

Pyrolysis of Cellulose in a Vacuum^{1 2}

S. L. Madorsky, V. E. Hart, and S. Straus

Samples of cotton, cotton hydrocellulose, and viscose rayon, both by themselves and impregnated with sodium carbonate or sodium chloride, were pyrolyzed at 250° to 397° C in a high vacuum. The volatile products were fractionated and the fractions analyzed in the mass spectrometer and by infrared absorption. The volatile fractions consisted mainly of CO, CO₂, water, and levoglucosan (tar). The residue consisted mainly of carbon (char). Impregnation of the cellulosic materials with salts caused a decrease in the yield of tar and an increase in the yields of CO, CO₂, H₂O, and char. Rates of thermal degradation of the same materials were investigated in the range 245° to 305° C by a loss-of-weight method, using a very sensitive tungsten spring balance enclosed in a vacuum. Plots of rates of loss of weight versus percentage of loss of weight, in the case of pure cellulosic materials, pass through maxima at about 13 to 23 percent loss of weight, then drop gradually to the carbonization end point. In the case of samples impregnated with sodium carbonate or sodium chloride, the initial rates of loss of weight are very high, but drop rapidly to the carbonization end point. The activation energies of thermal degradation of the pure cellulosic materials are much greater than those of the same materials impregnated with sodium carbonate or sodium chloride.

1. Introduction

An investigation of the thermal degradation or pyrolysis of cellulose in a vacuum was undertaken in connection with the problem of rendering cellulosic materials used in fabrics flame-resistant. Flaming of these materials takes place in two principal consecutive steps: (1) the cellulose first degrades under the influence of heat to form volatile and nonvolatile products; (2) the flammable constituents of the products ignite and the heat evolved promotes further decomposition of the cellulose. In rendering cellulosic materials resistant to flaming, the conditions of degradation are so altered as to increase the amount of the nonflammable products at the expense of the flammable products.

This paper deals with the first of the two steps enumerated above. The advantages of conducting pyrolysis in a vacuum, instead of in air or in an inert gas, are that the degradation products are prevented from reacting with oxygen (in the case of air) and that the volatile products are more quickly and completely removed from the hot zone, where they might otherwise undergo secondary reactions. In a vacuum the volatile products are more easily collected and fractionated for analysis.

Pyrolysis of cellulose at reduced pressures has been reported by several investigators [1, 2, 3, 4].³ Their results indicate the formation of tar, char, H₂O, CO₂, and CO in various yields, depending on conditions of pyrolysis. In this investigation a vacuum of 10⁻³ to 10⁻⁵ mm Hg was maintained during pyrolysis, and a study was made of the nature and proportion of the various products and also of the rates of degradation of pure cellulosic materials with or without additives. A considerable amount of research has been conducted in recent years at the Bu-

reau on the thermal degradation of vinyl, butadiene, and aromatic polymers; the methods and apparatus developed and used in this research have now been applied to the study of thermal degradation of cellulose. The method can be divided into two parts:

(1) Pyrolysis of a small sample in an evacuated apparatus, and subsequent investigation of the decomposition products.

(2) Determination of rates of thermal degradation at several temperatures, and calculation of the activation energies of the degradation reactions involved.

2. Materials Used

Three forms of cellulose were used: cotton cellulose, cotton hydrocellulose, and viscose rayon. The cotton, which was an Empire cotton obtained from the Southern Utilization Branch of the U. S. Department of Agriculture, was dewaxed by extraction with boiling alcohol. It was freed from pectic substances by immersion in boiling 1-percent sodium hydroxide in the absence of air for 2 hr, washed in distilled water, neutralized with dilute acetic acid, again washed in water, and dried in air at room temperature. The hydrocellulose was obtained by immersion of a portion of the purified cotton in 6 N HCl for approximately 15 hr. After washing with distilled water to remove the acid, the hydrocellulose was dried in air at room temperature. The viscose rayon was a commercial yarn, 900 denier, 100 filament. It was washed in warm dilute aqueous ammonia, rinsed in warm water, and dried in air at room temperature.⁴

In order to determine the amount of moisture and other volatiles adsorbed on the cellulosic materials, samples were "dried" to a constant weight in a vacuum at 100° C. It was found that this could be accomplished in about 60 min. Losses, in percentages of dry samples, were: 3.7, 4.1, and 8.6, for

¹ This work was performed as a part of the research project sponsored by the Office of Quartermaster General, Department of the Army.

² This paper was presented at the 128th National Meeting of the American Chemical Society in Minneapolis, Minn., September 12 to 16, 1955.

³ Figures in brackets indicate the literature references at the end of this paper.

⁴ The authors are indebted to Florence H. Forziati of the Textiles Section of the Bureau for supplying the purified cotton, hydrocellulose, and rayon.

cotton, hydrocellulose, and viscose rayon, respectively. In the actual pyrolysis experiments, the samples were dried in the above manner in the vacuum apparatus and the volatiles were pumped off prior to pyrolysis. The original weights of the samples were corrected for the above determined weight losses.

In some of the experiments, samples of cotton impregnated with NaCl or Na_2CO_3 and viscose rayon impregnated with Na_2CO_3 were used. The cellulose was impregnated with the salt in the following manner: A weighted amount of cellulose was placed in the container in which it was to be pyrolyzed. A weighed amount of salt was added to the same container. A small amount of water was then added and the water evaporated in an oven at about 80°C . Drying of the sample and additive was then completed in a vacuum in the same manner as for the nonimpregnated samples. All calculations of losses, yields, residues, etc., were made on the basis of dry celluloses.

3. Pyrolysis

3.1. Apparatus and Experimental Procedure

In order to obtain a detailed analysis of the volatile products of pyrolysis, these were separated into fractions. The following volatile and nonvolatile fractions were collected:

1. Residue.
2. Fraction V_{pyr} , volatile at the temperature of pyrolysis, but not at 25°C .
3. Fraction V_{25} , volatile at 25°C , but not at -80°C .
4. Fraction V_{-80} , volatile at -80°C , but not at -190°C .
5. Fraction V_{-190} , volatile at -190°C .⁵

⁵In previous work [5] on pyrolysis of polymers, fractions V_{pyr} , V_{25} , V_{-80} , and V_{-190} were designated as fractions II, IIIB, IIIA, and IV, respectively.

The pyrolysis apparatus is the same as that used in the thermal degradation of polytetrafluoroethylene [6], and is shown diagrammatically in figure 1.

In figure 1, A is a quartz tube, closed at one end and fitted into a larger quartz tube, B, also closed at one end. Tube B is attached to the vacuum system by means of a ground joint, C. A vacuum of about 10^{-3} mm of mercury could be obtained by means of a rotary oil pump, not shown in the figure, a liquid nitrogen-cooled trap, P, and a mercury-diffusion pump E. A cylindrical electric heater, not shown in the figure, could be moved in a fixed horizontal position so that tube A fitted approximately in the center of the heater muffle. The temperature was measured by means of a platinum versus platinum-10 percent rhodium thermocouple fixed permanently in the muffle of the heater, so that when the heater was moved in position for pyrolysis, the thermocouple came in contact with tube B approximately at a point where the sample was located in tube A near its closed end. The heater was so constructed that an essentially uniform temperature could be maintained over the entire specimen. The temperature could be maintained within $\pm 0.5^\circ\text{C}$ at pyrolysis temperatures.

After the cellulose specimen was placed in tube A and the tube inserted into tube B, the apparatus was evacuated overnight. When the heater, which had been kept at the desired temperature, but away from the apparatus overnight, was moved into position, tube A reached the desired temperature within a few minutes.

During pyrolysis the apparatus was cut off from the evacuation pump by means of stopcock D, while the mercury diffusion pump E remained in operation. The combined volatile fractions V_{25} , V_{-80} , and V_{-190} were confined between D and E. The mercury pump was rated to hold 25-mm back pressure, with a high vacuum on the inlet side; it was actually operated at a back pressure of not over

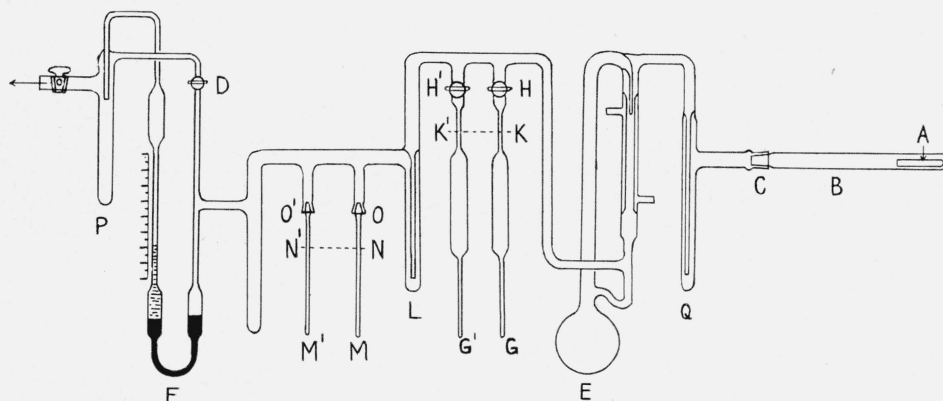


FIGURE 1. Apparatus for the study of thermal degradation of cellulosic materials.

A, Small quartz tube in which the sample is placed; B, large quartz tube; E, mercury diffusion pump; F, multiplying manometer; G, G', tubes for collecting fraction V_{-190} ; L, trap; M, M', tubes for collecting fractions V_{25} and V_{-80} ; P, liquid nitrogen cooled trap.

6 mm. The pressure was measured in the calibrated space between this mercury pump and stopcock D by means of a multiplying manometer, F, containing a low-vapor-pressure silicone oil in the left arm of the manometer, above a mercury column.

A sample of the gaseous fraction V_{-190} , noncondensable at the temperature of liquid nitrogen, was collected for analysis at the end of an experiment in the following manner. Liquid nitrogen was placed around trap L. The condensable material, consisting of combined fractions V_{-80} and V_{25} , was drawn into L, and a sample of the remaining gaseous fraction V_{-190} was then taken for analysis in 60-ml tube G or G' by sealing off the tube at K or K'. The weight of fraction V_{-190} was calculated from its volume, pressure, and composition.

After evacuating the excess fraction V_{-190} , the material that condensed in trap L was separated into two fractions, V_{-80} and V_{25} , with the aid of dry ice. These fractions were collected by means of liquid nitrogen in 3-mm tubes M and M', which were attached to the vacuum system by means of ground

joints O and O'. The tubes were sealed at N and N', weighed, and the contents analyzed in the mass spectrometer.

Fraction V_{pyr} , volatile at the temperature of pyrolysis but not at room temperature, deposited during pyrolysis as a yellowish tarry material in the quartz tube B just outside the heater. It was dissolved in methanol, transferred into a weighing bottle, the solvent evaporated, and the tarry material was then weighed.

The nonvolatile residue remaining in tube A was weighed in a weighing bottle. The total recovery weight of the products volatilized in each pyrolysis experiment was within a few tenths of a milligram of the loss in weight of the original dry sample. All weighings were made on a semimicro balance.

3.2. Results of Pyrolysis

Results of pyrolysis experiments are shown in table 1. Experiments 2a to 2g, inclusive, were carried out in consecutive steps on the same specimen

TABLE 1. *Pyrolysis of cellulose in a vacuum*

Experiment	Temperature	Weight of sample	Duration		Volatilization		Volatile fractions, of total volatilized part, for step			
			For step	Cumulative	For step	Cumulative	V _{pyr} (Tar)	V ₂₅ (H ₂ O)	V ₋₈₀ (CO ₂)	V ₋₁₉₀ (CO)
COTTON										
1	250	49.1	300	300	2.7	2.7	26.3	53.9	12.0	7.8
2a	280	83.3	38	38	3.3	3.3	33.9	50.7	10.5	4.9
2b	280	83.3	58	96	7.0	10.3	55.9	36.1	6.0	2.0
2c	280	83.3	53	149	9.1	19.4	63.8	29.6	5.4	1.2
2d	280	83.3	100	249	15.9	35.3	-----	-----	-----	-----
2e	280	83.3	77	326	9.8	45.1	70.2	23.6	4.7	1.5
2f	280	83.3	180	506	16.7	61.8	-----	-----	-----	-----
2g	280	83.3	155	661	7.8	69.6	70.8	21.9	5.5	1.8
3	321	39.5	9	9	22.0	22.0	65.2	28.2	4.3	2.3
4	397	13.8	159	159	91.4	91.4	69.6	22.5	6.2	1.7
HYDROCELLULOSE										
5a	280	80.0	35	35	4.3	4.3	40.6	49.7	6.7	3.0
5b	280	80.0	86	121	8.1	12.4	59.0	32.3	6.9	1.8
5c	280	80.0	72	193	9.3	21.7	62.4	31.5	4.7	1.4
5d	280	80.0	130	323	17.3	39.0	-----	-----	-----	-----
5e	280	80.0	120	443	13.1	52.1	73.7	20.9	4.0	1.4
5f	280	80.0	185	628	13.5	65.6	76.7	18.0	3.7	1.6
VISCOSE RAYON										
6a	280	85.6	7	7	3.3	3.3	19.6	61.7	11.7	7.0
6b	280	85.6	19	26	3.7	7.0	24.4	59.1	10.5	6.0
6c	280	85.6	22	48	5.3	12.3	39.5	48.4	8.7	3.4
6d	280	85.6	24	72	6.2	18.5	51.8	37.9	7.8	2.5
6e	280	85.6	65	137	16.3	34.8	-----	-----	-----	-----
6f	280	85.6	32	169	6.2	41.0	52.6	37.1	8.1	2.2
7	295	12.5	57	57	45.3	45.3	48.2	40.8	7.8	3.2
COTTON IMPREGNATED WITH Na ₂ CO ₃ (7%)										
8a	251	10.0	180	180	36.8	36.8	6.1	61.0	19.6	13.3
8b	291	10.0	30	a 210	14.6	51.4	15.3	54.6	22.7	7.4
COTTON IMPREGNATED WITH NaCl (8%)										
9	280	7.1	120	120	49.3	49.3	12.2	59.3	14.9	13.6

^a Cotton impregnated with Na_2CO_3 degraded initially so fast that it was not convenient to start experiment at 291° C. Instead, the sample was first heated for 180 min at 251°, with a resulting loss of 36.8%; the residue was then heated for another 30 min at 291°, with a further loss of 14.6%. Total loss in weight was 51.4%.

of cotton. Similarly, experiments 5a to 5f, inclusive, were carried out on the same specimen of hydrocellulose, and experiments 6a to 6f on the same specimen of viscose rayon. These three series of experiments were carried out at 280° C. A sample of cotton impregnated with Na₂CO₃ (7%)⁶ was pyrolyzed in two consecutive steps, at 251° and 291° C. A sample of cotton impregnated with NaCl (8%) was pyrolyzed in one step at 280° C. Fractions V₂₅, on mass-spectrometer analysis, were found to consist mainly of water mixed with a small amount of acetaldehyde, as is shown later. Fractions V₋₈₀ and V₋₁₉₀, also on mass-spectrometer analysis, were found to consist of CO₂ and CO, respectively. According to table 1, cotton and hydrocellulose behaved similarly on pyrolysis, whereas viscose rayon yielded more H₂O, CO₂, and CO, and less tar, than the first two cellulosic materials. The addition of NaCl or Na₂CO₃ had the effect of increasing the yields of H₂O, CO₂, and CO, and decreasing the yield of tar.

In table 2 cumulative yields of fractions are shown for 280° C (except in the case of purified cotton impregnated with Na₂CO₃, where the initial rate of degradation was so fast that the first 37% volatilization was carried out at 251° C and an additional 14% at 291° C). The data shown in table 2 were

⁶ The weight of the Na₂CO₃ was 7 percent of that of the dry cotton.

TABLE 2. Volatile fractions obtained in the pyrolysis of cellulose

Sample	Temperature	Time	Volatilization	Cumulative volatiles in the fractions ^a			
				V _{pyr} (tar)	V ₂₅ (H ₂ O)	V ₋₈₀ (CO ₂)	V ₋₁₉₀ (CO)
Cotton.....	° C	min	%	%	%	%	%
Hydrocellulose.....	280	661	70	65	27	6	2
Viscose rayon.....	280	628	66	66	27	5	2
Cotton impregnated with Na ₂ CO ₃ (7%) ^b	280	169	41	45	43	9	3
Cotton impregnated with NaCl (8%)	251	180	37	9	59	21	11
	291	30	14				
Cotton impregnated with NaCl (8%)	280	120	49	12	59	15	14

^a In percentage of total volatiles.

^b See footnote, table 1.

TABLE 3. Effect of temperature on yield of fractions in the pyrolysis of cellulose

Material	Experiment	Temperature	Volatilization, cumulative	Volatile fractions of total volatilized part			
				V _{pyr} (tar)	V ₂₅ (H ₂ O)	V ₋₈₀ (CO ₂)	V ₋₁₉₀ (CO)
Cotton.....	1	° C	%	%	%	%	%
	2a	250	2.7	26	54	12	8
	2a to 2c	280	3.3	34	51	10	5
	3	321	19.4	64	30	5	1
Viscose rayon.....	6a to 6f	280	41.0	53	37	8	2
	7	295	45.3	48	41	8	3

calculated on the basis of the data in table 1, interpolating where necessary.

The temperature effect on yields of the various fractions is shown in table 3, where a comparison is made of results obtained at different temperatures, but for about the same extent of degradation. According to this table the temperature effect through a range of about 250° to 321° C is not pronounced.

4. Analysis of Fractions

4.1. Mass Spectrometer Analysis

Mass-spectrometer analysis of fractions V₋₁₉₀ and V₋₈₀ showed them to consist of CO and CO₂, respectively. Similar analysis for fraction V₂₅, as shown in table 4, indicates that water is the main

TABLE 4. Mass-spectrometer analysis of fraction V₂₅

Component	Viscose rayon ^a		Cotton impregnated with NaCl (8%)	Cotton impregnated with Na ₂ CO ₃ (7%)	
	1	2		1	2
Water.....	Mole %	Mole %	Mole %	Mole %	Mole %
Acetaldehyde.....	84	92	97	97	91
	16	8	3	3	9

^a Analyses 1 and 2, in the case of viscose rayon, were made of fractions V₂₅ from experiments 6a and 7 (table 1); in the case of cotton impregnated with Na₂CO₃ (7%), analyses 1 and 2 were made of fractions V₂₅ from experiments 8a and 8b, respectively (table 1).

constituent. The only other constituent is acetaldehyde, which appears in amounts varying from 3 to 16 percent. The reason for this variation is not apparent from the present limited data.

Analysis of fraction V_{pyr} (tar) was performed by Bradt and Mohler in a 60° Nier mass spectrometer, using a method that they have developed [7]. The sample was heated in a vacuum-tube furnace that opened directly into the ionization chamber, and the temperature was increased step by step until there was no further evaporation. Mass spectra were recorded at each step. In addition to fraction V_{pyr}, these investigators also vaporized or pyrolyzed directly into the mass spectrometer filter paper, purified cotton, viscose rayon, cellobiose, and levoglucosan. There are no background patterns of pure compounds available for mass-spectrometer analysis of these substances, and the conclusions drawn on the basis of the mass spectra obtained must therefore be considered as tentative.⁷

Filter paper, cotton, and viscose rayon gave similar mass spectra. When heated above 100° C there was some evolution of H₂O, CO₂, and CO. At 240° and higher, a rather complicated mass spectrum extending to mass 144 appeared. Cellobiose appeared to degrade at 250° C, and the

⁷ The authors are indebted to P. Bradt and F. L. Mohler of the Mass Spectrometry Section of the Bureau for performing these analyses and for interpreting the results.

spectrum showed small peaks, indicating masses heavier than 144. Its spectrum was much like those of the cellulosic materials.

Levoglucosan evaporated in a narrow temperature range at about 130° C. Its mass spectrum showed peaks corresponding to H₂O, CO₂, and CO. These peaks were rather small as compared with those that were obtained for the celluloses.

The mass spectra obtained for fraction V_{pyr} (tar) from cotton and viscose rayon were similar. At an evaporation temperature of about 130° C, these spectra were almost identical with that from levoglucosan. However, there was in the tar a compound that was less volatile than levoglucosan and that degraded at higher temperatures to give a spectrum more like the product obtained from direct pyrolysis of cellulose into the mass spectrometer. It may be significant that all the spectra, whether from cellulose, levoglucosan, or tar, contained peaks for masses 126 and 144. These masses correspond to that of levoglucosan or of the cellulose structural unit, molecular weight 162, with 2 and 1 molecules of water, respectively, split off.

4.2. Infrared Analysis of Fraction V_{pyr}

Samples of pure levoglucosan and of fraction V_{pyr} (tar) from cotton were dissolved in methanol. Thin films were deposited on rock salt by evaporating the solvent, and infrared absorption spectra of the resulting films were obtained. As shown in figure 2,⁸ the only significant difference between the two spectra is the presence of an absorption band at 5.78 microns in the spectrum of fraction V_{pyr} (tar). This suggests that fraction V_{pyr} contained both levoglucosan and a compound that contains C=O groups.

⁸ The authors are indebted to Florence H. Forziati and Robert M. Brownell of the Textiles Section of the Bureau, for performing these infrared absorption analyses and for interpreting the results.

4.3. Average Molecular Weight of Fraction V_{pyr}

The average molecular weight of fraction V_{pyr} (tar) from cotton was determined by a microfreezing-point lowering method from a solution in phenol. Four determinations were made on this fraction and four on pure levoglucosan as a control. The molecular freezing-point lowering for phenol is given in the literature as 7.3° C. Sufficient sample was used in each determination to give a freezing-point depression of approximately 3° C. The molecular weight of levoglucosan was found to be 166±2 as compared with 162 theoretical. The average molecular weight of fraction V_{pyr} was found to be 152±1.

5. Rates of Degradation and Activation Energies

5.1. Rate Measurements in a Spring Balance

The rates of thermal degradation of cellulosic materials were determined by means of a very sensitive tungsten spring balance enclosed in a Pyrex housing, which could be evacuated to about 10⁻⁵ mm Hg. This apparatus and the method have been described previously [6] in connection with a study of the thermal degradation of a number of polymers. The method, briefly, consists in heating a sample of about 4 to 6 mg in a crucible suspended from the tungsten spring, and recording at regular intervals the loss in weight of the sample due to pyrolysis and evaporation, as indicated by a change in position of a crossline on a wire extension of the spring.

In preparing for a rate experiment the crucible containing the sample was suspended from the tungsten spring into a tube projecting down from the vacuum apparatus. The apparatus was pumped to a vacuum of approximately 10⁻⁶ mm Hg and left standing. In the meantime an electric furnace, kept in a position away from the projected tube, was heated overnight to the temperature required for the given experiment. In the morning the furnace was

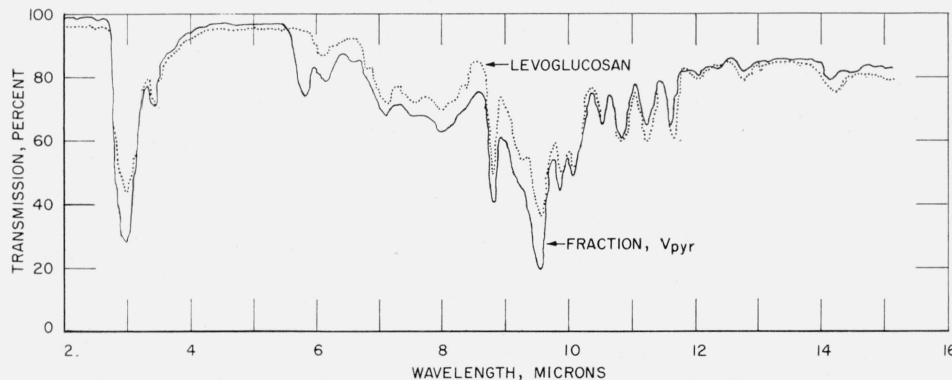


FIGURE 2. Infrared absorption spectra of the tarry fraction V_{pyr} and of levoglucosan.

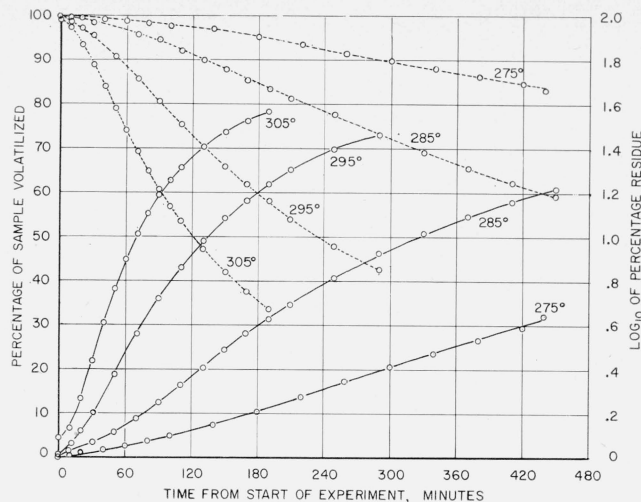


FIGURE 3. Thermal degradation of cotton.

—, percentage of sample volatilized versus time; ----, \log_{10} of percentage residue versus time.

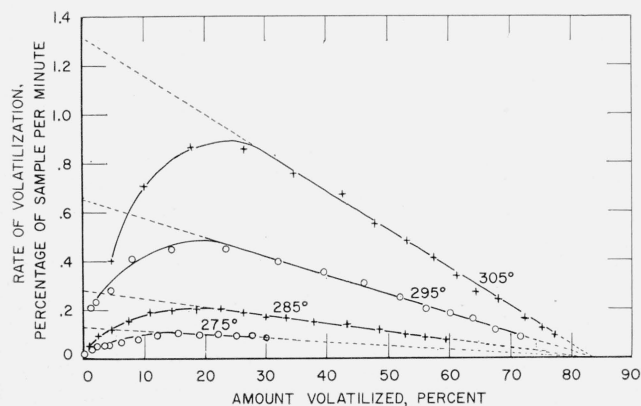


FIGURE 4. Rates of volatilization of cotton, in percentage of sample per minute, as a function of percentage volatilization (K_1 rates).

Dotted lines represent extrapolations of the rate curves.

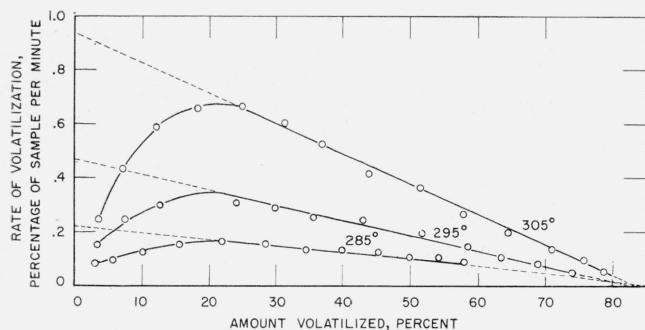


FIGURE 5. Rates of volatilization of hydrocellulose, in percent of sample per minute, as a function of percentage volatilization.

Dotted lines represent extrapolations of the rate curves.

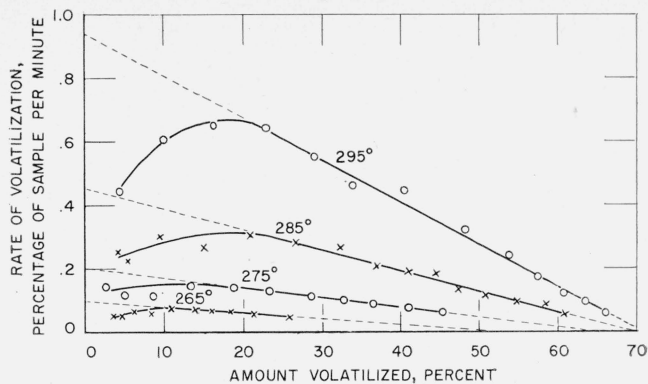


FIGURE 6. Rates of volatilization of viscose rayon, in percent of sample per minute, as a function of percentage volatilization.

Dotted lines represent extrapolations of the rate curves.

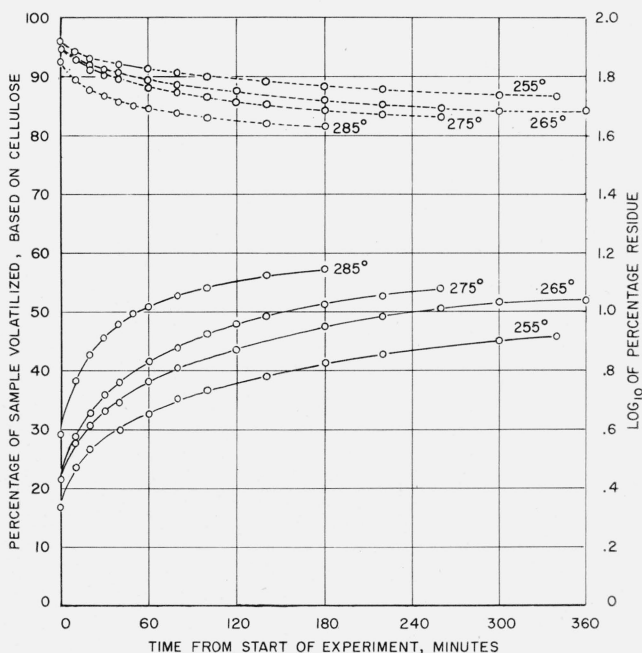


FIGURE 7. Thermal degradation of cotton impregnated with Na_2CO_3 (9%).

—, percentage of sample volatilized versus time; ----, \log_{10} of percentage residue versus time.

raised into position around the sample. It ordinarily took about 15 min for the crucible to reach the required temperature. Duration of the experiment was counted from the time this temperature was reached. The temperature was controlled by means of an electronic thermostat to within ± 0.2 deg C.

The results of rate experiments on cotton are shown in figures 3 and 4. The rates, K_1 , in percentage of the original dried cellulose per minute, are initially low and pass through maxima, beyond

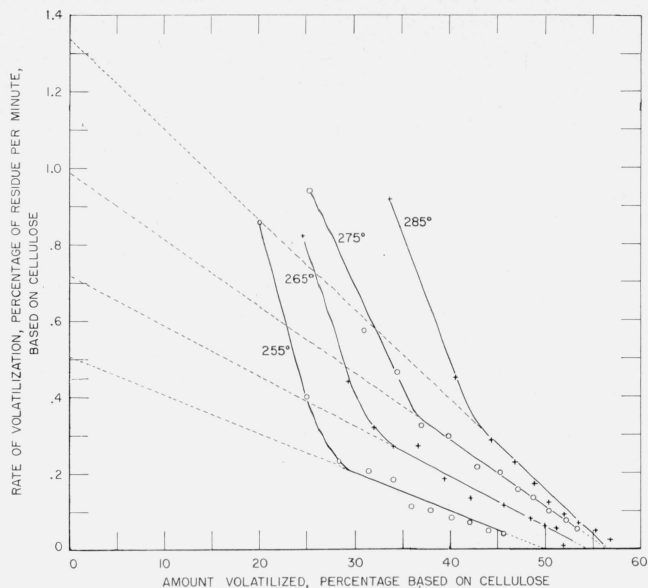


FIGURE 8. Rates of volatilization of cotton impregnated with Na_2CO_3 (9%), in percentage of cellulosic residue per minute, as a function of percentage volatilization (K_2 rates).

Dotted lines represent extrapolations of the rate curves.

which they follow straight lines. The points at which extrapolations of these lines intersect with the abscissas are defined as carbonization end points expressed in percentage of volatilization. The char yield, in percent of sample, for any particular temperature can be obtained by subtracting the carbonization end point from 100. By extrapolating the straight parts of the K_1 rate curves to the ordinate, the apparent initial rates were obtained. The importance of these apparent initial rates lies in the fact that the samples have the same composition only at zero degradation, and these rates can thus be used for the purpose of comparison or for calculating activation energies.

The curves obtained by plotting percentage of sample volatilized and logarithm of percentage residue against time for hydrocellulose and viscose rayon, were similar to the curves obtained for cotton, figure 2, and are not shown here. The K_1 rate of volatilization curves for hydrocellulose and viscose rayon are shown in figures 5 and 6, respectively. The apparent initial K_1 rates and the carbonization end points for hydrocellulose and viscose rayon were obtained by extrapolation, as in the case of cotton.

Results of rate experiments on cotton impregnated with Na_2CO_3 (9%) are shown in figures 7 and 8. The thermal stability of the cotton was greatly reduced as a result of the admixture with sodium carbonate. This reduction in stability was particularly great for the initial stages of the degradation. In the 15-min interval during which the cotton was raised from room temperature to the desired tem-

perature, about 18 to 30 percent of the cotton volatilized, depending upon the final temperature.

The rate curves for Na_2CO_3 -impregnated cotton are shown in figure 8. In this case the rates were expressed in percentages of residues existing at the instant (excluding Na_2CO_3) instead of percentages of the original samples and are designated as K_2 rates. This was done for the reason that the K_2 plots are straight lines beyond 30 to 40 percent volatilization, while the K_1 plots are curved through their whole extent. Extrapolated initial rates are the same whether they are obtained from K_1 or K_2 rate curves.

The plots showing percentage volatilization versus time and logarithm of percentage residue versus time for viscose rayon impregnated with Na_2CO_3 (9%) and cotton impregnated with NaCl (9%) are not shown here. These plots were similar to the corresponding plots for cotton impregnated with Na_2CO_3 (9%), shown in figure 7. The K_2 rate curves for viscose rayon impregnated with Na_2CO_3 and cotton impregnated with NaCl are shown in figures 9 and 10, respectively. The straight parts of the K_2 plots in figures 9 and 10 were extrapolated to obtain the apparent initial rates and the carbonization end points. In all cases, the plots of logarithm of residue versus percentage volatilization (shown in figs. 3 and 7 as dotted lines), were not straight lines, indicating that the over-all degradation reaction is not of first order.

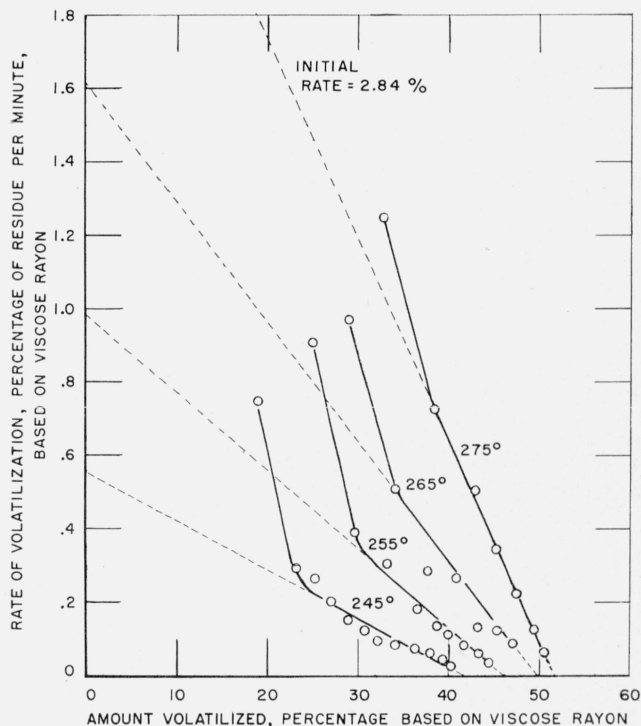


FIGURE 9. Rates of volatilization of viscose rayon impregnated with Na_2CO_3 (9%), in percentage of cellulosic residue per minute, as a function of percentage volatilization.

Dotted lines represent extrapolations of the rate curves.

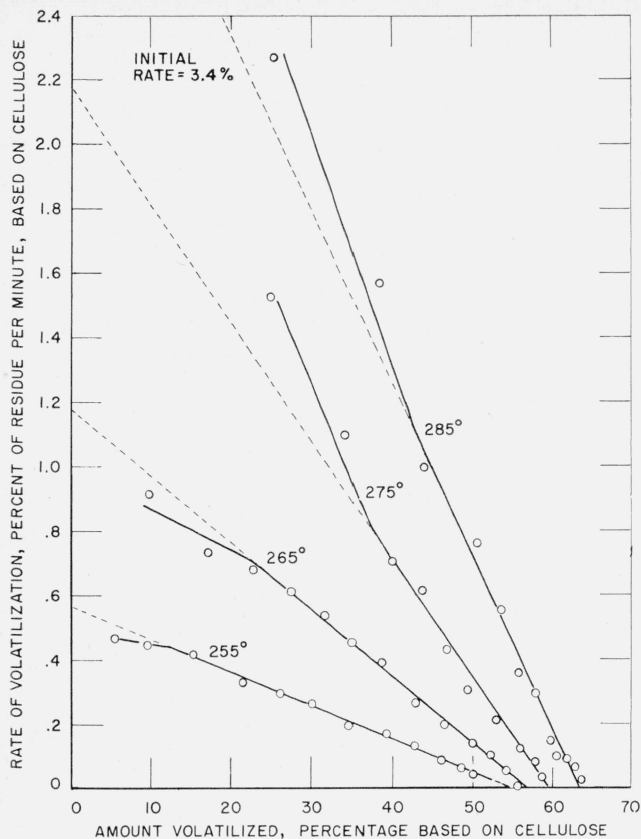


FIGURE 10. Rates of volatilization of cotton impregnated with NaCl (9%), in percentage of cellulosic residue per minute, as a function of percentage volatilization.

Dotted lines represent extrapolations of the rate curves.

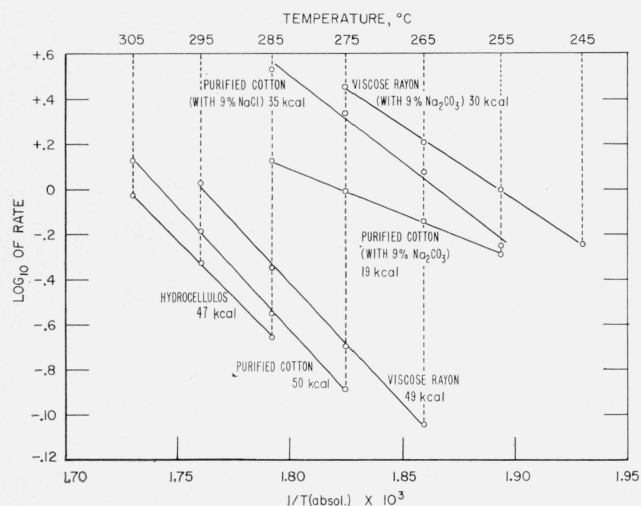


FIGURE 11. Activation energy of thermal degradation of cellulosic materials, based on extrapolated initial rates.

TABLE 5. Rates of thermal degradation of cellulose samples

Temperature	Heating duration	Loss of weight ^a	Apparent initial rate	Carbonization end point	Activation energy
COTTON					
$^{\circ}C$	<i>min</i>	<i>%</i>	<i>%/min</i>	<i>%</i>	<i>kcal/mole</i>
275	440	32	0.13	79	50
285	450	61	.28	81	
295	290	73	.65	82	
305	190	78	1.34	83	
HYDROCELLULOSE					
285	460	60	0.22	82	47
295	460	76	.47	82	
305	290	80	.94	83	
VISCOSE RAYON					
265	460	27	0.09	51	49
275	440	46	.20	64	
285	360	62	.45	69	
295	240	67	.94	71	
COTTON IMPREGNATED WITH Na ₂ CO ₃ (9%)					
255	340	46	0.51	49	19
265	360	52	.72	54	
275	260	54	.98	56	
285	180	57	1.34	57	
VISCOSE RAYON IMPREGNATED WITH Na ₂ CO ₃ (9%)					
245	300	41	0.55	42	30
255	220	45	.99	46	
265	140	48	1.61	50	
275	120	51	2.84	52	
COTTON IMPREGNATED WITH NaCl (9%)					
255	420	51	0.56	55	35
265	340	56	1.18	57	
275	240	59	2.18	60	
285	240	64	3.40	64	

^a Referred to dry cellulose.

Pertinent data on all the rate experiments by the loss-of-weight method in the tungsten-spring apparatus, are shown in table 5. The activation energies are shown in the last column of this table. These activation energies were obtained graphically, as shown in figure 11, by plotting the \log_{10} of the apparent initial rate at any given temperature versus $1/T \times 10^3$, where T is the absolute temperature. The over-all activation energy, E , in kilocalories per mole, is the slope of the straight line, obtained from the formula

$$E = -\frac{d \log K}{d(1/T)} \times 4.57 \times 10^{-3}.$$

A comparison of initial rates for all the materials investigated is given in table 6 for 275° and 285° C, the two temperatures at which the most complete data were obtained. Table 7 gives a condensed summary of data showing the effect of additions of Na₂CO₃ and NaCl on the yield of flammable and nonflammable fractions in the pyrolysis of cellulosic materials in a vacuum.

TABLE 6. Comparison of rates of thermal degradation of cellulose samples at 275° and 285° C

Sample	Initial rates, in percent of sample per min, at—	
	275°	285°
Cotton	0.13	0.28
Hydrocellulose	^a .10	.22
Viscose rayon	.20	.45
Cotton impregnated with Na ₂ CO ₃ (9%)	.98	1.34
Viscose rayon impregnated with Na ₂ CO ₃ (9%)	2.84	^a 5.48
Cotton impregnated with NaCl (9%)	2.18	3.40

^a Calculated on the basis of activation energy.

TABLE 7. Flammable and nonflammable volatile products and char obtained in the vacuum pyrolysis of cellulose materials (temperature of pyrolysis, 280° C)

Material	Flammable			Nonflammable			Char ^a
	Tar	CO	Total	H ₂ O	CO ₂	Total	
	%	%	%	%	%	%	%
Cotton	52	2	54	21	5	26	20
Hydrocellulose	53	2	55	21	4	25	20
Viscose rayon	30	2	32	29	6	35	33
Cotton impregnated with Na ₂ CO ₃ ^b	5	6	11	33	12	45	44
Cotton impregnated with NaCl	7	9	16	37	9	46	38

^a Since the carbonization end points were not determined experimentally at 280° C, the char values for this temperature were estimated from figures 4, 5, 6, 8, and 10.

^b Residue from pyrolysis for 180 min at 251° was pyrolyzed further for 30 min at 291°. Volatilization in the second step was from 36.8% (volatilized in the first step) to 51.4%, i. e., 14.6% (see table 1).

5.2. Rates Calculated from Pyrolysis Data

The data obtained in the step pyrolysis experiments at 280° C, shown in table 1, for cotton, hydrocellulose, and viscose rayon, were used in calculating the rates of volatilization in terms of averages for each individual step. Because in the pyrolysis experiments the degradation products were collected, weighed, and analyzed, it was possible to calculate rates of volatilization for each fraction, as well as for the total volatiles. These rates are shown plotted against percentage volatilization at 280° C in figures 12, 13, 14, and 15, for fractions V_{pyr}, V₂₅, V₋₈₀, and

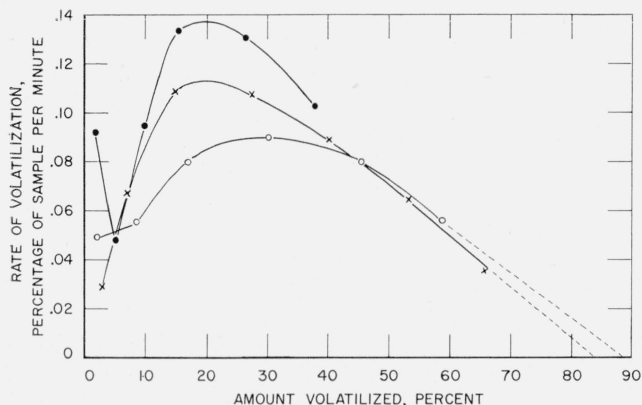


FIGURE 12. Rates of volatilization at 280° C calculated from pyrolysis data.

Rates of volatilization of the tarry fraction V_{pyr}, in percent of sample per minute, as a function of percentage volatilization for: ●, viscose rayon; ×, cotton; and ○, hydrocellulose.

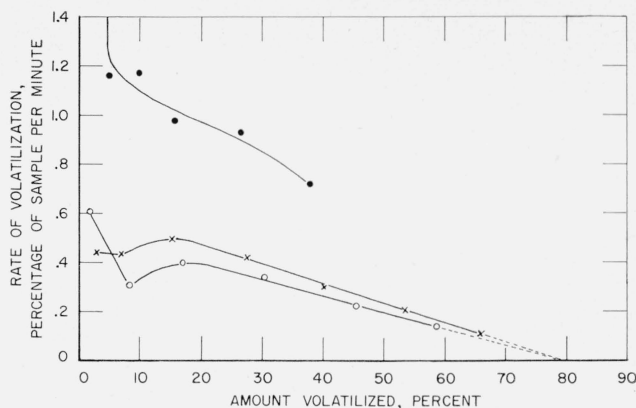


FIGURE 13. Rates of volatilization at 280° C calculated from pyrolysis data.

Rates of volatilization of fraction V₂₅, in percentage of sample per minute, as a function of percentage volatilization, for: ●, viscose rayon; ×, cotton; and ○, hydrocellulose.

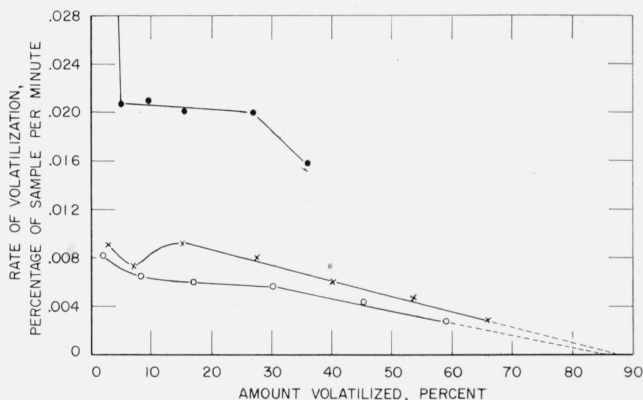


FIGURE 14. Rates of volatilization at 280° C calculated from pyrolysis data.

Rates of volatilization of fraction V₋₈₀, in percentage of sample per minute, as a function of percentage volatilization, for: ●, viscose rayon; ×, cotton; and ○, hydrocellulose.

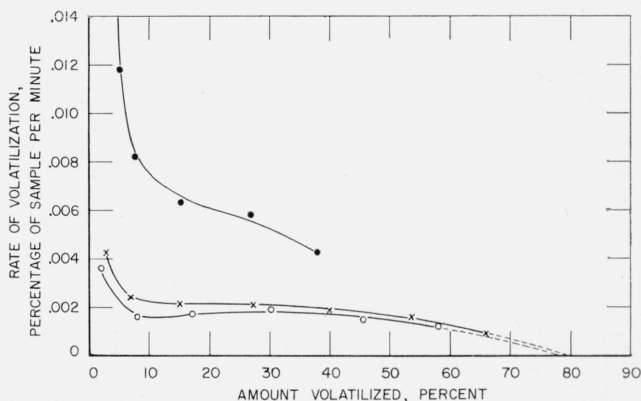


FIGURE 15. Rates of volatilization at 280° C, calculated from pyrolysis data.

Rates of volatilization of fraction V₋₁₀₀, in percentage of sample per minute, as a function of percentage volatilization, for: ●, viscose rayon; ×, cotton; and ○, hydrocellulose.

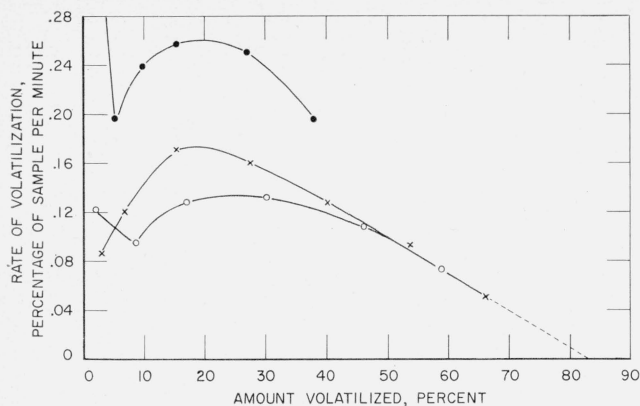


FIGURE 16. Rates of volatilization at 280° C, calculated from pyrolysis data.

Over-all rates of volatilization, in percentage of sample per minute, as a function of percentage volatilization, for: ●, viscose rayon; ×, cotton, and ○, hydrocellulose.

V_{-190} , respectively, and in figure 16 for the total volatiles. The rates shown in figure 16 do not differ much from the K_1 rates determined in the spring-balance apparatus and shown in figures 4, 5, and 6. Extrapolation of the rate curves for cotton and hydrocellulose in figures 12, 13, 14, 15, and 16 leads to similar carbonization end points as were found in the spring-balance rate experiments. In the case of viscose rayon, where pyrolysis at 280° C was carried only to 41 percent volatilization, the carbonization end point is not shown.

6. Discussion

Although the cotton used in this work had a lower crystallinity and higher degree of polymerization than the hydrocellulose, there is little difference in their behavior on pyrolysis, whether in regard to ratio of products or to rates of degradation. The crystalline forces seem to weaken at the pyrolysis temperature, and, therefore, have little effect on the results of pyrolysis. As to the effect of chain length, it was shown previously [8] in the case of a number of polymers that long chains break up on heating during the initial stage of thermal degradation, even before volatilization occurs. This tends to eliminate the effect of chain length on pyrolysis, except where polymers of very low degree of polymerization are involved. Viscose rayon has low crystallinity and low degree of polymerization, and the type of its crystalline structure is different from that of cotton and hydrocellulose. Results of pyrolysis of viscose rayon indicate a lower yield of tar, a higher yield of H_2O , CO_2 , and CO , and a faster rate of degradation than is the case with cotton and hydrocellulose. Further work will be required to determine the causes of the differences observed.

The presence of Na_2CO_3 or $NaCl$ in intimate contact with the cellulose has a profound effect on the

results of pyrolysis of cellulose. The tar yield is drastically reduced whereas the yield of H_2O , CO_2 , and CO is increased. Although the actual initial rates in the case of pure substances are low, rising to a maximum at about 15 to 20 percent volatilization, these rates in the presence of Na_2CO_3 and $NaCl$ start extremely fast and do not show any maxima. The apparent initial rates are also much higher in the presence of the salts than is the case with the untreated substances.

As shown in table 7, the char yield is about the same for cotton and hydrocellulose. In the presence of salts, the char yield is about doubled. In the case of viscose rayon the char yield is about 1.5 times as much as in cotton or hydrocellulose.

In the pyrolysis of untreated celluloses, up to about 20 percent volatilization, the yield of tar rises gradually, whereas the reverse is true of the yields of H_2O , CO_2 , and CO . Beyond about 20 percent volatilization the yields are stabilized and reach constant values. The data are insufficient to show whether the same is true with regard to the salt-impregnated celluloses.

Mass-spectrometer, infrared, and cryoscopic analysis of fraction V_{pyr} , all point to the conclusion that this fraction consists mainly of levoglucosan. However, there are definite indications that there is present in fraction V_{pyr} , in addition to levoglucosan, some small amount of other compound or compounds. These indications are: (1) a small part of fraction V_{pyr} is insoluble in H_2O , although all of it is soluble in methanol; (2) the infrared absorption spectrum of fraction V_{pyr} differs from that of levoglucosan in having an absorption band at 5.78μ ; (3) there are some differences in the mass spectra of fraction V_{pyr} and levoglucosan.

As shown in table 7, the yield of fraction V_{pyr} (tar) is 52 percent and 53 percent for cotton and hydrocellulose, respectively. This means that approximately 1 out of every 2 structural units in these celluloses vaporizes as a levoglucosan molecule. In viscose rayon, which yields 30 percent tar, approximately 1 out of every 3 structural units appears in the distillate as levoglucosan. The next largest volatile fraction is H_2O , which amounts to 21 percent for cotton and hydrocellulose, and 29 percent for viscose rayon. After discounting the hydrogen and oxygen that vaporize from cellulose as parts of levoglucosan, the highest possible theoretical yield of H_2O from the other cellulose structural units would be 27 percent from cotton and hydrocellulose and 37 percent from viscose rayon. The difference between the theoretical and actual yield of H_2O in the pyrolysis of the celluloses is accounted for by the formation of CO_2 and CO , and by the presence of H and O in the char. That the chars obtained at the carbonization end points at 280° C (20% for cotton or cellulose and 33% for viscose rayon, as given in table 7) contained volatile material was shown by experiments in which these chars were

heated in a quartz tube in a vacuum by means of a Meker burner to about 1,000° C. The loss in weight of the chars was roughly one-half for all the three celluloses.

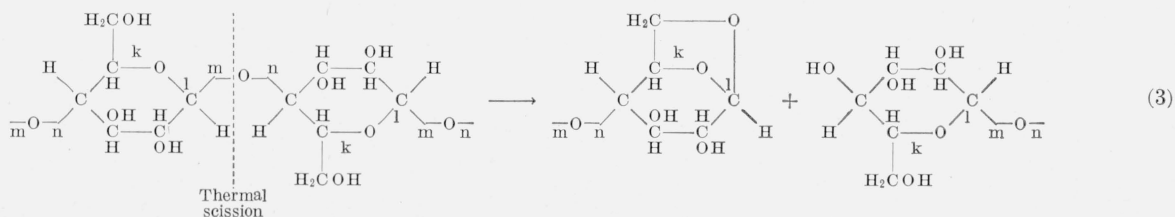
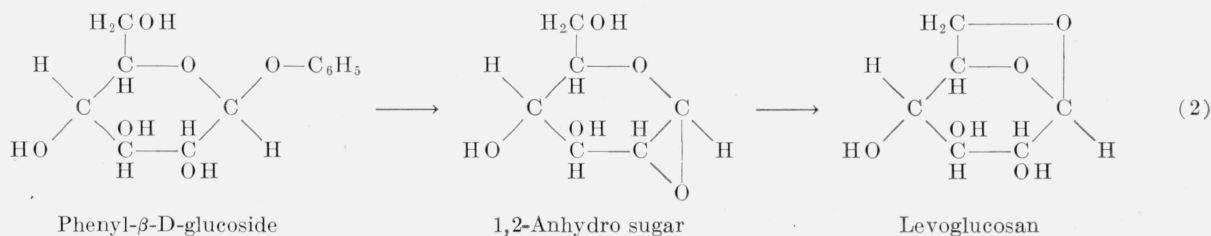
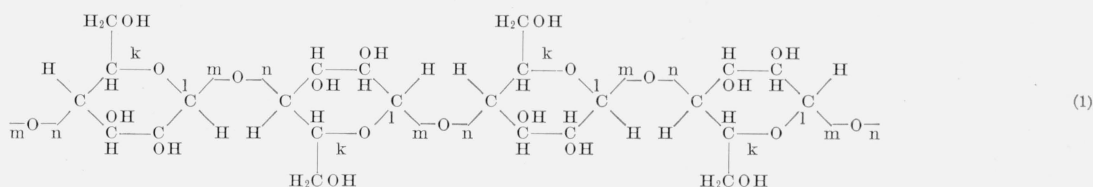
The results of pyrolysis suggest the following possible mechanism for the thermal degradation of cellulose in a vacuum. A dehydration process takes place randomly along the chain. Another process, which takes place simultaneously, consists in thermal scissions of the polymer chain resulting in the formation of levoglucosan, H₂O, CO₂, and CO. The C—O bonds in the chain are less stable thermally than the C—C bonds. This was shown by the present authors in a series of experiments on the pyrolysis of polyethylene, and polyethylene oxide. The polyethylene oxide was found to have a lower thermal stability and a lower activation energy of thermal degradation than polyethylene. The various C—O bonds in the chain are indicated in the structural formula (1) of the polymer as k, l, m, and n.

Random scissions of bonds k, l, or n result in a more or less complete breakdown of a part of the chain, yielding H₂O, CO₂, CO, and C. A random scission of

the C—O m bond may result in the formation of an oxygen linkage between carbons 1 and 6 by a process analogous to the formation of levoglucosan from phenyl-β-D-glucoside. McCloskey and Coleman [9] have shown in formula (2) that this reaction takes place in two steps.

Whether in the pyrolysis of cellulose this process takes place in one step [10], formula (3), or in two steps, is problematical. Pyrolysis is unlike hydrolysis in an aqueous alkaline medium and a close analogy between the two reactions is not justified. The formation of levoglucosan units in cellulose pyrolysis takes place when scission of the C—O m bonds occur one structural unit away from the ends formed through a random scission of a C—O m bond.

The presence of Na₂CO₃ and NaCl may have a catalytic effect on the dehydration and bond scissions taking place inside and outside the rings in the cellulose chain, resulting in increased yield of H₂O, CO₂, and CO at the expense of levoglucosan, and also in an increased rate of degradation of the celluloses, particularly in the initial stages.



7. References

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