A STUDY OF THE CHEMICAL UTILIZATION OF SCHOLLER LIGNIN THROUGH CHEMICAL MODIFICATION BY REACTION WITH CERTAIN AMMONIA TYPE NITROGEN COMPOUNDS

by

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FOREWORD

"Lignin is one of the world's greatest industrial waste and stream pollution problems. An enormous supply of lignin taxes our ingenuity to provide methods for disposal and challenges our scientific ability to determine its nature and possible use."

Edwin C. Jahn (14)

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A STUDY OF THE CHEMICAL UTILIZATION OF SCHOLLER LIGNIN THROUGH CHEMICAL MODIFICATION BY REACTION WITH CERTAIN AMMONIA TYPE NITROGEN COMPOUNDS

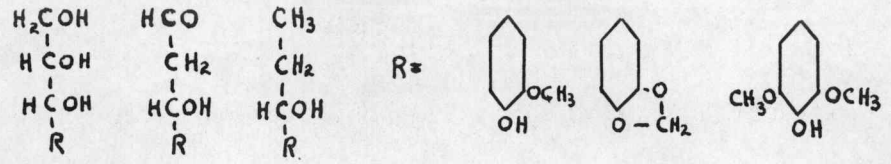
I. INTRODUCTION

Review of Lignin Chemistry

The abundance (14, 9) of lignin has proved for the past 100 years to be an incentive to research workers to determine its structure and a possible use. Lignin is usually defined as the non-carbohydrate portion of extractive-free woody plant materials. The structure is still unknown, an extensive use has not been found, and only an indefinite definition of lignin exists. All of these indicate the lack of fundamental knowledge about lignin. Lignins derived from different plants have common relationship, yet have definite differences. Even lignin from one plant can be separated into several fractions by different solvents. These facts, and the fact that lignin does not split into definite building units, have hindered the research chemist in establishing the correct structure of lignin and in developing a subsequent utilization.

A number of investigators (2, 12) give lignin a molecular weight of about 890 and many agree that softwood lignin has five hydroxyl groups of which one or two are aliphatic in nature (19, 2, 10). There are most certainly aromatic groupings in lignin as evidenced by aromatic compounds obtained from wood by alkali fusion (19), aromatic substances isolated by ethanolysis of lignin (13, 4), and aromatic derivatives obtained through high pressure catalytic hydrogenations (19, 11).

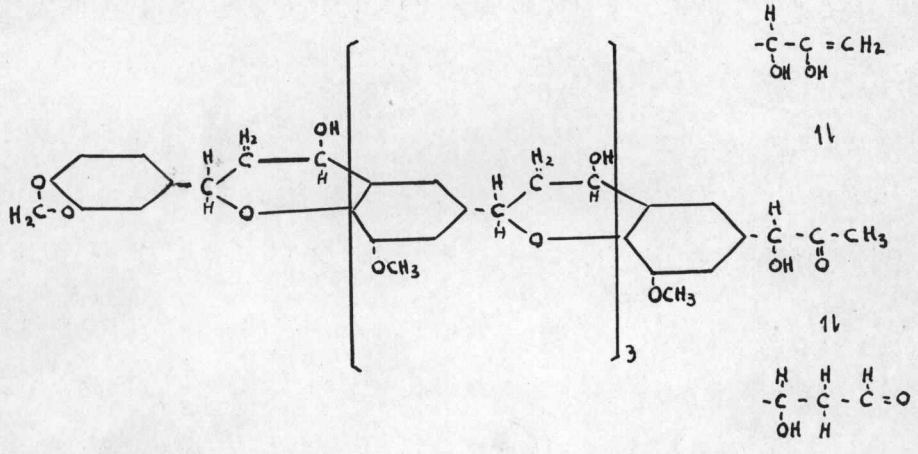
Freudenberg (7) has suggested that lignin is a product resulting from the etherification and condensation of the following units:



(a) (b) (c) (d) (e) (f)

Phenyl propane seems to be the fundamental structure.

A formula which seems to best fulfill the requirements set forth by the facts found and the theories propounded by lignin chemists is the following:



The above formula will be used to calculate any theoretical values although it is well understood that it may not represent exactly the structure found in Scholler lignin.

Within the past few years investigators have found the number of reactive groups and cleavage products and this knowledge has helped in the utilization of lignin. There are now a number of uses but most of them are of little importance. Among them are sulphite waste liquors for alcohol and yeast production, for roads, and for fertilizers; sulphite lignin for leather tanning; lignin for adhesives, fuels, in cements, in storage batteries, for removal of iron from water, for the production of vanillin (27) and for lignin plastics (25). This thesis deals primarily with the last of the above uses.

Review of the Scholler Process

In 1926, Scholler (22, 23, 8) in Germany developed a process for hydrolyzing wood to obtain a dilute solution of sugars which then could be fermented to alcohol or converted to feeding yeast (6). In the United States interest in this process has grown rapidly during the past few years because of our large war-time need for ethanol and protein feeds. In this method wood chips are hydrolyzed to wood sugars by subjecting the wood to hot dilute sulphuric acid (0.2-1.2%) at 170-180°C and about 150 pounds pressure. Nearly all the carbohydrate material is hydrolyzed and the lignin (25-30% of the wood) remains as an insoluble residue. This residual lignin has usually been used as a fuel at the plant, as a road binder, or dumped as waste. A flow sheet of the process is given in Figure 1.

The need for either product, alcohol or feeding yeast, is undoubted especially at the present time; however, the economic aspects

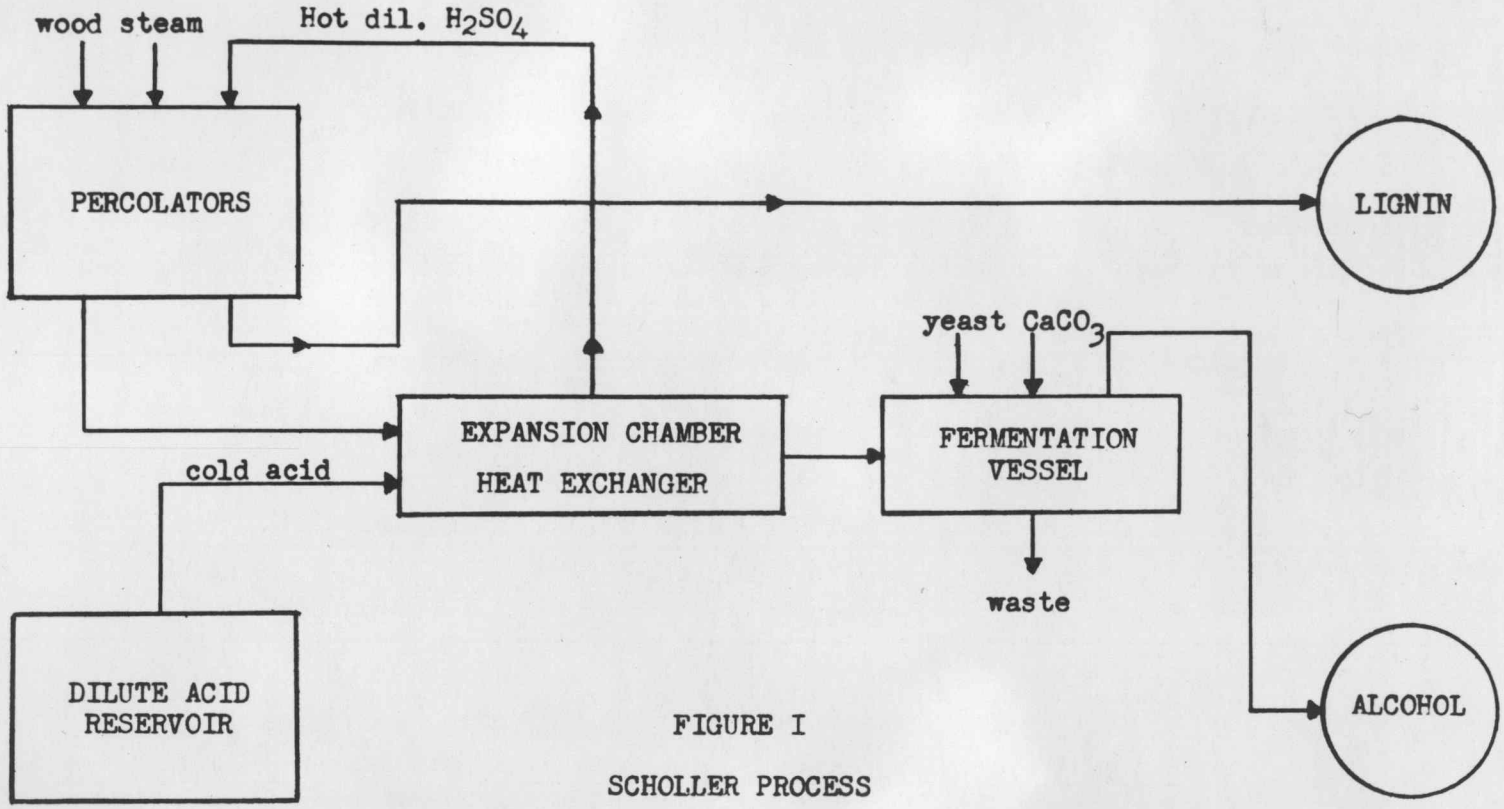


FIGURE I

SCHOLLER PROCESS

(16, 3) of the Scholler process have deterred the establishment of a plant in this country. The cost of manufacturing alcohol by this process is such as to yield a substantial profit at war prices, but exceeds the pre-war costs of making alcohol synthetically or from molasses. If a profit could be secured from the lignin, the future of the Scholler process in this country would be assured. The Pacific Northwest being an important lumber area has tremendous wood wastes which could be turned into alcohol or feeding yeast by the Scholler process. The lignin problem is then particularly pertinent to the chemists of this area.

II. EXPERIMENTAL PROCEDURE

Methods

The Scholler lignin as received was a brown powder admixed with chips that were only partially hydrolyzed. This material had been obtained in a pilot plant operation carried on by the U. S. Forest Products Laboratory and sent to Oregon State College for this study. The ligneous material was ground in an attrition mill to get it into a more usable state.

The moisture content was obtained by drying a weighed sample in an oven at 105°C., and the acidity of the lignin was determined approximately by a crude titration. One sample of lignin was shaken with water for five minutes and another for ten minutes. Both were filtered and aliquots titrated with standard sodium hydroxide.

The lignin content was determined by the standard procedure set up by the Forest Products Laboratory at Madison (21). Approximately two grams of air-dry material of known moisture content was weighed into a tared sintered glass crucible (G.3). The material was extracted for four hours in a Soxhlet apparatus with 95% ethyl alcohol, followed by extraction for four hours with alcohol-benzene solution (1-2 parts, respectively, by volume). The solvent was removed by suction, the residue washed with alcohol by suction to remove the benzene, and then extracted for three hours with hot water, and finally dried. The dried material was triturated in the crucible with 40 ml. of 72.0% sulfuric acid at 20°C. The acid was added in small portions and mixed thoroughly with the material, care being

taken not to allow the temperature to exceed 20°C. The resulting mixture was transferred to a two liter Erlenmeyer flask, diluted with 1500 ml. of distilled water, making the concentration of sulfuric acid exactly three percent, and boiled for three hours under a reflux condenser. The residue was filtered into the tared sintered glass crucible, washed free of acid by means of hot water, dried to constant weight at 105°C. in an oven, cooled in a desiccator, and weighed. The lignin content was calculated as a percentage of the oven-dry unextracted wood.

Solubility of the lignin was determined by adding 10.0 grams of lignin to 100 ml. of solvent and mixing for one hour on a shaking machine. The solution was filtered and an aliquot evaporated to dryness on a hot plate or under an evaporating lamp, dried in an oven at 105°C, desiccated over phosphorous pentoxide, and weighed. Where this method was not practical as in the case of sodium hydroxide, use of Nessler tubes proved practical for the color could be matched to the color of a solution of known concentration. The known was usually prepared as an ethanolamine solution. Solubilities are expressed as grams per 100 ml. of solvent.

Condensations of amine-lignins with formaldehyde were carried out by following the procedure described by D'Alelio (5). Formalin was placed in a one liter three necked flask fitted with mechanical stirrer and reflux condenser. To this solution were added sodium carbonate dissolved in water and 28% ammonium hydroxide. The reactants were mixed and a sample taken for formaldehyde testing. The

amine compound was next added, stirred, and sampled for formaldehyde. The reaction mixture was heated to a mild reflux and a sample taken for formaldehyde. Sampling and testing for formaldehyde were continued throughout a two hour reaction period. At the end of this period the reaction mixture was cooled to room temperature and the pH adjusted to between 6.5 and 6.8 with either citric acid or sodium carbonate solution. The reaction mass was then usually evaporated to dryness for molding purposes by a vacuum evaporation setup.

The test method for formaldehyde was also one suggested by D'Alelio (5). One ml. of the sample to be tested for aldehyde was added to 20 ml. of alcohol in a 125 ml. Erlenmeyer flask containing three drops of 1% alcoholic bromphenol blue. The solution was neutralized with acid or base which were approximately 0.5 and 0.3 N., respectively. 7 ml. of a 10% aqueous hydroxylamine hydrochloride were added, the solution shaken, and set aside for five minutes. It was then titrated to neutrality with standard sodium hydroxide. A blank was run on the reagents. The formaldehyde content is reported as grams of formaldehyde per 100 ml. of solution and was calculated by the following formula:

$$\frac{3.0 \times \text{ml. titrant} \times \text{N. of NaOH}}{\text{ml. of sample used}} = \text{grams } CH_2O/100 \text{ ml. sol'n.}$$

ml. titrant = Resin - blank

Apparatus

Preparation of derivatives usually required only standard laboratory equipment such as a three necked flask equipped with a mercury sealed stirrer and a reflux condenser. Ammoniations required the use of the bomb of the Parr hydrogenator. This was useful since it could stand the pressure developed, the action of the ammonium hydroxide, and temperatures could be controlled while the whole mass was mixing. Moldings required the use of a ten ton Carver press and a mold for a 5" X $\frac{1}{2}$" test bar.

Total nitrogen content was determined by a micro-Kjeldahl method using an apparatus built in the department. Reference to Figure II will illustrate the usefullness of this machine, for the digestion is done in the flasks which are then attached to the machine for the runs. The material, being usually anhydrous, was weighed from a pig onto a cigarette paper using a micro balance. About a 10 mg. sample was used; the paper being transferred to the digestion flask. Digestion mixture was one ml. of concentrated, nitrogen free sulphuric acid and a knife point of catalyst (1 K_2SO_4 plus 3 $CuSO_4$) (18). 10 ml. of standard hydrochloric acid were put under the condenser with the tip of the latter well into the liquid. The digestion flask was put on and 4 ml. of 40% sodium hydroxide run into it slowly by a cranking motion of the stopcock. Steam was turned into the flask by shutting off the clamp on the trap and steaming was continued for 4 minutes. After that the standard hydrochloric acid container was lowered so the tip of the condenser was just over the surface of the

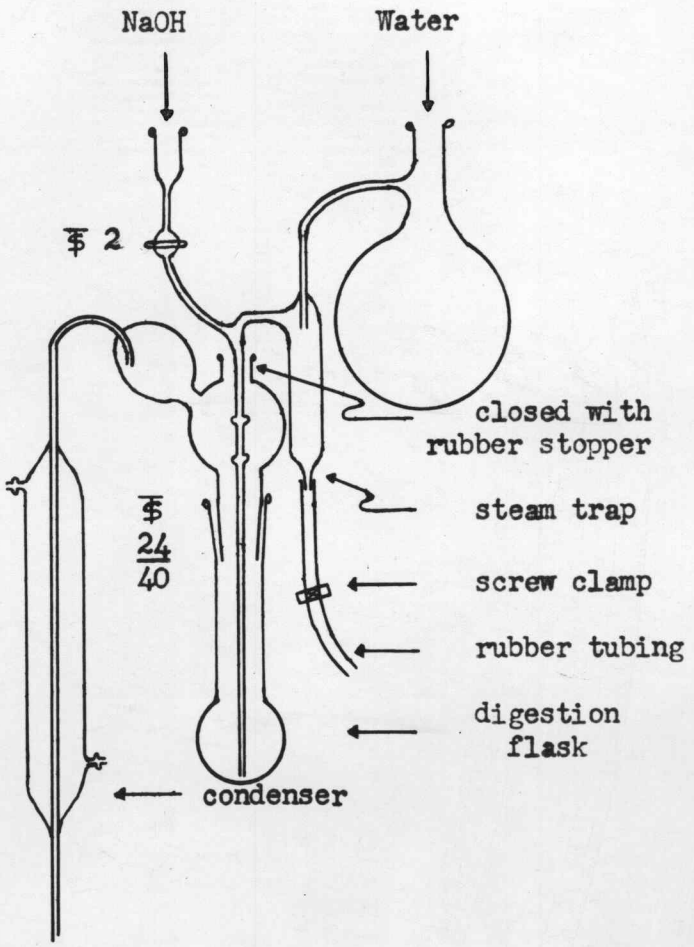


FIGURE II

KJELDAHL APPARATUS

liquid and the apparatus was steamed for one minute longer. The tip of the condenser was rinsed with distilled water and the hydrochloric acid container removed for titration. The digestion flask was removed and the male joint rinsed with distilled water to prevent any sodium hydroxide from sticking the next digestion flask onto the apparatus. The trap could be drained and the steam kept running through it until the next determination. This proved to be a very accurate and precise instrument. Titration of the hydrochloric acid was accomplished using one drop of methyl red indicator and a standard sodium hydroxide solution. The hydrochloric acid solution must be boiled for about 15 to 20 seconds before titration. 10 ml. microburrettes were used and the sodium hydroxide was titrated against potassium acid phthalate while the hydrochloric acid was standardized against the sodium hydroxide. The nitrogen content was calculated by the following formula:

$$\frac{\left[(\text{ml. of acid} \times \text{N. of acid}) - (\text{ml. titrant} \times \text{N. of base})\right] \times 14 \times 100}{\text{mg. of sample}} = \%N$$

ml. titrant = ml. base used + ml. base for blank

III. EXPERIMENTAL RESULTS

Initial Experiments

The lignin after grinding was a brown powder and some of the hydrolyzed wood could probably have been screened out here for it still had somewhat of a fibrous character. This was not desirable for fibrous particles could be utilized as a filler to give greater strength to any plastics formed.

The moisture content of the lignin was the same as that of the wood flour that is kept in the laboratory which is 7% on the basis of air dry weight. The lignin content (21) was of course high and reference to Table I will show it to be 77.7%. Since it is a fact that the higher the ratio of lignin to cellulose is, the more brittle but more water resistant the lignin plastic is; Scholler lignin plastics might be expected to be similar.

Scholler lignin proved to be only slightly soluble in all common laboratory reagents; the best solvents were ethanolamine, 5% sodium hydroxide solution, dioxane, and a 20% solution of ethanomaline in water. Table II presents a comparison of the different solvents used.

Several test tube reactions (26) were tried with lignin, of which only a few are worth mentioning. Bromine in carbon tetrachloride was decolorized. Scholler lignin gave none of the characteristic tests for an aldehyde linkage which include the Tollens, Fuchsin-aldehyde, and the Fehling tests. The Schotten-Baumann reaction took place vigorously while acetyl chloride and benzenesulfonyl

TABLE I

Lignin Determinations

	I	II
95% alcohol, alcohol-benzene, and hot water extractables	10.75%	10.63%
H_2SO_4 soluble material	11.55	11.64
Lignin content	77.70	77.72
	100.00%	99.99%

TABLE II

Lignin Solubilities

Solvent	g/100 ml.
Acetone	0.8
95% alcohol	0.8
n-amyl acetate	0.2
i-amyl alcohol	0.7
Benzene	0.2
n-butyl alcohol	0.4
Chloroform	0.3
Cyclohexane	0.1
Dioxane	1.2
Dioxane	1.1*
Ethanolamine	2.0
20% ethanolamine	1.2
10% ethanolamine	0.9
10% ethanolamine	1.3*
Ether	0.3
5% hydrochloric acid	0.5
Methanol	0.8
Nitroethane	0.3
Nitromethane	0.4
2-nitropropane	0.2
Petroleum ether	0.1
Pyridine	0.9
5% sodium hydroxide	1.8
Toluene	0.2
Water	0.4

*Refluxed for one hour with lignin, then tested for solubility.

chloride gave no apparent change. Periodic acid test for multiple hydroxyl groups was positive and phthalic anhydride with lignin lumped into a hard ball of material. These reactions, although few in number, tell much of the nature of Scholler lignin.

Aniline plastics (25) have been of interest to the lignin chemist for many years and yet the chemistry is not too well known. Several experiments were performed in order to analyze for any increase in nitrogen content upon treatment of lignin with aniline.

To 50 grams of dry wood in a three necked flask were added 400 grams of water and 10.5 grams of aniline; while to a second batch, in addition to the reactants of the first, 24.2 grams of concentrated hydrochloric acid were added. After four days of reaction at room temperature, samples of the first batch of wood (Product II) contained only 0.25% nitrogen and the second batch (Product III) contained 0.26%. This was only a slight gain as the original wood (Product I) had a nitrogen content of 0.13%. Both batches were refluxed for four hours, filtered, washed until washings were negative to an aniline color test, dried at 105°C., and desiccated over phosphorous pentoxide. A solution of bleaching powder added to a solution of aniline in water gives a violet color when concentrated and diminishes to a light blue and finally to a colorless solution as the aniline content decreases to zero (17). This has proved to be a very sensitive test. A Kjeldahl on the first batch showed that very little reaction had occurred during the four hour reflux period as the average nitrogen content was 0.27% (Product IV). The second

batch had 1.1% nitrogen (Product V).

Some aniline hydrolyzed wood prepared by the Forest Products Laboratory method (25) (Product VIII) contained 2.1% nitrogen. In this method wood is hydrolyzed in a digestor with aniline and water using a pressure of 160 psi. The resultant digested mass is filtered, washed with water, and dried. Even with this drastic treatment very little nitrogen has been combined.

To 50 grams of air dry lignin were added 396.5 grams of water and 10.5 grams of aniline. The material was refluxed for four hours and then filtered hot. The mass was washed alternately with two 25 ml. portions of alcohol and two 25 ml. portions of water until the water gave a negative color test for aniline. After the material was dried the nitrogen content was 1.15% (Product VI). The filtrate and washings were a murky, brown color and part of this filtrate was distilled until the distillate gave a negative aniline color test. The residue was concentrated and dried under an evaporation lamp, and the nitrogen content was determined as 4.5% (Product IX).

To 50 grams of air dry lignin were added 10.5 grams of aniline, 26.1 grams of concentrated hydrochloric acid, and 380 grams of water. The mass was treated the same as the preceding one. The washed aniline-lignin contained only 0.75% nitrogen (Product VII). The murky filtrate was neutralized with sodium hydroxide, a green colloidal precipitate was allowed to settle, and the top of the solution was decanted. The colloidal precipitate was washed with water using centrifuging and decantation. Then it was dried under the

evaporation lamp and a Kjeldahl gave the nitrogen content as 1.37% (Product X). The solid from the filtrate of the first aniline-lignin preparation was soluble in acetone while the solid from the colloidal precipitate of the filtrate from the second aniline-lignin preparation was not.

Ten grams of lignin with 2.1 grams of aniline were pressed in a one square inch circular mold at 175°C. and 1000 psi. The product was a dark brown, good looking, uniform disk. The disk was broken up and ground in an attrition mill to get it into a more usable state. The ground material was then steam distilled to get rid of any uncombined aniline. The mass was filtered hot and the residue dried while the filtrate was being evaporated to dryness. The residue from the distillate (Product XI) contained 0.97% nitrogen while the residue from the filtrate (Product XII) contained 1.75%. Table III gives the data of the above experiments.

Substitution Reactions

To introduce more nitrogen into the molecule it is necessary to put onto the structure some active groups that can subsequently react with amine type compounds. Since lignin decolorizes bromine in carbon tetrachloride an experiment was undertaken to substitute bromine atoms into benzene rings and also to saturate any aliphatic double bonds. From the theoretical structure of lignin the amount of bromine to be used can be calculated. If all the replaceable hydrogens

TABLE III

Kjeldahl Results of Aniline Reactions

Product	Reaction	% N in Product
I (a)	Blank on wood	0.13
(b)	" " "	0.13
II (a)	Wood + aniline + water	0.27
(b)	" " "	0.23
(c)	" " "	0.25
III (a)	Wood + aniline + water HCl	0.21
(b)	" " " "	0.31
IV (a)	Wood + aniline + water	0.25
(b)	" " "	0.29
V (a)	Wood + aniline + water + HCl	0.98
(b)	" " " "	0.87
(c)	" " " "	1.25
VI (a)	Lignin + aniline + water	1.14
(b)	" " "	1.15
(c)	" " "	1.15
VII (a)	Lignin + aniline + water HCl	0.76
(b)	" " " "	0.74
VIII (a)	Forest Products Lab. aniline hydrolyzed lignin	2.17
(b)	" " " " " "	2.04
(c)	" " " " " "	1.97
IX (a)	Solid from filtrate of VI	4.73
(b)	" " " " "	5.33
(c)	" " " " "	4.10
(d)	" " " " "	3.91
X (a)	Solid from filtrate of VII	1.37
(b)	" " " " "	1.38
XI (a)	Lignin + aniline (molded)	1.00
(b)	" " "	0.93
XII (a)	Solid from filtrate of XI	1.75
(b)	" " " " "	1.74

were substituted there would be eleven in number which would require eleven moles of bromine. There is only one possibility of addition which would require another mole. Using 0.1 mole of lignin, 1.2 moles of bromine, and 300 ml. of carbon tetrachloride to make a slurry, the experiment was carried out in a three necked flask equipped with separatory funnel, stirrer, and reflux condenser. The bromine was added to the lignin and carbon tetrachloride gradually and enough heat was used to start the reaction. The heat of reaction was then enough to carry the reaction until all the bromine had been added at which time heat was applied to bring the contents to a reflux. After one hour the water was drained from the condenser and it was used as an air condenser. Excess bromine and hydrogen bromide were carried off to a beaker of water. Some carbon tetrachloride was carried over with the excess bromine and therefore the reaction flask had to be replenished from time to time. When the color of bromine was no longer distinguished in the reflux condenser the reaction was stopped and the mass transferred to an evaporating dish where it was taken to dryness with an evaporation lamp. The bromlignin looked quite similar to the original but differed by being slightly darker in color. The bromlignin was found to contain 30.8% bromine which is in agreement with results of other investigators (12) on lignin obtained from a different source. These same investigators claimed that bromine substituted for hydroxyls and methoxyls on lignin as well as certain hydrogens. Bromlignin for all future reactions was prepared exactly as in the foregoing experiment.

The bromlignin was found to be very active as it would react with aniline in the cold and begin to set up. If aniline was added to bromlignin on a watchglass and placed in an oven at 95°C., the material would harden into a shiny, brittle, black solid. Aniline was reacted with bromlignin in much the same manner as it had been reacted with wood and the original ligneous material. Using a three necked flask equipped with a mechanical stirrer and a reflux condenser, a slurry of the bromlignin was formed with water. After the addition of aniline, the resulting mixture was allowed to react one hour at room temperature and then refluxed for three hours. The resulting material was cooled, neutralized with 40% sodium hydroxide, filtered, and washed with water. With constant stirring the mass was then steam distilled to get rid of any uncombined aniline; the distillate being tested with bleaching powder solution continuously until negative. The mass was filtered, washed, dried, and an analysis gave 3.28% nitrogen (Product XIII). The filtrate was distilled until the distillate was negative to aniline color tests and then evaporated to dryness. Analysis on this (Product XIV) proved 6.47% nitrogen combined. Another reaction of aniline with bromlignin using a four hour reflux period and no reaction time at room temperature showed only 3.2% nitrogen combined (Product XV).

In an effort to introduce more nitrogen into the ring, ammoniations were tried. Anhydrous ammonia was bubbled through a carbon tetrachloride slurry of bromlignin. Heat was given off at first but finally heat had to be applied to keep the mixture almost at the

boiling point. After a three hour reaction period the mass was transferred to an evaporating dish and dried under the lamp. The resulting material was washed free of ammonium bromide with water by detecting the bromide ion in the washings with silver nitrate. The material (Product XVI) after drying was tested for nitrogen and there was 2.0% found. In another experiment anhydrous ammonia was passed through for six hours and 5.0% nitrogen was combined (Product XVII).

The formation of primary amines of aliphatic compounds is possible by the above method but it is not feasible with aromatic compounds. A more drastic treatment was relied upon (28). 50 grams of bromlignin were reacted in the bomb of the Parr hydrogenator with 200 ml. of 28% ammonium hydroxide in the presence of about 0.5 grams cuprous oxide and 0.5 grams cuprous chloride. Reaction times were usually four hours. This method was used to prepare enough ammoniated lignin for other experiments. An average nitrogen content of all the ammoniated lignin products (Products XVIII through XXVII) was 7.7%. Data on Kjeldahl determinations of both the aniline-lignins and the ammonia-lignins are presented in Table IV.

Condensations and Moldings

Since certain ammonia type compounds undergo condensations with formaldehyde, such reactions of the lignin compounds were attempted. Table V shows a comparison of lignin, aniline-lignin, ammonia-lignin, and urea condensations with formaldehyde. The reactants were kept constant at 157 ml. of water, 43 ml. of formalin, 0.08 grams of sodium

TABLE IV

Kjeldahl Results of Aniline-Lignins and Ammonia-Lignins

Product	Reaction	% N in Product
XIII (a)	Aniline + bromlignin + water	3.31
(b)	" " "	3.24
XIV (a)	Solid from Washings of XIII	6.45
(b)	" " " " "	6.48
XV (a)	Aniline + bromlignin + water	3.34
(b)	" " "	2.97
XVI (a)	NH_3 + bromlignin + CCl_4 (3 hours)	1.94
(b)	" " " " "	1.87
(c)	" " " " "	2.13
XVII (a)	NH_3 + bromlignin + CCl_4 (6 hours)	4.97
(b)	" " " " "	5.03
XVIII (a)	NH_4OH + bromlignin + catalyst (4 hours)	7.93
(b)	" " " " "	7.97
(c)	" " " " "	8.15
XIX (a)	NH_4OH + bromlignin + catalyst (4 hours)	8.69
(b)	" " " " "	7.87
(c)	" " " " "	8.32
XX (a)	NH_4OH + bromlignin + catalyst (4 hours)	8.47
(b)	" " " " "	7.88
XXI (a)	NH_4OH + bromlignin + catalyst (4 hours)	8.73
(b)	" " " " "	8.87
XXII (a)	NH_4OH + bromlignin + catalyst (4 hours)	6.90
(b)	" " " " "	7.15
XXIII (a)	NH_4OH + bromlignin + catalyst (4 hours)	7.62
(b)	" " " " "	7.45
XXIV (a)	NH_4OH + bromlignin + catalyst (11 hours)	7.68
(b)	" " " " "	8.67

(Continued on next page)

TABLE IV (Continued)

Product		Reaction	% N in Product
XXV	(a)	NH_4OH + bromlignin + catalyst (3 hours)	7.04
	(b)	" " " " "	6.53
XXVI	(a)	NH_4OH + bromlignin + catalyst (3 hours)	7.13
	(b)	" " " " "	7.12
XXVII	(a)	NH_4OH + bromlignin + catalyst (3 hours)	7.47
	(b)	" " " " "	7.53

carbonate, and 2.14 ml. of 28% ammonium hydroxide. 53 grams of lignin were used in one reaction, 53 grams of ammoniated lignin used in another, 18 grams of urea used in a third, and the aniline-lignin resulting from reaction of 40 grams of bromlignin with aniline was used in the fourth. The amount of urea used was such that the nitrogen content in the condensation reaction would be similar to that in the ammoniated material. In Table V, oo represents a sample taken of the reactants, o a sample taken after the amine compound had been added, R a sample taken at reflux, and the numbers represent the reaction time in minutes (5). A blank run on the reagents used in the titration required 0.5 ml. of sodium hydroxide which is taken into account when calculating the amount of formaldehyde in solution.

Table VI presents data on the moldings of the compounds prepared and also on some miscellaneous moldings which were made for comparison, and on some of the tests run on these products. The molding conditions had to be regulated, and they were taken as 185°C. and 2000 psi. with a five minute reaction period at 185°C. The mold was heated as rapidly as possible with electric platens and cooled with air after the five minute period. The mold was always preheated to 60°C. before the reaction material was introduced. The pressure was never allowed to drop until the mold had cooled to 60°C. at which time the product was removed. About two hours were required to reach the 185°C. and about 30 minutes were also required for the cooling process. The mold parts were always dusted with zinc stearate for lubrication. The moisture content was always 3% based on the dry ligneous

TABLE V

Lignin Condensations

Samples	Lignin		NH_3 Lignin		Aniline-Lignin		Urea	
	A	B	A	B	A	B	A	B
oo	7.5	6.58	7.5	6.58	7.6	6.67	7.5	6.58
o	7.1	6.20	6.3	5.45	7.1	6.20	6.5	5.63
R	7.1	6.20	4.7	3.95	7.0	6.11	2.1	1.51
15	6.9	6.02	4.2	3.48	6.9	6.02	1.9	1.32
30	6.8	5.92	3.8	3.10	6.8	5.92	1.8	1.22
60	6.8	5.92	3.5	2.82	6.7	5.83	1.8	1.22
120	6.8*	5.92	3.0	2.35	6.5*	5.63	1.8*	1.22

A=ml. NaOH used in the formaldehyde test

B=HCHO content of the solution in grams per 100 ml. of solution

*=Not run but assumed.

TABLE VI

Molded Products

	Ligneous material	Grams other substance	W	R	Remarks
1.	25 g. lignin	—	24.8	*	brown color - little flow fair looking
2.	25 g. HCHO aniline-lignin	—	—	*	dark brown - little flow
3.	25 g. lignin	5.0 g. aniline 1.9 g. paraform	1.6	765	very good looking dark brown - hard
4.	25 g. aniline-lignin	4.8 g. furfural	8.6	*	good flow but brittle fairly good looking
5.	17.5 g. aniline-lignin 7.5 g. wood flour	2.0 g. aniline 3.4 g. furfural	2.1	*	flow but brittle fairly good looking
6.	25 g. lignin	5.0 g. aniline 6.0 g. furfural	0.8	*	very good looking brittle but hard
7.	25 g. NH_3 lignin	—	—	*	no flow - poor
8.	25 g. HCHO NH_3 lignin	—	—	*	no flow - poor
9.	25 g. NH_3 lignin	4.3 g. paraform	—	*	no flow - poor
10.	25 g. NH_3 lignin	13.75 g. furfural	—	*	no flow - poor

(Table continued on next page)

TABLE VI (Continued)

	Ligneous material	Grams other substance	W	R	Remarks
11.	10 g. lignin	10 g. aniline	—	—	extruded from mold with little pressure - black - brittle
12.	5 g. bromlignin 5 g. wood flour	5 g. aniline	—	—	reached decomp. point at 165°
13.	5 g. bromlignin 5 g. wood flour	5 g. aniline	22.7	*	black-hard - sawed easily ‡
14.	12.5 g. bromlignin	12.5 g. aniline	4.6	1083	black - good looking ‡
15.	25 g. lignin	6.25 g. urea 3.1 g. paraform	19.1	*	hard - brittle
16.	25 g. lignin	6.25 g. urea 6.0 g. furfural	2.7	*	hard - brittle good texture
17.	25 g. lignin	5.0 g. Phthallic anhydride	0.4	1160	black - good looking good flow and texture
18.	12.5 g. lignin 12.5 g. wood flour	4.0 g. Phthallic anhydride	1.4	997	hard - good texture.

* Broke coming out of mold
‡ Molded at 100°C

W=% water absorption after 24 hours immersion
R=Modulus of rupture.

material. Exceptions are those plastics which contain bromlignin for it was used with any equilibrium moisture it might have picked up in the laboratory.

The moisture absorption test, results of which are given in Table VI, was not the standard one but was done only for a means of comparison. A 1½ in. piece of the test bar was sawed off, weighed, immersed in water for 24 hours, taken out, excess water blotted off, and weighed. The percent absorption was based on the dry weight of the 1½ in. bar. The modulus of rupture was calculated by finding the breaking strength in pounds and substituting that into the following formula:

$$R=3PL/2bd^2$$

b=width
d=depth
P=load
L=length between centers
R=modulus of rupture

The test bar was always 5 in. long and ½ in. wide and was always broken through the ½ in. depth. The breaking machine always had 4 in. between centers. Therefore d always equalled ½ in. and L 4 in. This simplifies the formula to R=24P/b.

The urea was impregnated into the lignin by using a saturated solution of urea, mixing this with the lignin, and then drying in a vacuum oven. The phthallic anhydride was impregnated in a similar manner except the solvent was an alcohol-ether mixture.

IV. DISCUSSION OF RESULTS

The test tube reactions (26) tell something of the structure of the Scholler lignin. If bromine reacts by substitution there must be certain active groups on the rings to activate particular hydrogens. In the case of Scholler lignin these active groups are most likely hydroxyls and methoxyls. Any addition of bromine to the structure is covered by the evolution of hydrogen bromide; however, the ease of ammoniation by anhydrous ammonia of bromlignin signifies that some addition may have occurred (28). As has been said, certain investigators (12) claim that bromine displaces hydroxyl and methoxyl groups as well. The reason that acetyl-chloride and benzene-sulfonyl chloride did not react with lignin while the benzoyl chloride did might be explained through the conditions of the reactions (26). There is no nitrogen in the original lignin; therefore, there can be no amine groups. The existence of hydroxyl groups is indicated by the periodic acid test as well as by the Schotten-Baumann reaction. Acid chlorides react readily with primary and secondary amines; however, acylation takes place less readily with alcohols and phenols and, as a consequence, alkali is often used to accelerate the Schotten-Baumann reaction since it neutralizes the hydrochloric acid which is eliminated. Thus the Schotten-Baumann reaction might work while the conditions would not permit the others to do so.

The aniline-wood and aniline-lignin reactions proved that very little aniline is actually combined. It is believed by most lignin

chemists that the success of aniline plastics is due to an aniline-lignin complex. In making such plastics, a small amount of furfural is usually used in addition to the aniline. In an earlier related study of such plastics in this department, Clinton and Detering (Unpublished data) obtained results which led them to doubt the formation of the aniline-lignin complex and to believe that perhaps the aniline or an aniline-furfural complex plasticized the lignin plastic. Based on the results obtained in the present study both concepts are probably correct, but since only a small amount of nitrogen is combined most of the chemistry of aniline plastics is tied up in the aniline-furfural polymer.

The molding time is a serious disadvantage (15) of lignin products as compared to synthetic resins, and the only place where lignin plastics would now be useful would be as boards and panels for building materials. The condensation of the ammoniated lignin should have provided the molecules with groupings that during the molding time could have cross-linked and produced a thermosetting resin. This would not then require a very long molding period. Although the ammonia-lignin condenses with formaldehyde the product does not polymerize to form a good plastic. This might be due to extreme degradation of the lignin molecule by the drastic treatment during ammoniation or perhaps the molding conditions were unsuitable. It was hoped that the condensation and molding of ammonia-lignin would parallel the urea formaldehyde plastic to some extent. Even with the latter it is possible to produce an insoluble compound (24) that is

unsuitable for molding by failing to control the pH correctly during the condensation. This also may have happened with the lignin although it is not likely. No use of plasticizers was made in most of these moldings which may account for some of the poor results, since plasticizers are helpful in lowering the molding temperature.

When aniline and bromlignin were put into the mold the material started extruding at 75°C. and no pressure could be applied. The material could have been molded at 80°C. just as well as 100°C. This phenomenon has never previously been reported with lignin plastics. To the author's knowledge there has been no lignin plastic molded with good flow of the material under 150°C. The product was brittle and this was believed to result from salt formation when aniline combined with the bromlignin. As a result, after aniline reacted with the bromlignin the mass was neutralized, washed and molded. These plastics were not successful which might be accounted for by the possibility of incorrect reaction conditions.

There are two methods of modifying lignin; one, by substitution of the hydrogens in the molecule, and two, by replacement of the hydroxyl groups of the molecule. The work in this thesis has been done on the former; however, two plastics were made to prove the potentialities of the latter. Phthalic anhydride pressed with lignin gave the best plastic produced during this research, both as to water resistance and as to breaking strength. The bar was very good looking but the breaking strength, although good, was not as high as it should have been.

All the plastics produced were very hard but also very brittle. The incorporation of plasticizers, wood flour, or a change of molding conditions might alter these to produce better lignin plastics. Through a trial and error study of these variations some success may be attained. Most methods of the past have been to react the compounds in the mold with lignin or to react the amine compounds directly with the lignin (1, 25). Although that type of research has had some success, it has not produced a good thermosetting lignin plastic. This research has tried to first modify the lignin and then to react amine compounds with the modified product. It is believed that a thermosetting lignin plastic can be prepared by this method or by a replacement of the hydroxyl groups by some compound such as phthalic anhydride.

V. SUMMARY

A review of lignin chemistry and of the Scholler process is given.

Methods and apparatus used are described.

A chemical modification of Scholler lignin has been attempted and moldings have been made of the products.

Suggestions are offered for the production of improved Scholler lignin plastics from the modified products.

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