

AN ABSTRACT OF THE THESIS OF

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Title A PRELIMINARY INVESTIGATION OF THE CATALYTIC HYDRO-
GENATION OF SULFONATED LIGNIN -----

Abstract Approved: -----

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Much of the early work on lignin consisted of the study of methods of isolation and characterization of the active groups present in this isolated material. Although considerable progress has been made, the exact structure and good means of utilization of lignin are still unknown. Recently, a new method of attack, the catalytic hydrogenation of lignin, has been used. Structural investigations involving the use of hydrogenation have been made only during the past five years. It has been found that by hydrogenation of material isolated in the laboratory, the product obtained consisted principally of compounds containing nine carbon atoms. In one case it has been mentioned that phenolic substances were obtained by hydrogenation. In the case of soda lignin from commercial sources the product obtained does not consist of nine carbon atom units but primarily of larger units.

In this study a sulfonated lignin obtained from a commercial waste sulfite liquor was used. It has been thought that this material was impossible to hydrogenate due to the high percentage of sulfur, which readily poisons most catalysts. The purpose of this study was to attempt to find a suitable catalyst and conditions that would permit hydrogenation of this material. Raney nickel, copper chromite, molybdenum oxide, nickel sulfide and tetralin were used. The copper chromite gave the best results. It was also found that hydrogenation will not occur without a catalyst being present.

A quantity of material was hydrogenated with copper chromite, in order that an attempt might be made to identify some of the products obtained by hydrogenation. Of the lignin hydrogenated, 4.2 per cent was converted to a high boiling oil and solid. No alcohol was obtained. An acid containing from five to eight carbon atoms was present among the products.

A PRELIMINARY INVESTIGATION
OF THE CATALYTIC HYDROGENATION
OF SULFONATED LIGNIN

by

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A THESIS


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A PRELIMINARY INVESTIGATION OF THE CATALYTIC HYDROGENATION OF SULFONATED LIGNIN

I. INTRODUCTION

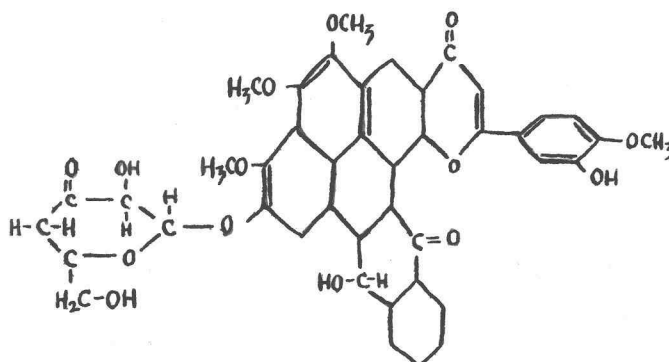
The investigation of lignin started over 100 years ago. Anselme Payen according to Phillips (37) was the pioneer investigator in this field. Payen was the first to attempt a separation of wood into its components. De Candole in 1833 (19) was the first to make use of the term lignin.

Lignin may be defined as the non-carbohydrate portion of woody tissue. Although this definition of lignin is rather indefinite it is perhaps one of the best that is available. With the exception of Brauns (11) of the Paper Institute no one claims to have isolated pure unchanged native lignin.

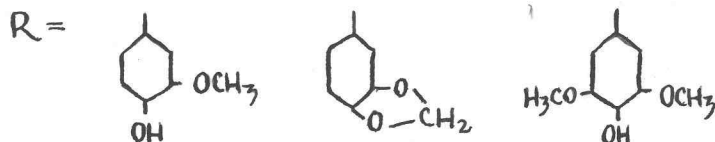
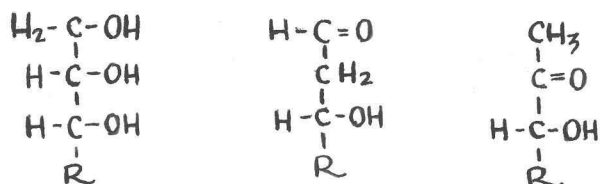
In almost all cases the isolation is accomplished by rather drastic means. Such means as 72 per cent sulfuric acid, 42 per cent hydrochloric acid and others have been employed. Brauns (11) used only ethanol in his procedure and extracted about 2-3 per cent of the total lignin in the wood. Bailey (3) has used butyl alcohol and sodium hydroxide as a solvent. Hibbert employed methanol and hydrochloric acid (12) in the isolation of lignin. Friedman (16) has used benzyl alcohol and hydrochloric acid in the preparation of lignin. All of these men have

made intensive studies on the material thus obtained.

The chemical constitution of lignin is at the present time unknown. Many formulas have been proposed for its structure. Fuchs (18) has proposed the following which is one of the most elaborate and admittedly incorrect.



Freudenberg (17) regards lignin as a product resulting from the esterification and condensation of the following units.



Phillips (38) is of the opinion that the fundamental building unit is n-propylguaiacol. That lignin is made up of the repetition of a definite structural unit seems to be pretty well agreed upon by most investigators. Brauns and Hibbert (12) and later Brauns (11) have even gone so far

as to give an empirical formula for lignin. This is not entirely justifiable until it has been definitely proven that lignin is homogeneous and not heterogeneous as was brought out in a recent paper by Bailey (4).

Lignin is a great importance because of its abundance and the possibility that it may serve as a source of aromatic compounds. The principal source of commercially available lignin is from the paper industry, where it is produced as a by-product in the manufacture of paper from wood. In the sulfite process about half of the weight of wood entering into the digestors is later dumped in the rivers as ligninsulfonic acids and soluble carbohydrates. This not only represents a considerable waste but also constitutes a source of pollution of the waters into which it is dumped. In the United States only one company, The Marathon Paper Mills Co., is utilizing this waste product. In their process the inorganic chemicals in the liquor are first precipitated and then the ligninsulfonic acids. The recovered chemicals are returned to the system and the lignin is sold for a variety of uses. However, this one company can more than supply the present needs of the United States.

In Europe, the principal means of disposal is to use the sugars in the waste liquor as a source of alcohol. In this country this is not feasible due to the low-cost

methods of production of alcohol.

Although many patents have been obtained for the utilization of lignin, none of the processes have solved the problem of the utilization and disposal of waste liquor.

Among the latest methods of studying the structure and disposal of lignin has been hydrogenation. Much of the work has been done on lignin prepared in the laboratory and very little on commercially available lignin. (This will be brought out in the following review on the hydrogenation of lignin.) Since ligninsulfonic acids contain an appreciable amount (5-7 per cent) of sulfur, it has been thought that it was impossible to hydrogenate this material. In all cases of hydrogenation a catalyst is necessary and sulfur is very effective in poisoning most of the catalysts in common use. It was the intention in this study to attempt to find conditions and catalysts that would give a satisfactory degree of hydrogenation and thus obtain either some product that would be of commercial use or that would throw some light on the structure of the material that was being hydrogenated.

II. REVIEW OF HYDROGENATION

The earliest work on the reduction of a lignin containing material was done by Berthelot (7) in 1869. He treated wood with hydriodic acid and obtained a mixture of hydro-carbon oils and some gaseous products. It was not until fifty years later that Fischer and Tropsch (15) did more work on lignin and lignin containing materials. Their work was mainly with coal and they made very little attempt to identify their products, but divided the material obtained into portions based on solubility in different solvents. In their work with lignin, their aim was to show a relationship between wood and coal.

In 1925 Fierz-David and Hanning (14) carried out a distillation of wood, lignin and several other materials with hydrogen at 300 atmospheres pressure and in the presence of nickel. According to these investigators an almost quantitative conversion to liquid or gaseous products resulted. The principal products found were water, phenols, ketones and alcohols. In a second study (13) on wood and cellulose, in the presence of nickel hydroxide ($\text{Ni}(\text{OH})_2$) heated at $450-700^\circ$, under a hydrogen pressure of 150-220 atmospheres, a yellow liquid containing essentially the same products as obtained in the earlier investigation was obtained.

Ipatiev and Petrov (27) in 1929 were interested in obtaining low-boiling products from the hydrogenation of wood tar. The results showed that the percentage of hydrocarbons and low-boiling fractions was high when wood tar was heated with hydrogen in the presence of a catalyst. The conditions they found for obtaining the largest possible yield of liquid products were a temperature of 440-60° and an excess of hydrogen in the presence of catalysts.

At about the same time Egloff (36) became interested in the cracking of wood tar in order to produce motor fuels. He found that pine tar was most suitable for solvents and paint thinners, hardwood tars could be utilized in the production of phenols, and Douglas fir tar produced a high antiknock motor fuel.

In 1930 Lindblad (29) obtained a patent for the production of aromatic compounds by hydrogenation of lignin-sulfonic acids precipitated from waste sulfite liquor. This is probably the first mention of the hydrogenation of waste sulfite liquor. He carried out several other investigations (30, 31, 32) on hydrogenation of wood and waste sulfite liquor and obtained patents as the results of these investigations. In one process (33) for the production of oils from wood by hydrogenation, a mixture of sawdust and waste sulfite liquor carbonized at 350° was used. He

tried a great variety of catalysts. Hydrogenation of the carbonized product gave 57.9 per cent oils, 17.4 per cent gas, 12.4 per cent water, 13.0 per cent organic residue and 4.0 per cent waste. The oils consisted of up to 36 per cent of saturated hydrocarbons of high boiling point.

Bergstrom and Cederquist (5) made a study of the hydrogenation of waste sulfite liquor. They heated dried sulfite liquor to a final temperature of 460° with dry gas purification mass under hydrogen pressure. On heating the residue obtained to 180° , they obtained by distillation from 200 grams of sulfite solids the following: 10.5 g. of oil, 63.0 g. of water, 50.5 g. of ether extract and 89 g. of residue. The tar was high boiling and very viscous at room temperature. Of the tar 28.8 per cent was soluble in 2N sodium hydroxide, 8.7 per cent separated as a rosin, 58.5 per cent neutral oils and 4.0 per cent losses. Of the neutral oils 31.9 per cent was insoluble in 80 per cent sulfuric acid, 14.2 per cent insoluble in 95.5 per cent sulfuric acid. After hydrogenation the greater part of the sulfur was present as sulfide and only 3 per cent as sulfate. They obtained a patent (6) for the preparation of materials for hydrogenation by heating under pressure at an elevated temperature in the presence of various hydroxides and carbonates.

Boomer, Argue and Edwards (9) found that the destruc-

tive hydrogenation of cellulose and fir wood sawdust could be carried out using tetralin as a carrier. The material was completely converted to a mixture of liquids and gases.

Isobe, Tanaka, and Ito (28) converted ground wood to an oil by heating it in a mixture with 5-30 per cent of coal tar petroleum, or wood tar at a temperature of 400° under a hydrogen pressure of 300 atmospheres.

A two-step hydrogenation was found by Trefil'ev and Filaretov (40) to give the best hydrogenation of wood tar. The fraction obtained on hydrogenation at elevated temperatures (180-300°) gave increased yields of benzene, toluene, dimethylbenzene and naphthalene.

In a recently issued French patent (26) it was found that oxides or sulfides of metals of groups 5-8 (periodic table) or of tin could be satisfactorily used as a catalyst in the hydrogenation of waste sulfite liquor.

An attempt to show something about the structure of lignin was made by Moldavskii and Vainshtein (35). Sulfuric acid lignin was hydrogenated in a horizontally rotating autoclave, electrically heated to 400-450°, with a cold hydrogen pressure of 50-70 atmospheres in the presence of molybdenum sulfide (MoS_2) as a catalyst. A complete transformation of lignin into liquid (44 per cent) and gaseous products was accomplished. The tar obtained was fractionated into three fractions: 24.2 per cent boiling

below 200°, 35.6 per cent between 200° and 300°, above 300° and losses 40.2 per cent. The products of hydrogenation of lignin showed the aromatic structure of the material. The oxidation of the liquid fraction of hydrogenation yields m-phthalic acid which shows that the aromatic hydrocarbons of this fraction have side chains in the 1,3-positions.

Hatihama, Zyodas and Umezu (24) prepared hydrochloric acid lignin from a soft wood. They methylated part of it and hydrogenated both the methylated product and the original material. They found that the methylated lignin had apparently lost its reactivity with hydrogen. On the original lignin best results were obtained, when it was hydrogenated using dioxane as the solvent, and nickel oxide as the catalyst. One mole of hydrogen was absorbed by 40-44 grams of lignin in 35-55 hours. The ether soluble portion amounted to 46.7 per cent of the weight of lignin and contained dihydroeugenol, protocatechuic acid, pyrocatechol and p-hydroxybenzoic acid. The latter three substances were considered to be secondary decomposition products of dihydroeugenol, which seems to have an important part in the construction of natural soft wood lignin. Aldehydes and other neutral substances were also found in the ether soluble portion. This work is of interest because the products found are different from those

found by others who have made hydrogenation studies and also because these products are the same as are usually found as the result of alkali fusion of lignin.

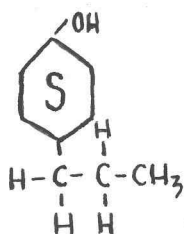
Bobrov and Kolotova (8) acidified sulfite waste liquor with sulfuric acid, passed steam into it at 100°, and then evaporated to dryness. This treatment served to remove half of the fixed sulfur as sulfur dioxide. This preliminary treatment led to a considerable saving of hydrogen. The yield of the initial material was 70.5 per cent of the weight of the dry residue obtained by direct evaporation of the original liquor. The treated material was suspended in heavy hydrogenation oil in a proportion of 2:1. Consumption of hydrogen was first observed at a temperature range of 140-70°. During further heating to 300° the consumption of hydrogen is inappreciable but appears again at higher temperatures. High yields of heavy oil and almost complete absence of light fractions were obtained at temperatures not over 340-50°, while a sharp increase in light fraction boiling below 150° was obtained by raising the temperature above 400°. By heating for 6 hours at 350-400° a total yield of 55 per cent oil was obtained. They concluded from their studies that wood, lignin, cellulose and similar products break down at temperatures above 270-280°.

The Forest Products Laboratory has made several in-

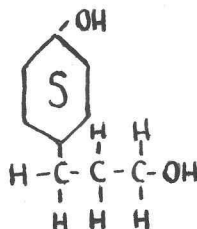
vestigations on the hydrogenation of lignin. Harris, D'Ianni and Adkins (21) hydrogenated methanol lignin obtained from aspen wood over copper-chromium oxide. They found that one mole of hydrogen was absorbed for each 25 grams of lignin. The reaction was carried out in dioxane at 250-260°, under 200-350 atmospheres of hydrogen during a period of 18 hours. The mixture of products resulting from the reaction is colorless or faintly yellow. They obtained from the hydrogenation of 80 grams of lignin, 22 g. of methanol, 9 g. of an alcohol b.p. 92-95° (7 mm), about 3 g. of a glycol b.p. 107-110° (1 mm), 20 g. of a glycol b.p. 125-127° (1 mm), 18 g. of a mixture of compounds b.p. 130° to 260° (1 mm).

The alcohol was identified as 4-n-propylcyclohexanol (I). The analysis of the glycols for carbon and hydrogen corresponds to the formula $C_9H_{18}O_2$. The one present in the larger amounts contains a primary hydroxyl group and has been oxidized to a keto acid, $C_9H_{14}O_3$. This glycol is 3-(4-hydroxycyclohexyl)-propanol-1(II). In a later paper by Adkins (10) he has synthesized this compound and showed that he was correct. The second glycol has been characterized as 4-n-propylcyclohexanediol-1,2(III). The analysis of the mixture of products distilling above 130° (1 mm) corresponds to the formula $(C_6H_{11}O)_n$. The weight of methanol isolated and the combined weight of the three

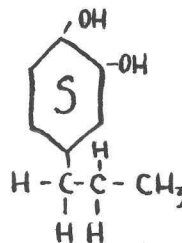
9-carbon atom compounds were about 28 and 44 per cent,



I



II



III

respectively, of the weight of the lignin submitted to hydrogenation.

In a later paper Harris and Adkins (20) showed that the same products could be obtained in about the same yields from methanol, hydrochloric acid, alkali and sulfuric acid lignin. The results of analysis on the high-boiling residue show that there are units in lignin containing 18 or more carbon atoms.

Harris and Sherrard (23) obtained a patent on the basis of their work with hydrogenation in aqueous medium. In this process they used an alkaline medium, using Raney nickel. In addition to the pulp which they obtained, methanol, propanol and several propylcyclohexane derivatives were obtained. The pulp obtained without further treatment was about the color of newsprint. It was quite free from shives and easily bleached by a mild treatment with chlorine.

In a later publication from the same laboratory (22), the experimental work of hydrogenation in aqueous medium

was discussed. They found that approximately 35 moles of hydrogen were taken up for each equivalent weight of lignin (900 grams), 1 mole/25 g. In this study they used methanol lignin, soda lignin, purified soda lignin (both from a commercial source), soda lignin prepared in the laboratory, sulfuric acid and cellosolve lignins. A similar type of product was obtained from all of the lignins. The resin obtained was fractionated into four fractions. Fraction I consisted chiefly of n-propylcyclohexane. Fraction II was identified as n-propylcyclohexanol by comparison with known material. Fraction III contained a mixture of two or more compounds containing the n-propylcyclohexane nucleus. Fraction IV, the residue, consisted of several substances having the general formula $(C_6H_{10} \text{ or } H_{11}O)_x$. This is in good agreement with their earlier work.

Adkins (2) made a study of the hydrogenation of a commercial soda lignin, over copper chromite in dioxane solution at 250-300°. In a typical fractionation there was obtained from 594 g. of lignin, 24 g. 55-85° (7 mm), 24 g. 85-112° (7 mm), 39 g. 76-145° (0.3 mm), 45 g. 145-190° (0.3 mm), 40 g. 190-235° (0.2 mm), and 147 g. residue boiling above 235° (0.2 mm). In order to be sure that the products were completely saturated, the larger share of them were then submitted to rehydrogenation over copper

chromite at 290° in dioxane solution.

In contrast with methanol lignin mentioned earlier, only 10 g. of a fraction boiling at 55° (7 mm) to 130° (1 mm) as against 45 g. for the methanol lignin was obtained from 100 g. of the lignins, thus indicating a qualitative as well as quantitative difference in the products from the two types of lignin.

While 10 per cent of the weight of the methanol lignin appeared as 4-n-propylcyclohexanol-1, only a few tenths of a per cent was isolated from soda lignin. Cyclohexanol, 4-methylcyclohexanol and 4-ethylcyclohexanol were also isolated and characterized by their boiling points and the melting points of their solid phenylurethans. A ten-carbon alcohol was isolated as its phenylurethan, but its structure has not yet been ascertained. No pure compound has as yet been isolated from the mixture of products of soda lignin boiling above the nine-carbon atom glycols (130° (1 mm)), which contained about half of the weight of the lignin submitted to hydrogenation and over 80 per cent of the products if water and methanol are disregarded. The material boiling above 200° (1 mm) is a clear rosin-like solid. It showed an average molecular weight of about 538.

Adkins (2) concludes that this information is in harmony with the concept that in methanol lignin units related to propylbenzene are joined in chains, while in soda

lignin cyclization has taken place during the process of isolation. Hydrogen over copper chromite cleaves the bond between successive C_9 units in methanol lignin, while with soda lignin the action of hydrogen is largely limited to hydrogenation of unsaturated rings and the hydrogenolysis of hydroxyl, methocyl and cyclic ether linkage, since the rings are stable toward hydrogenolysis.

III. EXPERIMENTAL PROCEDURE

Preparation of Lignin

Calcium lignin I (Ca L.I) was prepared from a commercial waste sulfite liquor (W.S.L. I) obtained from the Weyerhaeuser Pulp Co., Longview, Washington. The waste liquor was neutralized with sodium carbonate to precipitate calcium sulfite. It was then passed once through a counter-current dialyzer. The dialyzed material contained 5.95 per cent sulfur, as determined by the Parr bomb method (34).

Calcium lignin II (Ca L. II) was prepared from a second sample of commercial waste sulfite liquor (W.S.L.II) obtained from the Weyerhaeuser Pulp Co. This material was neutralized with sodium carbonate, dialyzed in a counter-current dialyzer, concentrated and redialyzed. When evaporated to dryness, the final product was black in color. It analyzed as follows: sulfur, 6.40 per cent, ash 12.4 per cent, moisture, 3.5 per cent. The sulfur, ash and moisture were determined by methods outlined by Mahin (34).

Desulfonated lignin (D.S.L.) was obtained from calcium lignin I. It was refluxed with Raney nickel in water solution. The final product contained 5.76 per cent sulfur, in spite of the fact that this treatment was supposed to remove sulfur. Apparently most of the sulfur is in such

form that it will not react with Raney nickel under the conditions used.

Lignin V (L.V.) Treatment of waste sulfite liquor with sodium hydroxide is one method of removing sulfur from the lignin compounds and under certain conditions can be used as a commercial method of making vanillin. Accordingly a sample for hydrogenation was prepared from W.S.L.I. Two liters of waste liquor were treated with 150 grams of sodium hydroxide. This solution was placed in an autoclave, heated to 200° and cooled rapidly. The resulting solution was neutralized to a pH of 4.6-5.2. The lignin is precipitated by acidification. The lignin is filtered off and used for hydrogenation.

Calcium waste sulfite liquor (Ca W.S.L.) was the dried solids from W.S.L. I.

Steam distilled lignin (S.D.L.) was obtained from W.S.L. II. The liquor was acidified with sulfuric acid and steam was passed into it until the odor of sulfur dioxide was no longer detectable. The solution was cooled and the inorganic material which precipitated was filtered off. The solution was evaporated to dryness in a vacuum evaporator.

Apparatus

For all of the experiments on hydrogenation a Parr

high pressure hydrogenator was used. Photographs and diagrams of this apparatus are shown in figure I, II, and III.

Catalysts

Raney nickel (NiR) was prepared by the procedure outlined by Adkins (1).

Copper chromite (CuCrO) was prepared by the method of Adkins (1).

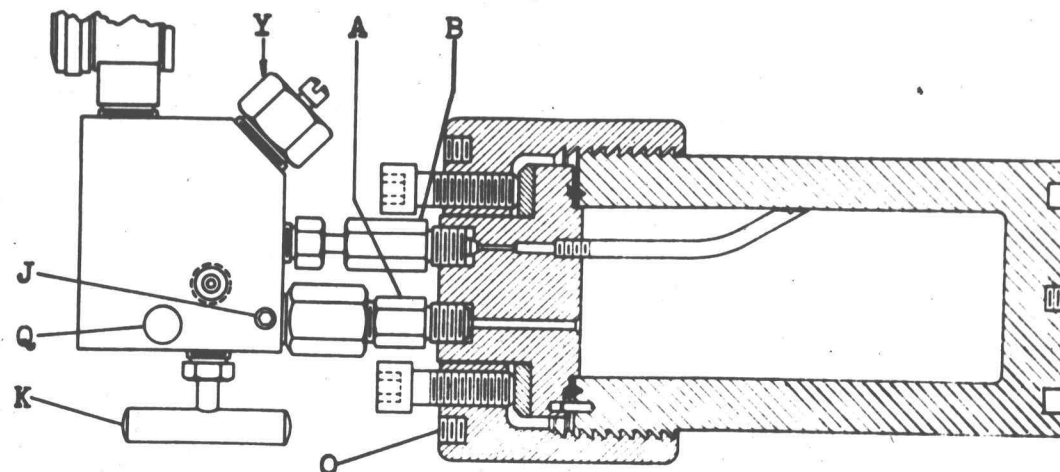
Molybdenum oxide (Mo_3O_4) was prepared by dissolving ammonium molybdate in water, heating to boiling, passing in hydrogen sulfide, then acidifying with sulfuric acid and continuing the addition of hydrogen sulfide. The precipitate was filtered off and ignited. The process was based partially on the procedure for the formation of colloidal molybdenum oxide (25).

Nickel sulfide (NiS) was prepared by dissolving nickel nitrate in water, heating to boiling, and passing in hydrogen sulfide. The precipitate was filtered and washed.

Commercial tetralin was used in the hydrogenation.

Hydrogenation

The procedure, in general, consisted of placing the dry solid in the bomb, adding solid sodium hydroxide and then water. The hydrogen was passed in to the desired



BOMB AND GAGE BLOCK ASSEMBLED, WITHOUT LINER

FIGURE I

The following parts are designated by letter on the photographs, pages 5 & 6, and in the above sketch. It is suggested that the user become familiar with the operation of each, before proceeding to use the apparatus.

A - Safety Plug
 B - Bomb-Gage connection
 C - Gage -Coil Connection
 D - Low Pressure Supply Connection
 E - High Pressure " "
 F - Tube Fitting
 G - " "
 H - " "
 J - Gage-Block Set Screw
 K - Gage-Block Valve
 L - Booster-Block Valve
 M - To Cylinder Valve

N - Lift-Out Handle
 O - Lift-Out Handle Socket
 P - Pin Wrench
 Q - Pin Wrench Socket
 R - Bomb Retainer Bolt
 S - Line Outlet
 T - Heater Cord
 U - Motor Switch
 V - Thermocouple
 W - Thermoregulator Knob
 X - Relay Cut-out Knob
 Y - Vapor Trap

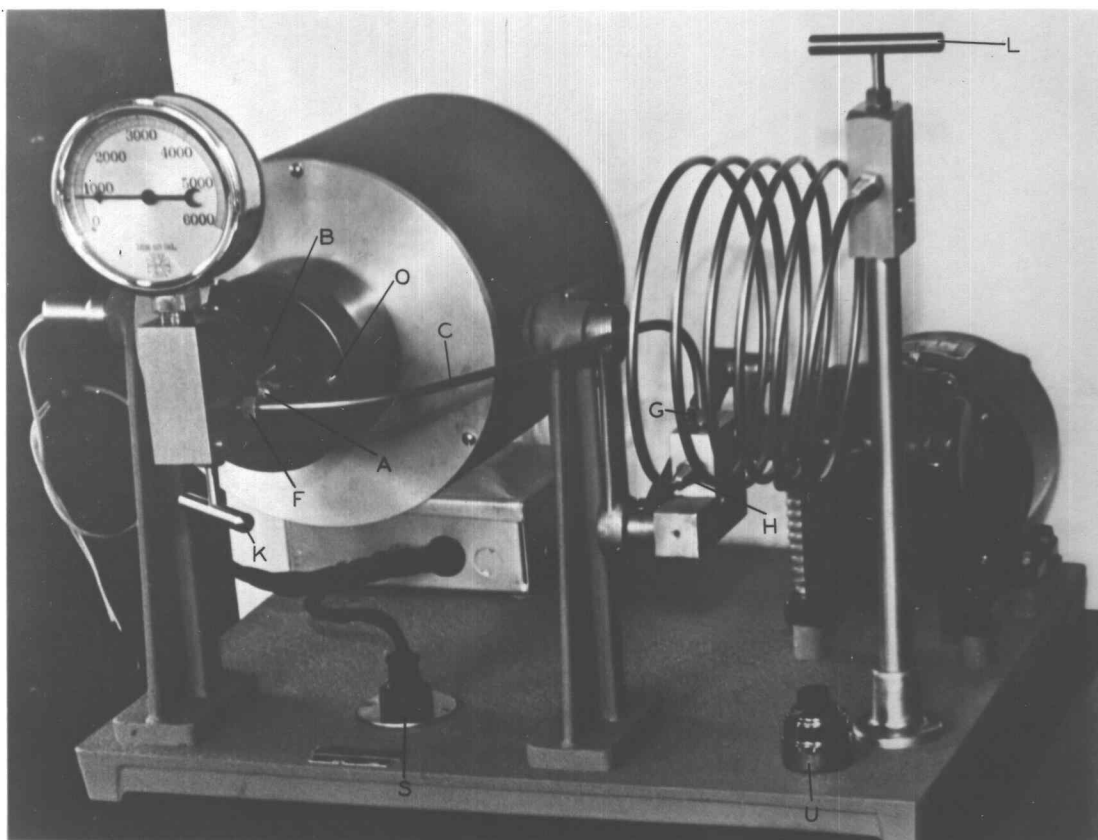


FIGURE II
FRONT VIEW OF HYDROGENATION APPARATUS

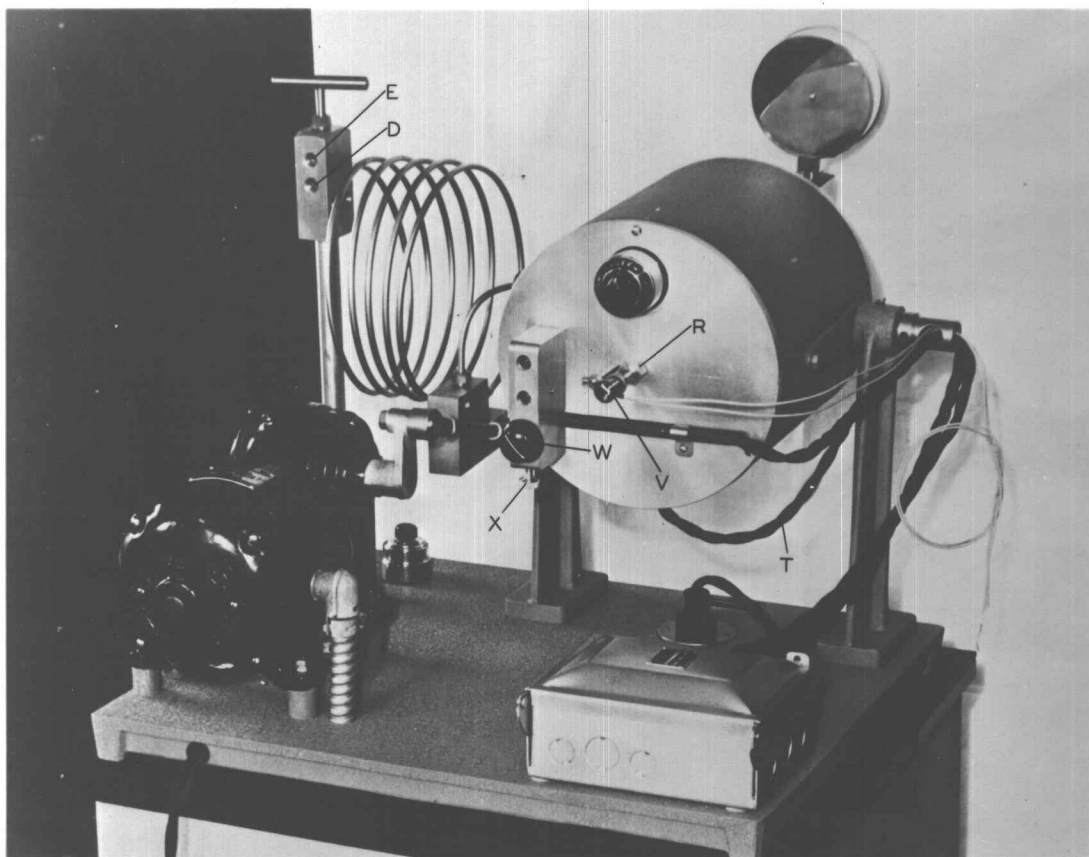


FIGURE III
REAR VIEW OF HYDROGENATION APPARATUS

pressure and the heat turned on. The bomb was shaken for the entire period of the hydrogenation and the heat was kept constant by means of a thermo-regulator on the bomb. The bomb was cooled at the end of the hydrogenation by immersing it in cold water until no further pressure drop was noticed. It was then opened and the material poured into a receiver. In the cases where some of the material adhered to the sides of the bomb it was removed by means of a metal scraper.

IV. EXPERIMENTAL RESULTS

Hydrogenations

Tables I, II and III give the data for the individual hydrogenations. The first three experiments shown in Table I gave products that were almost identical. The odor of the product was somewhat like that from the destructive distillation of wood. The only noticeable difference in the products was in number one, in that the material was adhering to the walls of the bomb. The product obtained was very light in color and the solution was clear.

In experiment four, Table I, the final product was all in solution, only catalyst remaining. A precipitate was obtained on acidifying the solution.

Experiment number five, Table I, was a double hydrogenation. The material was added and allowed to hydrogenate for 13.5 hours after which time the bomb was opened and the catalyst filtered off. Much of the lignin was adhering to the catalyst and was not returned to the solution, probably accounting for the low pressure drop in the second hydrogenation. From the second hydrogenation a clear solution was obtained by filtration. The residue on the filter paper was chiefly catalyst. On acidification of the filtrate a dark resinous precipitate formed. This

TABLE I

Hydrogenation of Lignin over Raney Nickel Catalyst

Material	Grams of Material	Grams of Catalyst	Temperature		Pressure Drop	Time Hours	Moles H Adsorbed	Grams of Material/ Mole of H
			Ave.	Max.				
1. Ca L.I	30	9	250	258	220	8.17	0.172	175
2. Ca L.I	5	9	240	270	000	6.0	0.00	---
3. Ca L.I	10	9	314	414	190	6.5	0.148	67.5
4. L. V.	15.6	8	230	250	140	9.0	0.110	141
5. Ca W.S.L.	30	8	250	258	300	13.5	0.532	56.4
		6	250	258	380	45		
					680	58.5		
6. D.S.L.	25	8	250	254	110	7	0.086	291

TABLE II

Hydrogenation of lignin over Copper Chromite Catalyst

Material	Grams of Material	Grams of Catalyst	Temperature Ave. Max.		Pressure Drop	Time Hours	Moles H Adsorbed	Grams of Material/ Mole of H
1. Ca L.II	30	5	235	254	520	4.66	0.406	73.9
2. Ca L.II	30	5	270	270	540	14	0.421	71.4
3. Ca L.II	30	5	258	264	570	8.5	0.445	67.5
4. Ca L.II	30	5	270	270	70	9.66	0.0546	550
5. Ca L.II	30	3	250	254	200	6.33	0.351	85.5
		3	250	254	250	23.67		
		6			450	30.00		
6. Ca W.S.L	30	5	250	258	300	13.5	0.531	56.5
		5	250	258	380	45		
		10			680	58.5		
7. D.S.L.	30	5	264	264	520	24	0.406	73.9
8. Ca L.II	30	5	400	410	630	23	0.493	61.0
9. Ca L.II	30	10	400	410	900	8	0.704	42.7
10. Ca L.II	30	10	400	410	500	8	0.390	77.0

TABLE III

Hydrogenation of Lignin with Miscellaneous and no Catalysts

Material	Grams of Mate- rial	Catalyst	Grams of Catalyst	Tempera- ture Ave. Max.	Pres- sure Drop	Time Hours	Moles H ad- sorbed	Grams of Material/ Mole of H
1. Ca W.S.L.	20	Tetralin	125 cc	250 258	180	24	0.141	143
2. Ca L.II	30	Mo ₃ O ₄	5	270 296	480	24	0.375	80
3. Ca W.S.L.	30	None	---	258 270	100	7	0.078	386
4. Ca W.S.L.	30	None	---	400 410	000	2	---	---
5. Ca L.II	30	NiS	10(wet)	250 254	110	17	0.086	349

precipitate was extracted with ether, but only a small portion was extractable. The first residue was also extracted with ether, but only a small portion of this was soluble.

Hydrogenation six of Table I gave a light brown clear solution with a residue of catalyst. When the solution was acidified a light gray resin formed. The remaining solution was clear and yellow in color.

Hydrogenations numbers one to four inclusive of Table II gave identical appearing material, regardless of the length of time of hydrogenation. The resulting products contained very little solid material other than the catalyst. This was separated from the solution by filtration. The solution was acidified and a precipitate formed. The precipitate and residue from hydrogenations three and four were combined and distilled in a Hickman still at one mm pressure. Some material collected in the distilling column, but not enough to identify. The solution was distilled in a Widmer column, but the initial boiling temperature was 100° , indicating that very little, if any, low-boiling material was present.

Hydrogenation number five of Table II consisted of a double hydrogenation. After the first hydrogenation the catalyst was filtered off. Air dry this weighed 4.4 grams. Three grams of catalyst were then added to the solution and

the hydrogenation repeated for about 24 hours. The final product was filtered and 7.0 grams of catalyst and residue were obtained. The solution was acidified and filtered to remove the precipitate that formed. This precipitate weighed 10.7 grams. An attempt was made to fractionate the solution by means of a Widmer column, but the first temperature of distillation was 100°.

In hydrogenation number six, Table II, the only item that was different from the previous hydrogenations with copper chromite was the gray precipitate that formed on acidification. The usual color of this precipitate was dark brown or black.

Hydrogenations numbers eight, nine and ten were similar. The product from the bomb had a dark black resinous layer on it and the solution had a dirty yellow color. The catalyst and some of the resin were adhering to the walls of the bomb and were very difficult to remove. This procedure was the basis for a more complete study of the products of hydrogenation and will be taken up later in that connection.

In the case of tetralin as a hydrogen carrier (No. 1, Table III) somewhat different results from any of the above were obtained. The odor of the gas given off was definitely that of hydrogen sulfide. The material in the bomb after hydrogenation consisted of an oil (tetralin), a water

layer and a carbonaceous residue. The mixture was filtered. The solution separated into two layers, water and oil. This was distilled and two principal fractions were obtained. The first boiled at 99° and the second at $202-7^{\circ}$, which is approximately the boiling point of tetralin (205°). There was left a small residue of a higher boiling material.

The hydrogenations using molybdenum oxide and nickel sulfide gave products that were very much like those obtained from the hydrogenation over Raney nickel.

When no catalyst was used the product obtained had a very foul odor, indicating that some decomposition or hydrogenation had occurred. The material in the bomb had carbonized and was a black solid. The solution after filtering was black in color. When number three, Table III, was acidified a small amount of dark gray precipitate formed. Number four was stopped because of trouble in the guage.

Products of Hydrogenation

After carrying out the preliminary hydrogenations, it was decided to hydrogenate a sufficient quantity of lignin, so that an attempt might be made to identify some of the products formed. For this investigation it was decided to use 30 g. of calcium lignin II, 10 g. of copper chromite,

6 g. of sodium hydroxide and 180 ml. of water. This mixture was placed in the bomb and hydrogenated at 400° for eight hours. The initial pressure was 1900 pounds.

These conditions were chosen because of the high pressure drop, the resinous layer on the top of the solution in the bomb and the fairly clear solution, plus an appreciable precipitate on acidification. The high temperature was employed in the hope of obtaining products that would consist of small molecules that could be more readily identified.

The use of sodium hydroxide was based on the work of Harris (22). In that paper he mentioned that alkali sped up the reaction, protected the catalyst from various impurities that may have been present in the solution and thereby made it possible to hydrogenate without purification samples that were readily obtained as by-products from pulping process. He also mentioned that the increased reactivity in alkaline solution may result from better contact between the hydrogen and the lignin, since the alkaline solution is a solvent for lignin, or it may be the result of a cleavage of the molecule promoted by alkali followed by the hydrogenation of the cleavage product.

The procedure was repeated under these conditions until a total of eight hydrogenations had been made. All of the products were collected in one container. A total

of 190 grams was obtained from a charge of 226 grams. The remainder was lost either as gas or was adhering to the bomb. The bomb was washed with hot water, but no attempt was made to scrape the inside clean between runs, because this was not thought to be necessary. Table IV gives the data from a typical hydrogenation of this series. The average pressure drop was 525 pounds. This varied within the range of 475 to 550 pounds.

A schematic outline of the procedure used for the separation of the material obtained is given in figure IV. The collected material from the eight hydrogenations was decanted, giving two parts. The first consisted of the solution, with a little catalyst and resin. The other part consisted of the catalyst and resin, with a little solution. Both of the fractions were then filtered and the residues combined. Harris (21) recommends centrifuging to remove the catalyst, but in this case, the resin would still be with the catalyst. Thus filtration was the preferred method of separation. The solutions were not combined because of the large volume. The residue, 120.0 g., was extracted with ether. A total of 16.9 g. was extracted.

An attempt was made to distill the ether extract in a molecular still, but due to considerable bumping this was found not to be feasible. The ether extract was then

TABLE IV

Hydrogenation of Calcium Lignin II over Copper Chromite

Time Hours	Pressure Pounds	Temp. °C.	Time Hours	Pressure Pounds	Temp. °C.
0.00	1000	20	4.30	4520	410
0.15	2520	103	4.45	4400	400
0.30	3350	216	5.00	4480	410
0.45	4300	338	5.15	4550	410
1.00	4750	380	5.30	4580	420
1.15	4850	400	5.45	4500	420
1.30	4900	400	6.00	4360	400
1.45	4975	410	6.15	4300	390
2.00	4750	400	6.30	4250	370
2.15	4900	410	6.45	4340	390
2.30	4720	410	7.00	4375	395
2.45	4780	400	7.15	4350	400
3.00	4650	400	7.30	4375	405
3.30	4750	400	7.45	4380	405
3.45	4750	430	8.00	4220	405
4.00	4680	430	Cold	1450	20
4.15	4500	420			

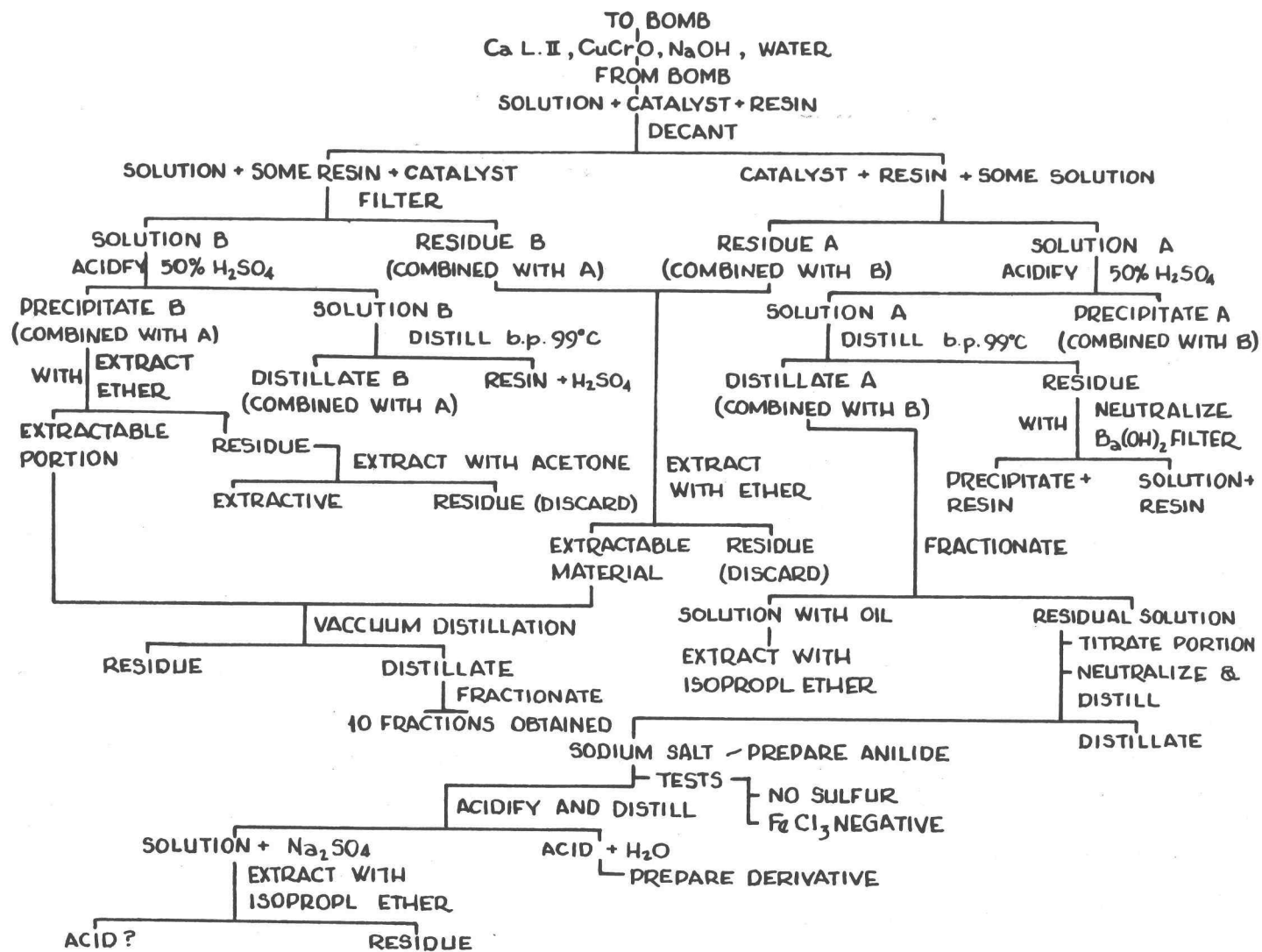


FIGURE IV
SCHEMATIC DIAGRAM OF PROCEDURE FOR ANALYSIS

placed in a distilling flask and distilled at a pressure of less than one mm. The first distillate that came over was clear and colorless. The temperature of the vapor was about 75° and that of the bath was 145° . On continued distillation the product coming over gradually changed in color from colorless to light yellow to red. A total of 5 grams was collected at this temperature and pressure. The receiver was then changed and the distillation continued until the temperature of the outside bath was 270° and that of the vapor 150° . This product was a solid. The first portion coming over was bright red, but on further distillation a dark brown solid was obtained. The yield obtained was 3 grams, making a total yield from the distillation of 8 grams.

These two distillates were later combined and an attempt was made to fractionate them in a low holdup column. Since the column had no thermometer to read the temperature of the vapor, very small fractions were taken off and the degree of separation was obtained by means of the refractive index of the material. Results of this distillation are given in Table V. The refractive indices were determined in a constant temperature bath at 25° .

The solutions obtained were distilled in a simple distillation apparatus. The first few drops coming over were cloudy and contained small colorless oil droplets.

TABLE V

Fractionation of Distillate from the Ether Extracts

Frac- tion	Temperature Bath Jacket		Color	Refractive Index	Weight of Fraction	Pres- sure mm.
1.	155	115	colorless	1.5229	1.0845	2.5
2.	158	122	yellow	1.5328	0.4710	3
3.	162	123	yellow	1.5382	0.4231	3
4.	175	140	red	1.5515	0.3608	3
5.	182	142	red	1.5635	0.2916	3.5
6.	215	125	red	1.5525	0.2400	3
7.	225	170	red	1.5571	0.5001	3
8.	234	184	brown	solid	0.6880	3
9.	235	183	brown	solid	0.2384	3
10.	250	195	black	solid	0.9880	3

The residue remaining contained enough resin to give it a black appearance. In one case this was partially neutralized with barium hydroxide to remove sulfuric acid. Due to the low solubility of this compound, great dilution results. The resin cannot be separated from the barium sulfate by filtration, but can be removed from the filter paper by dissolving in acetone.

The distillates were combined and fractionated in a column packed with glass helices. The temperature of the vapor was 99° . The first portion of the distillate contained yellow oil droplets and was cloudy. A fraction was taken off until the material being removed was no longer cloudy. This fraction amounted to about 75 cc. It was then extracted with isopropyl ether in an attempt to obtain the acid.

A portion of the residual solution was titrated against standard base. This solution was found to be 0.18 normal. The remainder was neutralized with sodium hydroxide and distilled. A solid sodium salt was obtained. A qualitative test showed that sulfur was absent. (This was the only possibility other than carbon, hydrogen and oxygen.) Ferric chloride also gave a negative test, indicating that the material was not a phenol. The preparation of the anilide was attempted. The product obtained was difficult to recrystallize. After three attempted re-

crystallizations a dark brown amorphous solid was obtained. It had an indefinite melting point of about 60-68°. A second portion of the salt was acidified with sulfuric acid. Only a very slight odor was noticed. To a faintly acid solution of the salt, phenylphenacylbromide was added. After refluxing the mixture for one hour and cooling, a white crystalline solid was obtained. Recrystallization four times gave an ester melting at 68-70°. The common acids whose phenylphenacyl esters melt in a comparable range are n-valeric (63°), iso-valeric (76°), caproic (65°), caprylic (67°) and heptylic (62°). The acid could not be obtained in sufficient purity to obtain its neutral equivalent. The procedures used for these analyses were obtained from Shriner and Fuson (39). In contrast to results obtained by other workers there was no indication of an alcohol in the fractionation.

V. DISCUSSION OF RESULTS

Table I tends to show that in a single hydrogenation Raney nickel does not catalyze the reaction. This is what would be expected since it is definitely known that a very small amount of sulfur will poison a large quantity of Raney nickel. The table also indicates that refluxing the lignin preparation with nickel does not aid in stopping the poisoning action. The analytical data also shows that the sulfur is not appreciably removed by refluxing. A double hydrogenation, with Raney nickel shows promise of giving a satisfactory hydrogenation. If we assume that the lignin content is about 50 per cent of the lignin containing material entering the bomb (30 per cent of the tree was lignin, about 50 per cent of the tree passed into solution and this material was merely the dried solids from a cook) then the value obtained for the number of grams of lignin per mole of hydrogen adsorbed would be about 28. This is in good agreement with any of the data that are given for hydrogenation.

In Table III, the only material that shows promise as a catalyst is the molybdenum oxide, but the value obtained for the grams of material per mole of hydrogen is higher, almost 50 per cent, than any given in the literature. This table shows definitely that no hydrogenation will occur

without a catalyst.

Hydrogenation number nine, Table II, cannot be considered valid, because repeated hydrogenations under the same conditions will not give a pressure drop above 600 pounds. Hydrogenation number four, Table II, also might be considered invalid. It is entirely possible that the bomb had not reached room temperature before the pressure was released. In general, it can be said that copper chromite will give hydrogenation of sulfonated lignin. While the amount of hydrogen absorbed is lower than that obtained by Harris (22), it is in better agreement with Hatihama (24), who obtained 40-45 grams of lignin per mole of hydrogen.

In the analysis of the products formed nothing definitely was found, but a few comparisons can be made. The total high-boiling distillate obtained was 8 grams. This represents 3.34 per cent of the lignin-containing material entering the bomb or 4.18 per cent of the lignin (80 per cent of material charged into bomb). Adkins (2) in his work obtained 6.57 per cent of material that distilled between 76° and 145° at 0.3 mm pressure. Since no account is made for losses, this is in fair agreement with the value obtained. However the total distillate is represented in this case and not in Adkins' work (2). If we assume that the total ether extract would distill below 235° (0.2 mm),

a second comparison is possible. The ether extract was 16.5 per cent of the lignin-containing material entering the bomb or 20.6 per cent of the lignin. Adkins obtained 29.2 per cent yield under the conditions stated. Again it will be noted that the agreement is fairly good. The refractive indices cannot be compared with Adkins, since none are given for his fractions. The values obtained by Harris (22) for the refractive indices of the normal propylcyclohexane derivatives range from 1.4615 to 1.4801. None of the refractive indices obtained in this work were less than 1.5229. This shows that the major part of the distillate is not the same as products obtained by Harris. The boiling points of the products obtained are not in good agreement with those found by Harris.

In the work with soda lignin, Adkins (2) presented the theory that cyclization of the lignin has occurred and therefore the small nine carbon atom compounds will not be found to any great extent. The meager evidence presented here would be in line with the idea that a similar change takes place during treatment of wood with sulfurous acid.

No alcohol was isolated by fractionation. Harris (22) obtained a 5 per cent yield of methanol. This also tends to show that the products obtained are different.

The one item found that neither Adkins nor Harris mentioned was an acid. From the behavior of the sodium salt

and the melting point of the phenylphenacyl ester, it is fairly certain that the acid is not acetic, but that it contains 5-8 carbon atoms. Since none of the dicarboxylic acids can be steamed distilled these are also ruled out. In the literature on lignin no mention is made of acids, other than the dicarboxylic, acetic and some aromatic acids. This is some evidence that the hydrogenation of sulfonated lignin does not produce the same products as the other lignin materials. Inasmuch as the purity of the lignin is not known the possibility of the acid being produced from material other than the lignin is not ruled out.

VI. SUMMARY

A brief discussion of lignin and some of the reasons for the interest in this substance have been presented.

A review of the literature on the hydrogenation of lignin has also been given, together with reasons for interest in this type of work.

Attempts have been made to hydrogenate sulfonated lignin over a variety of catalysts. Of those investigated, copper chromite was found to be the most satisfactory catalyst.

A few products were isolated and an attempt was made to identify them.

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