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Title The Dioxane Extraction of Lignin From Wood

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In order to determine the effect of acid and water concentrations on the rate of extraction of lignin, the desired quantities of wood and extracting liquor, made from the necessary amounts of technical grade dioxane, concentrated hydrochloric acid, and water, were placed in a flask fitted with a reflux condenser and boiled for the desired length of time, samples being withdrawn at intervals. The extraction rate increased with increasing acid concentrations up to 7 per cent anhydrous HCl, but then decreased with higher acid concentrations. The optimum concentrations so far as the yield and appearance of both lignin and pulp were concerned were found to be 5 per cent anhydrous HCl and 14 to 18 per cent water, the remainder being dioxane.

The yield of pulp varied from 45 to 55 per cent of the dry wood charged, while the lignin recovered was 25 to 30 per cent of the dry wood.

THE DIOXANE EXTRACTION OF LIGNIN FROM WOOD

by

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THE DIOXANE EXTRACTION OF LIGNIN FROM WOOD

OBJECT

The primary objective of this investigation was the determination of the influence of acid and water concentrations on the rate of extraction and ultimate yield of lignin from wood during a dioxane extraction. It was also desired to produce a sufficient quantity of product that work might be started on its utilization for plastics.

INTRODUCTION

Each year pulping liquors alone produce 1,500,000 tons of lignin, only a small part of which is recovered and used. Forest and sawmill wastes offer an additional source of several million tons annually (3).

It has been known for some time that dioxane will extract lignin from lignocellulose materials, but little is known about the rate of extraction and the final yield of product. In 1932, Wedikind and Engel (10) developed a process, but did not publish any details, for the delignification of wood at atmospheric pressure and about 90°C. (9) by using dioxane in the presence of a little HCl. The concentrations used were presumably 3 to 5 per cent concentrated hydrochloric acid, about 1 to 2 per cent anhydrous HCl (4).

Nikitin and Orlova (5) extracted 16 to 23.7 per cent crude lignin from spruce wood sawdust in 12 to 22 hours, using dioxane with 0.12 to 0.75 per cent HCl on a water bath. Their crude lignin was precipitated from the dioxane extract with ether and contained about 16 per cent pentosans. Aronovsky and Gortner (1) report that aspen sawdust extracted for four hours at 176°C. with dioxane removed 65.1 per cent of the lignin present, 4.8 per cent of the alpha cellulose, and 67.1 per cent of the pentosans. The residual pulp obtained was brown and quite pliant. A similar process was patented in the United States in 1935 by Henry Dreyfus (2), in which lignin is extracted from materials such as wood, straw, or grass with the use of an organic medium such as dioxane at an elevated temperature (170-200°C.) and at pressures above atmospheric.

Most of the experimentation using dioxane as an extracting liquor seems to have been directed toward the preparation of small quantities of lignin for laboratory purposes. However, the research department of Howard Smith Paper Mills Limited (7) has developed a process for the recovery of a moldable, low melting point form of lignin from waste liquors of the kraft pulping process. The material is used in the manufacture of a paper base laminate which is reported to be very tough and stable. The Handbook of Plastics gives a fairly complete list of the properties of plastics made from lignin (9, p. 74-76) and also presents a process for the manufacture (9, p. 743) of these plastics.

The work presented here was done with the hope that it will aid in the search for an economical method of obtaining lignin for the plastics industry.

Wood contains a number of so-called extractive materials which may be removed by treating the wood with various solvents (11, p. 385-440). When treated with water, substances such a cycloses, polysaccharides, sugars, and salts are removed. With alcohol, coloring matter, tannins, phlobaphenes, and some water solubles are removed, while ether will extract fats, fatty acids, phytosterol, resenes, resin acids, and waxes. An acid dioxane extraction would remove appreciable quantities of most of these substances as well as the lignin, but the use of water for precipitation and the subsequent washing will remove most of the water soluble materials from the lignin. Hilpert and Wisselinck (4) report that when the extraction is carried out on fructose instead of

wood, the fructose dissolves, immediately becomes brown, and, on dilution with water, gives a precipitate which when washed and dried turns to a black powder. Since tannins and phlobaphenes are phenolic in nature, their presence in lignin used for plastics would not be objectionable, and no attempt was made to remove them. It was first proposed to make an ether extraction on the lignin precipitate, but there proved to be such a small amount of ether soluble material present that the ether wash was discontinued. Throughout this thesis, the term lignin designates all the material which is precipitated from the dioxane extract by the addition of water.

The principal variables encountered in such an extraction process are: (1) acid concentration, (2) water concentration, (3) extraction temperature, (4) extraction time, (5) wood particle size, and (6) liquor ratio. In addition, it is desirable to determine the conditions which will give the greatest recovery of dioxane.

EXPERIMENTAL PROCEDURE

It was first proposed to perform the extractions in a large soxhlet apparatus, but considerable difficulty was encountered in getting good performance from the apparatus. Since such an extraction takes place at a much lower temperature than the temperature in the boiler, it took place at a very slow rate, and the extracted materials were subjected to high temperatures for long periods of time. The apparatus also requires a large supply of heat for operation. Therefore, the soxhlet was abandoned in favor of a reflux apparatus, which requires much less heat and which performs the extraction at a higher temperature.

Since the moisture content of wood changes over a period of time, the extractions were made with oven-dry wood so that they would be comparable with each other. After thus establishing the approximate range of optimum concentrations, further extractions were made on undried wood to establish the extraction rates.

The desired quantities of wood and extracting liquor, made from the necessary amounts of technical grade dioxane, concentrated hydrochloric acid, and water, were placed in a flask fitted with a reflux condenser and heated with a bunsen burner. The mixture was then kept at a slow boil (194°F.) for the desired length of time, samples being withdrawn at intervals. The samples were filtered through paper, cooled to 25°C., and a portion pipetted into about five times its volume of water. The resulting precipitate was filtered through a weighed fritted glass filter, washed with water, and dried to constant weight. The

percentage of extracted material was then readily calculated.

At the end of the extraction time, the pulp was filtered from the liquor, shredded, and washed twice with clean dioxane, which removed practically all of the extracted materials. This filtrate was then concentrated by distillation to 10 to 12 per cent lignin and poured slowly, with vigorous stirring, into about seven times its volume of water. The resulting precipitate was then filtered, washed thoroughly, and dried. The pulp material was washed with water to remove the dioxane present, four washings being used. The first such wash contained considerable extraneous materials, but the last three were sufficiently clean that they were used to make up part of the water used for precipitation of the lignin. Solid sodium hydroxide was then added slowly to the total volume of water solution collected, until the caustic concentration was 25 per cent. At this concentration, 95 to 97 per cent of the dioxane present in the water is salted out (6) and easily recovered.

The determination of the methoxyl content of the lignin was used as a measure of the quality of product obtained.

RESULTS

Figures 1, 2, 3, and 4 show graphically the effect of acid concentration, water concentration and time on the extraction of oven dried one half inch Douglas fir chips, with a liquor ratio of 10 milliliters per gram of wood. The rate is seen to increase with increasing acid concentration. However, above 7 per cent anhydrous HCl, the rate is again decreased. That the increase of HCl concentration allows an increased water concentration in the liquor can be seen from figures 5 and 6, the curves generally passing through a definite maximum. Figures 7 and 8 show the results of extractions performed on undried Douglas fir chips and sawdust. The moisture content of the chips was 9.4 per cent on the dry basis, while that of the sawdust was 11.3 per cent. The presence of moisture in the wood decreased the extraction rate somewhat, and also decreased the optimum water concentration. The water concentrations and liquor ratios shown include the moisture introduced with the wood.

At a liquor ratio of 10 milliliters per gram of dry wood, the extraction proceeded more rapidly with 7 per cent HCl than with 5 per cent HCl. However, this situation was reversed (Figures 7 and 8) when a liquor ratio of 5 to 1 was employed. Furthermore, the results were rather erratic, and the product obtained was nearly black at 7 per cent HCl. The water concentration was increased as far as practicable, consistent with good yields. The optimum concentrations, so far as yield and appearance of both lignin and pulp were concerned, were found to be 5 per cent anhydrous HCl and 14 to 18 per cent water, the

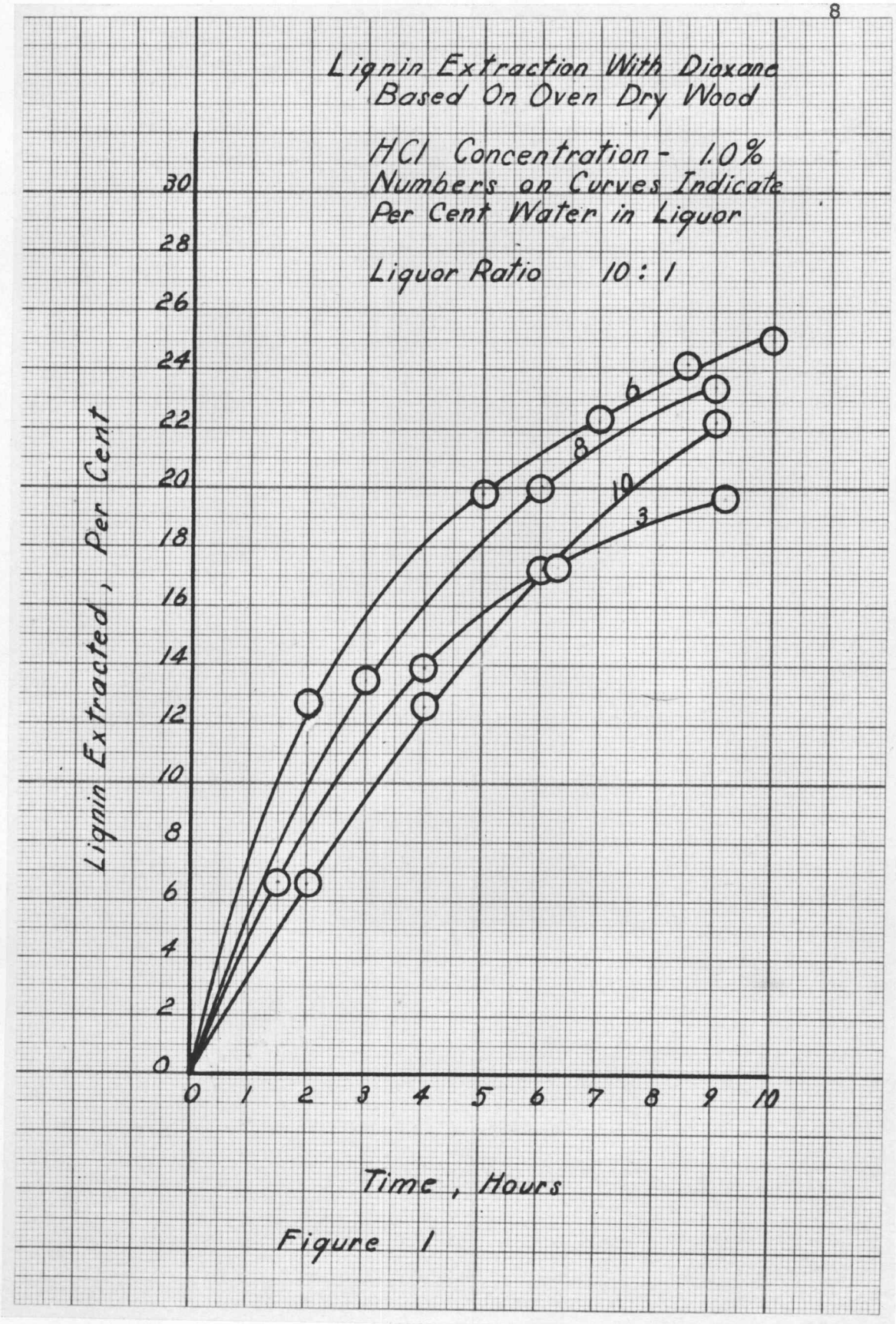
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration - 1.0%
Numbers on Curves Indicate
Per Cent Water in Liquor
Liquor Ratio 10 : 1
Lignin Extracted, Per Cent
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0 1 2 3 4 5 6 7 8 9 10
Time, Hours
6
8
10
3

Figure 1

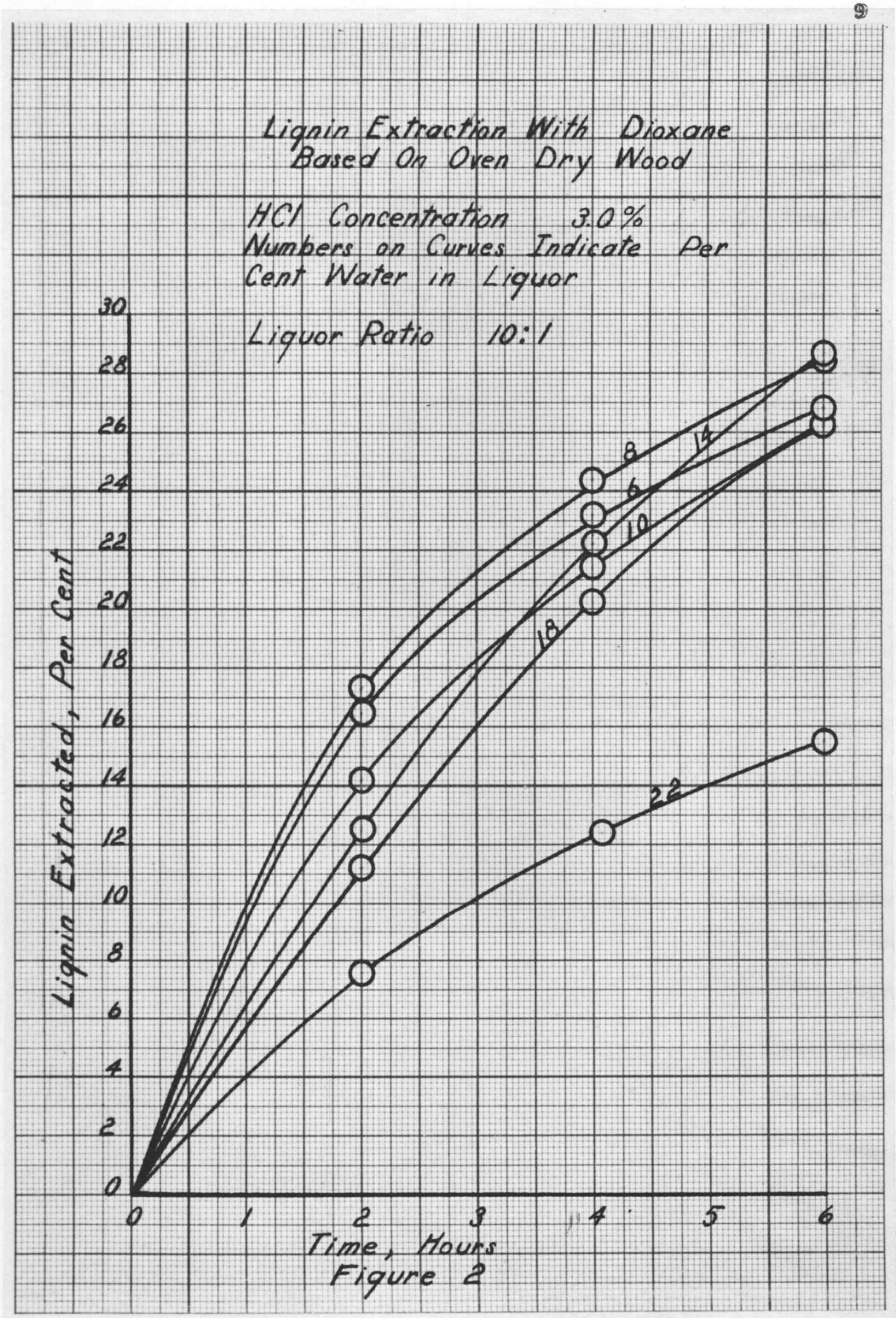
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration 3.0%
Numbers on Curves Indicate Per Cent Water in Liquor
Liquor Ratio 10:1
Lignin Extracted, Per Cent
Time, Hours
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
8
6
10
14
18
22

Figure 2

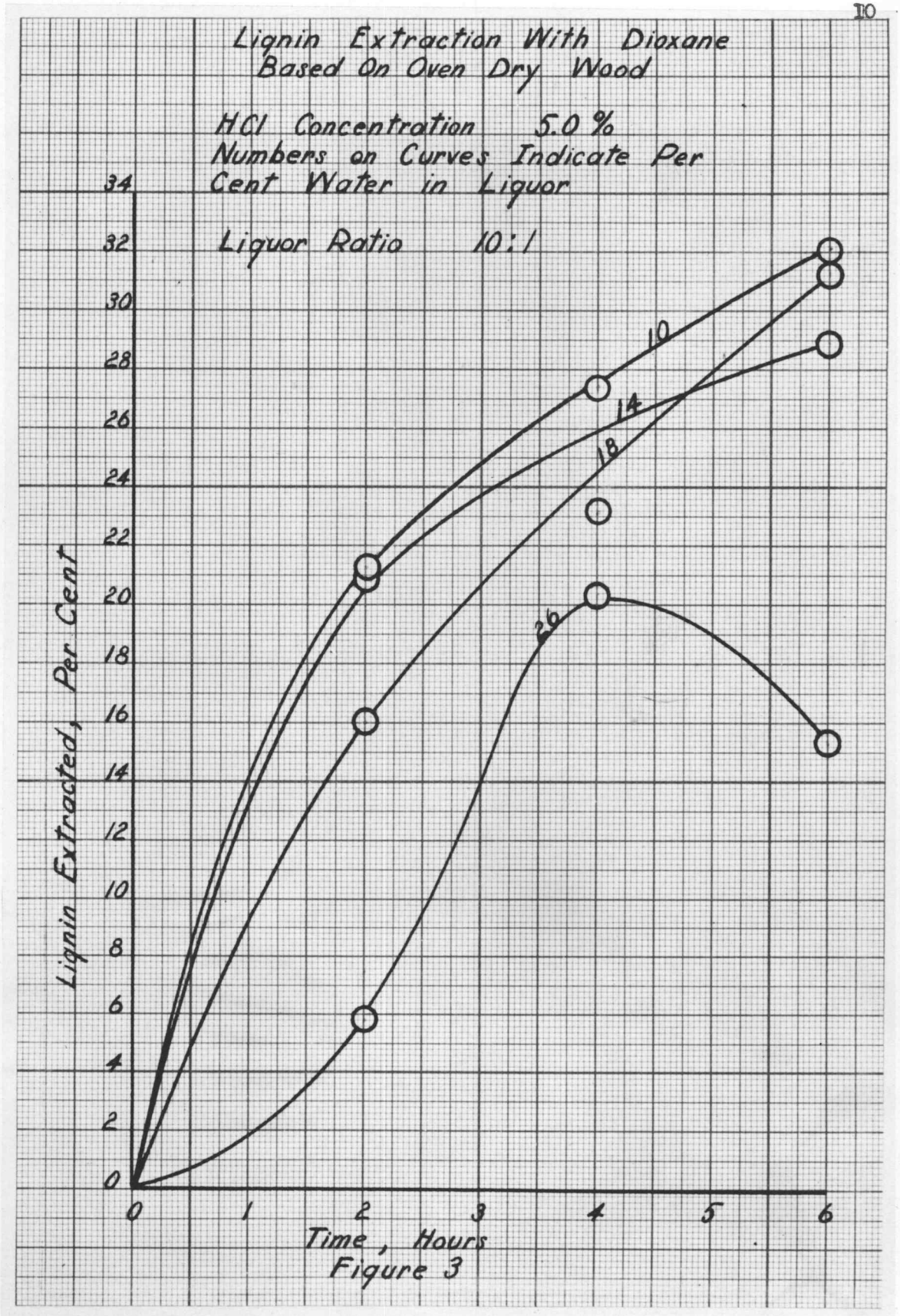
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration 5.0 %
Numbers on Curves Indicate Per Cent Water in Liquor
Liquor Ratio 10:1
Lignin Extracted, Per Cent
Time, Hours
10
14
18
26
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
0
1
2
3
4
5
6

Figure 3

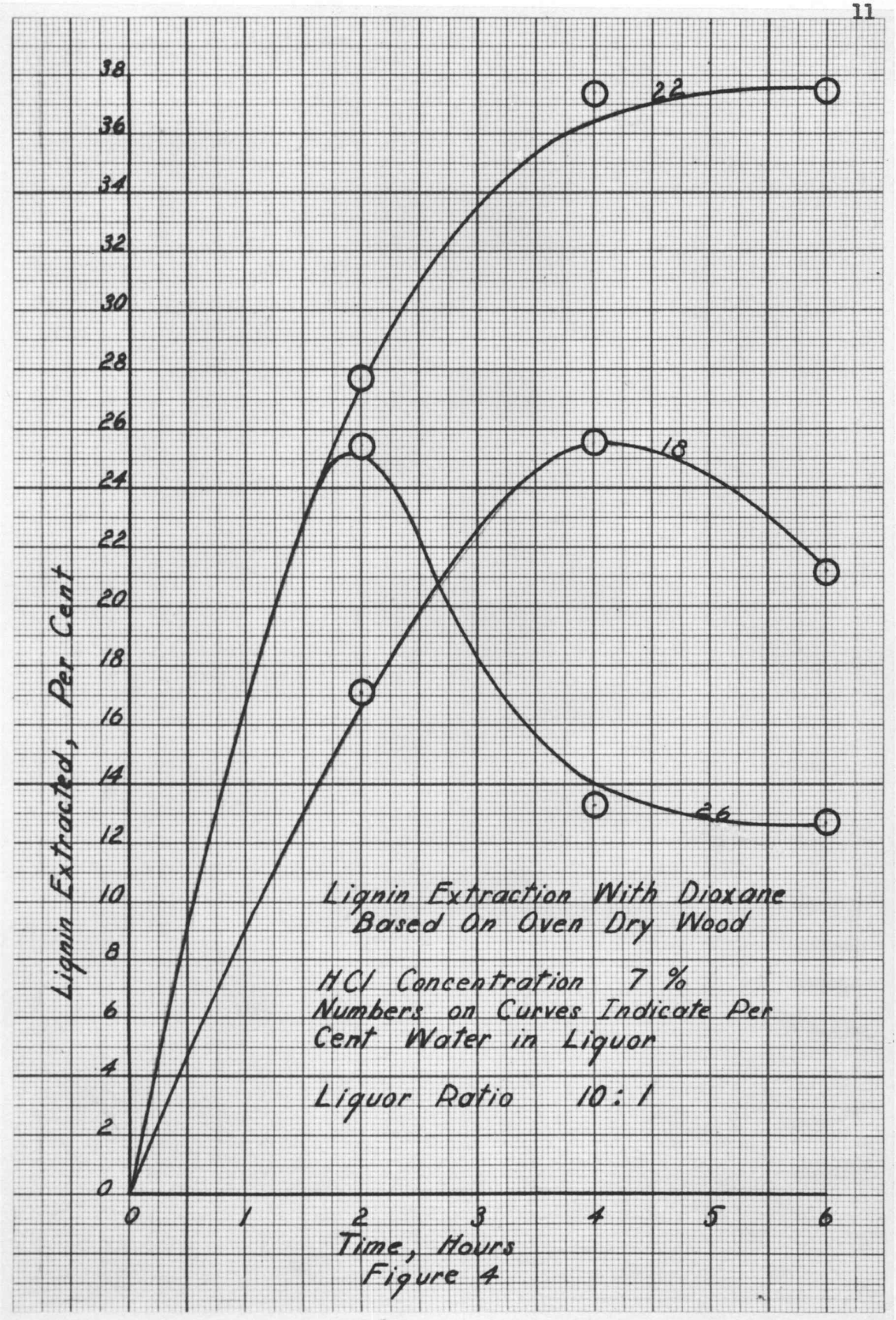
Lignin Extracted, Per Cent
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
0
1
2
3
4
5
6
Time, Hours
22
18
26
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration 7 %
Numbers on Curves Indicate Per
Cent Water in Liquor
Liquor Ratio 10 : 1

Figure 4

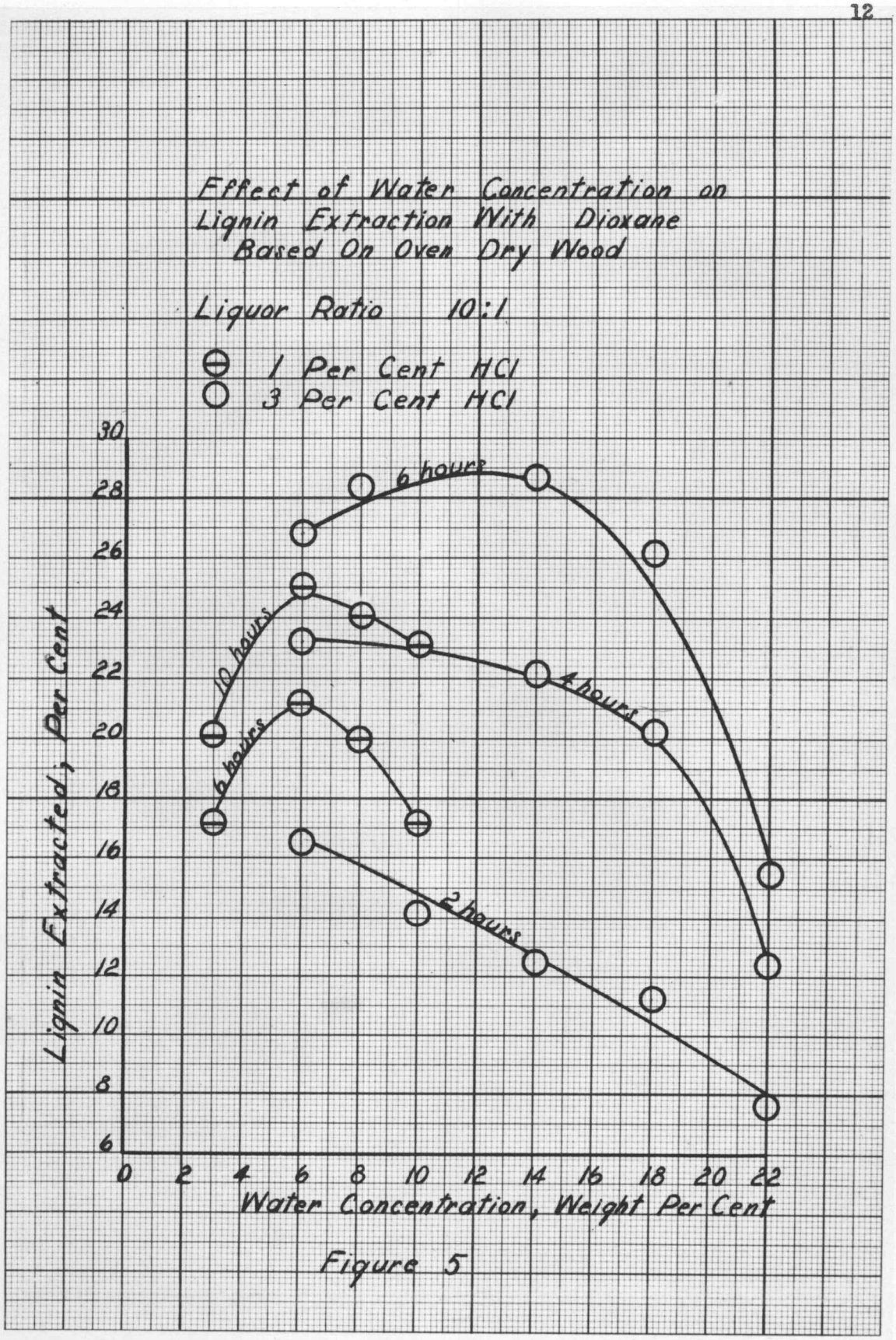
Effect of Water Concentration on
Lignin Extraction With Dioxane
Based On Oven Dry Wood
Liquor Ratio 10:1
1 Per Cent HCl
3 Per Cent HCl
6 hours
10 hours
4 hours
6 hours
2 hours
Lignin Extracted, Per Cent
Water Concentration, Weight Per Cent
30
28
26
24
22
20
18
16
14
12
10
8
6
0
2
4
6
8
10
12
14
16
18
20
22

Figure 5

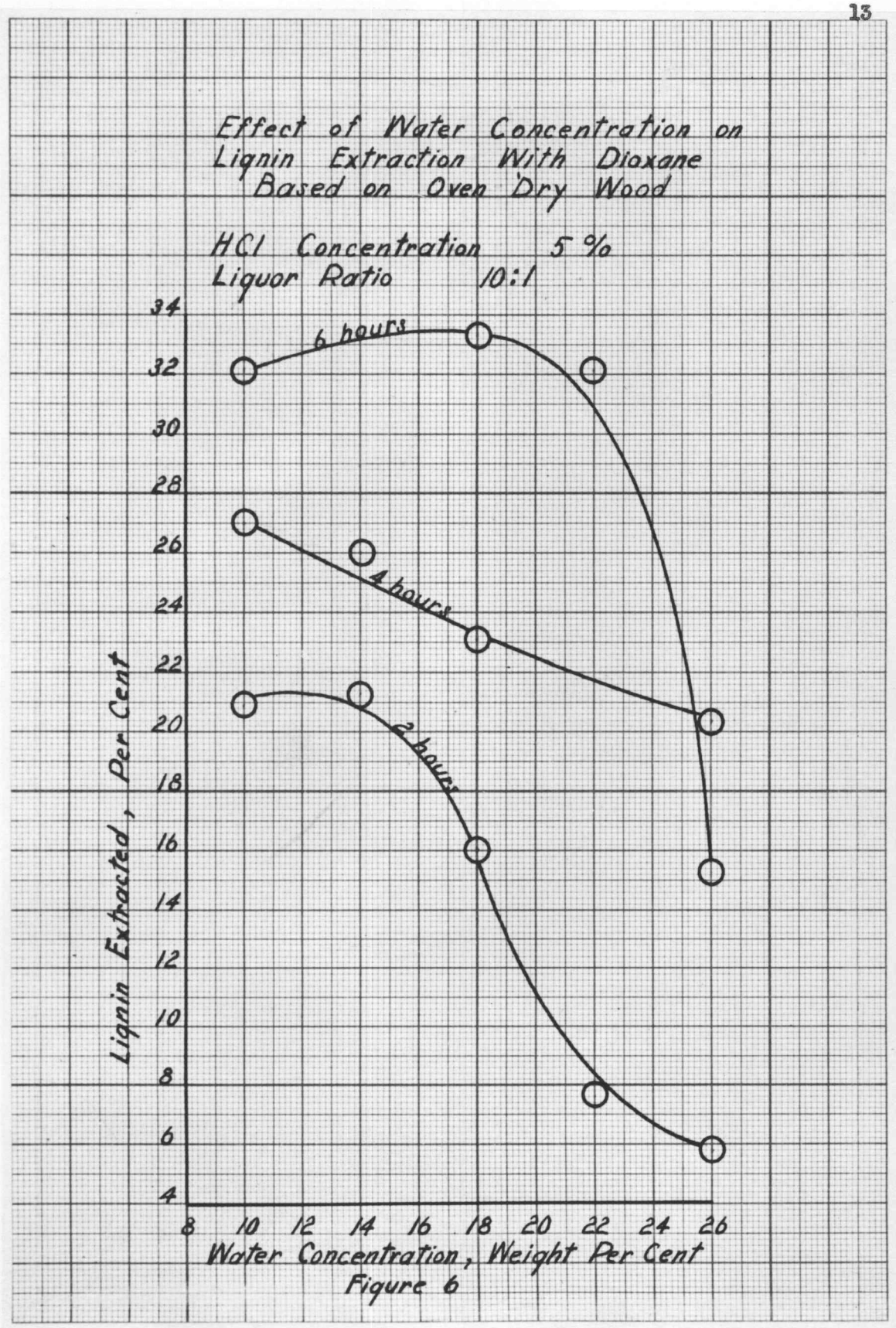
Effect of Water Concentration on
Lignin Extraction With Dioxane
Based on Oven Dry Wood
HCl Concentration 5 %
Liquor Ratio 10:1
6 hours
4 hours
2 hours
Lignin Extracted, Per Cent
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
8 10 12 14 16 18 20 22 24 26
Water Concentration, Weight Per Cent

Figure 6

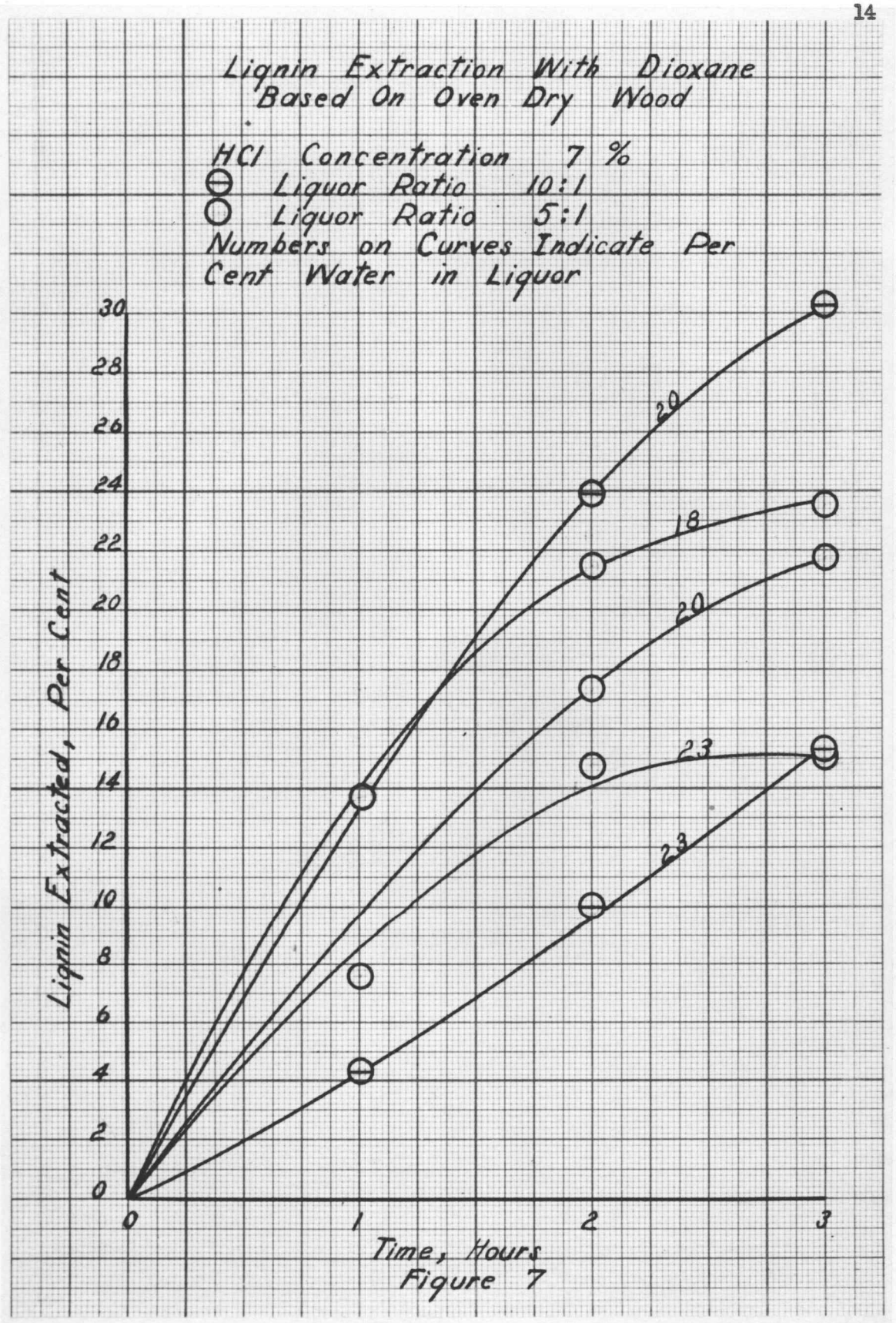
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration 7 %
Liquor Ratio 10:1
Liquor Ratio 5:1
Numbers on Curves Indicate Per Cent Water in Liquor
Lignin Extracted, Per Cent
Time, Hours
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
20
18
20
23
23

Figure 7

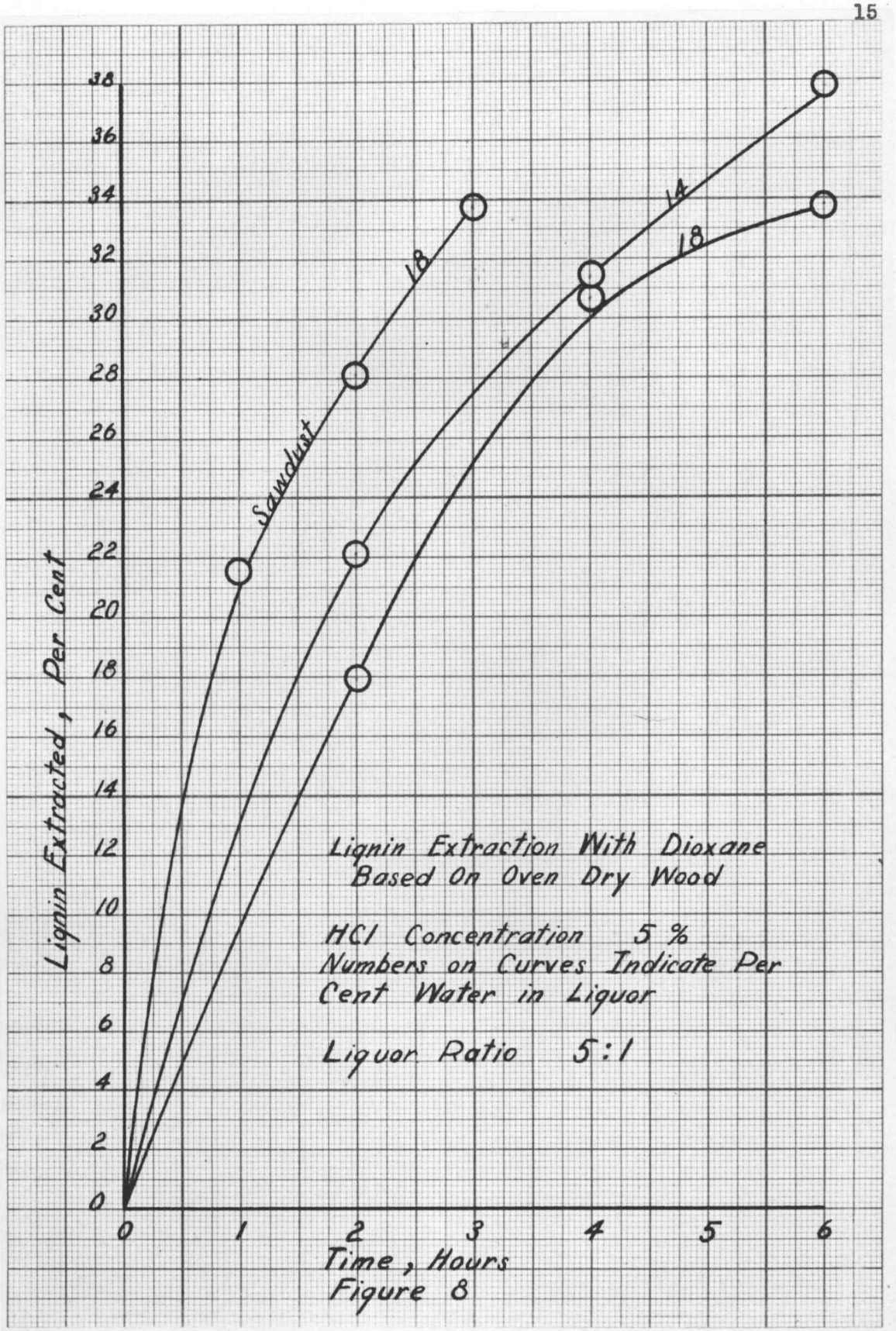
Lignin Extracted, Per Cent
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
0
1
2
3
4
5
6
Time, Hours
Sawdust
18
14
18
Lignin Extraction With Dioxane
Based On Oven Dry Wood
HCl Concentration 5 %
Numbers on Curves Indicate Per
Cent Water in Liquor
Liquor Ratio 5:1

Figure 8

remainder being dioxane. Four hours of cooking for the chips and two to three hours for the sawdust in such a liquor was sufficient to extract approximately 30 per cent of the dry wood weight as lignin.

At these concentrations, the liquor separates into two phases, the upper layer being nearly pure dioxane while the lower is approximately 75 per cent dioxane and contains most of the water and HCl. The two layers do not merge before the boiling point is reached, and the extraction is done with two intimately mixed liquid phases. Such a liquor performs at least four necessary operations during an extraction: (1) it diffuses into the wood particles, (2) it ruptures the bonds between the lignin and cellulose, (3) it dissolves the lignin, and (4) it serves as a vehicle for the diffusion of the lignin out of the wood particles. The rupture of the bonds between the lignin and cellulose is quite dependent on the hydrogen ion concentration. At low acid concentrations, the rate of extraction is increased with increasing HCl concentration. When the acid concentration is too high, it may actually bring about decomposition of the lignin, thus reducing the yield of product. Since the dielectric constant of dioxane (2.2) is much less than that of water (78.6), the addition of water to the liquor will increase the hydrogen ion concentration by reducing the attractive forces between hydrogen and chloride ions. This addition of water cannot be continued indefinitely, however, as the liquor soon loses its ability to dissolve the lignin, explaining the maxima shown in figures 5 and 6.

The substitution of an equivalent amount of sulfuric acid for

the HCl performs a much slower extraction, and the use of sodium hydroxide in place of HCl results in no extraction of lignin. The addition of an equivalent amount of a salt of a weak acid and strong base, such as sodium thiocyanate or sodium acetate, to a liquor containing HCl, increases the pH from between 1 and 3 to between 6 and 7 and reduces the extraction to a small fraction of that in the absence of the salt.

The loss of dioxane varied from 8 to 20 per cent of that used in the extracting liquor. Approximately one-fifth of that lost remained in the water solution due to incomplete salting out by the sodium hydroxide. Another 45 per cent remained in the pulp, and the rest was lost by evaporation during the filtering and washing of the pulp. Since, in a commercial application, the water used for washing the pulp and precipitating the lignin could be re-used after separation of the dioxane, this source of loss could be eliminated. The performance of the dioxane washings and filterings in a closed container would materially reduce the loss by evaporation, and it is felt that considerable improvement could be made on the recovery of the solvent.

The yield of pulp varied from 45 to 55 per cent of the dry wood charged, while the overall yield of alpha cellulose was 36 to 42 per cent of the dry wood. The cooked chips were medium to dark brown, and were very soft and pliant. From 25 to 30 per cent of the wood was recovered as a lignin powder which varied from light brown to dark brown in color, had a methoxyl content of 8.3 to 11.5 per cent, and a melting point of 185 to 200 degrees Centigrade.

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APPENDIX

Run No.	HCl Conc. %	Water Conc. %	Extraction Time Hours	Lignin Extracted % of Wood	Methoxyl Content of Lignin, %	Melting Point °C.
10	1	10	8	29.4	11.3	188
14	3	8	6	28.4	8.9	195
24	5	10	6	32.1	-	193
28	5	18	6	31.3	11.5	190
36	7	18	6	21.2	9.3	-
38	7	22	6	37.5	9.1	200
48	5	18	6	33.8	-	197
49	5	14	6	37.8	8.3	-
53	5	18	3	33.8	9.6	185

Run No.	HCl Conc. %	Water Conc. %	Liquor Ratio ml/gram	Extraction Time Hours	Lignin Extracted % of dry wood
		Runs 1 through 41 were made with oven dry wood. Runs 42 through 53 were made with un-dried wood.			
2	1	3	10	1.5	6.7
				4	13.9
				6	17.2
				9.2	19.8
3	1	6	10	2	12.7
				5	19.8
				7	22.2
				8.5	24.2
				10	25.0
8	1	10	10	2	6.6
				4	12.6
				6.33	17.3
				9	22.2
13	1	8	10	3	13.5
				6	20.9
				9	23.4
14	3	8	10	2	17.3
				4	24.4
				6	28.4
21	3	6	10	2	16.5
				4	23.2
				6	26.8
22	3	10	10	2	14.2
				4	21.4
				6	26.3

Run No.	HCl Conc. %	Water Conc. %	Liquor Ratio ml/gram	Extraction Time Hours	Lignin Extracted % of dry wood
25	3	14	10	2	12.5
				4.1	22.2
				6	28.7
27	3	18	10	2	11.2
				4	20.2
				6	26.2
29	3	22	10	2	7.6
				4.15	12.4
				6	15.5
24	5	10	10	2	20.9
				4	27.4
				6	32.1
26	5	14	10	2	21.3
				6	28.9
28	5	18	10	2	16.0
				4	23.1
				6	31.3
31	5	26	10	2	5.8
				4	20.4
				6	15.3
36	7	18	10	2	17.1
				4	25.5
				6	21.2
38	7	22	10	2	27.7
				4	37.4
				6	37.5
40	7	26	10	2	25.4
				4	13.3
				6	12.7

Run No.	HCl Conc. %	Water Conc. %	Liquor Ratio ml/gram	Extraction Time Hours	Lignin Extracted % of dry wood
41	8	22	10	1	5.8
				2	19.1
				4	21.1
42	7	23	10	1	4.3
				2	10.0
				3	15.3
43	7	23	5	1	7.6
				2	14.8
				3	15.0
44	7	20	10	2	23.9
				3	30.3
				4	16.5
45	7	20	5	2	17.3
				3	21.7
				4	20.5
46	7	18	5	1	13.7
				2	21.4
				3	23.5
47	7	16	5	1	15.7
				2	22.5
				3	33.2
48	5	18	5	2	17.9
				4	30.7
				6	33.8
49	5	14	5	2	22.1
				4	31.8
				6	37.8

Run No.	HCl Conc. %	Water Conc. %	Liquor Ratio ml/gram	Extraction Time Hours	Lignin Extracted % of dry wood
52*	5	18	5	1	20.5
				1.5	25.6
53*	5	18	5	1	21.6
				2	28.1
				3	33.8

*Sawdust