United States Patent Office 2,945,777
Patented July 19, 1960

2,945,777

PROCESS FOR THE SACCHARIFICATION OF SOFTWOOD SAWDUST

Theodor Riehm, Mannheim, Germany, assignor to Udic Société Anonyme, Lausanne, Switzerland

No Drawing. Filed Dec. 27, 1957, Ser. No. 705,515

1 Claim. (Cl. 127—37)

The invention relates to the saccharification of finely comminuted soft wood (coniferous wood), preferably sawdust, by means of hydrochloric acid and this application is a continuation-in-part of my application Ser. No. 540,643, filed October 14, 1955, now abandoned, for Process of Hydrolyzing Cellulosic Vegetable Materials.

In the hydrochloric acid hydrolysis of wood, it is of advantage to operate in two steps in order to recover the pure wood sugars, particularly the glucose, in high yields. One of the known methods consists in heating the cellulosic material in the prehydrolysis step with dilute 0.5 to 1.5% hydrochloric acid at a temperature of about 120° to 140° C. in order to dissolve the hemicelluloses and non-glucosic monosaccharides, whereupon the residue is treated with concentrated hydrochloric acid of at least 40%. Said method which is described in Patent No. 2,752,270, gives quite satisfactory results in the treatment of wood as long as the starting material is not in too finely divided form, for instance in the form of shavings. However, if the method is applied to sawdust i.e. to wood substance of a grain size of about .3 to 1.5 mm., the solid residue remaining from the prehydrolysis has disintegrated to such a fine flour that it forms in the subsequent main hydrolysis step with high concentrated hydrochloric acid a highly viscous paste which interferes with the passage of the hydrochloric acid and is unsuitable for further processing. Also, the prehydrolysis solution obtained under such conditions produces, after filtration and de-acidification, on concentration a syrup which represents a dark brown unappetizing bitter-tasting liquid.

It is a principal object of the invention to provide a two-step saccharification method for sawdust in which the material leaving the first hydrolysis step is still sufficiently compact and coherent to allow the ready passage and displacement of the hydrochloric acid in the second hydrolysis step.

Another object of the invention is to provide a method to obtain from sawdust a prehydrolysis sugar liquor which is suitable for the recovery of pure pentoses, particularly xylose.

Other objects and advantages will be apparent from a consideration of the specification and claim.

According to the invention, the difficulties of the procedures used heretofore are eliminated by subjecting sawdust of soft wood to a prehydrolysis at temperatures of about 15–30° C. with a hydrochloric acid of a carefully adjusted concentration of 34 to 37, preferably 35 to 37 percent HCl by weight. Only when employing said concentration, the obnoxious disintegration of the wood grains in the prehydrolysis is avoided; therefore, the subsequent main hydrolysis with high concentrated hydrochloric acid (40 to 42%) can be carried out without any difficulties, whereby particularly the 35 to 37% HCl of the prehydrolysis is easily displaced by the higher concentrated acid of the main hydrolysis. Under these conditions, 22 to 26% of the hemicelluloses are dissolved in the prehydrolysis and the liquor of the main hydrolysis is readily processed to glucose.

If a hydrochloric acid is used which has an HCl content only slightly in excess of 37%, also a substantial amount of the cellulose is dissolved so that the desired selective dissolution of the pentoses in the prehydrolysis and of the hexoses in the main hydrolysis takes place no longer. When using hydrochloric acid of less than 34%, only a low unsufficient percentage of the hemicelluloses is dissolved.

The method of the invention may be carried out as follows:

Pine wood sawdust is placed in a column and a current of 35% hydrochloric acid is passed upwardly through the sawdust. The formed prehydrolysis sugar solution is withdrawn from the top of the column. The prehydrolysis is generally terminated after about two hours, whereupon the residual 35% HCl remaining in the charge is displaced by passing high concentrated 40.5% HCl from the bottom of the column upwardly. The thus obtained main sugar solution is withdrawn from the top of the column, collected and processed to glucose in the conventional manner.

After concentration in vacuo, deacidification and purification, the prehydrolysis sugar solution yields a sweet tasting, light lemon yellow, clear syrup which is pleasantly distinguished from the dark brown bitter tasting syrup obtained on processing solutions formed by prehydrolysis with 1% HCl at 130° C. Said clear syrup contains a high content of xylose which can be readily recovered in the pure state.

The grain size of the wood substance prior to and after the described treatment is shown in the following table:

Grain sizes	Percentage of grain sizes in the—	
	original wood substance	remaining lignin
above 3 mm	0.6	0.0
3 to 1.2 mm	12.3	12.0
1.2 to .6 mm	49.8	56.0
.6 to .3 mm	24.6	21.0
below .3 mm	12.7	11.0
	100.0	100.0

The hemicelluloses contained in the wood are considered to serve as binder for the wood components, cellulose and lignin. Therefore, it has been believed to be impossible to dissolve the hemicelluloses out of very finely comminuted wood, such as sawdust, without inherently causing complete disintegration of the wood structure, and this belief has been strengthened by the failure of previous attempts to subject sawdust to saccharification on a commercial scale. My novel method shows that it is possible to extract the hemicelluloses also from sawdust when employing hydrochloric acid of a very narrow range of concentrations and thereby to solve the problem of converting sawdust to glucose.

The following Examples 1 and 3 show the results obtained when using for the prehydrolysis hydrochloric acid of a concentration outside the critical range, whereas Example 2 illustrates the method of the invention.

Example 1

Pine wood sawdust was hydrolized at 20° C. with the tenfold amount of 32% HCl for a period of two hours. The solution was then filtered off; it contained hemicelluloses in an amount corresponding to 14 percent of the dry wood substance. The wood residue was washed, dried, and subjected to the main hydrolysis with 41% HCl.

The acid solution obtained by said hydrolysis was processed as described in U.S. 2,752,270 to a syrup of

about 80 percent sugar content. Even though said syrup was inoculated with glucose crystals and stirred, crystallized glucose could not be obtained in commercially useful yields.

A similar negative result was obtained when the HCl concentration of the prehydrolysis step was increased to 33.7%. In this case, 15.5% of the hemicelluloses were dissolved but it was still not possible to crystallize glucose in any useful amount from the syrup of the main hydrolysis.

Example 2

The same type and amount of sawdust as used in Example 1 was hydrolyzed under the same conditions with ten times the amount of 34.5% HCl. The dissolved amount of hemicelluloses was 22.2 percent of the dry wood substance.

When processed as set forth in Example 1, the syrup obtained from the hydrolysis product of the main hydrolysis with 41% HCl yielded 25 percent crystallized glucose, calculated on the weight of the dry sawdust.

If 35.6% HCl was used for the prehydrolysis under otherwise equal conditions, 23 percent of hemicelluloses were dissolved and the yield of crystallized glucose increased to 27.6 percent.

With 37% HCl, the ratio of dissolved hemicelluloses remained the same, but the yield of glucose decreased slightly to 27.5 percent.

Example 3

The same sawdust as used in Examples 1 and 2 was treated in the same amount under the same conditions with 38.4% HCl. In this case, 68 percent of the dry wood substance were dissolved and the residue consisted

substantially only of lignin. Therefore, substantially all the cellulose of the wood substance had been dissolved already in the prehydrolysis step with the result that no longer separation of prehydrolysis sugars (substantially pentoses) and main hydrolysis sugars (hexoses) could be obtained.

It should be noted that the range of 34 to 37% HCl is critical only for the prehydrolysis treatment of sawdust from softwood, which wood has a relatively low content of pentoses. Said range is not suitable for the first step of the two-step hydrolysis of substances rich in pentoses, such as hardwood or bagasse; for such substances, hydrochloric acid of 30 to 34% HCl must be used.

I claim:

A process for the saccharification of soft wood sawdust comprising subjecting the sawdust at a temperature of about 15 to 30° C. to a prehydrolysis with hydrochloric acid containing 34 to 37 percent of HCl by weight for a time sufficient to dissolve substantially the hemicelluloses in an amount corresponding to about 22 to 26 percent of the dry wood substance, separating the obtained solution from the solid residue, subsequently treating in a main hydrolysis step the solid residue of said prehydrolysis with hydrochloric acid of about 40 to 42% HCl content, and recovering crystalline glucose from the sugar syrup obtained in said main hydrolysis.

References Cited in the file of this patent

UNITED STATES PATENTS

1,795,166	Farber	Mar. 3, 1931
1,851,822	Farber	Mar. 29, 1932
2,752,270	Specht	June 26, 1956