

Effect of Potassium Bicarbonate on
the Ignition of Cellulose by Radiation

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Introduction

Most combustion reactions of interest in the field of fire control involve cellulosic materials. For such materials the fire reactions may be considered as proceeding in essentially two steps—first, a pyrolysis of the solid phase which yields, among other things, combustible gaseous products and, second, a highly exothermic gas-phase oxidation reaction. Since most of the energy in the fire is produced in the gas-phase reactions (and incidentally, since simple gas-phase reactions lend themselves more readily to study), most research programs on fire extinguishment have considered primarily the gas-phase flame reactions.

Investigations into the action of flame extinguishing agents have established that, besides the obvious physical effects (cooling, smothering, etc.), a chemical effect, attributed to a chain-breaking reaction, also occurs in the gas phase. On the other hand, the possible chemical effect of the extinguishing agent on the pyrolysis reactions of the solid has frequently been overlooked in the fire extinguishing field (although such an effect forms the basis of the chemical theories of flame-proofing of wood and fabrics). However, fire extinguishment procedures generally attempt to bring the extinguishing agents in intimate contact with the solid fuel. Here the agents can affect pyrolysis to give gaseous products differing in kinds, amounts, proportions, or temperatures, and thus, so to speak, affect the gas-phase flame reactions before they occur. This possibility is strikingly illustrated by the observation that many of the highly recommended fire extinguishing materials, including potassium bicarbonate, can "catalyze" the combustion of carbohydrates (for example, make sugar cubes burn) (2).

The present report describes some of the results obtained in a series of experiments undertaken at the United States Naval Radiological Defense Laboratory (NRDL) to determine how impregnation of cellulose with small amounts of potassium bicarbonate alters the combustion characteristics of the material and the gaseous products evolved in the pyrolysis. Purified alpha-cellulose, in the form of specially prepared papers, had been in use for a number of years in studies of the thermal decomposition and ignition of cellulosic materials by thermal radiation (4, 6, 7), an important phase of the Laboratory's program investigating the effects of thermal radiation from nuclear detonations. Such papers had been selected for study in an attempt to insure reproducible results which could be of direct value in interpreting the behavior of heterogeneous, highly variable, natural fuels. The present experiments were undertaken when it became evident that the low ash content of these papers might give results which differed markedly from results obtained

with impure natural fuels and that indiscriminate application of fire-extinguishing and fire-proofing materials might lead to undesirable consequences.

Apparatus and Procedures

Test Materials

In 1953, the Forest Products Laboratory, Madison, Wisconsin, prepared, from a single batch of wood pulp, a series of alpha-cellulose papers (5) for use in the program of the Thermal Radiation Branch, Naval Radiological Defense Laboratory. These papers were made up in varying thicknesses and densities, and carbon black was added to some to provide a gradation in optical properties. The paper (No. 4095) chosen for the present experiments was made with 2.5% (dry weight basis) carbon black added to the pulp. The density of the dry paper was 0.67 g/cm^3 , its thickness was 0.54 mm, and its radiant absorptance for the spectral distribution of the radiant energy source was > 0.9 , as measured with a General Electric Model 8 PVI reflectometer.

Chemical analysis of this paper indicated an ash content of 0.15%, consisting largely of Ca, Mg, Na, Fe, and Si. As a result, it was decided that the minimum addition of KHCO_3 it would be profitable to investigate was 0.15%—doubling the ash content of the sample. To investigate the influence of more drastic changes in composition, a 10-fold increase—to 1.5%—was selected. Finally a few experiments were conducted with 15% KHCO_3 added to a limited number of samples.

Initial attempts were made to distribute the KHCO_3 throughout the cellulose by adding it in aqueous solutions. Because of the tendency of the paper to warp and swell when wet, this approach was abandoned in favor of one in which the KHCO_3 is produced within the cellulose by the neutralization of alcoholic KOH with moist CO_2 . With such a procedure no noticeable change in the appearance of the paper could be detected.

For the treatment, three solutions of KOH in anhydrous methanol were prepared—with concentrations 0.02 M, 0.2 M, and 2 M. The paper samples, $1\frac{1}{2}$ by $1\frac{3}{4}$ inches in size, weighed $0.63 \pm .02\text{g}$, so the treatment consisted of adding to each sample 0.5 ml of the appropriate solution from a repeating pipette and placing the samples immediately on racks in an atmosphere of CO_2 saturated with water vapor. The atmosphere was maintained by bubbling tank CO_2 through water and removing excess water from the stream by passing it through a cellulose filter. After an overnight exposure to the moist CO_2 atmosphere, the samples were mounted in standard holders and left exposed to the normal atmosphere until they were used.

In appearance, the treated samples were indistinguishable from the untreated samples, and no change in absorptance was detected with the reflectometer. Evidence that the treatment did indeed convert the KOH to KHCO_3 was obtained in two ways: (1) a number of samples were weighed before and after treatment, the weight changes being in accord with the stoichiometry, (2) the same samples were leached with a small amount of distilled water, and the pH of the resulting solution was compared with that of an aqueous KHCO_3 solution of the expected concentration. As a final check on the method of sample preparation, the effects of exposure to radiant energy were compared for a limited number of the samples treated with aqueous KHCO_3 solution and those treated with alcoholic KOH. The results showed only negligible differences between the two groups of samples.

Radiant Energy Source

For these experiments, samples were exposed to an intense beam of thermal radiation produced by means of a high current carbon arc and a relay-condenser optical system. This source (1) can provide a maximum irradiance level of 30 calories per square centimeter per second, uniform over a circular area of three square

centimeters. The spectral distribution of the thermal output from the source, as operated, approximates that of a 5,500° K black body emitter. Attenuation of the whole beam to the desired irradiance level was accomplished using Libby-Owens-Ford "color-clear" plate glass, ground to produce a diffusing surface of appropriate attenuation. Exposures were made by means of a high speed square-wave shutter capable of providing exposures as short as 0.1 seconds reproducible to 0.01 seconds. The samples of test materials were individually mounted for exposure in brass shim-stock holders through which an accurately centered 3/4-inch diameter hole had been punched. A water-cooled aperture with a slotted guide received the holders and automatically aligned them into the focal spot.

Phenomena Observed

The effect observed when a particular cellulose sample is exposed to radiant energy depends upon both the irradiance and the time of exposure. At sufficiently high irradiance, the first ignition phenomenon observed is transient flaming—a flaming which terminates promptly at the end of the exposure. For somewhat longer exposures at a particular irradiance level in this range, sustained flaming occurs—the flaming extends beyond termination of the exposure and results in the nearly complete combustion of the sample. At somewhat lower irradiance levels, transient flaming never occurs; whenever the exposure is sufficiently long to permit initiation of flaming, it is always sustained. At still lower irradiance levels a sufficiently long exposure produces glowing ignition, and the sample may be consumed without the appearance of flame.

Analytical Procedures

The principal evidence concerning the influence of KHCO_3 on the combustion characteristics of cellulose was obtained from visual observation of the effects on exposed samples. However, to gain some insight into possible explanations for the observed results, a few comparative measurements were made of the quantities of the principal volatile pyrolysis products generated by treated and untreated samples exposed to the same thermal input.

At two irradiance levels and exposure times chosen on the basis of the ignition effects in air, first an untreated sample and then a sample impregnated with KHCO_3 were exposed in a helium atmosphere. The volatile products were swept by the helium carrier into a two-stage gas chromatography system (8). As a means of confirming the identity of the components, the effluent stream from the liquid-partition stage of the two-stage system was monitored by a Bendix time-of-flight mass spectrometer. A combination of the chromatographic retention time and the mass spectrum gives ample proof, in general, of the identity of each component.

Results and Discussion

Method of Quantification

The result observed when a single test sample is exposed to one specified pulse of thermal radiation is a "go - no go" phenomenon. That is, for a given irradiance, if the critical exposure time (threshold for a particular effect) is exceeded, the effect will occur (a success); if the critical time is not exceeded, no effect, or a different, lesser effect will be observed (a failure). To obtain an estimate of the critical value, then, a series of samples must be exposed to different values of the variate. From the results, an estimate of the critical value, usually defined as that value for which just half of all samples would exhibit the effect, that is, the LD_{50} in biological experimentation, may be obtained.

For a given sample population, the value of the estimate depends upon such factors as the variability in sensitivity of the samples in the population and the variability of the population as a whole with external factors—temperature, humidity, etc. For experiments with the present exposure apparatus, additional variability is

introduced as a result of uncertainties in the delivered dose. The source is not equipped for continuous monitoring. It is calibrated by mounting a calorimeter in the position at which samples will subsequently be exposed. However, the irradiance is not invariate with time. It has short time fluctuations (1-2% in seconds as the carbons rotate) and long time fluctuations (5-10% over several minutes as the carbons feed in and out or as voltage drifts). Thus, the method of estimating a critical value must take into account all such variations.

The procedure that has been adopted in determining the critical value for a single material is the so-called "up-and-down" method (3). In this method, fixed increments of the variate, in this case exposure time, are selected. The result of each exposure then determines the next time setting. If a "success" is obtained, the time is set down one increment; if a "failure", the time is increased. Neglecting a long series of steps in one direction as the critical value is first approached, the final estimate is obtained by simply averaging all subsequent exposure times.

For comparing two materials whose critical values differ only slightly, a modified up-and-down procedure was adopted and will be described in a future report. Samples of the two materials are exposed alternately in quick succession, the time setting being adjusted only if the same effect is observed for both samples. Such procedures permit the use of one material as a control to minimize the effect of any long time fluctuations.

Critical Values

The regions of occurrence of the various ignition phenomena for the pure No. 4095 paper are delineated by the curves in Fig. 1. These curves represent the composite results of a large number of experiments on this paper and extrapolations from results obtained with the similar papers of different density and thickness. As may be seen, there is a critical irradiance for the material—a level below which ignition will not occur no matter how long the exposure. For sustained ignition at the high irradiance levels, so-called reciprocity is approached, the effect occurring at approximately the same total exposure regardless of the irradiance level. More obvious from a logarithmic plot than from Fig. 1 is the fact that for pure alpha-cellulose papers of the type used in these experiments, the occurrence of transient flaming may be expressed by a constant product of the irradiance and the radiant exposure. The value of the constant is a function of the thermal conductivity, the density, and the heat capacity of the material. For the pure No. 4095 paper the relationship is given by

$$HQ = H^2 t = 59 \quad (1)$$

where H is the irradiance in $\text{cal cm}^{-2} \text{sec}^{-1}$

Q is the radiant exposure in cal cm^{-2}

t is the exposure time in sec

For determination of the influence of KHCO_3 impregnation, four irradiance levels were chosen: 11 and 18 $\text{cal cm}^{-2} \text{sec}^{-1}$, where both transient and sustained flaming are observed for the untreated material; 4.2 $\text{cal cm}^{-2} \text{sec}^{-1}$, where only sustained flaming is observed; and 1.4 $\text{cal cm}^{-2} \text{sec}^{-1}$, where only glowing ignition is observed. At each irradiance level, parallel "up-and-down" sequences were obtained by alternating untreated and treated papers. The average irradiance to be used for the treated material was estimated on the basis of the average exposure time for the untreated samples. The results are presented as the points in Fig. 1. For those points at which the effects observed differed from those observed at the same irradiance level for the untreated material, the actual effect observed for the treated material is also indicated in the figure.

Several interesting observations may be noted in Fig. 1. First, if only 0.15% KHCO_3 is added, the effects are the same as for the untreated materials at

all irradiance levels used. At the highest irradiance level, little difference in sensitivity is found between the treated and untreated materials. At the intermediate irradiance levels slightly more energy is necessary to produce a given effect in the treated material. However, at the low irradiance level the treated material is appreciably more sensitive.

Second, under no conditions attainable with this source was it possible to induce a sustained flaming in material treated with 1.5% KHCO_3 . Transient flaming did occur, at exposure times slightly longer than for the untreated material, but all sustained ignitions were of the glowing variety and all occurred at times appreciably less than those necessary to produce sustained ignition in the untreated material.

Third, only at the highest irradiance level was it possible to obtain a transient flame from the material impregnated with 15% KHCO_3 , except that a brief transient flaming, presumably as the gaseous products of pyrolysis were ignited by the radiant beam, could be produced at the $12 \text{ cal cm}^{-2} \text{ sec}^{-1}$ level at an exposure well beyond that necessary to produce the first glowing ignition. On the other hand, the times to produce a sustained ignition were always much lower for the treated material than for the untreated material, and the minimum irradiance level necessary to produce ignition was much less.

One final point should be made. The highest irradiance levels measured on conventional fires are always less than $2\text{-}3 \text{ cal cm}^{-2} \text{ sec}^{-1}$. Thus, the largest differences in sensitivity between treated and untreated materials occur in the region of greatest interest from the point of view of fire spread, with the treated material always the more sensitive.

Analysis of Volatile Pyrolysis Products

Summary of the gas chromatography-mass spectrometry results is given in Tables I and II. In addition to the weight loss during exposure in a helium atmosphere for an untreated 100 mg α -cellulose sample and for an equivalent sample impregnated with 2 mg KHCO_3 , each table gives the measured weights of various pyrolysis products and their relative ratios (the ratio of weights of the specific constituent divided by the ratio of total weight change). Table I gives results obtained after exposure to an irradiance of $4.2 \text{ cal cm}^{-2} \text{ sec}^{-1}$ for 2.5 sec (a time intermediate between those necessary to produce sustained ignition in air for the two materials). Table II gives similar results after exposure to an irradiance of $11 \text{ cal cm}^{-2} \text{ sec}^{-1}$ for 1.4 sec (a time somewhat more than the minimum necessary to produce sustained ignition in air for both materials).

Under conditions of these experiments, pyrolysis of cellulose gives a large number of products ranging from the low molecular weight gases to high molecular weight tarry materials. As may be seen from the tables, the volatile fraction (boiling point less than about 150°C) includes only about 25% of the weight loss from the untreated samples but about 50% of the weight loss from the treated samples. As might be expected, the increased sensitivity of the treated material to radiant exposure results in a more complete pyrolysis (that is, to a larger fraction of low molecular weight materials) for the same exposure conditions.

The volatile materials may be broken into two categories: gases (boiling points less than 0°C) and vapors (boiling point $0\text{-}150^\circ \text{C}$). For the untreated material, CO_2 and CO constitute $>98\%$ of the gas fraction. For the treated material, the CO_2 and CO components are still quite large, but the other, combustible, gases show a marked increase. Since the treated samples do not exhibit sustained flaming, while the untreated samples do, this result is more than mildly surprising.

The principal constituent of the vapors is H_2O , which for both treated and untreated samples makes up about 80% of the vapor fraction. About 90% of the

materials in the "Other Vapors" category in the tables have been identified. They include acetaldehyde, acrolein, acetone, biacetyl, crotonaldehyde, furan, methanol, and propionaldehyde. Here, too, some of the results are rather surprising. Although KHCO_3 treatment does not change the relative ratio of most of the vapors, several constituents, notably acetone and biacetyl are increased by an order of magnitude, or more.

The apparent contradiction between the ignition behavior of the treated and untreated materials in air and the pyrolysis results in helium, gave impetus to a detailed study of the temperature behavior of the samples during exposure. Such experiments have now begun. Although no conclusive results are yet available, it appears that under ignition conditions in air a treated sample will attain a lower temperature than will an untreated sample during an identical exposure, but that in helium the treated samples attain a somewhat higher temperature than the untreated samples.

Summary

As part of a program investigating the mechanisms of action of fire extinguishing agents, a study has been started on the influence of potassium bicarbonate additives on the ignition behavior of cellulosic materials. Pure α -cellulose papers and others to which varying amounts of KHCO_3 had been added were exposed in air to the intense radiation flux of a refocused carbon arc beam, and the ignition thresholds were determined at several irradiances. Several samples were then similarly exposed in a helium atmosphere, and the gases and vapors generated were passed through a gas chromatography-mass spectrometry analytical system.

From the results of this experimental work it is concluded that adding potassium bicarbonate to α -cellulose papers prior to radiant heating reduces the sensitivity to transient flaming and, furthermore, that sustained flaming may be prevented without adding more than 1.5% by weight. Such an observation is in complete accord with the fact that the effectiveness of KHCO_3 as a fire extinguishing agent has been repeatedly demonstrated over the years and is beyond question. Not in accord with its proven value in firefighting is the fact that the addition of KHCO_3 increases the rate and degree of pyrolysis of cellulose to volatile substances, and, as an apparent consequence, greatly increases the sensitivity to glowing ignition. Further, KHCO_3 treatment markedly enhances the production of gases such as hydrogen, methane, ethane, and ethylene as well as organic liquids (at room temperature) such as acetone and biacetyl. These seemingly contradictory results may be resolved by careful temperature measurements during pyrolysis, and such measurements have now begun.

ACKNOWLEDGMENT

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Table I—Pyrolysis products of untreated α -cellulose and α -cellulose impregnated with 2% KHCO_3 , both exposed under helium to $4.2 \text{ cal cm}^{-2} \text{ sec}^{-1}$ for 2.5 sec.

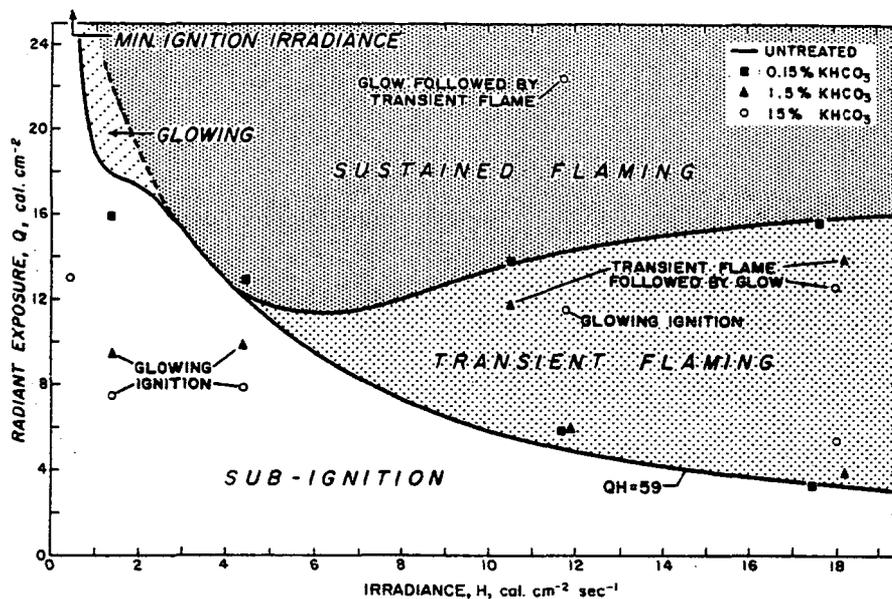
Product	Weight produced from—		Relative ratio
	Untreated sample	Treated sample	
	(mg.)	(mg.)	
Weight loss ^a	22.7	53.7	1
Total volatiles (B. P. <150° C)	6.2	26.9	1.8
Total gases (B. P. <0° C)	1.75	7.8	1.9
CO ₂	1.22	4.7	1.6
CO	0.53	3.0	2.4
H ₂	0.003	0.014	2
CH ₄	0.002	0.030	6
C ₂ H ₄	<0.001	0.026	> 10
C ₂ H ₆	<0.001	0.046	> 20
Water	4.0	16.5	1.8
Other vapors (B. P. 0-150° C)	0.48	2.6	2.3

^aOriginal sample weight = 100 mg.

Table II—Pyrolysis products of untreated α -cellulose and α -cellulose impregnated with 2% KHCO_3 , both exposed under helium to $11 \text{ cal cm}^{-2} \text{ sec}^{-1}$ for 1.4 sec.

Product	Weight produced from—		Relative ratio
	Untreated sample	Treated sample	
	(mg.)	(mg.)	
Weight loss ^a	68.1	79.3	1
Total volatiles (B. P. <150° C)	15.6	38.7	2.1
Total gases (B. P. <0° C)	4.3	13.0	2.6
CO ₂	2.54	6.3	2.1
CO	1.65	5.1	2.6
H ₂	0.015	0.3	17
CH ₄	0.020	0.66	28
C ₂ H ₄	0.034	0.51	13
C ₂ H ₆	0.007	0.19	23
Water	9.5	19.6	1.8
Other vapors	1.8	6.0	2.8

^aOriginal sample weight = 100 mg.



Ignition behavior of No. 4095 α -cellulose paper.
 Points indicate effect of KHC0_3 impregnation.

Figure 1