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EFFECT OF INORGANIC SALTS ON PYROLYSIS OF WOOD, CELLULOSE, AND LIGNIN DETERMINED BY DIFFERENTIAL THERMAL ANALYSIS

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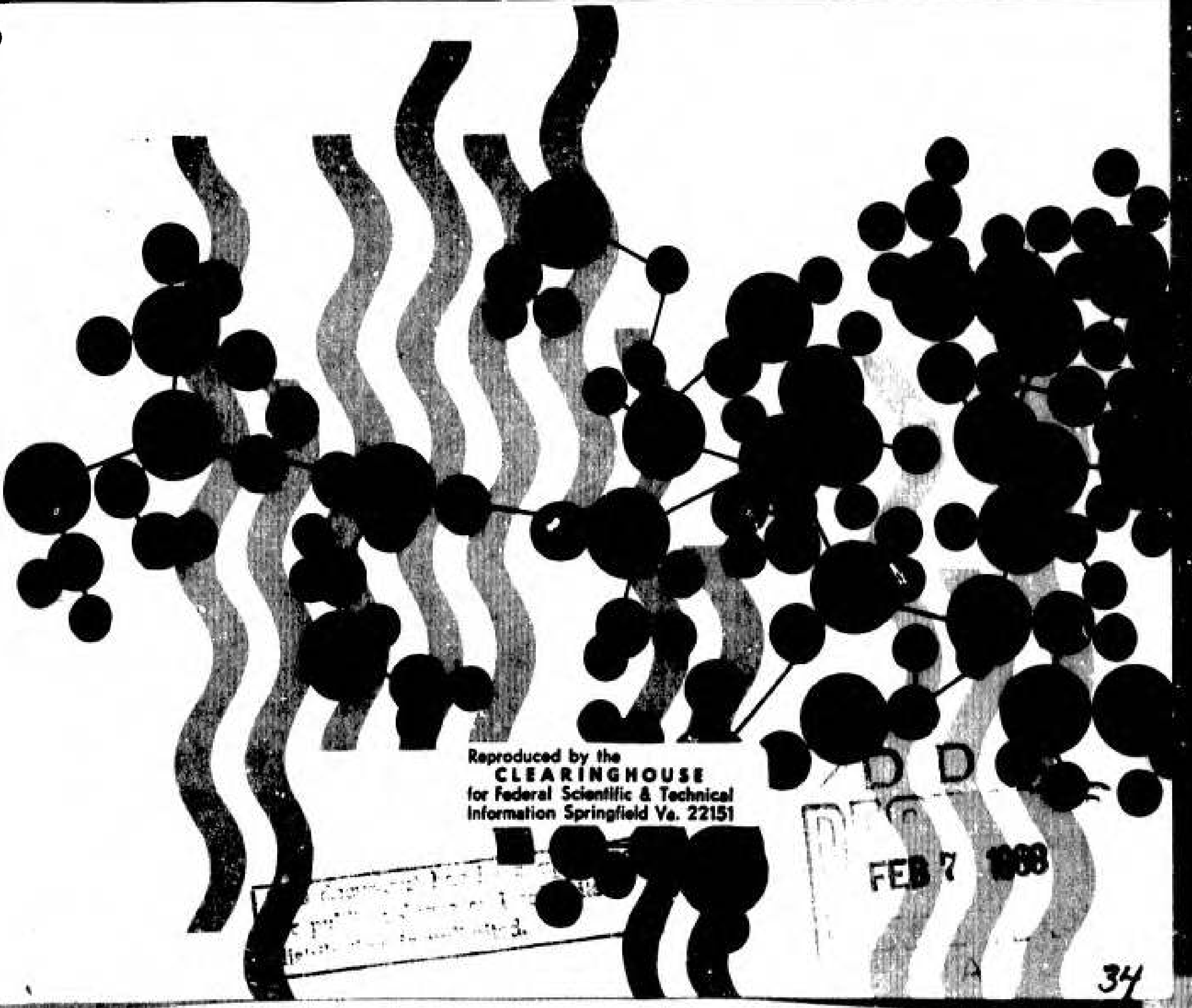

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SUMMARY

The wood-product and wood-treating industries are continually searching for more effective fire-retardant chemicals for use with wood. The development and application of these chemicals could mean further acceptance and use of wood products for certain uses in public and institutional buildings where only non-combustible materials are now accepted. To aid in this development, additional information is needed on the action of the chemicals in changing the pyrolysis and the combustion of wood and its components and on the physical and the chemical properties necessary for a chemical to be most effective in reducing flammability and glowing.

This work was part of a series to investigate the decomposition kinetics and the thermal reactions of the pyrolysis and the combustion of wood and its components. Differential thermal analysis was conducted in both helium and oxygen atmospheres on the thermal decomposition of wood, cellulose, and lignin, untreated and treated with 2 and 8 percent by weight of eight inorganic salts and an acid. Thermograms were obtained for the temperature ranges for endothermic and exothermic reactions, for the temperatures of maximum heat absorption or release, and for the heat intensities. These data combined with results of a previous work at the Forest Products Laboratory utilizing thermogravimetric analysis provide additional information on the characteristics of thermal decomposition.

In particular, these data show that the net heat of pyrolysis for untreated and treated cellulose is endothermic. The heat of pyrolysis for both wood and lignin is initially endothermic and later becomes exothermic. However, the net exothermic heat of pyrolysis for wood is only about 2 percent of the heat of combustion. The heat of combustion from wood is released by flaming of the volatiles with a maximum release at about 310° C. and a glowing of the solids with a second maximum release at about 440° C. The influence of the several types of effective and ineffective fire-retardant salts on the initial temperature of volatilization, rate of decomposition and heat release, transition temperatures of volatilization and heat release, and maximum heat intensities are also related by this work to theories that have been developed concerning the retarding of flaming and glowing reactions of wood and its components.

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Effect of Inorganic Salts on Pyrolysis of Wood, Cellulose, and Lignin Determined by Differential Thermal Analysis[1]

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INTRODUCTION

The wood and wood-product industries have long been and are becoming increasingly interested in the process of wood flammability and how it can be prevented or retarded by chemical treatments. Combustion of wood, cellulose, and lignin is preceded by pyrolysis to form gases and vapors and a solid charcoal residue. Some gases and vapors when mixed with air can burn by flame; charcoal can burn in air by glowing without flame. Ordinarily, fire starts when enough heat is applied to wood, cellulose, or lignin to make pyrolysis proceed rapidly enough for sufficient gases and vapors to become mixed with the surrounding air to reach flammable proportions, after which they become ignited by pilot flame or spark or ignite spontaneously. If enough of the heat of combustion is returned to the wood to maintain the pyrolysis and if the supply of oxygen is sufficient, the flaming may be sustained until the evolution of gases and vapors becomes feeble, after which glowing combustion may ensue until nothing is left except ash (17).[3]

Much of the information on pyrolysis and combustion reactions of wood and of the theories on how these reactions are controlled by using chemical additives has been reviewed in a Forest Products Laboratory report (4).

After analyzing this report and noting where information was lacking or inadequate, a program of basic investigation of the pyrolysis, ignition,

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[1] This paper is based on work performed in preparation of the Ph.D. thesis, "The Effect of Inorganic Salts on Pyrolysis, Ignition, and Combustion of Wood, Cellulose, and Lignin" (Chemical Engineering, University of Wisconsin, 1964), by Dr. Walter K. Tang, now of E. I. du Pont de Nemours & Co., Wilmington, Del. This work reported in the thesis was conducted at the Forest Products Laboratory under the supervision of Prof. Wayne K. Neill, Chemical Engineering Department, University of Wisconsin; Dr. Frederick L. Browne, Chemist, Forest Products Laboratory; and Mr. Eickner.

[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[3] Underlined numbers in parentheses refer to Literature Cited at end of this report.

and combustion of wood was initiated in 1960 at the Forest Products Laboratory. Investigations were made of the physical and the chemical factors of pyrolysis and the combustion reactions for untreated and treated wood and its components. Results of some of this initial research on the pyrolysis and combustion reactions of wood involving various means of analysis--thermogravimetric, differential thermal, heat of combustion, and pyrolytic product--have been published (2, 5, 6, 7, 10, 17, 18). It is believed increased information will help provide for a more systematic selection of new fire-retardant chemicals to replace the empirical method of selection.

As part of the Laboratory's program of basic investigation of pyrolysis and combustion, work was conducted on a doctoral thesis which, in part, is summarized in this paper. The kinetics of thermal decomposition of wood, cellulose, and lignin treated with chemicals are examined by DTA (differential thermal analysis) with samples exposed to both inert and oxidizing atmospheres.

PROCEDURE

For these differential thermal analyses on treated and untreated materials, a special specimen holder (fig. 1) was designed for use in the

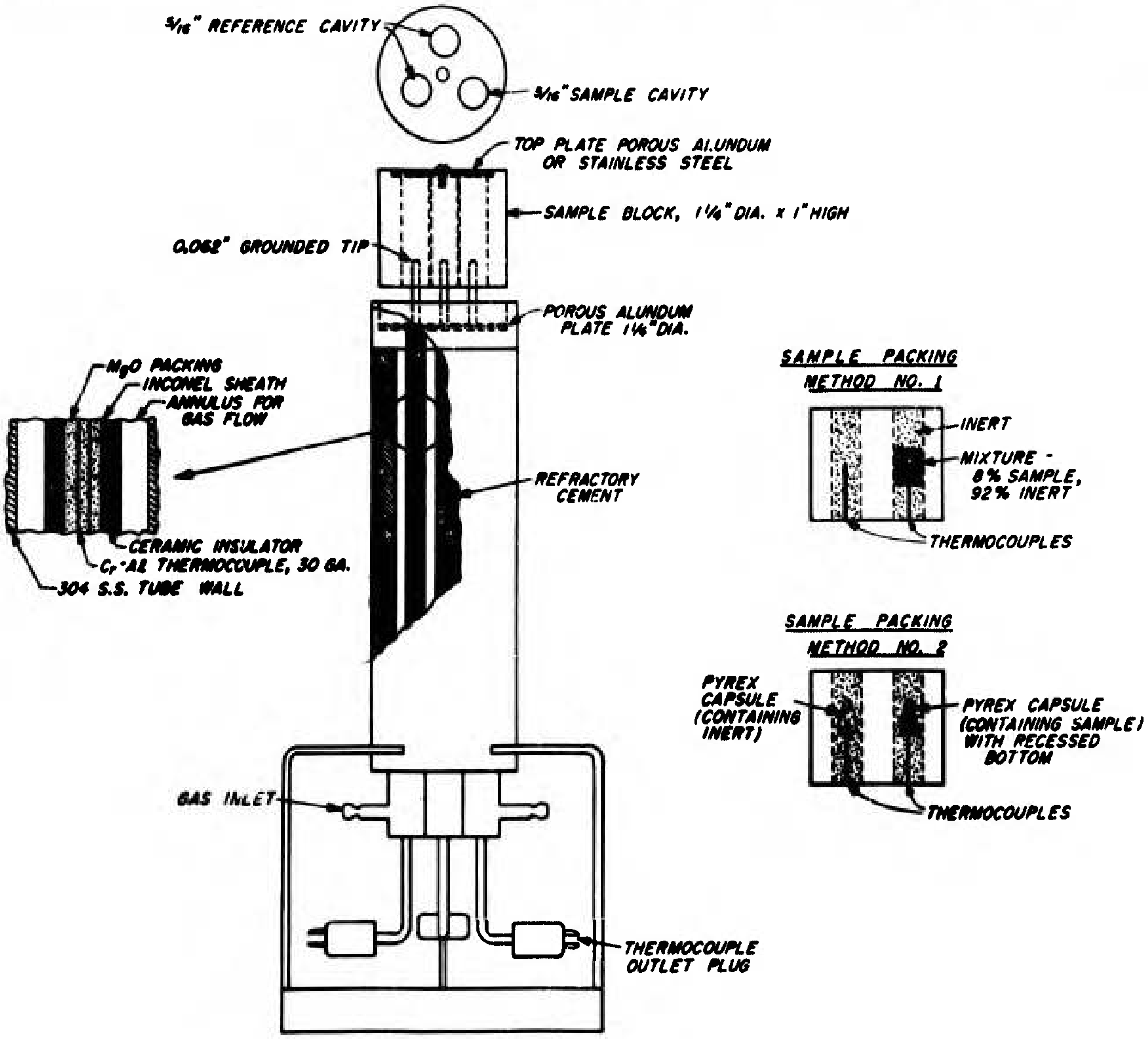


Figure 1.--Specimen holder for differential thermal analysis. (M 123 215)

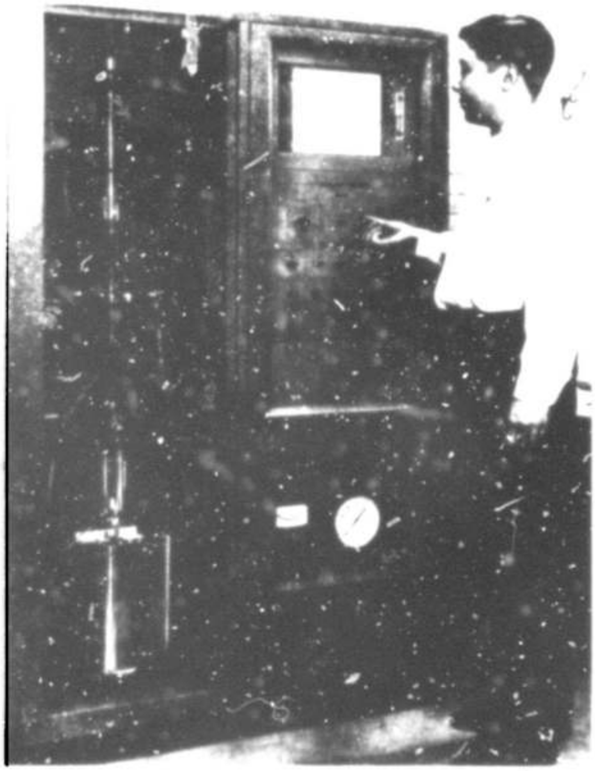


Figure 2.--Spring-type deflection thermogravimetric balance and recording equipment. Furnace shown in lower left and x-y recording equipment in upper right. (M 117 357)

furnace of a thermogravimetric balance (fig. 2) that controlled the rate of heating and provided recording equipment. Analyses were made in an inert helium atmosphere to represent the pyrolysis condition and in an oxidizing oxygen atmosphere to represent combustion.

Samples

Previous investigations (6, 18) showed that in addition to the size and mass of the holder, particle size, packing density, and specific heat of the samples could greatly influence DTA because of the effect on heat transfer to the interior of the samples and the escape of volatile products. To minimize the effects of mass and particle size, 20 to 100 milligram samples of ponderosa pine sapwood (40-mesh maximum), cellulose (Whatman cellulose powder, 99.3 percent cellulose), and lignin (sulfuric acid processed from spruce) were used.

Chemical treatment.--The samples were treated with chemicals by placing them on a glass filter, by washing repeatedly with an aqueous solution of the chemical aided by the application of vacuum, and then by drying and conditioning at 27° C. and 30 percent relative humidity.

The treatments were made so that the anhydrous retention of the following chemicals was 2 percent by weight for the pyrolysis samples and 2 and 8 percent by weight for the combustion samples:

Sodium tetraborate decahydrate
($Na_2B_4 0_7 \cdot 10H_2 0$)

Potassium bicarbonate ($KHCO_3$)

Sodium chloride ($NaCl$)

Aluminum chloride hexahydrate
($AlCl_3 \cdot 6H_2 0$)

Monoammonium phosphate ($NH_4H_2PO_4$)

These chemicals were also included in the previous investigation (17) on the pyrolysis and the combustion reactions by dynamic thermogravimetry. These salts were selected to represent both effective and ineffective fire retardants for wood and also different thermal decomposition classes for effect on volatilization of wood at 250° and 400° C. (7).

Combustion samples were also prepared with 2 and 8 percent retention by weight of boric acid (H_3B0_3) and at 8 percent retention by weight of disodium phosphate (Na_2HP0_4), ammonium sulfate ($(NH_4)_2S0_4$), and ammonium pentaborate octahydrate ($NH_4B_5 0_8 \cdot 8H_2 0$).

The low concentration of 2 percent was selected as a level low enough to modify the pyrolysis reactions of wood and its components, yet not so high that the thermal reactions of the chemicals themselves might mask other reactions.

Experimental Apparatus

A spring-type deflection thermogravimetric balance, the "Thermograv" (fig. 2), made by the American Instrument Company and used in previous TGA (thermogravimetric analysis) of the decomposition of wood, cellulose, and lignin

(6, 7, 17), was modified for use in differential thermal analysis.

Development of a specimen holder for DTA shown in figure 1 was the basic modification. The holder was designed to stand on the floor of the thermogravimetric balance where the cylindrical furnace could be lowered into place over the top of the holder and supply the proper rate of heating. The sample holder had three 5/16-inch-diameter, 1-inch-deep cavities--two for reference and one for sample materials. These cavities were above a porous Alundum plate with three 30-gage Chromel-Alumel thermocouples inserted with junctions in the center of each cavity. A controlled gas flow could be supplied to each of the cavities up through the lower porous Alundum plate.

A switch was provided in the X-Y recorder of the thermogravimetric balance to disconnect the input to the Y-axis from the weighing-system transducer. The output voltage of the differential thermocouples in one reference cavity and in the sample cavity was amplified by a Leeds and Northrup direct current microvolt amplifier and then used to actuate the Y-scale recording. The output from the thermocouple in the other reference cavity provided the X-axis recording voltage.

Differential Thermal Analysis Procedures

For DTA in an oxygen atmosphere, the sample block (fig. 1) was carefully positioned with reference to the thermocouple junctions at the top of the specimen holder. It was then packed with Pyrex glass beads (0.03 mm. in diameter) into the two reference cavities. In the sample cavity, 20 to 30 milligrams lignin or 40 to 50 milligrams wood or cellulose of sample material mixed with 92 percent glass beads was sandwich packed between the glass beads as illustrated in figure 1, packing method 1. The top of the sample block was covered with a porous Alundum disk. By including only the small percentage of sample in the cavity, differences in thermal diffusivity between the sample and reference materials were reduced, thus lowering thermal errors.

For DTA in the helium atmosphere, a larger size (100 mg.) sample was used, and both the sample and the reference were packed into stainless steel capsules placed in the sample block (fig. 1, packing method 2).

The specimen holder was then placed on the floor of the thermogravimetric balance so that the furnace unit could be lowered and could uniformly heat the specimen block. Proper connections were made to the gas inlet for flow rates through each of the packed cells of 5 milliliters per minute of helium for the pyrolysis analysis or of 30 milliliters per minute (27° C.) of oxygen for the combustion analysis. Helium was selected for the pyrolysis study because results of initial work indicated that available supplies of nitrogen were not sufficiently pure to be used in this type of analysis.

Connections were made from the thermocouples of the specimen holder to the X-Y recorder of the thermogravimetric balance. The thermocouples of one reference cavity were connected to the X-axis of the recorder, whereas the thermocouples in the other reference cavity and the sample cavity were connected so that the differential voltage was applied to the Y-scale through the microvolt amplifier. The sensitivity of the recorder system for measuring the differential temperature on the Y-axis was adjusted to 0.5° C. per inch for the pyrolysis in an inert atmosphere and 5.0° C. per inch for combustion in oxygen.

The furnace of the thermogravimetric balance was adjusted for a heating rate of 12° C. per minute and placed in position over the sample holder. Then, as the sample in the holder decomposed by heating, a thermogram curve was plotted on the X-Y recorder, indicating thermal changes at various temperatures. Triplicate runs were made for study of each of the variables--material, chemical, and concentration.

In studying the heat of pyrolysis with the high sensitivity (0.5° C. per in.), there was a base-line drift as illustrated in figure 3 for the untreated wood, cellulose, and lignin. This drift was caused by small differences between sample and reference material in physical properties, in heat transfer, and in the sensitivity of measurement. The location of the base line was estimated by blank runs (without reaction materials) and by repeated runs after the pyrolysis of the sample was completed. Appropriate changes were then made in the curves as illustrated in figure 4.

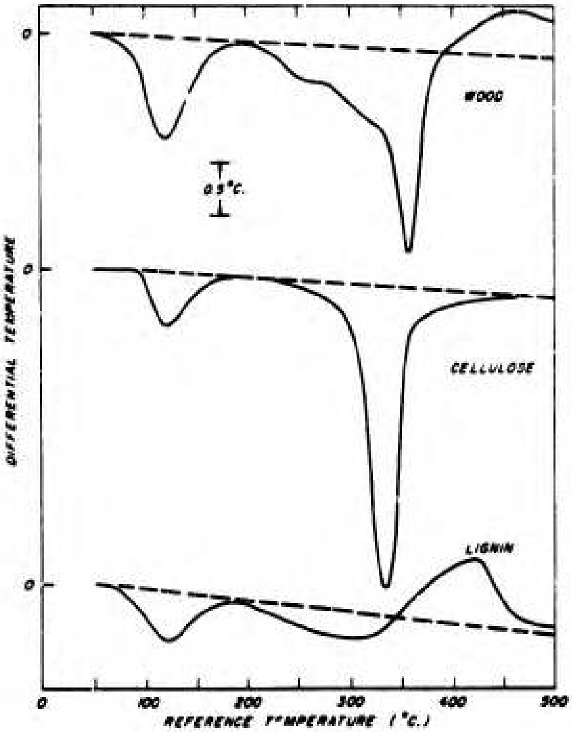


Figure 3.--Differential thermal analysis thermograms of pyrolysis of untreated wood, cellulose, and lignin showing baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles; Cellulose, 100-milligrams powdered Whatman cellulose; Lignin, 100-milligrams powdered (sulfuric acid processed spruce); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 544)

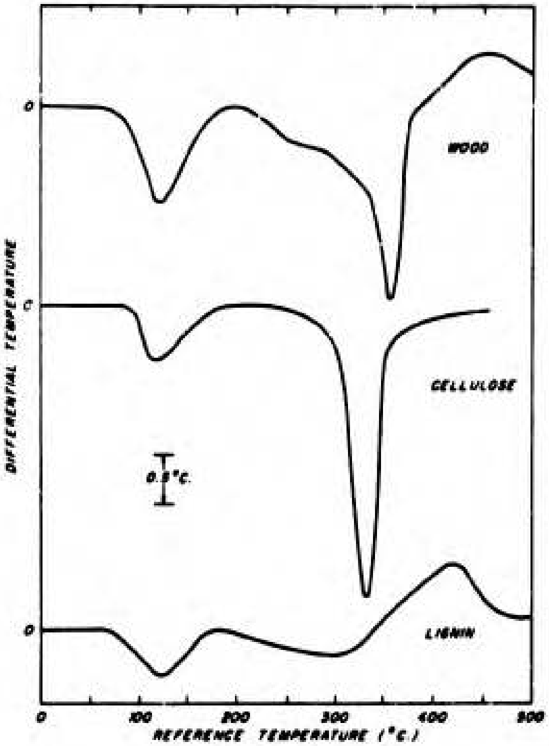


Figure 4.--DTA thermograms of pyrolysis of untreated wood, cellulose and lignin corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles; Cellulose, 100-milligrams powdered Whatman cellulose; Lignin, 100-milligrams powdered (sulfuric acid processed spruce); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 545)

RESULTS

Differential Thermal Analysis in Helium

The DTA thermograms for the pyrolysis of wood, cellulose, and lignin untreated and treated to 2 percent salt retentions are shown in figures 4 to 9.

In figure 4 for untreated wood, cellulose, and lignin, the first endothermic reaction, which occurred between room temperature and about 200° C. with the nadir at 125° C., was primarily from the evaporation of water and the desorption of gases. Above 200° C. active pyrolysis took place. The initial reaction of cellulose might be depolymerization, followed by competing reactions of decomposition, volatilization, aromatization, and others. The endothermic reaction shown by the curve, therefore, indicates that depolymerization and volatilization were dominating. When the temperature reached 335° C., these endothermic reactions either ceased or more probably were overpowered by competing exothermic reactions. This feeble exothermic course subsided quickly, indicating that the reactions were completed without evolving much exothermic heat.

The lignin specimens used in the experiments were previously degraded in separation by the sulfuric acid extraction method. Therefore, the depolymerization or fragmentation of lignin

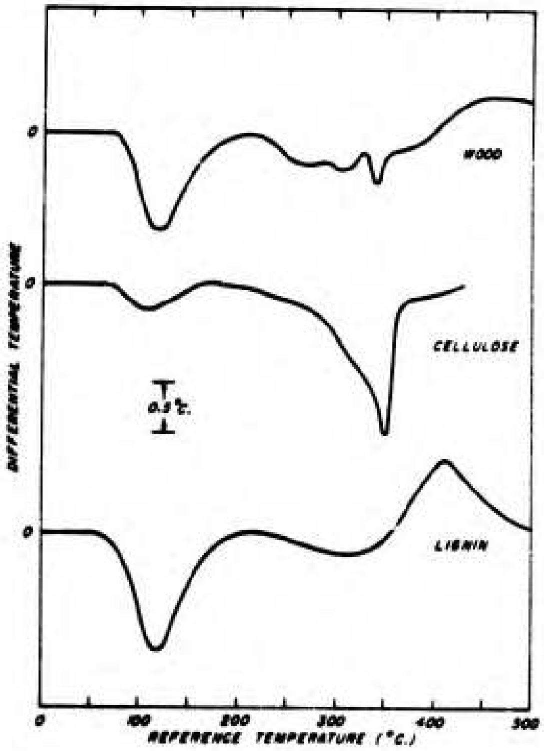


Figure 5.--DTA thermograms of pyrolysis of wood, cellulose, and lignin with 2 percent sodium tetraborate decahydrate corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles (treated); Cellulose, 100-milligrams powdered Whatman cellulose (treated); Lignin, 100-milligram powdered (sulfuric acid processed spruce) (treated); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters at 27° C. atmospheric pressure. (M 133 546)

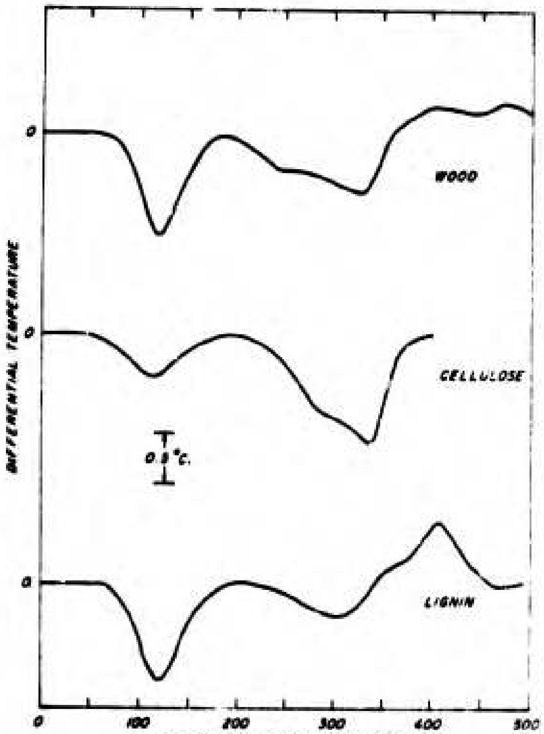


Figure 6.--DTA thermograms of pyrolysis of wood, cellulose, and lignin with 2 percent sodium chloride corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles (treated); Cellulose, 100-milligrams powdered Whatman cellulose (treated); Lignin, 100-milligrams powdered (sulfuric acid processed spruce) (treated); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 547)

macromolecules was accomplished to a certain degree before DTA, as inferred by the rather shallow and flat nadir. The endothermic reaction between 190° and 345° C. was the partial fragmentation to complete the decomposition of lignin. After this reaction, the fragments of smaller, nonvolatilized molecules would re-unite similarly as cellulose fragments do to form char, causing the exothermic reaction between 345° and 500° C. The exothermic formation of char of lignin exceeded the endothermic fragmentation.

The pyrolysis of wood began with the early decomposition of hemicelluloses, which began at 200° C. and reached a peak at 260° C., followed by the early stage pyrolysis of lignin and the depolymerization of cellulose. Therefore, products from pyrolysis of hemicellulose, such as acetic acid and perhaps formaldehyde (4), affected the pyrolysis of cellulose and lignin. The combination of these consecutive and simultaneous reactions shifted the nadir to a higher temperature than for either lignin or cellulose alone. The products of pyrolysis re-combined exothermically and exceeded the heat of endothermic reactions at 390° C. This exothermic reaction was not completed within the temperature range of the experimental equipment, but it was estimated to have been completed at about 600° C.

When wood, cellulose, and lignin were treated

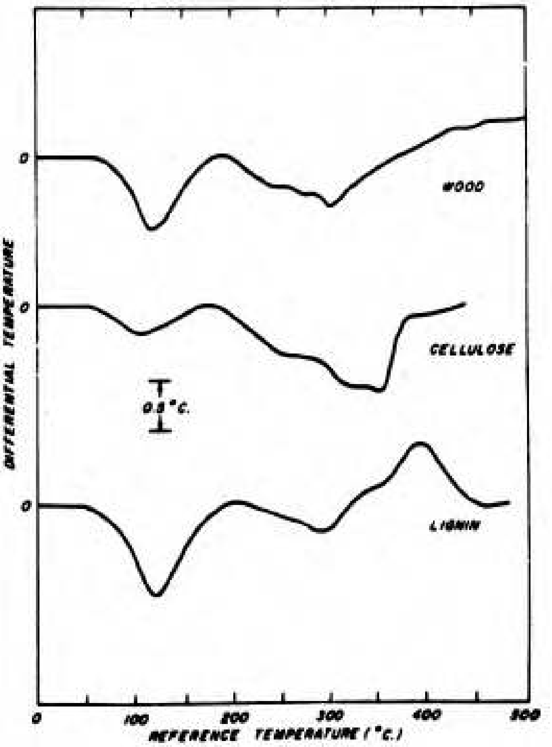


Figure 7.--DTA thermograms of pyrolysis of wood, cellulose, and lignin with 2 percent potassium bicarbonate corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles (treated); Cellulose, 100-milligrams powdered Whatman cellulose (treated); Lignin, 100-milligrams powdered (sulfuric acid processed spruce) (treated); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 548)

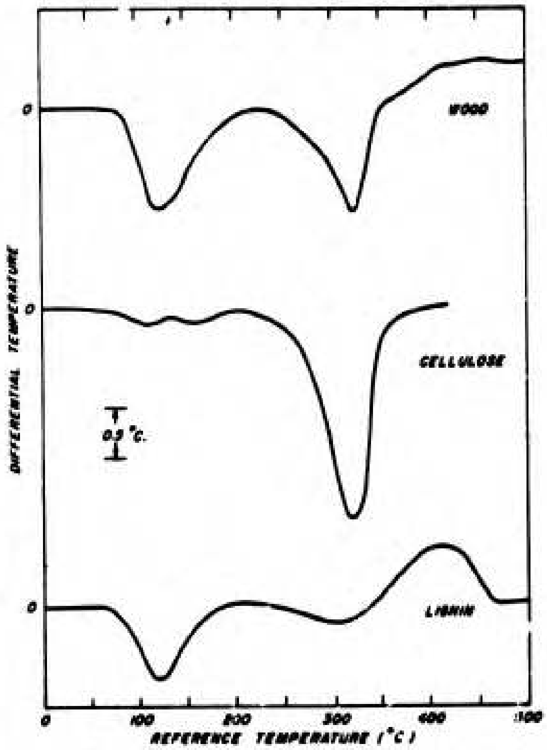


Figure 8.--DTA thermograms of pyrolysis of wood, cellulose, and lignin with 2 percent aluminum chloride hexahydrate corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles (treated); Cellulose, 100-milligrams powdered Whatman cellulose (treated); Lignin, 100-milligrams powdered (sulfuric acid processed spruce) (treated); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 549)

with inorganic chemicals, the pyrolysis reactions were modified by dehydration in decomposition and an increase in formation of char from pyrolysis products (figs. 5 to 9). The temperature ranges, nadirs, and peak temperatures in the pyrolysis of treated and untreated samples are listed in table 1.

Differential Thermal Analysis in Oxygen

When a constant sample weight and density of packing were maintained in DTA, the results varied with the oxygen supply and the heating rate. Experiments showed that the thermogram shape was very sensitive to these factors. The effects are shown in figures 10 and 11.

With only a trace of oxygen present, strongly exothermic oxidation was added to endothermic pyrolysis reactions. With a limited supply of oxygen there was a loss of unburned flammable volatiles because the lower flammability limit was not reached in the gas phase, and also because the ignition temperature may not have been reached. After ignition took place, combustion was confined to moderate smoldering because of the lack of oxygen, and the burning solids contributed mainly to the heat intensity. This reaction, as shown in DTA, occurred at

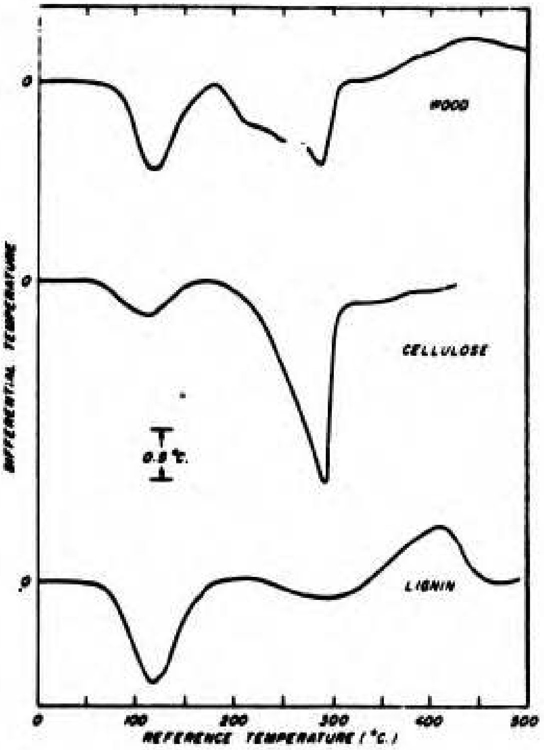


Figure 9.--DTA thermograms of pyrolysis of wood, cellulose, and lignin with 2 percent monoammonium phosphate corrected for baseline drift. Weight and form of samples in stainless steel capsules: Wood, 100-milligrams, 40-mesh ponderosa pine particles (treated); Cellulose, 100-milligrams powdered Whatman cellulose (treated); Lignin, 100-milligrams powdered (sulfuric acid processed spruce) (treated); Heating rate, 12° C. per minute by conduction; Atmosphere, helium flow 5 milliliters per minute at 27° C. atmospheric pressure. (M 133 550)

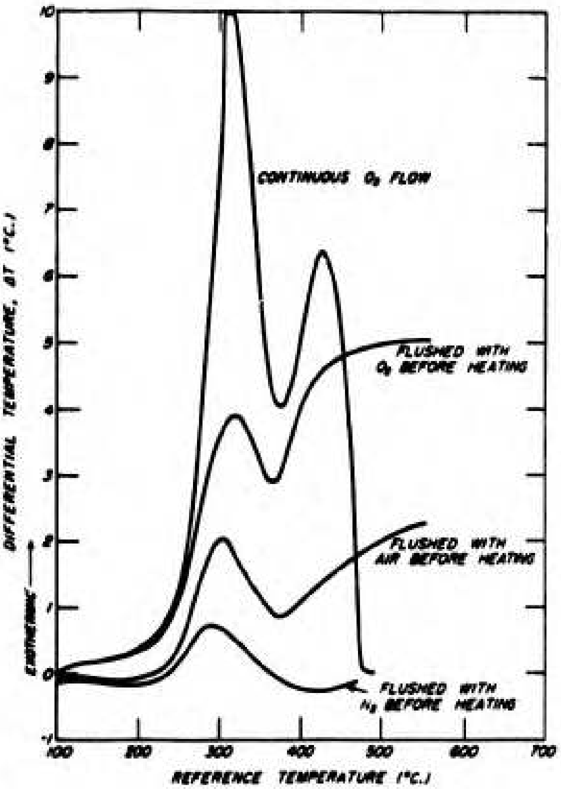


Figure 10.--Different degrees of oxidation of wood during heating varied with accessibility of oxygen (determined by differential thermal analysis). Specimen weight, 40 milligrams; Form of specimen, 40-mesh ponderosa pine particles; Heating rate, 12° C. per minute; Atmosphere, varying degree of oxygen and nitrogen supply at atmospheric pressure. (M 123 264)

a much higher temperature than does the burning in an oxygen-rich atmosphere.

In an atmosphere oxygen-rich or with continuous pure oxygen flow, the flaming of volatiles preceded and produced more heat than the glowing of solids. Thus, there were two peaks separated by a nadir near 375° C. With a high flow rate of oxygen, a considerable amount of flammable volatiles was carried out of the reaction chamber before burning and therefore reduced the heat contributed by the volatiles. For that reason, an optimum flow of oxygen was used to produce a condition of complete burning with the proper mixture of fuel and oxygen.

High heating rates increase the content of combustible tars in the products of pyrolysis. It could be expected to increase the flaming intensity, but the inadequate mixing of fuel and air and the rapid advance of the reference temperature on the X-axis revealed that the 32° C. per minute heating rate did not produce optimum conditions.

A low heating rate of 3° C. per minute showed that the slow formation of combustible volatiles caused an excessively low fuel-oxygen ratio and consequently a greater loss of heat because of incomplete combustion than with intermediate heating rates. The shift of exothermic peaks from 285° C. for 3° C. per minute to 315° C. for 32° C. per minute does not indicate a corresponding shift in ignition temperature. It is simply a mechanical effect in the coordination of differential temperature with reference tem-

Table I.--Temperature range, nadir, and peak temperatures of pyrolysis reactions[1]

Sample treatment[2]	Wood				Cellulose				Lignin			
	Endothermic		Exothermic		Endothermic		Exothermic		Endothermic		Exothermic	
	Range	Nadir	Range	Peak	Range	Nadir	Range	Peak	Range	Nadir	Range	Peak
	°C	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
No treatment	200-390	360	390-500	455	240-450	335	.....	....	190-345	305	345-500	425
2 percent sodium tetraborate decahydrate	200-395	340	395-500	470	180-420	350	.....	....	210-360	310	360-500	410
2 percent sodium chloride	190-360	325	360-500	410 475	200-400	335	.....	....	200-340	300	340-460	410
2 percent potassium bicarbonate	190-380	300	380-500	495	175-440	355	.....	....	200-325	290	325-450	395
2 percent aluminum chloride hexahydrate	220-350	320	350-500	460	200-410	320	.....	....	220-340	300	340-470	410
2 percent monoammonium phosphate	180-315	285	315-500	455	170-400	290	.....	....	220-340	295	340-455	410

[1] These values are for 100-milligram samples in stainless steel capsule in helium atmosphere determined by differential thermal analysis. Temperature deviation is ±5° C.

[2] Chemicals are 2 percent by weight.

perature and a chemical effect in fuel and oxygen mixing to initiate combustion.

The heating rate of 12° C. per minute was used because it produced thermograms with good resolution, and it was within the range of the ASTM E-119 standard time-temperature curve for "normal" fire exposures.

The DTA data for the wood, cellulose, and lignin obtained under these conditions of particle size, sample size and packing, rate of heating, and rate of oxygen flow are given in figure 12. The data for wood, cellulose, and lignin modified with 2 and 8 percent of the various salts are given in figures 13 to 26.

As wood burns, the cellulose fraction contributes most to the flaming combustion, whereas the lignin fraction supports most of the subsequent glowing combustion. This is shown by the DTA curve in figure 12. The sharp peaks at 310° C. for wood and 335° C. for cellulose are attributed to the flaming of volatile products in the initial pyrolysis; the flatter peaks at 440° C. for wood and 445° C. for lignin are due to glowing combustion of the residual char.

When wood, cellulose, and lignin were impregnated with 2 percent sodium tetraborate decahydrate (fig. 13), the flaming was reduced considerably, but the effect on glowing combustion was small, and a stimulated second glowing peak appeared at 510° C. In a visual observation in a separate experiment, a piece of 2 percent sodium tetraborate decahydrate-treated wood burned with flame. After the flame subsided, the black char glowed throughout, and the skeleton of gray char and ash glowed again if the environmental temperature remained in the 500° C. range.

The flaming of 2 percent sodium tetraborate decahydrate-treated cellulose was reduced, but its feeble glowing-combustion was increased and extended to higher temperatures than for the untreated cellulose. Two percent sodium tetraborate decahydrate actually promoted the glowing peak of lignin and showed a second glowing peak.

These results were exaggerated by increasing the concentration of this chemical to 8 percent (fig. 14). A second glowing peak also appeared in cellulose combustion.

The concentration of 2 percent sodium chloride reduced the flaming of both wood and cellulose (fig. 15). The effect on cellulose was particularly distinct. It also enlarged the glowing portion of cellulose decomposition. The peculiarity was that a weak endothermic reaction interrupted the exothermic glowing of wood and cellulose; at 420° C. for wood and at 425° C. for cellulose. The effect of 2 percent sodium chloride on lignin was not so obvious, but the high-temperature peak was shifted to a lower temperature and the intensity of both the low and high temperature peaks was increased.

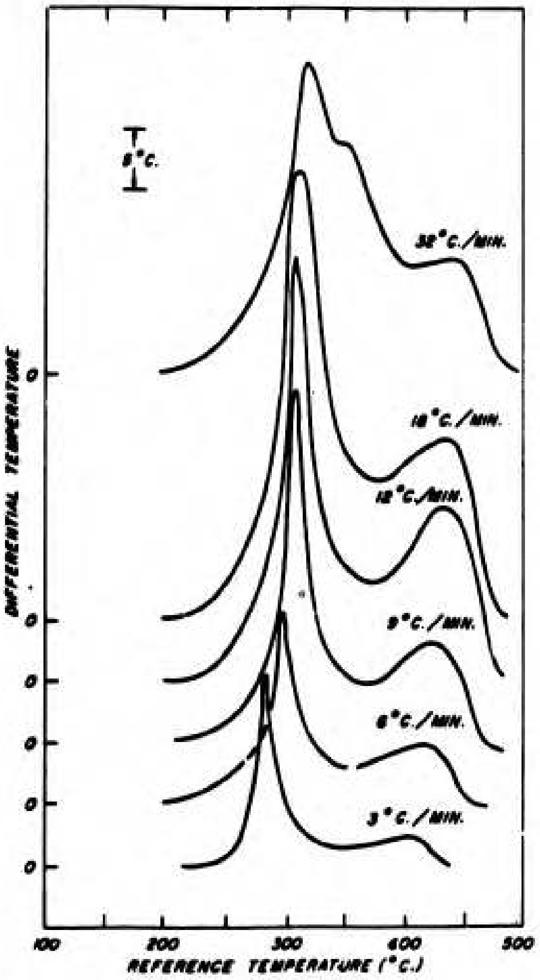


Figure 11.--Effect of heating rate of combustion on untreated wood by differential thermal analysis in oxygen. Specimen weight and form: Wood, 50 milligrams, 40-mesh; Heating rate, 3° to 32° C. per minute by conduction and convection; Pressure, atmospheric; Oxygen rate, 30 milliliters per minute at 27° C. through each of the three cavities. (M 133 551)

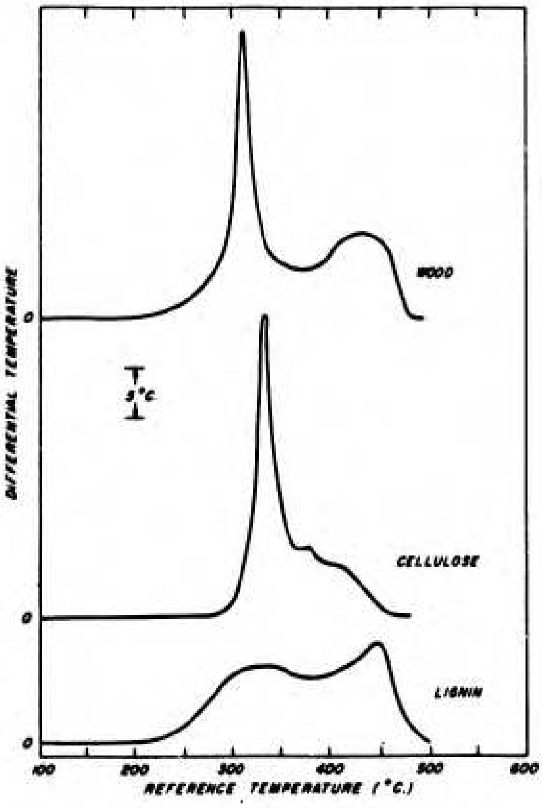


Figure 12.--The combustion of wood, cellulose, and lignin with no treatment (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh ponderosa pine particles; Cellulose, 50-milligrams Whatman cellulose powder; Lignin, 30-milligrams powdered (sulfuric acid processed spruce); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 552)

Sodium chloride at 8 percent concentration (fig. 16) promoted increased glowing peaks of wood and cellulose and shifted the peaks. It stimulated the combustion of lignin at 325° C., where volatilization became rapid. Flaming possibly took place also.

The combustion of 2 percent potassium bicarbonate-treated lignin exhibited (fig. 17) a trend similar to that of 8 percent sodium chloride-treated lignin. The flaming of wood and cellulose treated with 2 percent potassium bicarbonate decreased. Peaks were shifted as if the contribution to the flaming of wood was more from lignin than from cellulose derivatives. In the 400° C. range, there were minor exothermic reactions of wood and lignin in addition to the strong glowing of cellulose.

The effect of 2 percent potassium bicarbonate was further extended with an 8 percent concentration (fig. 18). The flaming of wood and lignin nearly coincided, and oscillations occurred at higher temperatures. The combustion of cellulose resembled that of untreated lignin, except for the presence of an endothermic nadir at 400° C.

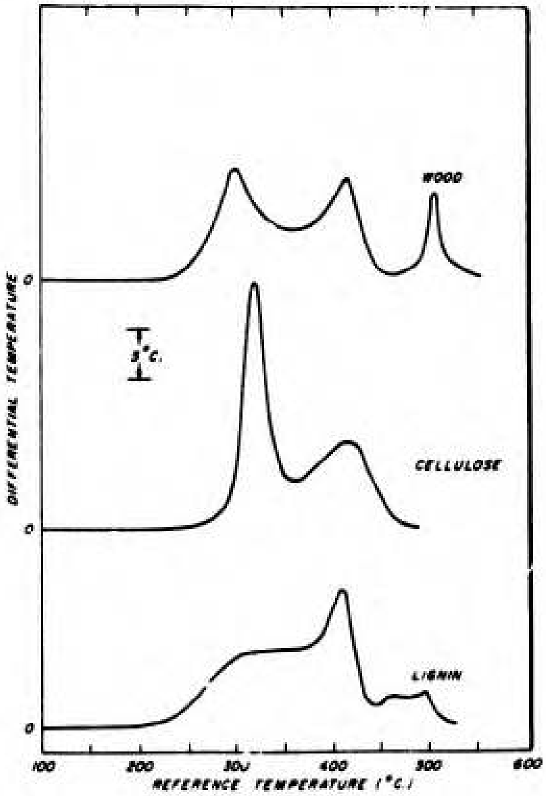


Figure 13.--The combustion of wood, cellulose, and lignin with 2 percent sodium tetraborate decahydrate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 553)

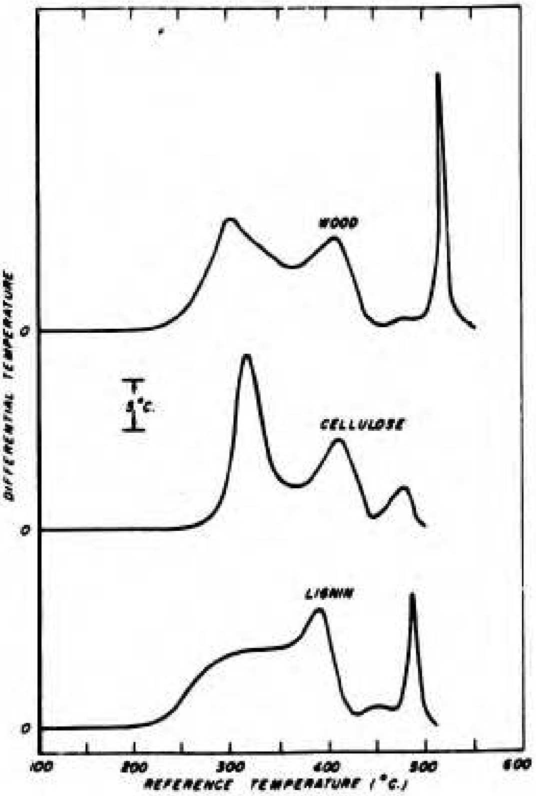


Figure 14.--The combustion of wood, cellulose, and lignin with 8 percent sodium tetraborate decahydrate (differential thermal analysis). Specimen weight and form: Wood, 50 milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 554)

The difference in concentration between 2 and 8 percent aluminum chloride hexahydrate (figs. 19 and 20) did not have much effect on the burning of wood, cellulose, or lignin. In both concentrations, cellulose seemed to dominate the combustion with reduced flaming and increased glowing. The reactions were similar to those of wood. There were pulses of stimulated glowing in lignin. Apparently lignin played a minor role in these cases; therefore, the burning of wood was not affected.

Ammonium phosphate, at both the 2 and 8 percent levels, caused the most effective reduction of all heat intensities for the flaming of wood, cellulose, and lignin (figs. 21 and 22) and the glowing of wood and lignin. It effectively extended the exothermic oxidation of cellulose to a higher temperature range.

The behavior of boric acid and ammonium pentaborate on wood, cellulose, and lignin was similar (figs. 23, 24, and 25). The effect was most noticeable on wood and cellulose. The flaming of wood and cellulose was somewhat suppressed at lower temperatures (about 300° C.).

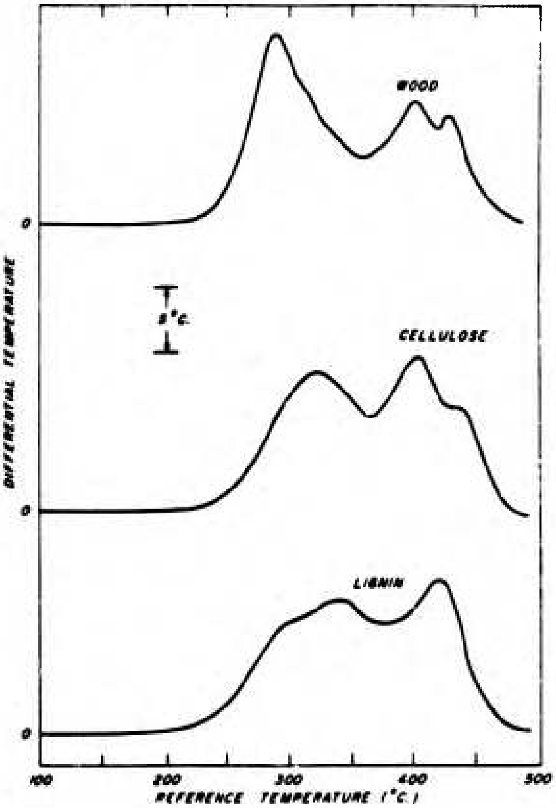


Figure 15.--The combustion of wood, cellulose, and lignin with 2 percent sodium chloride (differential thermal analysis). Specimen weight and form: Wood, 50-milligram, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 555)

The main effect was the reduction of the glowing of wood and cellulose as shown by the low heat intensity in the higher temperature range (350° to 500° C.). However, the flaming reduction by these chemicals was not as satisfactory as desired.

Samples with 8 percent disodium phosphate (fig. 26) showed remarkable similarity to those with 2 percent potassium bicarbonate (fig. 17) in differential thermal analysis. Ammonium sulfate falls in the same category as ammonium phosphate in its effectiveness as a fire retardant.

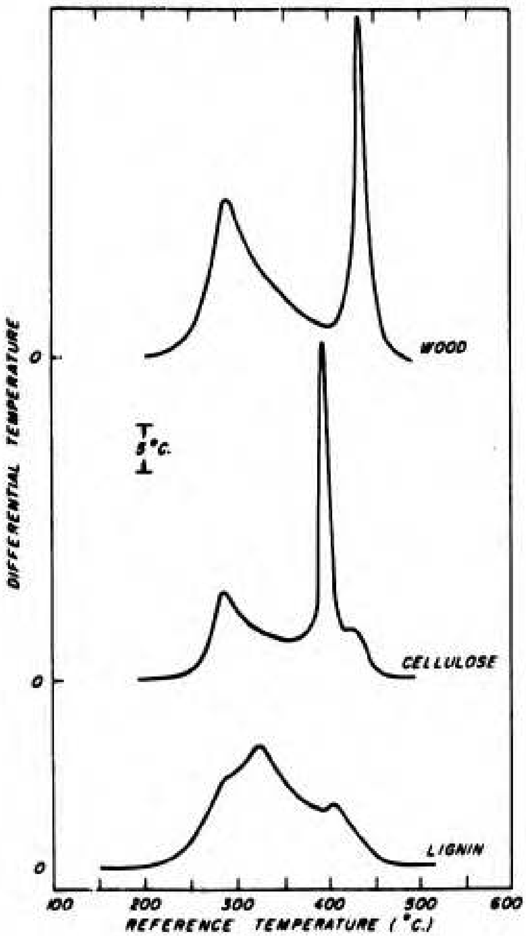


Figure 16.--The combustion of wood, cellulose, and lignin with 8 percent sodium chloride (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 556)

The thermograms (fig. 27) illustrate this similar behavior.

Thermochemistry of Reactions

In addition to defining the temperature range of thermochemical or thermophysical changes of a sample, quantitative differential thermal analysis can be used to estimate the magnitude

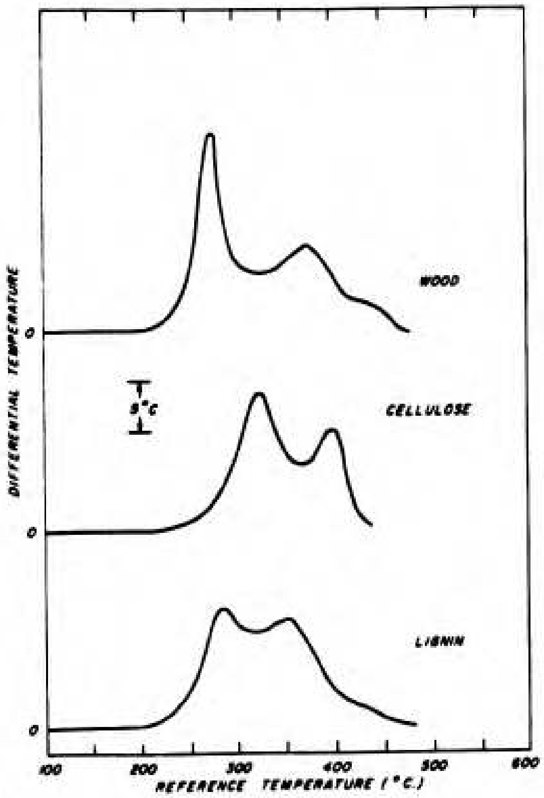


Figure 17.--The combustion of wood, cellulose, and lignin with 2 percent potassium bicarbonate (differential thermal analysis). Specimen weight and form: Wood, 50-milligram, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow, 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 557)

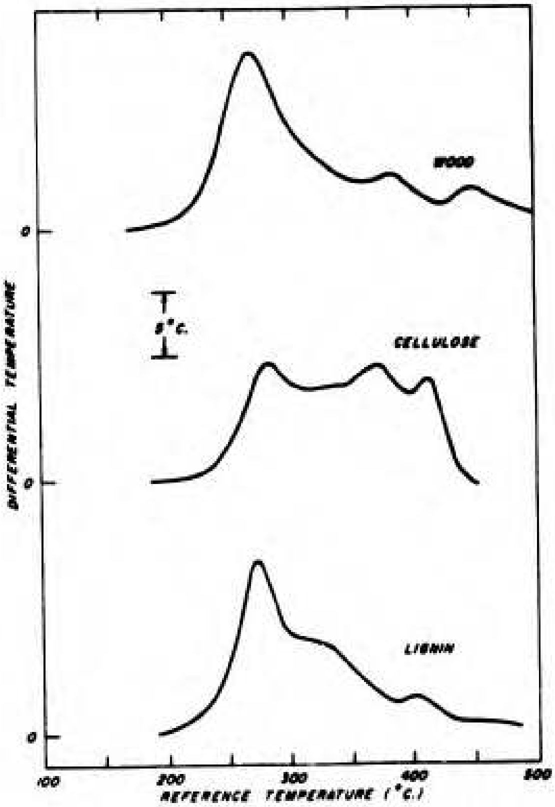


Figure 18.--The combustion of wood, cellulose, and lignin treated with 8 percent potassium bicarbonate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 558)

of energy absorbed or liberated.

A DTA approach (19) originally derived for the study of homogeneous reactions can also be applied to heterogeneous reactions of the type represented by the pyrolysis experiments, because (1) a small sample was used, (2) it was heated uniformly and with a negligible concentration gradient, (3) it decomposed uniformly and with a negligible concentration gradient, (4) the gas-to-solid reactions were localized without significant diffusion and mass transfer, and (5) the sample was in an essentially closed system.

This technique resulted quantitatively in the equation

$$(\Delta H)_s = \frac{A_s m_k}{A_k m_s} (\Delta H)_k$$

where

$(\Delta H)_s$ = heat of reaction of sample, calorie per gram
$(\Delta H)_k$ = known heat of reaction of a reference substance, calorie per gram
m_s, m_k = weight of sample and a reference substance, gram
A_s, A_k = areas under DTA curves, centimeter squared

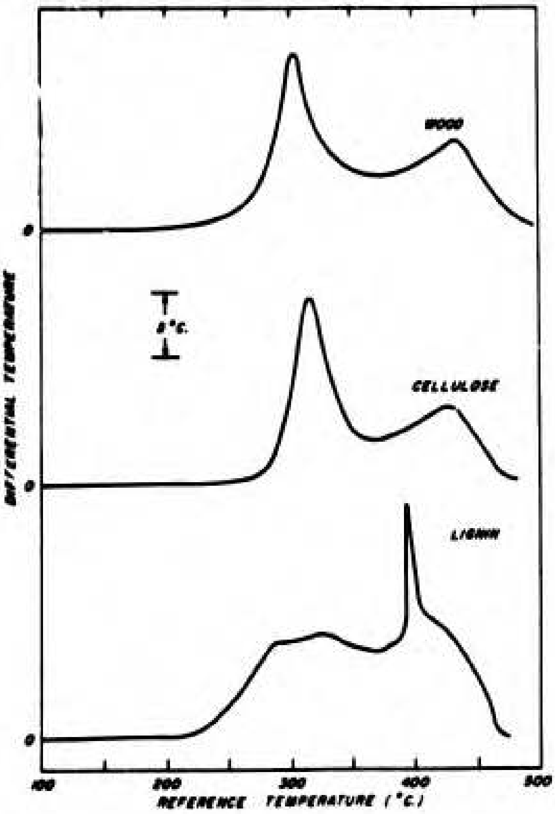


Figure 19.--The combustion of wood, cellulose, and lignin with 2 percent aluminum chloride hexahydrate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure.

(M 133 559)

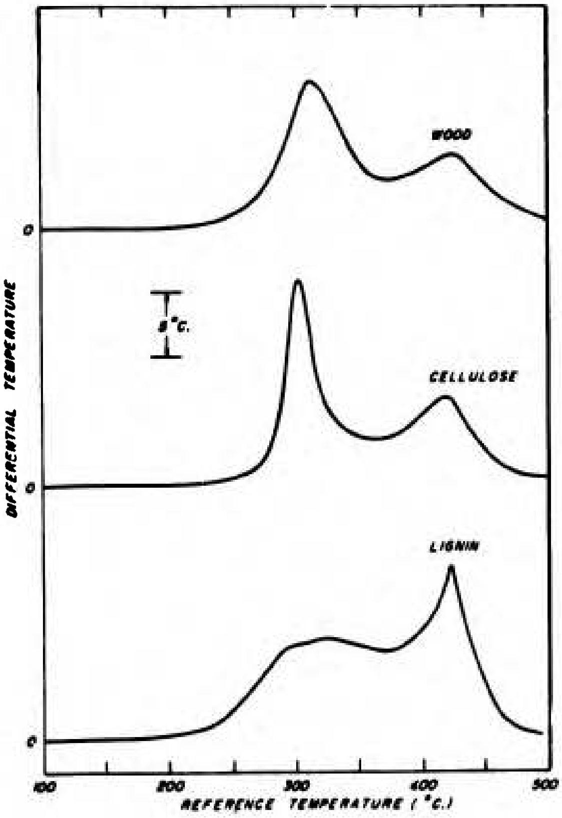


Figure 20.--The combustion of wood, cellulose, and lignin with 8 percent aluminum chloride hexahydrate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 560)

This equation was used to estimate the heat of pyrolysis from the areas of the thermograms (figs. 4 to 9). Differential thermal curves were obtained for the standard substances--silver nitrate, benzoic acid, and potassium nitrate--under the same experimental conditions as those of the wood, cellulose, and lignin samples. The areas for the thermograms of these compounds (with calibration values for the heat of fusion and melting points covering the range of 100° to 350° C.) were then compared to the thermograms of the wood samples. The values of heat of pyrolysis of untreated and treated wood, cellulose, and lignin under these conditions are listed in table 2.

The endothermic and exothermic heat changes indicated in table 2 are not to be taken as measures of individual homogeneous reactions. On the contrary, they revealed the overall results of various competing reactions. There may even have been both endothermic and exothermic reactions occurring in the same temperature range. For example, cellulose showed no apparent exothermic reaction (table 2); however, depolymeri-

Table 2.--Heat of pyrolysis of samples[1]

Sample treatment[2]	Wood				Cellulose				Lignin			
	Endothermic		Exothermic		Endothermic		Exothermic		Endothermic		Exothermic	
	T[3]	ΔH_{pyr}[4]	T[3]	ΔH_{pyr}[4]	T[3]	ΔH_{pyr}[4]	T[3]	ΔH_{pyr}[4]	T[3]	ΔH_{pyr}[4]	T[3]	ΔH_{pyr}[4]
	°C.	G.-cal. per g.	°C.	G.-cal. per g.	°C.	G.-cal. per g.	°C.	G.-cal. per g.	°C.	G.-cal. per g.	°C.	G.-cal. per g.
No treatment	200-390	77	390-500	31	240-450	88	.....	....	190-345	19	345-500	40
2 percent sodium tetraborate decahydrate	200-395	31	395-500	22	180-420	58	.....	....	210-360	13	360-500	35
2 percent sodium chloride	190-360	42	360-500	26	200-400	70	.....	....	200-340	17	340-460	25
2 percent potassium bicarbonate	190-380	38	380-500	19	175-400	72	.....	....	200-325	14	325-450	26
2 percent aluminum chloride hexahydrate	220-350	37	350-500	40	200-410	87	.....	....	220-340	9	340-470	34
2 percent monoammonium phosphate	180-315	45	315-500	36	170-400	78	.....	....	220-340	11	340-455	26

[1] 100-milligram samples in capsule in helium atmosphere by differential thermal analysis.

[2] Chemicals are 2 percent by weight.

[3] Temperature range of reactions; deviation, ±5° C.

[4] Heat of pyrolysis reactions; deviation, ±4 percent.

zation and decomposition occurred, implying that the values of the heat of pyrolysis are net values of opposing reactions.

The transition temperatures, endothermic to exothermic, of pyrolyzing lignin in table 2 are very close to the transition temperatures for lignin in the dual-segment kinetics mechanism in table 4 of the previous report on DTA (17). Thus, the transitional point of the kinetics mechanism may be the true transition between endothermic and exothermic reactions for wood, cellulose, and lignin rather than the apparent transition values shown on the DTA thermograms for wood and cellulose.

Untreated samples produce a greater endothermic heat of pyrolysis than do treated samples, and also have less char residue than the treated samples. There are two possible explanations:

1) Less gaseous products (less levoglucosan) may have been produced from treated than from untreated samples if the endothermic process is primarily the heat of volatilization of levoglucosan.

2) About as many gaseous products may have been produced initially, but some subsequently polymerized and recondensed as solids.

In explanation (1) the char would consist chiefly of charcoal. In (2) the content of charcoal would remain much the same for both treated and untreated samples, but there would be much tar coke among the solid residues from treated samples. However, the degree of change in heat of pyrolysis depended on the nature of the inorganic salts.

Heat of combustion.--If the combustion reaction goes to completion, the heat of combustion for treated wood, cellulose, and lignin samples, corrected for any heat effect produced by the chemical additive, must be the same as the heat of combustion of the untreated samples. In complete combustion, the end products of wood, cellulose, and lignin are the same (water, carbon monoxide, and carbon dioxide) for both untreated and treated samples. The effect of inorganic chemicals on the total heat of combustion in these cases is slight. Browne and Brenden (5) discussed this in their work on the heat of combustion of volatile pyrolysis products for untreated and treated wood.

In investigating the combustion of treated and

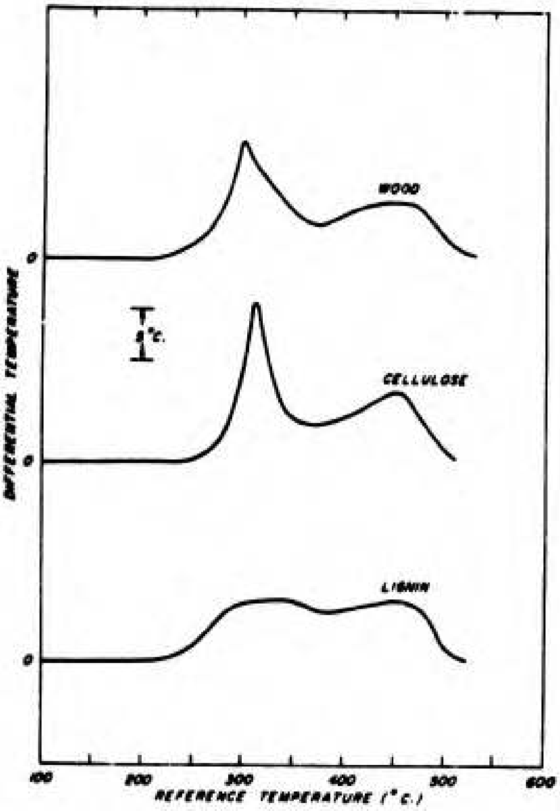


Figure 21.--The combustion of wood, cellulose, and lignin with 2 percent monoammonium phosphate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 561)

untreated cellulose, an attempt was made to use the latent heat of vaporization of ammonium chloride to calibrate the total heat of combustion. The DTA was run on ammonium chloride in flowing nitrogen instead of oxygen with all other conditions the same as in the DTA of the combustion of wood, cellulose, and lignin. The factor

$$\frac{m_k(\Delta H)_k}{A_k} = 2.2 \frac{\text{cal.}}{\text{cm.}^2} \text{ for } NH_4Cl$$

where

$$(\Delta H)_k = 39.6 \frac{\text{kcal.}}{\text{mole}} \text{ or } 740 \frac{\text{cal.}}{\text{g.}}$$

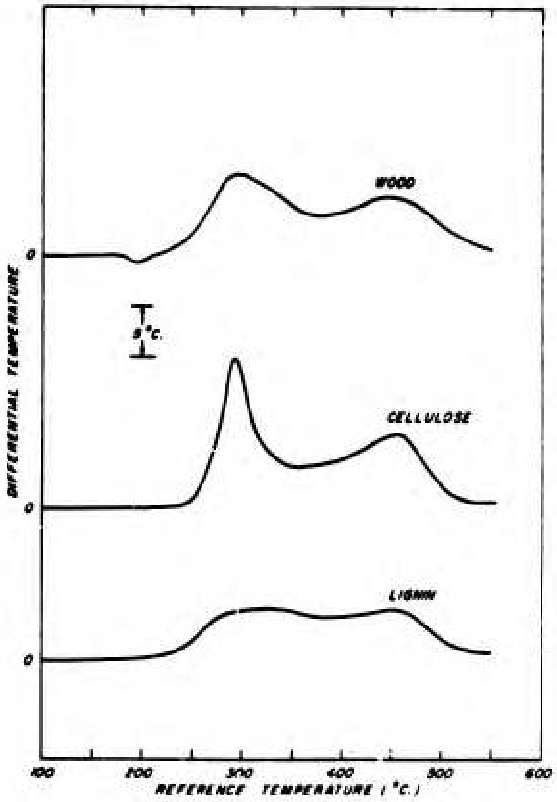


Figure 22.--The combustion of wood, cellulose, and lignin with 8 percent monoammonium phosphate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 562)

The DTA value for the combustion of cellulose with this calibration factor was about 12 percent lower than for the heat of combustion of untreated cellulose obtained in the oxygen-bomb calorimeter (-4030 cal./g.). A possible reason for the lower value is the loss of unburned volatiles in the gas stream. If the loss of combustible volatiles is proportional to the heat evolution and corrections are made accordingly, the maximum rate of heat generation may be estimated for untreated and treated wood, cellulose, and lignin. The values under these conditions are given in table 3.

Table 3.--Relative maximum heat intensity of combustion by differential thermal analysis for 50 milligrams wood and cellulose and 30 milligrams lignin in flowing oxygen

Sample treatment[1]	Temp.[2] and I_c[3]	Wood[4]			Cellulose[4]			Lignin[4]		
		Volatiles	Solids		Volatiles	Solids		Volatiles	Solids	
			First peak	Second peak		First peak	Second peak		First peak	Second peak
8 percent aluminum chloride hexahydrate	Temp.	310	425	......	305	420	......	330	425	......
	I_c	480	235	......	675	260	......	465	610	......
2 percent monoammonium phosphate	Temp.	300	450	......	315	450	......	335	455	......
	I_c	480	235	......	635	275	......	370	360	......
8 percent monoammonium phosphate	Temp.	295	450	......	290	455	......	330	455	......
	I_c	340	240	......	620	300	......	290	270	......
2 percent boric acid	Temp.	300	440	......	315	435	......	310	430	......
	I_c	650	190	......	830	205	......	465	540	......
8 percent boric acid	Temp.	315	440	......	320	445	......	320	435	......
	I_c	505	240	......	740	220	......	415	390	......
8 percent disodium phosphate	Temp.	280	390	440	310	395	......	295	375	440
	I_c	580	330	115	755	495	......	505	600	105
8 percent ammonium sulfate	Temp.	300	445	......	285	450	......	315	445	......
	I_c	300	200	......	460	260	......	365	390	......
8 percent ammonium pentaborate octahydrate	Temp.	310	440	......	325	440	......	310	425	......
	I_c	545	200	......	770	215	......	515	440	......

[1] Chemical percentages are by weight.

[2] Temperature at which the peak took place (±3° C.).

[3] Heat intensity of combustion, calories per gram-minute, at particular peak, variation ±5 percent.

[4] Predominantly volatiles or solids

These results show a definite suppression by the inorganic salts on the maximum rate of heat generation in the flaming of wood and cellulose. However, the degree of suppression by the salts does not indicate their relative effectiveness because they cannot be properly compared by a weight-percentage basis. Among these salts, sodium tetraborate indicated a definite two-stage stimulation of glowing combustion on the lignin fraction of wood, whereas a high concentration of sodium chloride strongly promoted the burning of chars of the cellulose fraction. Potassium bicarbonate and sodium chloride caused an early breakdown of lignin for volatile combustion. A stimulated glowing pulse appeared in the heat intensity of aluminum chloride-treated lignin. However, it was weak compared to the overall burning process of aluminum chloride-treated wood.

DISCUSSION OF RESULTS

For a more meaningful interpretation of the differential thermal analysis data obtained in oxygen and helium atmospheres, it is desirable to expand the comparison to include the TGA (thermogravimetric analysis) data (figs. 28 to 31) obtained in vacuum for the untreated and treated wood, cellulose, and lignin samples in the previously reported part of this investigation (17).

After the loss of water at about 100° to 150° C. in the initial stage of pyrolysis of untreated wood, the decomposition of hemicellulose started at about 200° C. (figs. 3, 12, and 28). Subsequently, hydrolysis of cellulose and pyrolysis of lignin and cellulose followed in order. All of these reactions took place endothermically by DTA and with the TGA weight loss. Ignition

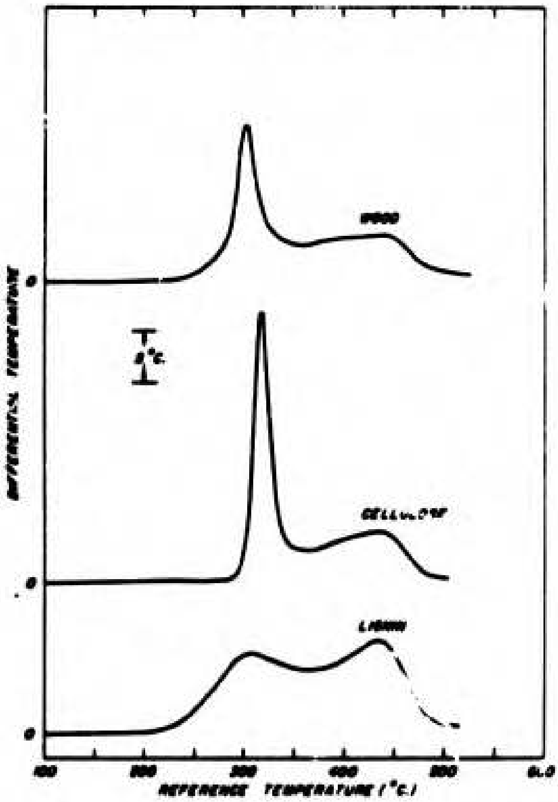


Figure 23.--The combustion of wood, cellulose, and lignin with 2 percent boric acid (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 563)

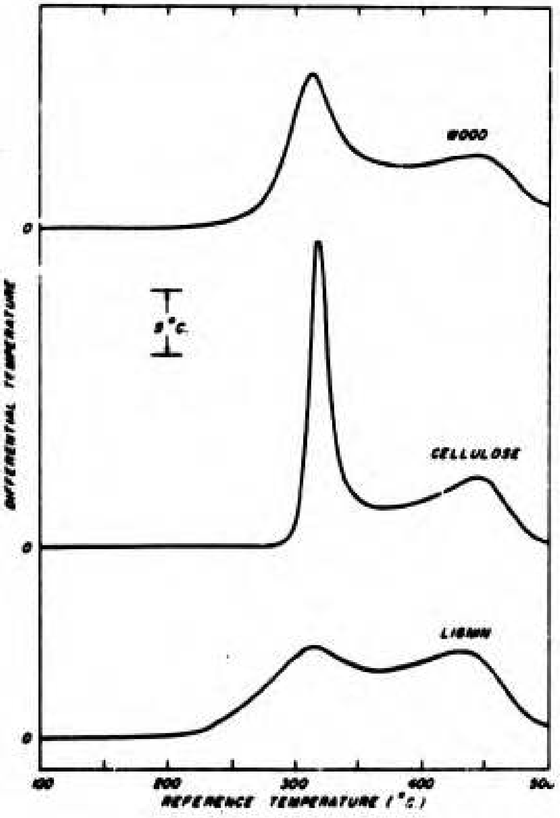


Figure 24.--The combustion of wood, cellulose, and lignin with 8 percent boric acid (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 564)

and combustion of volatiles took place at about 305° C. where the maximum rate of temperature rise occurs in oxygen DTA. About 25 percent of the volatiles (excluding the initial moisture) was involved in ignition. The flaming subsided at about 360° C. where the active endothermic reaction and the related weight loss were completed.

The pyrolysis DTA (fig. 4) showed an exotherm for the expected reactions in forming secondary char in a "closed" system. At 360° C. the burning of char took place, and the glowing ended at about 480° C. Depolymerization of cellulose took place without a weight loss from 200° to 270° C. and continued beyond 270° C., where the TGA curve began to show a significant weight loss. This may have involved volatilization of "monomeric" levoglucosan in the initial stage of pyrolysis.

In the final stage, the endotherm reached its nadir at 335° C. where the rate of weight loss reached its maximum, and the combustion exotherm reached a peak from combustion of volatile tars. Near 360° C., the pyrolytic endotherm and the weight loss indicated that active pyrolysis, with evolution of low-molecular-weight flam-

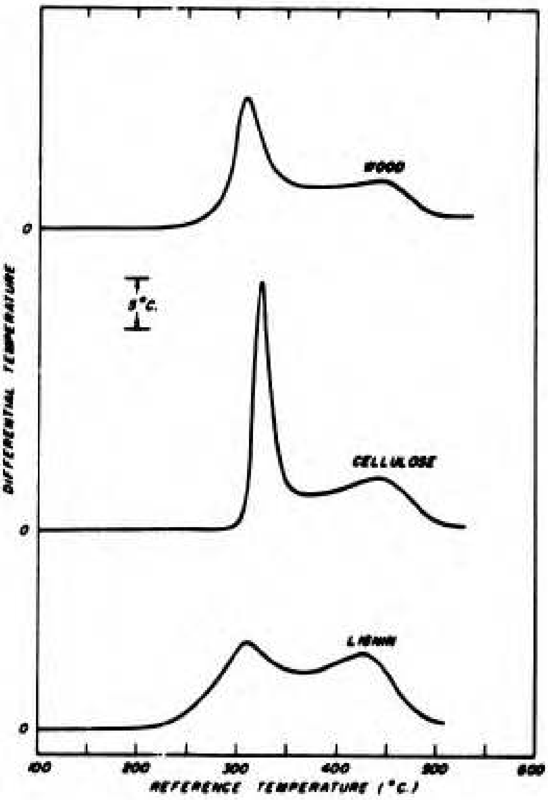


Figure 25.--The combustion of wood, cellulose, and lignin with 8 percent ammonium pentaborate octahydrate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure (M 133 565)

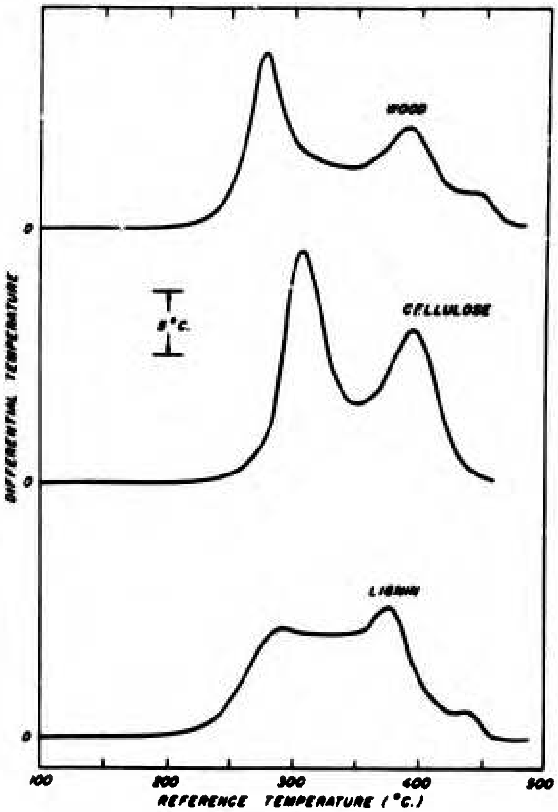


Figure 26.--The combustion of wood, cellulose, and lignin with 8 percent disodium phosphate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 566)

mable tars, was almost completed. In combustion in oxygen, however, an exotherm continued because the higher molecular-weight chars were being consumed by glowing until about 460° C., at which point the entire sample had been consumed.

Because of the nature of chemically degraded lignin, the pyrolysis of lignin showed only a weak endothermic reaction from 200° to 345° C., where the weight loss began and attained the maximum rate. Oxidation was weakly exothermic in that temperature range. The weight loss continued beyond 345 C., and the pyrolysis became exothermic until the active weight loss ceased. At that time, lignin chars were completely consumed by glowing combustion.

These reactions were modified to different degrees by inorganic salts as shown in figures 5 to 9 (DTA, pyrolysis), figures 13 to 27 (DTA, combustion), and figures 29 to 31 (TGA, pyrolysis).

Published information is not available on reaction mechanisms between wood, cellulose, lignin, and sodium tetraborate in the absence or presence of oxygen at high temperatures. Experimental results have shown that more char and

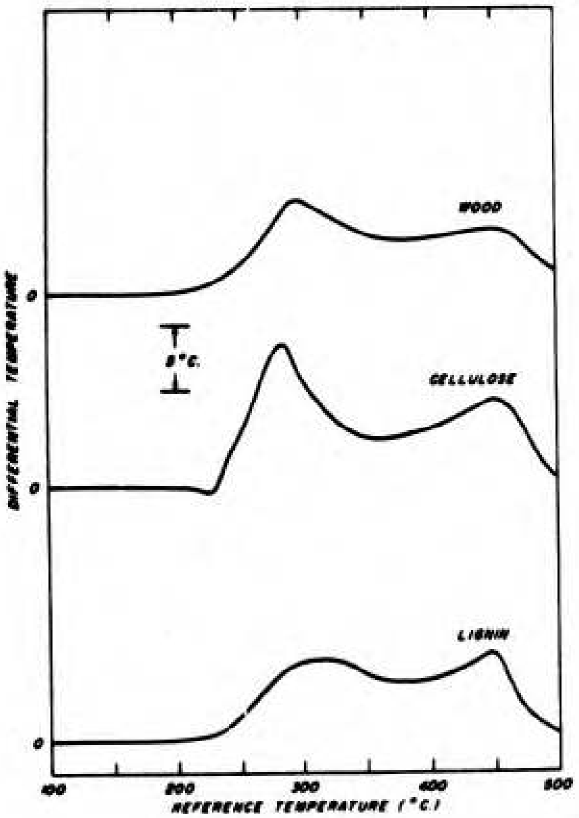


Figure 27.--The combustion of wood, cellulose, and lignin with 8 percent ammonium sulfate (differential thermal analysis). Specimen weight and form: Wood, 50-milligrams, 40-mesh treated ponderosa pine particles; Cellulose, 50-milligrams treated Whatman cellulose powder; Lignin, 30-milligrams treated spruce lignin powder (sulfuric acid processed); Heating rate, 12° C. per minute by conduction and convection; Atmosphere, oxygen flow 30 milliliters per minute at 27° C. to each cavity at atmospheric pressure. (M 133 567)

less tar are formed by the effect of sodium tetraborate on pyrolysis of wood (2) and cellulose (11, 12).

Low concentration solutions of sodium tetraborate contain predominantly monoborate ions.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 2Na^+ + 2B(OH)_4^- + 2H_3BO_3$$

Whereas at high concentrations tetraborate ions predominate

$$Na_2B_4O_7 \rightleftharpoons 2Na^+ + B_4O_7^{=}$$

Tetraborate ions may also be formed according to the equation:

$$B(OH)_4^- + 3H_3BO_3 \rightleftharpoons HB_4O_7^- + 6H_2O$$

wherein the acid tetraborate ion may be further ionized to the tetraborate ion (13). The uncharged species corresponding to these ions is the hypothetical tetraboric, or pyroboric, acid $H_2B_4O_7$, existing only in ionic form in solution (13). The behavior of sodium tetraborate may be considered favorable because it does not attack cellulose at low temperatures. When heated in air, sodium tetraborate dissolves in its own water of crystallization, swells to a frothy mass, loses water, and fuses to a clear melt (13).

It is evident from the TGA results that cellulose was not significantly attacked by sodium tetraborate below the active pyrolysis temperature of untreated cellulose (17).

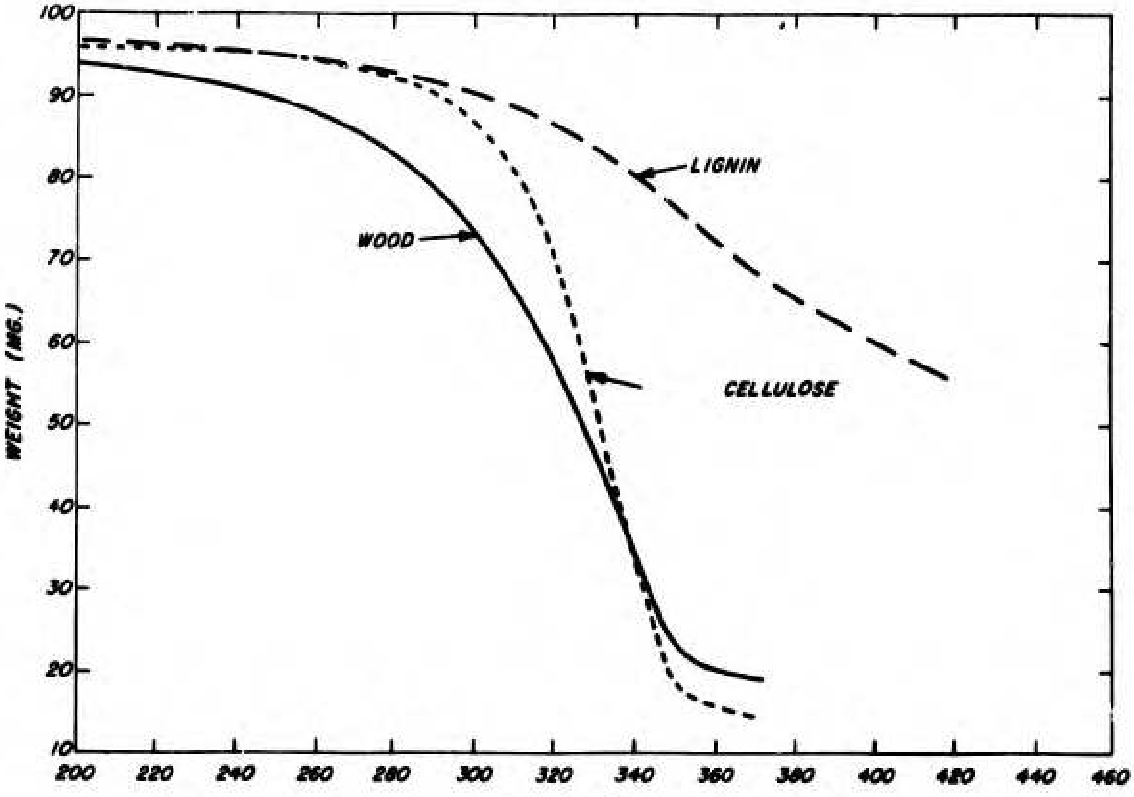
Sodium tetraborate probably dissociates in water with heating:

$$Na_2B_4O_7 + 2H_2O \rightleftharpoons 2H^+ + B_4O_7^{=} + 2Na^+ + 2OH^-$$

$$\text{and } 2Na^+ + 2OH^- \rightleftharpoons 2NaOH$$

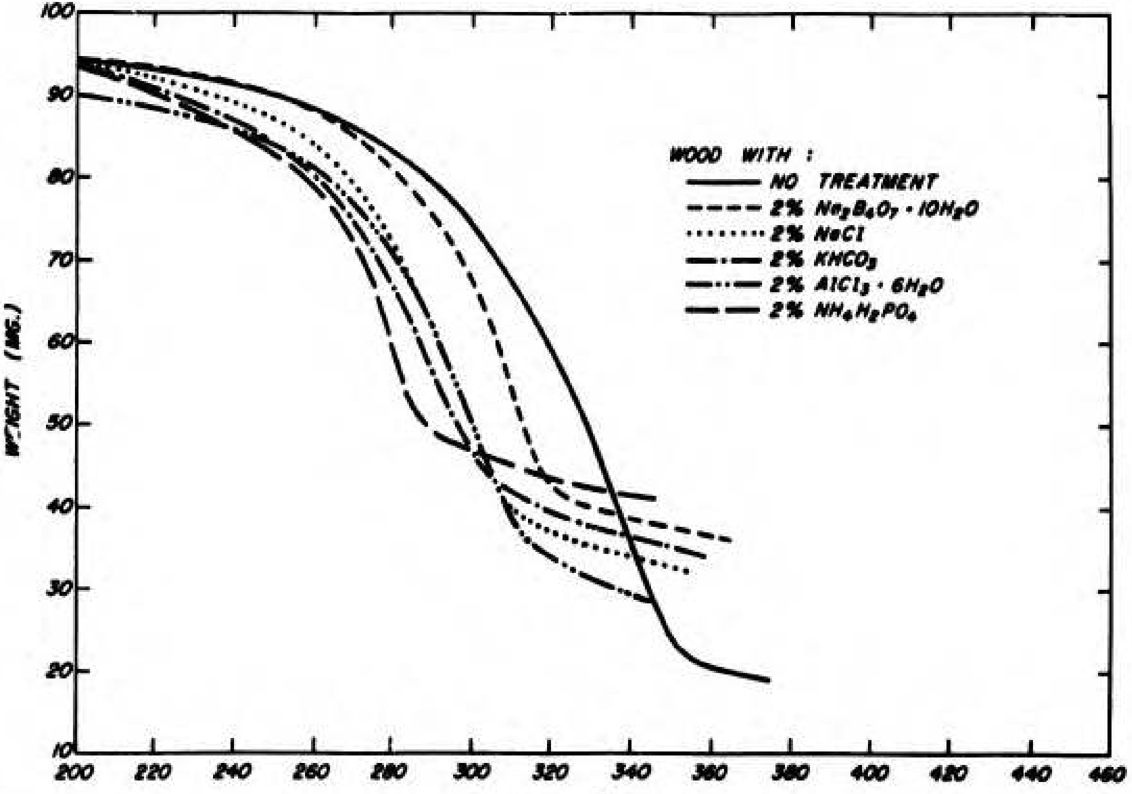
As the wood impregnant undergoing pyrolysis, sodium tetraborate acts as the ions of a salt of strong base and weak acid in water from the pyrolyzing wood. The hydroxyl anions, in accordance with the Lewis electron theory, cause dehydration of the glucose units of the cellulose molecule by the formation of carbanions (4, 16). Thus, it may be postulated that, unlike other dehydration mechanisms, sodium tetraborate does not dehydrate cellulose before depolymerization has taken place. It actually functions as a salt of strong base and weak acid in the initial stage of pyrolysis where weight loss becomes significant, and causes dehydration to compete with the formation of levoglucosan after scission of the cellulose C-O-C bonds. This Lewis base mechanism might be modified to apply to the numerous alcoholic hydroxyl groups of lignin by reactions similar to those attributed to cellulose. This was illustrated by TGA in the increase in char formation (17).

The DTA of sodium tetraborate-treated cellulose in oxygen (fig. 12) exhibits the expected reduction in flaming and increase in glowing. The curves for wood and lignin have two peaks stimulated in the glowing combustion range. The first is probably from the burning off of increased



(M 131 817)

Figure 28.--Relationship of increased temperatures to weight of untreated wood, cellulose, and lignin.



(M 131 815)

Figure 29.--Relationship of increased temperature to weight of wood with and without inorganic salts.

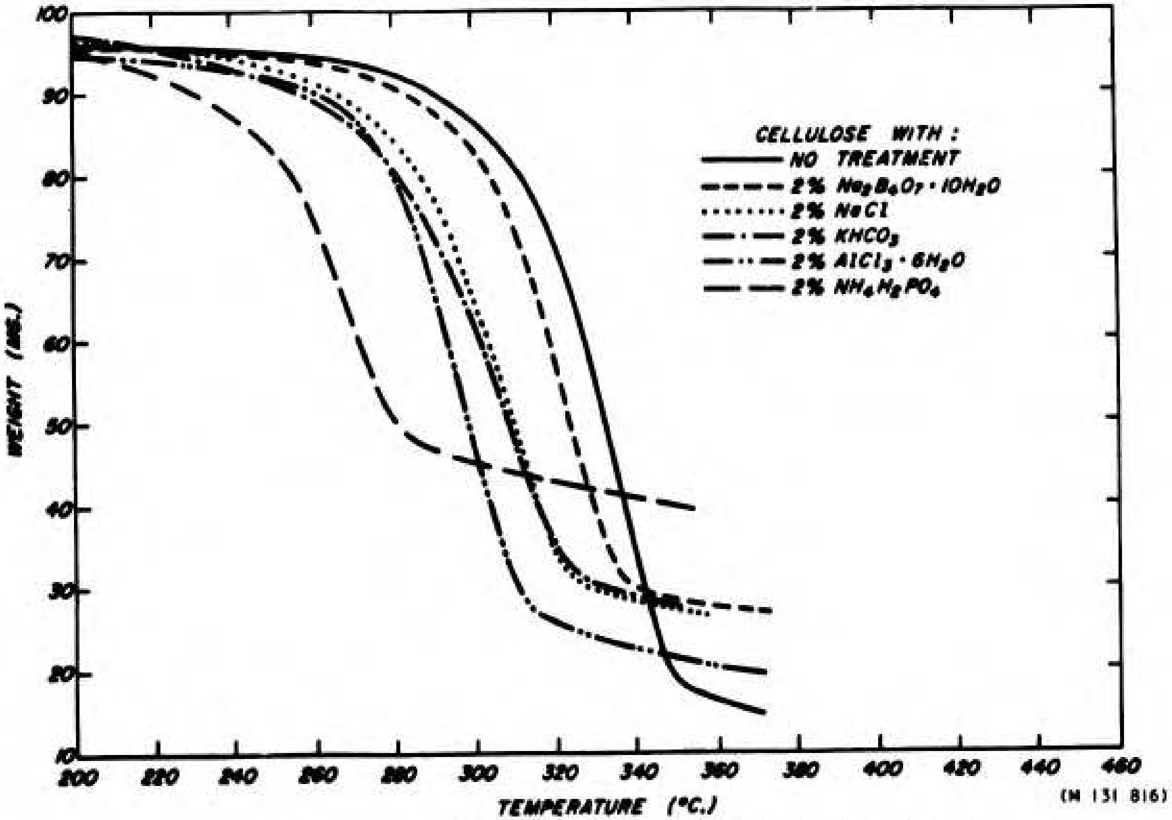


Figure 30.--Relationship of increased temperature to weight of cellulose with and without inorganic salts.

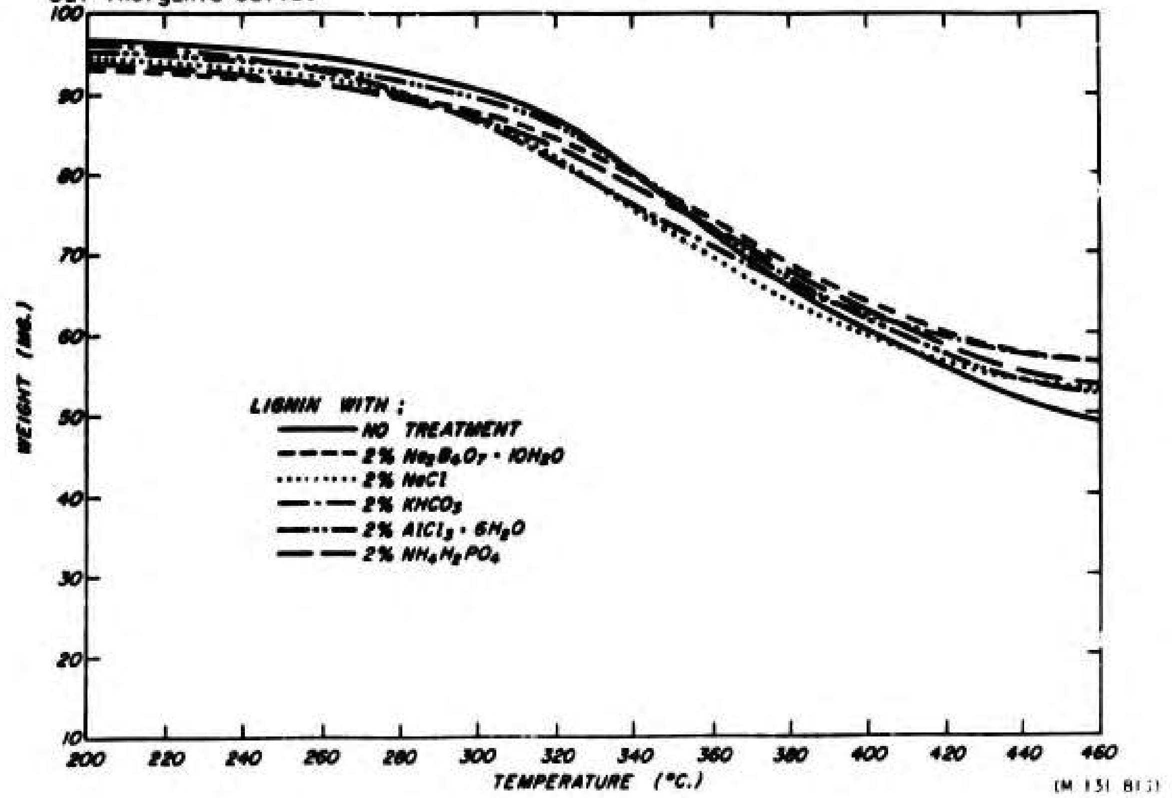


Figure 31.--Relationship of increased temperature to weight of lignin with and without inorganic salts.

char due to the chemical treatment. The second glowing peak is characteristic of sodium tetraborate. The intensity increases with an increase in borate concentration. The second peak was at first attributed to the crystallization of anhydrous borax. However, that would be expected to occur at a higher temperature, greater than 600° C. (3).

In the literature on the DTA of borax, none of the authors mentions an exotherm near 500° C. (1, 8, 9). The DTA for a mixture of sodium tetraborate and Pyrex bead reference material showed no effect in oxygen up to 600° C. Therefore, it was concluded that this exothermic reaction was the catalyzed burning of lignin char residues because it occurred in lignin and in wood but at a temperature at which cellulose was completely consumed.

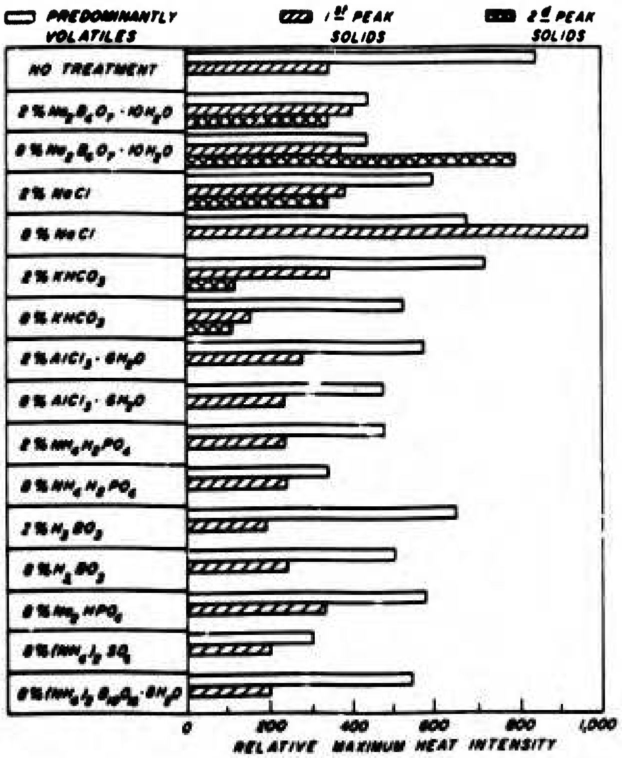
Sodium chloride also showed some ability to reduce tar and increase char in the pyrolysis of wood (2) and cellulose (16). Madorsky et al (15) proposed that sodium chloride could have a catalytic effect on dehydration and bond scissions taking place inside and outside the rings of the cellulose chain, resulting in an increased yield of water, carbon dioxide, and carbon monoxide at the expense of levoglucosan, and could also cause an increased rate of degradation of cellulose, particularly in the initial stages.

The catalytic effect attributed to sodium chloride is by no means limited to pyrolysis. At the low concentration of 2 percent, there was an apparent endothermic reaction that occurred during the combustion exotherm at about 425° C. for both cellulose and wood (fig. 16), but lignin heated in oxygen was not affected much. At the higher concentration of 8 percent, however, lignin was catalyzed and burned at a lower temperature in the volatilization range (fig. 16), and the chars of cellulose and wood were catalyzed at an extremely high-intensity combustion at temperatures where lignin has already been consumed. From this evidence, sodium chloride acts as a retardant in pyrolysis. However, when oxidation is involved, the effect reverses to stimulate burning.

When 2 percent potassium bicarbonate was added to cellulose, an increased weight loss and endothermic effect occurred between 100° and 200° C., presumably from reactions initiated by the decomposition of potassium bicarbonate to potassium carbonate, carbon dioxide, and water. The endotherm (fig. 7) indicated that a series of complex reactions probably took place between 200° and 350° C. The depolymerization of cellulose was expected to compete with a dehydration reaction by a Lewis base formed in the dissociation of potassium carbonate in water from pyrolysis, leading to an increased rate of formation of carbon dioxide, carbon monoxide, and char at the expense of tar. The combustion curve (figs. 17 and 18) for treated cellulose shows decreased flaming but increased glowing in comparison to untreated cellulose.

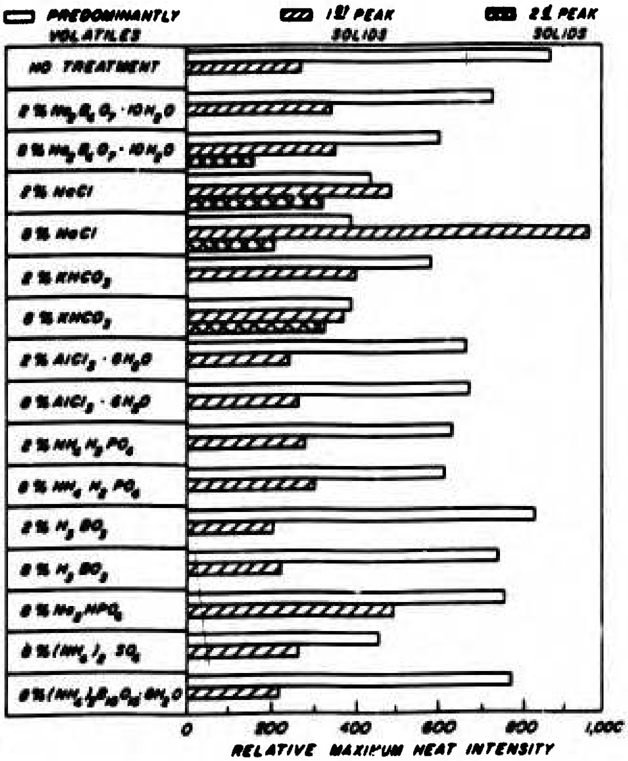
The effect of potassium bicarbonate on cellulose is not as distinct as the effect [illegible]ed with lignin and wood. The combustion of treated lignin took place in the temperature range of its volatilization, about 100° C. lower than the temperature for combustion of untreated lignin. The burning temperature of treated wood was also lowered. These phenomena were exaggerated with the higher concentration, 8 percent, of potassium bicarbonate. Lignin assumed the major role in the combustion of wood, as is shown by the similarity of the combustion of treated lignin and wood. It is possible that the Lewis base had a great effect on the numerous hydroxyl groups and that it further degraded the pyrolyzed molecule to fragments consumed by oxidation at lower temperatures.

The DTA curves (figs. 8, 19, and 20) of aluminum chloride hexahydrate-treated samples show a similar trend of reduction of the endothermic nadir for pyrolysis and reduction of exothermic flaming peak. Glowing of lignin was sharply stimulated, but this stimulation was apparently minor and did not affect the burning of wood, even with the higher salt concentration of 8 percent. There was little difference in performance between 2 and 8 percent salt concentration. Aluminum chloride hydrate breaks down to aluminum oxide, hydrochloric acid, and water between 100° and 180° C. (from TGA data (17)). Aluminum chloride and aluminum oxide are both Lewis acids (16). TGA and DTA suggest that the Lewis acid dehydration mechanism was initiated during the decomposition of aluminum chloride hexahydrate. This catalytic process was sustained by aluminum oxide. The pyrolysis temperature of cellulose and wood was lowered by hydrochloric acid, but these reactions caused no change in the rate of weight loss of cellulose. The hydrate of aluminum chloride apparently has its primary effect on the cellulose portion of wood.



(M 133 569)

Figure 32.--Maximum heat intensity of combustion of wood (from DTA data).



(M 133 568)

Figure 33.--Maximum heat intensity of combustion of cellulose (from DTA data).

The decomposition of monoammonium phosphate yields ammonia and phosphoric acid at 166° C., and phosphoric acid further decomposes by:

$$2H_3PO_4 \xrightarrow{216^\circ\ C.} H_2O + H_4P_2O_7$$

$$\text{and } H_4P_2O_7 \longrightarrow 2H_2O + P_2O_5$$

The formation of phosphoric acid and possibly phosphorous pentoxide later would dehydrate cellulose by reacting with the hydroxyl groups (4). Ammonium phosphate is extremely effective in both flaming and glowing retardance for both cellulose and lignin as shown in figures 9, 21, and 22. Ammonium sulfate produced similar results, probably by the same mechanism.

Ammonium pentaborate and boric acid were mainly effective in glowing retardance. Ammonium pentaborate, capable of being dissociated to ammonia and boric acid, behaved like boric acid in pyrolysis of wood, cellulose, and lignin. Disodium phosphate, which dissociates in water, had an effect similar to that of potassium bicarbonate. It probably functioned as a Lewis base with strong sodium ions and weak acid phosphate ions.

The histograms in figures 32, 33, and 34 represent the effect of inorganic chemicals on combustion. All of the tested inorganic chemicals reduced the flaming of wood (fig. 32). If a comparison is made on a weight-percentage basis, sodium tetraborate and ammonium phosphate were the most effective, whereas sodium chloride, potassium bicarbonate, and disodium phosphate were the least effective. Sodium tetraborate and sodium chloride stimulated glowing, whereas boric acid, potassium bicarbonate, and ammonium salts most effectively suppressed glowing.

All chemicals reduced the flaming of cellulose in different amounts (fig. 33). If comparison is made on the basis of chemical concentration, sodium chloride, potassium bicarbonate, ammonium sulfate, and ammonium phosphate are most effective, whereas boric acid, ammonium pentaborate, and disodium phosphate are the least effective. However, all chemicals reduced volatiles and increased char and promoted glowing except for boric acid and the ammonium salts. Sodium chloride and disodium phosphate stimulated the most pronounced glowing of cellulose.

The volatile flaming peak of lignin is rather meaningless because normally only lignin glows. However, with potassium bicarbonate, sodium tetraborate, and sodium chloride, the heat inten-

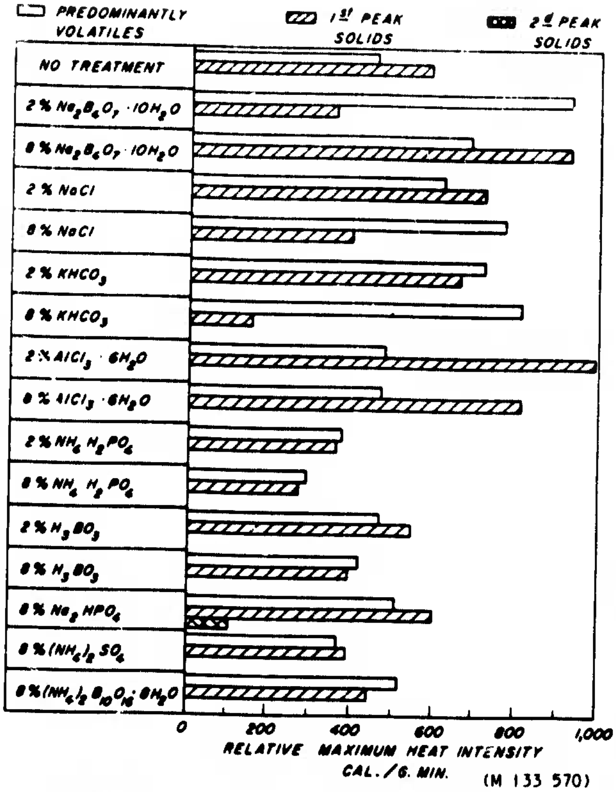


Figure 34.--Maximum heat intensity of combustion of lignin (from DTA data).

sity suggests that flaming may occur even with the slow volatilization rate of lignin. If flaming did not occur, the glowing combustion would be extensive. Ammonium phosphate and ammonium sulfate suppress these reactions.

CONCLUSIONS

Four types of reaction in the pyrolysis of cellulose (14) may be postulated from these observations:

1) A dehydration, first observed at about 220° C.; cellulose reacts in a process involving loss of water to yield a partially dehydrated cellulose. Such loss of water was confirmed by mass spectrometric thermal analysis.

2) A depolymerization, with volatilization of the product (tar, largely levoglucosan), first evident at about 280° C.; previously unreacted cellulose breaks into smaller molecules that volatilize via an endothermic process competitive with the dehydration.

3) A decomposition of the "dehydrocellulose" formed in the first process--by one or more exothermic reactions into a number of gaseous products and residual char. At lower temperatures the decomposition is slower than rate of formation of the dehydrocellulose, but the decomposition rate increases rapidly with temperature.

4) A condensation of simpler substances from the decomposition products.

The initial dehydration of untreated cellulose may be quantitatively estimated from 220° to 280° C. to consist of one hydroxyl group from every four glucose units. The hydroxyl to glucose ratio is increased when cellulose is treated with retardants. The outstanding example is cellulose treated with ammonium phosphate from which about 1-1/4 hydroxyl groups are taken from each glucose unit. This increase in dehydration results in more water and char at the completion of active pyrolysis. The dehydration and the char-forming reactions are at the expense of the depolymerization reaction that produces levoglucosan.

Dehydration also occurs in lignin; however, instead of the depolymerization that takes place in cellulose, lignin or dehydrated lignin probably undergoes fragmentation and decomposition. Inorganic salts evidently increase the dehydration reaction and the char formation.

The decomposition of the wood shows the additive effects of cellulose and lignin reactions with the cellulose predominant as expected from the relative proportions of cellulose and lignin in wood.

From the study of pyrolysis kinetics (17), it appears that wood, cellulose, and lignin volatilize with dual-stage pseudo-first-order mechanisms. In untreated and treated cellulose, the initial stage may also fit pseudo-zero-order (18). Random scission and terminal cleavage of macromolecules in the initial pyrolysis would account for this observation. However, with the pseudo-first-order reaction, volatilization of the fragments would be expected for all three types of samples. The activation energies for the treated samples were either equal to or lower than those for the untreated samples. Sodium tetraborate primarily affected lignin. Sodium chloride lowered the activation energies for the second stage of wood and cellulose pyrolysis. Aluminum chloride changed the values in the first stage for lignin and in the second stage for wood pyrolysis.

In pyrolysis, inorganic compounds have much more effect on wood or cellulose than on lignin.

The decomposition of cellulose begins with dehydration, and several possible mechanisms (14) may follow. These include the decarbonylation, dehydration, and decomposition of simpler compounds. Some of the products of such decomposition could undergo intermolecular condensations, for example, aldehydes with acids, further dehydrations, and other decompositions to form complex materials of char (tar coke). The four major types of reaction in pyrolysis of cellulose compete with one another, and the thermochemical values for the pyrolysis of cellulose from DTA result from the interaction between these reactions. The relative proportions of the four types vary with the conditions under which pyrolysis takes place, particularly when inorganic additives are present.

Effective flame retardants minimize the depolymerization that produces flammable tars, such as levoglucosan, and stimulate dehydration that produces water and char. These phenomena are illustrated thermochemically by DTA pyrolysis thermograms. The pyrolysis of wood is affected by inorganic additives in much the same manner as cellulose by the direction of the four types of reactions, although wood is complicated by the presence of lignin.

It has often been thought that the pyrolysis of wood and other cellulosic materials is highly exothermic. The results of this thermochemical work show that the net heat of pyrolysis of untreated and treated cellulose is endothermic. The pyrolysis of both wood and lignin is initially endothermic and later exothermic. The heat produced in these reactions is small. However, a trace of oxygen may upset all endothermic processes causing them to become highly exothermic.

The endothermic heat of pyrolysis for cellulose is 88 calories per gram, whereas its heat of combustion is -4030 calories per gram. The heat of pyrolysis then is actually about 2 percent of the heat of combustion. The change in the heat of pyrolysis by chemicals depends on the nature of the chemicals. The heat of dehydration and the heat of depolymerization of cellulose must be about the same, because the change in the ratio of these two reactions as influenced by inorganic salts does not effectively change the net heat. However, sodium tetraborate promotes the least dehydration but catalyzes decomposition and recondensation of the depolymerized species reducing the heat of pyrolysis of cellulose from the exothermic heat from secondary polymerization and aromatization. Chemical treatment greatly reduces the endothermic heat of wood pyrolysis by perhaps the same mechanism with the presence of lignin. These results contradict the assumption that pyrolysis is strongly exothermic. The pyrolysis must be preempted by oxidation to become strongly exothermic.

Combustion adds subsequent and competitive oxidation reactions to the existing four types of pyrolysis reactions (14). Water from dehydration does not contribute to oxidation, but the products of depolymerization, 1, 4-anhydro-α-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, and levoglucosan, are strongly oxidized in flaming. Volatile products from the decomposition of partially dehydrated cellulose would also contribute to the gas-phase oxidation. However, depolymerization produced most of the material for the gas-phase burning, whereas char from dehydration and secondary decomposition and condensation oxidizes, burning only in the solid phase by glowing without flaming. Therefore, cellulose, which undergoes little initial dehydration but yields much levoglucosan by depolymerization, burns predominantly by flaming. When dehydration is increased by the effect of inorganic salts, more solid-phase oxidation, or glowing of char, takes place at the expense of flaming.

Lignin, with decomposition products that are primarily solids in the combustion range, contributes little or nothing to flaming but supports the oxidation of solids by glowing. In the complexity of the pyrolysis and combustion of wood, the cellulose and lignin components retain their individual characteristics. The effect of chemicals accentuated these individualities.

In the combustion of wood, cellulose, or lignin, treated with sodium tetraborate or sodium chloride, the individualities of cellulose and lignin are clearly defined. In the range of 400° C. to above 500° C., the tar products formed initially broke down into secondary charcoal or tar coke, adding to the primary charcoal first formed. In this stage, the individualities of cellulose and lignin diminish. In the DTA, combustion of charcoal treated with sodium tetraborate and sodium chloride followed a course different from treated cellulose or lignin. Therefore, the char from treated wood, which shows the individualities of treated cellulose and lignin, must have been formed in the earlier stage of pyrolysis and combustion. Thus, sodium tetraborate causes intensive glowing of char from the lignin fraction, whereas sodium chloride stimulates the glowing of the cellulose portion of wood.

In contrast to the early formation of compounds that are oxidized at high temperatures, potassium bicarbonate and disodium phosphate produce an immediate breaking down of lignin and oxidize its fragments at lower temperatures.

Boric acid and ammonium pentaborate cause little dehydration and depolymerization of cellulose, but reduce the oxidation of solid decomposition and condensation products, limiting the glowing of cellulose.

In samples treated with ammonium phosphate, dehydration apparently predominates in both cellulose and lignin. Even the char of the decomposition products is not easily oxidized.

The pyrolysis and the combustion of cellulose parallel each other in that the maximum rate of weight loss, the endothermic nadir, and the exothermic peak occur at about the same temperature. The addition of other materials such as lignin and inorganic salts shifts this parallelism. This shift also seems to indicate the mechanism of pyrolysis and combustion of each treatment. Sodium tetraborate, which causes the least dehydration, shifts the endothermic nadir to a higher temperature at which the weight loss and flaming have almost ceased. In contrast, ammonium phosphate, which causes the most dehydration of cellulose, has its nadir at a lower temperature. This is near the end of the weight loss but before the full intensity of flaming. Other treatments fall between these extremes.

Treated wood shows effects similar to those occurring with cellulose. The endothermic pyrolysis nadirs of untreated and treated lignin occur at the beginning of active weight loss. However, the exothermic peaks of both pyrolysis and combustion occur near the completion of weight loss except for the potassium bicarbonate and disodium phosphate treatments from which the combustion peaks are found in the intermediate weight-loss range.

It is difficult to relate the fire-retardant effectiveness of chemicals from the results of this work solely on the basis of weight loss and char yield because other effects noted in the thermochemical results and side reactions are caused by certain chemicals. Generally, the thermogravimetric data indicated that sodium tetraborate, boric acid, aluminum chloride, ammonium phosphate, and ammonium sulfate were all in the effective fire-retardant classification (17). However, sodium tetraborate stimulates the glowing of lignin, and boric acid or ammonium pentaborate is relatively ineffective in flame retardation, but the mixture of these two compounds results in an effective fire retardant used commercially.

The results here agree with previous work in that ammonium sulfate and ammonium phosphate are effective retardants but that they increase the volatilization of wood at relatively low temperatures. Other chemicals such as potassium bicarbonate, disodium phosphate, and aluminum chloride are not effective. Sodium chloride is entirely ineffective even though it reduces flaming in the early stage of combustion.

It is difficult to generalize on the effectiveness of all the chemicals because the phenomena differ. However, it may be postulated that salts of a strong base and a weak acid have a pronounced effect on lignin, promoting glowing or even flaming. The salts of a strong acid and a weak base suppress the flaming of both cellulose and lignin, especially cellulose. The salts of a strong base and a strong acid are effective catalysts in forming more char and less tar, but stimulate glowing combustion. Salts of a weak base and a weak acid or a weak acid alone are apparently effective in preventing low flames but do not retard them. Finally, all salts reduce the formation of levoglucosan to a certain degree, reducing flaming.

These results may be related to the theories of the mechanism of flame retardance that have been advanced in the literature, particularly chemical theories that the chemicals directly alter the pyrolysis of wood. Following is a quotation from Browne and Tang (7):

> a. Since thorough dehydration of cellulose leaving only carbon in an ideal reaction for the purpose, useful chemicals are likely to be highly hydrophilic and soluble in water.
>
> b. Since strong acids and strong bases tend to attack cellulose, salts of strong acids with weak bases or of weak acids with strong bases, which dissociate readily when heated, are likely to be effective.

c. More specifically, the action of acids and bases is postulated as a condensation at the hydroxyl groups of cellulose (or lignin) with splitting off of water followed by pyrolysis to regenerate the acid or base, leaving carbon.

d. Still broader application of the theory of acids and bases is gained on the basis of the electron donor-acceptor theory (Lewis theory) of acids and bases with intermediate formation of carbonium ions or carbanions.

e. Many of the effective flame retardants contain groups capable of hydrogen bonding. such as -O, -OH, or $-NH_2$ groups, hence by their hydrogen bonding they may tend to hold the carbon atoms of cellulose and lignin together in char instead of allowing their escape in volatile fragments. A variant of the theory relies on polyfunctionality of phosphates, borates, sulfates, etc., to accomplish the same purpose.

In applying these theories, consideration must be given to the stimulation of burning of char by sodium tetraborate and sodium chloride and the promotion of combustion of lignin by potassium bicarbonate and disodium phosphate. These side reactions should not be overlooked.

For complete fire retardance, flaming is not the only form of combustion that should be controlled. Furthermore, if flaming combustion is entirely attributable to the volatilization of the cellulose monomer, the treatment for its elimination should not be limited to promoting dehydration. Any mechanism that would interfere with depolymerization or would lead to a nonvolatile depolymerization product would also reduce the flaming process, such as was demonstrated by sodium chloride.

Some effects that are secondary to the chemical reaction theories definitely influence fire retardance. For example, a coating of chemicals may prevent the escape of volatile products that are converted by secondary pyrolysis to more char and less tar. The coating may prevent oxygen from reaching the wood surface. Improved thermal properties of wood result from alteration of the pyrolysis path in forming products that increase fire retardance. Dilution of the combustible gases by noncombustible gaseous pyrolysis products and catalytic inhibition of flaming by free radicals capable of breaking the reaction chains of normal gaseous combustion are effective mechanisms. They perhaps originate in solid wood during pyrolysis, but achieve their flame suppression in the gas phase. Thus, in searching for effective fire-retardant chemicals, the criteria should not be limited to those that only cause dehydration of cellulose and lignin. Gas-phase reactions should be emphasized. This requires further research to fully characterize the reactions and intermediate products.

◆

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37 p. (U.S. FS res. paper FPL 82)

Pyrolysis and combustion reactions of wood are analyzed by differential thermal analysis conducted in both helium and oxygen atmospheres on wood, cellulose, and lignin, untreated and treated with 2 and 8 percent by weight of eight inorganic salts and an acid.

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