THE HYDROLYSIS OF WOOD

by

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INTRODUCTION

The production of sugars from cellulosic materials, such as straw, linen, cotton, peat, wood, and, in fact, all plant fibers, has engaged the attention of chemists and technologists for nearly a century. It is only within the last two decades, however, that serious attempts have been made to utilize wood wastes for this purpose. The production of sugars from wood has, of course, been an intermediary process, as the final product desired in every case was alcohol.

In recent years, the processing of wood wastes to give sugars and alcohol has received much attention and a great deal of money has been spent in its technical development. Quite a few plants have been built in this country, but only two have achieved even moderate success, and none are in operation at the present time. The failure of these plants has been due largely to the fact that none of the equipment designed in this country has worked efficiently, and also, to the fact that, from an economic standpoint, the process could not compete with the other alcohol processes. In only one instance, a plant at Georgetown, South Carolina, did these factors seem to be conquered, but an unfortunate fire destroyed the large sawmill which was the chief source of wastes for the plant, and it was never rebuilt.

The problem of waste disposal is of great importance to the lumber industry, and as this process seems to offer the only solution, the Forest Service has investigated each of the different processes, and the plants that have been built, in order to, so far as possible, learn the causes of former failures, and aid in the development of the process.

The amount of wood waste produced by converting a tree into lumber depends, of course, upon the tree and the efficiency of the sawmill. The following tabulation shows that more than half of the contents of the tree itself is wasted:

	Percent
Entire Tree	100
Stump	2
Top	18
Sawdust	12
Bark	10
Slabs	8
Edgings	8
Shavings	4
Total	62

This includes limbs, top, and stump, the parts of the tree left in the woods, in addition to the waste at the mill itself. Neglecting

the portions left at the place of cutting, which would not be available without extra transportation, the wastes at the mill itself are of great interest. The mill wastes of an efficiently run sawmill have been estimated by Margolin[2] as:

	Percent
Sawlog	100
Bark	13.0
Sawdust	13.5
Edgings and Trimmings	8.7
Slabs	8.7
Careless cutting	3.5
Loss in cutting to standard sizes	1.7
Total	49.1

Thus, it is certain that even in the final sawing of the wood, there is almost 50 percent waste.

The disposal of this waste is a problem for the large mill which is not located near a city, for the waste produced is greatly in excess of its fuel requirements; in fact, a mill with an efficient power plant will only be able to utilize about 40 percent of its sawdust, and some method of disposal must be found.

In most cases, this disposal is effected by a waste burner, and this not only destroys any value of the wood, but also calls for a certain charge for operation. From data gathered by the Forest Products Laboratory[3], a minimum estimate of the cost of disposal of wood wastes in this country is said to be well over six million dollars.[4] This, of course, does not include the value of the wood itself, but simply the cost of disposing of it.

There are many limitations to the utilization of wood waste, the chief one of which is its bulk, which makes transportation impractical except by fans or belts. These methods obviously cannot be used for long distances, so utilization on the spot is a necessity.

The form of the waste presents another difficulty, in that as the length of the wood fiber has been reduced, it has also been lacerated to an extent that will destroy its value for pulp and paper production. The form of the waste also prohibits destructive distillation, because the size of the particle makes it a very poor conductor which resists charring, and also, the charcoal produced is so finely divided that it is difficult to handle.

Therefore, it is obvious that in a search for some use for these wood wastes, it is necessary to find a process in which neither the bulkiness of the sawdust, nor the lacerated fibers of cellulose would be

a hindrance. This would seem to point to a chemical utilization of the sawdust rather than some physical method. A chemical utilization of the sawdust would overcome all of the previously stated objections as to the form of the material, and the length of the fiber.

HISTORICAL

The first recorded attempts to produce sugars and alcohol from vegetable fiber were those of Braconnet[5] in 1819. Little is known of his work, with the exception of the fact that he obtained a 98 percent conversion of cellulose into reducing sugars, using concentrated sulphuric acid.

No work was done subsequent to this until Simonsen[6] carried out his investigations in 1898. Simonsen's experiments were very thorough and he worked not only with sulphite cellulose, but also with sawdust, using sulphuric acid as an inverting agent. From the results of his experiments, he concluded that the best conditions for the inversion of sawdust were:

Time of inversion .....15 minutes

Strength of acid .....0.5% H_2SO_4

Proportion of wood to liquid .....1 to 4

Pressure .....9 atmospheres

Although Newman[7] questioned Simonsen's work, Korner[8] later verified his yield of alcohol, and showed also that the yields of alcohol and sugars were in proportion to the total cellulose content of the material used.

A. C. Classen[9], a German, developed a new process in which SO_2 was used, although his first patent covered a mixture of sawdust and

concentrated sulphuric acid (of 50-60° B), in which the mixture was subjected to great pressure in a hydraulic press. Originally Classen used an aqueous solution of sulphurous acid, although he later obtained patents in which chlorine, air or oxygen were used as oxidizing agents to convert the sulphurous acid to sulphuric acid. After this, he obtained patents covering the use of sulphuric anhydride, and also a patent covering the process of heating this mixture to 123-125° C.

Classen[12] also patented the use of a smaller amount of a more concentrated solution of sulphurous acid, as he claimed the acid recovery was more effective when the sawdust in the digester was only slightly moist. In 1914, he patented the use of platinum,[13] ferric oxide, etc. as catalysts to convert the sulphurous acid into sulphuric in the digester. The results of this work were corroborated by M. Taffin,[14] who, after experimenting for several months to satisfy himself of the practicability of the Classen process, purchased the French rights and organized a company to promote it.

During this era of expansion, the organization worked out a process whereby the acetic acid formed during the hydrolysis could be recovered along with a greater part of the sulphurous acid. This organization perfected, too, a special type of digester, which was later used in this country in a plant at Port Hadlock, Washington.

These plants were operated until about 1909, and in 1908 made a number of runs on American woods in order to try to interest American

capital. No record can be found of the results obtained, however, and shortly afterward these plants ceased commercial operations.

In 1903, the patent rights for America were sold to the Classen Lignum Company of Chicago. This company erected an experimental plant, with a capacity of about two tons of sawdust per 24 hour day, and later built a plant at Hattiesburg, Mississippi, to operate on sawdust and waste of longleaf pine.[15]

Some of the disadvantages of this process lay in the length of time (about 6 hours for two tons of wood), the large quantity of acid required, and also, the action of the sulphuric acid formed on both the sugars and the equipment was particularly troublesome.

The first American work on this project was undertaken by Ewen and Tomlinson,[16] two engineers who were associated with the Classen process. Their method shortened greatly the hydrolysis time (from 6 hours to 45 minutes), and produced other improvements, among them: 1) the treated wood waste was obtained in a form which could easily and quickly be extracted; 2) a digester was devised which was not affected by the reactants; 3) the quantity of acid needed was reduced; 4) a large yield of fermentable sugars was obtained from the wood.

These improvements were accomplished in part by adding SO_2 in a gaseous form, and by using steam as a source of both heat and moisture. This shortened the heating period considerably, and gave a product which could be more easily extracted.

In 1909 Ewen and Tomlinson[17] were granted a patent for the production of fermentable sugars from lignocellulose. In essence, they were using Simonsen's method, especially as to the ratio of acid to wood.

In a process which was worked out in 1910 by W. P. Cohoe of Canada, HCl is used as the hydrolytic agent, and its use is preferred because of its volatility. Cohoe claimed a yield of 25 to 28 percent of fermentable sugars, and also claimed that he could effect complete recovery of the acid from the wood by blowing it out with steam. Other claims by Cohoe[18] were: 1) 1 to 2 percent of acetic acid can be recovered by a preliminary steaming of the sawdust; 2) preliminary steaming gives a constant moisture content regardless of the initial condition.

The chief apparent flaw in Cohoe's work, however, lies in the fact that in his paper he reports a yield of about 20 percent, while his patents give an increased yield - over 10 percent more of the original weight of the material as reducing sugars.

In 1907, Hafner and Krist[19] worked out a process for the production of sugar from amylaceous or cellulose substances. They mixed their raw material with water, acidulated or not, under a pressure of 2 atmospheres, and at a temperature of 100°. Then they passed an electric current of 100 volts through the mass. No yields from this process are reported, so nothing is known of its efficiency.

P. G. Ekstrom[20] devised in 1907, a method for the conversion of cellulose into sugar using sulfite back water as a diluent for the process. This sulfite back water was boiled for five hours with 70 - 80° H_2SO_4. By using this, Ekstrom claimed that a cellulose was formed which was soluble in water, and which could be converted into sugar by simply boiling with dilute acids. The excess acid was then neutralized with a fresh portion of the sulfite back water. A 40 percent conversion of the weight of the original cellulose present was claimed.

R. N. Miller and W. H. Swanson[21] next experimented on the hydrolysis of wood, using powdered spruce wood as the cellulose containing material. First extracted with a mixture of ethyl alcohol and benzene, the wood was then subjected to hydrolysis at 96° for six hours by means of HCl of concentration varying from 0.05 percent to 3.0 percent. The cellulose, based on wood, in the residue (58.88 percent in wood) was diminished to 51.18 percent, 48.31 percent and 48.70 percent by the use of 3.0 percent, 0.75 percent and 0.05 percent HCl respectively. The reducing sugars formed were extracted, and the residue again subjected to hydrolysis. The use of 3.0 percent HCl produced 16.15 percent of sugar (based on the weight of the wood) on this second hydrolysis.

More concentrated acids gave no increase in yield in this experiment. A part of the cellulose was hydrolyzed rapidly, leading to the theory that the wood particles became coated, thus resisting further hydrolysis. After two complete hydrolyses, all of the wood could be accounted for as stable cellulose, lignin, and reducing sugars.

The use of salts of strong acids in addition to "sulfite acid" appeared to speed up the hydrolysis; salts of weak acids had a contrary effect, suggesting the influence of the hydrogen ion concentration.

A Russian, V. M. Kulikov,[22] carried out a hydrolysis of cellulosic materials which used neither concentrated nor dilute acid. The reaction was carried out in an autoclave, in the presence of hydrogen, and the neutralized produce was blown with air. No details concerning conditions of the reactants, or the amounts of the yields could be obtained, however.

On the theory that lignin may arise by the unsaturation of glucose, W. Fuchs[23] oxidized pinewood meal with perbenzoic acid. Subsequent hydrolysis with H_2SO_4 gave greater yields of glucose than were given by the unoxidized wood. Under the same conditions, the following amounts of glucose were obtained: untreated wood, 60 percent; treated wood, 66 to 70 percent; filter paper, 88 percent. (It is not stated whether these yields are calculated on the weight of the wood, or the weight of the cellulose present.) Fuchs' conclusion is that unsaturated compounds of the nature of glucal are present in lignified tissue.

An experiment using alcohol to decompose wood chips was performed by T. Kleinert and K. Tayenthal[24] in 1929. The alcohol solution (25-80 percent alcohol) under pressure, and at temperatures above 150°

(with the addition of a small proportion of an acid or base) was used to facilitate the recovery of substances such as lignin and sugar. No definite data from the experiment were given.

Eduard Farber[25] experimented with the hydrolysis of wood using hydrochloric acid. The wood is first treated with HCl and HCl gas in quantities insufficient to effect complete conversion into sugar, and then is transferred to a diffusion battery, and allowed to stand with no agitation. The conversion was completed by treatment with HCl of a lower concentration than that first used. This second acid was of a concentration of well over 35 percent, however. The sugar was simultaneously withdrawn along with this conversion, but, again, no yields were given.

Gallagher and Mork[26], in this country, next experimented with the saccharification of wood. The sawdust and reaction products were put into a digester, and the pressure raised to 60 - 135 lbs. per square inch. Then a solution formed of H_2O and 1 percent each H_2SO_4 and NaCl, or 1.5 percent each H_2SO_4 and $CaCl_2$ was added. The maximum yields of reducing sugars were obtained in from 15 to 60 minutes. A yield of 25.8 percent sugars is claimed, but it is not stated whether this is based on the weight of the wood, or on the weight of the cellulose present.

Fridrich Bergius[27], discoverer of the process that bears his name, experimented with the use of concentrated HCl. By his method, dry shavings were sent through a battery of 18 diffusion vessels, meeting

concentrated HCl in a counter current. From 60 to 70 percent of the material was converted into sugars, and about 30 percent was retained as lignin, which was collected on built-in porous plates.

A current of hot oil vapors was then blown through the sugar solution, removing most of the HCl and a large part of the water. Syrup and oil were separated by centrifuging, and the syrup was dried by means of a spray evaporator. The now dilute HCl was concentrated to its former strength of 40 percent.

Two by-products are said to make this process an economic success. The lignin remaining is briquetted directly, with no binder, and is used for fuel. Acetic acid is recovered in the same yields as in the destructive distillation of wood.

The use of alkali in hydrolysis is recorded in the work of Yrjo Kauko[28], who used it in his runs on peat. It was necessary, however, to follow this with dilute H_2SO_4, so there is doubt as to whether any advantages were obtained from the use of the alkali. The yields from this work are not reported.

In 1930, J. V. Tamchyna and H. M. Fanto[29] also used concentrated HCl in the hydrolysis of wood, although their work never reached the same state of advancement as did Bergius'. Wood was just dried and pulverized, then heated with concentrated HCl in vessels made of tar and quartz. Heating of the mixture was carried out by finely dispersed oil which does

not dissolve the sugar or HCl, and separation was effected in a centrifuge. The final product, in this work, appeared either as a dark brown syrup, or as brown crystals.

The carbohydrate yield of this experiment is said to be 60 - 70 percent of the wood, and the lignin about 30 percent. A 4 percent yield of acetic acid is claimed.

Using a pressure of 120 lbs. per square inch, J. Wiertelak[30] obtained a higher yield of sugars at 180 minutes, but from 30 minutes on the sugar yield increased very slowly. From his experiments, he found that, at the same pressure, hydrolysis with water produced about half the amount of reducing sugars obtained when 0.5 percent acid was used.

Karl Fredenhagen and Gustav Cadenback[31] experimented with the use of hydrofluoric acid as a hydrolytic agent in the saccharification of wood. Theoretically, they formed glucosyl fluoride by the splitting of the O links, which in turn was changed into glucose by H_2O. The solution they obtained, however, gave polyglucosans, which necessitated a dilute acid boil to change all of the material into glucose. Although they do not mention the fact, this acid boil in all probability aided the hydrolysis greatly. No quantitative yields of the sugars obtained are given in their report.

In 1933, Bergstrom and Cedarquist[32], using 2 periods of hydrolysis, obtained about 27 percent of the weight of the wood as reducing

sugars. The temperature was 180°, and each hydrolysis period 15 minutes, using 0.5 percent H_2SO_4 as the hydrolytic agent. The proportions were 5 parts of liquid to 1 part of wood, and some experiments were carried out in which the time and temperature were varied. It was found that the maximum yield could be obtained in 15 minutes at 180°, but at 160°, 50 minutes were required for hydrolysis in order to obtain the same amount of reducing sugar.

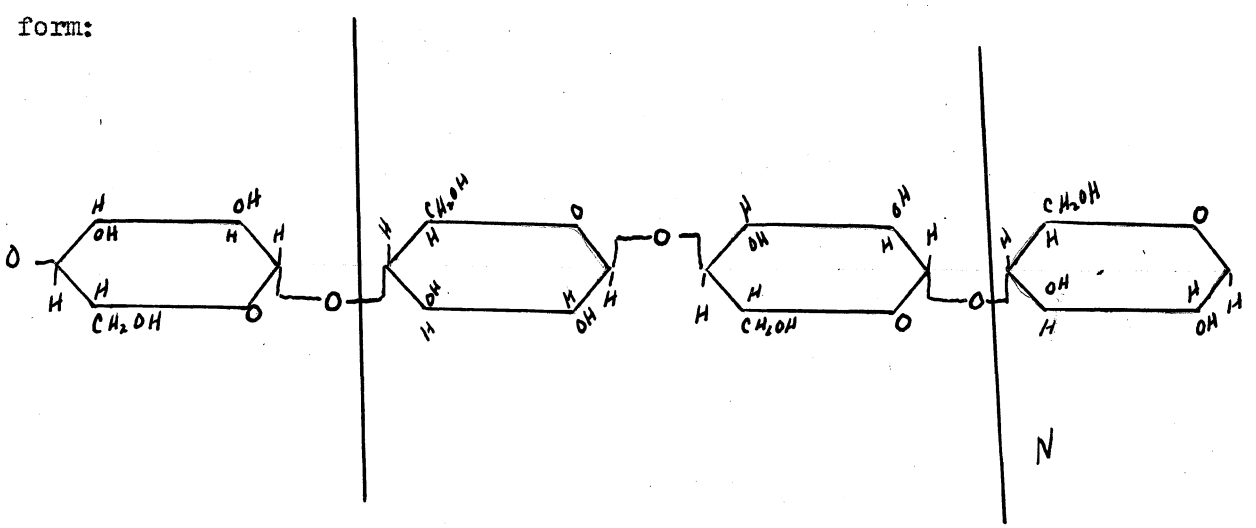
Many experiments using catalysts were carried out by Shenand and Gauger[33] in a search for a substance that would increase the speed of sugar formation and retard the decomposition reaction. In a series of over 70 experiments, the best results were obtained with oxalic acid, and benzenesulphonic acid, but no truly appreciable gain in the yield of sugars obtained from wood was found. The two conclusions reached by Shenand and Gauger were: 1) the salts of any one group of elements behave similarly and 2) that the greatest possibilities lie in the field of hydrolytic catalysts, since the use of highly dissociated acids such as formic and tri-chloracetic lowered the yields.

THEORETICAL

In any process for the saccharification of wood there are two integral steps; first, the separation of the lignin and cellulose, and second, the hydrolysis of the cellulose to sugars.

Lignin represents the non-carbohydrate part of the wood wastes - that is, the part which cannot be hydrolyzed to give sugars. The structure of lignin is uncertain, and, to date, no lignin has been isolated unchanged, which makes any study of it extremely difficulty. Chemically, lignin is considered to be the material remaining when a cellulosic material is extracted with seventy-two percent sulphuric acid.[34]

Cellulose is probably the most complicated of the polysaccharides, no agreement having yet been reached as to its structure. The fact that it can be hydrolyzed to glucose in quantitative yields would indicate that the glucose molecule is essentially anhydroglucose of the structural form:



Hydrolysis degenerates the cellulose and produces hydrocellulose and glucose by breaking the O-bonds between anhydro glucose units. Because of the uncertainty regarding the structure of cellulose, any equation for the reaction would, of necessity, have to be written:

$$(C_6H_{10}O_5)_n \quad \underline{HOH} \quad N \; C_6H_{12}O_6$$

Hydrolysis of cellulose has been effected by four means: 1) use of water and pressure alone; 2) use of certain salts, with and without pressure; 3) by regeneration from esters; 4) use of acids, both with and without pressure.

The use of acids seems to offer the best possibilities, as it can best be effected without using pressure. Acids, however, depending upon their nature and strength, may first cause hydrolysis to simple sugars, then dehydration to hydroxymethyl furfural.[36]

According to Schorger[37], saccharification is of more narrow scope than hydrolysis and refers to the conversion to the simple sugars. He states also that saccharification always appears to take place through the intermediate formation of dextrins.

EXPERIMENTAL

The experimental work on this project was divided into four divisions, 1) hydrolysis with concentrated acid; 2) hydrolysis with bases; 3) hydrolysis with dilute acids; 4) perfecting an extraction method from the data secured in the first series of experiments.

In all of these experiments, seasoned, second-growth, southern yellow pine sawdust was used unless it is otherwise stated. The analysis of the sawdust is as follows:

Table I

Composition of Yellow Pine Sawdust

Total Cellulose	53.0%
CCl_4 extract	4.0%
Lignin	34.2%
Moisture	5.1%
Ash	0.43%

The cellulose was determined by the method of Cross and Bevan,[38] and the lignin was determined by the procedure devised by Becker.[39]

The first set of experiments was run using concentrated sulphuric acid as the hydrolytic agent. The procedure was as follows:

1. Forty grams of sawdust were treated with 200 cc of concentrated sulphuric acid. The reaction was carried out at 0^{o} - 5^{o} by cooling the reaction vessel with an ice-salt mixture. The reaction was carried out in a 800 cc beaker, and the reactants were agitated by an electric stirrer. The resultant mixture was diluted with water.

2. The resultant mixture was filtered, using glass wool as a filter medium.

3. The filtrate was treated with Na_2SO_4, in order to precipitate the sugars formed.

4. The solution was again filtered, and the residue was combined with the washings from the first filtration.

5. The sulfates were then precipitated with $Ca(OH)_2$ and again filtered.

6. The final filtrate was evaporated, and tested for sugars. The determination was made using Fehling's solution by the method of Munson and Walker.[8]

The results obtained from the above outlined experiment were as follows:

Table II

Concentrated H_2SO_4 as Hydrolytic Agent

Run	Cms. Sawdust	CC Acid	Grams Glucose
1	40	200	.0393
2	40	200	.0406
3	40	200	.0375
4	40	200	.0371
5	40	300	.0341
6	40	300	.0352
7	50	200	.0506
8	50	200	.0516
9	30	200	.0315
10	30	200	.0326
11	20	200	.0215
12	20	200	.0215

Another set of experiments was run, using ammonium sulfate as the precipitating agent in place of the sodium sulfate. The conditions and procedure were exactly as above, with the exception of the substitution of precipitating agents. The results of this experiment are:

Table IIA

Concentrated H_2SO_4 as Hydrolytic Agent

Run	Gms. Sawdust	CC Acid	Gms. Glucose
1	40	200	.0375
2	40	200	.0381
3	40	200	.0364
4	40	200	.0378
5	40	200	.0399
6	40	200	.0380

These experiments were a notable failure and only one reason for such a lack of formation of glucose could be observed. Despite the low temperature, charring was observed, and the distinctive odor of burnt sugar was present. The assumption was therefore made that the sugars were actually formed, but were decomposed by the strong acid used.

The next series of experiments were run using sodium hydroxide as the hydrolysis agent. Although Groggins[39] states that cellulose could not be hydrolyzed by bases, it was decided to try the effect of different concentrations of a base on the sawdust.

This reaction was carried out in a five liter flask fitted with a reflux condenser. The sawdust was put in the flask with the alkali, and the hydrolysis carried out at the B. P. for different lengths of times. The sugars were analyzed as before and the following results were obtained.

Table III

Sodium Hydroxide as Hydrolytic Agent

Run	Time	Gms. Sawdust	CC Alkali	% Alkali	Gms. Glucose
1	3 hrs.	50	500	1%	trace
2	3 hrs.	50	500	5%	.0216
3	3 hrs.	50	500	10%	.0325
4	2 hrs.	50	500	15%	.0326
5	2 hrs.	50	500	20%	.0404
6	2 hrs.	50	500	25%	.0400
7	4 hrs.	50	500	30%	.0311
8	4 hrs.	50	500	35%	.0287
9	5 hrs.	50	500	40%	.0100
10	1 hr.	50	500	20%	.0421

The amounts of sugar obtained in every case were negligible when calculated on a percentage basis, as, for instance, the percentage in Run #2 would be 0.04%. The conclusion drawn from this experiment

was that the alkali had no hydrolytic effect upon the cellulose, but that the small amounts of sugars obtained were due to the heat and the water. Although it was not checked, it was assumed that the same amounts of sugar could have been obtained had water alone been used.

The next experiment was an attempt to combine the first two series of experiments, and perhaps obtain some quantitative yield of sugars from a combination of the two.

In the first experiment, the sawdust was first treated with alkali, then carefully filtered and washed. The residue was then treated with concentrated acid, filtered and washed. The filtrates and washings were then mixed and evaporated to a volume which could be easily handled. The solution was then neutralized and analyzed for sugars.

The procedure for this experiment was as follows: 50 grams of sawdust and 500 cc of 20% NaOH were heated at the boiling temperature for two hours in a 5 liter Erlenmayer flask fitted with a reflux condenser. Then the mixture was filtered, and the filtrate set aside, together with the washings. The residue was then treated, as in the first set of experiments, with 200 cc of concentrated H_2SO_4 at from 0° - 5° with constant agitation. The mixture was agitated until it appeared uniform throughout, and was then diluted, filtered and washed. The filtrate and washings from both reactions were combined, neutralized, and filtered through charcoal to remove as much of the brown coloring present as was possible. The results obtained from this experiment were:

Table IV

Successive Treatment with NaOH and H_2SO_4

Run	Gms. Sawdust	CC Alkali	CC Acid	Gms. Glucose
1	50	500	200	0.271
2	50	500	200	0.306
3	50	500	200	0.308
4	50	500	200	0.372
5	50	500	200	0.361
6	50	500	200	0.351

Although this reaction appeared to be very vigorous, it was decided to try the same experiment, but to repeat the treatment of the sawdust by the alkali and the acid. The procedure was the same as above, except that after the first two hydrolyses, the entire procedure was repeated - giving two alkali and two acid reactions. The results from this experiment were as follows:

Table IVA

Successive Treatment with NaOH and H_2SO_4

Run	Gms. Sawdust	CC Alkali	CC Acid	Gms. Glucose
1	50	500 + 500	200 + 200	0.741
2	50	500 + 500	200 + 200	0.634
3	50	500 + 500	200 + 200	0.742
4	50	500 + 500	200 + 200	0.834
5	50	500 + 500	200 + 200	0.881
6	50	500 + 500	200 + 200	1.071

The results from the combination of these two experiments was still far from satisfactory, although one run (#6) gave the best yield of sugars so far obtained. This, however, was barely over 2% of the weight of the wood used, so it was decided to abandon the strong acid and the alkali experiments, and to try the use of dilute acids.

The plan of investigation adopted for the use of dilute acids was to treat dry, seasoned sawdust with 1%, 5%, 10%, 15%, and 20% sulphuric acid at the boiling point of the mixture. The treatment was to go for eight hours; samples to be taken at the end of 1/4 hr., 1/2 hr., 1, 2, 4, 6, and 8 hours. From this arrangement, the variance of the yield of sugar with the time of reaction and the strength of the reagent could be obtained.

The above procedure was then to be repeated using HCl.

The entire experiment, as described above, was then to be repeated using green, unseasoned sawdust just as it is cut from the tree.

No variation of the temperature was to be tried, for from all of the literature it was assumed that the heat was an integral part of the reaction, so all experiments were carried out at the boiling point of the mixture.

From the outlined plan of investigation the optimum conditions could be obtained - the time, concentration of the reagent,

the best reagent, and the condition of the wood which would all combine to give the maximum yield of sugars.

The procedure for this experiment was to put 20 grams of the sawdust into a 1000 cc Erlenmeyer flask fitted with a reflux condenser, and add 400 cc of the acid. Heat was applied so as to keep the mixture agitated, so no mechanical stirrer was necessary. Ten cc samples were withdrawn by means of a pipette, and a careful measurement of the volume of acid solution was made at the end of the experiment in order to calculate the yields correctly. The samples for analysis were neutralized and analyzed as before. Two reactions were run as a check. The following are the results obtained:

Table V

Effect of Concentration and Time on Hydrolysis by Dilute H_2SO_4 and HCl

% Acid	Time	%Glucose from H_2SO_4	% Glucose from HCl
1	¼ hr.	3.2	3.5
1	¼	3.2	3.6
1	½	4.2	4.6
1	½	4.3	4.5
1	1	4.5	4.5
1	1	4.7	4.5
1	2	4.1	4.3
1	2	3.9	4.1
1	4	3.7	4.0
1	4	3.7	4.1
1	6	3.5	3.6
1	6	3.7	3.5
1	8	3.5	3.0
1	8	3.4	3.1
5	¼	6.3	8.1
5	¼	6.5	8.2
5	½	5.7	9.5
5	½	5.5	9.0
5	1	5.4	8.9
5	1	5.5	9.0
5	2	4.9	8.1
5	2	5.2	8.5
5	4	5.0	9.1
5	4	4.9	10.0
5	6	4.5	8.2
5	6	4.8	8.5
5	8	4.2	9.0
5	8	4.4	5.3

Table V (Continued)

% Acid	Time	% Glucose from H_2SO_4	% Glucose from HCl
10	¼	4.2	3.9
10	¼	4.1	3.0
10	½	4.2	3.3
10	½	4.3	3.0
10	1	4.0	3.0
10	1	4.2	2.1
10	2	3.9	2.9
10	2	3.8	2.1
10	4	3.7	3.0
10	4	3.5	2.9
10	6	3.4	2.0
10	6	3.5	1.6
10	8	3.9	2.3
10	8	3.6	2.2
15	¼	3.4	2.9
15	¼	3.2	2.6
15	½	2.5	2.1
15	½	3.0	3.0
15	1	3.0	2.7
15	1	2.9	2.8
15	2	2.8	2.5
15	2	2.9	2.8
15	4	2.8	1.5
15	4	2.8	0.8
15	6	2.7	2.1
15	6	2.7	2.2
15	8	2.5	2.3
15	8	2.1	2.1
20	¼	2.1	2.5
20	¼	2.1	2.2
20	½	2.0	2.2
20	½	2.0	2.2
20	1	1.9	2.9
20	1	1.0	2.1
20	2	1.2	2.4
20	2	1.1	2.0
20	4	1.5	2.0
20	4	2.1	2.1
20	6	1.0	1.7
20	6	1.0	1.5
20	8	.05	1.5
20	8	1.0	1.5

Table VI

Effect of Concentration and Time on Hydrolysis by H_2SO_4 and HCl on Green Sawdust

% Acid	Time(hrs)	% Glucose from H_2SO_4	% Glucose from HCl
1	¼	3.1	3.5
1	¼	3.2	3.4
1	½	3.9	4.1
1	½	4.0	4.3
1	1	4.1	4.2
1	1	4.1	4.2
1	2	3.0	4.0
1	2	3.1	4.1
1	4	3.2	2.9
1	4	3.6	4.0
1	6	3.5	3.1
1	6	3.0	3.4
1	8	3.0	3.2
1	8	3.1	3.2
5	¼	6.2	8.3
5	¼	6.0	7.8
5	½	5.9	9.1
5	½	5.8	8.7
5	1	5.8	8.8
5	1	5.8	8.6
5	2	5.4	8.0
5	2	6.0	8.5
5	4	5.4	9.1
5	4	5.4	10.0
5	6	4.6	9.0
5	6	4.8	9.2
5	8	4.6	9.0
5	8	4.9	9.4

Table VI (Continued)

% Acid	Time(hrs.)	% Glucose from H_2SO_4	% Glucose from HCl
10	¼	3.2	2.8
10	¼	3.6	2.6
10	½	4.0	2.4
10	½	3.2	2.2
10	1	3.0	2.6
10	1	3.1	2.7
10	2	3.0	3.0
10	2	3.0	2.4
10	4	2.9	2.2
10	4	2.0	2.3
10	6	2.0	2.8
10	6	2.0	2.0
10	8	2.0	2.6
10	8	2.0	2.1
15	¼	3.5	3.0
15	¼	3.8	2.9
15	½	3.0	2.6
15	½	3.2	2.7
15	1	2.9	2.5
15	1	2.9	1.4
15	2	3.0	2.0
15	2	3.1	2.1
15	4	2.8	2.3
15	4	2.1	2.4
15	6	3.0	2.6
15	6	2.8	2.8
15	8	2.7	2.1
15	8	2.1	1.9
20	¼	2.4	2.4
20	¼	2.3	2.1
20	½	2.1	2.0
20	½	2.3	2.0
20	1	2.0	2.6
20	1	1.6	2.4
20	2	1.9	2.0
20	2	1.7	1.6
20	4	2.0	1.8
20	4	1.8	1.6
20	6	1.6	1.4
20	6	1.6	1.6
20	8	1.5	1.4
20	8	1.4	1.4

As a result of this experiment it was seen that the best concentration of acid to secure a maximum yield of sugars lay between 5 and 10%, and the optimum time between 15 minutes and 1 hour. There was no marked difference between the yields obtained from the dry wood and the green wood, except that the yield from the green wood were usually a percent lower. One fact was noted which was of interest, however, and that was the marked decline in yield upon treatment of the green wood with 10% acid. This appeared in the 10% solutions of both acids, and no explanation is known.

Another point of interest is that in some instances the sugar content was higher after a period of from 15 minutes to 2 hours than it was after 6 or 8 hours. The explanation offered for this is that the continued heating with the hydrolysis agent destroyed some of the product formed.

The percentage of sugars obtained from this wood was still far from what other investigators had obtained from similar woods (or woods having a similar percentage of cellulose), and it was thought that perhaps the lignin and cellulose were not separated completely enough. Chlorine gas separates lignin and cellulose, forming lignin chloride and leaving the cellulose. It was decided to try an experiment in which the moist wood was treated with chlorine, and then hydrolyzed. The procedure involved putting 10 grams of moist sawdust in a large funnel fitted with a cover, and with a plug of glass wool at the

lower end. This smaller end of the funnel was inserted into a chlorine generator, in which MnO_2 was treated with concentrated HCl. The upper end was fitted to a condenser, to take care of the fumes. Chlorine was passed through the moist sawdust, and then the sawdust was hydrolyzed as in the previous experiment. Seven percent sulphuric acid was used, since it was decided to concentrate on sulphuric acid because of its cheapness. The time selected for chlorine treatment was one hour, followed by washing with water, and then a hydrolysis of one hour. Results were:

Table VII

Prechlorination and Yield of Glucose

Run	% Glucose	Run	% Glucose
1	6.8	4	9.3
2	7.4	5	8.2
3	6.4	6	8.0

As an average higher yield of sugars was obtained by this method than by any heretofore tried, it was decided to double up on it - that is, two treatments with chlorine, each followed by a hydrolysis.

Table VIII

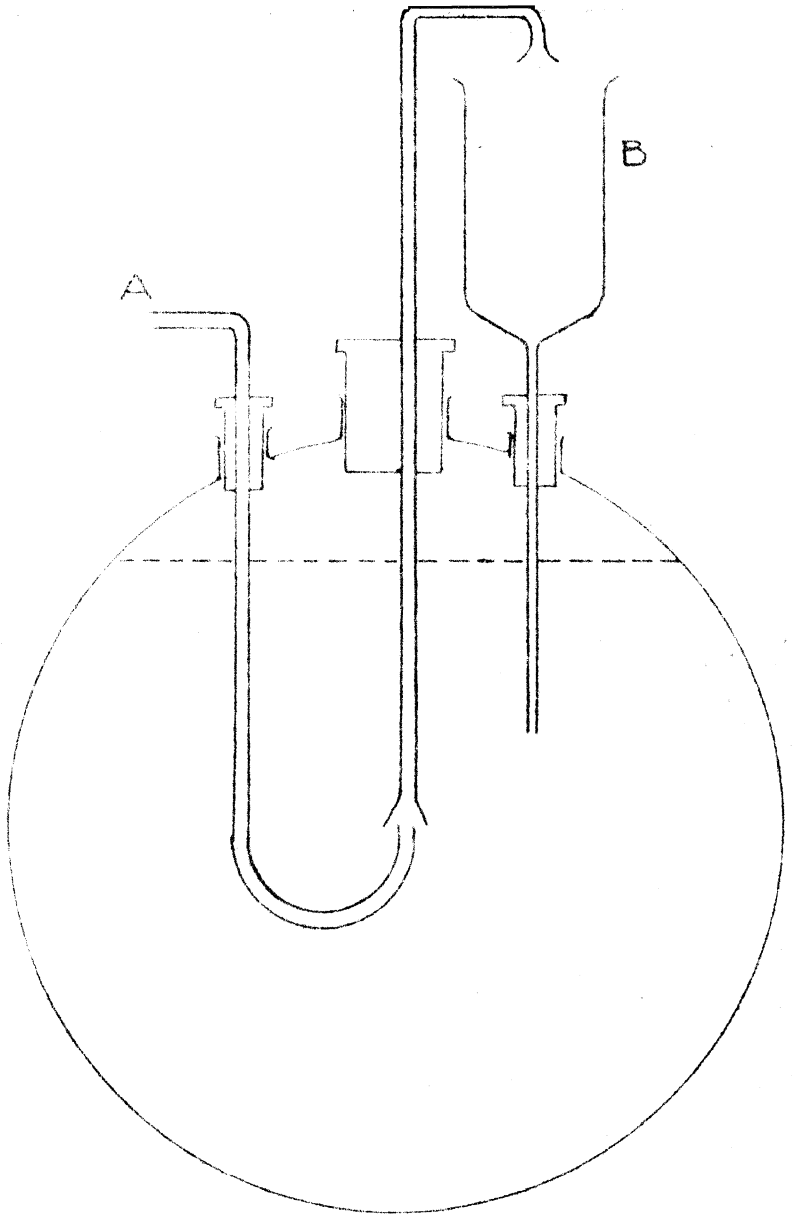
Prechlorination and Hydrolysis - Repetition of Process

Run	% Glucose First Hydrolysis	% Glucose Second Hydrolysis	Total %
1	8.4	5.6	14.0
2	7.8	5.4	13.2
3	8.0	5.2	13.2
4	8.2	5.0	13.2
5	8.0	5.1	13.1

These runs gave a high yield as compared to most of the previous ones, so it was decided to devise some method of extraction, other than simply mixing the two substances and heating them. Some device along the lines of a percolator was desired, and the apparatus shown in the accompanying diagram was devised. The flask was heated, and a jet of air through the inlet at the left forced the hot liquid up the tube, and over the sawdust, from whence it fell back into the reaction vessel.

The analyses of the solutions, all made up to this time by the use of Fehling's solution, were now made with a polariscope.

It was decided, with the new extractor, to determine again the conditions which would give a maximum yield - that is, the time of extraction, and the number of chlorinations and hydrolyses. The procedure in this experiment was as follows:



A - AIR INLET
B - CONTAINER FOR SAWDUST

1) 10 grams of moist sawdust was put into the previously described funnel for chlorination, and treated with chlorine for the designated period of time.

2) The chlorinated sawdust was washed thoroughly, and the wash water set aside to be later added to the sugar solution.

3) The chlorinated sawdust was hydrolyzed in the extractor with dilute H_2SO_4.

4) The solution was neutralized and evaporated for analysis.

As potassium permanganate is a good solvent for lignin salts, it was decided to try washing the chlorinated sawdust with a 10 percent solution of permanganate instead of the washing with water. The first six runs in Table IX used water as the wash liquid, while the last six used the permanganate solution. Results were:

Table IX

Yields of Glucose from Continuous Chlorination and Hydrolysis

Run	% Acid	Time Chlorine (hrs.)	Time Acid (hrs.)	% Glucose
1	7	2	6	7.2
2	7	2	6	6.9
3	7	2	6	7.4
4	7	2	6	6.8
5	7	2	6	7.2
6	7	2	6	7.4
7	7	2	6	7.0
8	7	2	6	7.2
9	7	2	6	6.9
10	7	2	6	6.8
11	7	2	6	7.2
12	7	2	6	7.1

These results did not differ appreciably from the results obtained without the permanganate wash, so it was decided to discard this step.

With the idea of increasing the sugar yield, it was decided to intersperse a treatment with alkali between the chlorination and the acid hydrolysis step. The procedure was to chlorinate as before, wash the

chlorinated sawdust and save the wash water. Then the sawdust was treated with 10% NaOH for two hours, followed by an acid hydrolysis. The wash water was then added to the acid solution, and the whole was neutralized, filtered and analyzed. The following results were obtained:

Table X

Effect of Alkali Treatment After Chlorination

Run	% Alkali	Time Alkali	% Acid	Time Acid	Time Chlorine	% Glucose
1	10	2 hrs.	7	1 hr.	1 hr.	6.5
2	10	2	7	1	1	6.3
3	10	2	7	1	1	7.0
4	10	2	7	1	1	6.2
5	10	2	7	1	1	6.1
6	10	2	7	1	1	5.8

As these values were even lower than the percentage obtained by the same procedure without the alkali treatment, it was eliminated. The reason advanced for the lower yield of sugars was that there could possibly have been a protective coating formed on the sawdust by the reaction between two of the reagents used.

Another attempt was made to increase the yield of reducing sugars by varying the strength of the acid used. The procedure was the same as previously described - ten grams of sawdust were chlorinated,

washed, and then hydrolyzed in the extractor. The results of this experiment were:

Table XI

Effect of Acid Concentration on Yields of Glucose

Run	% Acid	Time Acid	Time Chlorine	% Glucose
1	1	1 hr.	1 hr.	6.1
2	1	1	1	5.4
3	5	1	1	6.6
4	5	1	1	6.7
5	7	1	1	7.5
6	7	1	1	7.8
7	10	1	1	6.0
8	10	1	1	4.2
9	15	1	1	5.8
10	15	1	1	5.3
11	20	1	1	4.2
12	20	1	1	2.8

From the above results it was determined that from 5 to 7 percent acid was the best strength to use.

It was decided to successively chlorinate and hydrolyze, to see if repeated hydrolysis would increase the yield. The procedure was the same as

before, chlorination followed by extraction, except in this case it was repeated. The experiment is outlined below:

Table XII

Effect of Repitition of Treatment on Yield of Glucose

Run	% Acid	Hydrolysis Time Acid	Time Chlorine	No. of Hydrolyses and Chlorinations	% Glucose	Total
1	7	1 hr.	1 hr.	2	7.2 + 6.9	14.1
2	7	1	1	2	7.1 + 5.8	12.9
3	7	1	1	2	6.9 + 5.3	12.2
4	7	1	1	2	7.2 + 6.3	13.5
5	7	1	1	3	10.9 + 1.4 + 2.1	15.4
6	7	1	1	3	11.1 + 3.2 + 4.2	18.5
7	7	1	1	3	12.0 + 3.0 + 4.0	19.0
8	7	1	1	3	11.6 + 3.4 + 3.6	18.6
9	7	1	1	4	9.8 + 3.1 + 6.0 + 0.9	19.8
10	7	1	1	4	10.1 + 3.8 + 5.4 + 0.8	20.1

From this experiment, it was seen that successive hydrolysis increased the yield of sugar considerably over anything that had yet been tried. A yield of 20.1%, based on the weight of the wood itself, is a yield of about 37% of the total cellulose present. As successive hydrolysis seemed to be one of the factors which would give an increased yield, it was decided to vary the time, and perhaps obtain some higher percentage of sugars by this method.

It was also decided to cut down on the chlorination time, to see if the same effect could not be obtained with a much shorted interval of time. This experiment was run using only one hydrolysis, as the primary interest was in the chlorination:

Table XIII

Effect of Time of Chlorination on Yield of Glucose

Run	% Acid	Time Acid	Time Chlorine	% Glucose
1	7	1 hr.	1 hr.	7.5
2	7	1	1	7.6
3	7	1	3/4	7.4
4	7	1	3/4	7.8
5	7	1	1/2	7.7
6	7	1	1/2	7.2
7	7	1	1/4	7.4
8	7	1	1/4	7.6

On comparison with results of Table XI it was determined that the time of treatment with chlorine could be cut to 15 minutes without lessening the yield of sugar, so this was done in subsequent experiments.

The variation of the time of hydrolysis using this new chlorination time, was now carried out. The procedure followed was to chlorinate and hydrolyze four times, changing the time of hydrolysis. A sample of

each hydrolysis acid was kept and analyzed, and the total percentage of glucose obtained from the four analyses is reported:

Table XIV

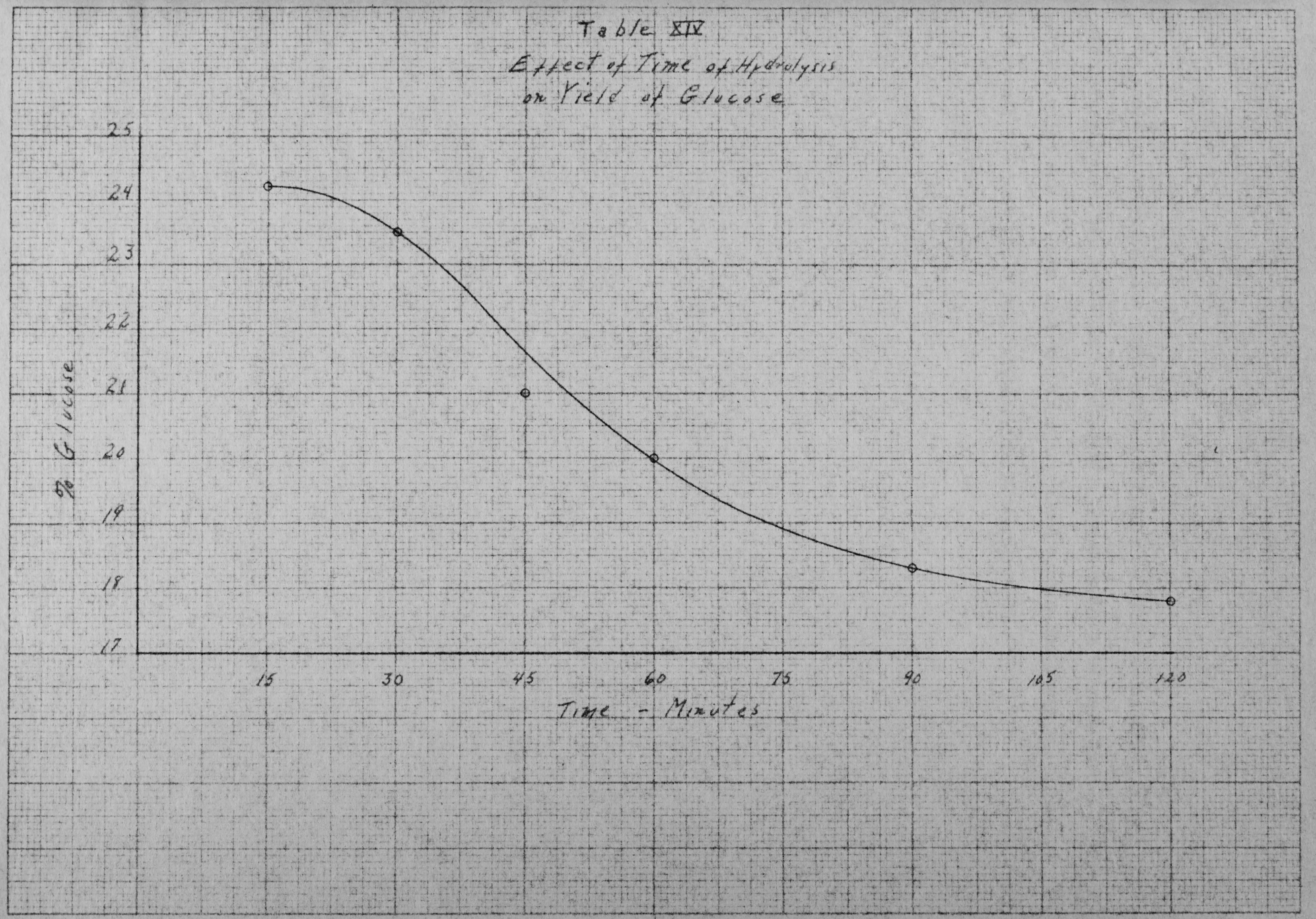
Effect of Time of Hydrolysis on Yield of Glucose

Run	% Acid	Time Acid	Time Chlorine	No. of Hydrolyses & Chlorinations	% Glucose
1	7	1/4 hrs.	1/4 hrs.	4	24.2
2	7	1/4	1/4	4	24.6
3	7	1/2	1/4	4	23.2
4	7	1/2	1/4	4	24.1
5	7	3/4	1/4	4	21.2
6	7	3/4	1/4	4	20.9
7	7	1	1/4	4	19.9
8	7	1	1/4	4	20.2
9	7	1 1/2	1/4	4	14.2
10	7	1 1/2	1/4	4	15.7
11	7	1 1/2	1/4	4	17.9
12	7	1 1/2	1/4	4	18.4
13	7	2	1/4	4	17.8
14	7	2	1/4	4	18.0

It was noted that the maximum yield was obtained after a hydrolysis period of only 15 minutes, so this cut the time of hydrolysis considerably.

Table XIV

Effect of Time of Hydrolysis on Yield of Glucose



The yield increased as the time decreased from 2 hours to 15 minutes, with the exception of the 1 1/2 hour hydrolysis, but a recheck of that gave a value which was in line with the others. Based on the amount of cellulose present, the best yield represents a 45% conversion.

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CONCLUSION

As a result of this investigation, the following conclusions were reached:

1. Concentrated acid gives no appreciable yield of glucose from sawdust, doubtless due to the caramelizing effect.

2. Alkali hydrolysis is of no value with wood wastes.

3. The best yields of reducing sugars can be obtained from the use of dilute acid under these conditions:

Time of Chlorination	15 minutes
Time of Hydrolysis	15 minutes
Number of Chlorinations	4
Number of Hydrolyses	4
Strength of Acid	7%

Should any more work on this problem be attempted, it is recommended that:

1. In the use of concentrated acids, some inhibiting agent be found, in order to prevent charring of the sugars formed.

2. In any use of dilute acids it is most likely that the hydrolysis should be carried out under pressure in order to give any increase in yield of reducing sugars.

BIBLIOGRAPHY

1. The Lumber Industry, Part IV, Bureau of Corporations, U. S. Dept. of Commerce.

2. Margolin, E. H. Report of the National Conservation Commission 1923 Vol. 2 p. 104.

3. Kressman, F. W. U. S. Dept. of Agric. Bull. 983. The Production of Ethyl Alcohol from Wood Wastes 1922 p. 12.

4. Kressman, F. W. ibid p. 14.

5. Branconnet, H. Reducing Sugars from Cellulose Gilberts' Annalen der Physik 1819 p. 348.

6. Simonsen, E. Hydrolysis of Cellulose Z. Angen Chem 111 (1898) p. 219.

7. Newman, H. Hydrolysis of Wood with Dilute Acid Chem Ztg. Vol. 34 (1910) p. 461.

8. Korner, T. Hydrolysis of Cellulosic Materials Z. Angen Chem. 21 (1908) (2353 - 2359)

9. Classen, A. German Patent 111,868 1901.

10. Classen, A. German Patent 118,842 1901.

11. Classen, A. German Patent 118,544 1901.

12. Classen, A. German Patent 118,543 1902.

13. Classen, A. German Patent 121,869 1902.

14. Taffin, M. German Patent 130,980 1903.

15. Kressman, F. W. U. S. Dept. of Agric. Bull. 983. The Production of Ethyl Alcohol from Wood Wastes 1922 p. 10.

16. Ewen, M. F. and Tomlinson, G. H. U. S. Patent 1,101,061 1906.

17. Ewen, M. F. and Tomlinson, G. H. U. S. Patent 1,101,062 1906.

18. Cohoe, W. P. U. S. Patents 985,725 and 985,728 1907.

19. Ruttan, R. F. Saccharification of Cellulose - Containing Substances Jour. of the Soc. of Chem. Ind. 1908 p. 1920.

20. Ekstrom, P. G. Hydrolysis with Sulfite Back Water Jour. of the Soc. of Chem. Ind. 1912 p. 513.

21. Miller, R. N. and Swanson, W. H. Hydrolysis of Wood Ind. Eng. Chem. Vol. 17 1925 p. 843-847.

22. Kulikov, V. M. Russian Patent 846 1914.

23. Fuchs, W. Ber. 60B 1927 776-82 1915.

24. Kleinert, T. and Tayenthal, K. British Patent 357,821 1929.

25. Farber, E. French Patent 383,776 1930.

26. Gallagher, F. and Mork, E. U. S. Patent 763,472 1930.

27. Bergius, F. Twenty Years of Hydrolysis Chem. Trade Jour. 1933 Vol. 93 p. 356-358.

28. Kauko, V. Przemysl Chem. 1933 Vol. 17 p. 1-5.

29. Fanto, H. and Tamchyna, J. Chem. Listy Vol. 24 1930 p. 105-106.

30. Wiertelak, J. Effect of Time Upon the Hydrolysis of Wood by Dilute Acid Am. Acad. Sci. Fennicae Vol. No. 14 (1927) p. 313.

31. Cadenbeck, G. The Use of Hydrofluoric Acid in Hydrolysis Angen. Chem. Vol. 46 1933 p. 113-117.

32. Bergstrom, K. and Cedarquist, G. Successive Hydrolysis in the Production of Alcohol from Wood No. 1 1933 p. 3-25. Iva.

33. Sherrard, E. C. and Gauger, W. H. Catalysts in Hydrolysis Jour. of Ind. Eng. Chem. Vol. 15 1923 p. 164.

34. Schorger, A. W. Chemistry of Cellulose and Wood McGraw-Hill 1926 p. 70.

35. Ibid p. 331.

36. Ibid p. 343.

37. Ibid p. 345.

38. Ibid p. 368.

39. Ibid p. 399.

40. Groggins, P. H. Unit Processes in Organic Synthesis McGraw-Hill 1935 p. 544.