U.S. FOREST SERVICE
RESEARCH PAPER
FPL 71
JANUARY 1967

Effect of Inorganic Salts on Pyrolysis of Wood, Alpha-Cellulose, and Lignin Determined by Dynamic Thermogravimetry

U.S. DEPARTMENT OF AGRICULTURE ≀ FOREST SERVICE ≀ FOREST PRODUCTS LABORATORY ≀ MADISON, WISCONSIN

SUMMARY

The use of wood and wood-base interior finish materials in the construction of public and institutional buildings is often restricted because of the flammability of the pyrolytic products of wood. The wood product and treating industries have empirically developed chemical fire-retardants for wood that retard flammability and the spread of fire over lining surfaces. To improve these treatments systematically, additional information is needed on the action of the chemicals in changing the pyrolysis and combustion processes of wood and its components and the physical and chemical properties necessary for a chemical to be most effective in reducing flammability.

In this study, a part of a series of investigations on pyrolysis and combustion reactions of wood, dynamic thermogravimetric analyses were conducted under vacuum on pyrolysis of wood, of alpha-cellulose, and of lignin, untreated and treated with 2 percent by weight of five inorganic salts.

Data for weight loss and for rate of weight loss were obtained to indicate the principal decomposition ranges for the wood and the wood components, the effect of the chemicals on volatilization at various temperature ranges, and the kinetics of the decomposition reactions. The difference method of Freeman and Carroll was first examined as a means for obtaining the order of the reactions, the frequency factors, and the activation energies. However, because of amplified errors in this method, a pseudo first-order Arrhenius plot was finally used for determining frequency factors and activation energies.

Effect of Inorganic Salts on Pyrolysis of Wood, Alpha-Cellulose, and Lignin

DETERMINED BY DYNAMIC THERMOGRAVIMETRY [1]

by

WALTER K. TANG, Chemical Engineer

Forest Products Laboratory [2]
Forest Service
U.S. Department of Agriculture

INTRODUCTION

The use of many interior finish products in the construction of public and institutional buildings is restricted because these products are flammable. Therefore, wood and wood products industries have long been and are increasingly interested in the process of wood flammability and how chemical treatment can prevent or retard it.

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.

A review of much of the information on the pyrolysis and combustion reactions of wood and of the theories on how these reactions are controlled by using chemical additives has been summarized in a Forest Products Laboratory report (5)[3]. Based on this review, noting where information was lacking or inadequate, a program for basic investigation of pyrolysis, ignition, and combustion of wood was initiated in 1960 at the Forest Products Laboratory. In addition to the study of physical and chemical factors of pyrolysis and combustion for untreated wood and its major components, similar studies were made on the effect on thermal decomposition of adding chemicals to wood. It was believed that this increased information would help provide a basis for a more systematic selection of new fire-retardant chemicals, rather than the purely empirical selection that has been used.

---

[1] This paper, prepared by Herbert W. Eickner, Chemical Engineer in charge of Fire Research at the Forest Products Laboratory, is based on part of the Ph.D. thesis, "The Effect of Inorganic Salts on Pyrolysis, Ignition, and Combustion of Wood, a-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. The 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.

Results of some of this initial research on the pyrolysis and combustion reactions of wood involving various means of analyses--thermogravimetric, differential thermal, heat of combustion, and product--have already been published (6,7,8,9,21).

This paper summarizes part of the results of work conducted for a doctoral thesis.[1] For this report, the kinetics of thermal decomposition of wood, alpha-cellulose, and lignin treated with chemicals were studied by dynamic thermogravimetric analyses with samples exposed under vacuum.

PROCEDURE

As a part of the investigation on the influence of chemical additives on pyrolysis and combustion reactions for wood, alpha-cellulose, and lignin, dynamic thermogravimetric analyses were conducted on these materials, all of which had been given chemical treatments.

Samples

The wood samples used in these experiments were ponderosa pine sapwood, 0.14 millimeters thick and 100 milligrams in weight. The alpha-cellulose samples were 0.15 millimeter thick, of Whatman's grade 1 chromatography paper, containing at least 99.3 percent alpha-cellulose.

The lignin samples were powdered lignin (sulfuric acid process) from spruce.

Chemical Treatment

The samples were impregnated with the various salts by immersing in an aqueous solution of suitable concentration to obtain 2 percent by weight anhydrous chemical in the sample. They were evacuated for 30 minutes, approximately 2 inches absolute mercury pressure, left immersed at atmospheric pressure for 2 hours; removed; wiped to remove excess solution; and then conditioned to equilibrium weight at 27° C. and 30 percent relative humidity,

The inorganic salts used were:

Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$)

Sodium chloride (NaCl)

Potassium bicarbonate ($KHCO_3$)

Aluminum chloride hexahydrate ($AlC1_3 6H_2O$)

Monobasic ammoniumphosphate ($NH_4H_2PO_4$)

The low concentration level for the inorganic salts was selected as an effective level for modifying the pyrolysis reactions of wood and its components, yet not so high that it would result in excessive weight changes from the thermal decomposition of the chemicals themselves.

Thermogravimetric Analysis

The dynamic thermogravimetric analysis was conducted using a spring-type deflection balance (fig. 1), the "Thermograv," made by the American Instrument Company. A schematic diagram for this apparatus is shown in figure 2. The use of this equipment is described in previous reports (7,8,9,21).

In using this equipment, the sample (100 milligrams) to be pyrolyzed is suspended from a calibrated spring within a Pyrex glass enclosure. The enclosure can be evacuated or supplied with a gas flowing at a controlled rate.

The lower portion of the glass enclosure, the pyrolysis reaction chamber, can be quickly encompassed by an electric furnace, preheated to constant temperatures up to 1000° C. or programed to rise in temperature at a rate from 3" to 18" C. per minute. The changes in weight of the specimen result in a displacement of the suspension to the weighing spring, this is picked up by a transducer and demodulator, and the impulse is transmitted to the Y-axis of the XY recorder. The X-axis can be set to record temperature measured by a thermocouple located 5 millimeters below the sample in the reaction chamber or it can be set to record time.

In this study, the Y-axis of the recorder was calibrated so that the full weight of the sample just spanned 200 divisions of the graph paper, and the X-axis was set to span the range in sample temperature of 0° to 500° C.

The furnace, still unheated, was raised into position enclosing the pyrolysis chamber. Heating was started at a programed linear rate of 3° C. per minute under a vacuum exposure of 0.3 millimeters of mercury within the system, A

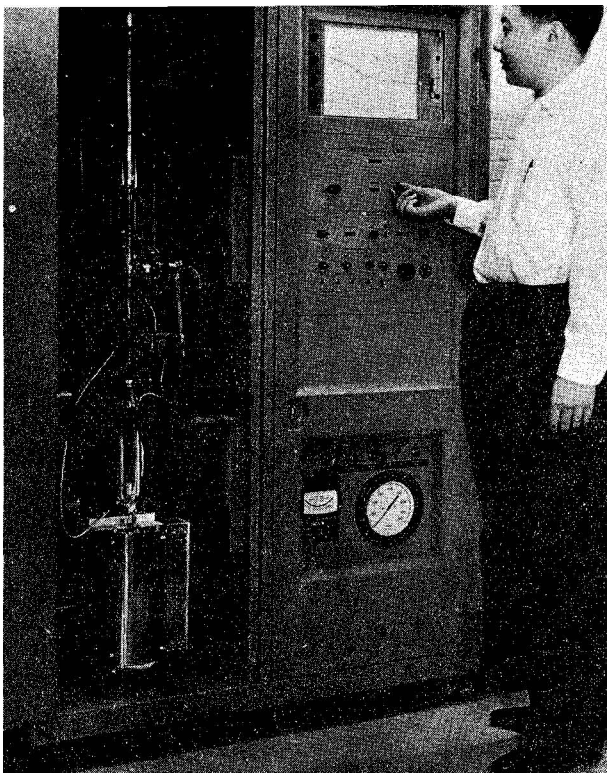

Figure 1.--Spring-type deflection balance and recording mechanism used for dynamic thermogravimetric analyses.

M 117 351

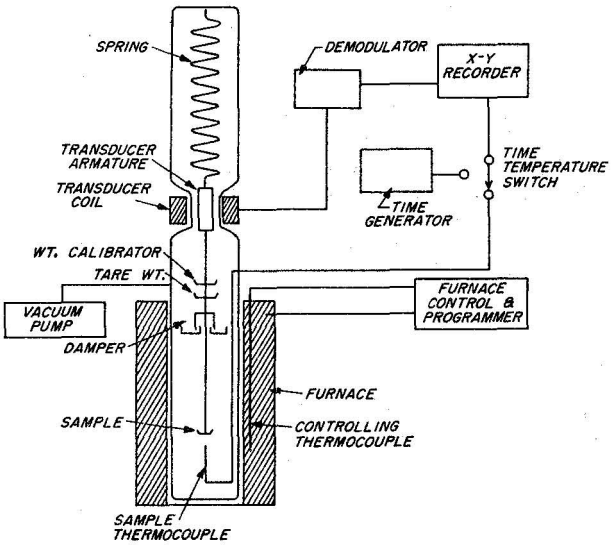

Figure 2.--Schematic diagram of the thermogravimetric balance.

M 123 212

recording mechanism was set in motion, and the recorders scribed the decrease in sample weight in percent of its initial weight against the temperature attained by the sample.

All runs were made in triplicate.

RESULTS AND DISCUSSION

The thermogram curves with the decomposition characteristics for untreated wood, alpha-cellulose, and lignin are shown in figure 3, and the curves illustrating the effect of low concentration of salts on the decomposition of wood, alpha-cellulose, and lignin are in figures 4, 5, and 6. Weight corrections for the chemical retained in the samples have been made in each curve.

Regardless of the treatments, lignin generally pyrolyzed at a slow rate, whereas wood and alpha-cellulose did so at a much faster rate. After the initial loss of moisture, further loss in weight attributable to pyrolysis began at about 220° C. for both untreated wood and lignin, but for cellulose this further loss was not until 275° C. The pyrolysis of cellulose, however, proceeded very rapidly as temperature rose still further, whereas the pyrolysis of lignin still proceeded very slowly. The pyrolysis of cellulose was essentially complete at 360° C. with a yield of char of only 16 percent. At 360° C., lignin still was 73 percent unvolatilized, and at 420° C. was 56 percent unvolatilized. Wood completed its pyrolysis at 360° C. with a yield of 21 percent char.

Two reactions, the relatively sudden fragmentation of cellulose within a narrow range of temperature and the slower disintegration of lignin over a broad range of temperature, perhaps, are explainable from the nature of the macromolecules of cellulose and lignin. Cellulose, as a repeating polymer of a single monomer of moderate size, may well follow a shorter and less involved path to complete pyrolysis than the more intricate macromolecule of lignin with its more varied composition of aromatic nuclei connected by straight-chain links.

The indication (7) that the threshold temperature of pyrolysis is lower for lignin than for cellulose seems at first to conflict with much of the literature (5), which holds that hemicellulose in wood pyrolyzes most readily, cellulose less

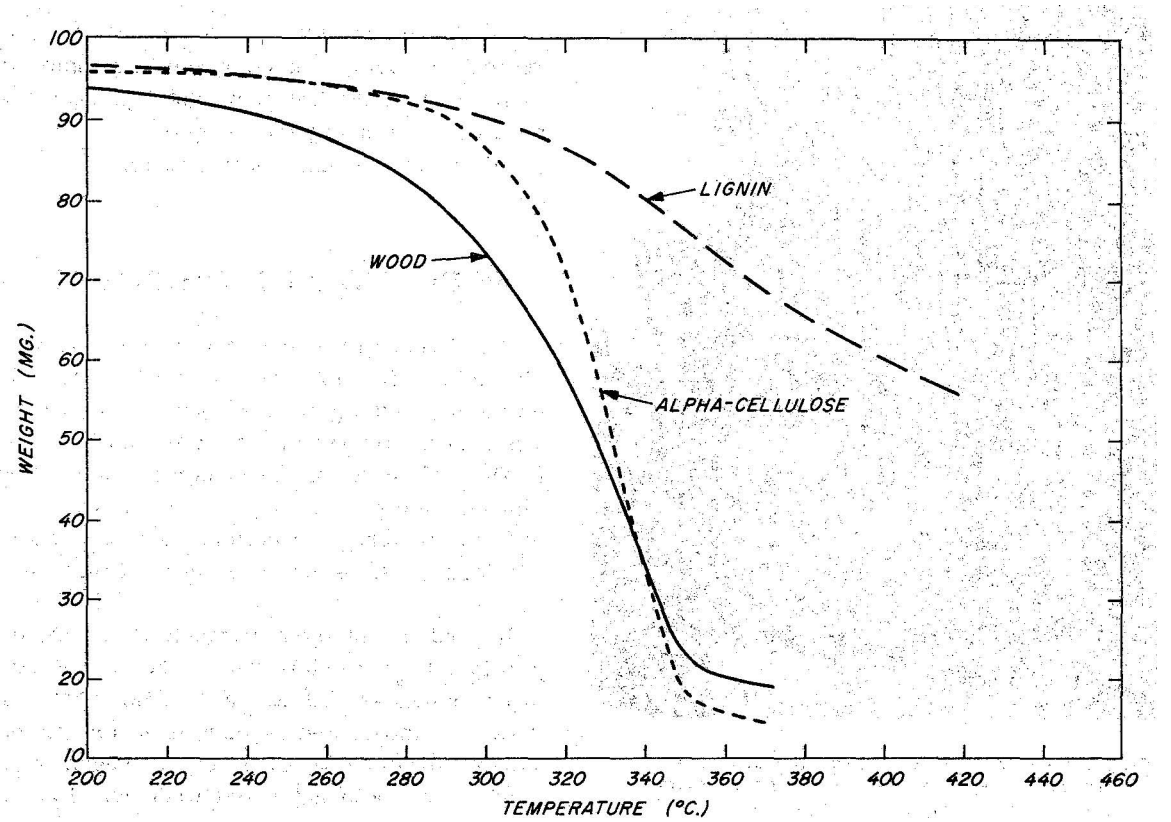

Figure 3.--Relationship of increased temperatures to weight of untreated wood, alpha-cellulose, and lignin. M 131 817

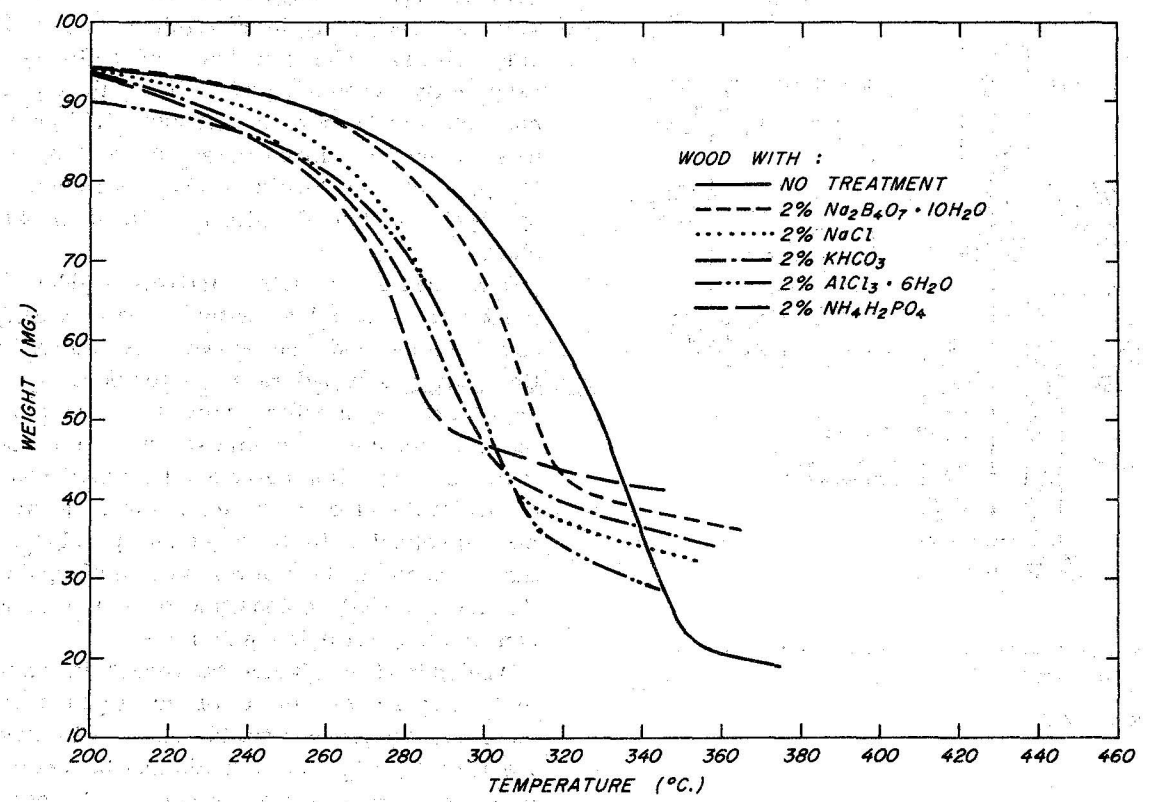

Figure 4.--Relationship of increased temperature to weight of wood with and without inorganic salts. M 131 815

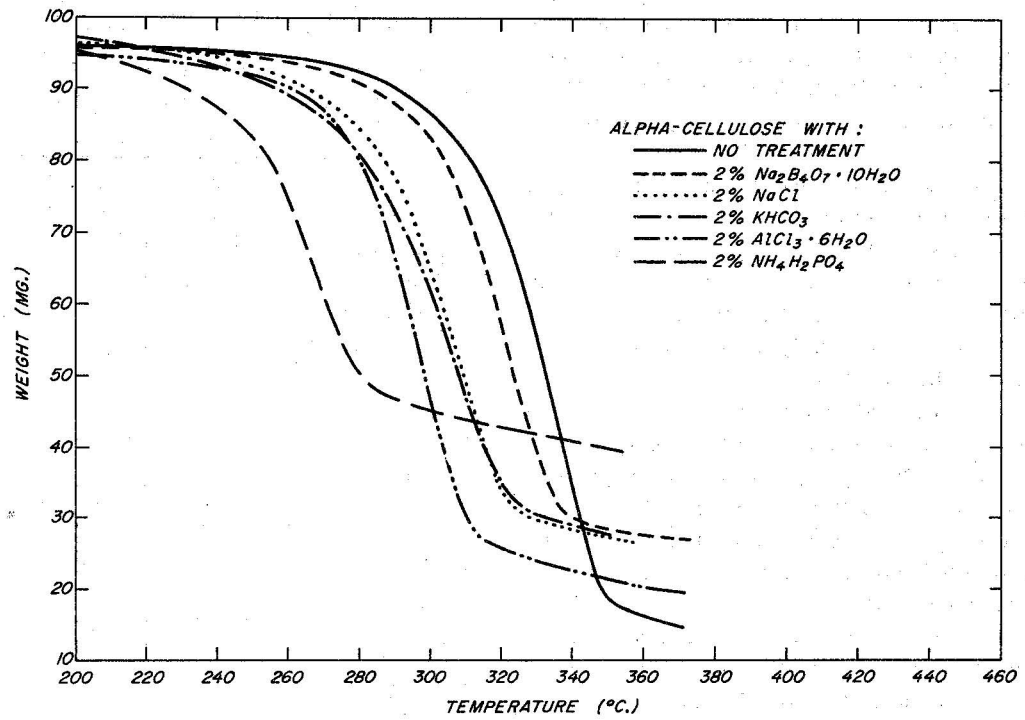

Figure 5.--Relationship of increased temperature to weight of alpha-cellulose with and without inorganic salts.

M 131 816

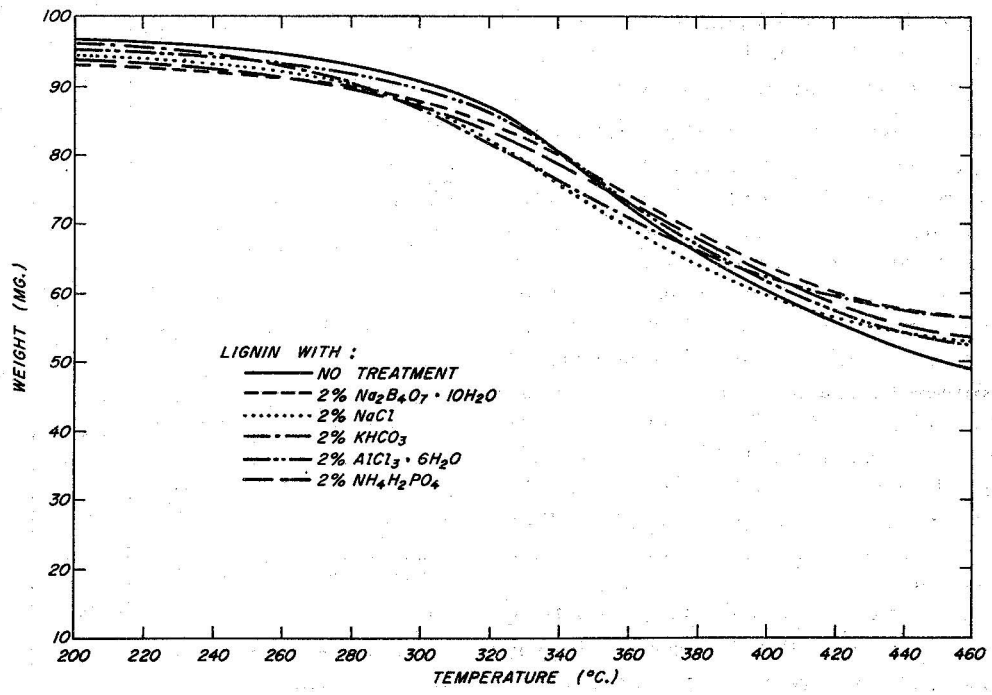

Figure 6.--Relationship of increased temperature to weight of lignin with and without inorganic salts.

M 131 813

so, and lignin least readily. The apparent conflict, however, is easily reconciled because only a small fraction of lignin has been lost at temperatures at which cellulose is already completely pyrolyzed.

For all of the salts used for treatment in this study, with the exception of aluminum chloride, it may be assumed that weight loss for test samples while the temperature rose to the region of 200° C. came chiefly from loss of moisture and some early-stage pyrolysis of hemicellulose in the wood.

For aluminum chloride-treated wood, the weight loss not only came from loss of free moisture and water of crystallization in the salt itself, but also from the hydrolytic attack of the hemicellulose portion by hydrochloric acid formed from decomposition of aluminum chloride hexahydrate at about 200° C.

For samples treated with salts that contain water of crystallization (sodium tetraborate, aluminum chloride), the actual loss of water by dehydration of salt amounted to only a fraction of a percent of the total weight, since the total salt concentration was 2 percent. Corrections were made for the content of salt in sample.

The effect of chemicals on the volatilization of wood, alpha-cellulose, and lignin is also shown in tables 1, 2, and 3 for weight of sample remaining at different temperatures of pyrolysis.

The weight loss values for wood and alpha-cellulose treated with sodium tetraborate were closest to the values for untreated samples until the temperature reached 300° to 350° C. and pyrolysis in these samples was almost complete. All other salts decreased the temperature when weight loss began to be rapid and increased the weight loss in a wide range of temperatures below 350° C. The departure from the weight loss values for untreated wood and cellulose was greatest for samples treated with monobasic ammonium phosphate. Weight loss values for the other salts fell between the values for the sodium tetraborate-treated and the monobasic ammonium phosphate-treated.

Beyond about 350° C., the weight of remaining samples of wood and cellulose treated with any one of the salts (corrected for salt content) exceeded the weight of char from untreated samples.

In contrasting with comparable values between untreated and treated wood and alpha-cellulose,

Table 1.--Effect of chemicals on volatilization of wood

Chemical--2 percent by weight	Weight of sample[1] in vacuum at--			
	200° C.	250° C.	300° C.	350° C.
	Mg.	Mg.	Mg.	Mg.
No treatment	94	90	74	23
Sodium tetraborate decahydrate	94	90	68	37
Sodium chloride	94	88	49	33
Potassium bicarbonate	94	84	46	35
Aluminum chloride hexahydrate	90	84	49	28
Monobasic ammonium phosphate	93	82	46	40

[1]Original sample was 100 mg.

Table 2.--Effect of chemicals on volatilization of alpha-cellulose

Chemical--2 percent by weight	Weight of sample[1] in vacuum at--			
	200° C.	250° C.	300° C.	350° C.
	Mg.	Mg.	Mg.	Mg.
No treatment	96	95	87	19
Sodium tetraborate decahydrate	96	95	83	29
Sodium chloride	95	93	65	28
Potassium bicarbonate	96	92	62	28
Aluminum chloride hexahydrate	95	92	46	21
Monobasic ammonium phosphate	95	83	45	40

[1]Original sample was 100 mg.

Table 3.--Effect of chemicals on volatilization of lignin

Chemical--2 percent by weight	Weight of sample[1] in vacuum at--			
	200° C.	300° C.	400° C.	450° C.
	Mg.	Mg.	Mg.	Mg.
No treatment	97	91	60	51
Sodium tetraborate decahydrate	93	88	64	57
Sodium chloride	94	88	60	53
Potassium bicarbonate	96	87	63	57
Aluminum chloride hexahydrate	95	90	62	53
Monobasic ammonium phosphate	94	87	63	53

[1]Original sample was 100 mg.

lignin showed that the low concentration of salts had much less effect on the volatilization of lignin than on the volatilization of wood and cellulose. At temperatures below 350° C. all treated lignin volatilized more than untreated lignin. But at temperatures above 350° C. the trend reversed; treated lignin yielded more char than untreated lignin. However, the maximum difference was only 6 percent between untreated and treated lignin compared with the maximum differences of 17 percent for wood and 21 percent for cellulose.

The salt treatments had the greatest effect on alpha-cellulose and the least effect on lignin. The effect on wood seemed to be a combination of the effects on alpha-cellulose and lignin. Thus, from these data, cellulose did show the controlling position in the pyrolysis of wood, with and without treatment.

Kinetics

Kinetic parameters have been derived from the weight loss data obtained in either dynamic or static thermogravimetric analysis. Methods for deriving kinetic parameters have been discussed fully by Farmer (10) using dynamic thermogravimetric data and Madorsky et al. (15,16,17) using static thermogravimetric measurements. Since, in this study, dynamic thermogravimetric analysis was applied, Farmer's (10) methods of analyses were considered.

The complex mechanisms of decomposition of wood, alpha-cellulose, and lignin are not sufficiently well understood to permit formulation of exact analytical expressions. Therefore, empirical kinetics must be used.

For a study of empirical kinetics, the rate expressions should be reasonably simple and adaptable to measurement techniques. Wood, alpha-cellulose, and lignin may show highly complex mechanisms. They may not be amenable to a simplified empirical analysis, because simple expressions are not sufficiently general to define all decomposition with the desired degree of accuracy. It must be realized that in the study various complex, concealed, and cumulative effects may limit the applicability of empirical kinetics to a mere close approximation of the procedural measurement conditions, unless experimentally proved otherwise.

For assumed pseudo-order homogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant may be expressed[4]

$$-\frac{dw}{dt} = kw^n \tag{1}$$

at a constant temperature.

The Arrhenius-type relation between k and T is taken as

$$k = Ae^{-E/RT}$$

where k and A are for a weight fraction basis, and the rate parameters, A and E, will be treated as constants.

For an experimental dynamic thermogravimetric analysis at a constant sample heating rate dT/dt, the rate of conversion is given by

$$-\frac{dw}{dt} = -\left(\frac{\partial w}{\partial t}\right)_T - \left(\frac{\partial w}{\partial T}\right)_t \frac{dT}{dt} \tag{3}$$

for the empirical assumption that decomposition depends only on temperature and time. Therefore, the total derivative may be expressed as

$$-\frac{dw}{dt} = kw^n = -\left(\frac{dw}{dT}\right)\left(\frac{dT}{dt}\right) \tag{4}$$

The rate of change of w with temperature, the final differential equation, is

$$-\frac{dw}{dt} = -\left(\frac{dw}{dT}\right)\left(\frac{dT}{dt}\right) = Aw^n e^{-E/RT}$$

This equation may be integrated and solved by an infinite. series solution (10) or the difference method of Freeman and Carroll (11) and Anderson and Freeman (3). In the difference method, the equation was derived wherein:

$$\frac{-\frac{E}{2.3R}\,\Delta\left(T^{-1}\right)}{\Delta \log W_r} = -n + \frac{\Delta \log (dw/dt)}{\Delta \log W_r}$$

This involves taking the differences among the logarithms of equation (5) and plotting

$$\frac{\Delta \log \frac{dw}{dt}}{\Delta \log W_r} \text{ vs. } \frac{\Delta (1/T)}{\Delta \log W_r}$$

where W_r is weight remaining at time t. This plot should result in linear relationship having a slope of $-E/2.3R$ and an intercept corresponding to n.

[4] Nomenclature used is defined at the end of this report.

In the process of evaluating dynamic thermo-gravimetric data from this study, the rate of weight loss was calculated by the relation

$$\frac{dw}{dt} = \left(\frac{dw}{dT}\right)\left(\frac{dT}{dt}\right) \qquad (6)$$

from the thermograms shown in figures 3, 4, 5, and 6. The increments of the curve used are from 3" to 10" C., depending on the rate of weight loss. In the faster weight loss region, 3" C. increments were used. The results of calculated rates are shown in figures 7, 8, and 9 for untreated and treated wood, alpha-cellulose, and lignin,

These rate data were used together with the calculated remaining weight W_r from the relation

$$W_r = W_d^{1} - W \qquad (7)$$

where W_r = residue weight of sample at time t,

W_d^{1} = weight loss at completion of the reaction, and

W =weight loss at time t

in the difference method plot. A sample of this type of plot is shown in figure 10. The primary reason for using the difference method was to approximate the pseudo order of reaction, n. Figure 11 was derived from figure 10 to show that the pseudo first order may be obtained for untreated alpha-cellulose.

However, a major limitation of the difference method lies in its amplification of small errors that may exist in the available data. Therefore, there is much scattering of data points in the lower temperature region where the rate of

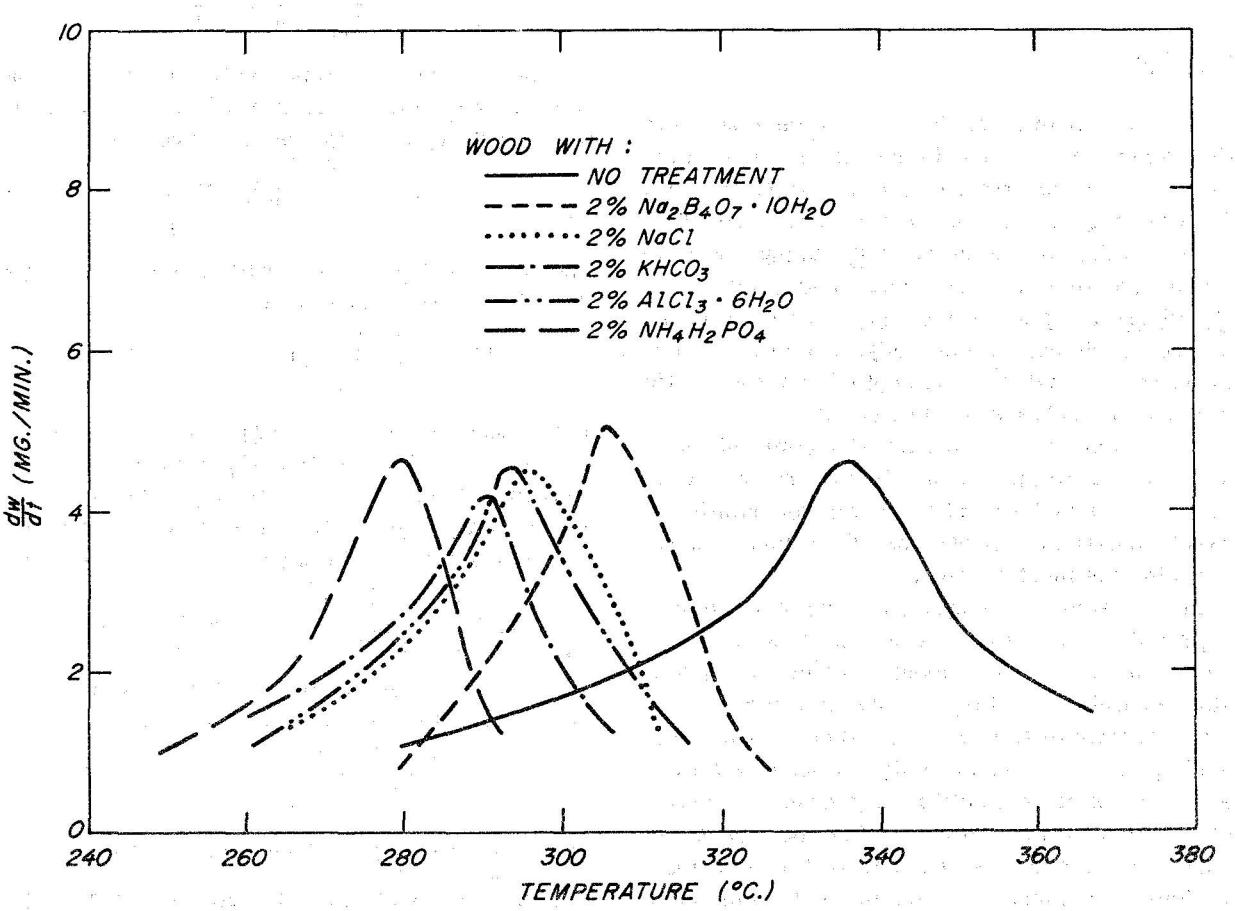

Figure 7.--Effect of temperature on rate of weight loss of wood untreated and treated with inorganic salts.

M 131 814

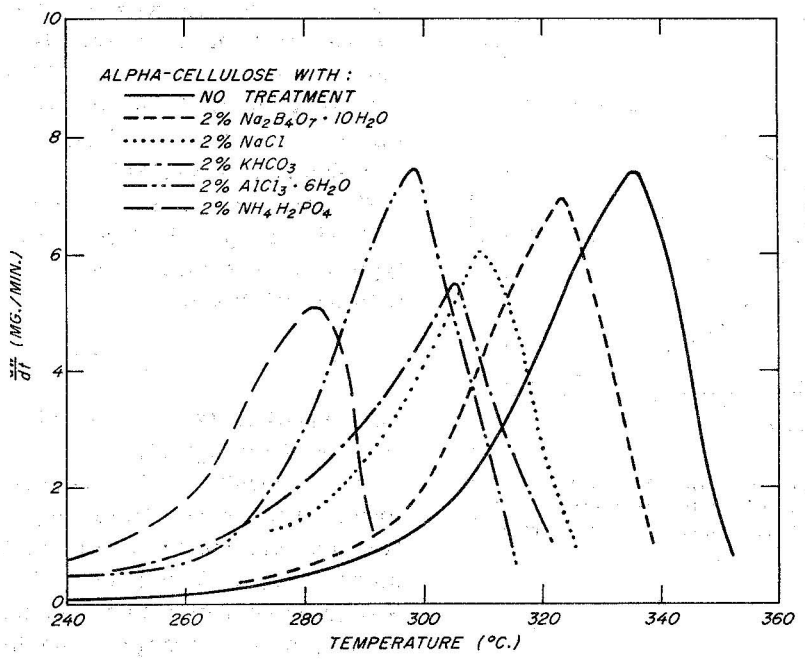

Figure 8.--Effect of temperature on rate of weight loss of alpha-cellulose untreated and treated with inorganic salts.

M 131 824

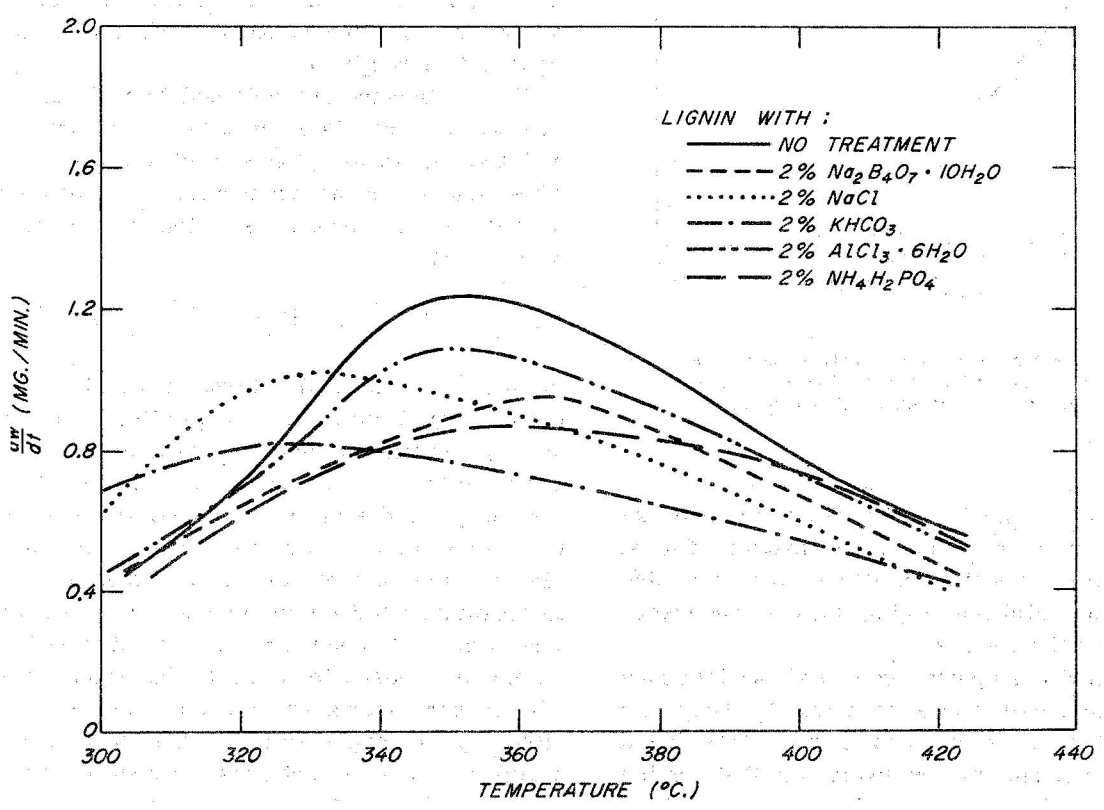

Figure 9.--Effect of temperature on rate of weight loss of lignin untreated and treated with inorganic salts.

M 131 825

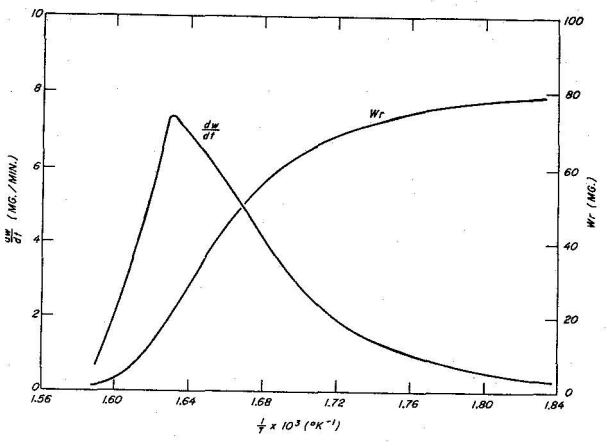

Figure 10.--Sample plot of rate of weight loss and remaining weight for difference method of calculating kinetics for untreated alpha-cellulose.

M 131 822

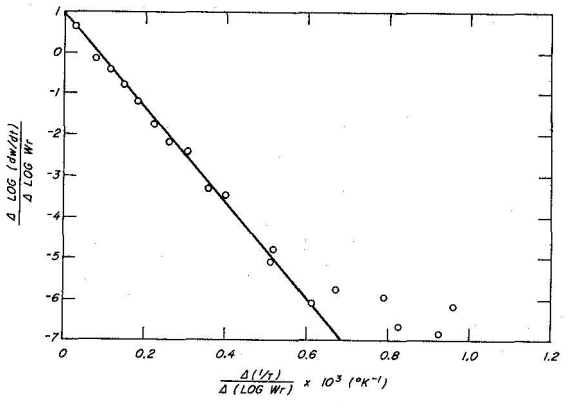

Figure 11.--Sample plot of difference method to determine order of reaction and activation energy for untreated alpha-cellulose.

M 131 823

weight loss is smaller. The use of an approximate statistical method, as the method of least squares after rejection of all data points outside 95 percent confidence limits, does not necessarily improve the results.

These scattered points exert a strong influence on the calculated values of A and E. They also suggested to Freeman and Carroll (11) that a different mechanism was involved in that portion of the plot. This was also found to be true for alpha-cellulose. Additional calculations by this method for the pyrolysis of the treated alpha-cellulose have been given (21). These plots show good conformance to pseudo first-order reaction during most of the pyrolysis, but a scattering during the initial stages. When the difference data for these initial stages were plotted according to pseudo zero-order reaction, excellent conformity was obtained.

To avoid the amplified errors of the difference method, the pseudo first order of Arrhenius-type plots was made directly from the rate data with the relation of

$$\frac{dw}{dt} = kW_r \tag{8}$$

and equation (2). These plots are shown in figures 12 through 15.

In all results, a dual segment approximation proved necessary, indicating the possibility of two mechanisms controlling in different temperature ranges. The points of inflection of the straight-line segments are indicated on the plots.

In figures 7 through 9, the distant-hill type of comparison of rates and of temperature relations shows that the effect of treatment is greatest on alpha-cellulose. Wood is next sensitive, and lignin, the least sensitive. This is also shown in the comparison of Arrhenius plots in figures 13 through 15.

Kinetic parameters obtained from figures 12 through 15 are listed in table 4 for untreated and treated wood, alpha-cellulose, and lignin. These dual-segment mechanisms could be represented by a general equation suggested by Martin (18).

$$-\frac{dw}{dt} = \left(k_1 + k_2\right) W_r^{\,1} = \left(A_1 e^{-E_1/RT_1} + A_2 e^{-E_2/RT_2}\right) W_r$$

to show an expected alteration in kinetics on passing from slow to fast pyrolysis for wood and alpha-cellulose and vice versa for lignin.

The effect of chemical treatment showed most distinctly in the kinetic parameters throughout the temperatures for alpha-cellulose, in the higher temperatures for wood, and in the lower temperatures for lignin. In the lower temperature range of wood, only 2 percent monobasic ammonium phosphate seemed to have much effect. Kinetic parameters remained in the same magnitude for the higher temperature range of lignin pyrolysis. This effect was pronounced in the frequency factors because they are exponentially magnified from the effect of activation energies.

Most published results of kinetic parameters for pyrolysis of untreated wood, alpha-cellulose,

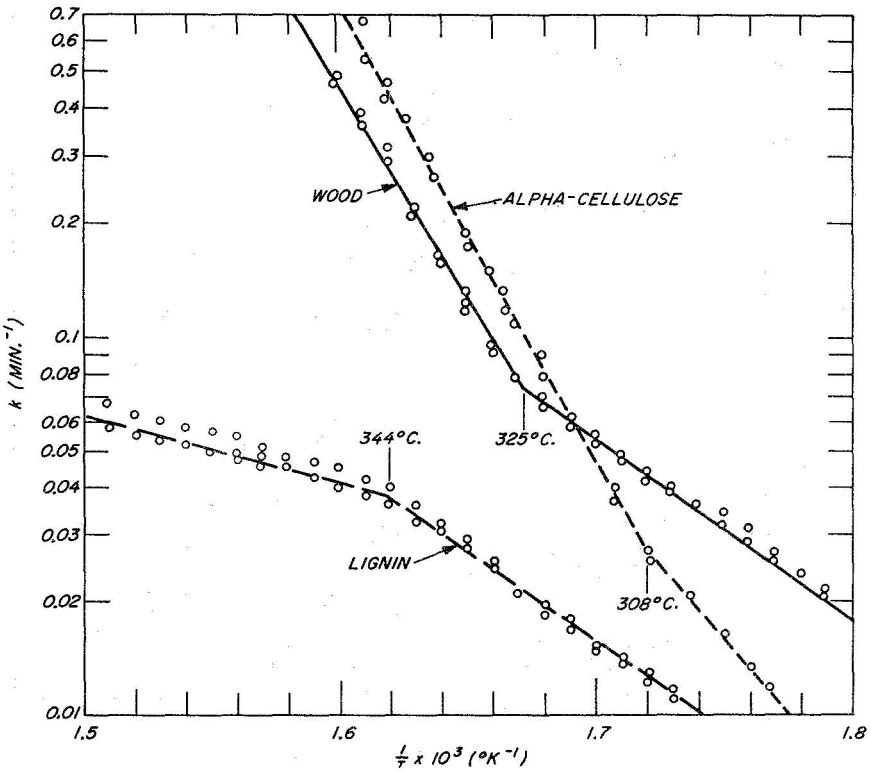

Figure 12.--Arrhenius plot for pseudo first-order kinetics of pyrolysis of wood, alpha-cellulose, and lignin with no treatment from data of dynamic thermogravimetric analyses and rate of weight loss.

M 131 819

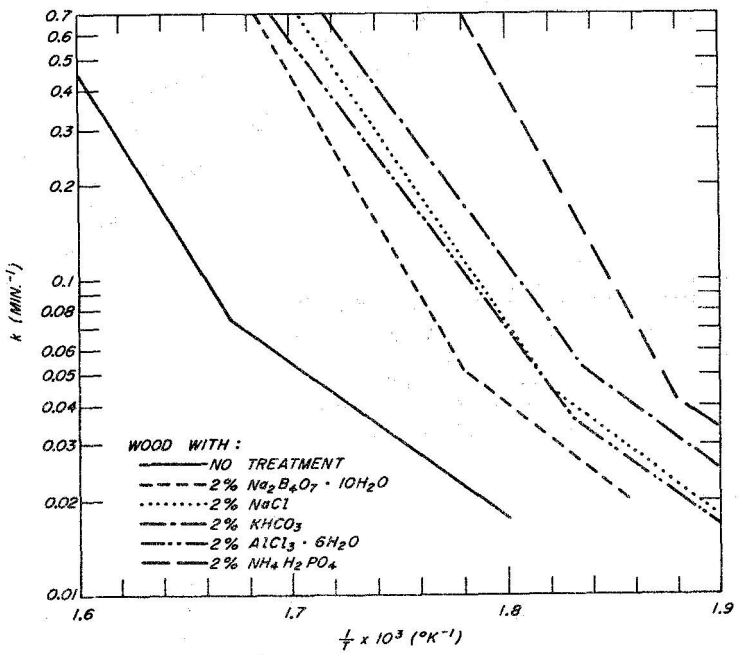

Figure 13.--Comparison of Arrhenius relations of untreated and treated wood.

M 131 821

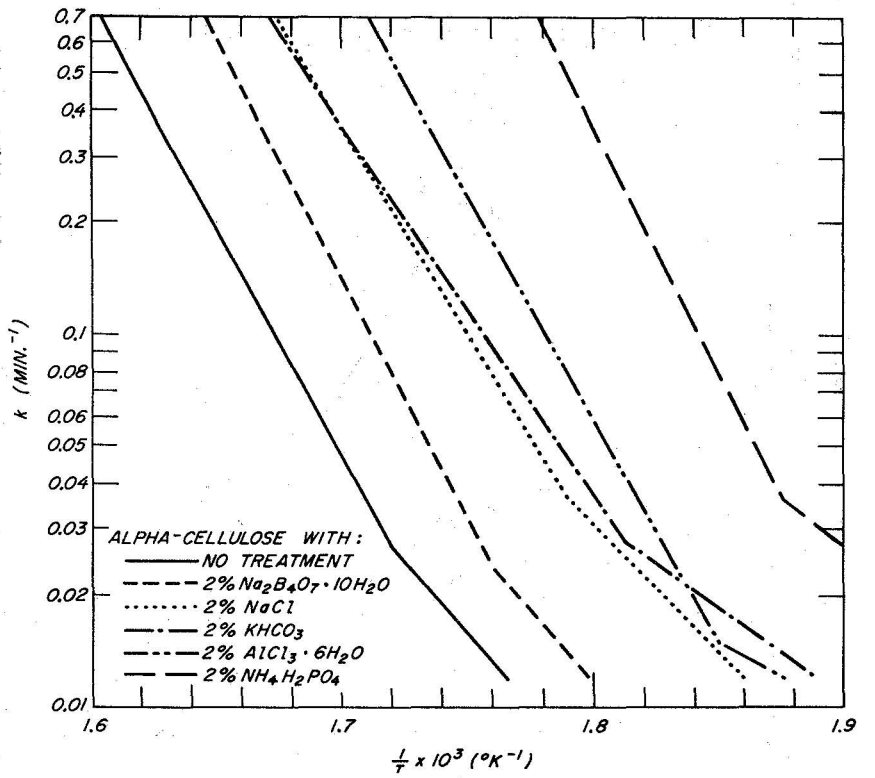

Figure 14.--Comparison of Arrhenius relations of untreated and treated alpha-cellulose.
M 131 820

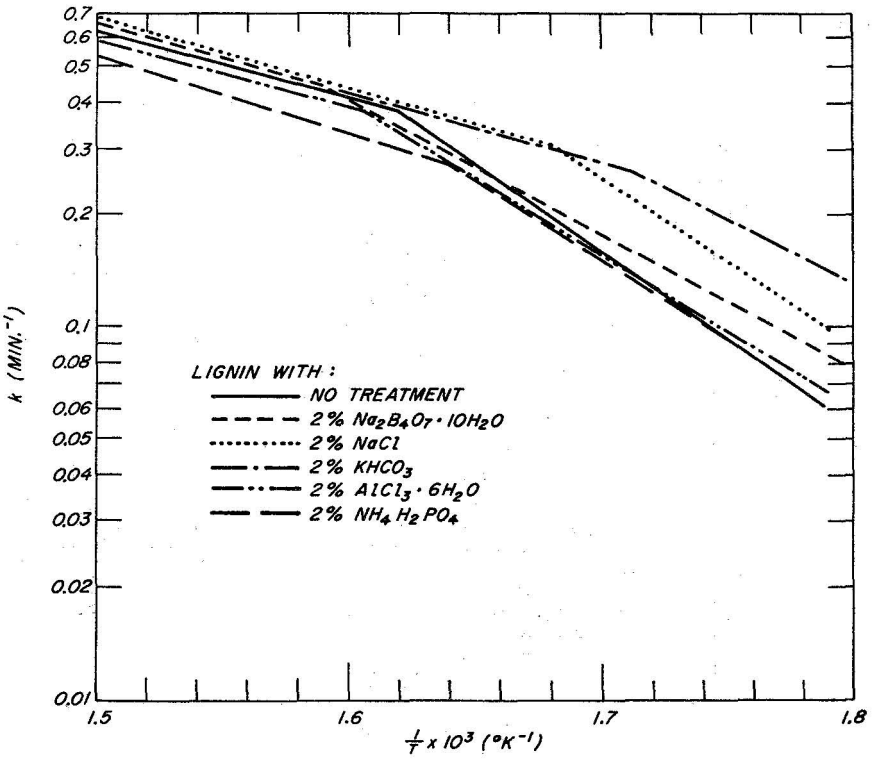

Figure 15.--Comparison of Arrhenius relations of untreated and treated lignin.
M 131 818

Table 4.--Kinetic parameters of pyrolysis and their effective temperature range[1]

Chemical--2 percent by weight	Wood						Alpha-cellulose						Lignin					
	First stage			Second stage			First stage			Second stage			First stage			Second stage		
	T_1	A_1	E_1	T_2	A_2	E_2	T_1	A_1	E_1	T_2	A_2	E_2	T_1	A_1	E_1	T_2	A_2	E_2
	°C.	Min.$^{-1}$	Kcal/mole	°C.	Min.$^{-1}$	Kcal/mole	°C.	Min.$^{-1}$	Kcal/mole	°C.	Min.$^{-1}$	Kcal/mole	°C.	Min.$^{-1}$	Kcal/mole	°C.	Min.$^{-1}$	Kcal/mole
No treatment	280-325	1.93×10^{7}	23	325-350	3.92×10^{18}	54	240-308	3.85×10^{11}	35	308-360	2.37×10^{19}	56	280-344	9.86×10^{5}	21	344-435	5.60×10	9
Sodium tetraborate decahydrate	260-289	4.50×10^{7}	23	289-320	1.86×10^{19}	53	230-295	4.54×10^{10}	32	295-345	1.59×10^{19}	54	280-356	1.58×10^{4}	16	356-440	5.79×10	9
Sodium chloride	250-276	6.35×10^{7}	23	276-315	8.19×10^{16}	46	260-286	1.74×10^{12}	35	286-325	2.76×10^{18}	51	280-322	1.59×10^{6}	21	322-425	2.69×10	8
Potassium bicarbonate	245-271	1.32×10^{7}	21	271-305	3.62×10^{15}	42	200-279	5.65×10^{6}	21	279-330	1.24×10^{15}	42	280-312	1.10×10^{4}	15	312-430	2.61×10	8
Aluminum chloride hexahydrate	250-272	2.32×10^{7}	22	272-310	2.25×10^{15}	42	210-267	3.44×10^{11}	33	267-320	2.11×10^{20}	55	280-349	1.87×10^{5}	19	349-430	2.44×10	8
Monobasic ammonium phosphate	235-259	2.75×10^{6}	19	259-290	6.77×10^{20}	54	190-260	2.24×10^{6}	19	260-300	1.18×10^{21}	55	290-336	3.50×10^{4}	17	336-435	4.63×10	9

[1]For 100 mg. sample in vacuum (0.3 mm. Hg abs.):
T_1, T_2, Temperature range in first and second stage (°C.).
A_1, A_2, Frequency factor in first and second stage (min.$^{-1}$).
E_1, E_2, Activation energy in first and second stage (kcal/mole).

and lignin seemed to reveal a single mechanism in the lower temperature range (1,4,12,15,16,17, 18,19,20) below or at the border of the temperatures of inflection found in the dual mechanism in this study. These published values are well within the magnitude of the results of this research.

The dual-mechanism concept of pyrolysis of wood was first introduced by Akita (1), who found the two-segment correlation of wood existing in the Arrhenius-type plot. This was also found by Tang in an earlier static thermogravimetric analysis. The activation energy was higher in the lower temperature segment and lower in the higher temperature segment. These results by Tang were discussed later by Browne and Tang (7) who considered the static thermogravimetric data not quite satisfactory owing to the excessive loss of weight, as much as 35 percent during the preheating period, so that the initial rate measurement was unreliable.

In this study, the trend was reversed for wood; the activation energy was found to be lower in the lower temperature segment and higher in the higher temperature segment. Alpha-cellulose followed the same trend, but lignin showed the reverse results.

From his results, Akita (1) proposed the summation of the rates of its components

$$\frac{dw}{dt} = \sum_i k_i \left(W_{di} - W_i\right)$$

Martin (18), on the basis of the data of Stamm (20) and that of Kujirai and Akahira (14), saw evidence of an expected alteration in kinetics on passing from slow pyrolysis below the exothermic region to fast pyrolysis above it for wood and alpha-cellulose. Heinrich and Kaesche-Krischer (13), in their more recent work, suggested that at least three different partial reactions are observed in thermogravimetric analysis.

By combining the postulation of Akita (1), Martin (18), and Heinrich and Kaesche-Krischer (13), a model

$$\frac{dw}{dt} = \sum_j k_j \left(W_d - W\right)^{n_j} = \sum_j k_j W_{r_j}^{n_j}$$

may be applied to the pyrolysis of wood, alpha-cellulose, and lignin.

The experimental results reduced the pseudo order to $n_j = 1$. Thus, the model would be the same as that suggested by Martin (18) for wood and cellulose.

In published results of kinetic parameters there are no materials with chemical treatments comparable to those used in this study. However, the kinetic parameters reported for treated materials all show decrease in activation energy

in agreement with the trend observed in this study. Results here showed that the reduction in activation energy depended on the nature of the salts.

For activation energy, 2 percent potassium bicarbonate and ammonium phosphate seemed to have the largest effect on wood and cellulose pyrolysis. Since all chemicals lower the pyrolysis temperatures of wood and cellulose, the frequency factor, combining the effect of change of temperatures and activation energy, showed the magnified difference exponentially even when some salts had little effect on activation energy.

Lignin was the least affected component in pyrolysis in the presence of chemicals. The largest reductions were shown in the activation energies of lignin with 2 percent sodium tetraborate decahydrate, 2 percent potassium bicarbonate, and 2 percent ammonium phosphate.

For a more complete understanding of the effect of inorganic salts on the pyrolysis and combustion of wood, it is necessary that these thermogravimetric results be combined with results from differential thermal analyses made in helium and oxygen.

NOMENCLATURE

A_1, A_2	= Frequency factor
dt	= Change in time
dT	= Change in temperature
dw	= Change in weight
E, E_1, E_2	= Activation energy of pyrolysis reactions
k, k_1, k_2, k_i	= Specific rate constant measured by weight changes
T	= Absolute temperature of a specimen at an isothermal pyrolysis
t	= Time at particular point of the reaction
w	= Fraction of weight of sample at particular point of the reaction
w_d, w_{di}	= Equilibrium weight fraction of volatilized specimen at a certain temperature (component i)
w_i	= Fraction of weight of component i at particular point of the reaction
w_r^1, W_r	= Residue weight of sample at time, t
W_d^1	= Weight loss at completion of the reaction
n	= Number of order of reaction
R	= Universal gas constant

LITERATURE CITED

1. Akita, Kazuo
   1959. Studies on the mechanism of ignitionof wood. Rpt. of Fire Res. Inst. of Japan. 9:(1–2).
2. American Instrument Company
   1960. Operating manual for thermogravimetric balance. American Instrument Company, Silver Springs, Md.
3. Anderson, D.A., and Freeman, E.S.
   1961. The kinetics of the thermal degradation of polystyrene and polyethylene. J. Polymer Sci. 54: 253–260.
4. Bowes, P.C.
   1956. Estimates of the rate of heat evolution and of the activation energy for a stage in the ignition of some woods and fiberboards. Joint Fire Res. Organ. Britain Note 266.
5. Browne, F.L.
   1958. Theories of the combustion of wood and its control. U.S. Forest Prod. Lab. Rpt. 2136. 69 pp., illus.
6. _____, and Brenden, J.
   1964. Heat of combustion of the volatile products of pyrolysis of ponderosa pine. U.S. Forest Serv. Research Paper FPL 19. 15 pp., illus.
7. _____, and Tang, W.K.
   1962. Thermogravimetric and differential thermal analysis of wood and of wood treated with inorganic salts during pyrolysis. Fire Res. Abst. and Revs. 4:(3).
8. _____, and Tang, W.K.
   1963. The effect of various chemicals on the thermogravimetric analysis of ponderosa pine. U.S. Forest Serv. Res. Paper FPL 6. 20 pp., illus.
9. Eickner, H.W.
   1962. Basic research on the pyrolysis and combustion of wood. Forest Prod. J. 2(4): 194-199.
10. Farmer, R.W.
   1963. U.S. Air Force aeronautical systems division report ASD-TDR-62-1043.

11. Freeman, E.S., and Carroll, B.
1958. The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J. of Phys. Chem. 62: 394–397.

12. Gross, D., and Robertson, A.F.
1958. Self–ignition temperatures of materials from kinetic–reaction data. J. of Res., Natl. Bur. of Standards 61(5): 413–417.

13. Heinrich, H.J., and Kaesche–Krischer, B.
1962. Contribution to the explanation of the self–ignition of wood. Brennstoff–Chemie 43(5): 142–148.

14. Kujirai, T., and Akahira, T.
1925. Effect of temperature on the deterioration of fibrous insulating materials. Scientific Papers, Inst. of Phys. and Chem Res. (Tokyo) 2: 223–252.

15. Madorsky, S.L., Hart, V.E., and Straus, S.
1956. Pyrolysis of cellulose in a vacuum. J. of Res., Natl. Bur. of Standards 56(6): 343–354.

16. _____
1958. Thermal degradation of cellulosic materials. J. of Res., Natl. Bur. of Standards 60(4): 343–349.

17. _____, and Straus, S.
1961. Stability of thermoset plastics at high temperatures. Modern Plastics (Feb. 1961).

18. Martin, S.
1956. The mechanisms of ignition of cellulosic materials by intense radiation. R. and D. Rpt. USNRDL D1–TR–102–NS081–001.

19. Murphy, E.J.
1943. Gases evolved by the thermal decomposition of paper. Trans. Electrochemical Soc. 82: 161–173.

20. Stamm, Alfred J.
1956. Thermal degradation of wood and cellulose. Indust. and Eng. Chem 48: 413–417.

21. Tang, W.K., and Neill, W.K.
1964. Effect of flame retardants onpyrolysis and combustion of alpha–cellulose. J. of Polymer Sci. (C6): 65–81.