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PROCESS OF HYDROLYZING WOOD IN PREPARING CRYSTALLINE GLUCOSE

Hugo Specht, Mannheim-Rheinau, Germany, assignor to Deutsche Bergin-Aktiengesellschaft, Mannheim-Rheinau, Germany

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The invention relates to improvements in the preparation of crystalline glucose by the hydrolysis of wood and is a continuation-in-part of my copending application, Serial No. 242,172, filed August 16, 1951, now abandoned.

Several processes have already been proposed for the recovery of crystalline glucose from wood sugar solutions, but they could not be economically operated on a large scale.

It has also been proposed to crystallize glucose from solutions which are obtained by the hydrolysis of wood and contains 5 to 10 per cent of mannose, calculated on the total sugar present. According to this known method, wood is first extracted at a temperature of about 100° C. with dilute 2% sulfuric acid, and the residue is washed and dried. Following this prehydrolysis, the residue is then hydrolyzed with 40% hydrochloric acid; the strongly acidic sugar solution obtained by this main hydrolysis is separated from the insoluble matter (lignin) and evaporated to dryness, whereby mainly water soluble polymeric carbohydrates are obtained. The dried product is then converted into a solution which contains 25 per cent of sugar and 1 per cent of hydrochloric acid. By heating, said sugar is converted into monoses. Subsequently, the solution is filtered, neutralized and evaporated in vacuo until the concentration reaches 65–75% sugars. This syrup is seeded with some pure crystals of glucose, and the crystallization is carried out at raised temperature while slowly stirring the mass.

I have found that the presence of 5 to 10% of mannose in the solution to be crystallized is not favorable for the crystallization of glucose. For instance, if a sugar solution obtained from softwood is adjusted to a mannose content of 8 per cent, there are always present other sugars such as xylose, galactose, fructose, in such amounts that they make up about 18 to 20 per cent of the total sugar content. In the case of hardwood, the amount of the non-glucose sugars retained in the residues of the prehydrolysis is still larger. If the solid residue of the prehydrolysis is subjected to the hydrolysis proper with cold superconcentrated (40%) hydrochloric acid, the obtained acidic sugar solution contains about 18 to 20 per cent of sugars which are not glucose. If said acid sugar solution is evaporated to dryness in the known manner and if then the dried product is subjected to the after-hydrolysis by heating in weakly acid solution and neutralized, the yields of crystallized glucose are at best about 30 per cent, calculated on the total sugar available.

Careful investigations have shown that the wood sugar solutions prepared according to the known methods always contain relatively large amounts of:

(1) Non-glucosic monosaccharides, such as mannos, xylose, galactose, fructose and arabinose;
(2) Oligosaccharides and soluble polysaccharides;
(3) Organic substances other than sugars, such as formic acid, levulinic acid, and others;
(4) Inorganic compounds formed by the neutralization of the residual hydrochloric acid, such as alkali metal or alkaline earth metal chlorides.

These impurities impair the crystallization of the solutions for the recovery of glucose; on the one hand, they increase the solubility of the glucose in the solvent, and on the other hand they retard the growth of the glucose crystals which remain so small as to be very difficult to separate from the syrup. I have found that crystalline glucose can be obtained in good yields only when the wood sugar solution subjected to crystallization is so prepared as to consist essentially of glucose and to be free as far as possible from the recited impurities, including mannose. According to the invention, cellulosic material, for instance wood, is essentially freed from hemicelluloses; the residue should contain not more than about 5–6 per cent of sugars other than glucose, calculated on the total content of carbohydrates, and is then hydrolyzed with superconcentrated (39–42%) hydrochloric acid. The thus obtained strongly acidic sugar solution is freed from hydrochloric acid by evaporation so as to leave only a small residue of the acid; the mass is then diluted to form a liquor containing about 10 to 15 per cent, preferably about 12 per cent of sugar, and said liquor is heated for about 1 to 3 hours at a temperature of about 110 to 130° C., preferably about 120° C., so as to convert the polysaccharides into glucose. In this after-hydrolysis, the acid concentration is about 0.4 to 1 per cent, preferably about 0.5 per cent. It is essential that the liquor subjected to said after-hydrolysis contains not more than 15 per cent of sugar. A higher sugar content reduces the yield of crystallized glucose.

When a liquor prepared and treated as above described is then neutralized and subjected to crystallization in the conventional manner, crystallized glucose is obtained in yields up to about 60 per cent, which yield is about double the yield obtainable heretofore. This yield can be further increased by subjecting the after-hydrolyzed liquor, before crystallization, to an additional purification by means of ion exchangers.

By the treatment of the sugar solutions with ion exchangers, preferably with anion exchange resins, it is possible to remove substantially the total amount of organic acids, residual hydrochloric acid, and salts of said acids still present in said solutions. The thus obtained solutions have such a high degree of purity as to give yields of about 85 per cent of crystalline glucose.

As set forth hereinabove, the removal of hemicellulose from the cellulosic starting materials is critical because the presence of hemicellulose during the hydrolysis results in the formation of monoses, which affect the processing and particularly the crystallization.

According to the invention, the cellulosic starting material such as wood and the like is freed from hemicellulose in a prehydrolysis step by a treatment with dilute acids at elevated temperatures under such conditions that the total sugar in the solid residue separated from the solution contains not more than about 6 per cent of non-glucose sugars. For this purpose, it is necessary to carry out the prehydrolysis with a dilute mineral acid at a temperature of at least 120° C., for instance at about 120 to 135° C. If dilute hydrochloric acid is used, it should have a concentration of about 0.5 to 1.5 per cent; in the case of sulfuric acid, the required concentration is about 1 to 3 per cent. The treating time depends on the starting material, for instance the type of wood used, the acid concentration and the temperature. The more concentrated the solution, and the higher the temperature, within the recited ranges, the shorter may be the treating time. Generally, the duration of the prehydrolysis in the treatment of wood is, under the recited conditions, about 1½ to 3 hours.

In the known process mentioned in the introductory statement of this specification, pine wood is first extracted with 2 per cent sulfuric acid at a temperature of about 100° C.; the resulting residue is hydrolized with cold 40 per cent hydrochloric acid and the obtained solution is, after removal of the lignin, evaporated to dryness. Comparative tests show that such pretreatment of wood with dilute sulfuric acid at 100° C. does not result in a sufficient removal of hemicellulose and leaves solid residues which contain still about 18 to 20 per cent of non-glucose sugars; in the succeeding hydrolysis proper with cold super-concentrated hydrochloric acid, said non-glucose sugars are carried over into the sugar solution and impair, together with other impurities such as organic acids and salts, the crystallization from the sugar solution resulting from the after-hydrolysis.

My invention is illustrated by the following examples:

Example 1

1,000 kg. of comminuted pine wood were heated with 6 cu. m. of 1% hydrochloric acid for two hours at 130° C. There were dissolved about 300 kg. of wood substance containing mannose, xylose, some glucose, galactose, rosins, salts, and acetic acid. After removal of said solution, the remaining wood contained still 5 per cent of non-glucose sugars, calculated on its total content of carbohydrates; it was washed, dried and hydrolyzed with cold 41% hydrochloric acid. The bulk of the hydrochloric acid was removed from the thus obtained sugar-hydrochloric acid solution by distillation in vacuo. The remaining syrup contained about 370 kg. of sugars in polymeric form and still about 15 kg. of HCl. The syrup was then diluted to a volume of 3 cu. m., so as to contain about 12 per cent by weight of sugar, and heated in an autoclave for 3 hours at 120° C. Bentonite was added to the solution for clarification and precipitation of colloids; the solution was then filtered and passed through a bed of a suitable decolorizing resin. The thus obtained liquor was then passed through an anion exchange resin to remove all free acids, i. e. hydrochloric acid and organic acids, particularly levulinic acid. Subsequently, the liquor was passed through a cation exchange resin to remove all cations derived from the wood. The acidic liquor leaving the cation exchanger was passed through a second anion exchange filter and finally through a second decolorizing filter. By this purification process, a water-clear glucose solution was obtained, which was completely free of acids and salts. Said pure solution was now evaporated under reduced pressure to a syrup of about 80 per cent sugar content, and the syrup was inoculated with some glucose crystals. The crystallization was carried out with stirring, 310 kg. of crystalline glucose were obtained, which were readily separated from the liquid by centrifuging. The yield was 85 per cent of crystallized glucose, on the basis of total sugar input.

Similar yields were obtained when the prehydrolysis was carried out at 120° C. for 3 hours with 1.5% hydrochloric acid or 2 to 3% sulfuric acid.

However, if the wood was heated at only 100° C. for 3–4 hours with 1% hydrochloric acid, the resulting prehydrolyzed wood contained about 20 per cent of non-glucose sugars. If this wood was then further processed in exactly the same manner as set forth above, a yield of only 110 to 120 kg. of crystalline glucose was obtained, as compared with 310 kg. for the same wood when prehydrolyzed under otherwise equal conditions but at 130° C.

Example 2

A syrup containing about 370 kg. of sugars in polymeric form and about 15 kg. of HCl was prepared from wood under exactly the same conditions as described in Example 1. However, said syrup was then diluted only to a volume of 1.4 cu. m., corresponding to a sugar concentration of about 25 per cent. In view of the higher acid content, the syrup was after-hydrolyzed in an autoclave at 120° C. only for 1½ hours, which period had been established as the optimum time for said concentrations. The further processing corresponded to that of Example 1. The yield was 250 kg. of crystalline glucose, i. e. 68 per cent of the total sugar input.

Example 3

1000 kg. of comminuted beechwood were prehydrolyzed with about 6 cu. m. of ½% hydrochloric acid for two hours at 130° C. Hereby about 380 kg. of wood substance, comprising xylose, mannose, some glucose, galactose, rosins, salts, and acetic acid, passed into solution. The remaining wood contained about 5 per cent of non-glucose sugars and was processed in the same way as described in Example 1. Also in this case, 310 kg., i. e. a yield of 85 per cent of crystalline glucose, calculated on the sugar input, was obtained.

When beechwood was treated in the same way as described above with the only difference that the hydrolysis with ½% HCl was carried out for 3–4 hours at 100° C., the remaining wood contained 18 per cent of non-glucose sugars, and the final yield of crystalline glucose was only 120 to 130 kg.

Example 4

Beechwood was treated as described in Example 3, but, as in Example 2, the syrup was diluted only to a volume of 1.4 cu. m., having a sugar concentration of 25%. The after-hydrolysis was carried out as in Example 2, and also in this case, the yield of crystalline glucose dropped sharply to 250 kg.

The foregoing examples show that the invention can be applied with equal success to softwood and hardwood. But also other cellulosic products may be used as starting material, such as straw, reed, bagasse, and the like.

Various modifications of the invention, other than specifically described herein, will be evident and are included within the scope of the appended claims.

What I claim is:

1. In the process of preparing crystalline glucose by prehydrolyzing a vegetable cellulosic material with a dilute mineral acid, separating the treated residue, hydrolyzing the residue with cold concentrated hydrochloric acid, distilling off the bulk of said concentrated hydrochloric acid, diluting the remaining syrup and heating the thus obtained sugar solution in a final hydrolysis step for the production of glucose, the improvement which comprises heating the cellulosic material in the prehydrolysis step with a member of the group consisting of dilute sulfuric acid and dilute hydrochloric acid at temperatures of about 120 to 140° C. until the monosaccharides contained in said cellulosic material have been substantially dissolved, and adjusting in said final hydrolysis step the sugar solution to a sugar concentration of about 10 to 15 per cent by weight, and heating said sugar solution at a temperature of about 110–130° C. for a time sufficient to convert the polysaccharides contained in said solution substantially into glucose.

2. In the process of preparing crystalline glucose by prehydrolyzing a vegetable cellulosic material with a dilute mineral acid, separating the treated residue, hydrolyzing the residue with cold concentrated hydrochloric acid, distilling off the bulk of said concentrated hydrochloric acid, diluting the remaining syrup and heating the thus obtained sugar solution in a final hydrolysis step for the production of glucose, the improvement which comprises heating the cellulosic material in the prehydrolysis step with a member of the group consisting of dilute sulfuric acid and dilute hydrochloric acid at temperatures of about 120 to 140° C. until the monosaccharides contained in said cellulosic material have been substantially dissolved, and adjusting in said final hydrolysis step the sugar solution to a sugar concentration of about 10 to 15 per cent by weight, and to a hydrochloric acid concentration of about 0.4 to 1 per cent, and heating the solution at a temperature of about 110–130° C. for a time suffi-

cient to convert the polysaccharides contained in said solution substantially into glucose.

3. In the process of preparing crystalline glucose by prehydrolyzing wood with dilute mineral acids, separating the treated residue, hydrolyzing the residue with cold concentrated hydrochloric acid, distilling off the bulk of said concentrated hydrochloric acid, diluting the remaining solution and heating the same in a final hydrolysis step for the production of glucose, the improvement which comprises heating the wood in the prehydrolysis step with a member of the group consisting of dilute sulfuric acid and dilute hydrochloric acid at temperatures of about 120° to 140° C. until the monosaccharides of the wood have been substantially dissolved.

4. The method of claim 3, wherein dilute hydrochloric acid having a concentration of 0.5 to 1.5 per cent is used.

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