Pyrolysis of Untreated and APO-THPC Treated Cotton Cellulose During One-Second Exposure to Radiant Flux Levels of 5-25 cal./cm.²-sec.

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INTRODUCTION AND BACKGROUND

The mechanism of degradation of polymers under conditions of high thermal stress is of basic interest for the understanding of bond strengths and molecular structure, and of practical importance for the development of flame-resistant clothing, re-entry vehicles, and solid propellant binders. The pyrolytic decomposition of cellulose is of particular concern due to the widespread use of cotton as a clothing material.   The investigation reported here was undertaken to elucidate the mechanism of thermal degradation of untreated and APO-THPC flame-retardant treated cotton cellulose during 1-sec. exposures to thermal flux levels of 5-25 cal./cm.²-sec. The work constituted one aspect of a Quartermaster Corps program aimed at the development of summer weight clothing that would provide adequate protection from the thermal effects of nuclear weapons.

Prior work on the thermal decomposition of cellulose includes both isothermal degradation studies at temperatures between 200 and 375°C. for times of 9 to 360 min., and degradation studies under millisecond flash illuminations of 430 cal./cm.²-sec.   Our experimental conditions lie between the two extremes.   Heating times were of the order of seconds, and the heat source was a carbon arc or solar furnace that delivers radiant energy of 5-25 cal./cm.²-sec., primarily in the visible.

Studies of the pyrolytic degradation of untreated cellulose in the 200-375°C. region were conducted in 1954-57 by Pascu and Schwenker,[1] and more recently by Madorsky, Hart, and Strauss.[2]   Similar investigations of untreated and flame retardant treated cottons have been reported by Holmes and Shaw.[3]   All three groups heated their samples in Pyrex tubes surrounded by electrical resistance furnaces.   Pascu and Schwenker pyrolyzed in an air stream moving at 500-900 cm./min., collected products condensable at 0°C. in cold traps, and analyzed them chemically.   Mador-

sky's group pyrolyzed in vacuum, separated the products into five fractions
by a series of cold traps, and analyzed each fraction by mass and infrared
spectroscopy. Holmes and Shaw used an experimental arrangement sim-
ilar to Madorsky's and analyzed the products by infrared and wet-chemical
analysis. Our samples were heated in a helium stream by a radiant source,
and the products were separated into four fractions that were analyzed by
vapor phase chromatography and infrared spectroscopy.

The picture of cellulose pyrolysis developed from the low-temperature
studies[1,2] is that the cellulose molecule polymerizes with scission of the 1,4-
glycosidic C—O bonds, and that the fragments undergo an intramolecular
rearrangement to levoglucosan.

Pascu and Schwenker believe that levoglucosan then participates in two
competing reactions: (1) polymerization and aromatization to form char,
and (2) destructive distillation to tars, volatile gases, and water.

Madorsky's group favors random scissions of C—O bonds and simultane-
ous dehydration along the cellulose chain. Thus, neither the char, tars,
volatiles, nor water need necessarily form exclusively from a levoglucosan
intermediate. On the other hand, Madorsky did find that the pyrolysis
mechanism seemed to be independent of the degree of crystallinity and the
degree of polymerization of the cellulose. To explain this result, he pos-
tulated that the application of heat tends to break up long chains prior to
volatilization. It is perfectly reasonable to suppose that levoglucosan is
the principal product in this early depolymerization stage and that, there-
fore, a large percentage of the volatile products originate from this inter-
mediate.

The effect of the APO-THPC flame retardant on the long-time, low tem-
perature pyrolysis of cellulose[3,4] is to increase the percentage of solid char
and to decrease the percentage of tar in the total product yield. In addi-
tion, the flame retardant accelerates the rate of formation of volatile prod-
ucts.[4]

The high-intensity millisecond flash pyrolysis of untreated cellulose was
studied by Nelson and Lundberg.[5] Homogeneous photolysis in their ex-
periments was minor compared to violent heterogeneous decompositions
centered about particulate impurities. However, under their conditions,
all polymers, regardless of composition, behaved in the same way. Frag-
mentary work in identification of decomposition products suggests that
the distribution of species is very different under flash illumination from
what it is under conventional heating conditions. A detailed mechanism
for cellulose pyrolysis was not worked out by the Nelson group, nor was
any attempt made to look for levoglucosan among the products. Exten-
sive studies are in progress, however, in Dr. S. B. Martin's laboratory in
San Francisco.[6]

EXPERIMENTAL

Apparatus

For the experiments described in this report, the very simple pyrolysis
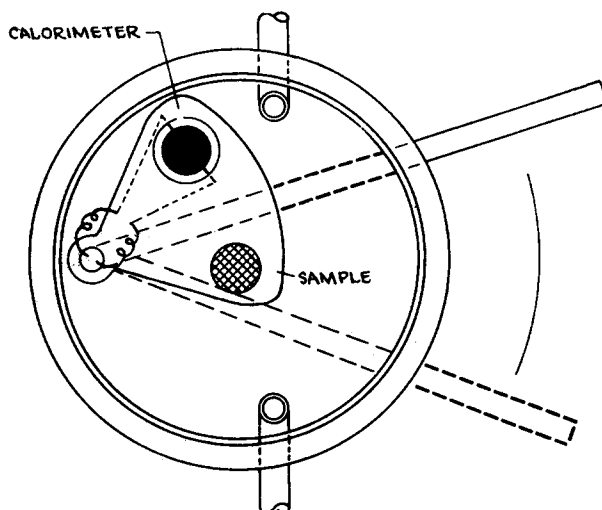cell shown in Figure 1 was constructed in which fabric samples could be

Fig. 1. Pyrolysis cell.

exposed to radiant fluxes of 5–25 cal./cm.^{2}-sec. for periods of 0.5–2 sec. under a controlled atmosphere in an arc imaging or solar furnace. The design is very similar to one that has been reported previously.[7] The sample and calorimeter mount is a Micarta sector with two holes cut in it. In one hole, the sample is held taut by a hoop of spring wire. In the other, a blackened copper disc calorimeter,[8] $1/_2$ in. in diameter, is mounted with iron-Constantan thermocouple wires. The wires are soldered to the rear face of the disc, cemented into slots in the Micarta block, and are fed into a Sanborn recorder for measurement of thermal flux.

The entire assembly is attached to the rear plate of a stainless steel cell, and can be pivoted by means of an outside handle so that either the sample holder or the calorimeter is in position at the center of the cell. An optically-flat quartz plate that clamps onto the stainless steel section through an O-ring completes the pyrolysis chamber.

Figure 2 is a schematic diagram of the flow system into which the pyrolysis cell is incorporated. Helium flows from tank A through a regulating valve B to a pressure gage C. The gas stream diffuses into the reference side D of a thermal conductivity cell and flows past the sample at F. The volatile products of thermal decomposition are swept sequentially through a copper U-tube and a copper coil, both immersed in a mixture of Dry Ice and acetone at G. Gases that fail to condense in the traps impinge upon a chromatography column at K, where the components are separated and allowed to enter the sample side (L) of the thermal conductivity apparatus. A rotameter at M measures the rate of flow of gas through the system. It is possible to by-pass the pyrolysis cell if necessary or desirable by closing valves E and H, and opening valve J. The entire system is mounted in a carbon arc imaging furnace[9] so that the center

of the pyrolysis cell coincides with the focal point of the furnace, and an automatic timing shutter is placed at the cross-over point of the furnace to regulate exposure times.

Procedure

Prior to exposure, samples are weighed, mounted in the sample holder, and positioned in the arc imaging furnace. With a battery-operated flash-light bulb substituted for the arc, and the calorimeter disc at the center of the cell, adjustments are made so that the calorimeter surface is well illuminated. The flow system is pressurized with helium to 20 p.s.i. and sealed off at both B and M in order to test for leaks. Helium is then al-lowed to flow through the by-pass valve, J, with E and H closed, while the pyrolysis cell and traps are simultaneously evacuated through N. Finally, the entire system is purged with helium and the traps are cooled to $-80°C$. with Dry Ice and acetone. The calorimeter is swung into position, and the attenuator of the arc imaging furnace is adjusted until the desired flux, as indicated on the recorder chart, is achieved at the sample plane. The Micarta sector is pivoted to shift the sample into the same position that was previously occupied by the calorimeter, and the fabric is irradiated under identical conditions of radiant flux and exposure time as the copper disc. The carrier-gas flow rate is maintained at about 500 cc./min. during each experiment.
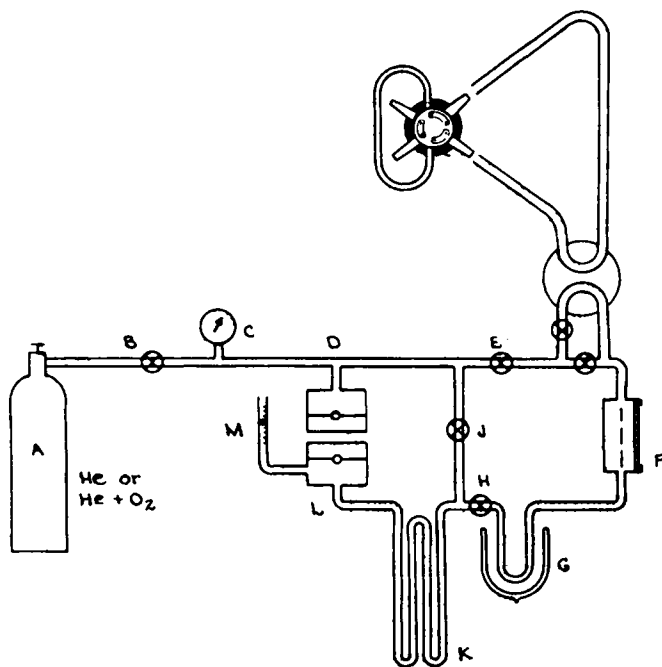

Fig. 2. Pyrolysis system.

The products of pyrolysis are divided naturally into four major fractions that can be analyzed separately. They will be designated in a way that facilitates comparison with previous work. Fraction $(V_{-80} + V_{-190})$ consists of the volatile products that fail to condense at $-80°C$. in the Dry Ice–acetone traps. It is swept onto a chromatography column and analyzed immediately. Fraction V_{rt} is contained in the cold traps and consists of products that are volatile at room temperature but condensable at $-80°C$. The tar fraction, V_{pyr}, condenses on the quartz window of the pyrolysis cell and contains products that are volatile at the surface of the exposed sample but not at $25°C$. . Finally, the *residue* or *char* fraction is the solid ash that constitutes the remains of the original exposed sample.

Samples

The samples investigated were an untreated O.G. 107 cotton poplin, 0.023 g./cm.^{2} (nominally 7 oz./yd.^{2}) and the same material treated with a 40% add-on of an APO-THPC flame retardant. The fabrics were supplied by the U. S. Army Quartermaster Corps in Natick, Massachusetts, and were used without pretreatment. Both materials were run in 1-sec. exposure at several flux levels between 5 and 25 cal./cm.^{2}-sec., and the products were analyzed as the four fractions previously described.

RESULTS

Fraction $(V_{-80} + V_{-190})$—Light Gases

The light gases were analyzed by vapor phase chromatography with a Perkin-Elmer model 154 instrument connected directly to the pyrolysis cell. Two meter columns of activated charcoal, silica gel, and molecular sieve 5A were used in the initial experiments. Typically, as shown in Figure 3, two peaks appeared with the charcoal column, four with the silica gel, and two with the molecular sieve. In duplicate runs, the effluent stream from the silica gel column was passed through a liquid nitrogen trap, and the condensate was analyzed in the mass spectrometer. From the known column characteristics and the mass spectrometer results, the silica gel peaks were identified, in order, as CO, CH_4, CO_2, and ethylene. The activated charcoal peaks are therefore CO and CH_4, while the molecular sieve peaks are CH_4 and CO. The assignments were verified by running known gases under conditions closely similar to those used with the unknowns.

For quantitative calibration, the apparatus shown in Figure 4 was constructed. It enabled us to fill the standard Perkin-Elmer constant volume gas sampling valve with known gases at various pressures. In this way, a series of gas samples of different weights could be introduced into the apparatus, and calibration curves of peak area vs. sample weight could be constructed. All of these were straight lines passing through the origin for a given flow rate and current setting.
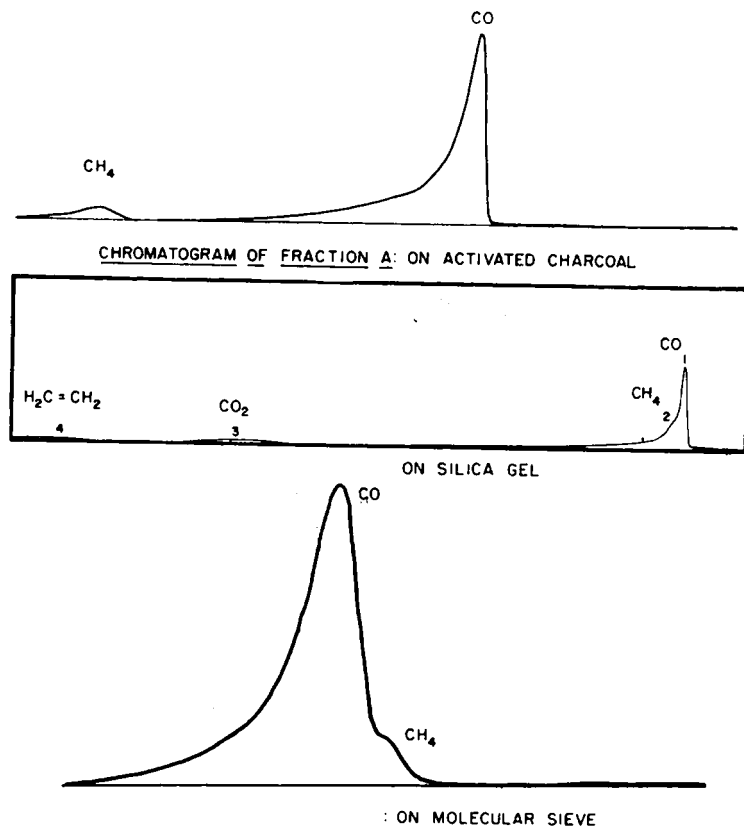
Fig. 3. Chromatogram of Fraction A on activated charcoal, silica gel, and molecular sieve.

A comparison of results for the untreated and flame-retardant treated cotton poplin is shown in Figure 5. Least square straight lines have been drawn through the experimental points. In general, the flame-retardant treated cotton gives a higher yield of volatile products than the untreated cloth, but also shows higher total weight losses, on the average. At all flux levels, the treated materials show slightly higher absolute concentrations of CO_2 and ethylene, and equal concentrations of CO. However, for both treated and untreated fabrics, the light gases account for approximately 5% of the total product at 5 cal./cm.²-sec., and for 18% of the total at 18–20 cal./cm.²-sec.

Fraction V_{rt}—Vapors Condensable at −80°C. but not at 25°C.

At the end of each experiment, Fraction V_{rt} was isolated in copper cold traps. These were maintained at Dry Ice-acetone temperature, and analyzed by vapor-phase chromatography within a few days of the pyrolysis experiment. 1 cc. of Wesson oil was added to the material in each trap,
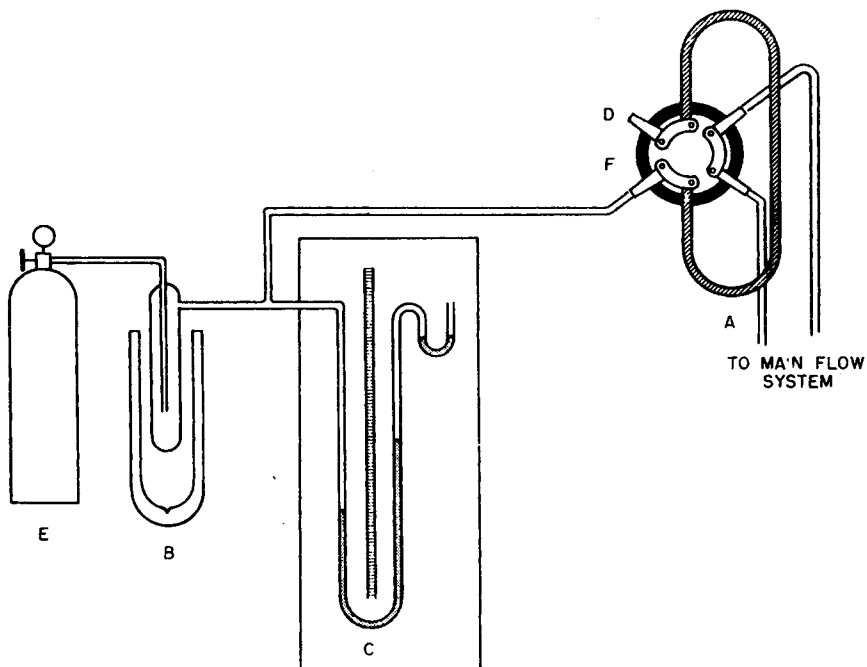
Fig. 4. Apparatus for introducing known quantities of permanent gases into the vapor phase chromatograph.

and the trap was allowed to warm to room temperature. The oil was poured out of the trap into a rubber gasket-sealed vial. Water was always present in copious amounts, but only the oil layer was sampled for analysis. A 0.02-cc. aliquot of contacted oil was run on an 8-ft. Resoflex R-296 column, with argon as an elution gas. The flash-heater temperature was 200°C., the column temperature 47 ± 1°C., and the cell temperature 210°C.

For purposes of calibration, a number of known substances was run under the same chromatographic conditions. Results are plotted in Figure 6 as logarithms of the retention time vs. the boiling point of each substance. It is characteristic of the Resoflex column that for many classes of polar organic materials (aldehydes, ketones, esters, alcohols, etc.) such a plot is a straight line. This observation was used to estimate the boiling points of the unknown pyrolysis products.

The number of possible gases in Fraction $(V_{-80} + V_{-190})$ is so limited that it is relatively easy to identify components with a considerable degree of certainty. The possible constituents of Fraction V_{rt}, which have a finite vapor pressure at 25°C. and a negligible vapor present at −80°C., are almost unlimited in number. Therefore, the only identification given is qualitative and based on approximate boiling points. Previous experience has shown that a peak height of unity corresponds to $5 \pm 4 \times 10^{-9}$ gs.

TABLE I

Concentration Numbers[a] for Fraction B: Untreated and APO-THPC Treated Cotton Poplin

Sample number	Incident flux	Boiling-point range, °C																			Total
		14–34	30–50	46–66	52–72	64–84	79–99	70–90	92–104	103–110	108–116	116–124	120–130	130–138	138–144	144–148	155–160	167–169	170–175	176–178	
						Untreated 7-oz. O.G. 107 Cotton Poplin															
32	20.2 (9 oz.)					2,100			150	250											2,500
34	16.06	60			1,275			235	755			45	40	140				110	200		2,860
35	11.88	60	15		100	525		240	80	30					190		90			150	1,475
36	7.21	50			1,685		155	180	4,775				10		250					460	7,570
						APO-THPC Treated 5-oz. O.G. 107 Cotton Poplin															
24	20.5					90,000				18,500											108,500
33	19.89				50	75	150			1,500											1,775
23	15.71					100,000	1,100		1,110												12,200
25	10.23				145,000	125,000				90,000											360,000
26	5.29					120,000			1,250												121,250

[a] A concentration number of one corresponds to approximately $5 \pm 4 \times 10^{-9}$ g.
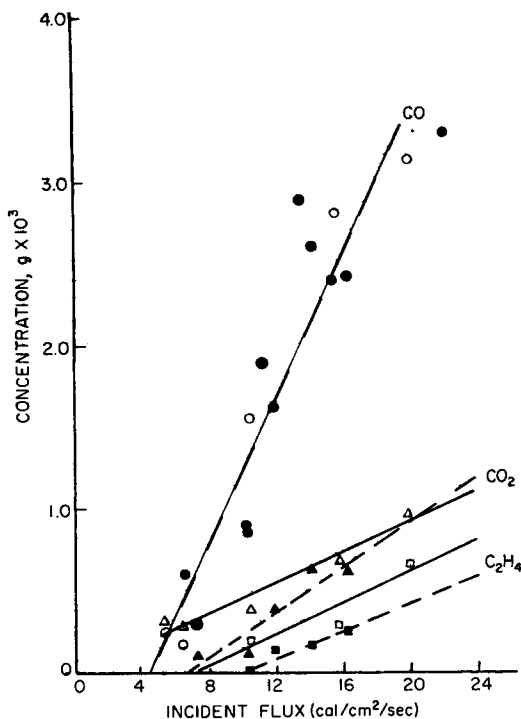
Fig. 5. Components of Fraction ($V_{-90} + V_{-180}$).

	CO	CO$_2$	C$_2$H$_4$
APO-THPC(——)	O	△	□
Untreated 7 oz. (- -)	●	▲	■

Results are shown in Table I. Although reproducibility is not good, it is clear that three to twelve polar organic constituents (aldehydes, ketones, esters, alcohols, etc.) with boiling points between 14 and 178°C. were found for every sample. It is also apparent that the number of grams of product in Fraction V_{rt} is roughly 30 times greater for the APO-THPC treated cotton than for the untreated, although the treated fabric is only 1.4 times heavier than the untreated.

Fraction V_{pyr}—Products Condensable at 25°C.

Fraction V_{pyr} is the tarry material found at the bottom of the quartz face plate after exposure is completed. It is therefore volatile at pyrolysis temperatures, but condenses rapidly at room temperature. It is the fraction that was found to contain levoglucosan in the longer-time, low-temperature pyrolyses of Madorsky.

Figure 7 compares the infrared spectra of our Fraction V_{pyr} from the pyrolysis of 7 oz. O.G. 107 cotton poplin at 20 cal./cm.^{2}-sec. with Madorsky's Fraction V_{pyr}, obtained from the pyrolysis of untreated cellulose at 350°C.
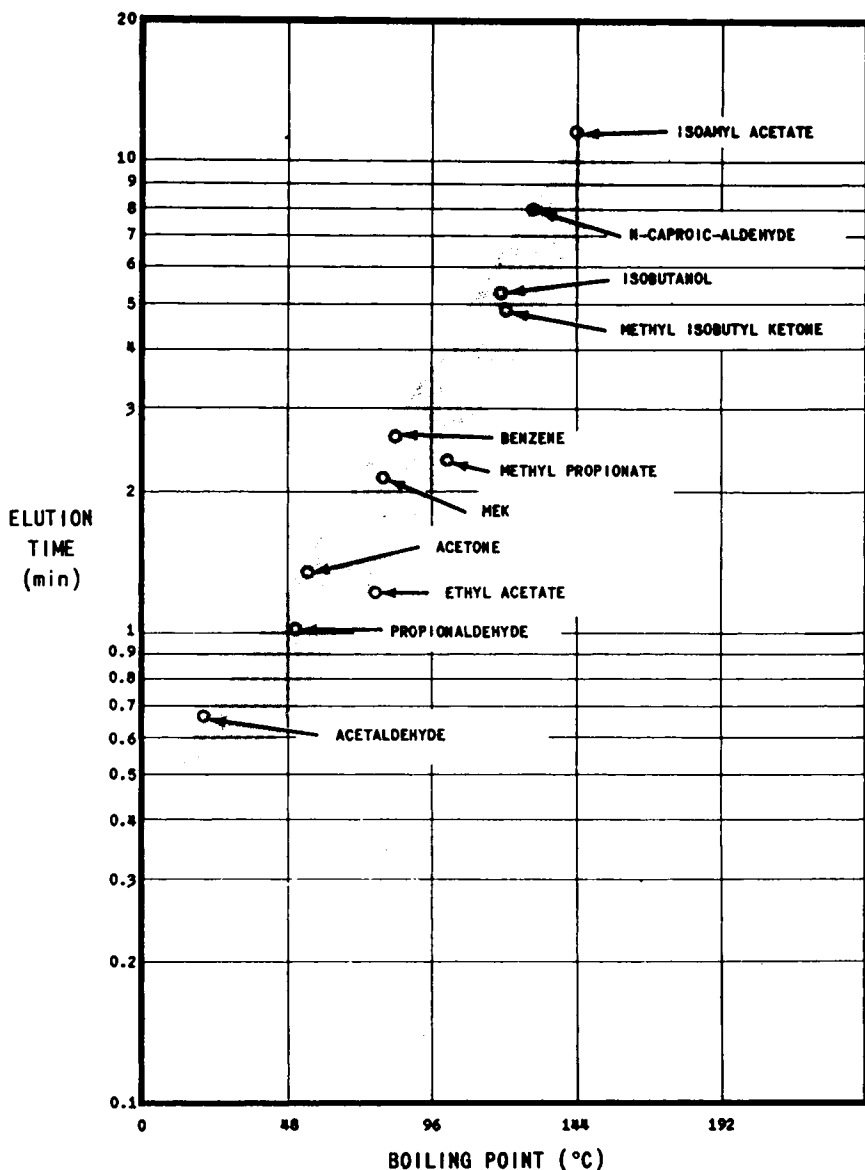
Fig. 6. Relationship between observed retention times and boiling points for known
organic molecules on a Resoflex R-296 column.

The spectra are identical, except for insignificant differences in band in-
tensities. The principal component has been identified as levoglucosan,
while the 5.8 μ band indicates that a second component, containing a
carbonyl group, must be present also.

The tar spectrum from the degradation of APO-THPC treated cotton at
20 cal./cm.^{2}-sec. also shows the prominent bands in the 10–12 μ region that
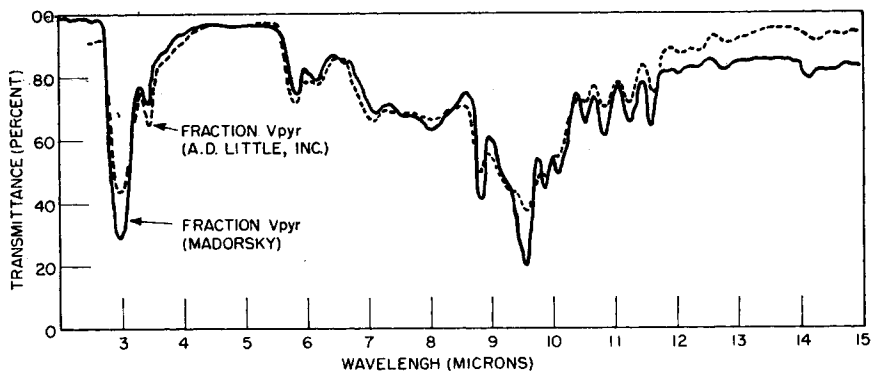
Fig. 7. Infrared spectra of Fraction V_{pyr}.

are characteristic of levoglucosan, and this is again unquestionably the principal component of the V_{pyr} fraction. The principal differences between the spectra of treated and untreated material lie in the 6.2, the 6.9, and the 8 μ regions, where the untreated cloth has well-developed absorption bands, while the treated material shows either no absorptions (8 μ) or mere shoulders (6.2 and 6.9 μ).

Char Fraction

The weight of residual char was calculated by estimating the weight of the exposed area of cloth and subtracting the net weight loss. The area

Fig. 8. Percentage of residual char for treated and untreated cotton.

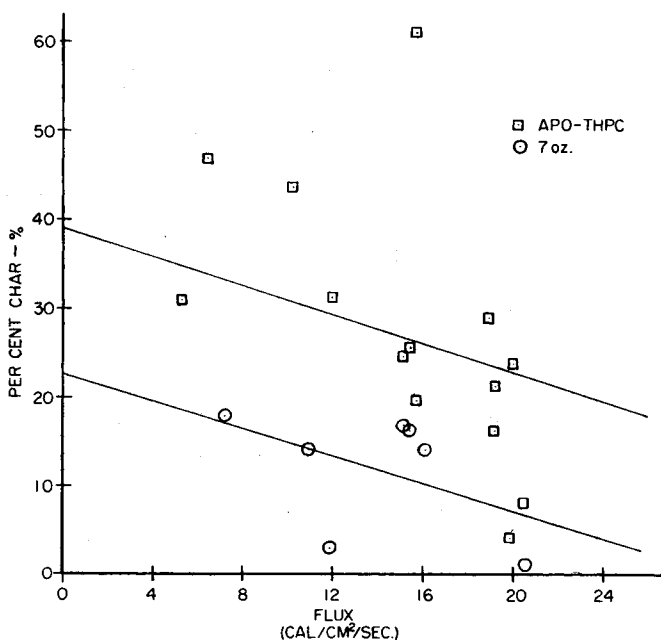exposed is roughly circular and approximately 10 ± 1 mm. in diameter. Since a 1-mm. or 10% error in diameter is translated into a 20% error in area, the calculated percentages of char, shown in Figure 8, are not highly accurate. However, in spite of the lack of precision in the data, two conclusions can be drawn. The lines are least square straight lines through each set of data and mean very little. However, it is clear, first, that the squares lie above the circles on the average; i.e., that the percentage of char is higher for the treated than for the untreated fabric. Second, it is also apparent that for both fabrics the percentage of product in the form of nonvolatile char decreases with increasing flux level.

CONCLUSIONS

A comparison of our pyrolysis results, under conditions of high thermal flux (5–25 cal./cm.^{2}-sec.) for 1 sec. with the results obtained in 9–60 min. exposures at 200–420°C., for either the treated or un-treated cloth, reveals no fundamental qualitative difference in the pyrolysis mechanism.

In the low-temperature degradations, the rate-controlling step is believed to be formation of levoglucosan by scission of the 1,4-glycosidic linkages of cellulose, and subsequent intramolecular rearrangement of the fragments.[2] Some of the levoglucosan, in turn, is thought to undergo dehydration and polymerization to form char, while some is believed to undergo destructive distillation to form volatile organics, permanent gases, and water vapor.

The principal products at low temperatures have been established as:

Fraction (V_{-80} + V_{-190}): carbon dioxide, carbon monoxide, methane, ethylene, hydrogen.

Fraction V_{rt}: water vapor, acetic acid, acetone, formic acid, formaldehyde, glyoxal, glycolic acid, lactic acid, and dilactic acid.

Fraction V_{pyr}: levoglucosan.

Char: unidentified.

In the high-intensity work reported here, levoglucosan has been identified as an important pyrolysis product, although it has not been established that its formation is the rate-controlling step in the degradation process. The light gases, identified chromatographically, appear to be CO_2, CO, CH_4, and ethylene, in agreement with the low-temperature work. Hydrogen was not found; water vapor is produced copiously. In addition, twelve aldehydes, ketones, acids, esters, etc., containing three to six carbon atoms have been identified, at least with respect to boiling point. The results of Fraction V_{pyr} cannot be compared directly to the low-temperature data, because the chromatographic method of analysis was not used in the low temperature experiments. However, the general assumption of destructive distillation of levoglucosan to fragments of lower molecular weights during pyrolysis fits the low and high temperature data equally well. It is, of course, quite possible that the relative quantities of light gases, simple organic molecules, and levoglucosan produced under high and low temperature pyrolysis are very different.

The effect of APO-THPC flame retardant on the pyrolysis products of cotton cellulose is also similar in both high and low temperature experiments. In both, the flame retardant causes an increase in the percentage of char in the degradation products, and therefore a decrease in the percentage of total volatile products. There is some evidence, however, that the distribution of volatile products among the various fractions may depend upon the heating conditions. This distribution, and the rate of formation of product species, may be critical factors in determining the protective effect of a fabric additive.

THEORETICAL MODEL OF CELLULOSE PYROLYSIS

The thermal degradation of cellulose produces a minimum of 18 products—at least 4 permanent gases, more than 12 simple polar organic molecules containing 1–6 carbon atoms, levoglucosan, and water. When a reaction is so complex, it is valuable to speculate in some detail on a conceivable degradation mechanism, to anticipate probable pyrolysis products, and to devise experiments to test the specific hypotheses.

A kinetic process is usually best understood if it can be described as a sequence of elementary steps. The first step in cellulose pyrolysis has been described as the formation of levoglucosan. Little consideration has been given, however, to subsequent steps in the degradation process that might ultimately lead to the observed multitude of products.

Structurally, levoglucosan is an acetal and should decompose with the formation of an aldehyde. A decomposition and isomerization reaction that splits off formaldehyde as follows might be postulated:

(levoglucosan)

(enol form)

(keto form)
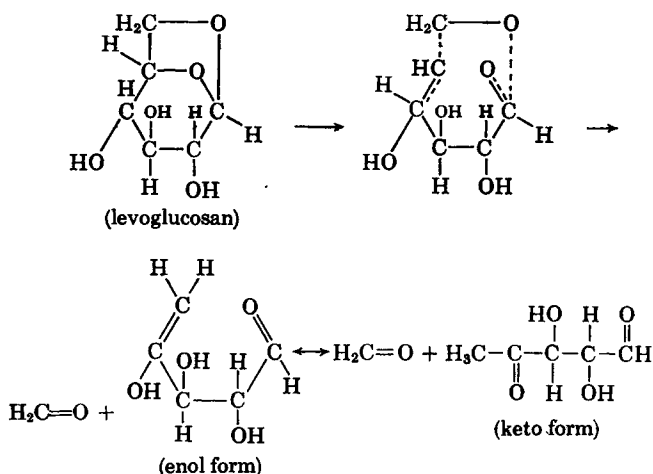
In addition one must postulate a decomposition of levoglucosan to CO_2 and $H_2C\!=\!CH\!-\!CHOH\!-\!CHOH\!-\!CH_2OH$ to account for CO_2 formation.

Many long-chain aldehydes and ketones are known to decompose by both free radical formation and molecular rearrangement.[10] In the first mech-

anism, the carbonyl group tends to weaken the adjacent C—C bond, which breaks with formation of radicals. The competitive rearrangement occurs by scission of the α C—C bond and accompanying hydride shift from the β-C atom. It is thus possible to predict free-radical degradations of the form:

$$
\underset{\substack{\| \\ O}}{H_2C}—\underset{\substack{| \\ H}}{C}—\underset{\substack{| \\ OH}}{C}—\overset{\substack{O \\ \|}}{C}—H \rightarrow H_2C—\dot{C}{=}O + \cdot\underset{\substack{| \\ H}}{C}—\underset{\substack{| \\ OH}}{C}—\overset{\substack{O \\ \|}}{C}—H
$$

$$
\rightarrow H_2C—\underset{\substack{\| \\ O}}{C}—\underset{\substack{| \\ H}}{C}—\underset{\substack{| \\ OH}}{C}\cdot + \cdot CHO
$$

$$
\rightarrow H_2C—C\cdot + \underset{\substack{| \\ H}}{\overset{OH}{C}} = \underset{\substack{| \\ OH}}{\overset{H}{C}} + \cdot CHO
$$

$$
\updownarrow
$$

$$
\overset{O}{\underset{\|}{HC}}—CH_2OH
$$

$$
\overset{O}{\underset{\|}{HC}}—CH_2OH \qquad \rightarrow \cdot CHO + \cdot CH_2OH
$$

Probable rearrangement reactions of the same intermediate are:

$$
H_2C—\underset{\substack{\| \\ O}}{C}—\underset{\substack{| \\ H}}{C}—\underset{\substack{| \\ OH}}{C}—\overset{\substack{O \\ \|}}{C}—H \rightarrow CH_2—OH—CHO + H_2C—\underset{\substack{\| \\ O}}{C}—\overset{\substack{O \\ \|}}{C}—H
$$

$$
\rightarrow H_2C—\underset{\substack{| \\ O}}{C}—CH_2OH + CHO—CHO
$$

The products postulated thus far are:

Molecular Species	Radicals
Levoglucosan	.CHOH—CHOH—CHO
CH₃—CO—CHOH—CHOH—CHO	CH₃—CO—CHOH—CHOH
H₃—CO—CHO (methyl glyoxal)	CH₃—Ċ=O
CH₃—CO—CH₂OH (acetol or hydroxy-acetone)	CHO
CHO—CH₂OH (glycolic aldehyde)	CH₂OH
CHO—CHO (glyoxal)	
CH₂O (formaldehyde)	
H₂C=CH—CHOH—CHOH—CH₂OH	

These species can undergo further reaction in almost endless variety. By simple application of the Rice-Herzfeld mechanism, all observed products can be explained, and many others can be predicted. Among the

latter are ethane, ketene, $CH_3—CH_2—CO—CHO$, $(CH_2CO—CHO)_2$,

$$H_2C \underset{\diagdown CO—CH_3}{\overset{\diagup CO—CHO}{}}$$, acetaldehyde, and methanol.

There is apparently need for studies on the thermal decomposition of pure, crystalline levoglucosan, as well as similar studies on any of the intermediates, or mixtures of them. Gas phase or gas liquid chromatography, particularly in conjunction with rapid scan infrared analysis of the separated products, would seem to be well suited for such work.

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Synopsis

Samples of untreated and APO-THPC flame-retardant treated cotton cellulose were pyrolyzed in a helium stream by exposure to flux levels of 5–25 cal./cm.²-sec. for 1 sec. in a carbon arc imaging furnace. The reaction products were separated naturally into four fractions, which were analyzed separately. Fraction ($V_{-190} + V_{-80}$) comprised volatile products that failed to condense in cold traps at $-80°C$. It was swept onto a chromatography column and analyzed immediately. For both fabrics, it consisted of a mixture of CO, CO_2, CH_4, and ethylene. These light gases accounted for approximately 5% of the total product at 5 cal./cm.²-sec. and for 18% of the total product at 18–20 cal./cm.²-sec. Fraction V_{rt} was contained in cold traps, and consisted of products volatile at room temperature, but condensable at $-80°C$. It was found by gas-liquid partition chromatography to contain 12 polar organic constituents which were identified with respect to boiling point. The percentage of total product in Fraction V_{rt} was approximately 20 times greater for the treated than for the untreated fabric. The tar

fraction, V_{pyr}, was found condensed at the bottom of the pyrolysis cell, and therefore contained products volatile at the surface of the sample but not at 25°C. It was found in infrared analysis to consist of levoglucosan and an unidentified carbonyl compound. Finally, the weight of residual char was estimated from the weight loss and the area of burn. For both fabrics, the percentage of char decreased with increasing flux level. At every flux level, the average percentage of char was higher for the treated than for the untreated fabric. The mechanism of pyrolysis is similar for both treated and untreated cloth, and for both high and low temperature degradation. A critical step is the formation of levoglucosan by scission of the 1,4-glycosidic linkages of cellulose. A mechanism for subsequent decomposition of levoglucosan to lower molecular weight compounds is considered.

Résumé

On a pyrolysé des échantillons de coton cellulosique comme tel et traité par l'APO-THPC qui retarde l'inflammation. La pyrolyse s'effectue dans un courant d'hélium en exposant à des degrés d'intensité de 5 à 25 cal./cm²·sec pendant une seconde dans un four à arc de carbone. Les produits de réaction sont séparés naturellement en 4 fractions, analysées séparément. La fraction $(V_{-190} + V_{-80})$ contient des produits volatiles qui empêchent la condensation dans des trappes refroidies à −80°C. Ils ont été acheminés vers une colonne de chromatographie et analysés immédiatement. Dans les deux cas il s'agit d'un mélange de CO, CO₂, CH₄, et CH₂=CH₂. Ces gaz légers entrent pour approximativement 5% dans le produit total à 5 cal/cm² sec. La fraction V_{rt} est condensée dans des trappes refroidies en contient des produits volatiles à température de chambre, mais condensables à −80°C. On a trouvé par séparation par chromatographie gaz-liquide que la fraction contenait 12 constituants organiques polaires qui ont été identifiés en tenant compte du point d'ébullition. Le pourcentage du produit total dans la fraction V_{rt} est approximativement 20 fois supérieur dans le cas du produit traité par l'APO-THPC par rapport au produit non-traité. La fraction goudronneuse V_{pyr} est condensée du fond de la cellulose de pyrolyse et contient dès lors des produits volatils à la surface de l'échantillon, mais non à 25°C. L'analyse I-R a mis en évidence qu'elle est constituée de lévoglucosane et d'un composé carbonylique non identifié. Enfin, le poids du résidu carbonisé est estimé à partir de la perte en poids et la surface brûlée. Dans les deux produits le pourcentage de carbonisation diminue avec une augmentation du degré d'intensité. Pour chaque degré d'intensité le moyenne du pourcentage de carbonisation est supérieure dans le cas du produit traité que dans celui du produit non-traité. Le mécanisme de la pyrolyse est identique pour les deux échantillons et pour des dégradations à haute et basse températures. Une étape critique est la formation du lévoglucosane par rupture des liens 1-4 glucosidiques de la cellulose. On a étudié un mécanisme de la décomposition ultérieure du lévoglucosane en produits de poids moléculaires inférieurs.

Zusammenfassung

Proben unbehandelter und APO-THPC-flammenschutz-behandelter Baumwollzellulose wurden in einem Heliumstrom bei Einwirkung eines Flusses von 5–25 cal/cm² sek durch eine Sekunde in einem Kohlebogenofen der Pyrolyse unterworfen. Die Reaktionsprodukte fielen in vier Fraktionen an, die getrennt analysiert wurden. Die Fraktion $(V_{-190} + V_{-80})$ bestand aus flüchtigen, in der Kühlfalle bei −80°C. nicht kondensierbaren Produkten. Sie wurde auf eine chromatographische Säule überführt und unmittelbar analysiert. Sie bestand bei beiden Geweben aus einer Mischung von CO, CO₂, CH₄ und H₂C=CH₂. Diese leichten Gase machten bei 5 cal/cm² sek ungefähr 5% des Gesamtproduktes aus und bei 18–20 cal/cm² sek etwa 18%. Fraktion V_{rt} lag in der Kühlfalle vor und bestand aus bei Raumtemperatur flüchtigen, bei −80°C. aber kondensierbaren Produkten. Mit Gas-Flüssig-Verteilungschromatographie wurden darin zwölf polare organische Bestandteile nachgewiesen, die in bezug auf ihren Siede-

punkt identifiziert wurden.   Der prozentuelle Anteil der Fraktion V_{rt} am Totalprodukt war beim behandelten Gewebe etwa 20 mal grösser als beim unbehandelten.   Die Teerfraktion V_{pyr} fand sich kondensiert am Boden der Pyrolysezelle und enthielt daher Produkte, die sich an der Probenoberfläche verflüchtigten, aber bei 25°C. nicht flüchtig waren.   Infrarotanalyse zeigte, dass sie aus Laevoglukosan und einer nicht identifizerten Karbonylverbindung bestand. Schliesslich wurde das Gewicht des Verkohlungs-rückstandes aus dem Gewichtsverlust und der Brennfläche bestimmt.   Bei beiden Geweben nahm die prozentuelle Verkohlung mit steigendem Fluss ab.   Bei gleicher Flusshöhe war die mittlere prozentuelle Verkohlung beim behandelten Gewebe grösser als beim unbehandelten.   Der Mechanismus der Pyrolyse ist bei behandeltem und unbehandeltem Material und für hohe und niedrige Temperatur ähnlich.   Eine kritische Phase ist die Bildung von Laevoglukosan durch Spaltung der 1,4-glykosidierten Bind-ungen der Cellulose.   Ein Mechanismus für die darauf folgende Zersetzung von Laevo-glukosan zu niedrigermolekularen Verbindungen wird erörtert.