CHAPTER IV

THE DECOMPOSITION OF WOOD BY ACIDS. WOOD SACCHARIFICATION

I. Introduction

The utilization of the carbohydrates of wood as a raw material for sugar manufacture is a scientific, and especially a technical problem of more than 100 years' standing. Just as Kirchhoff's discovery in 1811 that starch could be transformed into sugar by heating with acids was epoch-making for starch chemistry, so was the observation made several years later in 1819 by Braconnot, that cellulose is transformed into sugar on treatment with concentrated sulfuric acid, of fundamental importance for the chemistry of cellulose. Extreme practical importance was attached to this discovery at that time, for it was thought that it would be possible in this way to carry out an economically feasible saccharification of cellulose. However, despite much work in this field, it has not yet been possible to achieve an economically practicable solution of the problem of wood saccharification by Braconnot's method.

Realizing the difficulty of converting wood to sugar economically with strong acid, Melsens in 1855 made the first attempt to carry out the conversion with dilute sulfuric acid at elevated temperatures and pressures.

Several investigators and inventors have worked along these lines right up to the most recent times, and the procedure has been repeatedly tested on a commercial scale. A single treatment of the wood, which was employed in these procedures, gave poor yields of sugar, and this might well be the reason why all attempts to achieve the saccharification of wood by this method have failed.

The idea of converting wood to sugar by heating with dilute acid was not given up, however. A new path was opened up by the procedure of H. Scholler, which is often called the Scholler-Tornesch process, after the town of Tornesch, where the first factory was erected. In contrast to the earlier procedures, this one involves complete digestion of the carbohydrates by

systematic extraction under pressure, so-called "pressure percolation." This process will be described in detail later on.

All procedures for the saccharification of wood with dilute mineral acids yield dilute sugar solutions, containing relatively great amounts of impurities, which makes the isolation of crystalline sugar economically impossible. At the present time, the solutions can be used only as fermentation substrates. Furthermore, the degree of saccharification obtained is less than that theoretically possible. Only by the use of strong hydrochloric acid has it thus far been possible to obtain a nearly quantitative conversion to sugar, and at the same time to isolate the sugar as such. It has required decades of work to perfect the technical details of this process—the so-called "Rheinau process," and to make the procedure economically feasible.

II. Saccharification with Hot Dilute Acids

G. F. Melsens (1) who was the first to saccharify wood with hot, dilute acid, treated the wood in an autoclave at about 180°C with 3-5% acid. However, experiments carried out in France on a technical scale were unsuccessful (2). A Payen (3) hoped to obtain fermentable sugar along with paper pulp by using 10% hydrochloric acid. Bachet and Marchard (2) had, however, already proposed the use of dilute hydrochloric acid. W. Thorn (4) later reported that he had succeeded in this way in obtaining a yield of 18-25% of sugar. C. G. Zetterlund (5), working on a large scale, obtained 19% of fermentable sugar with five parts of 0.7% hydrochloric acid to one part of wood, and a reaction time of 8 hours at 0.1 atmospheres gage pressure.

A more thorough study of the saccharification of wood with dilute mineral acids was made by E. Simonsen (6), who investigated the effects of the strength of acid, the pressure, and the time of the reaction on the yield of sugar.

Simonsen concluded from his experiments that the following conditions gave the highest yield of sugar (about 22% of the weight of the wood for a single treatment): acid strength, 0.5%; pressure, 9 atm.; reaction time, 15 min. He also recommended that the quantity of acid be five times the weight of the wood, although the yield of sugar was not much affected if the quantity of acid was reduced to 2.5 times the weight of the wood. Simonsen believed that the cellulose was the sugar-forming constituent of the wood, because the yield of sugar was proportional to the cellulose content of the raw material.

By further hydrolysis of the unsaccharified residue less sugar was obtained than in the first saccharification, the yield amounting to only 13% of the original wood weight. Fermentation of the sugar solutions yielded about 6.5 l. of alcohol per 100 kg. of wood. On a technical scale the yield was less, amounting to only 2-6 l. per 100 kg.; this fact caused the operation of the factory to be suspended.

A. Classen (7) patented a series of procedures for wood saccharification, in which sulfurous acid was used as a hydrolyzing agent, either alone, or with the aid of such oxidizing agents as chlorine, oxygen, etc.

E. Reiferscheidt (8) carried out a series of experiments with a view to confirming the results of Simonsen and Classen, and obtained, in agreement with Simonsen, a yield of 6 l. of alcohol per 100 kg. of wood. [This result was also confirmed by Koerner (9)]. According to Classen, the best results with sulfurous acid were obtained when 9% acid was allowed to react for one hour at 140-150°C. Koerner (9) found that sulfurous acid did not give particularly good yields of sugar, and that oxidizing agents, with the exception of hydrogen peroxide, were harmful. Sulfurous acid was also used for a time by M. F. Ewen and G. H. Tomlinson (10), but they soon gave up this procedure, because of the difficulties involved, and later employed dilute sulfuric acid, like Simonsen (11).

Since the economic success of the saccharification with dilute acids is dependent on the quantities of water employed, i. e., on the relationship between the amount of acid and the amount of wood, E. Hägglund (12) investigated this matter more thoroughly. He found that decreasing the amount of acid to three times the quantity of wood did not affect the yield of fermentable sugar. Smaller quantities of liquid decreased the yield. The maximum yield per 100 kg. of dry wood corresponded to 8.7 l. of alcohol. The Classen sulfurous-acid procedure gave smaller amounts of fermentable sugar.

F. W. Kressman (13), following up the experiments of Simonsen, also determined the optimum conditions, and found the highest yields when the temperature was not raised above the point corresponding to a pressure of 7.5 atm. At the same time, the quantity of sulfuric acid was kept within the limits 1.8-2.5% of the weight of the wood, and the ratio of water to wood was 1.25 : 1.0. This last figure is not quite in agreement with the results of other investigators. Kressman also confirmed the fact that a rapid raising of the temperature (15-20 min.) and a short reaction time (15-20 min.) gave the best results. The yield of sugar and alcohol proved to be extremely dependent on the type of wood used, as may be seen from the following (abbreviated) table:

Type of Wood	Reducing Sugar in % of the Weight of Wood	Fermentable Sugar in % of the Total Sugar	Alcohol Yield in % of the Weight of Wood
Softwoods			
Western white pine	21.0	74.5	7.8
Red spruce	20.5	74.2	7.6
Red spruce	22.1	72.7	8.0
White pine	20.0	75.7	7.4
Longleaf pine	23.1	73.3	8.3
Longleaf pine	23.3	72.5	8.3
Lodgepole pine	21.9	67.4	7.2
Norway pine	25.6	66.9	7.7
Western larch	29.7	37.9	5.0
Western larch	30.5	57.9	8.7
Western larch	26.2	54.7	6.9
Western hemlock	21.2	77.6	7.6
Sugar pine	18.0	72.6	6.3
Sugar pine	20.2	66.5	7.1
White spruce	23.6	71.4	8.5
Douglas fir	21.1	67.4	6.8
Douglas fir	21.1	75.2	7.9
Hardwoods			
Birch	20.5	46.3	4.3
Sugar maple	18.9	34.0	3.0
Silver maple	20.7	47.2	4.7
Beech	21.2	22.2	2.0
White oak	17.3	50.5	4.1
Red oak	18.4	30.4	2.7
Sycamore	18.3	38.9	3.2
Slippery elm	16.6	26.8	1.4
Red gum	20.4	38.8	3.7
Cotton wood	18.2	32.9	2.4

Although the yield of reducing sugars from hardwood is not much smaller than that from softwood, the alcohol yield from the former is on the average less than half of that from the latter. This is due to the presence of large quantities of non-fermentable pentoses in the sugar from hardwood.

The poor fermentability of the sugar from "western larch" is attributable to the fact that this sugar is very rich in galactose, which is fermented only poorly or not at all by the strain of yeast used by Kressman (14). E. C. Sherrard (15), however, succeeded in fermenting galactose by using a Hungarian brewer's yeast, and thus raised the yield of alcohol to 10.8 g. per 100 g. of wood, with an average sugar yield of 29 g. Sherrard and G. W. Blanco (16) determined anew the optimum conditions for saccharification, and found the following for white spruce: 7.8 at. (175°C); 15 min. reaction time; 2.5% sulfuric acid (referred to the weight of the wood); 2 parts water to 1 part wood.

It has long been known that acetic and formic acids arise during the hydrolysis of wood (cf. p. 349). Sherrard and Blanco determined the quantity of acetic acid which is formed during the saccharification of

white spruce. By analyzing the residue, they further determined the amount of methyl alcohol split off, and the changes in the content of ash, cellulose, and pentosan.

According to their figures, 90% of the acetic acid, 80% of the pentosan, 30% of the cellulose, and 16% of the methoxyl are solubilized by the saccharification procedure. The lignin is evidently not dissolved.

Per Cent of the Weight of the Wood Before Hydrolysis

	Ether Extract-able	Acetic Acid on Hydro-lysis	CH_3O	Pento-san	Methyl-pento-san	Cellu-lose	Lig-nin	Ash
Before hydrolysis..	0.96	1.32	4.75	10.76	2.61	58.33	29.19	0.26
After hydrolysis...	1.08	0.116	3.99	1.79	3.06	39.67	29.63	0.06

W. P. Cohoe (17) thought that he could make the hydrolysis easier by a short pretreatment with steam. He also found that coarse sawdust was more suitable than fine.

Repeated attempts have been made to increase the yield of sugar by the addition of certain materials, which are alleged to have a catalytic effect.

As has been mentioned above, Classen attempted to convert sulfurous acid to sulfuric by the addition of oxidizing agents, with the evident hope of achieving an effect due to a "nascent" state. R. Gentzen and L. Roth (18) thought that they could conclude from their experiments that oxidizing agents had a favorable effect on the formation of sugar, even in the absence of sulfurous acid, but this conclusion is evidently wrong, to judge by later investigations (19). The problem has been studied particularly carefully by E. C. Sherrard and W. H. Gauger (19), who investigated a very large number both of organic and of inorganic materials, including ferric sulfate, copper sulfate, sodium bisulfite, zinc sulfate, potassium aluminium sulfate, nickel sulfate, manganous sulfate, cobalt sulfate, naphtholsulfonic acids, etc. In no case was an appreciable catalytic effect demonstrated; indeed most of the substances decreased the yield of alcohol.

A number of wood saccharification plants constructed in Germany during World War I used a modified Classen sulfurous-acid process. The modification consisted in the use of hydrochloric and sulfuric acids along with the sulfurous acid (20).[1] One to two per cent of SO_2 and HCl plus 3-4% of H_2SO_4, calculated on a dry weight basis, were added to a charge of 1,000 kg. of wood chips, and the temperature was raised rapidly to 165-170°C, corresponding to 7-8 atm. The hydrolysis was stopped after

[1] Voerkelius (21) could not detect any favourable result from adding sulfurous acid to a solution containing 0.2-2% of sulfuric acid at temperatures of 120-180°C.

20 minutes, and the contents of the digester were drawn off as rapidly as possible. The mass was extracted in diffusers, and yielded a 6-8% sugar solution. About 6-8 l. of alcohol were obtained per 100 kg. of dry wood in continuous operation.

Quite large quantities of unchanged carbohydrates remained in the residue, but it proved unprofitable to carry out repeated saccharifications.

The technique used here was obviously the same as that introduced much earlier in Georgetown by Ewen and Tomlinson. This procedure has been described by G. Foth (22) and especially by R. v. Demuth (23). Recently a summary has been given by E. C. Sherrard and F. W. Kressman (24). It was possible by appropriate procedure to obtain 6.4 l. of alcohol per 100 kg. of wood.

Certain by-products are formed during the saccharification of wood with dilute acid, and attempts have been made to recover them, in order to make the process more attractive economically (25). These products are acetic acid, methyl alcohol, acetone, aliphatic aldehydes, furfural, terpenes, and aromatic hydrocarbons, and part of them came over with the steam when the digester was blown off. The vapors were freed of acid constituents in a lime tower, and then condensed. The total amount of alcohols and aldehydes obtained on a technical scale was less than 1% of the weight of the wood. α-Pinene and p-cymene were found to be present in the terpene fraction, to the extent of 5% of the crude oil. Furfural was obtained from the condensate blown off from the digester. The yield was small—only 1% of the weight of the wood. Although the recovery of furfural was profitable, it was not sufficient to make the over-all production of alcohol from wood sugar economically practicable in peacetime, and the factories were shut down after the end of the war.

There are evidently several reasons, not all of them now known, why it is not possible to obtain more than 8-9 l. of alcohol (16-18% of fermentable sugars) from 100 kg. of wood by hydrolysis with hot, dilute mineral acids, although it should theoretically be possible to obtain about four times as much. It should be emphasized first of all, that the easily hydrolyzable carbohydrates which first become saccharified are rapidly decomposed by further cooking at the high temperatures used. It is true that the cellulose and the other wood polyoses yield further quantities of sugar, but under certain conditions the rate of sugar decomposition may become greater than the rate of hydrolysis. The decomposition has been shown to proceed faster in concentrated solutions than in dilute ones, so that it is advisable not to make the ratio of water to wood too small.

The ratio between the rates of the hydrolysis of cellulose and the decomposition of glucose, previously studied by H. Lüers (26), H. Scholler (27)

and F. Thiersch (28) (cf. p. 94), has recently been reinvestigated by J. F. Saeman (29) (cf. p. 397).

E. C. Sherrard and W. H. Gauger (19) attempted unsuccessfully to achieve a better yield by increasing the acid concentration from 5 to 30% H_2SO_4, while keeping the other conditions unchanged (15 min. at 175°C) (16). Nearly all the cellulose in the wood went into solution when the sulfuric acid concentration was raised, to be sure, but the quantity of sugar nevertheless decreased, as the following figures show:

Grams H_2SO_4 per 100 g. Dry Wood	Per Cent of the Weight of the Wood			
	Total Reducing Sugar	Fermentable Sugars	Cellulose in Residue	Dissolved Cellulose
5	21.98	16.29	31.7	26.5
10	21.54	18.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

The gradual decrease in the quantities of sugar obtained by repeated hydrolysis of the residues from earlier treatments is shown in the following table by J. Neuman (9):

Experiment No.	Sugar %	Alcohol %	Actual Yield of Alcohol in % of the Theoretical	Comments
1	18.3	5.1	50	Ordinary saccharification with hydrochloric acid; 100 g. dry sawdust gave about 80 g. dry residue
2	16.4	7.2	100	Hydrolysis of the residue from No. 1, (0.5% sulfuric acid for 15 min. at 175°C)
3	13.1	5.5	100	Same as No. 2, using residue from No. 2
4	12.9	6.3	100	Same as No. 2, using residue from No. 3

The idea of obtaining sugar from wood by the action of hot, dilute acids was not given up, however. H. Scholler (30) developed a method for saccharifying all of the carbohydrate of wood, which was based on his previous studies of the effect of reaction conditions on the saccharification of cellulose with dilute acid (27) (cf. p. 94).

The wood chips are brought to the cooking vessels (or percolators) by elevators and packed into them by steam pressure. Warm (170°C) 0.4% sulfuric acid is pumped through from top to bottom, and the heat of the sugar solution which is drawn off is used to pre-heat the acid. After a time a certain amount of the hydrolyzate is drawn off and an equal quantity of fresh acid is pumped in, thus preventing part of the sugar dissolved from being destroyed by the hot acid. The process is continued until all the carbohydrate of the wood has reacted. After neutralization the solution is used for fermentation or for the manufacture of yeast.

When soft woods were used, a 3-4% sugar solution was obtained. However, the sugar was by no means completely fermentable, for the yield of alcohol was approximately 1.2 l. of 100% alcohol per 100 l. of solution.

There is no doubt that all of the carbohydrate is dissolved by hydrolysis, for the residue corresponds to a normal yield of lignin, but an appreciable amount of the sugar formed is destroyed in the medium, so that the maximum yield of fermentable sugar from soft wood does not exceed about 40%, although the theory calls for about 66%. Accordingly, about 20 l. of pure alcohol are produced per 100 kg. of dry wood. The higher the concentration of sugar, the more it is degraded. However, it is more profitable to produce alcohol or yeast from a more concentrated sugar solution than from a dilute one, so that there is an optimum economic concentration for the over-all process—saccharification plus fermentation. This optimum lies at approximately $2\frac{1}{2}$% of fermentable sugar, i.e., at about the same sugar concentration as that found in the waste liquors from the sulfite pulping process.

A procedure developed by O. Ant-Wuorinen (31) is similar to that of Scholler in that a sort of percolation is employed. The percolation lasts for 40 minutes at 145-185°C, and a sulfurous acid solution containing 0.2-2% of SO_2 is used instead of dilute sulfuric acid. In this process, too, it is impossible to avoid the loss of sugar by decomposition, but the losses are obviously less than those caused by the use of 0.5% sulfuric acid. The use of the acid sugar solution to saccharify new wood (also considered by Scholler) which would constitute a sort of diffusion process, would hold out greater promise of sucess with the use of SO_2 solutions (32). However, the old rule that the higher the sugar concentration, the greater the decomposition of the sugar, holds here, too. Ant-Wuorinen gives the following figures for his pilot plant:

Sugar Concentration %	Total Yield of Sugar, in % of the Weight of the Wood (Pine)
1.7	54-55
3.4	52
6	45

A yield of 60 l. of alcohol per cubic meter (0.27 cords) of pine wood was obtained. This corresponds to something more than 21 l. per 100 kg. of wood, a yield which is not markedly higher than that obtained with the Scholler process.

The saccharification of wood for the purpose of obtaining alcohol by fermentation became technically important because of the great industrial demand for alcohol during the war years (1939-1945) especially in America.

In this connection J. F. Saeman (29) has measured the reaction velocity

for the hydrolysis of various American woods by dilute sulfuric acid at high temperatures, and investigated the speed of the decomposition of the sugar at the same time. It turned out, as previously had been shown for glucose (26), that the decomposition of all the types of sugars studied were first-order reactions. The activation energy of the decomposition of glucose was 32,800 cal. and did not depend on the acid concentration within the limits 0.4-1.6%. An increase of 10° in temperature between 170-190°C caused a 125% increase in the rate of decomposition. Doubling the acid concentration doubled the speed of decomposition. It was further found, in agreement with the results of Lüers (26) and Thiersch (28), that the hydrolysis of pure cellulose in the form of cotton or of wood which had been freed of wood polyoses by pre-hydrolysis was a reaction of the first order. Doubling the acid concentration in the range 0.4-1.6% increased the velocity of hydrolysis by about 150% at 170-190°C. A 10° temperature rise increased the hydrolysis rate 186% in this temperature range. From these data it is apparent that raising either the temperature or the concentration of acid results in a greater increase in the rate of hydrolysis of cellulose than in the rate of destruction of glucose. Hence, the efficiency of conversion of cellulose to reducing sugar is increased by increasing acid concentration and temperature.

R. H. Plow, J. F. Saeman, H. D. Turner, and E. C. Sherrard (33) have reported experiments made on a pilot-plant scale in spherical rotary digesters with a capacity of about 230 l. Repeated cookings of the residue yielded 19-23 l. of alcohol per 100 kg. of wood (Douglas fir), or just as much as saccharification in a stationary percolator. No fewer than 15 successive cookings were required, but the time for each was short, so that only about 2½ hours were consumed in all. A sulfuric acid concentration of 0.25-0.6% was employed at 170-185°C, using a ratio of wood to liquid of 1 : 3.

This procedure naturally has only academic interest, since, among other things, the residue must be washed completely free of sugar between the cookings.

A modification of the old one-stage process led to an increase in the yield of alcohol from 8.5 to about 11.5 l. of 95% alcohol per 100 kg. of wood. This "modified American process" is characterized by the use of high temperature (185-190°C), a sulfuric acid concentration of 1-2%, and a wood to liquid ratio of 1 : 2. If the process is repeated three or four times, and the digester held at the maximum temperature for 3-6 minutes each time, as much as 29% of fermentable sugar (based on the weight of the wood) can be obtained, corresponding to 16.5 l. of 95% alcohol per 100 kg. of wood. The original "American process" is the Tomlinson method mentioned

above, in which, according to Kressman, 100 parts of wood, 125 of water, and 1.8-2.5 of H_2SO_4 are heated to 173°C for 30-40 min. by the direct application of steam.

In the so-called "Madison wood sugar process" (34) 0.5-0.6% H_2SO_4 at 180°C is allowed to flow through the charge of wood continuously, rather than in batches as in the Scholler process. The sugars produced are removed more rapidly, saccharification is accomplished in less time, and steam consumption is therefore lower than in the German process. Using Douglas fir sawmill wood waste, the reducing sugar obtained with a reaction time of 2.7-3 hours amounted to about 50% of the bark-free wood, and the sugar concentration in the hydrolyzates was about 5%. Fermentation resulted in a yield of 24.5 l. 95% ethanol per 100 kg. wood, compared with 21 l. obtained in the Scholler process with a reaction time of 13-20 hours.

Alcoholic fermentation of wood sugar solutions, obtained by hydrolysis of Douglas fir waste wood with dilute sulfuric acid, has been thouroughly studied by E. E. Harris and co-workers (35). They point out that in agreement with previous findings (36, 37) removal of furfural (for example by flashing the hydrolyzate after neutralization) aids to fermentation. They also found that fermentation is facilitated, if the wort is clarified with aluminium sulfate. It is probable that a lignin-like substance, which is otherwise deposited on the yeast cells, is removed by this procedure (38). The alcohol yield from hydrolyzates containing 5% sugar was about 40% of the total reducing substance.

Production of yeast from wood sugar has been investigated by H. Fink, R. Lechner and E. Heinisch (39, 40), who used hydrolyzates from both the Scholler and Rheinau processes. *Torula utilis*, which ferments both hexoses and pentoses, and requires only ammonia as a source of nitrogen, was obtained in a yield of 40% of the total reducing sugars present in the wort. The high nutritive value of torula fodder yeast, especially as a source of protein and vitamins, has been pointed out by several authors (41). W. H. Peterson, J. F. Snell and W. C. Frazier (42) have also examined the conditions for a successful aerobic fermentation of wood hydrolyzates with torula yeasts, and found that an appropriate clarification and detoxification of the solutions is as necessary as in alcoholic fermentation (35). Hydrolyzates from different wood species, especially Douglas fir, spruce and Southern yellow pine, were investigated. The yeast yields (dry) obtained ranged between 35 and 42% of the total reducing sugar.

The suitability of wood hydrolyzates for the production of butanol and acetone by *Clostridium acetobutylicum* and of 2,3-butylene glycol by *Aerobacter aerogenes* has been studied by E. E. Harris, E. Beglinger, G. J. Hajny and E. C. Sherrard (43).

In the wood saccharification process, as outlined above, a lignin residue is obtained, for which no satisfactory use has yet been found. Lignin from the Scholler process has been used for soil improvement and its conversion into plastics has been attempted, but evidently with only little success (40, 44). A process consisting of a partial hydrolysis of wood, especially hard wood wastes, has been developed by Sherrard and his co-workers at the U. S. Forest Products Laboratory (45) with the purpose of obtaining lignocellulose residues suitable for plastic molding. The hydrolytic action in this process is confined chiefly to a dissolution of the hemicelluloses, and the resulting lignin-enriched residue shows some plastic flow, which makes it suitable for pressure molding, especially after incorporation of "plasticizing" agents such as aniline or furfural. A similar process, working continuously, has been developed by R. Katzen and D. F. Othmer (46). It has been shown (47) that the lignocellulose material obtained in this process contains about 55% lignin, part of which is soluble in organic solvents. Methanol dissolved 36%, dioxane 38%, and glycol monomethyl ether, 60% of the total lignin present. R. Katzen and co-workers (48) have also examined the possibilities of obtaining furfural and organic acids by heating the hydrolyzates at a pressure of 100 pounds per square inch for 15 minutes and then extracting with high-boiling solvents.

III. Saccharification with Concentrated Mineral Acids

A. SULFURIC ACID

In connection with his attempts to saccharify cellulose, H. Braconnot (49) also investigated the behavior of wood toward concentrated sulfuric acid, and found that large quantities of sugar were formed. Braconnot used a large excess of sulfuric acid, which naturally precluded any possibility of making the process economically practicable. The extent of saccharification was determined by means of the Flechsig method (50) by G. A. Voerkelius (21). He used seven parts of 70% sulfuric acid to one part of wood, and obtained 67% of sugar, 70% of which was fermentable. This gave 24.8 g. of alcohol per 100 g. of dry wood. The saccharification was evidently complete, since the lignin residue from the same amount of wood was 30 g.

It had been recognized even before this that economic practicability was out of the question unless the quantity of sulfuric acid could be reduced without reducing the yield of sugar. Experiments along this line were undertaken by J. E. Arnould (51), who used 100 parts of sawdust to 110 parts of concentrated sulfuric acid. His report that 80-90% of the wood was converted into soluble material is either wrong, or is due to the fact that too concentrated acid was used. A. Classen (52) found that high

pressure could initiate an exothermic reaction in a mixture of one part of sawdust and $^3/_4$ parts of sulfuric acid of 57° Bé. Treatment of the mass with hot water resulted in the conversion of up to 60 % of the wood to sugar. G. Ekström (53) also attempted to saccharify sugar with small quantities of strong sulfuric acid, both at low temperatures and at a temperature of 80° C.

E. Hägglund (12) determined the yields of sugar from sawdust and 70% sulfuric acid at various temperatures and with various reaction times. When the quantity of 70% sulfuric acid used was 100% of the weight of the wood, approximately 55% of sugar could be obtained at ordinary temperature.

These questions have recently been reinvestigated and large scale experiments have been carried out (54). It was found that quite good yields of sugar could be obtained with small amounts of acid, provided that the wood was used in a sufficiently finely divided form. Using a wood : acid ratio of 2 : 1 the sugar yield was 56% of the wood substance. The residue amounted to 35%, proving that only a small amount of unsaccharified material remains. Fermentation produced 48 l. of alcohol per 100 kg. of sugar.

It will be noted that the weight of sulfuric acid consumed is somewhat less than that of the sugar produced.

Low viscosity sulfite pulp ("fodder cellulose") could also be converted to sugar with a small amount of sulfuric acid. In a special experiment, for every 1.185 kg. "fodder cellulose," corresponding to 1 kg. dry pulp, 0.94 kg. concentrated sulfuric acid was used, the final concentration of the acid thus being about 80%. The sugar yield was 0.9 kg., which corresponded to about 90% yield, when the carbohydrate content of the pulp was taken into consideration. Since the sulfite pulping can be carried out in such a way that losses of sugar can be kept low, there is here a possibility of practically completely saccharifying the carbohydrates of the wood.

M. Giordani (55) believed that before saccharification with strong sulfuric acid could be made to occur economically it would be necessary to remove the wood polyoses and to degrade the cellulose completely to a "hydrocellulose" by pre-hydrolysis with 0.5-5% sulfuric acid at 135-150°C. However, this is by no means necessary, as has been shown above.[1]

Even if it seems possible to obtain a quantitative yield of sugar from wood, it would entail the consumption of a considerable quantity of

[1] For other methods, see K. Mitterbiller-Epp (56). He pulps with 50% sulfuric acid, and precipitates the dissolved carbohydrates with water. The products so obtained are said to be suitable for fodder. Since these are cellulose dextrins, they can be fed only to animals which digest cellulose. Such animals can also digest pulp itself, which would be simpler.

sulfuric acid, and an equivalent amount of lime, since the solution has to be diluted, heated, and then neutralized with lime or chalk to remove the sulfuric acid, which precipitates as calcium sulfate. If the calcium sulfate is not utilized, it accumulates in huge quantities. It would undoubtedly be possible to reconvert it to sulfuric acid, but this would not be profitable except on a very large scale—far exceeding that of any imaginable factory for the saccharification of wood.

For the sake of completeness, it may be mentioned that the recovery of the sulfuric acid by dialysis through a copper ferrocyanide membrane has been proposed (57). This method would hardly be of any more value than a previous attempt to utilize the sulfuric acid of the hydrolysis solution for the preparation of soluble phosphates. The Th. Goldschmidt Co. procedure for recovering the acid in the form of hydrogen sulfide is out of the question, and it is also impossible to effect the recovery by electrolysis (58).

B. HYDROCHLORIC ACID

A. Béchamp (59) discovered as early as 1856 that fuming hydrochloric acid dissolved cellulose, and that sugar appeared in the solution after some time. The conditions for the formation of sugar were not precisely given, and Béchamp made no attempt to make a technical application of these important findings. In the eighties, however, E. S. Dangevilliers (60) reported a procedure for saccharifying wood with strong hydrochloric acid. He passed hydrogen chloride into moist sawdust until complete conversion to sugar had occurred. The excess hydrogen chloride was pumped off in a vacuum, and the mass treated with water and cooked, in order to complete the hydrolysis of the dissolved carbohydrates. The equipment used is fully described in the patent. It was impossible to recover the hydrochloric acid in this procedure, because of faulty arrangements for the heat transfer during the evaporation, and especially because of unsuitable equipment for the saccharification.

R. Willstätter and L. Zechmeister (61) in 1913 gave exact data as to the strength of hydrochloric acid required to achieve smooth dissolution and saccharification of cellulose. Willstätter patented the preparation of cellulose solutions. According to this patent, one part of sawdust is treated with seven parts of acid of specific gravity 1.209-1.213 (at 15° C, corresponding to 40-41% hydrochloric acid). After one hour the lignin is filtered off and the cellulose precipitated from the solution with water, salt solution, or alcohol. No mention of the extent of saccharification is made in the patent, but in the article by Willstätter and Zechmeister there are some

statements to the effect that complete saccharification of cellulose is possible only with a very great excess of hydrochloric acid. The dissolving power of the acid increased with its strength, but even 41% hydrochloric acid can give only a 15% solution of cellulose.

This slight dissolving power of concentrated hydrochloric acid compared with that of concentrated sulfuric acid is indeed a great disadvantage in the technical conversion of wood to sugar. While it is possible to effect complete saccharification with equal parts of concentrated sulfuric acid and wood, equal quantities of 40% hydrochloric acid and of wood give at most 21.6% of sugar, and this yield is achieved only after 24 hours. The time could be cut to 4 hours if the temperature was kept at 40° C, but prolongation of the reaction time did not increase the yield above 23.5%. With larger quantities of hydrochloric acid, the yield of sugar increased slowly, as the following figures show (62):

Relative Amount of Hydrochloric Acid, by Volume	Yield of Sugar, in % of Weight of the Wood, at 15° C
1	21.6
2	30.0
3	44.4
4	54.5
5	61.4
6	66.5
7	67.2

The yield could be increased only slightly by intimate mixing, kneading etc.; nor was any greater improvement noted when very fine sawdust was used.

When the excess of acid was kept as small as possible, i.e., when the concentration of the carbohydrate in solution was high, there occurred a strong reversion of the sugar first formed. Hence the advantage ascribed by Willstätter to the hydrochloric acid process over that with sulfuric acid, namely, that the hydrolysis could be followed polarimetrically from start to finish, is only a limited one. The polarimetric measurements, according to Willstätter, are best made on solutions which are quite dilute with respect to sugar.

The saccharification with hydrochloric acid, like that with sulfuric acid, must be considered as a two-stage process: solution in concentrated acid, and hydrolysis with dilute acid. H. Ost (63) has called attention to this fact.

The initial reactions occurring between cellulose and hydrogen chloride in the absence and in the presence of water have been studied by Schlubach and by Hess and their co-workers. Their results have been discussed in Chapter III (p. 101).

Willstätter's process leads to solutions which contain at most 3-4% of

sugar. It is unthinkable that the problem of converting wood to sugar could be solved in this way, for in the first place, solutions high in hydrogen chloride can not be evaporated in technical operation, and in the second place, even if it were possible to separate the sugar from the hydrochloric acid in this way it would still be uneconomical at such low concentrations of sugar.

A discovery essential for the development of the process was that of E. Hägglund, who found that hydrochloric acid solutions which showed no more dissolving power regained their activity when brought into contact with fresh sawdust. The saccharification stopped again when a certain quantity of carbohydrate had gone into solution; a new "equilibrium" had been established. The solution could then again take up carbohydrate from fresh sawdust. In this way it proved possible to obtain simultaneously both complete saccharification and concentrated sugar solutions, containing 30 g. of sugar or more per 100 cc. of solution. When the concentrated sugar solutions had been obtained in this way, the possibility arose of carrying out on a technical scale the separation of the acid from the sugar by vacuum distillation, and of doing it economically. This presupposes, however, that the sugar is stable enough to permit the solution to be heated to the temperature necessary for the distillation at the vacuum technically obtainable. The sugar solutions could actually be heated to 70°C without being decomposed in the time necessary for the distillation. So high a temperature is not necessary in practice.

Repeated saccharification in several successive reaction vessels and recovery of the hydrochloric acid by vacuum distillation of the sugar solutions are characteristic of the Rheinau process. The principles of this process were patented as long ago as 1917 (64), but it required a great deal of courage to put the principles into practice, for it could be forseen that the most serious difficulties would arise in perfecting the apparatus for such a process.

The technical details of the process can not be discussed here. The difficulties connected with the apparatus were overcome in the course of many years. A large number of chemists and engineers have made significant contributions to the development of the process (65, 66). The essential steps of the process are shown schematically in Fig. 65.

The wood, consisting of any waste wood (or firewood) is shredded into pieces somewhat larger than the particles of ordinary sawdust, and dried to 5–10 per cent water content in a revolving drum, which is heated by means of the stack gases of the boiler plant. The dried wood is conveyed to the diffusion battery, which consists of a series of iron containers equipped with acid-proof linings.

A countercurrent system is used in the hydrolysis. The dried wood is mixed in the first diffuser with an acid-sugar solution which already has passed through the preceding diffusers. The fresh acid containing 40 per cent hydrogen chloride is brought into contact with a charge, which is already practically completely saccharified and extracted. It then proceeds
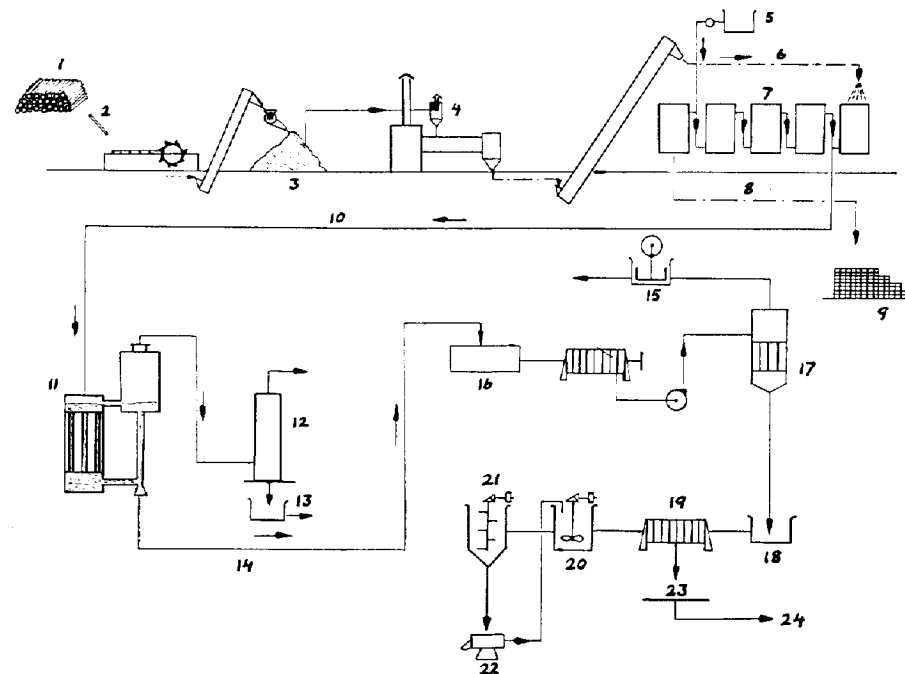

Fig. 65. Flow Diagram of the Rheinau Process.

1. Wood supply
2. Wood shredder
3. Chips
4. Wood dryer

Saccharification steps:
5. Hydrochloric acid
6. Dried wood chips
7. Diffusion battery
8. Lignin
9. Lignin-briquetting process

Evaporation steps:
10. Sugar solution
11. Evaporator for hydrochloric acid
12. Condenser
13. Hydrochloric acid
14. Sirup

Crystallization steps:
15. Vacuum pump
16. Inversion

17. Evaporator
18. First crystallization
19. Filter press
20. Solution vat
21. Recrystallization
22. Centrifuge for pure crystals
23. Sirup filtrate (mother liquor)
24. To alcohol (by fermentation)

through the battery, successively meeting charges with increasing carbohydrate content and taking up more and more sugar. Finally, when it has been in contact with the fresh wood for a time, it is drawn off, and then contains about 32 per cent by volume of reducing sugar. From the last diffuser practically carbohydrate-free lignin is obtained, which is freed of hydrochloric acid by systematic washing. It can be briquetted without a binder and used as fuel or converted into charcoal. The use of the lignin residue in thermosetting plastics has also been proposed (67).

So far, however, there has evidently been no significant utilization of this lignin (40).

The operation may be explained as follows: We assume that the acid-sugar solution in one diffuser is in equilibrium with wood which still contains undissolved carbohydrate. Acid with a higher HCl content, coming from the preceding diffuser, displaces this solution into the next diffuser, which contains wood with a higher carbohydrate content. If this process is carried out systematically, the sugar content of the solution rises from one diffuser to the next, as is shown in Fig. 66. The curve is not linear; this fact shows clearly that the last traces of cellulose are not easily converted into sugar.
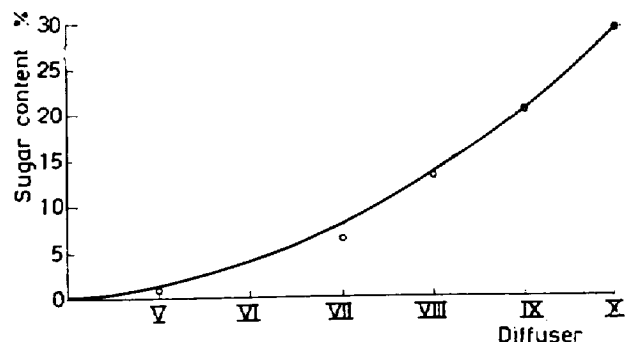

Fig. 66. Sugar content of the hydrochloric acid solutions in the various diffusers.

The sugar concentration of the final solution is dependent primarily on the number of the diffusers; Fig. 66 shows that seven diffusers would be required to achieve a concentration of 30%, at temperatures of 15-20°. (It should be noted that the "percentages" used here mean grams of sugar per 100 cc. of solution.) The discovery (68) that the quantity of hydrogen chloride decreased as that of sugar increased was also significant. The ratio of HCl to $(HCl + H_2O)$, which was initially about 40% had decreased to about 32% in the last diffuser. This behavior may be attributed to the absorption of hydrogen chloride by the lignin. The relationship between the concentrations of sugar and hydrogen chloride are illustrated in Fig. 67.

A study of the processes in the diffusion battery gives the impression that there must exist an equilibrium involving the sugar content of the solvent and the carbohydrate content of the residue. This would be difficult to understand, however. The controlling factor is the concentration of the hydrochloric acid. An increase in the HCl content of the sugar solution increases the extent of saccharification and accelerates the process (68).

A reversion of the sugar occurs along with the saccharification, the extent of the reversion increasing with the sugar concentration. Apparently, the reversion proceeds to a mixture of oligosaccharides, mainly containing
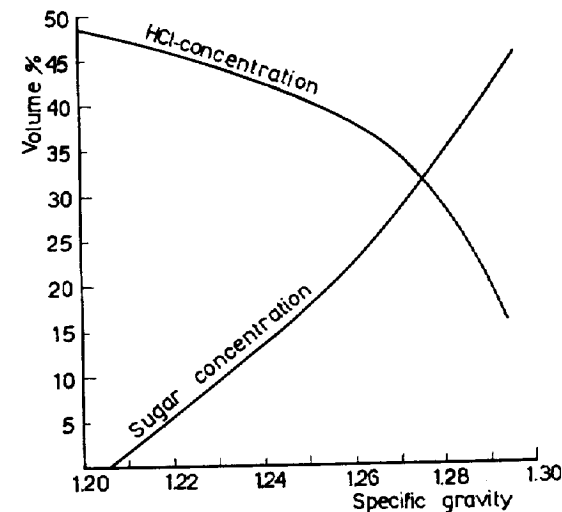

Fig. 67. Relationship between the hydrogen chloride and the sugar concentrations in saccharification solutions of different specific weight.

more than two monosaccharide units. The connection between the sugar concentration and the amount of reversion products may be seen from the following figures:

Per cent of carbohydrate in solution (calcd. as glucose)	7.6	15.6	32.2	46.6
Per cent of carbohydrate present as reversion product	26.6	32.5	47.1	54.2

After inversion, the sugar obtained from fir and pine (in yields of 65-70% of the wood) had the following composition:

	%
Glucose	61.9
Mannose	24.7
Galactose	4.0
Fructose	1.4
Xylose	8.0
	100.0

The sugar solution obtained from the battery is distilled under vacuum. Distillation is carried out by indirect steam heating and with rapid agitation of the solutions. The evaporators are equipped with tubes of a special acid-proof material of good heat conductivity. The hydrochloric acid is condensed and re-used in the hydrolysis step.

To separate the hydrochloric acid as far as possible, steam is blown into the concentrate at the end of the vacuum distillation. A sirup, consisting of sugars and their r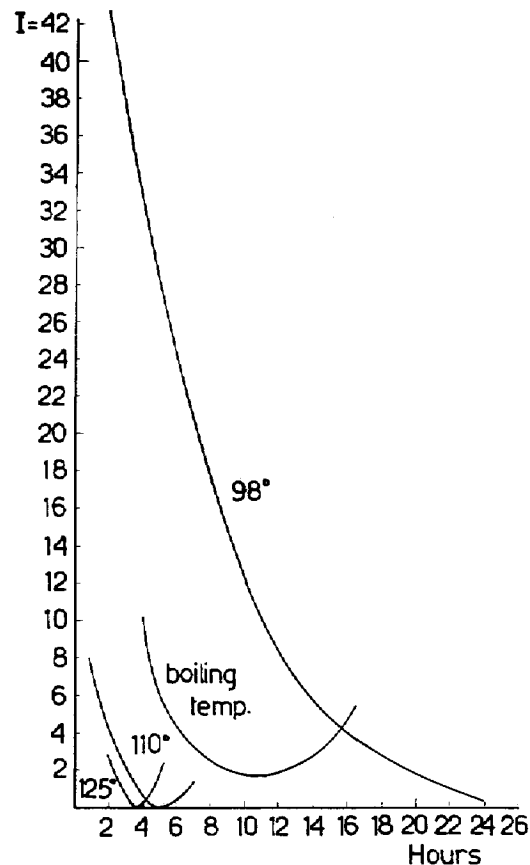eversion products (see above, p. 407) is thus obtained. It contains only about 3% of HCl, calculated on the amount of sugar present.

If the sugar is to be used for fermentation or for the production of crystalline sugar, the reversion products have to be inverted. For this purpose the raw hydrolyzate, which still is slightly acid, is diluted by three times its volume of water and heated for about half an hour at 120° C. The speed of inversion in 10% sugar solutions with 1% of HCl is shown in Fig. 68. The ordinate represents the inversion factor I, defined by:

$$ I = \frac{(a - b)\,100}{a}, $$

where a is the glucose content when the inversion is complete, and b the glucose content at any given time. Neutralization and concentration yield crystalline sugar which can be used as fodder. The remaining molasses may be utilized in fermentation processes.

Fig. 68. The speed of hydrolysis of crude wood sugar at various temperatures.

The suggestion has been made (69) that the hydrochloric acid could be removed by systematic dialysis instead of by distillation. However, there are no technically applicable membranes which will permit such a separation without the loss of excessive quantities of sugar from solutions containing large amounts of monosaccharides. It should also be emphasized that the hydrochloric acid recovered by dialysis would in any case be a dilute solution which would be of no value for the further operations.

In the past 10 or 20 years repeated attempts have been made to solve

the saccharification problem by the method of Dangevilliers, too. A. Wohl and H. Krull (70) immersed 5 g. of wood in 15 cc. of water, and saturated the mixture with hydrogen chloride. After 5 hours of hydrolysis, the hydrochloric acid was distilled off in a vacuum, leaving behind only small amounts of HCl. The mass was diluted with water to a volume of 100 cc., cooked for 8 hours, neutralized, treated with yeast nutrients, and fermented. The following results were obtained:

Raw Material	Sugar %	Alcohol %	Yield of Alcohol in % of the Theoretical (Calculated on Basis of Sugar)
Cotton	94.4-97.9	44.3-46.6	90.7-91.7
Mechanical pulp	62.65	15.48	50.0
Unbleached sulfite pulp	84.9	29.0	68.6
Unbleached soda pulp	88.7	25.3	60.0
Spruce wood	59.3-62.6	17.2-18.8	60.0-61.5
Rye straw	59.4-59.6	6.8-7.1	23.0-30.0

This process is out of the question for technical operation because of the heat developed when the hydrogen chloride is absorbed. In order to reduce this heat as much as possible, it has been suggested (71) that the wood be immersed not in water or in dilute HCl, but in 40% HCl, and that HCl gas then be led in until saturation is reached.

Nearly quantitative solution was obtained when the amount of hydrogen chloride was 80% of the weight of the wood. According to the patent, not only sugars, but also hydrolyzable dextrins are obtained. When the saccharification is complete, part of the hydrogen chloride is recovered by evacuation.

The Swiss chemists H. Terisse and M. Levy (72) used a method which is the same in principle as that described above. Dry sawdust was mixed with an equal weight of 40% hydrochloric acid, and the temperature was kept down to 25 °C by cooling. The concentration of hydrochloric acid was then increased by passing in a quantity of gas equal to 10-20% of the weight of the wood. This can be done because of the adsorption of HCl by the wood. It must also be noted here that heat is developed, and must be removed. The inventors of the process attempted to do this by water cooling, using an apparatus similar to a mechanical roasting oven. The plates were hollow, and water circulated through them, cold in the upper part, and hot in the lower. The wood was kept in motion by stirring, and was conveyed from top to bottom, while the HCl gas streamed through in the opposite direction. Excess hydrogen chloride was driven off with hot air in another oven which was similarly constructed. The yield from this process was, however, so poor that it was necessary to close down the plant. With this failure, the solution of the problem of wood saccharifi-

cation according to the Dangevilliers' principle may well be considered to have been proved impossible.

J. W. Darboven (73) has proposed another solution to the problem of heat removal during the solution of hydrogen chloride. According to his method, the saccharification occurs in a solution of hydrogen chloride in an organic solvent. After the saccharification, the hydrogen chloride and the organic solvent are removed by heating, and the sugar is extracted from the residue. As yet, this process seems not to have been carried out on a commercial scale.

Many inventors have made proposals for increasing the yield of sugar and of shortening the reaction time. Wohl and Krull investigated the possible advantages of a pretreatment with chlorine. The reducing power of the product increased, to be sure, but this did not indicate an increased yield of sugar, but rather a decreased yield of alcohol. Treatment with sodium hydroxide, with or without the addition of chlorine, proved equally valueless.

A. Classen (74) has suggested improving the hydrolysis with hydrochloric acid by the use of certain catalysts, but tests have shown that the materials proposed have no noticeable effect.

C. Other Procedures with Concentrated Acids

The use of mixtures of concentrated acids instead of sulfuric or hydrochloric acid alone has been repeatedly proposed for digesting wood. It has already been mentioned that mixtures of hydrochloric and phosphoric acids are used to dissolve carbohydrates in the isolation of lignin.

Such a mixture was first proposed by R. Langhans (75), who also used mixtures of hydrochloric and sulfuric acids. These saccharification mixtures were patented by the Waldhof Cellulose Works and V. Hottenroth (57), Z. Ostenberg (76), and others. So far as is known, these mixtures were never used in pilot plant operations. Procedures in which hydrochloric acid is mixed with dehydrating agents, like zinc chloride (77) have also had no practical value thus far.

As has already been mentioned in another connection (cf. p. 101), K. Fredenhagen and G. Cadenbach (78), inspired by the experiments of B. Helferich, have converted cellulose to sugar with hydrogen fluoride. Hydrogen fluoride from fluorite and sulfuric acid is led over dry, finely divided wood, and is adsorbed. About 1 kg. of hydrogen fluoride is used per kg. of dry wood. After the digestion, the hydrogen fluoride can be recovered by pumping it off (79).

So far as is known, the procedure has had no practical results, chiefly,

no doubt, because the problem of designing suitable apparatus has been extremely difficult. Lüers (80), however, has reported that H. Hoch and H. Bohunek have succeeded in saccharifying wood in an economically practicable way with hydrogen fluoride (81). No factory is known to have been erected yet, however.

H. H. Schlubach's procedure (82) with 100% hydrochloric acid (cf. p. 101) has also not yet proved adaptable to technical operations.

A detailed description of German activities in the field of wood saccharification has been given by J. F. Saeman, E. G. Locke and G. K. Dickerman (40). For a recent review on wood saccharification see also E. E. Harris (83).

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