THE SOLVENT EXTRACTION OF LIGNIN WITH DIOXANE

by

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TABLE OF CONTENTS

List of Figures

SOLVENT EXTRACTION OF LIGNIN WITH DIOXANE

OBJECTIVE

The basic aim of this investigation was to find an economical method of producing a commercial lignin which would be a suitable raw material as an extender in the production of plastics.

It was hoped that the experiments and work completed would provide the essential information necessary to develop the method and process further.

INTRODUCTION

Each year there is a lignin production of over 2,500,000 tons, most of which is burned or run down the sewer. Some of this lignin is recovered by treating the waste liquors from pulp mills with acid and obtaining a powdered lignin resin. This resin is used as an extender with phenolic resins. However, the amount of lignin used by this means is not large.

Up to the present time no large measure of success has been achieved in using it alone or as a reaction product in a commercial plastic. As a plastic the lignin obtained by present methods lacks flow characteristics so necessary for a satisfactory molding material. The specific properties of the plastic are limited when using lignin obtained by present methods.

Lignin is also used as a binder in a lignin enriched fibrous cellulose. The resulting mixture is pressed into sheets and used in the building industry.

If an economical method could be found for recovering the waste lignin and yet produce a suitable product whose properties are better than those obtained by present means, the major problem would be solved.

N. B. Pewter has developed a method (4, P. 106-109) of obtaining lignin from the Soda or Kraft pulp-making process and they claim that the product has a low melting

point and is moldable. It is used for a paper base laminate in the manufacture of table tops. The color is a deep walnut brown and the resulting product is very tough and stable.

It is hoped that the work in this thesis will help in finding an economical process of obtaining a lignin with good properties for use as an extender and as a resin.

The methods of isolating lignin may be divided into two classes: (1) those that depend on the removal of the cellulose and other components, leaving the lignin as an insoluble residue, and (2) those that depend on the removal of lignin from the cellulose and other substances.

The methods of class one, as mentioned above, use a rather drastic treatment of the wood generally with a strong acid. Class two includes the sulfite method which is the basis of the sulfite pulping process, an alkali method which is used in the production of paper pulp, separation by alcoholysis including the dioxane method, and extraction with phenols and other miscellaneous methods.

In whatever method used, it is difficult to obtain a lignin which is similar to the native lignin. Brauns seems to have been the most successful in obtaining a native lignin on a very small scale suitable for laboratory purposes. The discussion here is concerned with

commercial scale production methods. The methods of class one are rather drastic and seem to give a polymerized lignin. The sulfite method of class two gives a lignin not in the free state but in the form of water soluble sulfonic acids. The alkali method of class two seems to give an undesirable polymerized lignin. Separation by alcoholysis is objectionable because in all cases a product is obtained containing the alkyl or aryl group in combination with the lignin.

It was decided that the work in this thesis would be confined to the extraction of lignin with dioxane. Dioxane contains no hydroxyl groups, is unreactive, is a good solvent, and has reasonable cost.

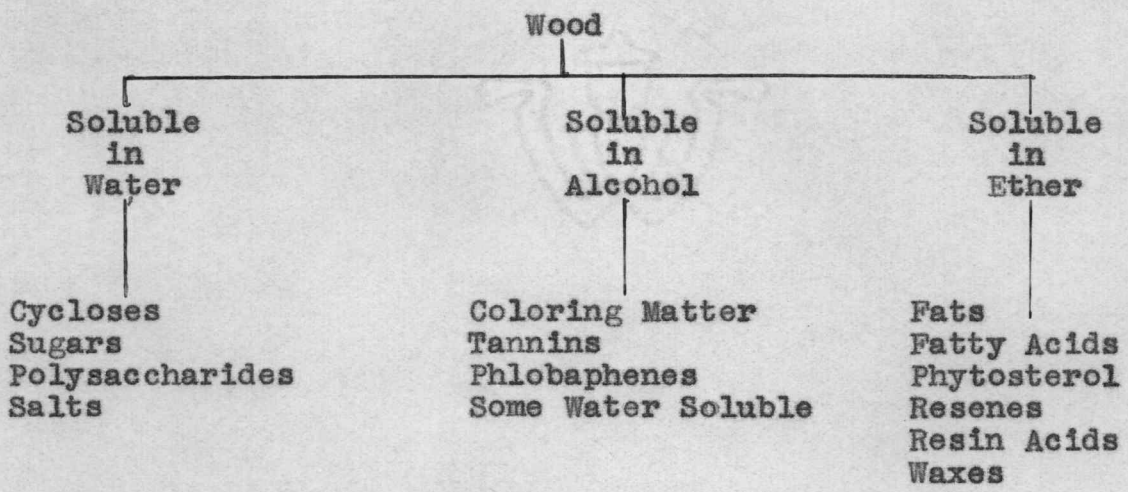
The method of separation of lignin from wood with dioxane was patented in Germany by Engel and Wedekind in 1932. However, the efforts of these German scientists seem to have been chiefly directed toward obtaining a lignin for laboratory purposes.

Since it is known that dioxane offered a good possibility as a solvent for the extraction of lignin, it was decided to use it and determine how the various variables would affect the process.

In the method (3, P. 2434-8) used by Engel and Wedekind the wood was warmed with dioxane in the presence of small quantities of catalysts, HCl or HAc, on a

water bath for 12 to 22 hours after which the lignin was precipitated by ether. The equipment seems to have been a flask with a reflux condenser. The presence of a catalyst seems to be essential. The German scientists have not attempted to determine the exact effect of varying the concentration of acid used as a catalyst or the length of the extraction time. Engel and Wedekind used 100° C as the extraction temperature.

The materials comprising the extractives of wood are multitudinous and when wood is extracted with dioxane it can be assumed that there will be a complex mixture of many components in the solution. In general these components can be divided into three classes as listed below with the various components in each class.



In the dioxane extract there would probably be an appreciable amount of each of the components listed. The

components which are soluble in water and in ether are undesirable and it is evident that these components can be removed from the lignin precipitate by treatment with warm water and ether. If the lignin precipitate were treated with alcohol, the tannins, phlobaphenes and others could be removed but in so doing the alcohol would also dissolve a considerable amount of the lignin. Since the tannins and phlobaphenes are phenolic in character, it would not seem objectionable to have them present in the commercial lignin for use in plastics. Therefore, the alcohol treatment was eliminated.

There have been numerous studies and structural formulas proposed for lignin, but this thesis was not concerned with the determination of formulas for lignin. The main objective of this study was to obtain a product which showed good promise of being a suitable raw material for the plastics industry. The quantitative determination of the methoxyl groups present serves as an indication of the nature of the product as well as the color of the product obtained. Numerous color reactions can be used to determine whether or not the product is lignin.

The variables encountered in the extraction of lignin are: (1) concentration of the acid used as a catalyst, (2) extraction time, (3) temperature, (4) pressure. Those conditions which are the most economical and

give a suitable product would be the ones to use. There seems to be nothing in the literature which would indicate exactly how all these variables affect such an extraction. Engel and Wedekind completed their extraction at 100° C. They varied the acid concentration but have not indicated in detail what its effects were. They have also indicated that in from 12 to 22 hours of extraction a certain per cent of lignin was obtained, but it is not known definitely how it varies with time. The experiments performed by the German scientists were completed at one atmospheric pressure.

If the method proposed in this thesis is to be of value, it is necessary to know in detail how the variables affect the extraction. The effect of acid concentration and time can be determined by means of extractions in a Soxhlet extractor. To determine the effect of temperature and pressure, it will be necessary to use some type of a pressure vessel, probably an autoclave. The work in this thesis is directed toward finding how the variables of acid concentration and time affect such an extraction.

Aronovsky and Gortner (1, P. 1270) have done some work on the extraction of lignin with dioxane using an autoclave. Their extractions were completed at a pressure of 60 psi. The per cent lignin obtained by this

method was approximately 15.

A considerable amount of experimental work remains to be done using an autoclave at various pressures. The conditions encountered while using an autoclave will more closely approach those which might be used in an industrial process.

The chief value of the work in this thesis is as follows: (1) to determine a feasible method of extracting the lignin, recovering the dioxane, precipitating the lignin, filtering, treating the residue, etc., (2) to determine how the acid concentration and time affect the extraction, (3) to determine an economical means of recovering the dioxane from the water solution, (4) to determine how various percentages of water in the dioxane will affect the extraction, (5) to investigate the peroxide formation in the dioxane, (6) to determine how much dioxane is absorbed by wood chips, (7) to determine how concentrated a lignin extract can become before lignin commences to precipitate, and (8) to determine the dilution of concentrated lignin extract necessary to recover 100 per cent of lignin.

The boiling point of dioxane is 101.6° C and therefore it is very difficult to separate dioxane and water by ordinary distillation. It was found that dioxane can be separated from water by salting the dioxane out of

solution and that this method would seem to offer the best possibility for success. Various bases and salts were used in these experiments.

Ethers tend to form peroxides if exposed to air for any considerable length of time. When these ethers are distilled, explosions frequently occur. If dioxane is to be used, a means must be found to inhibit this peroxide formation and make the dioxane safe to distill. It was found that a small amount of water in the dioxane will inhibit this peroxide formation and will probably be satisfactory providing a reasonable per cent yield of lignin is obtained. There is a method (2,P.52-54) of removing peroxides from dioxane by passing the dioxane through activated Al_2O_3.

PROCEDURE

Procedure for Obtaining a Representative Sample of Wood

A few extractions were completed using White Fir and the majority of the extractions were completed using Western Hemlock since it is the chief source of pulp for the paper industry.

The samples of wood were obtained from the forestry department at Oregon State College. They were cross sections of trees about 10 or 12 inches in diameter. The wood was solid and all the bark was removed. Chips, about $\frac{1}{2}$ inch long and from $\frac{1}{4}$ to $\frac{1}{2}$ inch wide, were prepared from these samples of wood.

Moisture Determination in Wood Sample

A representative sample of wood was ground into sawdust and a small sample was placed in a weighing bottle. The sample was dried at a temperature of approximately 100° C for two hours. From the loss in weight the per cent of moisture was readily calculated.

These results were checked several times.

Lignin Extraction

The wood sample was cut into chips approximately $\frac{1}{2}$ inch long and from $\frac{1}{4}$ to $\frac{1}{2}$ inch wide and this sample was

then weighed. The weighed chips were placed in a 300 ml. Soxhlet extractor. Approximately 450 cc. of technical grade dioxane were placed in the Soxhlet extractor with enough concentrated HCl to make the desired acid concentration in the dioxane. The extractor was heated by means of a hot plate and the heat was so adjusted that there were between 4 and 8 siphonings per hour. The heat for all comparative samples was so adjusted that each apparatus siphoned at the same interval of time. Thus the results are comparative.

At the end of the desired extraction time the extract was filtered and distilled. The distillation was continued until only 10 or 15 cc. of concentrated solution remained in the flask. The condensed, distilled dioxane was re-used after purification. The concentrated extract was diluted with warm water in the ratio of approximately 10 to 1. This water precipitates the lignin plus numerous other substances. A very small amount of NH_4Cl was added each time to help precipitate the lignin. Warm water was used since it was thought it might help to prevent the precipitation of sugars along with the lignin.

The solution containing the lignin was filtered through a weighed fritted glass filter using a Bailey ring and a suction flask. The lignin precipitate was washed with warm water to dissolve any sugars and other

carbohydrates which were precipitated with the lignin. This lignin precipitate was dried at approximately 70°C for about 3 hours and then washed repeatedly with ethyl ether until further washings with clean ethyl ether produced no coloration of the ether.

The lignin precipitate was then dried for several hours at approximately 60°C until further drying produced no additional loss in weight. The glass filter and lignin precipitate were then weighed. The per cent lignin residue was then calculated.

Lignin Extraction With a Certain Amount of Water Added to the Dioxane

The procedure for the extraction was the same as with pure dioxane except for a certain amount of water being present in the dioxane. The amount of water added varied from 3% to 30%.

Recovery of Dioxane from Water Solution

The boiling point of dioxane is 101.6°C and water 100°C. Therefore the separation of these two substances by distillation is impossible.

It was decided to try the method of salting the dioxane out of the solution. Various salts and bases were used including NaOH, NaCl, NH_4Cl, ZnO, Na_2CO_3, and $CaCl_2$.

The procedure when using NaOH was to prepare a

concentrated NaOH solution about 11 normal. This solution was standardized. Fifteen cc. of H_2O and 10 cc. of dioxane were placed in each of several gas burettes. Concentrated NaOH was added to each burette in an amount which would make the desired concentration of the water layer. The concentration varied from 10 to 30 per cent. The number of cc. of dioxane recovered was determined and the per cent dioxane recovery calculated.

The procedure when using the remaining salts was to add the required amount of dry salt to each of several burettes containing 15 cc. of H_2O and 10 cc. of dioxane such that the resulting water layer would be of a certain concentration of salt. The cc. of dioxane recovered was then noted. The concentrations of the water layers were varied.

The experiments were repeated until the results clearly indicated the exact nature of the separation.

Recovery of the Dioxane Absorbed by the Chips

The procedure for determining the exact amount of dioxane absorbed per unit weight of chips was as follows:

After the completion of the dioxane extraction of the lignin, the dioxane solution was completely removed from the Soxhlet extractor containing the chips. About 450 cc. of water were added to the Soxhlet extractor and

the extraction was continued for four hours. The water solution containing the dioxane removed from the chips was drained from the Soxhlet and the dioxane was recovered by salting the water-dioxane solution with NaOH. The dioxane was separated in a separatory funnel and measured in a burette. Since the original weight of the dry chips and the cc. of the dioxane recovered were known, the cc. of dioxane absorbed per unit weight of chips was now also known.

At the end of the four-hour water extraction the above experiment was repeated with fresh water to determine whether or not all the dioxane had been removed from the chips in the first four-hour extraction.

The above experiment was repeated with other samples of chips until the results were nearly the same.

Procedure for Determining How Much to Dilute the Concentrated Lignin Extract in Order to Recover 100% of the Lignin in Solution

A small amount of the lignin precipitate was weighed and placed in a beaker. One hundred cc. of dioxane were added to dissolve the lignin. Then water in the ratio of 3 parts of water to 1 part of dioxane was added. The solution was filtered in a fritted glass filter. Additional water was added to the filtrate in the ratio of 5 to 1 and the resulting solution filtered in a clean

filter. This procedure of dilution and filtration was repeated. Each filter was dried and weighed and the weight of lignin obtained from each dilution was obtained.

Duplicate samples were run in all cases.

Peroxide Determination

A small amount of KI is dissolved in a small amount of dilute acid so that HI will be formed. The solution to be tested is mixed with this HI solution and if there are peroxides present the free iodine will be liberated which is tested with starch solution. This is not an exact quantitative test, but it does give comparative results. The more peroxides present, the darker will be the color when tested with starch solution.

RESULTS

Lignin Extraction With Pure Dioxane

Samples 1 to 5 inclusive were white fir sawdust and the acid content varied from 0.1% HCl to 0.2% HCl. Extraction time varied from 12 to 23 hours. The results of these 5 extractions offer no conclusive results, but they do indicate that a 0.1% acid concentration does not give a good extraction. 0.2% HCl gives somewhat better results, giving as much as 21.54% lignin residue in 23 hours of extraction.

Samples 6 and 7 were performed with western hemlock sawdust and with an acid concentration of 0.1% for sample 6 and 0.3% for sample 7. The results of these two extractions give results similar to those of samples 1 to 5 in that they show 0.1% HCl as giving a low yield while 0.3% HCl gives a reasonably good yield.

Figure I indicates the rate of extraction for the remaining samples using western hemlock chips and pure dioxane. An acid concentration of 0.2% seems to be too low. The rate of extraction for those samples with an acid content of 0.4% to 2.0% seems to be approximately the same. Higher acid concentrations such as 1.5% and 2.0% give a higher rate of extraction during the first 4 hours, after which the rate decreases. All samples

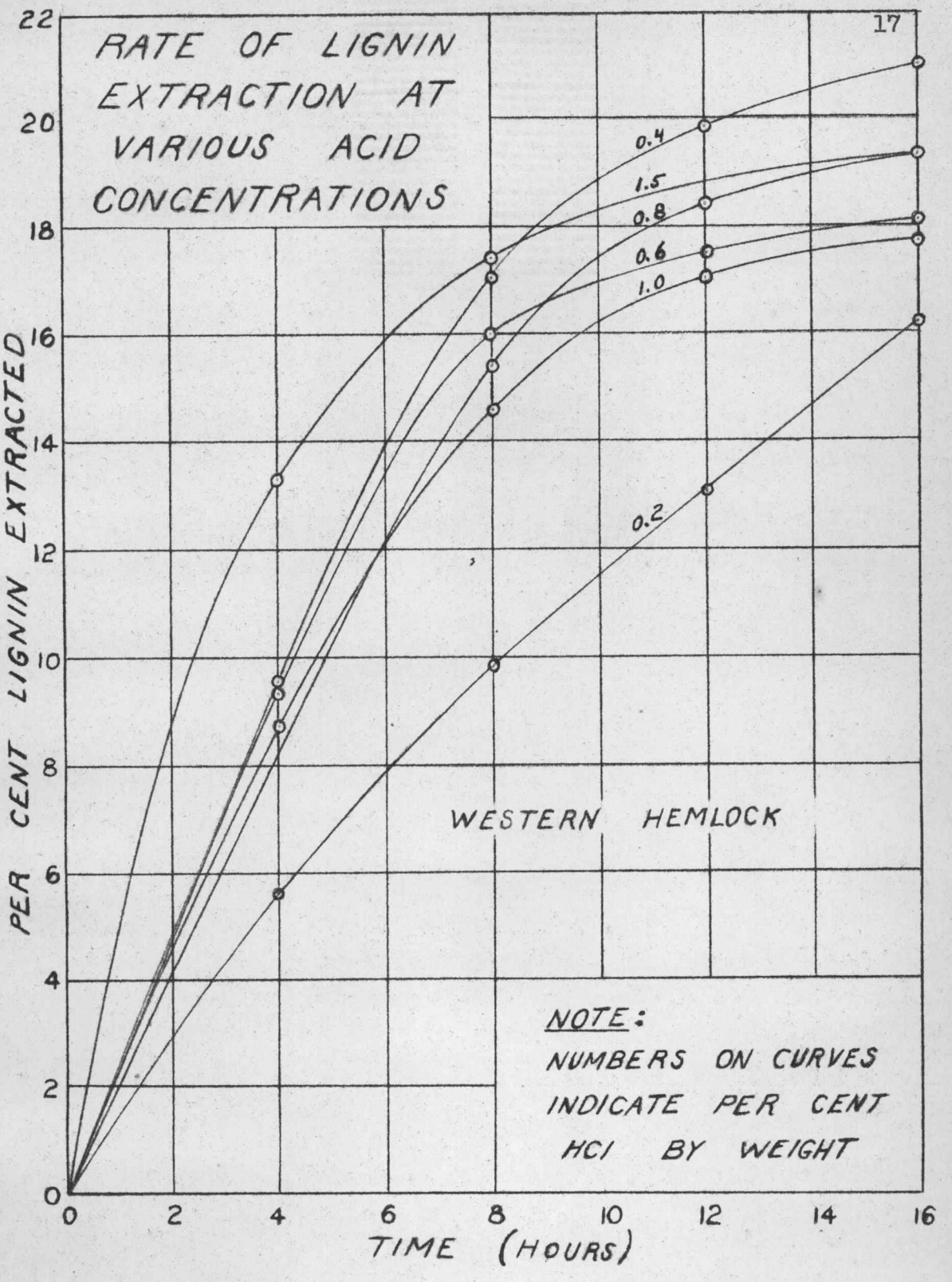

RATE OF LIGNIN EXTRACTION AT VARIOUS ACID CONCENTRATIONS
PER CENT LIGNIN EXTRACTED
TIME (HOURS)
0.4
1.5
0.8
0.6
1.0
0.2
WESTERN HEMLOCK
NOTE:
NUMBERS ON CURVES INDICATE PER CENT HCl BY WEIGHT
0
2
4
6
8
10
12
14
16
18
20
22

FIGURE I

seem to give a fairly rapid rate of extraction during the first 8 hours. It is to be noticed that a 0.4% acid concentration gives as good a yield as 1.5% acid concentration at the end of 8 hours and a higher per cent yield at the end of 16 hours.

The color of the lignin residue obtained starts with a very light brown at a low acid concentration of 0.2% or 0.4% HCl and becomes progressively darker as the acid concentration is increased. 1.5% or 2.0% HCl gives a very dark product. This is expected since higher acid concentration causes greater polymerization.

Lignin Extraction With Water Added to the Dioxane

Since dioxane tends to form peroxides and is dangerous to distill, it was thought that the addition of a certain per cent of water to the dioxane would inhibit the peroxide formation and yet give a satisfactory yield of product.

From the results of the extractions with pure dioxane, 0.4% HCl concentration was chosen as the optimum acid concentration since it gives the most satisfactory yield and the color of the product obtained is light in color.

Samples 19 through 24 inclusive were extracted with a 0.4% HCl concentration and with varying percentages of

water in the dioxane. Sample 25 was completed with 1.0% HCl. The results of the extractions are shown in Table VIII and Figure II. From these results it is apparent that a small percentage of water in the dioxane will yield as high a per cent of lignin as pure dioxane. Sample 25 with 3% water present yields 16.6% lignin at the end of 8 hours' extraction time which is nearly the same yield as that obtained using pure dioxane and an acid concentration of 0.4% HCl. Sample 15 with pure dioxane and 0.4% HCl yields 17.08% lignin at the end of 8 hours.

From these results it is indicated that a water concentration of as high as 3% can be used in the dioxane with satisfactory yields. The presence of this amount of water would inhibit the peroxide formation and make the dioxane solution safer to handle.

The color of product obtained is light brown.

Results of Dioxane - Water Separation

The method of salting the dioxane out of solution was used. Several salts and bases were used in these experiments including NaOH, NaCl, NH_4Cl, ZnO, $CaCl_2$, and Na_2CO_3.

The NaCl concentration in the water layer was varied

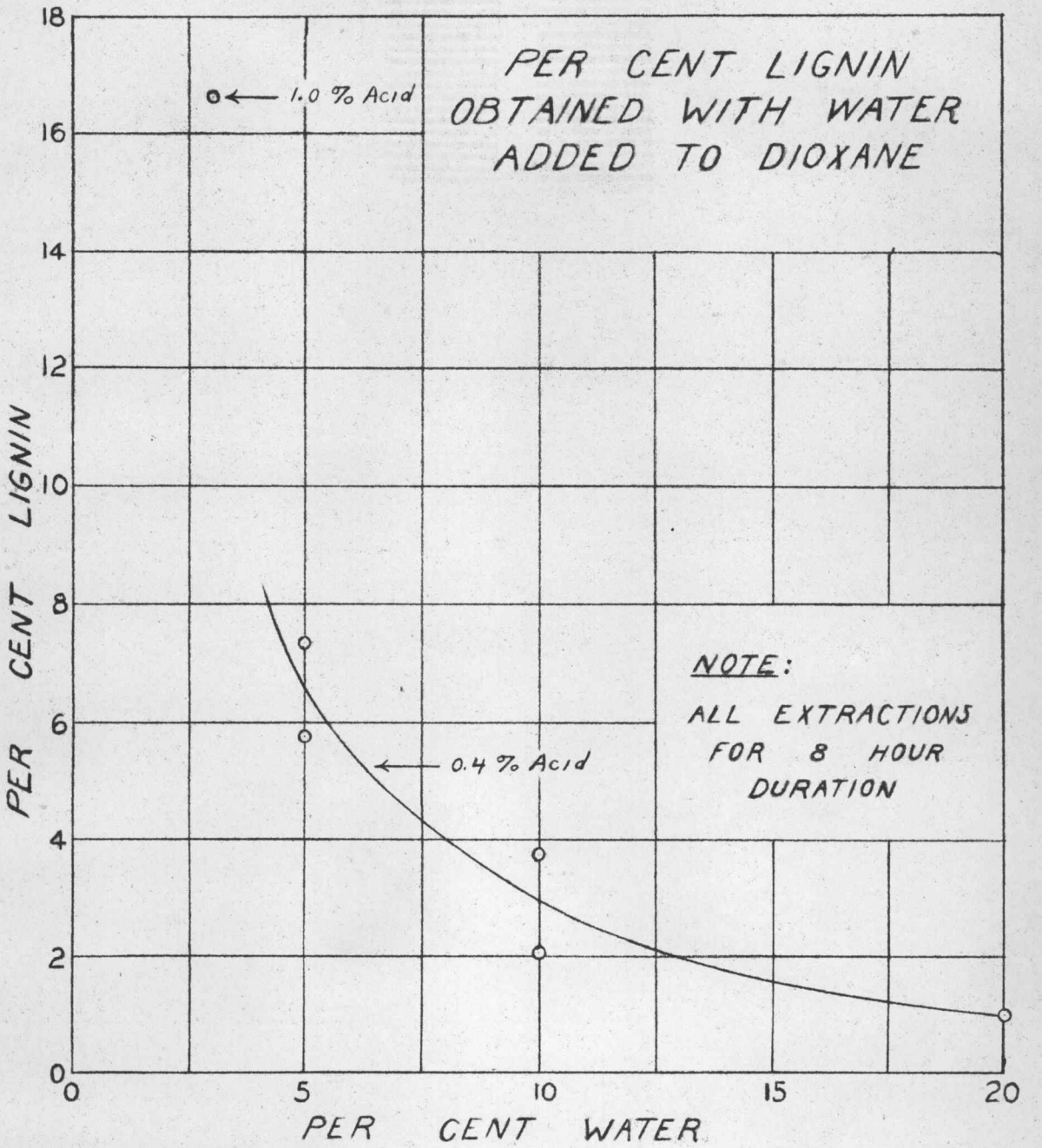

PER CENT LIGNIN OBTAINED WITH WATER ADDED TO DIOXANE
1.0 % Acid
0.4 % Acid
NOTE:
ALL EXTRACTIONS FOR 8 HOUR DURATION
PER CENT LIGNIN
PER CENT WATER
0
2
4
6
8
10
12
14
16
18
0
5
10
15
20

FIGURE II

from 14% to 26% with no separation of dioxane. At 26% concentration, crystals of NaCl formed in the bottom of the burette.

There was no separation using NH_4Cl, ZnO and $CaCl_2$. The $CaCl_2$ concentration was increased to as high as 40%.

Na_2CO_3 gives a separation into two layers. The results using Na_2CO_3 are shown in Table III. The concentration of Na_2CO_3 was varied from 14% to 24%. A large amount of water separates with the dioxane layer even at a high concentration of Na_2CO_3 and this is not satisfactory. The use of sodium carbonate as a salting out agent seems to be unsatisfactory.

Sodium hydroxide seems to give satisfactory results. The results using NaOH are shown in Tables IV and V and also in Figure III. If the concentration of NaOH in the water layer is increased to 24% or higher it is possible to recover 96% to 100% of the dioxane originally in solution.

These experiments were repeated several times in order to verify that the results as shown are accurate.

Experiments to Determine the Necessary Dilution of the Concentrated Lignin Dioxane Solution in Order to Precipitate all of the Lignin

The results of these experiments are shown in Table VI and differ somewhat in regard to the per cent recovery

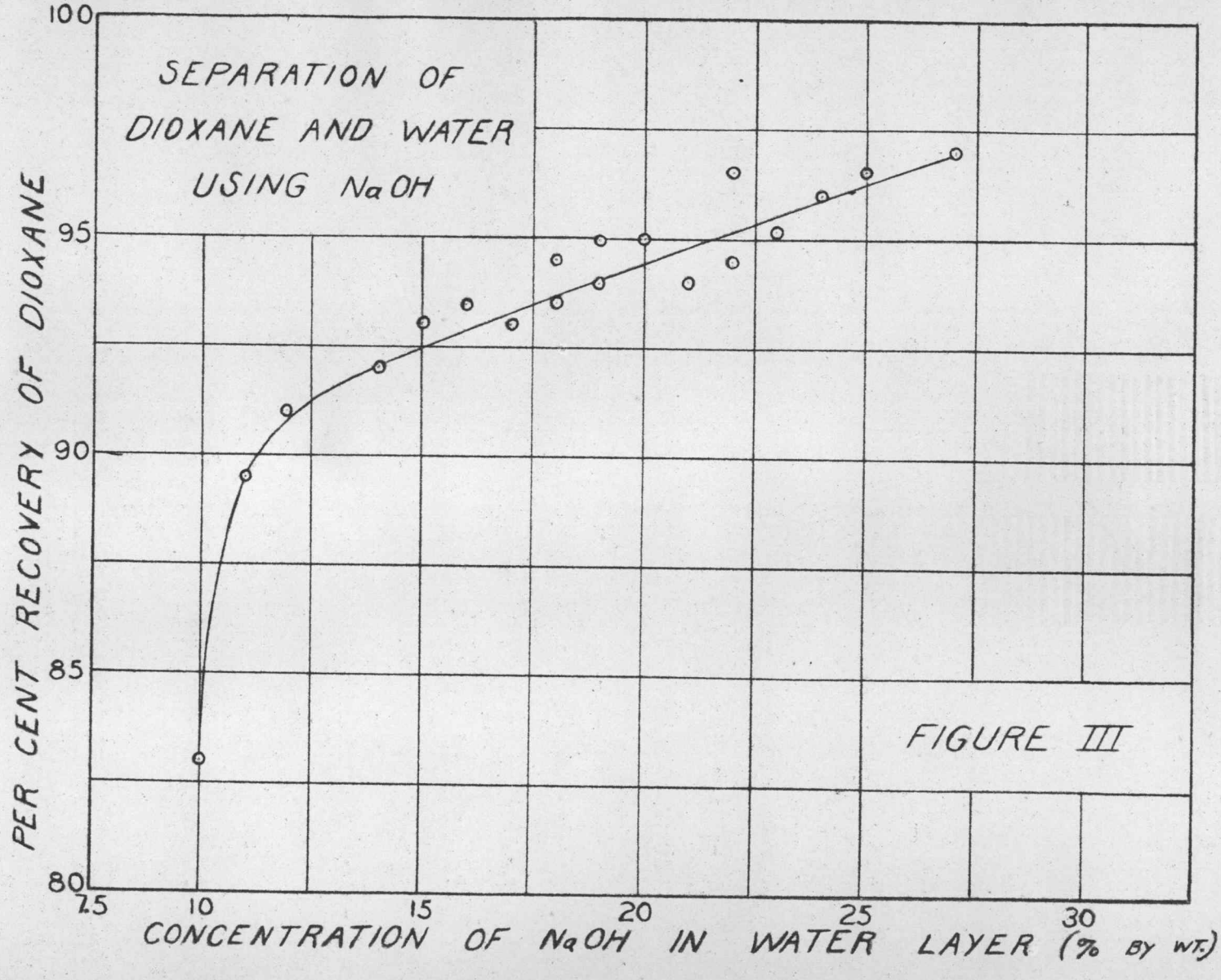

SEPARATION OF
DIOXANE AND WATER
USING NaOH
PER CENT RECOVERY OF DIOXANE
100
95
90
85
80
2.5
10
15
20
25
30
CONCENTRATION OF NaOH IN WATER LAYER (% BY WT.)

FIGURE III

of the lignin, possibly due to experimental error. Duplicate runs on redissolved lignin solutions indicated that it required a 7 to 1 dilution of the original concentrate in order to recover 100% of the lignin. From 77% to 97% of the lignin was recovered with a 3 to 1 dilution.

These results were verified on an original extracted solution.

Results of Experiments to Determine the Amount of Dioxane Absorbed by the Chips and Later Recovered

These results are shown in Table VII. The average amount of dioxane absorbed per gram of wood chips on the dry basis is 1.09 cc.

Results of Experiments to Determine How Much a Dioxane Lignin Solution can be Concentrated Before Lignin Precipitates

With all extractions the dioxane lignin solution was concentrated to about 15 cc. before any lignin precipitated. The amount of lignin residue in these solutions varied from 0.1 to 1.8 grams.

Therefore it is possible to concentrate the solution to 10% or 12% lignin by weight before the lignin residue commences to precipitate. Concentrating these solutions too much might tend to cause greater polymerization and be harmful to the product. Also if the

solution is concentrated too much it would be more dangerous since increased peroxide concentration might result in an explosive mixture.

Result of Peroxide Determination

This test was performed on technical grade dioxane and also on the dioxane recovered from the distillation of the lignin dioxane solution.

The technical grade dioxane was found to contain some peroxides. This experiment does not give an exact quantitative determination but just comparative results.

CONCLUSIONS

The results of this investigation may be summarized in a few general conclusions.

One: It is possible to extract lignin with pure dioxane and obtain 60% to 70% of the lignin in a reasonable length of time.

Two: It is possible to obtain a good yield of lignin with 3% of water present in the dioxane.

Three: Lower acid concentration such as 0.2%, 0.4% and 0.6% give lighter colored products. Higher acid concentrations such as 1.5% and 2% give very dark-colored products probably due to greater polymerization.

Four: An acid concentration of 0.4% HCl seems to give as good yields as higher acid concentrations while any concentration lower than 0.4% does not give a good yield.

Five: Dioxane can be recovered from the water solution by salting the dioxane out of solution with sodium hydroxide. A 30% NaOH concentration in the water layer will give nearly 100% separation of the dioxane.

Six: It requires about a 7 to 1 dilution of the concentrated lignin extract in order to precipitate all

of the lignin in solution.

Seven: The amount of dioxane absorbed by the chips averages approximately 1 cc. per gram of chips, and this dioxane can be recovered.

Eight: The lignin extract can be concentrated to approximately 10% to 12% lignin by weight in solution before lignin commences to precipitate.

Nine: There are considerable amounts of peroxides present in technical grade dioxane. These can be removed and it is believed that a small amount of water present will inhibit further peroxide formation.

Ten: The color of the product obtained at a lower acid concentration appears good. The methoxyl content is approximately 15%.

BIBLIOGRAPHY

1. Aronovsky, S. I. and Gortner, R. A. Pulping properties of certain organic reagents. Industrial engineering chemistry 28: 1270, 1936.

2. Dasler, Waldemar and Bauer, Clifford D. Removal of peroxides from dioxane. Industrial engineering chemistry, Analytical edition 18: 52-54, 1946.

3. Engel, O. and Wedikind, E. Extraction of spruce wood with dioxane and the composition of natural lignin. Chemical abstracts: 1199, 1937 and Bericte 69B: 2434-2438, 1936.

4. Powter, N. B. Canada develops new form of lignin. Modern plastics 24: 106-109, Apr. 1947.

5. Simonds, Herbert R., Bigelow, M. H. and Sherman, Joseph V. The new plastics. 2nd ed. New York, D. Van Nostrand co., 1945. 320p.

6. Winding, Charles C. and Hasche, Leonard R. Plastics theory and practice. New York, McGraw and Hill book co., 1947. 280p.

7. Wise, Louis E. Wood chemistry. New York, Reinhold publishing corp., 1944. 900p.

APPENDIX

TABLE I

Lignin Extraction With Pure Dioxane

Sample Number	Wood Used	Form of Sample	Acid	Time (Hrs.)	Yield	Color of Product
1	White Fir	Sawdust	0.1	8	3.7	Light Br.
2	White Fir	Sawdust	0.1	12	8.2	Light Br.
3	White Fir	Sawdust	0.2	16	13.56	Light Br.
4	White Fir	Sawdust	0.1	16	9.8	Light Br.
5	White Fir	Sawdust	0.2	23	21.54	Light Br.
6	West. Hem.	Sawdust	0.1	24	7.6	Light Br.
7	West. Hem.	Sawdust	0.3	24	20.97	Light Br.
8	West. Hem.	Chips	0.3	*		
9	West. Hem.	Chips	0.2	*		

* Samples 8 and 9 were discarded.

TABLE II

Lignin Extraction With Pure Dioxane

(Western Hemlock Chips)

Sample Number	% Acid	Cumulative % Lignin Residue* 4 Hrs.	8 Hrs.	12 Hrs.	16 Hrs.	24 Hrs.	30 Hrs.	Color of Product
10	0.2	3.34	8.68	11.82	13.61	15.3	15.9	Light Br.
11	0.6	9.43	16.00	17.55	18.17			Med. Br.
12	1.0	5.26	9.36	11.76	13.12	14.6		Dark Br.
13	1.0	8.74	14.57	17.03	17.75			Dark Br.
14	1.5	13.28	17.40	18.53	19.33			Dark Br.
15	0.4	9.61	17.08	19.87	21.00			Light Br.
16	0.2	5.70	9.83	13.10	16.19			Light Br.
17	0.8	6.60	15.43	18.37	19.30			Med. Br.
18	2.0	12.63						

* Based on moisture-free sample.

TABLE III

Results of Dioxane Water Separation Using Na_2CO_3

Con. Na_2CO_3 in H_2O Layer	cc. Water	cc. Dioxane Used	gms. Na_2CO_3 Added	cc. in Dioxane Layer
14	25	5.65	4.07	13.8
16	25	5.65	4.76	12.6
20	25	5.65	6.25	10.6
24	25	5.65	7.90	9.2

TABLE IV

Results of Dioxane Water Separation

Conc. H_2O Layer	cc. H_2O Used	cc. Dioxane Used	cc. NaOH* Added	cc. Dioxane Recovered	% Recovery
10	15	10	4.80	8.95	89.5
12	15	10	5.37	9.25	92.5
13	15	10	5.98	9.30	93.0
14	15	10	6.62	9.35	93.5
15	15	10	7.30	9.30	93.0
16	15	10	8.02	9.35	93.5
17	15	10	8.83	9.30	93.0
18	15	10	9.65	9.45	94.5
19	15	10	10.50	9.50	95.0
20	15	10	11.45	9.50	95.0
21	15	10	12.46	9.40	94.0
22	15	10	13.52	9.65	96.5
24	15	10	15.92	9.60	96.0
26	10	10	12.50	10.00	100.0
28	10	10	14.81	10.00	100.0

* Normality = 11.105

TABLE V

Results of Dioxane Water Separation

Conc. H_2O Layer	cc. H_2O Used	cc. Dioxane Used	cc. NaOH* Added	cc. Dioxane Recovered	% Recovery
10	15	10	4.6	8.30	83.0
12	15	10	5.86	9.10	91.0
14	15	10	7.26	9.20	92.0
16	15	10	8.90	9.25	92.5
18	15	10	10.71	9.35	93.5
19	15	10	11.74	9.40	94.0
20	15	10	12.89	9.30	93.0
21	15	10	14.08	9.40	94.0
22	15	10	15.35	9.45	94.5
23	15	10	15.75	9.52	95.2
24	15	10	18.38	9.60	96.0
25	15	10	20.05	9.65	96.5
26	15	10	21.90	9.63	96.3
27	15	10	24.0	9.70	97.0

* Normality = 11.105

TABLE VI

Results of Dilution of Concentrated Extract With Water

Run No. 1			Run No. 2		
Dilution	Weight of Residue	% Recovery	Dilution	Weight of Residue	% Recovery
3 to 1	0.896	97.1	3 to 1	0.226	77.1
5 to 1	0.013	1.41	5 to 1	0.016	5.46
7 to 1	0.024	2.6	7 to 1	0.007	2.37
9 to 1	None		9 to 1	None	

TABLE VII

Dioxane Absorbed by Chips

Sample Number	Weight of Wood Sample (gms.)	cc. Dioxane Recovered	cc. Dioxane Absorbed per Gram of Wood
16	13.710	13.55	0.987
17	12.612	13.34	1.06
18	13.823	16.90	1.22

TABLE VIII

Lignin Extraction With Water and Dioxane

(Western Hemlock Chips)

Sample Number	% Acid	% Water	Time (Hrs.)	% Lignin Residue	Color of Product
19	0.4	10	8	2.06	Light Br.
20	0.4	20	8	0.955	Light Br.
21	0.4	30	8	0.818	Light Br.
22	0.4	5	8	7.35	Light Br.
23	0.4	10	8	3.78	Light Br.
24	0.4	5	8	5.77	Light Br.
25	1.0	3	8	16.60	Med. Br.

SAMPLE CALCULATIONS AND DATA

SAMPLE NO. 15 (Typical for all extractions)

Wt. of wood sample and beaker	=	51.501 gms.
Wt. of empty beaker	=	38.706 gms.
Wt. of sample	=	12.795 gms.
Per cent moisture	=	9.25
Wt. of sample on dry basis	=	11.615 gms.
Acid content	=	0.4 %

Wood used - Western Hemlock
Form of wood sample - Chips
Amount of 37% HCl to add to 150 cc. = 1.407 cc.*

Extraction Time (hours)	1-4	5-8	9-12	13-16
Time started	5:27	5:15	4:45	9:05
Time ended	9:27	9:15	8:45	1:05
Wt. of filter and treated residue	31.844	26.423	26.401	24.751
Wt. of empty filter	30.726	25.555	26.077	24.620
Wt. of lignin residue	1.118	0.868	0.324	0.131
Per cent lignin	9.61	7.47	2.79	1.13
Cumulative % lignin	9.61	17.08	19.87	21.00

* Calculation of cc. of 37% HCl (Sp. gr. = 1.188) to add to 150 cc. of dioxane to make 0.4% HCl

$$\text{Sp. gr. of dioxane} = 1.03$$

$$\frac{x}{(150)\ (1.03) + x} = 0.004$$

$$x = 0.618 \text{ gm. HCl}$$

$$\frac{0.618}{0.37}(1.188) = 1.407 \text{ cc. } 37\% \text{ HCl}$$

MOISTURE DETERMINATION

Wt. of wood sample = 1.969 gms.
Wt. of dried sample = 1.787 gms.
Loss in weight = 0.182 gms.

$$\text{Per cent moisture} = \frac{0.182\ (100)}{1.969} = 9.25\% \text{ wet basis}$$