

PARTIAL PYROLYSIS of WOOD

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► ► ► When oak wood is heated in an atmosphere of steam at atmospheric pressure, partial pyrolysis commences below 180° C. At 240° C. the modified wood retains its crushing strength and shows smaller volume changes than the original wood when its moisture content is varied. At that temperature the pentosans have been almost completely decomposed, but two thirds of the cellulose remains and the lignin shows an apparent increase. Three quarters of the total acid and half of the furfural, but no methanol, appear in the condensate. The temperature range of 240–260° C.

is critical in spite of control of exothermic reactions. At 260° C. the pyrolyzed wood has a decidedly lower crushing strength and commences to show charring. The cellulose has been almost completely destroyed and the lignin cannot be determined because of the presence of charcoal. Only one third of the methanol has been evolved at 260° C. Most of it is evolved above 280° C. The products at 400° C. show substantially the same methanol as in commercial practice and 25 per cent more acids, the main increase being in formic and propionic acids.

NO ACCURATE studies have been made of the pyrolysis of wood at temperatures below those necessary for the formation of charcoal. This paper presents the results of small-scale experiments in this field. In 1850 Violette (4) heated small pieces of alder wood in an atmosphere of steam to various temperatures and found that 280° C. was necessary to obtain a residue which resembled charcoal. This temperature was confirmed by Chorley and Ramsey (2) and Klason (3), who also showed that a pronounced exothermic reaction took place when wood was heated in absence of air to about 280° C. Klason's results indicated that there was little decomposition of wood by heat at temperatures below 250° C., but in his experiments the temperature was raised rather rapidly. Experiments have also been made on the effect of temperature up to 150° C. in connection with the kiln drying of wood. The wood becomes stiffer and more brittle, but there is no evidence of destructive distillation. There is lack of information on the behavior of wood when heated in the absence of air at temperatures between 200° and 275° C.

Pyrolysis of Oak

The exothermal reaction was recognized to be so great that special precautions would be required to dissipate the heat and keep the temperature uniform. Therefore, heating should be slow, and heat should be applied mainly through a vapor; steam was chosen. It acts partly as an inert gas but also as a reactive agent. The wood was heated in a steel retort set in an electrically heated jacket. Steam at atmospheric pressure was passed through a pipe in the jacket space and so was superheated when it entered the retort. All runs were made at atmospheric pressure. Two thermocouples were used within the retort; one was placed in the vapor space surrounding the blocks and one was inserted in a 1/16-inch hole bored in the top of one of the blocks. The temperature of the two thermocouples did not vary over 5° C. from each other except in one test when the temperature difference amounted to 10°. The temperature of the thermocouple within the wood is reported as the temperature of the run in these tests. After the desired temperature was reached, it was not allowed to vary over 5° during the run. The one exception is run 14 when the temperature was purposely raised to 400° C. as the run progressed.

Kiln-dried red oak was the wood tested. In order to measure volume changes during heating, blocks approximately 1 × 1 × 4 inches in size were used. The nine blocks comprising the change were dried at 105° C., cooled, weighed and measured, and placed

in the cold retort. The retort was heated by the external heat from the jacket until the temperature had risen to 150° C. Superheated steam at atmospheric pressure was then passed in and the temperature raised in 2 hours to that at which the pyrolysis was to be conducted. This fixed temperature was maintained for 10 hours, superheated steam at atmospheric pressure being introduced throughout the run. The steam and volatile products passed through a condenser and into a receiver where the watery distillate was collected. At the end of the period the retort was allowed to cool to 200° C. before it was opened. The only exception to this method of procedure was run 14 in which the temperature was raised from 270° to 400° C. so as to determine the yields of products when charcoal was formed. Since steam was being employed as a heating agent, the quantity used was large. Its weight was always greater than that of the wood. The duration of the heating period was determined somewhat arbitrarily. Pyrolysis is an irreversible reaction, and therefore it was not feasible to run to equilibrium. The most rapid pyrolysis always occurred at the beginning of a run and was still progressing at a diminished rate at the close of the 10-hour period at the temperature of the test.

Changes in Properties of Oak

The shrinkage of bars sawed tangentially is shown in Figure 1. There is little shrinkage parallel to the grain of the wood, and at the lower temperatures there may be even slight expansion. Figure 2 indicates that the weight and volume decrease rather regularly between 205° and 240° C., quite sharply between 240° and 260°, with a slower decrement to 280° and small decreases from 280° to 400° C.

The compressive strength of the wood was measured on pieces sawed from the test blocks to be approximate cubes which were placed in the testing machine so that the stress was applied parallel to the grain. The effect of partial pyrolysis up to 240° C. was to increase the crushing strength (Figure 2). The strength dropped rapidly after heating only 20° more to 260°. The color of the wood became progressively darker with each increase in temperature, and at 280° it commenced to show a charred appearance.



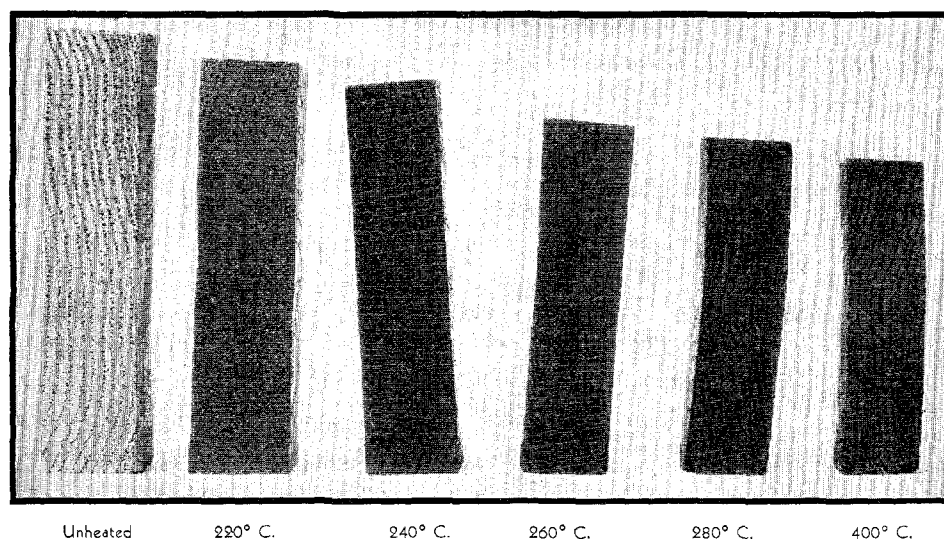


Figure 1. Changes in Size and Appearance of Blocks of Oak Wood Due to Partial Hydrolysis

The volume changes of the partially pyrolyzed wood on exposure to a damp atmosphere are shown in Figure 3. The sample which had been heated to 210° C. gained only half as much weight and expanded only half as much as the sample which had been dried at 105°. The graphs for the samples heated to 240° and 260° parallel that for 210° so closely that the curves for change in length could scarcely be separated.

Volatile Products

The initial temperature of partial pyrolysis cannot be determined readily. A preliminary run at 180° C. showed that about one quarter as much acid was evolved in 10 hours as would be obtained at 400° in the same time. The data for six runs at temperatures varying from 205° to 400° C. are reported in Table I, as well as the analysis of a liquor from a commercial wood distillation plant for comparison. The changes in the more important products are shown in Figure 4. At 205° C. about two thirds of the maximum amount of acetic acid and 40 per cent of the furfural had been evolved. At 240° C. the liquid products contained 80 per cent of the maximum yield of acetic acid with considerable additional amounts of formic and propionic acids, but no methanol. In the interval 240–260° C. the exothermic reaction is reported to begin. The damping influence of the steam prevented any uncontrolled rise in temperature in these tests, but the run at 260° C. marked the first appearance of methanol in the condensate. The amount of furfural also increased sharply and showed a maximum at this temperature. The run at 280° showed rather small increases in all of the products but furfural. In run 14 the temperature was allowed to rise slowly to 400° C. The acids increased to a small extent, and furfural decreased slightly. Two thirds of the methanol was evolved above 280° C. The commercial plant (run C, Table I) apparently obtained only 80 per cent as much acetic acid and only a small fraction as much formic and propionic acids as our partial pyrolysis with steam yielded. The quantity of methanol was about the same in the two methods of treatment. The analysis of the fixed gases showed about three times as much

carbon dioxide as monoxide. Hydrogen and hydrocarbons could not be detected in any of the gases analyzed. This would be expected from the large amount of oxygen in the raw material and the low temperature of the operations.

Chemical Changes

Chemical analyses were made on sawdust obtained from blocks during some of the runs (Table II). The methods were those developed by Schorger and his successors at the Forest Products Laboratory as compiled by Bray (1). The material

soluble in cold water and that soluble in hot water were both decreased to about 40 per cent of the original value at 210° and to about 20 per cent at 240° C. The material soluble in one per cent sodium hydroxide, after deduction of the amount soluble in hot water alone, behaved in the reverse way. The quantity of material soluble in one per cent caustic was one third greater after treatment at 210° than it was in the untreated wood; although it became somewhat less at the higher temperatures, it was still greater after treatment at 240° C. than in the original wood.

The pentosans yielded most readily to heat; over 75 per cent was eliminated by heating to 210° C., and the remainder disappeared at a slower rate in the runs made at successively higher temperatures until at 260° C. the pentosan content was very small. The acetic acid formed by hydrolysis of the treated wood followed much the same course as the pentosans. Only 25 per cent had disappeared in the product obtained at 210° C. and 35 per cent from the product at 240° C. However, when heated only 20° hotter to 260°, almost all of the cellulose was broken down. A further analysis of the cellulose was made on a single sample heated to 210° C. It showed that the pentosans in the cellulose had dropped to about one sixth of the initial figure (12.4 to 2.0) and that the alpha-cellulose had dropped to one third (32.1 to 10.5) while the total cellulose had decreased only from 55.4 to 43.0.

The lignin showed an apparent increase of 20 per cent in the product that had been heated to 210° and stayed about

Table I. Volatile Products of Partial Pyrolysis

Yield, as % by Wt. of Unpyrolyzed Wood Dried at 105° C.

Run No.	Temp., ° C.	Total acids	Formic acid	Acetic acid	Propionic acid	Methanol	Furfural	CO	CO ₂
8	205	3.82	0.34	3.48	0.00	None	1.54	^a	^a
11	220	4.25	0.43	3.89	0.43	None	2.08	0.64	2.25
10	240	5.30	0.55	4.15	0.60	None	2.45	^a	^a
13	260	5.88	0.70	4.46	0.70	0.68	4.44	2.4	5.2
12	280	6.32	0.62	4.76	0.94	0.93	4.12	2.4	8.1
14	270–400	6.82	0.73	5.37	0.71	2.25	3.95	^a	^a
C ^b	400–450	4.70	0.10	4.36	0.24	2.2	^a	^a	^a

^a Quantity not measured.

^b The data in run C are computed from the analysis of the liquor from a commercial wood distillation plant operating on oak. The liquor was analyzed in the same way as the distillates from the experimental work, and the yield was calculated on the assumption that one cord of wood weighed 3200 pounds.

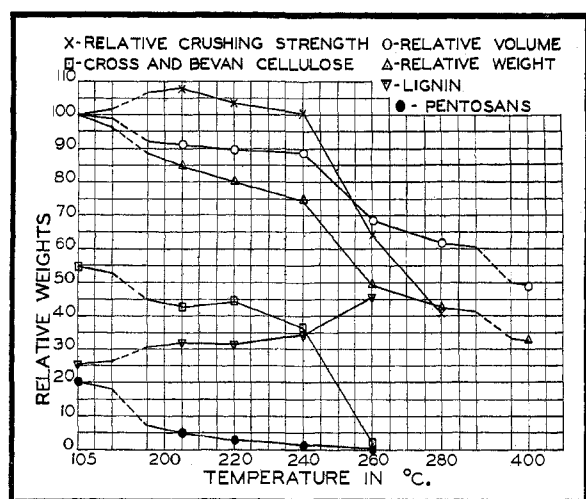


Figure 2. Changes in Oak Wood during Partial Pyrolysis (on Basis of Wood Dried at 105° C.)

at that level in the products heated to 220° and 240° C. Contrary to analyses on the other substances, the lignin apparently increased at the higher temperature of 260°. However, the method for lignin determination consists in treatment with 72 per cent sulfuric acid at room temperature for 16 hours followed by dilution to 3 per cent acid and boiling for 2 hours. The material remaining undissolved is called "lignin". It is probable that some material was becoming insoluble in the acid treatment and so was reported as lignin. This becomes more evident in the product of the 260° run; it obviously contains some charcoal which, being insoluble in acid, is reported as lignin. The decomposition of the wood was so evident in the product heated to 260° C. that no attempt was made to analyze the somewhat charred residue of the 280° run.

An independent check of lignin decomposition is given by the change in percentage of methoxyl groups in the wood after treatment to the several temperatures, together with the amount of methanol found in the distillate. It is usually held that the methanol resulting from pyrolysis of wood comes from the methoxyl groups in the lignin. The data for this discussion are found in Table III. There was a disappear-

ance of 20 per cent of the methoxyl groups of the wood at 220° C., and one third disappeared after heating to 240° C. without the appearance of any methanol in the distillate in either case. Another third of the methoxyl groups disappeared from the sample heated to 260° C., and methanol corresponding to only 10 per cent of the methoxyl groups appeared in the distillate. A further small increase in methanol in the distillate and decrease in methoxyl occurred at 280°, but it is only at temperatures above 280° and below 400° C. that the main portion of the methanol is formed.

Table III. Change in Methoxyl Groups Compared with Yield of Methanol from Oak Wood

Run No.	Temp., °C.	Methoxyl Content, % ^a	Methanol Yield, % ^a
Not heated	105	5.87	None
11	220	4.72	None
10	240	4.19	None
13	260	2.33	0.68
12	280	1.94	0.93
14	270-400	...	2.25

^a Based on unpyrolyzed wood dried at 105° C.

Table IV. Ultimate Analyses of Oak and Its Products

Run No.	Temp., °C.	Composition		O (by difference)
		C	H	
Wood and Products of Partial Pyrolysis				
a	Not heated	50	6	44
10	240	56.2	5.4	38.4
13	260	69.5	5.1	25.4
12	280	73.6	4.0	22.4
Charcoal (Crossett Chem. Co.)		86.6	3.2	10.2
Lignin Isolated with 72% H ₂ SO ₄				
	Not heated	65.8	5.0	29.2
10	240	68.2	5.2	26.6

^a An average composition of hardwood from the literature.

Ultimate Analysis

Ultimate analyses (Table IV) were made of the wood as modified by heating to 240°, 260°, and 280° C. An analysis was also made of a modern commercial charcoal for comparison. The carbon increased and the oxygen decreased progressively as the temperature of pyrolysis rose; the largest change occurred between 240° and 260° C. The greatest change in the hydrogen came, however, between 260° and 280° C.

The lignin (Table IV) from the wood dried at 105° C. contained considerably more carbon and less oxygen than the wood from which it was derived. The lignin from the wood modified by treatment at 240° C. contained still more carbon and less oxygen, but the hydrogen was almost unchanged.

Products of Partial Pyrolysis and of Commercial Carbonization

In commercial carbonization the wood is heated to a final temperature of 400-450° C. and steam is not intentionally introduced into the retorts. It is present in large amounts during the early stages of the run while the wood is being dried but becomes much less during the later stages when pyrolysis is taking place. When the exothermic reaction starts, the temperature rises rapidly to temperatures approaching 400° C. Commercial carbonization differs from



Table II. Chemical Analysis of Partially Pyrolyzed Wood

	Yield, % of Unpyrolyzed Wood Dried at 105° C.				
	Dried 105° C.	Run 8, 210° C.	Run 11, 220° C.	Run 10, 240° C.	Run 13, 260° C.
Loss in wt. due to pyrolysis	...	18.6	19.3	25.6	50.7
Solubility in					
Cold water	5.0	1.8	1.4	1.0	a
Hot water	8.1	3.2	3.0	1.6	a
1% NaOH	24.8	25.5	22.5	19.6	10.3
1% NaOH, cor. ^b	16.7	22.3	19.5	18.0	a
Ether	0.5	0.4	0.3	0.2	Trace
Alcohol-benzene	6.3	6.2	5.8	4.0	1.6
Total pentosans	20.0	4.5	2.9	1.1	0.2
Acetic acid by hydrolysis	4.0	0.7	0.6	0.2	a
Cross & Bevan cellulose	55.4	42.4	44.5	36.4	1.2
Lignin	25.7	32.4	31.1	34.7	45.3 ^c

^a Quantity not measured.

^b Corrected for hot water solubility; value obtained by subtracting % hot-water-soluble material from that soluble in 1% alkali.

^c Includes both lignin and charcoal.

the experimental method reported here in at least three evident ways—the final temperature, the rapid rise in temperature due to the exothermic reaction, and the amount of steam present throughout the run.

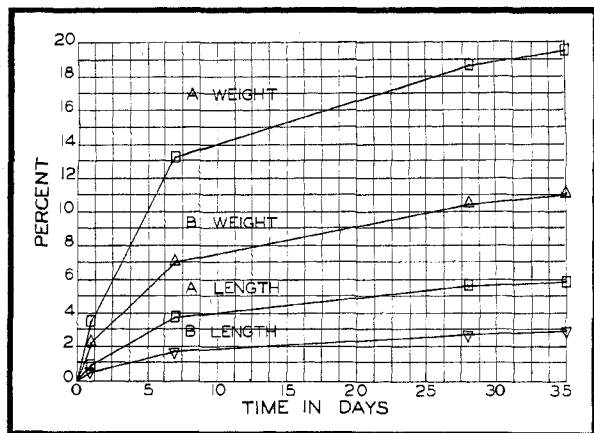


Figure 3. Changes in Length and Weight in Damp Atmosphere

Blocks of wood, $1 \times 1 \times 4$, sawed tangentially and placed in air of 95–100 per cent humidity at $24\text{--}26^\circ\text{C}$. A = average of 3 samples dried at 105°C ; B = average of 3 samples after partial pyrolysis at 210°C .

The effect of increasing the final temperature was tested in run 14 where the temperature was brought to 270°C in 2 hours in the usual way. Instead of holding the wood at that temperature, it was raised at a uniform rate in 6 hours to 380° and then to 400°C in 4 hours more. Data of this run are given in Table I and Figure 2. The solid product was charcoal. The yield of total acid was not much greater, and the furfural was slightly less than at 280°C . The methanol was more than twice as great at 400° as at 280°C .

The results from a commercial carbonization plant operating on oak wood (Table I, run C) indicate that the commercial retort gave substantially the same amount of methanol as our small unit when the temperature in the experimental unit was raised gradually to 400°C . However the experimental unit gave nearly 50 per cent more total acids. The analysis of these acids shows that a considerable part of the increase was in formic and propionic acids. The actual acetic acid was only 20 per cent greater than was found in commercial operation; the amount of propionic acid was three times as great and that of formic acid was seven times as great as in commercial operation. A more detailed analysis of this product at 210° (not given in the table) showed that the pentosans in the Cross and Bevan cellulose decreased from 12.4 in the dried wood to 2.4 in the 210°C product; the alpha-cellulose decreased from 32.1 to 10.5 per cent. A larger proportion of formic and propionic acid was found in the results with the experimental unit at each temperature. They may be due to the controlled rate of temperature rise or, as seems more probable, to the hydrolytic action of the steam on aldehydes. The larger yield of acetic acid may be explained in the same way.

Progressive Reactions during Partial Pyrolysis

The experimental data reported give a picture of the products formed and the changes in oak wood in the tempera-

ture range $180\text{--}280^\circ\text{C}$. In these tests the wood was held for 10 hours at the temperature indicated, in an atmosphere of steam. The reactions were still continuing at a reduced rate after 10 hours, as was to have been expected from an irreversible reaction.

The chemical changes in the wood may be followed in Figure 1 and Table II. The constituents soluble in cold and in hot water dropped to 40 per cent of their initial value when heated to 210°C . The amount of material soluble in one per cent sodium hydroxide increased over 40 per cent, after deduction was made for the amount soluble in hot water. The constituents soluble in ether and in the alcohol-benzene mixture were stable up to 140°C . The most noticeable change at 210°C was in the pentosans, which had decreased to 4.5 per cent from the 20.0 per cent in the dried wood. The quantity of acetic acid yielded by hydrolysis of the wood decreased in almost the same proportion as the pentosans. The cellulose showed greater stability than the pentosans. The Cross and Bevan cellulose decreased about 20 per cent on heating to 210°C . These experiments confirm the conclusions of previous investigators that the pentosans, both free and associated with the cellulose, are the first of the important wood constituents to break down on pyrolysis.

The lignin was one third greater at 210° than in the unheated wood. This also corresponds to the results of other investigators. We made no studies to determine the chemical nature of this material which is isolated as lignin by the usual method of analysis, except as indicated by the ultimate analysis in Table IV.

There is somewhat more pyrolysis at 220°C but the trends noted at 210° continue. The modified wood shows little change in lignin content and in Cross and Bevan cellulose in the modified wood. The pentosans in the wood decrease further and the total acid in the distillate increase moderately.

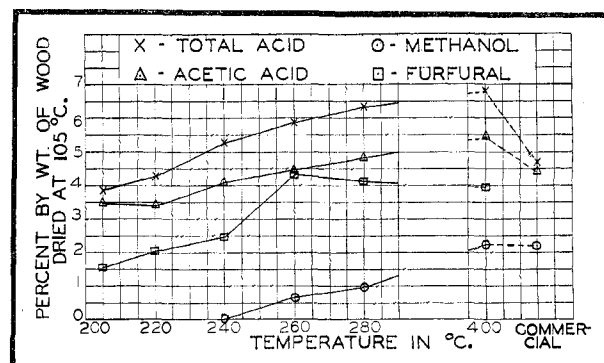


Figure 4. Volatile Products of Partial Pyrolysis of Oak Wood Compared with Results from Commercial Practice

The results at 240°C show further pyrolysis without any marked change in the character of the products. The quantities of acids and of furfural increase and so does the reducing power of the distillate, as evidenced by its reaction with Fehling solution. No measurable amount of methanol appears in the condensate. One hundred pounds of the original wood contained 8.1 pounds of material soluble in hot water. Only 1.6 pounds survived in the modified wood at 240°C . Similarly, only 36.4 pounds of the 55.4 pounds of Cross and Bevan cellulose survived. The 25.7 pounds of lignin have, however, apparently increased to 34.7 pounds. Thirty per cent of the methoxyl groups of the original wood have disap-



U. S. Dept. Agr. Photograph by Forsythe

An Alabama Sawmill in Full Swing

peared, apparently to form complex groups in the distillate since no measurable amount of methanol was found. The change in the composition of the lignin is shown by the ultimate analysis of Table IV. The apparent lignin at 240° has 2.8 per cent more carbon, 0.2 per cent more hydrogen, and 2.6 per cent less oxygen than the dry lignin isolated from the unheated wood. Calculation indicates that a modified product has been formed whose composition is 75.4 per cent carbon, 5.7 hydrogen, and 19.2 oxygen. There are no indications as to the structure of this compound or complex, but since it is insoluble in 72 per cent sulfuric acid, it is reported as lignin.

The temperature range of 240–260° C. is critical in that the exothermic reaction is supposed to start here. The heating in our work was controlled carefully and the volume of steam was large enough so that no rise in temperature was shown by the thermocouple embedded in the wood. The run at 260° C. showed somewhat more acid in the condensate, but the noteworthy feature was the appearance of methanol to the amount of one third of the maximum yield obtained by carbonization to 400° C. The methoxyl groups in the modified wood from the 260° run were little more than half as great as they were in the residue from the 240° run. The Cross and Bevan cellulose dropped from 36.4 per cent in the 240° product to 1.2 in that from the run at 260° C. The physical properties of the wood modified by heating to 260° C. showed great change. The wood residue at 240° had a somewhat higher compressive strength than the original wood, but the residue at 260° was only 70 per cent as strong. A visual examination of the 260° solid residue showed it to be almost black. An analysis for lignin showed an apparent increase of that constituent from 34.7 to 45.3 based on the weight of the undried wood. However, charcoal, like lignin, is insoluble in 72 per cent sulfuric acid, and it is not easy to separate them. Therefore it is impossible to say how much lignin and how much charcoal were present in the product. The run at 280° C. showed somewhat more acid and methanol. The compressive strength of the wood residue dropped to 41 per cent of that of the original wood.

The only run at a higher temperature was 14, whose temperature was raised slowly from 270° to 400° C. When compared to the 280° run, there was a minor increase in the acid

and a slight decrease in the furfural in the condensate. The methanol, however, rose from 0.93 to 2.25 per cent of the weight of the original dry wood.

Commercial Possibilities

The wood distillation industry has traditionally had three major products—charcoal, methanol, and acetic acid. The work reported here indicates the possibilities of an industry with two major products—acids and modified wood residue—obtainable by partial pyrolysis of wood in an atmosphere of

superheated steam at temperatures below 260° C. This paper has presented data only on oak wood, but other tests on maple, birch, spruce, and Georgia pine indicate that the same general type of products may be obtained. The yield of acetic acid may be somewhat larger and the amounts of formic and propionic acid several times as large as those now obtained in commercial charcoal plants. Direct condensation of the vapors would give a dilute liquor, but circulation of the vapors through a hot tar oil scrubber, as in the Suida process, would permit the removal of the acids without condensing the steam and allow the steam to be recirculated after being superheated. The time reported here—10 hours at the temperature of the test—was made long in order to carry the reactions reasonably near to completion. Other experiments have shown that with smaller pieces comparable results may be obtained in 1 hour.

A piece of dried wood cut with its long dimension parallel to the grain of the wood will not change in length materially, but it will shrink quite uniformly in cross section. The modified wood from the treatment at 220–240° C. will be stronger and have a higher apparent elastic limit but will be somewhat more brittle than the original wood. It will have smaller volume changes with changes in humidity. The modified wood is brittle enough to be crushed rather readily to yield a wood flour stable at 240° C., which may be incorporated into molding compounds.

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