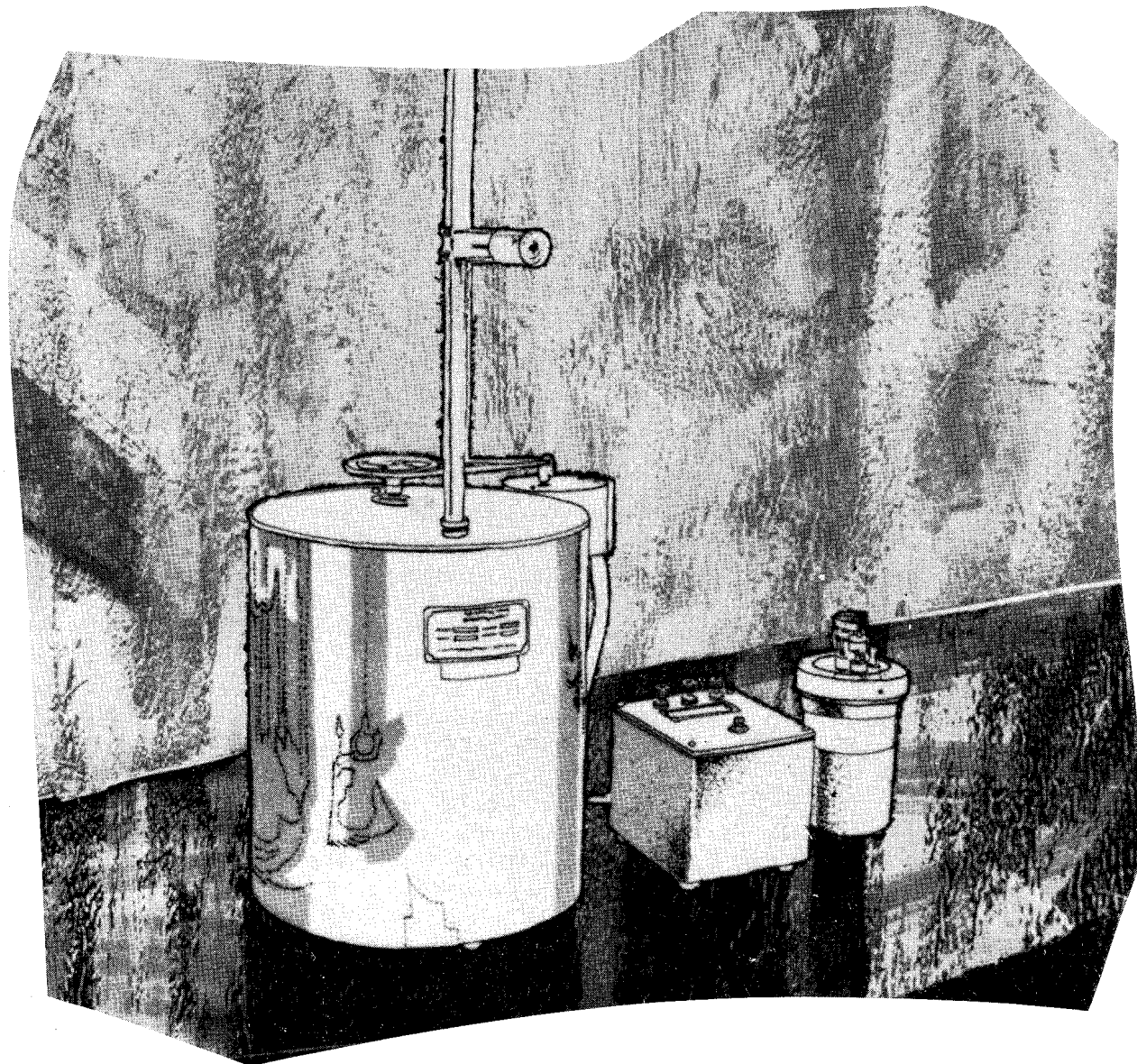


HEAT OF COMBUSTION OF THE VOLATILE PYROLYSIS
PRODUCTS OF FIRE-RETARDANT-TREATED
PONDEROSA PINE



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SUMMARY

The heats of combustion of the volatile pyrolysis products released up to various stages of volatilization from untreated and chemically treated ponderosa pine were determined. This heat of combustion of the volatile products was calculated as the difference between the heat of combustion of the original unpyrolyzed (treated or untreated) wood and the heat of combustion of the char residue left after partial pyrolysis.

The results show that for untreated wood the heat of combustion was proportionally low for the first products evolved as compared to a pure chemical compound undergoing a single decomposition reaction, and materially increased during the later stages of volatilization. Up to a 20 percent weight loss, the average heat of combustion was about -2,800 calories per gram of volatiles released (representing 10 percent of the total heat of combustion), and at 40 percent weight loss about -3,000 calories per gram (representing 29 percent of the total heat of combustion). When 85 percent weight loss was reached, the average heat of combustion had reached -4,000 calories per gram of volatiles released (representing 75 percent of the total heat of combustion).

The effect of the fire-retardant treatments was to reduce the average heat of combustion for the volatile pyrolysis products released at the early stages of pyrolysis below the value associated with untreated wood at comparable stages of volatilization. For example, at 40 percent volatilization, where untreated ponderosa pine had released in the volatile components 29 percent of its total heat of combustion, the fire-retardant-treated ponderosa pine had released only 10 to 19 percent of its total heat of combustion.

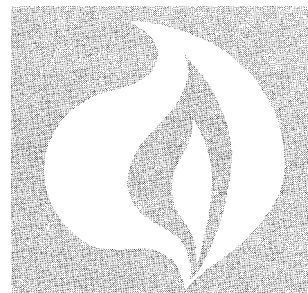
Data for sodium chloride-treated wood fell on the same curve as untreated wood when the percent of total heat released was related to the percent of volatilization.

HEAT OF COMBUSTION OF THE VOLATILE PYROLYSIS PRODUCTS OF FIRE-RETARDANT-TREATED PONDEROSA PINE¹

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INTRODUCTION

Many fire-retardant treatments for wood have been developed, and it is often questioned whether these treatments change the rate of heat release during a fire exposure. Studies at the Forest Products Laboratory by Browne and Tang (3)³ and Brenden⁴ of the pyrolysis reactions for fire-retardant-treated wood indicate that these treatments influence the development of the relative proportions of the decomposition products: char, flammable tars, water, and noncondensable gases. These treatments decrease the amount of flammable volatile tars which can contribute to the flaming reaction and increase the yield of the solid char residue which may contribute to later glowing reactions.

It was, therefore, the purpose of this study to determine whether the volatile products released at the initial stages of volatilization in the pyro-

lysis of wood treated with several individual fire-retardant treatments have heats of combustion less than for untreated wood.

If wood samples are first partly pyrolyzed and then the resultant char and volatile products are burned separately to carbon dioxide and water, the total heat resulting from the thermal decomposition of the wood would be:

$$\Delta H_{\text{C wood}} = \Delta H_{\text{C char}} + \Delta H_{\text{C volatiles}} + \Delta H_{\text{pyrolysis}}$$

where ΔH is the heat change (increment of enthalpy H) of the individual reactions. Because the heat of pyrolysis is relatively small, found to be less than 5 percent of the heat of combustion in studies of the destructive distillation of wood by Klason (4) and also in recent work at the Forest Products Laboratory by Tang using differential

¹Work here reported was initiated and financed in part by a grant of the National Science Foundation, with Dr. F. L. Browne, now retired, as principal investigator.

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

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

⁴Brenden, John J. The influence of inorganic salts on the products of pyrolysis of ponderosa pine. M.S. Thesis, Chemical Engineering Department, University of Wisconsin, 1963.

thermal techniques, it can be neglected and therefore:

$$\Delta H_C \text{ volatiles} = \Delta H_C \text{ wood} - \Delta H_C \text{ char}$$

On this basis, the heat of combustion for the

volatile products obtained up to various stages of volatilization can be computed as the difference between the heats of combustion of the original wood sample and of the char residues at these volatilization stages.

EXPERIMENTAL PROCEDURE

The general procedure in this study was to pyrolyze untreated and chemically treated wood samples to different degrees of volatilization under carefully controlled time and temperature conditions, and then to determine the heat of combustion of the residual char. The difference between the original heat of combustion of the undecomposed wood samples and the heat of combustion of the pyrolyzed residues then represented the heat of combustion of the volatiles released at the various degrees of volatilization.

Specimens

Specimens for the experimental work described in this report were 1/4-inch-diameter ponderosa pine cylinders, approximately 1 inch long. Test specimens weighed approximately 0.5 gram when the wood was brought to equilibrium conditions at 80° F. and 30 percent relative humidity, prior to treatment. After being brought to equilibrium, the specimens were stored in polyethylene film bags.

Chemical Treatments

The specimens were treated with two general types of chemicals: inorganic salts and a resinous polymeric material. Treatment with inorganic salts was accomplished by impregnating the specimens with the following saline water solutions: (1) Sodium tetraborate, 6 percent; (2 and 3) diammonium phosphate, 6 and 12 percent; (4) sodium chloride, 1.2 percent. After impregnation with the solutions the specimens were dried.

The actual impregnation was accomplished in a desiccator by a pressure-vacuum technique at room temperatures under the following conditions:

(1) The atmosphere above the salt solution to which the specimens had just been added was evacuated to about 2 inches of mercury for 15 minutes.

(2) The desiccator was opened to the atmosphere for 15 minutes.

(3) Steps 1 and 2 were repeated three times.

(4) Specimens were then removed, drained, and dried to moisture equilibrium in an atmosphere of 80° F. and 30 percent relative humidity.

The analysis to determine the exact amount of salt retained in the wood specimens treated according to the aforementioned procedure presents difficult problems. Therefore, for the purpose of this report, the resulting "treatment level" was simply calculated from the gain in weight of the specimens after they had been treated as indicated in steps 1 through 4, including the conditioning to equilibrium at 80° F. and 30 percent relative humidity. This gain in weight was then expressed as a percentage of the treated and conditioned weight of the specimen.

In this analysis, it was necessary to make an allowance for the water-extractable portion of the wood which is dissolved by the treating solution. This water-extractable portion was assumed to be 0.48 percent of the untreated but conditioned weight of the wood. It was also found that there was some variation in the amount of chemical retained from specimen to specimen although the same salt concentration and treatment cycle was used. To help eliminate possible treatment level distribution effects, an attempt was made to distribute similar treatment levels evenly among replicate runs.

The resinous polymeric material also included in this investigation was prepared by reacting tetrakis (hydroxy methyl) phosphonium chloride (THPC) with methylol melamine and urea using an ethanalamine buffer.⁵ The specimens were

⁵Much of the development work of the tetrakis (hydroxymethyl) phosphonium chloride (THPC) resin system and its application to textiles was done at the Southern Regional Research Laboratory, Southern Utilization Research Branch, Agricultural Research Service, USDA.

treated by impregnating them with resin monomers, using the following procedure:

(1) Two solutions were made of:

Solution A: tetrakis (hydroxymethyl) phosphonium chloride, 27.2 grams; water, 7.5 grams; and ethanolamine, 1.5 grams.

Solution B: trimethylol melamine (unmethylated), 15.5 grams; urea, 7.3 grams; and water, 17.8 grams.

(2) Solution A was added to solution B, and the resultant mixture was immediately added to 316 grams of water.

(3) The specimens were added to the solution formed in (2), and the pressure-vacuum procedure previously described was used to impregnate this solution into the specimens,

(4) After completion of the pressure-vacuum impregnation, the specimens were removed from the excess solution and placed in a room at 80° F. and 30 percent relative humidity where the monomers polymerized and water was evaporated from the resultant polymer.

Pyrolysis Procedure

Partial pyrolysis of the specimens was accomplished in a thermogravimetric balance.⁶ The thermogravimetric balance and its use is described by Browne and Tang (3). It was possible when using this equipment, to heat the specimens to any temperature between 240° and 822° C., for almost any period of time, to achieve a desired volatilization (loss in weight). This thermal decomposition was accomplished in an atmosphere of nitrogen. A group of four specimens, selected to have a closely matched treatment level, was pyrolyzed at each condition of time and temperature.

Calorimetry

The determination of the heat of combustion and heat of reaction of many substances is described in the literature (7). In the present work, a standard oxygen bomb calorimeter was used to determine the heat of combustion of the original wood specimens and residues. The bomb was

fired under 300 pounds per square inch oxygen (gage) pressure, and the resulting heat evolution caused an approximate 1° C. rise in temperature in the 1,900 grams of water surrounding the bomb. There were several corrections to be applied.

They were:

(1) During a determination, heat is transferred to and from the measured quantity of water in the calorimeter because the calorimeter is not at exactly the same temperature as its surroundings. This heat transfer was corrected for by taking a series of temperature readings of the calorimeter water before igniting the wood sample in the bomb, and also after the maximum water temperature had been reached.

The observed temperature rise (the difference between the maximum water temperature and the firing temperature) was then corrected by assuming that the heat transfer rate, before firing, prevailed for approximately 20 percent of the time from firing until the maximum temperature was reached. It was also assumed that the heat transfer rate at the maximum temperature prevailed for 80 percent of this time. It can be shown that this approximation does not lead to serious errors.

(2) When the bomb was filled with oxygen, some residual nitrogen from the atmosphere remained in the bomb. Under the high temperatures of combustion and the oxidizing conditions of the bomb, this nitrogen was completely converted to nitrogen dioxide (NO₂). To correct for the heat of this reaction, approximately 2 millimeters of distilled water were placed in the bomb prior to firing so that the nitrogen dioxide would dissolve in the water, forming nitric acid (HNO₃).

After completion of the temperature measurements, the bomb was opened and the nitric acid solution was titrated with a 0.0725 normal sodium carbonate solution. This solution was made SO that 1 millimeter is equivalent to 1 calorie given off in the nitrogen-dioxide reaction. This titration correction was then subtracted from the total heat of combustion.

(3) In addition to the two previous corrections, allowance was made for the heat given off by the burning fuse wire. This amounted to 2.3 calories per centimeter of the fuse wire burned.

⁶Special acknowledgement is given to W. K. Tang, Forest Products Laboratory chemical engineer, who aided the work by pyrolyzing samples with the thermogravimetric balance.

Calculations

If W_1 is the weight of the unpyrolyzed (treated or untreated) specimen in equilibrium at 80° F. and 30 percent relative humidity, and W_2 is the weight of the char left after pyrolysis, the degree of volatilization is given as:

$$\text{Percent weight loss} = V = \frac{W_1 - W_2}{W_1} \times 100$$

If ΔH_c is the standard heat of combustion per gram of the original wood specimens and ΔH_s is the heat of combustion per gram of the char left after pyrolysis, the decrease in the heat of com-

bustion of the solid phase is given by:

$$W_1 (\Delta H_c) - W_2 (\Delta H_s) \text{ calories}$$

the percent decrease in heat of combustion of the solid phase is given by:

$$\frac{W_1 (\Delta H_c) - W_2 (\Delta H_s)}{W_1 (\Delta H_c)} \times 100 \text{ percent}$$

and the heat of combustion calculated for the volatile products is:

$$\frac{W_1 (\Delta H_c) - W_2 (\Delta H_s)}{W_1 - W_2}$$

in calories per gram of volatile products.

RESULTS

The heat of combustion of the ponderosa pine material from which all specimens were taken and which was in equilibrium at 80°F. and 30 percent relative humidity was found to be -4,626 calories per gram, ± 0.83 percent. This is the result of six measurements.

Table 1 gives data on the decrease in the heat of combustion of untreated wood specimens pyrolyzed to increasing degrees of volatilization, and the corresponding increase in the heat of combustion calculated for the volatile products. Tables 2 through 6 present similar data for the chemically treated wood specimens. The minus sign (-) associated with the heat of combustion (indicating that heat is given off) has been omitted from all these tables and subsequent figures. The values in table 1 for untreated wood correspond to temperatures from 240° to 822° C., and for degrees of volatilization from about 13 to 85 percent weight loss. As a rule, these data represent four replicates at each temperature of pyrolysis and approximate degree of volatilization.

The arithmetic average heat of combustion of the volatile products was computed and plotted versus the arithmetic average of degree of volatilization for the corresponding specimens (fig. 1). These data are also shown differently with the percent of the total heat of combustion released in the volatile pyrolysis products plotted against the percent of volatilization of the samples

(fig. 2). The 45° line shown in figure 2 represents a simple chemical compound undergoing a single reaction where the amount (or percent) of the total heat change is directly related to the amount (or percent) of the material reacted.

It appears from these data that the heat of combustion of the volatile products of untreated wood is relatively low at the outset of pyrolysis. For example, at 20 percent weight loss, the average heat of combustion was about -2,800 calories per gram of volatiles released (representing 10 percent of the total heat of combustion); at 40 percent weight loss, about -3,000 calories per gram (representing 29 percent of the total heat of combustion); and at 85 percent weight loss about -4,000 calories per gram (representing 75 percent of the total heat of combustion).

It appears in figure 1 that the heat of combustion of the volatile products at any given degree of volatilization is independent of the temperature at which the pyrolysis occurs (at least for temperatures above 270° C.). For example, at 263° C. the heat of combustion for the volatile products corresponding to 27.7 percent volatilization was -2,835 calories per gram, and at 290° C. the heat of combustion corresponding to 25.3 percent volatilization was -2,810 calories per gram.

At 290° C., when pyrolysis was continued to 57.4 percent, the heat of combustion was -3,273 calories per gram, in close agreement with an interpolation of the data for: 62.6 percent volatil-

Table 1.--Heat of combustion of volatile pyrolysis products from 1/4-inch-diameter dowels of ponderosa pine, as a function of temperature and extent of pyrolysis (weight loss) (heat of combustion of unpyrolyzed ponderosa pine, 4,626 calories per gram)

Temperature : (°C.)	Volatilization : (loss in weight) : Percent	Decrease in heat : of combustion : Percent	Heat of combustion : of volatile products : Calories per gram of wood	Heat of combustion : of volatile products : Calories per gram of volatile products
273	22.42	9.42	424	1,891
	23.81	13.44	605	2,536
	23.80	12.78	575	2,416
	24.53	9.75	439	1,782
Mean	23.65			2,156
280	51.71	35.17	1,625	3,140
	46.56	30.17	1,395	2,990
	43.87	29.35	1,360	3,100
	39.23	27.78	1,285	3,270
Mean	45.34			3,125
290	25.63	15.69	725	2,830
	25.01	14.51	671	2,680
	24.89	15.51	718	2,880
	25.73	15.86	733	2,850
Mean	25.31			2,810
290	26.33	16.33	755	2,870
	26.54	16.84	780	2,940
	26.53	13.00	601	2,270
	25.17	18.65	862	3,420
Mean	26.14			2,875
290	20.42	11.16	516	2,520
	20.23	11.98	554	2,740
	21.50	12.21	565	2,630
	21.50	12.35	571	2,660
Mean	20.91			2,638
240	12.72	5.75	266	2,090
	14.56	8.32	384	2,640
	16.36	7.96	368	2,250
	14.01	6.86	318	2,270
Mean	14.41			2,312
260	17.37	7.88	364	2,100
	17.24	7.43	344	2,000
	17.03	8.59	396	2,320
	17.32	7.37	341	1,970
Mean	17.24			2,098
263	28.42	17.87	826	2,900
	27.10	15.89	735	2,720
	26.45	15.87	735	2,780
	28.70	18.26	845	2,940
Mean	27.67			2,835
270	18.07	9.63	445	2,460
	21.17	14.42	667	3,150
	22.53	15.82	731	3,250
	20.60	11.39	526	2,550

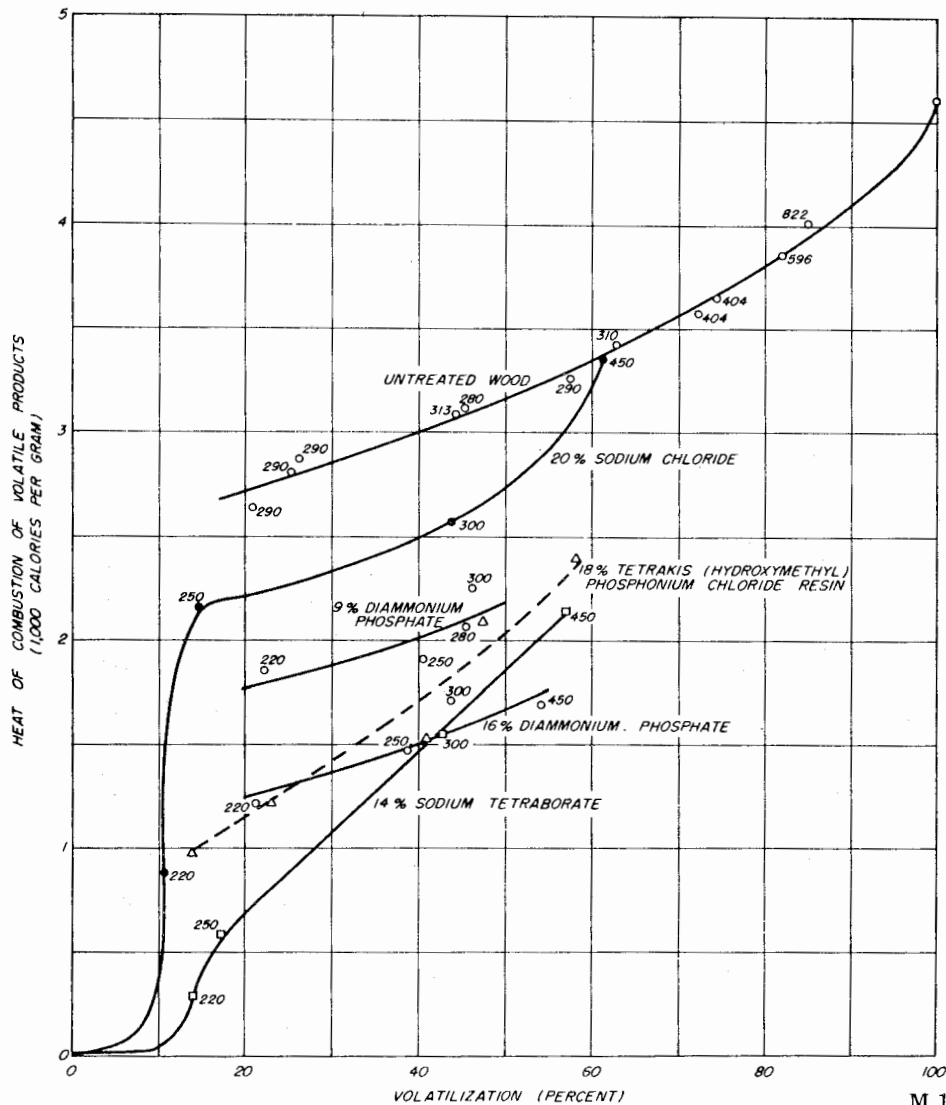
Temperature : (°C.)	Volatilization : (loss in weight) : Percent	Decrease in heat : of combustion : Percent	Heat of combustion : of volatile products : Calories per gram of wood	Heat of combustion : of volatile products : Calories per gram of volatile products
Mean	20.59			2,852
273	35.22	24.23	1,120	3,180
	32.63	22.19	1,025	3,140
	31.90	22.13	1,122	3,510
	31.78	20.98	970	3,050
Mean	32.88			3,220
290	57.59	41.14	1,905	3,300
	58.54	40.47	1,870	3,190
	56.16	40.46	1,870	3,330
Mean	57.43			3,273
310	64.30	47.30	2,185	3,400
	65.11	47.15	2,180	3,340
	64.94	45.96	2,120	3,270
	56.14	45.25	2,095	3,730
Mean	62.62			3,435
313	43.77	30.22	1,400	3,200
	38.31	25.23	1,170	3,060
	47.34	34.34	1,588	3,350
	47.77	28.67	1,327	2,780
Mean	44.30			3,097
404	71.90	55.30	2,560	3,570
	72.31	56.53	2,620	3,620
	72.15	56.06	2,600	3,600
	72.45	55.97	2,585	3,575
Mean	72.20			3,591
404	74.30	58.29	2,700	3,640
	73.92	58.76	2,720	3,680
	74.39	59.34	2,745	3,690
	74.50	58.87	2,720	3,650
Mean	74.28			3,665
596	82.02	68.81	3,180	3,880
	81.59	68.30	3,160	3,870
	82.24	69.02	3,200	3,890
	81.69	67.59	3,130	3,840
Mean	81.88			3,870
822	85.16	74.47	3,440	4,040
	83.93	72.16	3,340	3,980
	85.02	73.53	3,400	4,000
	85.02	75.33	3,480	4,080
Mean	84.78			4,025

ization at 310° C. of -3,435 calories per gram °C, and 45.3 percent volatilization at 280° C. of -3,125 calories per gram °C. There was also the close agreement between this latter value and 44.3 percent volatilization at 313° C. of -3,097 calories per gram.

The curve for untreated wood in figure 1 can be extrapolated to -4,626 calories per gram at 100 percent volatilization, because if it were possible to pyrolyze the wood entirely to volatile products, their heat of combustion would necessarily be equal to that of the untreated wood before pyrolysis. On tracing the curve backward,

it must drop rapidly to zero calories per gram at some point before zero percent volatilization is reached, because most of the 6 percent moisture in the wood, prior to pyrolysis, is surely given off well before any combustible volatile products appear. It may be that the relation expressed in figure 1 accurately applies only for temperatures of pyrolysis above the so-called exothermic point, approximately 270° C.

This observation, that the heat of combustion of the volatile products is independent of the temperature of pyrolysis, may mean that the course of the successive chemical reactions in



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Figure 1.--Heat of combustion of volatile pyrolysis products as a function of the degree of pyrolysis for untreated and chemically treated ponderosa pine. (Numbers adjacent to points on the curve indicate the temperature in °C. at which the samples were pyrolyzed.)

the pyrolysis of wood is essentially the same at all temperatures above the exothermic point. It is, however, difficult to accept such a theory because the overall pyrolysis of wood is the sum of many individual reactions for which the temperature coefficients of the reaction velocity constants presumably vary appreciably. Further work with wood samples of different geometry, particularly thin veneer, will therefore be desirable.

There were two indications that the geometry of the test specimen may have an effect on the results. The first was some runs made in an exploratory test at 290° C. in which 1/2-inch-diameter cylinders were used. The data for these

specimens were below those shown on the curves for 1/4-inch wood specimens. Secondly, some preliminary experiments were also made with thin veneer samples which gave data at low degrees of pyrolysis that were somewhat above those shown in the figures.

The deviation in the heat of combustion for the volatiles released from the 1/4-inch cylinders and veneers was approximately 160 calories per gram at a volatilization of 35 percent, and 130 calories per gram at 45 percent. The tentative curve for the veneers merged with that for the 1/4-inch cylinder specimens at approximately 80 percent volatilization. These two considerations, then,

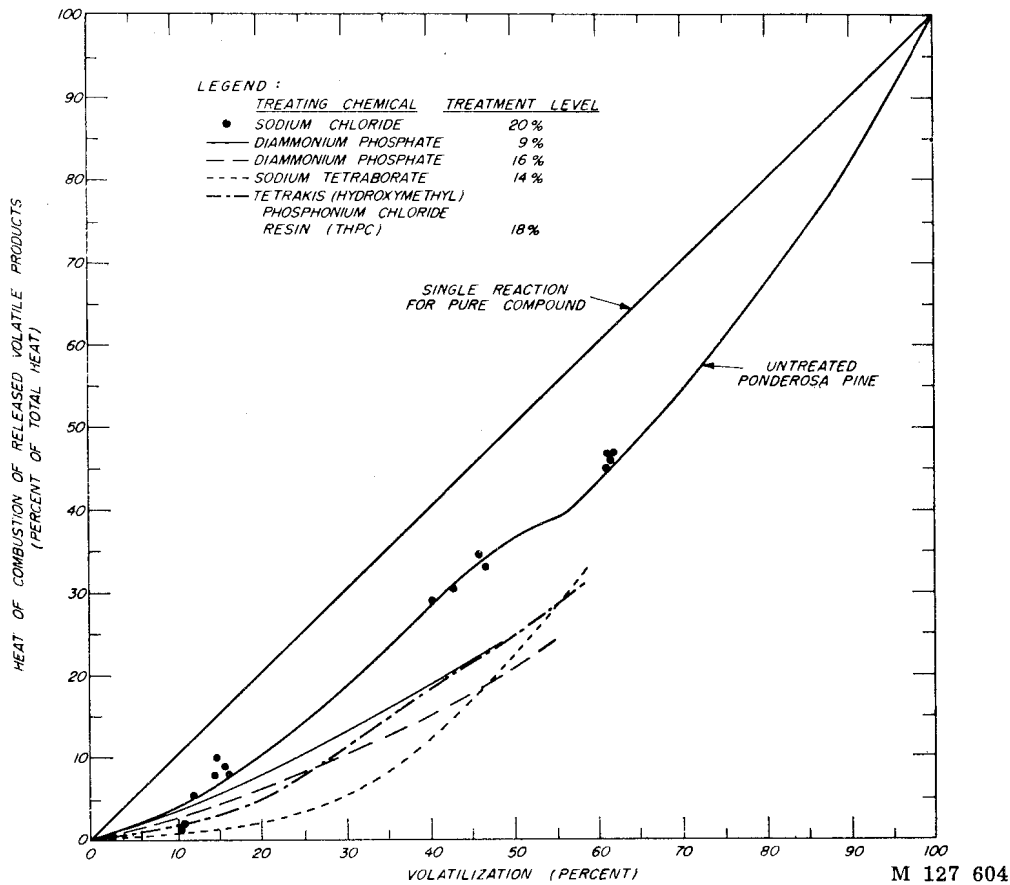


Figure 2.--Heat of combustion of released volatile products (percent of total heat) as a function of the degree of pyrolysis (volatilization) for untreated and chemically-treated ponderosa pine.

tend to show that the heat of combustion of the volatile pyrolysis products, as measured under the assumptions of this study, decreased as the diameter of the specimen increased.

The data for volatile products of pyrolysis of chemically treated wood specimens extend only to 50 to 60 percent volatilization because treated wood yields upon pyrolysis much less volatile material and correspondingly more char than untreated wood. Extrapolation of the curves for treated wood specimens (figs. 1 and 2) to hypothetical 100 percent volatilization therefore is not justifiable.

It is, however, in the earlier part of the pyrolysis that the heat of combustion of the volatile products is most significant for flaming combustion, which is commonly more important than the glowing combustion of char for the onset and initial spread of fire. Nevertheless, the heat of combustion of the treated but unpyrolyzed wood specimens, which affords the sum of the heats of combustion of volatile products and of char, was

determined directly and the results are recorded in the titles of tables 2 through 6.

The heats of combustion of the several kinds of treated but unpyrolyzed ponderosa pine differed among themselves and from the -4,626 calories per gram found for untreated and unpyrolyzed ponderosa pine. Unpyrolyzed wood treated with any one of the strictly inorganic salts evolved less heat on combustion than the untreated wood. The difference was due largely to the bulk of the inorganic salt in the treated wood specimens. The magnitude of the bulking effect can be calculated reasonably close from the mean treatment levels of the salts recorded in tables 2 through 6. When that is done small discrepancies still remain, amounting to -91 calories per gram of treated wood for the treatments with 6 percent diammonium phosphate, -90 for 12 percent diammonium phosphate, +107 for 6 percent sodium tetraborate, and +137 for 12 percent sodium chloride.

These discrepancies, which amount to 2 to 4

Table 2.--Heat of combustion of volatile pyrolysis products from 1/4-inch ponderosa pine dowels treated with 6 percent diammonium phosphate solution (heat of combustion of the treated but unpyrolyzed wood, 4,287 calories per gram of treated wood)

Treatment level	Temperature of pyrolysis (°C)	Volatilization (loss in weight) Percent	Decrease in heat of combustion Percent	Heat of combustion of volatile products Calories per gram of wood	Calories per gram of volatile products
8.83	220	23.14	9.75	418	1,806
9.10		21.28	9.39	402	1,891
9.26		22.51	9.81	420	1,868
Mean		22.31			1,855
9.20	250	40.78	16.90	725	1,777
9.30		39.90	18.50	793	1,988
9.10		40.93	19.15	821	2,006
8.81		40.80	17.75	761	1,865
Mean		40.60			1,909
8.93	280	45.66	22.26	954	2,091
9.50		45.35	22.43	962	2,121
9.39		45.51	21.80	973	2,054
9.93		45.71	22.38	960	2,099
Mean		45.56			2,066
9.54	300	46.28	24.08	1,032	2,230
9.99		46.16	24.51	1,051	2,277
9.39		46.19	24.56	1,053	2,280
8.90		46.87	23.26	997	2,128
Mean		46.38			2,254

Table 4.--Heat of combustion of volatile pyrolysis products from 1/4-inch ponderosa pine dowels treated with 6 percent sodium tetraborate solution (heat of combustion of the treated but unpyrolyzed wood, 3,866 calories per gram of treated wood)

Treatment level	Temperature of pyrolysis (°C)	Volatilization (loss in weight) Percent	Decrease in heat of combustion Percent	Heat of combustion of volatile products Calories per gram of wood	Calories per gram of volatile products
14.03	220	13.78	0.35	16	100
13.57		13.98	1.06	47	293
13.76		13.67	.92	41	261
15.08		14.64	1.92	87	507
Mean		14.02			290
13.65	250	17.22	1.58	70	354
13.42		16.75	4.39	185	950
15.40		17.88	1.25	60	288
14.33		16.97	3.29	148	750
Mean		17.21			585
14.77	300	42.88	18.06	815	1,628
14.28		43.30	17.87	802	1,596
13.71		41.79	15.65	698	1,412
Mean		42.66			1,545
13.40	450	56.99	30.34	1,347	2,057
13.60		56.88	31.84	1,418	2,165
14.13		57.05	32.52	1,457	2,204
Mean		56.97			2,142

Table 3.--Heat of combustion of volatile pyrolysis products from 1/4-inch ponderosa pine dowels treated with 12 percent diammonium phosphate solution (heat of combustion of the treated but unpyrolyzed wood, 3,967 calories per gram of treated wood)

Treatment level	Temperature of pyrolysis (°C)	Volatilization (loss in weight) Percent	Decrease in heat of combustion Percent	Heat of combustion of volatile products Calories per gram of wood	Calories per gram of volatile products
15.04	220	21.39	3.44	161	641
15.63		20.46	7.88	368	1,523
15.77		20.84	6.39	298	1,212
15.38		22.35	8.20	383	1,457
Mean		21.26			1,208
17.81	250	38.43	14.72	647	1,477
15.53		39.26	14.90	685	1,481
15.10		38.52	14.50	677	1,499
15.66		38.80	13.91	649	1,418
Mean		38.75			1,469
16.83	300	43.60	18.30	853	1,635
16.22		43.12	17.71	827	1,614
15.73		43.48	20.30	948	1,847
15.34		44.65	19.47	909	1,731
Mean		43.71			1,707
15.12	450	54.30	24.08	1,124	1,765
17.49		53.43	24.47	1,142	1,772
15.53		54.41	22.83	1,066	1,663
16.07		54.88	21.77	1,016	1,562
Mean		54.26			1,691

Table 5.--Heat of combustion of volatile pyrolysis products from 1/4-inch ponderosa pine dowels treated with 12 percent sodium chloride solution (heat of combustion of the treated but unpyrolyzed wood, 3,596 calories per gram of treated wood)

Treatment level	Temperature of pyrolysis (°C)	Volatilization (loss in weight) Percent	Decrease in heat of combustion Percent	Heat of combustion of volatile products Calories per gram of wood	Calories per gram of volatile products
21.01	220	10.54	1.85	82	615
21.30		9.87	.99	44	350
18.84		11.36	5.50	251	1,799
20.33		10.26	2.12	95	740
Mean		10.56			876
20.02	250	15.55	8.00	359	1,855
18.79		14.28	9.79	447	2,552
20.42		13.97	7.76	347	1,983
18.38		15.03	8.94	410	2,238
Mean		14.71			2,157
19.94	300	45.82	34.54	1,551	2,725
20.23		40.05	28.62	1,281	2,564
20.73		42.55	30.19	1,342	2,512
21.10		46.41	32.94	1,456	2,487
Mean		43.71			2,572
19.62	450	60.89	56.63	2,555	3,388
18.71		61.15	55.81	2,550	3,406
19.19		61.54	56.90	2,583	3,408
19.94		60.64	54.79	2,462	3,266
Mean		61.06			3,367

percent of the measured heats of combustion, are not large enough to be considered significant. They may arise from thermal effects due to decomposition and volatilization of the salts during combustion in the oxygen bomb.

The heat of combustion of unpyrolyzed ponderosa pine treated with tetrakis (hydroxymethyl) phosphonium chloride (THPC), -4,508 calories per gram, approached the -4,626 calories per gram for untreated wood much more closely than

Table 6.--Heat of combustion of volatile pyrolysis products from 1/4-inch ponderosa pine dowels treated with 18 percent tetrakis (hydroxy-methyl) phosphonium chloride-urea-methylolmelamine resin (heat of combustion of the treated but unpyrolyzed wood, 4,508 calories per gram of treated wood)

Treatment level	Temperature of pyrolysis	Volatilization (loss in weight)	Decrease in heat of combustion	Heat of combustion of volatile products
Percent	°C.	Percent	Percent	Calories per gram of wood
18.56	220	13.61	2.79	153
17.63		16.00	5.50	301
18.00		12.33	.38	32
18.21		13.80	3.69	202
Mean		13.94	3.14	974
18.04	250	21.51	5.19	284
18.42		22.89	5.84	321
17.75		24.28	6.99	382
17.46		23.25	6.78	370
Mean		22.98	6.20	1,215
18.07	300	41.62	15.88	870
17.57		40.52	14.62	804
18.36		40.54	12.51	687
18.94		40.70	13.31	733
Mean		40.85	14.08	1,532
17.04	350	47.16	22.84	1,245
18.16		47.37	21.05	1,154
18.49		47.72	21.71	1,193
17.66		47.55	22.47	1,228
Mean		47.45	22.02	2,097
18.39	450	59.15	32.36	1,776
18.17		58.01	30.11	1,358
17.50		58.47	31.64	1,728
17.00		57.16	29.38	1,601
Mean		58.20	30.87	2,397

did the heat of combustion for any of the strictly inorganic salts. When allowance is made for the 18 percent bulk of the THPC already described for the other salts, the result is a difference of -715 calories per gram of wood as compared with untreated wood. Such difference is clearly significant and is due to decomposition of the THPC and combustion of its organic components during combustion of the THPC-treated wood in the oxygen bomb.

Thus, fire retardants that contain organic components such as THPC may greatly decrease the heat of combustion of the volatile products evolved in the first part of pyrolysis and yet themselves

contribute to the heat produced when combustion has consumed the char as well as the volatile products.

The data show that treatment of wood with any one of the chemicals studied materially diminished the heat of combustion of the volatile products released during the early stages of pyrolysis. In figure 1, in which the average heat of combustion of the volatile products released is plotted against the extent of volatilization, the curves show that sodium chloride, which is not usually considered a fire retardant, is not nearly so effective as diammonium phosphate, sodium tetraborate, or THPC resin in reducing the heat of combustion of the volatile products released in the early stages of volatilization.

In fact, in figure 2 where the data are plotted with the percent of total heat of the sample contained in the released volatile products as a function of the percent of volatilization, sodium chloride-treated wood falls on the same curve as untreated wood. The failure of the points for sodium chloride to coincide with the curve for untreated wood in figure 2 also is due partly to the bulking effect of the inert chemical and partly to inherent differences between the types of plots involved.

However, the data for the other treatments definitely fall below the line for untreated wood as plotted in both figures 1 and 2. This indicates that these treatments cause a smaller proportion of the original heat of combustion to be released in the form of heat of combustion of volatile products at any pyrolytically attainable degree of volatilization.

For example, at 40 percent volatilization where there is a significant difference, untreated wood specimens had lost about 29 percent of their heat of combustion as the heat of combustion of the released volatile pyrolysis products; wood specimens treated with the various effective fire-retardant treatments had lost only 11 to 19 percent of their heat of combustion.

CONCLUSIONS

The results of this investigation indicate that fire-retardant treatments tend to lower the heat of combustion of the volatile pyrolysis products of treated wood below the value associated with the

untreated wood at the same stage of pyrolytic volatilization.

This means that the combustible volatile products, which are the usual source for the ignition

and spread of fire, would have considerably less available heat when produced from the pyrolysis of fire-retardant-treated wood than when produced from untreated wood. When combustion has been completed by the consumption of the char by glowing, inorganic fire retardants alter the total amount of heat released (flaming and glowing combustion together) from the wood itself only to the extent of any heat effects caused by decomposition or volatilization of the treating chemical,

which is usually insignificant in relation to the total heat released.

Fire retardants that have organic components, however, after greatly reducing the heat evolved in flaming combustion of volatile products formed in the early stages of pyrolysis, may themselves contribute to the total heat set free when combustion reaches the stage of complete consumption of the char.

APPENDIX

Discussion of Relevant Data in the Literature

Further insight can be gained from consideration of relevant data found in the literature of other workers.

Klason (4) heated 800-gram samples of birch wood in a retort at atmospheric pressure, heated 100-gram samples in a vacuum apparatus, collected the products of the destructive distillation, and analyzed them in detail. He determined the heat of combustion of the original wood, the charcoal, and the tar, and then calculated the thermal relations for the pyrolysis.

In one run at atmospheric pressure the rate of heating was such as to take 8 hours for the temperature of the charge to rise from 250° C., where pyrolysis was considered to begin, to 400° C., where pyrolysis and distillation were considered complete. In another run at atmospheric pressure, heating was so slow that 14 days were required for the charge to reach 400 C. The run in vacuum was completed in about 6 hours. A rearrangement of Klason's results is presented in table 7.

For pyrolysis in vacuum, where volatile products evidently escaped from the hot zone rapidly enough to minimize secondary pyrolysis, and therefore the yield of tar was maximum and the yields of charcoal, water, and carbon dioxide were minimum, the heat of combustion of the volatilized material, -3,794 calories per gram at a volatilization of 80.46 percent, was practically identical with the present finding (fig. 1) of 3,830 calories per gram at 80 percent volatilization. For Klason's pyrolyses of wood in bulk at atmospheric pressure, the yields of charcoal, water, and carbon dioxide were greater, the yield of tar

less, and therefore the heat of combustion of the volatilized material was less the slower the distillation.

This finding, in conjunction with the finding (fig. 1) that the heat of combustion of the volatilized material at any given extent of volatilization seems to be nearly independent of temperature, suggests that the initial thermal decomposition of wood may be a surprisingly simple reaction independent of temperature within certain limits and that complexities appear when the products of the initial breakdown undergo secondary pyrolysis.

In view of comments made later, it is observed that the heat of combustion contributed by the flammable fixed gases (carbon monoxide, hydrocarbons, and formaldehyde) amounts to less than 10 percent of the total heat of combustion of volatilized material for the distillation in vacuum and to less than 15 percent in the slow 14-day distillation in which there was greatest opportunity for secondary pyrolyses.

Table 8 presents data of Klason, Heidenstam, and Norlin (5) for distillation of cellulose from cotton and for sulfite cellulose from pine (*Pinus sylvestris*) in a manner similar to the 8-hour distillation of birch wood reported in table 7. The celluloses produced more water and less tar than the birch wood and, as a result, the heat of combustion of the material volatilized from cellulose was only half that of the volatilized material from wood. Apparently the heat of the pyrolysis reaction was somewhat greater for cellulose than for wood.

Madorsky, Hart, and Straus (6) pyrolyzed cotton cellulose in very small samples (not more than 85 milligrams) and in vacuum, so that there could be practically no secondary pyrolysis. By

Table 7.--Rearrangement of data by Klason (4) on the thermal relations of pyrolysis during destructive distillation of birch wood

Pyrolysis product or group of products	Yield of product and its heat of combustion					
	6-hour distillation in vacuum		8-hour distillation, atmospheric pressure		14-day distillation, atmospheric pressure	
	Percent by weight	Calories per gram	Percent by weight	Calories per gram	Percent by weight	Calories per gram
Charcoal (solid residue)	19.54	1,528.0	30.85	2,428.3	39.44	3,193
Water	16.64	0	20.48	0	26.08	0
Carbon dioxide	5.95	0	10.17	0	12.62	0
Nonflammable gases and vapors	22.59	0	30.65	0	38.70	0
Carbon monoxide	3.28	79.7	3.57	86.8	2.19	53.2
Methane	.91	118.8	.98	128	.67	83.5
Ethylene	.20	23.7	.25	29.6	.10	11.9
Formaldehyde	1.30	59.2	1.00	45.7	.70	31.9
Flammable gases	5.69	281.4	5.80	290.1	3.66	180.5
Other flammable vapors ¹	15.00	709.1	15.76	892.5	16.39	961.8
Flammables other than tar	20.69	990.5	21.56	1,182.6	20.05	1,142.3
Tar	37.18	2,062.4	16.94	1,025	1.81	114.8
Total volatilized material	80.46	3,052.9	69.15	2,207.6	60.56	1,257.1
Heat of combustion of 1 gram of volatilized material		3,794		3,192		2,076
Heat of combustion of wood		4,704		4,895		4,791
Heat of combustion of products		4,580.9		4,635.9		4,450.1
Heat of pyrolysis reaction		123.1		259.1		340.9

¹Comprised of acetic acid, formic acid, methyl alcohol, acetone, and "oil distilled over." Listed individually in the original; lumped together for purposes of this tabulation.

means of suitable cold traps they determined the yield of products volatile at -190° C., -80° C., and 25° C., respectively, and condensable at 25° C. The fractions were found by analysis to be chiefly carbon monoxide, carbon dioxide, water, and tar, respectively. The water contained some acetaldehyde, and the tar appeared to be levoglucosan containing some contaminant with a ketone group. Some of the results are given in table 9 together with the heat of combustion of 1 gram of volatilized material calculated on the basis of -2,410 calories per gram of carbon monoxide and -6,780 calories per gram of tar.

Madorsky, Hart, and Straus in their vacuum pyrolysis of very small samples obtained much larger yields of tar and lower yields of water and carbon dioxide, and consequently a higher heat of combustion of a gram of volatilized material than was found by Klason, Heidenstam, and Norlin in their distillation of larger samples of cotton and of pine cellulose. This outcome par-

Table 8.--Rearrangement of data of Klason, Heidenstam, and Norlin (5) on the thermal relations of pyrolysis during destructive distillation of cotton cellulose and of sulfite cellulose from pine (*Pinus sylvestris*)

Pyrolysis product or group of products	Yield of product and its heat of combustion			
	Cellulose from cotton		Cellulose from pine	
	Percent by weight	Calories per gram	Percent by weight	Calories per gram
Charcoal (solid residue)	38.82	2,930.9	36.93	2,855
Water	32.39	0	34.17	0
Carbon dioxide	10.35	0	12.83	0
Nonflammable gases and vapors	42.74	0	47.00	0
Carbon monoxide	4.15	100.8	3.40	82.7
Methane	.27	35.3	.27	35.3
Ethylene	.17	20.2	.21	24.9
Flammable gases	4.59	156.3	3.88	142.9
Other flammable vapors ¹	.073	5.3	.08	5.9
Flammables other than tar	4.66	161.6	3.96	148.8
Tar	13.78	748.4	12.11	820.8
Total volatilized material	61.18	910.0	63.07	969.6
Heat of combustion of 1 gram of volatilized material		1,487		1,535
Heat of combustion of cellulose		4,188		4,170
Heat of combustion of products		3,840.9		3,824.6
Heat of pyrolysis reaction		347.1		345.4

¹Comprised of acetic acid, acetone, and methyl acetate. Listed individually in the original; lumped together for purposes of this tabulation.

Table 9.--Heat of combustion of volatilized material calculated from yields obtained by Madorsky, Hart, and Straus (6) in the pyrolysis of less than 0.1-gram samples of untreated and treated cotton cellulose in vacuum

Treatment applied: to the cotton	Temperature of pyrolysis:	Yield (by weight) of					Total volatilized:	Heat of combustion of 1 gram of volatilized material
		Water	Carbon dioxide:	Carbon monoxide:	Tar			
	°C.	Percent	Percent	Percent	Percent	Percent	Calories	
None	250	1.5	0.3	0.2	0.7	2.7	1,970	
.....	280	1.7	.3	.2	1.1	3.3	2,420	
.....	280	3.7	.6	.2	5.8	10.3	3,830	
.....	280	5.8	1.0	.2	12.4	19.4	4,350	
.....	280	10.6	2.1	.7	31.7	45.1	4,800	
.....	280	15.2	3.8	1.3	49.3	69.6	4,850	
.....	321	6.2	.9	.5	14.4	22.0	4,470	
.....	397	20.6	5.6	1.6	63.6	91.4	4,770	
Sodium carbonate (7 percent)	291	28.0	11.7	3.8	7.9	51.4	1,220	
Sodium chloride (8 percent)	280	29.3	7.3	6.7	6.0	49.3	1,150	

allels Klason's finding of the difference between vacuum and atmospheric distillation of wood (table 7).

If with the data of table 9 the heat of combustion of the volatilized material is plotted as a function of the extent of volatilization, the curve resembles figure 1 in that the heat of combustion seems to depend on extent of volatilization only and to be independent of temperature. Further, the heat of combustion drops off precipitously when the extent of volatilization falls below about 25 or 20 percent. Thus there is a reasonable similarity between wood and cellulose.

For the entire region above 20 percent volatilization, however, the heat of combustion reported for cellulose by Madorsky, Hart, and Straus exceeds that reported for wood by Klason (table 7) or by the authors (fig. 1). Moreover, the data of table 9 indicate that the heat of combustion of the volatiles from cellulose reaches a maximum in the vicinity, perhaps, of 70 percent volatilization, which substantially exceeds the heat of combustion of pure cellulose which is probably between

4,000 and 4,200 calories per gram.

Table 9 shows that treatment of cellulose with inorganic salts reduces the heat of combustion of the volatile products even more drastically than is shown for wood (fig. 1). Moreover, sodium chloride effects its striking reduction despite the fact that it is an ineffective flame retardant for either wood or cotton.

Broido and Martin (1) pyrolyzed pure α -cellulose (filter paper) and cellulose containing 2 percent of added potassium bicarbonate in helium by irradiating thin sheets at two different levels, 10.5 and 15.4 calories per square centimeter, from a carbon arc source that was equivalent to a 5,500° K. black body emitter. The highest irradiance levels measured in conventional fires are 2 to 3 calories per square centimeter per second. The loss in weight was determined, and the volatilized products other than tar were analyzed by gas chromatography and mass spectrometry with the results reported in table 10. In this table, a calculated yield of tar has been added, based on the difference between the total weight loss and

Table 10.--Heat of combustion of the volatile products of pyrolysis of a-cellulose or of α -cellulose impregnated with 2 percent of potassium bicarbonate, when irradiated at two different intensities, based on data of Broido and Martin (1)

Pyrolysis product or group of products	Heat of combustion	Yield of product and its heat of combustion							
		Untreated cellulose irradiated by ¹				Treated cellulose irradiated by ²			
		10.5 calories per square centimeter	15.4 calories per square centimeter	10.5 calories per square centimeter	15.4 calories per square centimeter				
	Calories per gram	Percent by weight	Calories per gram	Percent by weight	Calories per gram	Percent by weight	Calories per gram	Percent by weight	Calories per gram
Water	0	4.0	0	9.5	0	16.5	0	19.6	0
Carbon dioxide	0	1.22	0	2.54	0	4.7	0	6.3	0
Nonflammable gases	0	5.22	0	12.04	0	21.2	0	25.9	0
Carbon monoxide	2,410	.53	12.8	1.65	39.8	3.0	72.3	5.1	123.0
Hydrogen	34,180	.003	1.0	.015	5.1	.014	4.8	.3	102.5
Methane	13,200	.002	.3	.020	2.6	.030	3.9	.66	87.0
Ethylene	11,800	--	--	.034	4.0	.026	3.1	.51	60.1
Ethane	12,280	--	--	.007	.9	.046	5.6	.19	23.3
Flammable gases		.535	14.1	1.726	52.4	3.116	89.7	6.76	395.9
Other vapors	37,000	.48	33.6	1.8	126.0	2.6	182.0	6.0	420.0
Tar (by difference)	6,780	16.5	1,120.0	52.5	3,560.0	26.8	1,818.0	40.6	2,755.0
Total weight loss		22.735	1,167.7	68.066	3,738.4	53.716	2,089.7	79.26	3,570.9
Heat of combustion per gram volatilized:			5,130		5,500		3,890		4,500

¹Irradiation with 4.2 calories per square centimeter per second for 2.5 seconds.

²Irradiation with 11 calories per square centimeter per second for 1.4 seconds.

³The products found among the other vapors, reported as acetaldehyde, acrolein, acetone, biacetyl, crotonaldehyde, furan, methanol, and propionaldehyde, vary from 5,340 to 7,740 calories per gram in their heat of combustion.

the sum of all other products reported by the authors. To the table has also been added the heat of combustion of each component of the products, calculated from data given in the handbooks (the heat of combustion of tar from pine cellulose is taken from reference (5)). Finally, table 10 records the calculated heat of combustion of 1 gram of the products volatilized from cellulose.

Broido and Martin found that treatment of cellulose with potassium bicarbonate, which imparts marked resistance to flaming, very greatly increases the relative proportions of the highly flammable gases, hydrogen and the hydrocarbons. This anomalous finding might be resolved by the fact that they probably did include the tar products which many workers consider the most important source of flammability (2). Table 10 indicates that the tar provided three-fourths of the weight loss and more than 95 percent of the total heat of combustion for untreated cellulose; for cellulose treated with potassium bicarbonate the yield of tar dropped to half the weight loss but still accounted for more than three-fourths of the total heat of combustion.

The significant decrease in heat of combustion

of the volatile products brought about by the treatment bears a close relation to the improvement in resistance to flaming. The increase in production of flammable fixed gases such as hydrogen and hydrocarbons is probably not important, because they are still present in too small an amount to contribute greatly to the heat needed to support flaming.

Comparison of the pyrolysis of untreated cellulose by strong irradiation of thin sheets (table 10) with that by destructive distillation in bulk (table 8) shows that, at nearly the same level of volatilization, strong irradiation produces less water, carbon dioxide, and flammable fixed gases but more tar and vapors other than tar (oxygenated organic liquids) than does destructive distillation. In both cases, however, the contributions to both weight loss and heat of combustion made by the flammable gases and by the vapors other than tar are very much less than the contributions made by the tar.

The heat of combustion of the material volatilized by strong irradiation of untreated cellulose (table 10) is even greater than that observed for a comparable degree of volatilization by heating

small samples in a furnace (table 7). The extent to which the heat of combustion for 15.4 calories per square centimeter irradiation (-5,500 calories per gram) exceeds the value for 10.5 calories per square centimeter irradiation (-5,130 calories per gram) is no greater than would be expected from the more advanced degree of volatilization (68.0 rather than 22.7 percent), judging from the findings reported in table 9.

Although the evidence suggests that pyrolysis by irradiation may be more complicated, producing more fragments of low molecular weight than slower pyrolysis in a furnace, both fast and slow pyrolysis may be subject to the same rule that the heat of combustion of the volatile products varies with the extent of volatilization but is relatively independent of the temperature at which the pyrolysis takes place.

The calculations of tables 9 and 10, however, present a serious anomaly. If the heat of combustion of the volatile products is as great as the calculations indicate, the pyrolysis of the cellulose must be strongly endothermic, of the order of 1,000 to 2,000 calories per gram. The data in table 8, on the other hand, indicate a moderately exothermic condition, of the order of -150 to -160 calories per gram. There must be

a systematic discrepancy in the analytical data of Madorsky, Hart, and Straus and of Broido and Martin, or in the present interpretation of them, or else some important thermal factor is still escaping consideration,

In tables 9 and 10 the yields of water from untreated cellulose appear surprisingly low and those of tar correspondingly high. Despite such uncertainty, however, certain conclusions find striking confirmation from several groups of workers following very different methods of experimenting. It seems clear that the heat of combustion of the volatilized material from wood or cellulose depends little if any on the temperature at which pyrolysis takes place, that it increases as the degree of volatilization increases (with cellulose perhaps a maximum is passed through), and that it may be reduced markedly by treatment of wood or cellulose with inorganic additives.

The relative independence of temperature suggests that the initial step in pyrolysis of wood or cellulose may be a simple one (in the case of cellulose the formation of levoglucosan), and that the conditions become complicated when secondary pyrolyses set in.



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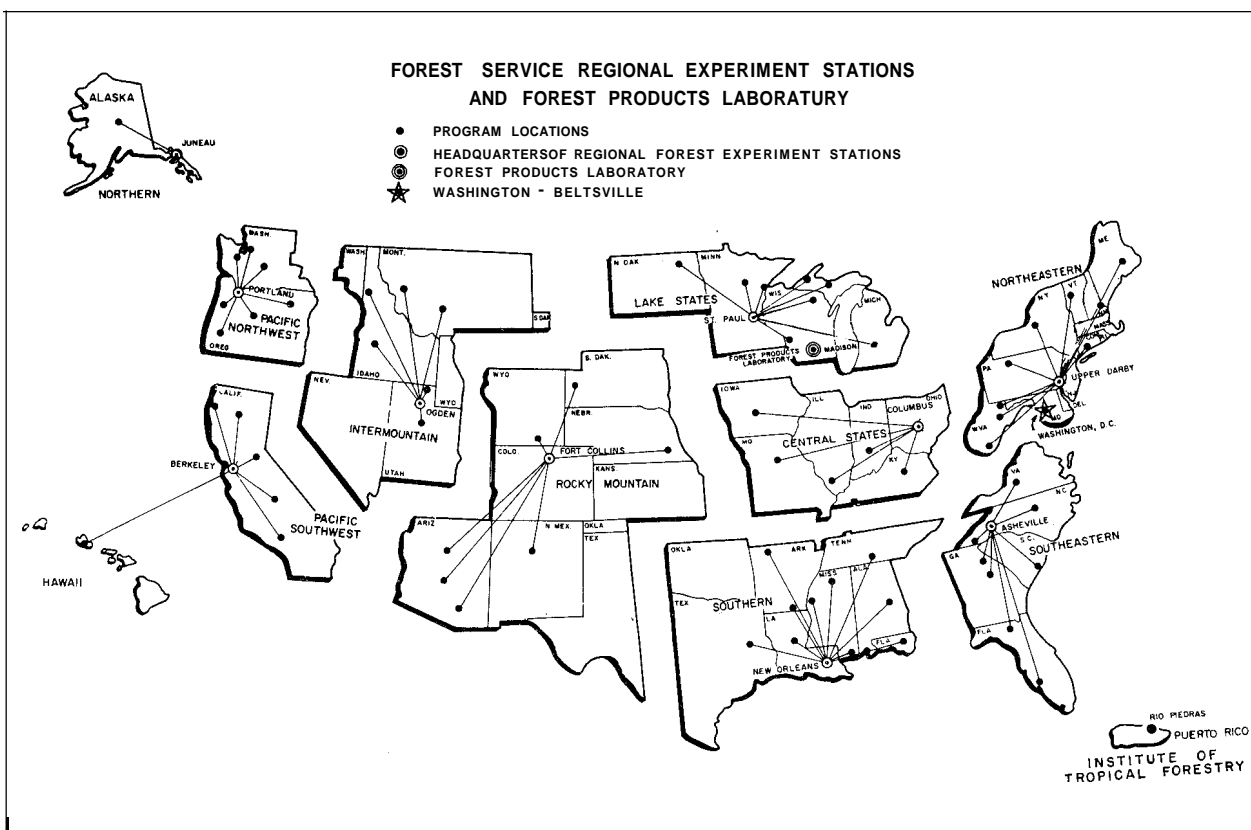
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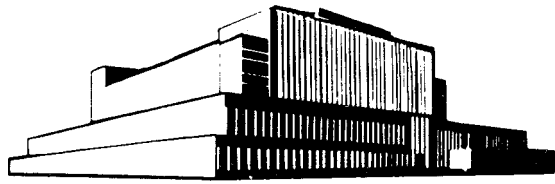
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