HYDROLYSIS OF HEMICELLULOSE AND ALPHA-CELLULOSE TO PRODUCE SUGAR

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The invention herein described may be manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereto.

This invention relates to the production of sugars from wood by hydrolysis of cellulose in the presence of acid. Processes based upon such hydrolysis have been used extensively abroad. For instance, about twenty plants were known to be in operation in Germany in 1941 according to the Scholler process, described in Industrial and Engineering Chemistry 37, 9—11 (1945). This process is very slow, operates batchwise, is characterized by high maintenance costs and low yields of sugars per unit volume of equipment, and requires so much labor as to be uneconomical except where labor is very cheap.

The United States Forest Products Laboratory has developed an improved process in which wood chips are charged to a digester, the charge is submerged rapidly in hot dilute sulfuric acid, and hot dilute acid is percolated continuously through the charge under high pressure until the sugar concentration in the hydrolyzate is about 5 percent. The pressure on the hydrolyzate is then reduced to about 30 p.s.i., and it is neutralized and filtered continuously under pressure. The product may be evaporated to form molasses or may be fermented directly to alcohol or may be used for the production of commercial yeast, but there is continuous destruction of sugars as the hydrolysis progresses.

It is an object of this invention to provide a process for the hydrolysis of wood in which destruction of sugars produced is greatly reduced.

Another object is to provide such process which can be made continuous, is simple in operation, has low labor costs, and which may be carried out in simple and cheap apparatus.

Still another object is to provide such process wherein improved operability and improved quality of the sugar product are attained.

Other objects and advantages will become apparent as this disclosure proceeds.

It has been long known that the cellulose contained in wood may be divided into two fractions, namely, a fraction that may be hydrolyzed by acid under relatively mild conditions of heat and pressure, and a fraction that requires more severe conditions of heat and pressure for this reaction. These fractions are substantially identical with those called hemicellulose and alphacellulose, respectively, by many workers in this field, although the separation into hemicellulose and alphacellulose is frequently based upon other reactions such as solubility in alkali.

We have found that a principal cause of the low yields or impure sugars obtained in other methods is the destruction or degradation of sugars produced by hydrolysis of the easily hydrolyzed or hemicellulose fraction when they are subjected to conditions of heat and pressure sufficiently severe to hydrolyze the more difficultly hydrolyzed, or alphacellulose fraction. We have also found that the sugars produced by hydrolysis of the alphacellulose fraction have sufficient chemical stability that they are not destroyed to any appreciable extent by exposure to conditions of hydrolysis sufficiently severe to cause hydrolysis of hemicellulose. We have developed a simple method for increasing the purity of sugars by application of those principles.

Briefly, this method comprises treating wood with a recycled dilute sulfuric acid-sugar solution under conditions of heat and pressure sufficiently severe to cause hydrolysis of the more easily hydrolyzed portion of the cellulose (hemicellulose), separating the resulting hydrolyzate from solid residue, neutralizing and withdrawing the hydrolyzate for evaporation to molasses, fermentation, or any other use desired. The solid residue is then treated with a second portion of dilute sulfuric acid under conditions of heat and pressure sufficiently severe to cause hydrolysis of the more difficultly hydrolyzed portion of cellulose (alphacellulose). The resulting acid hydrolyzate is separated from a solid residue composed principally of lignin and is recycled at lower temperature and pressure to serve as hydrolysis reagent for a fresh batch of wood chips. We have found that sugars of higher purity are obtained by making all withdrawals from the system immediately after the hemicellulose hydrolysis step.

The attached drawing is a flow sheet illustrating diagrammatically one preferred method employing principles of our invention. With reference thereto, the numeral 1 indicates mixing zone or vessel equipped with a stirrer 2. Means for introducing controlled quantities of wood chips, sulfuric acid, water, and steam for heating purposes are indicated by the arrows designated 3, 4, 5, and 6 respectively. A line 7 also is provided to conduct liquid from an alphacellulose hydrolysis step to mixing vessel 1.

The full quantity of hot liquid produced in the hydrolysis of alphacellulose is introduced into vessel 1 via line 7 and is there mixed by action of the stirrer 2 with a fresh charge of wood chips introduced at 3. Sufficient sulfuric acid and make-up water are introduced if necessary via 4 and 5 respectively to form a mixture of wood chips suspended in at least 8 times their weight of liquid containing from 0.5 to 2.0 percent, or preferably about 1.0 percent, of sulfuric acid.

It is desirable to use the minimum amount of liquid required to produce a pumpable slurry. A quantity of liquid at least 8 times the weight of the wood chips will be necessary to form such slurry and often a weight of liquid 10 to 12 times that of the chips may be required. The resulting mixture is rapidly heated to near its boiling point by steam introduced at 6 and is passed into a hemicellulose hydrolysis zone 8. Pressure of about 15 to 25 p.s.i. in excess of that required to maintain liquid state is maintained in this zone; the rate of flow is such that the material passes through zone 8 in about 3 to 5 minutes. High-pressure steam is introduced at some convenient point 9 in quantity sufficient to maintain the temperature at about 265° to 285° F. during the time the material remains in the hemicellulose hydrolysis zone. Zone 8 preferably is a coil of pipe as illustrated in the drawing. The length and diameter of this tubular zone are chosen so that the rate of flow under the conditions just described is such that the retention time in zone 8 is from about 3 to 5 minutes.

The material is then discharged into a flash tank 11 and is there flashed to atmospheric pressure. Next it is passed to a separation step 12 where the liquid hydrolyzate is separated from solid residue. A rotary filter is the preferred equipment for conducting this separation.
step, although other types of separation apparatus may be used if desired. Separated liquid hydrolyzate is withdrawn at 14 and is neutralized, evaporated to molasses, fermented, or used in any other manner desired.

The solid residue from the separation step 12 is introduced into a second mixing zone 17. Sulfuric acid, water, and steam are also introduced via lines 18, 19, and 20 respectively to form a mixture of residue in at least 8 times its weight of dilute aqueous sulfuric acid having an acid strength in the range from about 0.5 to 2.0 percent, and preferably about 1 percent. This mixture then is passed into a heater 21 and on through an alphacellulose hydrolysis zone 22 under a pressure about 15 to 25 p. s. i. in excess of that required to maintain liquid state, at a temperature in the range from 360° to 390° F. and at a rate of flow such that the mixture passes through zone 22 illustrated as a coil of pipe, in a retention time of about 4 to 6 minutes. The mixture is then introduced into a flash tank 23 and is flashed to atmospheric pressure.

The mixture is then conducted to a separation step 24 where the liquid hydrolyzate is separated from a solid residue composed principally of lignin. This residue is withdrawn at 25 and the entire liquid hydrolyzate is recycled via line 7 to mixing vessel 1 to serve as hydrolysis medium for a fresh batch of wood chips.

Principal advantages gained in our process are (a) a good yield of sugars; (b) the operating conveniences obtained by making all separations of hydrolyzate from residues at atmospheric pressure; (c) higher concentration of sugars in the hydrolyzate withdrawn for neutralization and use; (d) improved operability due to minimized production of sludge by decomposition of sugars; and (e) a sugar product of improved quality due to the small quantity of decomposition products contained therein.

Example

The method developed by the United States Forest Products Laboratory is believed to be the most efficient process for production of sugars from wood that was available prior to the development of our process. An average of 29 runs reported by that laboratory, using their process and Douglas fir, had shown total sugar recovery of 50.3 percent of the bark-free dry wood and an average concentration of sugars in the final hydrolyzate of 5.0 percent.

In a pilot plant constructed at Wilson Dam, Alabama, we operated according to that process to determine its efficiency in respect to other woods. Using mixed hardwoods, we obtained a total sugar recovery of 51.1 percent; in good agreement with the results reported by the Forest Products Laboratory, but with a concentration of only 3.8 percent sugars in the final hydrolyzate.

These results are to be contrasted with those obtainable by the method as calculated below on the basis of one ton of dry mixed hardwoods as starting material.

One ton of dry mixed hardwoods contains approximately 456 pounds of bark and 1544 pounds of dry wood substance; it contains an amount of easily hydrolyzed cellulose and the like) equivalent to 230 pounds of reducing sugars and an amount of more stable cellulose (alphacellulose and the like) equivalent to 923 pounds of reducing sugars.

This quantity of wood is chipped, introduced into a mixing vessel equipped with a stirrer, as shown at 1, and is there mixed with a sufficient amount of recycled hydrolyzate from an alphacellulose hydrolysis step 22 to form a pumpable slurry. About 8 parts or more of liquid will be required for each part of wood chips. The physical properties of the slurry will determine the amount of hydrolyzate that must be added: the slurry must be pumpable in order to carry out the remainder of the process without excessive difficulties in operation, but addition of excess water is to be avoided as it results in dilution of the final hydrolyzate and increases the cost of recovering sugars from it. The slurry preferably has an acid content of about 1 percent sulfuric acid.

The slurry is then heated to or near its boiling point and is passed into a hemiacetolose hydrolysis zone 8, at a pressure about 15 p. s. i. in excess of that required to maintain liquid state. High-pressure steam is introduced at 9 to maintain the temperature at about 275° F. in this zone. The slurry is passed through this zone at such a rate that its retention time in the zone is about 4 minutes. This period of time is preferred for mixed hardwoods, but other woods may require somewhat longer retention times. The retention time should be as short as is compatible with complete hydrolysis of the hemiacetolose fraction in order to minimize decomposition of the sugars formed.

Under these conditions all the easily hydrolyzed cellulose is converted into sugars, and 230 pounds are thus formed. The more resistant cellulose fraction is not affected appreciably and is retained as such in the chips. The sugars contained in the recycled alphacellulose hydrolyzate are not attacked to any appreciable extent, as these are the more resistant sugars. Decomposition of sugars in this step is well under 1 percent, and this loss is included in the over-all loss from the process, as shown below, which is about 10 percent of the yield. The average sugar concentration in solution withdrawn at 14 is about 5.1 percent.

The partially hydrolyzed chips are then separated from the liquid hydrolyzate which has an average concentration of about 5.1 percent total reducing sugars. The separated chips are reslurried with water to which sulfuric acid has been added. These chips contain resistant cellulose equivalent to 923 pounds of reducing sugars.

The resulting slurry is then passed through an alphacellulose hydrolysis zone 22 at a pressure somewhat in excess of that required to maintain liquid state. The temperature is maintained at 400° F., acid concentration is 1 percent, and retention time is 3.5 minutes. This retention is that at which the net yield of reducing sugars from this particular material is at a maximum. Under these conditions only about three-fourths of the more resistant cellulose fraction is hydrolyzed and decomposition of sugars formed is such that the net yield is only about 50 percent of the amount equivalent to the cellulose content. Thus 461 pounds of reducing sugars are received in the hydrolyzate from this stage.

A longer retention time would, of course, result in more complete hydrolysis of the cellulose, but it will be found that whatever type of wood is used there is a point of maximum yield, since the same conditions of heat and acid concentration that result in hydrolysis of the resistant alphacellulose fraction also result in decomposition of the sugars formed. It is therefore impractical to proceed beyond the point at which the rate of sugar decomposition becomes substantially equal to the rate of sugar formation.

The hydrolyzate is then separated from the spent chips (lignin) and is recycled to vessel 1 where it is used to produce slurry with fresh chips. Water lost in flashing to atmospheric pressure is compensated for by water added to the solution by washing the lignin residue.

The over-all yield of the two-stage hydrolysis is about 230 pounds of reducing sugars from the hemiacetolose hydrolysis step plus 461 pounds from the alphacellulose hydrolysis step: a total of 691 pounds of reducing sugars from one ton of dry mixed hardwoods. There is usually an over-all loss of about 10 percent in slurry and subsequent processing of the solution. The yield actually obtained thus becomes about 622 pounds of reducing sugars per ton of dry mixed hardwoods, or 53.9 percent of the potential reducing sugars in the charge. In terms of 50 percent molasses, the yield is 1244 pounds or 107 gallons per ton of dry wood.
It will thus be seen that our process results in a good over-all yield. Also, the quality of the sugar product is high because of the presence of relatively small proportions of decomposition products. Operational difficulties due to decomposition are minimized, and the small quantity of decomposition products present makes possible the production of a molasses that is highly palatable to livestock.

Although our process is described above as a continuous process it is not restricted to continuous operation, but could be carried out batchwise if desired. Other modifications also may be made without departing from the spirit of our invention, which is limited only by the attached claims.

We claim as our invention:

1. A process for the production of sugars from wood which comprises mixing wood residue from a hereinafter described hemicellulose hydrolysis step with at least 8 times its weight of 0.5 to 2.0 percent aqueous sulfuric acid; passing the resulting mixture at a temperature in the range from about 360° to 400° F. through a tubular alphasaccharolose hydrolysis zone under a pressure about 15 to 25 p. s. i. in excess of that required to maintain liquid state, at a rate of flow such that the mixture passes through the hydrolysis zone in a retention time of about 3 to 20 minutes; flashing the resulting mixture to atmospheric pressure; separating the solid residue composed essentially of lignin from said mixture; passing the resulting liquid mixture to a mixing zone; therein mixing it with wood chips, water, and acid to form a mixture of wood chips in from 10 to 12 times their weight of liquid containing from 0.5 to 2.0 percent sulfuric acid; passing the resulting mixture through a tubular hemicellulose hydrolysis zone at a temperature in the range from about 265° to 285° F, under a pressure about 15 to 25 p. s. i. in excess of that required to maintain liquid state, at such rate of flow that is passes through the hemicellulose hydrolysis zone in a retention time of about 3 to 5 minutes; flashing the mixture to atmospheric pressure; separating the mixture into liquid high in wood sugars and a solid residue; recycling the solid residue; and withdrawing and neutralizing the liquid high in wood sugars.

2. The process of claim 1 wherein the concentration of sulfuric acid in both hydrolysis steps is about 1 percent.

3. The process of claim 1 wherein both separation steps are conducted at atmospheric pressure.

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