

ACID HYDROLYSIS OF WASTE WOOD FOR USE IN PLASTICS

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ACID HYDROLYSIS OF WASTE WOOD FOR USE IN PLASTICS^{1/}

By CYRUS O. GUSS, Chemist

Summary

The manufacture of molding powders and board materials from acid-hydrolyzed sawdust or chips has been studied with the purpose of furthering the utilization of waste wood. The product, known as hydrolyzed wood, or hydrolyzed lignocellulose, is a material whose lignin content is increased by removal of some of the carbohydrates present in wood. In addition, the lignin is partially converted into a form in which it functions as a plastic. When hydrolyzed sawdust is reduced to a powder, it can serve as a semiplastic filler for phenolic molding compounds similar to the wood-flour filled phenolics. One special property of this material is its acid resistance. The hydrolysis of chips provides a stock containing fibers from which a sheet or a board can be made. The sheet can be laminated, with or without the addition of auxiliary resin, but its low wet strength and tear resistance make it troublesome to handle. The board made from the hydrolyzed wood is similar in properties and appearance to some commercial hardboards.

Although none of these products is produced commercially by this process, products of the same type made by somewhat different processes are available from commercial sources. Products made by the acid-hydrolysis process have shown few advantages over the commercial materials.

Introduction

Two-thirds to three-fourths of the volume of a tree is lost as waste in the normal logging and lumbering conversion process. A large part of this waste is left in the forest and is definitely a liability there. While some use can be made of the waste from sawmills and wood-fabrication plants (10) the enormous quantities available far surpass the market demands. It is apparent, therefore, that the problem of profitable utilization or disposal exists. The research reported here represents an effort to develop one form of waste wood utilization.

^{1/}This report is intended to replace the information and recommendations given in a previous report (7) on acid hydrolyzed wood, to present new and more complete data on hydrolyzed-wood molding powders, and to describe procedures for making laminating sheets and boards from hydrolyzed wood.

Wood as a Material for a Derived Plastic

Wood is made up of carbohydrate material (cellulose plus hemicelluloses), often referred to as holocellulose, and lignin, together with various extraneous materials or extractives. Extractive-free wood contains approximately 25 percent lignin and 75 percent holocellulose. Maple, for example, which has been extensively used in this research, is made up of 60 percent cellulose, 18 percent hemicelluloses, and 22 percent lignin.

Cellulose is the fibrous constituent of wood. It is not only fibrous in a macro sense but also in a molecular sense, since it is made up of long threadlike molecules with a high molecular weight, which accounts for its desirable sheet-forming and strength properties.

Cellulose itself cannot be formed into useful shapes under heat and pressure. When heat is applied to it, the cellulose decomposes at a temperature below its softening point. The forces holding the cellulose molecules together are so strong that the material cannot soften below the temperature that produces decomposition by cleavage of primary chemical bonds. After replacing a large part or all of the hydroxyl groups of cellulose with acid groups (esterification), or with ether groups (etherification), however, the forces of attraction between the resulting molecules are considerably reduced, and the softening points of these derivatives lie below their decomposition points. This has enabled cellulose esters, such as cellulose acetate, and cellulose ethers, such as ethyl cellulose, to become useful commercial plastics.

Lignin is a colloidal material of relatively high molecular weight. It is intimately associated with the carbohydrates in wood -- probably involving a chemical bond -- and in this state does not exhibit any well-defined plastic properties. Dry sawdust, for example, when pressed alone at high pressures and at temperatures below incipient decomposition, does not show any of the properties common to plastic materials. Only a small portion of the lignin can be extracted from wood with polar organic solvents unless some acid or base is present. The lignin isolated from wood by various methods, including the pulping processes, however, shows from small to complete solubility in polar organic solvents and aqueous alkali. Although several of these isolated lignins can be molded under heat and pressure, the products so obtained are relatively low in strength. Such material does not appear to have any utility as a plastic unless it can be used together with some other material that will contribute strength, or unless it can be modified in some manner to develop increased strength properties.

It is apparent, therefore, that the cellulose in wood must be modified if it is to function as a plastic; and if the lignin is to function as a plastic, it probably must first be freed from its bond with the carbohydrates in wood. This liberated lignin need not necessarily be separated from the cellulose. Preferably, in its new form, the lignin should serve as a bonding agent to reunite the particles of wood or cellulose fiber. Finally, the possibility exists that the cellulose may be converted into a derivative, or the lignin may be freed, and perhaps, altered chemically, or both. These changes may be accomplished in one or more steps either successively or simultaneously.

Acid Hydrolysis of Wood

Theoretical Aspects

When wood is heated in the presence of a dilute mineral acid, an attack on the carbohydrates occurs. It is well known that cellulose is degraded by such a treatment, a sugar, glucose, being the ultimate end product (11, Chapter 6). The hemicellulose in wood is even more susceptible to hydrolytic degradation. On the other hand, the lignin is resistant to the solubilizing action of the aqueous mineral acid.

The purpose of the dilute-acid treatment in the process to be described (3) is to convert the lignin into a form in which its plastic properties can be utilized. A concomitant reaction, which presumably includes breaking of the cellulose-lignin bond, is the hydrolysis of the carbohydrates. A gradual solubilization of the carbohydrates accompanied by a modification of the lignin occurs. The reaction is allowed to continue until the lignin has developed plastic properties commensurate with the application in mind. The lignin content in the product is increased, not because lignin is added, but because the carbohydrates are removed as water solubles.

Figure 1 illustrates the action of the dilute acid hydrolysis on maple wood when the end product is intended for use in a molding powder, as a sheet for laminating, or as a board.

Hydrolysis Process

The basic piece of equipment used in this work was a 17-gallon, bronze, cylindrical, rotary digester pictured in figure 2. In operation, this digester rotated six times per minute. Steam was admitted into the interior of the digester through a trunnion as shown in the figure.

In making the first of a series of runs, or a solitary run, the digester was first closed and preheated with steam. The purpose of this preheating was to reduce the amount of steam condensate in the run that followed. After preheating, the digester was vented, the condensate emptied out, and the charge introduced immediately.

The wood, as sawdust or chips, was introduced into the hot digester, and then the dilute acid solution, at room temperature or below, was poured over the wood. The cover was put in place at once and securely bolted down.

After the digester was started rotating, the steam was turned on full until the desired temperature, as indicated by the gage pressure, was reached. A period of from 1 to 3 minutes was required to bring the charge to operating temperature. The timing of the cook commenced when the pressure indicated on the gage had reached the desired value. The cooking process was terminated by stopping the rotation of the digester in an upright position and venting at once through the lid into a duct. The pressure drop to nearly zero could be attained in 1 minute + 30 seconds. The end of the cooking period was marked at the moment the venting valve was opened.

The condensation of steam during the run diluted the acid and accounted for, roughly, a 60 percent increase in the weight of the final liquor over that originally present. Acid concentrations mentioned in this report refer to original concentrations.

The cooked wood was dumped into a screen box and washed with warm water until free from acid. The filtrate, which contains sugars, organic acids, and furfural, and which undoubtedly has some commercial value, was not studied in this investigation. When chips were used, it was found difficult, if not impossible, to wash them free from acid. This difficulty could be circumvented by grinding the cooked chips and rewashing. Hydrolyzed sawdust was washed easily. The drip-free hydrolyzed sawdust contained about 75 percent water by weight.

The hydrolyzed wood was dried, when it was to be used for molding powder, by spreading it on trays and placing them in a kiln or a circulating-air oven at about 70° C. (158° F.). In general, a period of about 24 hours was required to dry the material at this temperature.

A Wiley mill was used for grinding the dry hydrolyzed wood to a powder. About 85 percent of the ground material was between 20 and 80 mesh in most of the experiments for which the hydrolyzed wood served as a semiplastic filler in phenolic molding powders.

Analytical Procedures

In this work, it was customary to analyze the washed, dried, and ground hydrolyzed wood for lignin content, pH, and methanol solubility.

Lignin.--The lignin content was determined by a modification of the 72 percent sulfuric acid method (1). A 0.5-gram sample of known moisture content (about 5 percent or less) was weighed exactly and transferred to a 50-milliliter Erlenmeyer flask. To this was added 7 milliliters of cold, 72-percent sulfuric acid. The flask was immediately stoppered, shaken vigorously, and placed in a water bath at 35° C. (95° F.) for 30 minutes. The flask was removed from the bath and shaken at intervals of about 10 minutes. The contents of the flask were then completely washed into a 250-milliliter Erlenmeyer flask, diluted to 125 milliliters, and boiled gently for 30 minutes on an electric hot plate. The lignin was then transferred to a tared, fritted-glass-bottom crucible by suction filtration, washed until free from acid, dried at 105° C., for 2 hours, and weighed after cooling in a desiccator. A precision of ± 0.5 percent was easily obtained.

pH.--The pH of hydrolyzed wood was determined by heating a 2-gram sample in 50 milliliters of distilled water to boiling in a 125-milliliter Erlenmeyer flask. The cooled water was decanted off, and its pH was determined with a glass electrode. When the pH was below 5, as measured by this method, the material was considered to be too acid for use. The result was qualitative and served only to eliminate an inadequately-washed hydrolyzed wood.

Methanol solubility.--The methanol solubility of the hydrolyzed wood was determined by extracting it in a conventional Soxhlet-type apparatus. About

3 to 5 grams of the hydrolyzed wood of known moisture content were weighed into a tared, alundum crucible. The crucible and contents were then placed in the extractor and extracted with 99 percent methanol for 6 to 8 hours. The crucible was then removed and dried at 105° C. (221° F.), until it attained a constant weight. The decrease in weight represented extracted material and moisture loss. These data permitted the calculation of the percentage of methanol solubles based on the weight of the original hydrolyzed wood when dry. Check runs of this analysis usually agreed within 1 or 2 percent. The soluble lignin ratio (abbreviated SLR (4)) was often used as a guide in following the effect of cooking variables on the plastic properties. The SLR is the quotient of the percent methanol solubility divided by the percent lignin content, multiplied by 100. The SLR expresses the percent of the total lignin that is methanol-soluble lignin.

Properties of Acid-hydrolyzed Wood

The acid-hydrolyzed wood, as usually prepared, was brown in color. It retained practically the same physical form as the original wood. Excessive hydrolysis causedⁱⁿ the color to darken. The lignin content could easily be estimated to within a few percent by the color of the dried material. Hydrolyzed wood with a relatively high lignin content (50 percent lignin for maple) was friable and tended to disintegrate badly in the digester. Acid hydrolysis lowered the strength of the cellulose considerably, so that acid-hydrolyzed maple chips of, for example, 40 percent lignin content could easily be broken cleanly across the fiber direction.

The removal of the hemicellulose during the hydrolysis process eliminated the most hygroscopic portion of the wood. This explains the fact that acid-hydrolyzed wood was relatively less hygroscopic than wood, itself. In a few tests, the acid-hydrolyzed wood gave an equilibrium moisture content of 7.0 percent at 65 percent relative humidity and 80° F. (26.67° C.) in contrast to 12 percent for normal wood.

Acid-hydrolyzed maple was analyzed separately for lignin and cellulose and was found to consist entirely of these two components (3). The major portion of the lignin content of the hydrolyzed wood arose from the lignin in the original wood. It was shown (3), however, that some of the material in the hydrolyzed wood consisted of decomposition products of the sugars formed during the hydrolysis. These decomposition products appear as lignin in the analysis.

The solubility of acid-hydrolyzed maple in various organic liquids is indicated in table 1. The conditions of hydrolysis, that is, temperature, acid concentration, and time of hydrolysis, were found to affect the solubility of the hydrolyzed wood. As shown in the table, the material extracted from the hydrolyzed wood by the solvents was essentially lignin. A small amount of the lignin is soluble in water; thus the washing of the hydrolyzed wood tends to reduce the lignin content.

Previous work demonstrated that acid hydrolysis did not affect the methoxyl content of the lignin (3).

The Effect of Variables in the Process

The variables in the process to be considered are acid concentration, temperature, and time of hydrolysis. An increase in either the acid concentration, the temperature, or both, resulted in an increased rate of hydrolysis.

The fact that the acid solution was diluted by the condensed steam during the run is to be kept in mind in interpreting the data to be presented.

Variation of Acid Concentration

Table 2 shows the data obtained when the acid concentration was changed and the temperature and time of hydrolysis were held constant (3). The increased rate of hydrolysis with increased acid concentration is apparent. Data are also given in this table for the calculated and observed lignin content, which show that the formation of lignin-like material from the cellulose is appreciable only when the hydrolysis of the wood is more drastic than that which is here recommended for use in wood plastics.

Variation of Temperature

In table 3 are recorded the data for a series of runs in which the temperature (steam pressure) was varied with the acid concentration held constant at 1.2 percent of the weight of the water. Rather than use a constant time of hydrolysis, in this series, the hydrolyses were continued sufficiently long to yield products of approximately the same lignin content, that is, 40 percent lignin. The temperature of hydrolysis is clearly a rate-determining factor.

Factors Affecting the Solubility of Acid-hydrolyzed Wood

In a large number of runs, data for which are shown in tables 4, 5, 6, 7, and 8, the effect of acid concentration, temperature, and time of hydrolysis on the solubility of the lignin in the hydrolyzed wood was studied. From these data it was deduced that, (a) the hemicellulose portion of wood is easily solubilized, (b) lignin in wood is converted into a methanol-soluble form during the acid-hydrolysis process, but the hydrolysis environment causes this soluble lignin to be converted into an insoluble form that differs from the original lignin with the observed result that the methanol-soluble lignin fraction of the total lignin rises to a maximum and then decreases during any given hydrolysis, (c) the higher the temperature and the greater the acid concentration, the higher is the SLR maximum but the shorter is the time interval that the SLR is near the maximum. These conclusions are in general agreement with the results of others (4).

Studies with softwoods indicated that appreciably less methanol-soluble lignin was produced during their hydrolysis than during the hydrolysis of hardwoods. Since, as will be indicated later, the methanol-soluble lignin

content of the hydrolyzed wood is important with regard to the use of the material in molding powders, laminating sheets, and boards, the hardwoods are preferred.

The methanol-soluble lignin content of the acid-hydrolyzed wood was materially reduced by heating to temperatures near 150° C. (302° F.) in the dry state.

Miscellaneous Variables

In all of the work reported here, sulfuric acid was the acid used. The kind of acid used did not appear to have any effect on the quality of the hydrolyzed wood. Other acids gave a different rate of hydrolysis per equivalent, but there was not any selective action on the amount of methanol-soluble lignin produced at the same degree of hydrolysis.

The ratio of dilute-acid solution to wood in the digestion was varied over a wide range without affecting the quality of the product appreciably. In most of the work, the water-to-wood ratio was held between 0.5 and 2.5.

Acid-hydrolysis cooks made in the presence of methanol or phenol gave products having a high methanol-soluble lignin content. In some cooks over 90 percent of the lignin in the hydrolyzed wood was methanol soluble. Acid hydrolysis in the presence of formaldehyde or aniline gave considerably less methanol-soluble lignin than identical runs in the absence of these compounds.

Use of Acid-hydrolyzed Wood in Molding Powders

Hydrolysis Conditions

The hydrolysis of hardwoods, such as maple or sweetgum, to a material having about a 40 percent lignin content was preferred when the product was to be used to replace wood flour in phenolic molding powders. Conditions that give a higher lignin content cause increasing cellulose degradation and loss in strength. At a lignin content of 35 percent, for example, the plastic properties of the lignin are not sufficiently developed for this use. The 40 percent choice is a compromise between plastic properties of the lignin and strength properties of the cellulose, sometimes referred to as "resin" and "filler" effects.

Many different conditions of hydrolysis were used to produce materials having a lignin content near 40 percent. Thus, the hydrolyses were carried out at different temperatures and acid concentrations, and for various periods of time. When the methanol solubility of maple and sweetgum hydrolyzed woods, all with 40 percent lignin but prepared under a wide variety of conditions, was compared, it was found that some were nearly 20 percent methanol soluble, and others were less than 10 percent soluble. Furthermore, when an attempt was made to mold these hydrolyzed woods, those with the highest methanol solubility were found to be the most satisfactory with regard to flow under heat and pressure.

The following hydrolysis conditions gave satisfactory lignin solubility and flow:

- 2 parts hardwood sawdust, dry weight
- 1 part water
- 0.012 part concentrated sulfuric acid
- 190 to 200 pounds per square inch steam pressure for 15 minutes

A hydrolyzed wood prepared in this manner had a 38 to 40 percent lignin content and was 18 to 20 percent methanol soluble (SLR = 47.4-52.6). The yield was about 60 percent. Various other combinations of acid concentration, temperature, time, and water-to-wood ratio were also used to produce a material having analytical values within this range.

Hydrolyzed Wood-phenolic Resin Compositions²

The hydrolyzed wood obtained under the conditions described in the preceding paragraph was definitely not a complete molding powder. Experiments indicated that only the soluble lignin contributed to the plastic properties of the material. Thus, only about one-half of the lignin was effectively utilized. Since the material was more moldable than plain wood flour, however, the possibility of substituting hydrolyzed wood for wood flour in phenolic molding powders was investigated.

It was found that compositions containing 70 to 75 parts hydrolyzed wood and 25 to 30 parts phenolic resin gave moldings comparable in appearance and properties to those made from commercial molding powders containing 50 parts wood flour and 50 parts phenolic resin (fig. 3).

With water-soluble phenolic resins, the following formula was satisfactory:

- 350 grams acid-hydrolyzed wood
- 150 grams water-soluble phenolic resin, based on solids content
- 2.5 grams zinc stearate

The resin solution was diluted with water to a volume of 350 milliliters. This solution was added to the hydrolyzed wood-stearate mix in a Werner-Pfleiderer type mixer. The wet mix was then dried at 70° C. (158° F.) to a moisture content of 3 to 4 percent. The dried material was ground and was then ready for molding. Alternatively, the wet mixture was sometimes dried to about a 10 percent moisture content, then put through differential milling rolls at 100° to 110° C. (212-230° F.) for not more than 30 seconds to produce a sheet about 0.040 inch thick. This sheet was then ground and adjusted to a 3 to 4 percent moisture content before molding. When small quantities of carbon black and a blue dye were used in this formula, the moldings had a better appearance.

²-These compositions have been called "Hydroxylin" by the Forest Products Laboratory.

With powdered phenolic resins, the formula used was:

1,400 grams acid-hydrolyzed wood
600 grams powdered phenolic resin
20 grams carbon black
10 grams dye
15 grams zinc stearate

This mixture was rod-milled for 45 minutes. Then 12 grams hexamethylene tetramine in 200 milliliters water were added, and rod-milling was continued for another 10 minutes. The powder was then put through the differential milling rolls and the process completed as described for the previous formula.

For comparative testing purposes, these molding powders were molded at 155° C. (311° F.) and 4,000 pounds per square inch.

Standard tensile, flexural, and impact specimens were molded for 10 minutes and removed from the mold while hot. Water absorption disks, 2 inches in diameter and 1/8 inch thick, were molded for periods from 1 to 10 minutes in order to determine the rate of cure. The test specimens were conditioned and tested according to (tentative) standard methods² for this type of plastic. The values given in table 9 are typical for the properties of the molded material as made in this manner.

These acid-hydrolyzed wood-phenolic resin compositions have no advantages in strength over the wood-flour filled phenolics for general purpose applications, but where acid resistance is a requirement, the hydrolyzed wood compositions are believed to be superior.

Hydrolyzed-wood Sheet for Laminating

Hydrolysis Conditions

The hydrolysis of hardwoods for conversion into a sheet required chips as the starting material because longer fibers were necessary. Extensive experimentation showed that the hydrolysis should be conducted to give about a 32 percent lignin content in the product. This lignin content, which is lower than that used in molding compounds, is permissible because less flow is needed in the press. With lignin contents below 32 percent, the bonding action became increasingly poor; with higher lignin content, the fibrous structure and strength diminished because of excessive cellulose degradation.

Sweetgum and alder were used the most successfully. These woods, in the form of chips about 3/4 inch long and up to 1 inch wide, were cooked as follows:

²ASTM Standards on Electrical Insulating Materials.

1 part chips
1 part water
0.006 part concentrated sulfuric acid
190 to 200 pounds per square inch steam pressure for 10 minutes

Under these conditions, the product contained 32 to 33 percent lignin and was 13 to 15 percent methanol soluble. The yield was about 70 percent.

Laminated Hydrolyzed-wood Sheet

The chips were washed until acid-free, and then reduced to a pulp in a double-rotating disk mill. The pulp was screened and run over a Fourdrinier paper machine at a Schopper-Riegler freeness of 500 to 700 without further refining. The resulting sheet was made fairly thick (10 to 12 mils) in order to overcome its inherently low wet strength and tear resistance.

An acid-hydrolyzed wood sheet (alder), containing 6 to 7 percent moisture was laminated at 2,000 pounds per square inch, and 175° C. (347° F.) The resulting panel, removed from the press cold, had a mottled brown-black appearance and possessed the properties given in table 10.

After impregnation of the hydrolyzed-wood sheet with water-soluble phenolic resin to an 18.5 percent resin content, the laminating was effected at 163° C. (325° F.) and 2,000 pounds per square inch to give a uniformly black panel possessing the properties recorded in table 10. The addition of phenolic resin has but little effect upon the strength properties other than laminar shear. The prime object in adding phenolic resin is to improve the water resistance, dimensional stability, and minimize the tendency to delaminate. Smaller amounts of phenolic resin can be used when a smaller improvement in these properties is satisfactory.

Hardboard Made from Acid-hydrolyzed Wood

Hydrolysis Conditions

Hardwood chips, when hydrolyzed under the same conditions used in making the sheet described in the preceding section, served as the stock for making a hardboard.

Hydrolyzed Wood Hardboard

The hydrolyzed chips were pulped in a double-rotating disk mill or in a beater, and then put through a 40-cut screen. A pulp slurry was formed into a thick wet mat (10 by 10 inches) in an experimental handsheet machine. The wet mat, containing 70 to 80 percent water, was placed on a slightly oversize screen to allow for the escape of moisture during the pressing operation. The wet mat and screen were placed between cauls in a hydraulic press. Without turning on the heat in the press platens, the press was slowly closed to 300 to 500 pounds per square inch pressure to remove the excess water from the

mat. The pressure was then lowered to 65 pounds per square inch which was maintained while the platens were heated to a temperature of 185° C. (365° F.). The wet mat dried out and became further compressed under the combined heat and pressure. About 20 minutes was required to process a 1/4-inch board from an approximately 1-1/2 inch thick mat. The density of the board was determined by the press pressure used. A sweetgum pulp pressed by this method gave a board having a specific gravity near 1. Sometimes a sizing agent, that is, rosin and alum, was added to the pulp to improve the water resistance of the board.

These boards had the properties and appearance of commercial hardboards made by the "explosion process" (2, 9). The properties of a board made from sweetgum are given in table 11. The properties of the boards could be varied considerably. Douglas-fir was also used to make boards, although the strength properties, in the few cases attempted, were not so good as those indicated for sweetgum.

Evaluation of Acid-hydrolyzed Wood

Samples of acid-hydrolyzed wood and products made therefrom have been sent to various interested people by this Laboratory, but as yet no market for the material has developed. Molding powder, laminate and board are all in competitive fields (2, 5, 6, 9) in which they have little, if any, advantage. The use of acid-hydrolyzed wood as a semiplastic filler for phenolic resins must apparently be exploited on the basis of special properties rather than as a general purpose material. This fact tends to limit the market for the material and makes the process less attractive in the waste-wood utilization program. Since both the sheet and board are made from chips, they are confined to the utilization of only certain forms of waste. The sheet is rather difficult to handle because of its low wet strength and tear resistance. The board has the best potentialities, but it does not have any known advantage over some commercial hardboards, either in regard to quality or cost.

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Table 1.--Solubility of hydrolyzed maple sawdust in various organic solvents (Soxhlet extraction)

Run number	Extractant ¹	Lignin content of hydrolyzed wood	Soluble content of hydrolyzed wood	Experimental lignin content of residue from extractant	Calculated lignin content of residue ²
		Percent	Percent	Percent	Percent
1083-1109	Methanol	39.4	12.0	31.2	31.1
1149	Methanol	40.0	13.4	30.8	30.7
1605	Methanol	38.0	19.4	25.2	23.1
1605	Ethanol	38.0	19.1	24.7	23.4
1605	n-Butanol	38.0	19.5	24.0	23.0
1605	Dioxane	38.0	22.8	20.6	19.7
1605	Ethyl acetate	38.0	13.5	28.8	28.3
1605	Cellusolve	38.0	24.0	19.3	18.4
1605	Benzene	38.0	2.2	35.6	36.6
1605	Carbon tetra-chloride	38.0	0.0	36.8	38.0
1605	Acetone	38.0	16.1	27.0	26.1
1605	Heptane	38.0	0.0	36.8	38.0
1149	Water	40.0	4.5	37.0	37.2
1083-1109	Water	39.4	2.8	37.4	37.6
1149	Ethylene dichloride	40.0	7.7	34.2	35.0
1083-1109	Ethylene dichloride	39.4	7.4	33.2	34.5

¹Commercial-grade chemicals.

²On basis that only lignin is dissolved.

Table 2.--Acid hydrolysis of maple:¹ variation of acid concentration

H_2SO_4^2	: Yield of	:	Analysis of hydrolyzed wood			
(on basis of	: hydrolyzed	:	-----			
weight of	: product	:	Cellulose	Lignin	:	Lignin, calculated ³
water)	:	:	:	:	:	
	:	:	:	:	:	

Percent	:	Percent	:	Percent	:	Percent

120 p.s.i. steam pressure (177° C. -- 350.6° F.) for 30 minutes						
0.4	:	64.95	:	63.4	:	33.9
.8	:	62.30	:	61.9	:	35.3
1.2	:	60.10	:	59.6	:	36.6
1.6	:	58.95	:	57.1	:	37.3
2.0	:	56.90	:	55.6	:	38.7
2.8	:	54.18	:	52.0	:	40.6

135 p.s.i. steam pressure (181° C. -- 357.8° F.) for 30 minutes						
.4	:	63.70	:	66.0	:	34.5
.8	:	61.83	:	63.0	:	35.6
1.2	:	59.81	:	61.0	:	36.8
1.6	:	59.74	:	58.5	:	36.8
2.0	:	56.80	:	55.0	:	38.7
2.4	:	55.72	:	54.4	:	39.5
2.8	:	54.00	:	49.9	:	40.8

150 p.s.i. steam pressure (186° C. -- 366.8° F.) for 30 minutes						
.4	:	62.87	:	64.6	:	35.0
.8	:	60.52	:	61.6	:	36.4
1.2	:	58.24	:	58.5	:	37.8
1.6	:	57.20	:	55.4	:	38.5
2.0	:	56.55	:	52.5	:	38.9
2.4	:	54.03	:	49.4	:	40.7
2.8	:	52.00	:	43.0	:	42.3
	:		:		:	

¹Data from Harris and Mitchell (3).

²Water-to-wood ratio was 2.5 to 1.

³Obtained by dividing 22 percent (lignin content of maple) by the percent yield. The assumption is made that no lignin is lost or gained in the hydrolysis process. The difference between the observed and calculated lignin value is a measure of the amount of lignin-like products formed during the process.

Table 3.--Acid hydrolysis of maple: variations with temperature and time at a constant sulfuric acid concentration of 1.2 percent based on weight of water and on initial water-to-wood ratio of 2.5

Run number	Time of hydrolysis	Steam pressure	Temperature		Lignin content
	Minutes	Lb. per sq. in.	° C.	° F.	Percent
1145	450	50	147	296.6	42.6
1138	75	100	170	338.0	40.2
1150	68	110	173	343.4	39.9
1147	56	120	177	350.6	40.8
1148	45	130	180	356.0	40.3
1149	32	140	183	361.4	41.6
1146	22	150	186	366.8	40.9
1153	15	160	188	370.4	39.0
1441	10	200	198	388.4	40.0

Table 4.--Hydrolysis of maple sawdust at 50 pounds per square inch steam pressure (147° C. -- 296.6° F.) (3 percent acid, equal parts water and wood)

Run number	Time	Lignin content	Methanol soluble: lignin	SLR ¹
	Minutes	Percent	Percent	
1203	30	34.1	3.4	10.0
1204	60	35.5	4.6	12.9
1205	120	36.1	5.8	16.0
1377	150	35.5	8.3	23.4
1378	180	36.2	8.4	23.2
1379	210	36.1	6.5	18.0
1380	240	37.5	7.3	19.5

¹Soluble lignin ratio, percentage of methanol soluble lignin in total lignin.

Table 5.--Hydrolysis of maple sawdust at 135 pounds per square inch steam pressure (131° C. -- 357.8° F.) (1.2 percent acid, 2.5 parts water per part of wood)

Run number	Time	Lignin content	Methanol soluble: lignin	SLR ¹
	Minutes	Percent	Percent	
1345	5	35.0	10.6	30.3
1346	10	35.4	12.4	35.0
1347	15	36.1	12.0	33.3
1348	20	38.0	14.2	37.4
1349	25	38.3	14.1	36.8
1350	40	40.0	15.0	37.5
1351	50	40.7	15.9	39.1
1352	60	41.1	14.9	36.3
1353	90	43.1	14.5	33.7
1354	120	45.0	13.3	29.6
1361	150	43.7	12.4	28.4
1362	180	45.1	12.2	27.0

¹Soluble lignin ratio, percentage of methanol soluble lignin in total lignin.

Table 6.--Hydrolysis of maple sawdust at 200 pounds per square inch steam pressure (198° C. -- 388.4° F.) (1.2 percent acid, 2.5 parts water per part of wood)

Run number	Time	Lignin content	Methanol soluble: lignin	SLR ¹
	Minutes	Percent	Percent	
1360	6	37.2	15.6	41.9
1365	10	41.4	19.5	47.1
1371	15	43.6	19.5	44.7
1372	20	46.0	20.2	43.9
1373	30	50.3	21.4	42.3
1374	40	57.0	20.2	35.4
1375	50	57.8	20.4	35.3
1376	60	60.5	19.8	32.7

¹Soluble lignin ratio, percentage of methanol soluble lignin in total lignin.

Table 7.--Hydrolysis of maple sawdust at 200 pounds per square inch steam pressure (198° C. -- 388.4° F.) (3 percent acid, equal parts of water and wood)

Run number	Time	Lignin content	Methanol soluble: lignin	SLR ¹
	Minutes	Percent	Percent	
1381	1	38.2	17.2	45.0
1382	3	40.2	19.0	47.3
1383	5	44.8	23.5	52.4
1388	10	50.6	23.4	46.2
1389	15	58.5	24.2	35.3

¹Soluble lignin ratio, percentage of methanol soluble lignin in total lignin.

Table 8.--Hydrolysis of maple sawdust, at 200 pounds per square inch steam pressure (198° C. -- 388.4° F.) (0.6 percent acid, 2.5 parts water per part of wood)

Run number	Time	Lignin content	Methanol soluble: lignin	SLR ¹
	Minutes	Percent	Percent	
1391	10	34.8	12.7	36.5
1366	20	37.3	16.9	45.3
1385	30	36.0	14.3	39.7
1386	45	40.0	14.2	35.5
1387	60	41.8	15.9	38.0

¹Soluble lignin ratio, percentage of methanol soluble lignin in total lignin

Table 9.--Properties of hydrolyzed-wood phenolic moldings

Property	:	Value
Tensile strength.....	p.s.i.:	5,000-6,000
Flexural strength.....	p.s.i.:	7,000-9,000
Impact strength (Izod).....	ft.lb.per in.of notch:	0.3-0.4
Shear (Johnson-type shear tool) ¹	p.s.i.:	8,000
Hardness (Rockwell-M).....	:	100-110
Specific gravity.....	:	1.35-1.40
Water absorption ² (24 hours).....	percent:	0.25-0.5

¹Specimens, 1/2 inch in width by 1/4 inch in thickness by 3 inches long.

²Specimens, disk 2 inches in diameter and 1/8 inch in thickness.

Table 10.--Some average strength and related properties¹ of parallel-laminated hydrolyzed alder sheets

Test and property		Unimpregnated laminate		Phenolic resin impregnated laminate	
		Lengthwise	Crosswise	Lengthwise	Crosswise
Tension ²	3 tests:				
Ultimate strength.....	p.s.i.:	15,000	8,240	17,560	13,400
Proportional limit stress.....	p.s.i.:	6,010	3,730	7,690	5,150
Modulus of elasticity.....	1,000 p.s.i.:	2,165	1,406	2,032	1,352
Elongation immediately before fracture.....	percent:	1.21	1.36	1.02	1.18
Flexure (flatwise) ^{2, 3}	3 to 4 tests:				
Modulus of rupture.....	p.s.i.:	20,010	12,860	17,040	13,220
Proportional limit stress.....	p.s.i.:	10,340	6,210	10,150	5,830
Modulus of elasticity.....	1,000 p.s.i.:	1,993	1,248	1,907	1,320
Compression (edgewise) ⁴	4 tests:				
Ultimate strength.....	p.s.i.:	14,010	13,490	17,200	18,170
Proportional limit stress.....	p.s.i.:	4,200	3,440	4,050	4,030
Modulus of elasticity.....	1,000 p.s.i.:	1,876	1,272	1,454	1,194
Impact strength (Isod) ⁴	5 tests:				
Flatwise, notch on face.....	ft.lb.per in.of notch:	1.89	1.21	1.38	0.97
Edgewise, notch on edge.....	ft.lb.per in.of notch:	.57	.50	.38	.33
Shear (Johnson-type shear tool) ²	3 to 4 tests:				
Shearing strength (flatwise).....		9,680	8,660	10,570	10,600
Specific gravity.....		1.42	1.42	1.39	1.39
Water absorption ⁵	percent:		4.9		1.3
Hardness (Rockwell).....	M-numbers:	100	100	112	112

¹Properties here reported were obtained from specimens prepared, conditioned, and tested in accordance with Federal Specification L-P-406a for Plastics (sheet materials) Organic; General Specifications (Methods of Tests).

Lengthwise and crosswise refer to the orientation of the predominant direction (machine direction or "grain") of fibers in the constituent sheets of hydrolyzed-wood sheet with respect to the length of the specimen. Thus values of shear for "lengthwise" and "crosswise" are respectively, perpendicular and parallel to the predominant fiber directions. Flatwise refers to load applied to a surface of the original laminate, that is, in the direction of molding pressure. "Edge-wise" refers to load applied on the edges of the laminations, that is, in a direction perpendicular to that of the molding pressure.

²Tests at room temperature on nominal 1/4-inch material.

³1/2- by 1/4- by 6-inch specimens tested under center loading over a 4-inch span.

⁴Tests at room temperature on nominal 1/2-inch material.

⁵Specimens 1 by 3 by 1/8 inch.

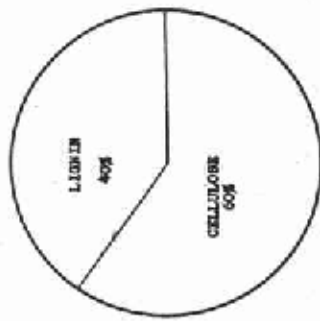
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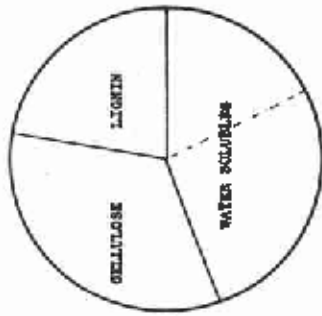
Table 11.--Properties of a hardboard made from acid-hydrolyzed sweetgum
(with rosin-alum size)

Property		Number: of tests	Average value
Tensile strength.....	p.s.i.:	4	5,610
Flexural strength.....	p.s.i.:	4	7,170
Modulus of elasticity in tension.....	p.s.i.:	1	1,240,000
Modulus of elasticity in flexure.....	p.s.i.:	1	850,000
Elongation, in tension.....	percent:	1	0.59
Compressive strength, flatwise.....	p.s.i.:	3	23,430
Impact, Izod, notched edgewise... ft.lb.per in.of notch:		1	0.61
Specific gravity.....		4	1.04
Hardness (Rockwell-M).....		7	15
Water absorption ¹	percent:		
24 hours.....			12.5
240 hours.....			25.9

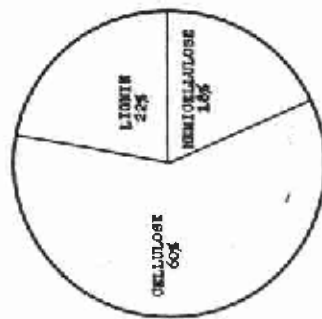
¹Specimens 1 by 3 by 1/4 inches.



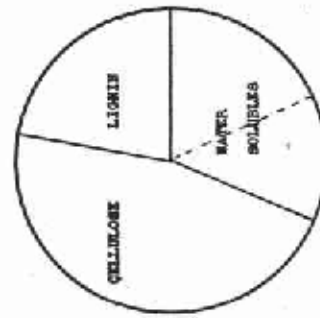
COMPOSITION OF PRODUCT
FOR MOLDING POWDER.



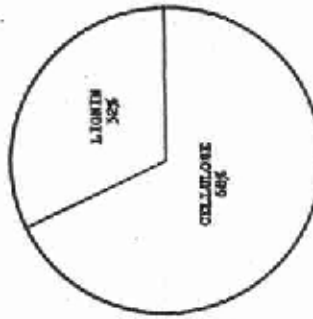
RESULT OF HYDROLYSIS PROCESS



COMPOSITION OF
MAPLE WOOD.



RESULT OF HYDROLYSIS PROCESS



COMPOSITION OF PRODUCT
FOR SHEET AND BOARD.

Figure 1.--Action of hydrolysis process and composition of products.

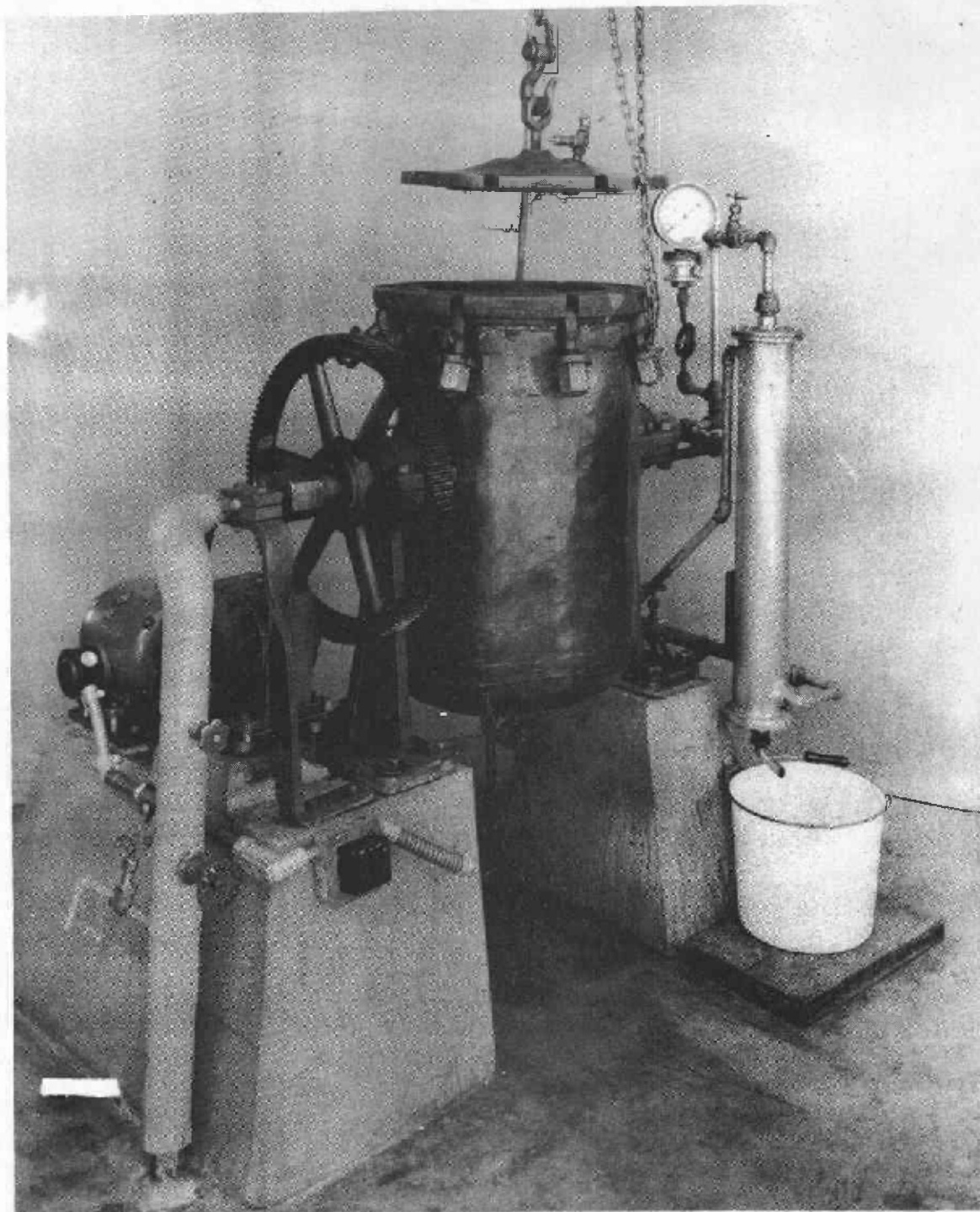


Figure 2.--A 17-gallon, bronze, cylindrical, rotary digester.

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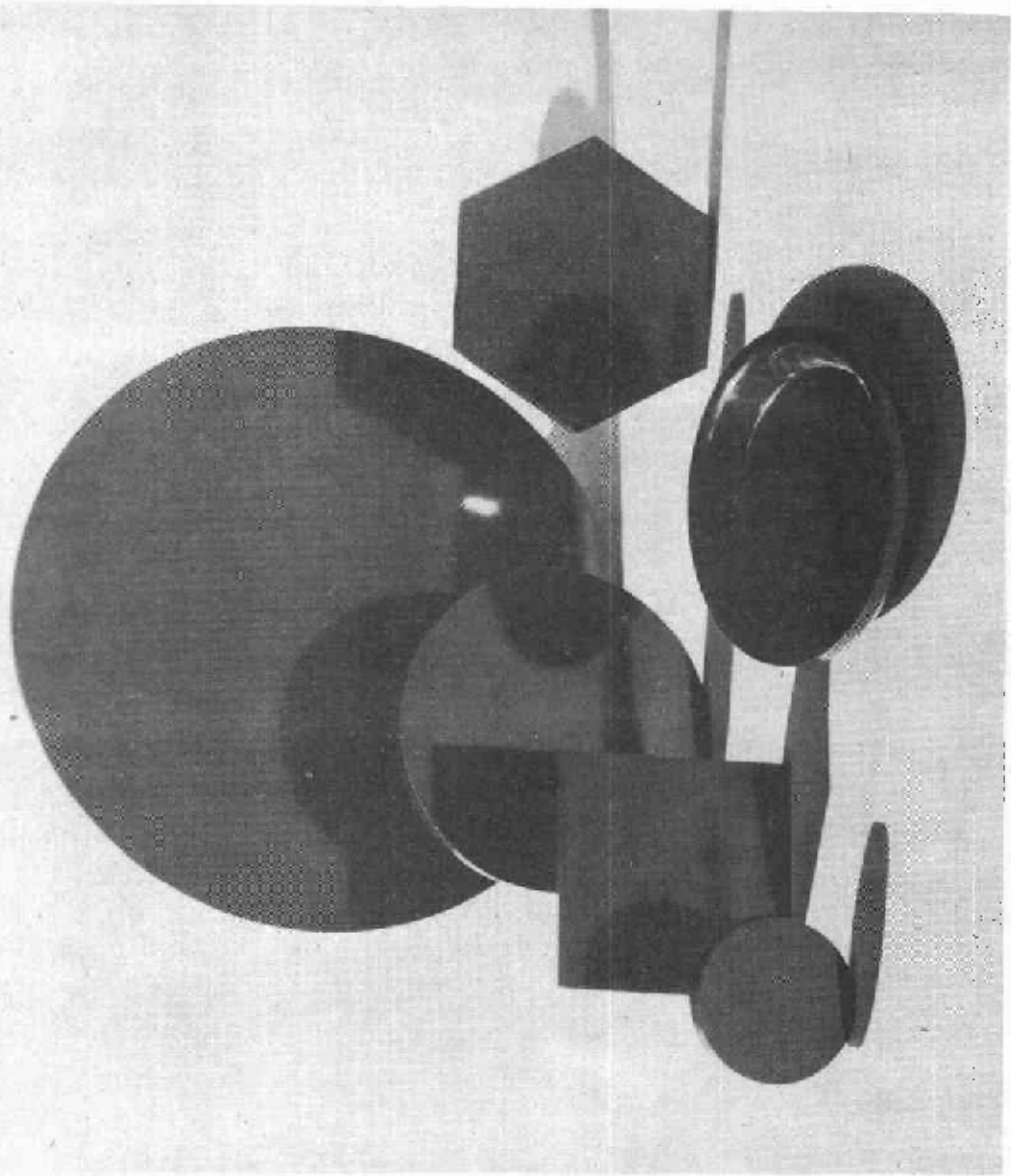


Figure 3.---Samples of hydrolyzed wood-phenolic molded plastics.

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