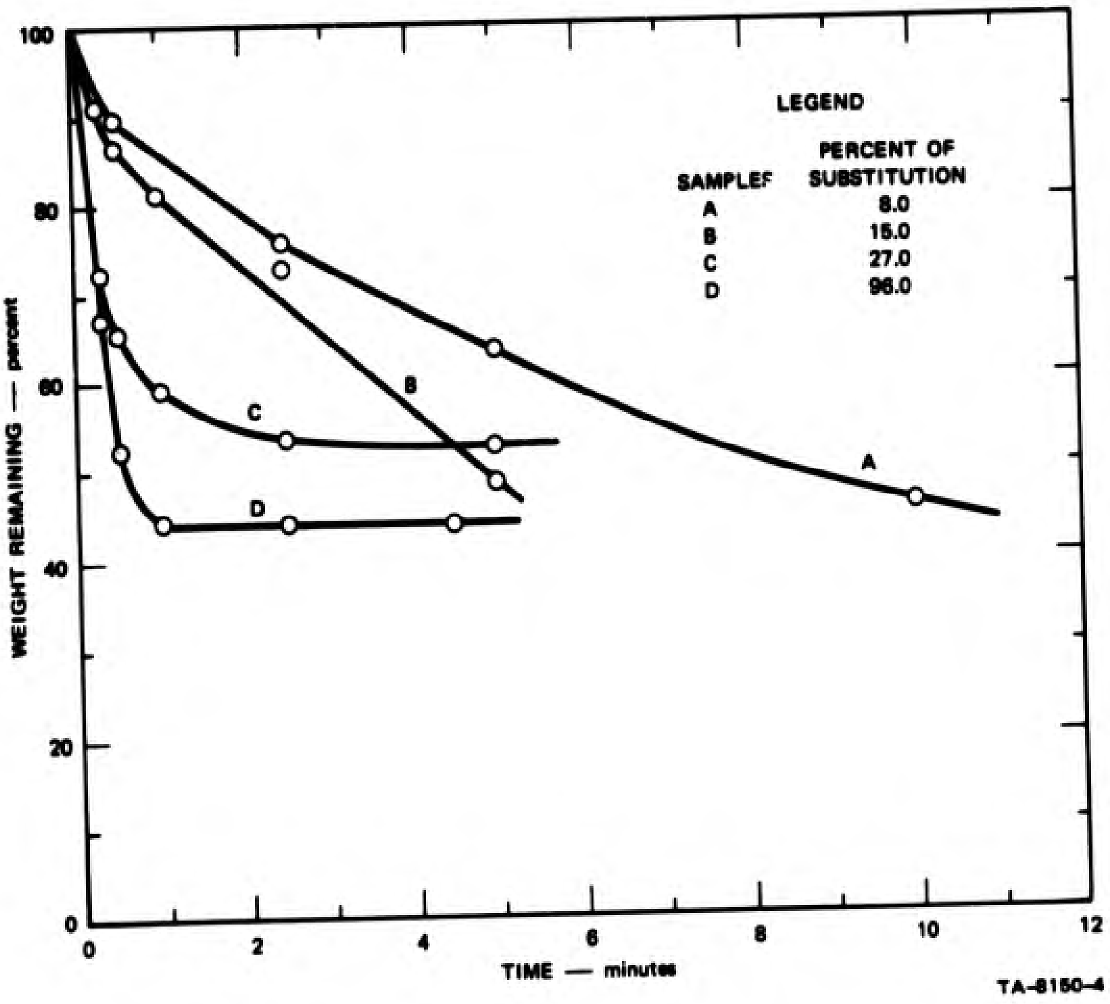
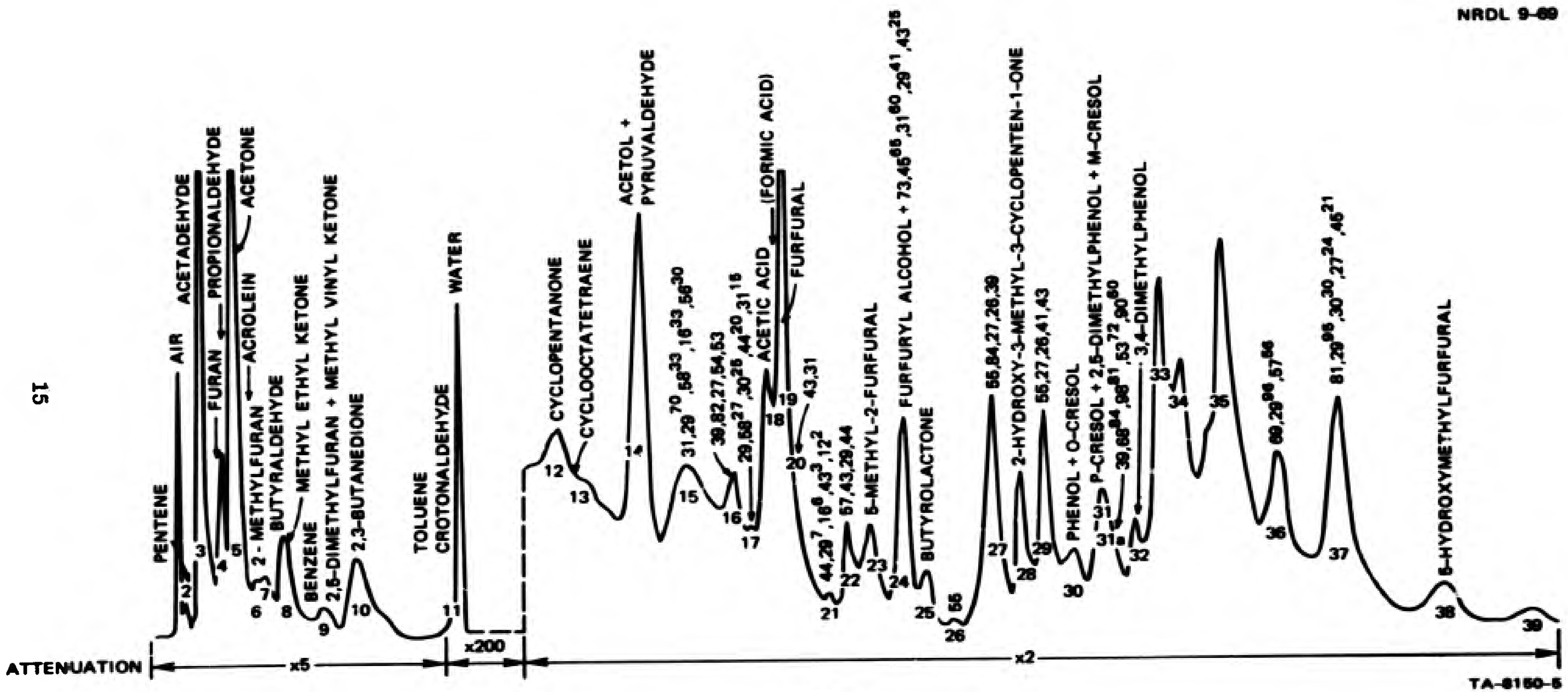
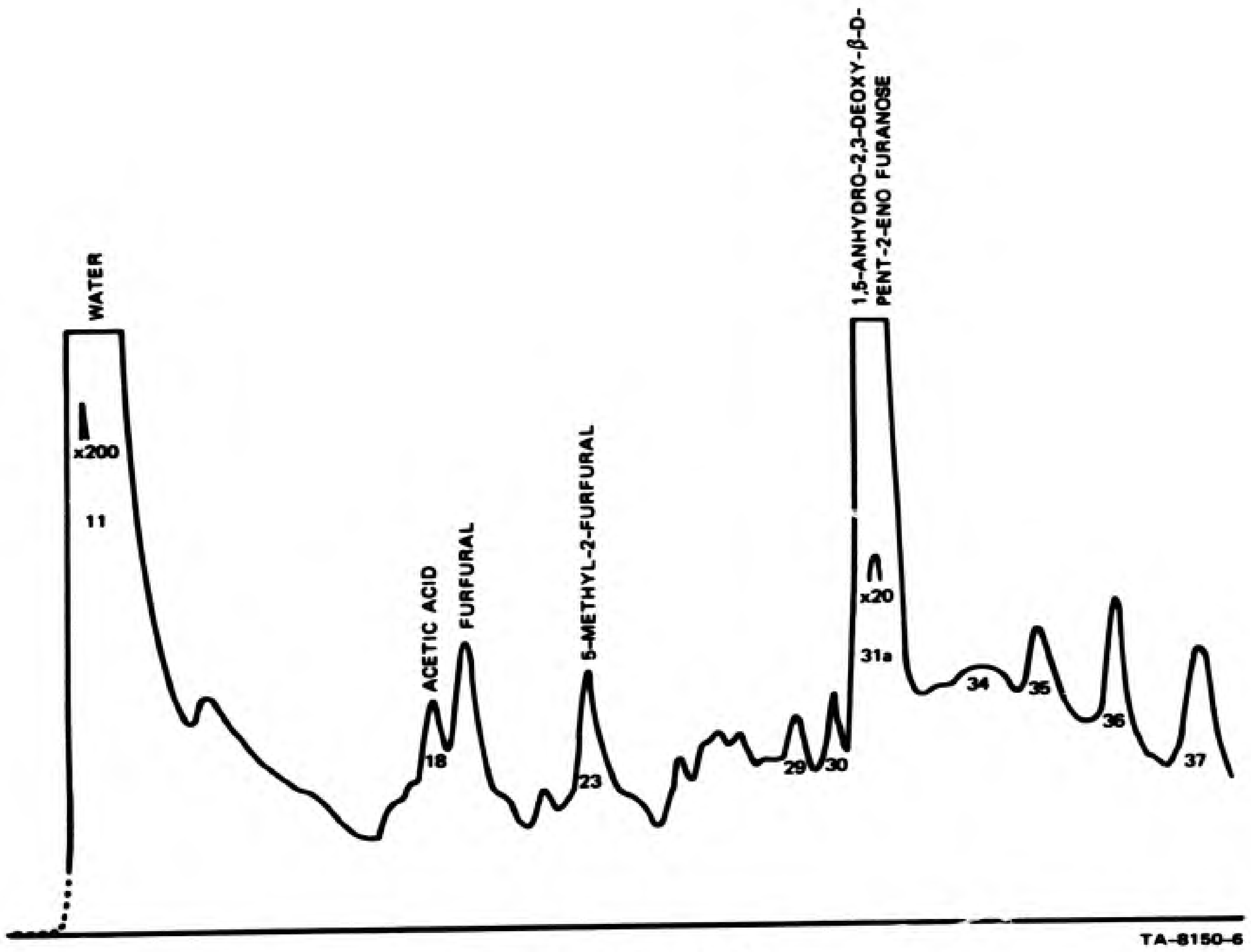


FIGURE 4 ISOTHERMAL PYROLYSIS OF BENZHYDRYLATED THEN IODINATED WHITE α-CELLULOSE IN NITROGEN AT 288°C



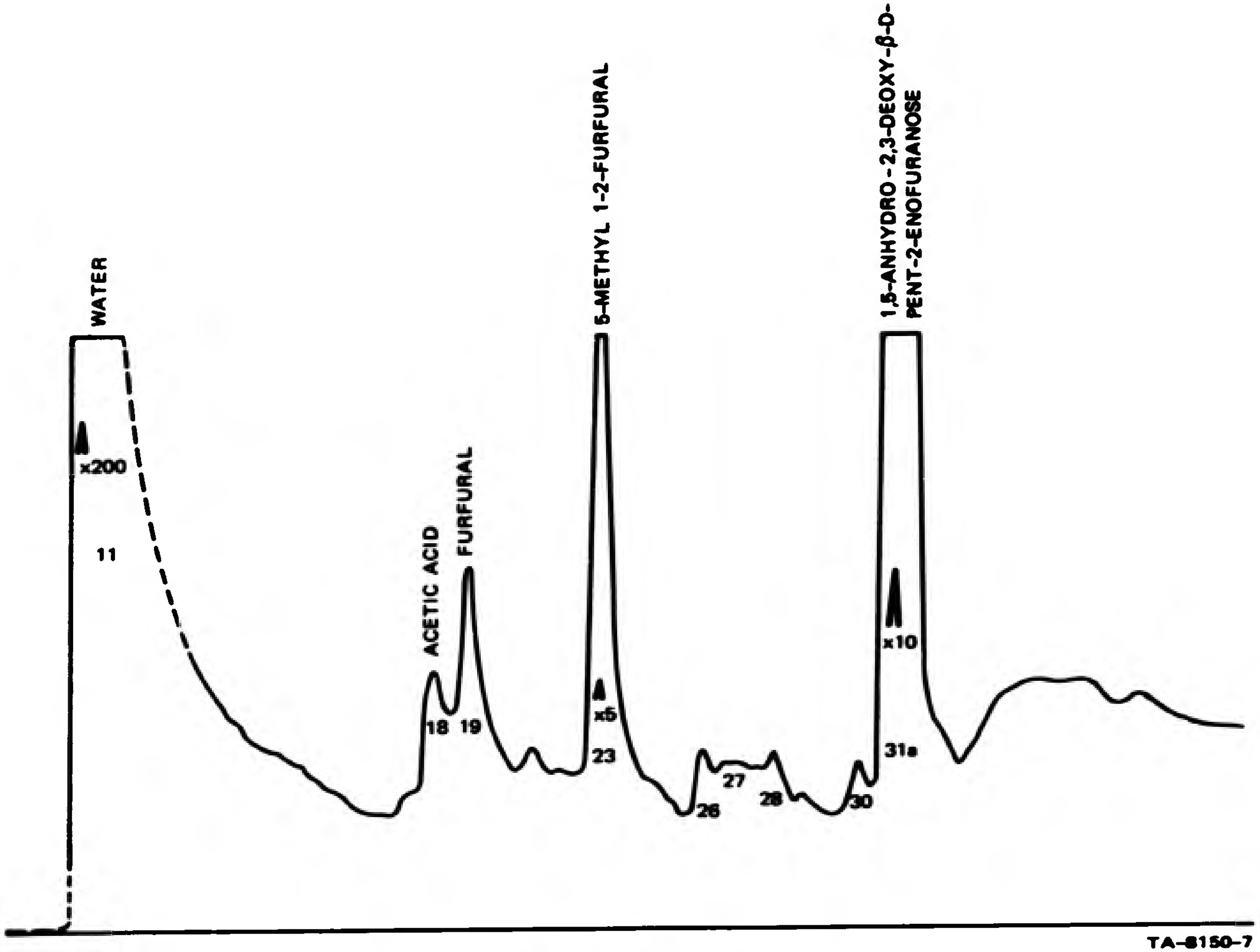
(A) UNTREATED

FIGURE 5 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED AND CHEMICALLY SUBSTITUTED α-CELLULOSE



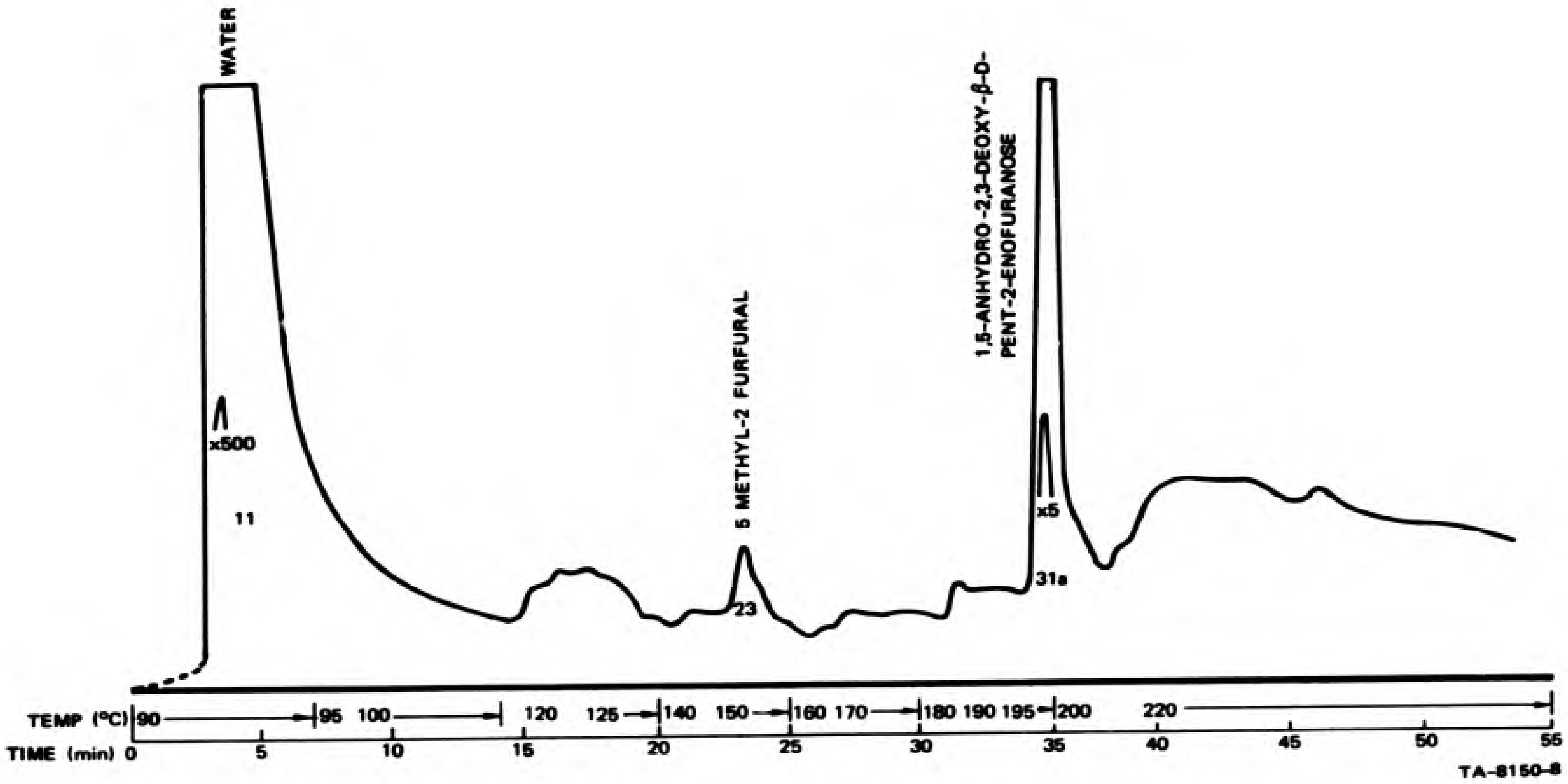
(B) 6% BENZHYDRYLATION

FIGURE 5 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED AND CHEMICALLY SUBSTITUTED α-CELLULOSE



(C) 4% IODINATION

FIGURE 5 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED AND CHEMICALLY SUBSTITUTED α-CELLULOSE



(D) 5% BENZHYDRYLATION—4% IODINATION

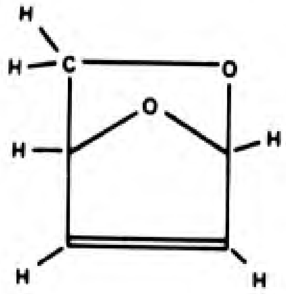
FIGURE 5 GAS CHROMATOGRAMS OF THE VOLATILE PRODUCTS FROM THE PYROLYSIS OF UNTREATED AND CHEMICALLY SUBSTITUTED α-CELLULOSE

CM^{-1}	Identification
2800 - 2900	CH_2
1680 - 1725	C = C stretching
1090 - 1100	C - O
960 - 976	C - H bending
873 - 893	
825 - 833	

The NMR spectrum consisted of:

δ	Number of protons	
3.85	2	Multiplet
5.02	1	Triplet
5.35	1	Singlet
6.12	1	Doublet
6.30	1	Multiplet

Based on the above results the structural formula assigned to this compound was:



It is now important to determine the mechanism for its formation and to establish its role in the scheme of decomposition of cellulose.

CONCLUSIONS AND RECOMMENDATIONS

1. There is an optimum swelling time in the 20% NaOH to achieve the highest percent of substitution. Longer pretreatments result in extensive changes in the crystalline lattice which in turn seem to lower the accessibility of the hydroxyl groups to the chemical reagents. For benzhydrylation, the optimum length of alkaline soaking was 30 seconds which led to 34% substitution; for iodination, 75 seconds with 8% substitution and for benzhydrylation followed by iodination, the optimum soaking time was 10 seconds which gave 27% as a total percent of substitution. The possibility of using another swelling agent such as Cadoxen should be investigated for higher percentages of substitution.

2. The overall weight loss pattern of the chemically substituted samples is similar to the untreated ones. The increased rate of weight loss in the treated cellulose is due partly to an increased percentage of the amorphous regions in the samples and probably to a reduction in the molecular weight. Measurements of the molecular weight distribution of the substituted samples and cellulose soaked in NaOH should be performed to determine the extent of the reduction.

3. Of the three types of treatments tried, iodination renders the most effective retardant in terms of weight loss rate and char production.

4. The addition of benzhydryl to the iodinated sample seems to decrease rather than increase its char producing property.

5. Since the action of the chemically bonded retardants on the rate of degradation is similar to that of basic and acidic salts, it is reasonable to assume that the action of the chemically bonded retardants on the char is also similar to that of the basic and acidic salts, where the action is primarily on the levoglucosan rather than the cellulose molecule itself. Char determinations on benzhydrylated and iodinated levoglucosan would clarify this action.

6. In general, the three kinds of derivatives drastically decrease the number of thermal degradation products of molecular weights lower than 150; untreated cellulose gave 59 compounds as opposed to only 5 compounds rendered by the chemically bonded cellulose. Of these, water and peak 31a (1,5-anhydro-2,3-deoxy β-D-pent-2-eno-furanose) are highest in concentration. The largest amount of water is produced by the combined treatment.

Additional differences in the action of these retardants might be detected by the gas chromatographic analysis of the trimethy silyl derivatives of the degradation products of molecular weight higher than 150.

7. Since compound 31a appears in large quantities only in the degradation products of treated cellulose (chemically bonded as well as treated with basic and acidic salts) and also increases in the products of treated levoglucosan, it is important to determine the mechanism of its formation and its role in the decomposition of cellulose. Compound 31a is a furanose derivative, therefore it is possible that it might be formed by the action of the retardants on 1,6-anhydro-β-D-glucofuranose or 1,5-anhydro-β-D-ribofuranose. Since these compounds have been identified among the degradation products of treated and untreated cellulose, g.c. analysis of the pyrolysis products of treated and untreated 1,6-anhydro-β-D-glucofuranose and 1,5-anhydro-β-D-ribofuranose should be performed.

   On the other hand, compound 31a might be one of the primary decomposition products of levoglucosan, which is stabilized by the presence of a retardant and hence appears in larger quantities in treated samples. Gas chromatographic analysis of the degradation products of treated and untreated 31a should therefore be performed.

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13. ABSTRACT

Cellulose samples were subjected to various degrees of iodination, benzhydrylation and benzhydrylation followed by iodination. The effect of these treatments on crystallinity, rate of thermal degradation, char production and pyrolysis products was investigated. Results indicated that in general the crystallinity index varies inversely with the percent of substitution, rate of weight loss, and amount of residual char. Although the rates of weight loss of the substituted samples increased from 0.3%/min. to as high as 108%/min. depending on the type and percent of substitution, the overall weight loss pattern of the treated cellulose was similar to that of the untreated samples. Of the three types of retardants tried, iodine was the best flame retardant in that the residual char increased by a much larger factor for a given increase in rate. The addition of benzhydryl to the iodinated sample seemed to decrease rather than increase the char producing ability. All three treatments drastically reduce the number of degradation products of molecular weights lower than 150; untreated cellulose gave 59 components whereas the substituted cellulose led to five major compounds; water, acetic acid, furfural, 5 methyl-2-furfuraldehyde, and 1,5 anhydro-2, 3-doxy-beta-D-pent-2-eno-furanose. Of the water and the furnose derivative were the major components.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Flammability						
Alpha-cullulose						
Benzhydrylation						
Iodination						
Pyrolysis						