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THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF POTASSIUM BICARBONATE CONTAMINATED CELLULOSE†

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Abstract—When samples undergo a complicated set of simultaneous and sequential reactions, as cellulose does on heating, results of thermogravimetric and differential thermal analyses are difficult to interpret. Nevertheless, careful comparison of pure and contaminated samples, pyrolyzed under identical conditions, can yield useful information. In these experiments TGA and DTA curves were obtained, in air and in an inert atmosphere (nitrogen), with "ash-free" cellulose (ash content $<0.01\%$), "pure" cellulose (ash content $\sim 0.15\%$), and "treated" cellulose (1.5% $KHCO_3$ added). The results show that as little as 0.15% inorganic contamination can significantly affect the pyrolysis reactions undergone by cellulose. The addition of 1.5% $KHCO_3$ lowers by some 80 °C the temperature at which significant decomposition begins, but essentially eliminates the flame-producing reactions in favor of those leading to glowing combustion.

INTRODUCTION

EVEN when a single pure substance undergoes a clearly defined reaction to give a unique product, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results are influenced by many factors associated with the apparatus, technique, and physical state of the materials under investigation.[1–4] When a sample undergoes a complicated set of simultaneous and sequential reactions, TGA and DTA results can become quite complex and an unequivocal interpretation well nigh impossible. Nevertheless, careful comparison of nearly identical samples, pyrolyzed under identical conditions, can yield useful information.

After it was shown[5] that impregnation of cellulose with small amounts of potassium bicarbonate could significantly alter the combustion characteristics of the material and the gaseous products evolved in the pyrolysis, the effect of such treatment on the TGA and DTA curves for pure cellulose became of interest. Apparatus being used in research

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on the flame-proofing of wood at the U.S. Forest Products Laboratory in Madison, Wisconsin, was made available for a limited number of experiments. These experiments were intended to check the effect of small amounts of impurity in nominally pure cellulose and thus to complement the work already underway at Madison on the effect of much larger concentrations of flame retardants.

APPARATUS AND MATERIALS

The TGA thermograms were obtained with 0.5-gram paper samples suspended by a nichrome wire attached to the spring-type deflection balance of the American Instrument Company Thermograv described by Tang and Neill.[6] The samples, in an atmosphere of air or nitrogen, were centered in the reaction tube mounted in a vertical tube furnace. The furnace temperature, programmed usually for a 6 °C/min rate of increase, but with occasional experiments at 3 °C/min or at 12 °C/min, was plotted on the X-axis of an X-Y recorder, and the sample weight, expressed as percent of original weight, on the Y-axis. For the experiments in air, the atmosphere was drawn, by natural convection in most cases, directly from the constant-temperature, constant-humidity room in which the apparatus was mounted. For the experiments in an inert atmosphere, the reaction chamber was flushed three times with water-pumped nitrogen (maximum oxygen concentration, 0.1 %) and a nitrogen flow of two liters per minute was maintained through the course of the experiment.

The thermograph apparatus as modified by Tang[7] was also used for the DTA experiments. For this purpose, two wells were drilled into a brass heating block so that a sample tube and a reference tube could be symmetrically placed within the Thermograv furnace. The weight signal to the Y-axis of the recorder was replaced by the e.m.f. from a differential thermocouple mounted with one junction in the sample tube and the other junction in the reference tube.

For the DTA experiments, about 5 grams of shredded paper were placed in the sample tube to completely surround the thermocouple well, and the reference tube was packed to an equal depth with aluminum oxide. The nitrogen or air entered the tube through a glass sleeve at a point slightly above the level of the sample and was discharged from the top of the tube.

The standard "pure" material used in these experiments was the same paper used in the earlier work on ignition by thermal radiation:[5] an

alpha-cellulose paper containing 2.5% (dry weight basis) carbon black. The density of this paper was 0.67 grams per cubic centimeter, its thickness was 0.54 millimeters, and its ash content was 0.15%. As in the previous experiments, to provide a higher ash material, here called "treated" cellulose, samples of this paper were uniformly contaminated to a concentration of 1.5% $KHCO_3$ by adding an appropriate amount of KOH in anhydrous methanol and promptly neutralizing in an atmosphere of CO_2 saturated with water vapor.

To check the effect of even 0.15% ash, samples of "ash-free" cellulose, Schleicher and Schuell No. 589 White Ribbon analytical filter paper (ash content $<0.01\%$) were also used. This filter paper differed from the other papers in its physical properties, e.g., thickness and color. As a check on the effect of such changes, a limited number of experiments were performed with paper identical to the standard, but of thickness 0.05 millimeters, and with papers made from the identical pulp but without the addition of carbon-black.

Samples of the standard paper consisted of pieces 5 centimeters long and $2\frac{1}{2}$ centimeters wide. The thinner papers were folded to give a pleated sample of the same length and width. For the DTA experiments, 10 such samples were shredded into the sample tube.

RESULTS

Averaged DTA and TGA curves for "ash-free" cellulose, "pure" cellulose, and "treated" cellulose in nitrogen are given in Figure 1. As may be seen from Figure 1A, the TGA curve for "ash-free" cellulose, after an initial drop in weight attributable to evaporation of extracellulosic water, shows a first detectable weight loss at about 285°C. The weight drops rapidly over the next 100°C, then tails off toward a 10% residual "char" at higher temperatures. In the temperature region below 360°C, the corresponding DTA curve indicates several additional reaction zones. The initial endothermic dip attributable to extracellulosic water is followed by a recovery which may mask a slight exotherm. The slight dip starting at about 220°C may mark an endothermic reaction or just recovery after an exothermic reaction. The much sharper endotherm at about 280°C and the sharp exothermic upswing beginning at about 320°C clearly indicate distinct reactions.

By either TGA or DTA techniques, the detection of a reaction depends, of course, upon the sensitivity of the instrumentation and the speed of transition through the particular temperature interval.

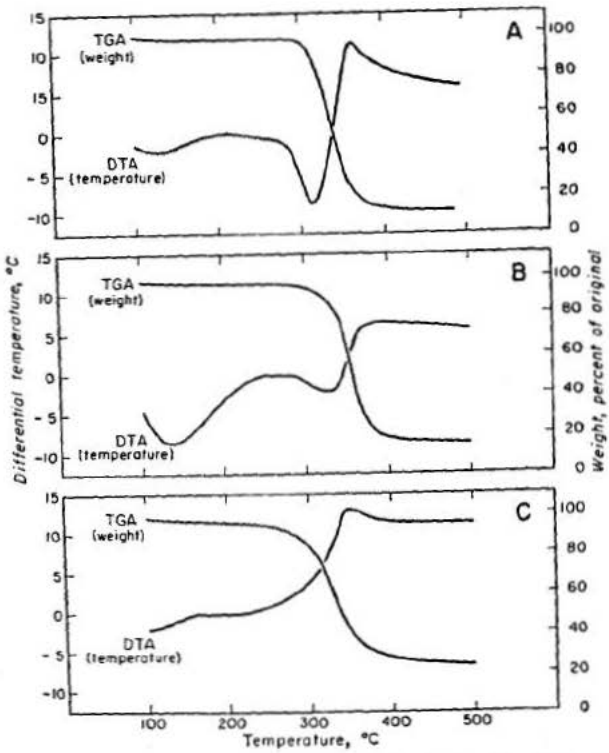

Figure 1.—DTA and TGA Results for (A) "Ash-Free"; (B) "Pure"; and (C) "Treated" Cellulose in Nitrogen Atmosphere.

Although DTA can detect reactions involving no weight change, and thus undetectable by TGA, additional experiments can distinguish such cases from those resulting from differences in sensitivity. For example, it can be simply demonstrated that the process indicated by DTA to occur at temperatures near 220 °C is concurrent with a slow weight loss even though the TGA results imply a rearrangement without weight change. After heating a sample of the "ash-free" cellulose at 230 °C for a 24-hour period, a loss corresponding to about 10% of the starting weight is observed. In comparing the temperature of onset of change in the DTA and TGA curves, it is important to remember, too, that the amount of sample and the geometry of heating in the two cases are different, and that such differences might well account for several degrees of misalignment of one curve with respect to the other.

The various samples of "pure" cellulose gave quite consistent results,

confirming the validity of direct comparison of the curves for "pure" cellulose with the corresponding curves for the "ash-free" material. As shown in Figure 1B, the first weight change following the initial loss of water is observed at about 260 °C. This weight loss is not accompanied by a corresponding change in the DTA curve—indicating that two competing processes may be just balancing energy inputs until about 290 °C, where the endothermic one predominates to produce the dip in the DTA curve. Apparently both the endotherm and the subsequent sharp exotherm are involved in the major weight loss reactions for the sample. As may be seen, the amount of residual "char" is significantly greater than that produced from the "ash-free" cellulose.

For the "treated" cellulose (Figure 1C), the TGA curve seems to drop continuously from the initial water loss—although there is an indication of a possible leveling-off in the temperature range 150–200 °C. Starting at about 220 °C, the DTA curve climbs rapidly, with no indication of the sharp endotherm observed with the other two samples. Again, the residual "char" is considerably higher than that obtained from the more-pure samples.

Similar curves for the three materials in air are given in Figure 2. For the bulk of these experiments, both the inlet and outlet tubes to the reaction chamber were simply open to the room. The curves obtained in this way with the "ash-free" and "pure" cellulose samples were again quite reproducible, but, as may be seen from Figure 2C, the central portion of the TGA curve for treated cellulose was highly variable.

For "ash-free" cellulose, the detectable weight loss begins about 265 °C, presumably with an exothermic reaction which compensates the endotherm produced in nitrogen. After about 290 °C, the endotherm predominates momentarily until the rapid temperature rise occurs. The amount of residual "char" from the "ash-free" cellulose is slightly greater in air than in nitrogen.

With the "pure" cellulose, the "first" exothermic reaction predominates sooner than it does with the "ash-free" cellulose, and to such an extent that the DTA curve never again crosses the differential temperature axis. From this curve it is impossible to determine whether two exothermic reactions occur on either side of an endothermic reaction or the endothermic process just predominates in one portion of a continuous exothermic reaction domain. The amount of residual "char" is again greater than both that from the "ash-free" cellulose in air and from the "pure" cellulose in nitrogen.

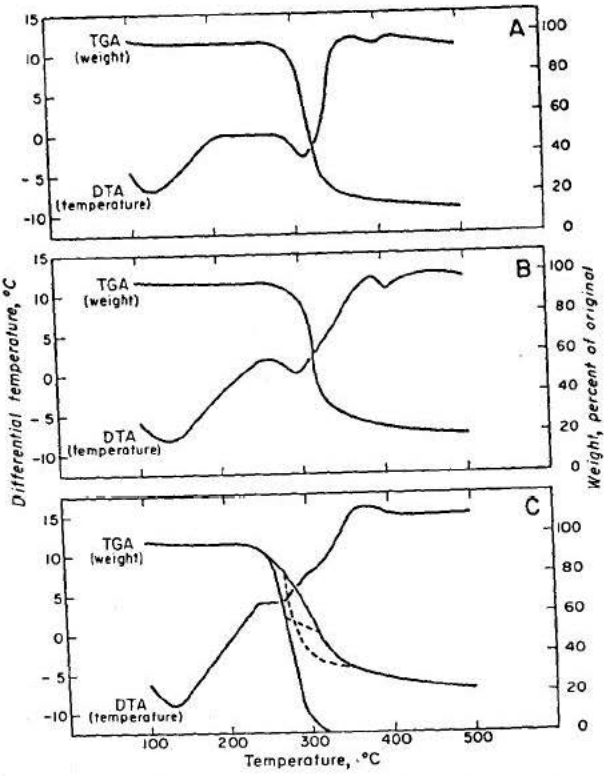

Figure 2.—DTA and TGA Results for (A) "Ash-Free"; (B) "Pure"; and (C) "Treated" Cellulose in Air.

The DTA curve for the "treated" cellulose shows an almost continuous exotherm from the minimum attributable to the evaporation of the extra-cellulosic water. The TGA curve starts off in rather routine fashion, but frequently, and at a different temperature for each sample, an abrupt change occurs—with a much sharper rate of weight loss until an equally sudden leveling-off. Looking into the furnace at these transition points reveals that the sample suddenly begins to glow. The consequent rapid evolution of pyrolysis and combustion products subsequently quenches the combustion process, and the sample returns to its standard rate of weight loss. If, instead of relying upon natural convection, a gentle air flow is maintained through the vessel by connecting the exit tube from the reaction chamber to an aspirator, the sample continues to burn in a glowing process until it is essentially completely consumed.

DISCUSSION

Ideally, a thermogravimetric curve provides a convenient way of obtaining kinetic parameters (*e.g.*, reaction order, activation energy) for a decomposition reaction.[8] Thus, if the curve is given in terms of the fraction of reactant remaining, F, the value of F at maximum reaction velocity, *i.e.*, maximum (negative) slope, can be used to determine the order of a simple pyrolysis reaction. For example, if, at maximum reaction velocity, F is 0.368, the reaction is first order. Again, for such a reaction a plot of log log $1/F$ against $1/T$ (where T is the absolute temperature) gives a straight line whose slope provides a simple and accurate estimate of the activation energy. Unfortunately, for reactions as complicated as those with cellulose, the parameter values which may be obtained from the TGA curves are largely a function of the assumptions which may be made about the curves.

In order to express a TGA curve in terms of the fraction of reactant remaining, the "final" weight (the weight after the desired reaction is complete and only product remains) must be determined. With cellulose the weight curve does not level off—the "char" continues to react as the temperature increases. As a result, not only activation energies, but even the *number* of reactions indicated by analysis of the cellulose TGA curve can be affected by the selection of the leveling-off weight and the assumptions about weight change in the "char" product. Unequivocal interpretation of the results is particularly difficult because of the inherent inaccuracies in determining the small weight changes which occur at the start of the major drop in weight (as a result of low temperature) and at the end (as a result of the small amount of residue).

Although the curves in Figures 1 and 2 cannot be used to establish unequivocally the kinetic parameters of the pyrolysis and combustion reactions of cellulose, they do serve several useful purposes. As a negative example, they show quite clearly that even the small amount of ash present in the so-called "pure" cellulose has a marked effect on the pyrolysis and combustion behavior of such samples. This, of course, raises serious questions about any data obtained with more or less pure samples in cases where the importance of such impurities has not been recognized.

A more positive example of the utility of such curves is their use in explaining, at least in a qualitative way, the known temperature behavior of cellulose.[9] Apparently, very pure cellulose can pyrolyze in at least two competing sequences of reactions, one of which occurs at a slow

but measurable rate at temperatures above 200 °C, and the other of which predominates at temperatures about 300 °C and leads to a rapid endothermic volatilization of the sample. It seems obvious from examination of all the data, that the effect of the ash constituents of cellulose is to catalyze the first reaction, which can predominate if the cellulose is contaminated by sufficient "catalyst." This first reaction, which results in considerable "char" formation, leads to a sequence whose manifestation in air is glowing combustion. On the other hand, the

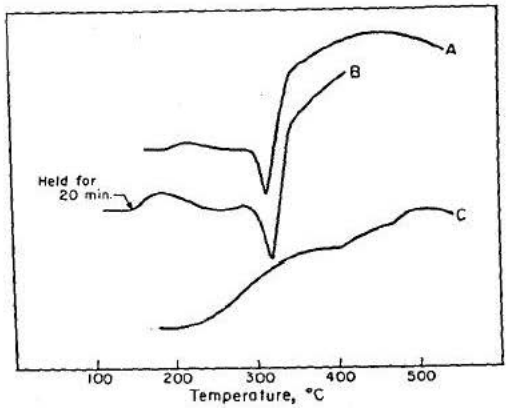

Figure 3.—Thermograms of: (A) Whatman's Cellulose; (B) Same, but Held for 20 minutes at 150 °C; and (C) Same, but Held for 2 hours around 250 °C. (From Reference 10.)

rapid endothermic volatilization is most likely responsible for the flaming combustion of cellulose. Treatment of the cellulose with fire retardants, then, appears to catalyze the glowing combustion process at the expense of the flaming combustion reactions.

If the above explanation is correct, the effect of the inorganic contaminants should be duplicated by holding very pure cellulose at a relatively low pyrolysis temperature until sufficient reaction can occur. Indeed, the thermograms obtained by Berkowitz[10] and reproduced in Figure 3 show a rather obvious similarity to the effect of contaminants indicated in Figure 1. In the same way, this general scheme seems to provide an explanation for many of the observations found with pure and treated cellulose, and some preliminary speculations about the specific reactions involved has been attempted.[9] However, much more work is needed to fully characterize the individual reactions and to isolate and determine the structure of unidentified intermediates.

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