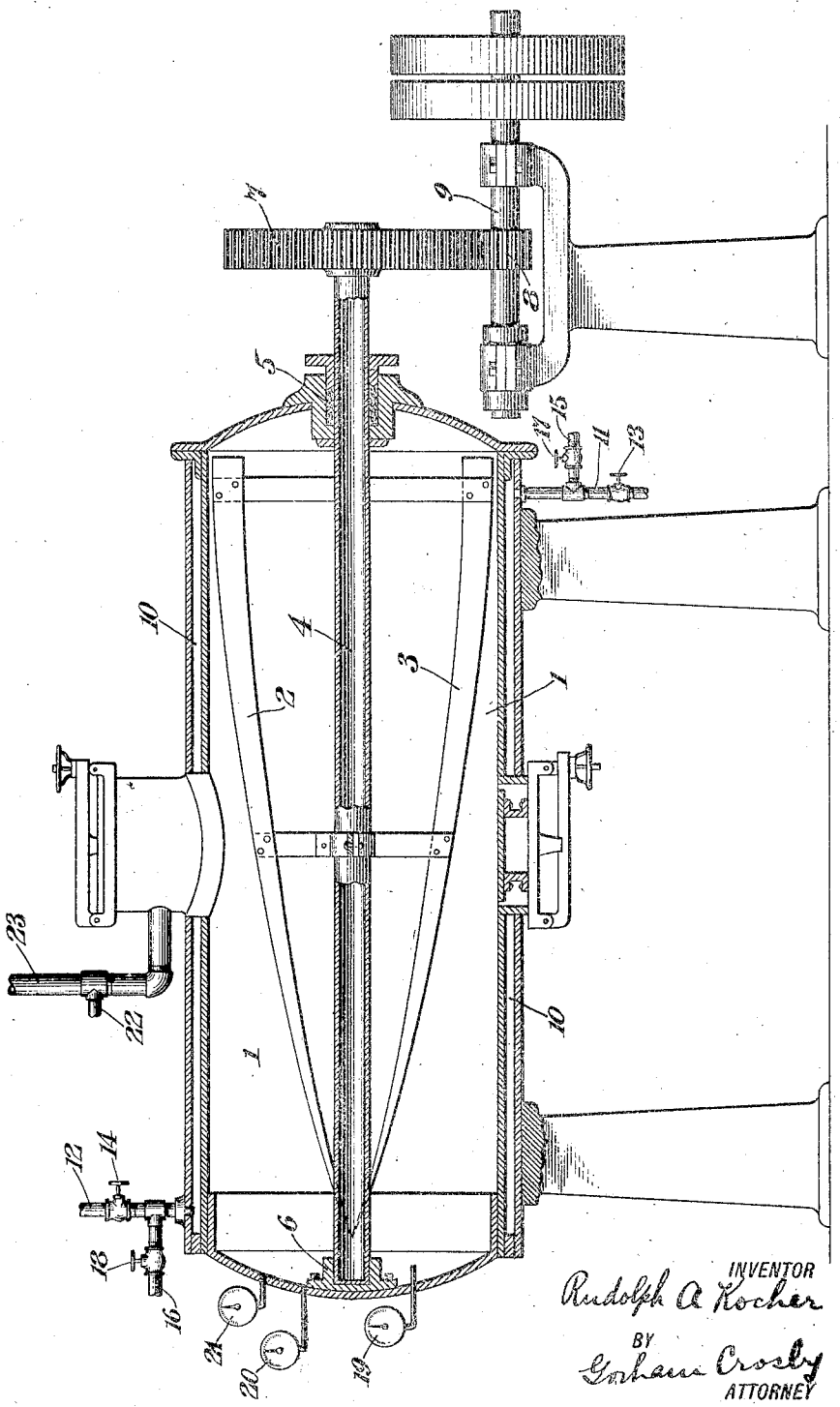
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PROCESS FOR CONVERTING CELLULOSE.

APPLICATION FILED MAR. 21, 1917.

1,374,928. Patented Apr. 19, 1921.



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To all whom it may concern:

Be it known that I, RUDOLPH A. KOCHER, citizen of the United States, and resident of San Francisco, in the county of San Francisco and State of California, have invented certain new and useful Improvements in Processes for Converting Cellulose, of which the following is a specification.

My invention relates to improvements in processes for converting cellulose and is particularly adapted to the conversion of cellulose into sugar or sugars such as glucose or similar fermentable products which may be treated by fermentation methods for the production of alcohol. This application is a continuation in part of my prior application Ser. No. 65676 filed Dec. 8, 1915, and a continuation in part of my prior applications Ser. No. 130563 filed Nov. 10, 1916, and Ser. No. 132584 filed Nov. 21, 1916.

It has been known that cellulose can be converted to glucose by suitable treatment with acids such as sulfuric acid, sulfurous acid and hydrochloric acid. But in every instance, so far as I am aware, the selection of reagents and conditions have been such that either the cellulose has only been partly converted or else the acid reagent has been largely lost or so difficult to recover or separate that the processes have failed in commercial operation.

When suitable cellulose material is converted according to my process, not only is the desired large yield obtained, but the treating reagent is used in so small an amount that the most of it is easily recovered, so that it may be used over and over again and also the reaction is more efficiently obtained. Further objects, features and advantages will more clearly appear from the detailed description given below, taken in connection with the accompanying drawing which forms a part of this specification and which illustrates a converter, largely in section, adapted to carry out the process in one form.

According to one mode of carrying out the process, cellulose material, such as saw dust or wood chips containing 30% to 40% by weight of moisture (water) are fed in to the airtight converter 1 through top manhole opening. Such saw dust or wood chips may contain about 70% of cellulose, based on the dry weight of the wood.

The converter 1 is provided with a stirrer or agitator comprising two spiral blades 2 and 3 which run close to the cylindrical wall of the converter. The scraper blade 2 has such a curvature that it tends to force the material longitudinally of the converter in one direction while the scraper blade 3 is curved in the opposite direction so as to tend to force the material in the opposite direction longitudinally of the converter. Preferably there is another pair of blades similar to the blades 2 and 3 but arranged on the opposite side of the converter. The agitating blades are carried by a hollow central shaft 4 passing through a stuffing box at 5 and having a bearing at 6 inside the converter. A gear 7 is secured on the end of the shaft 4 which gear meshes with a gear 8 on a shaft 9 which is driven from any suitable source of power. The converter is provided with a jacket 10, through which water or other cooling fluid may be circulated by means of pipes 11 and 12 by opening the valves 13 and 14; or the converter may be heated by circulating steam or other heating fluid through the jacket by means of pipes 15 and 16 by operating the valves 17 and 18. If desired, a heating fluid or a cooling fluid may be introduced into the hollow shaft 4. A thermometer 19, a pressure gage 20 and a vacuum gage 21 are connected to the converter to indicate the conditions of temperature, pressure and exhaustion therein.

After the sawdust or other cellulose material, containing about 30% or 40% of moisture has been charged into the converter, the air is exhausted from the converter by any suitable evacuating apparatus connected with the pipe 22. After the removal of the air, hydrochloric acid gas is admitted to the converter through the pipe 23 during agitation of the cellulose material. Although the pressure in the converter may be little or nothing above atmosphere pressure, the sawdust and the water therein will, under these conditions, absorb so much of the hydrochloric acid gas that liquid hydrochloric acid will be formed of a strength of 39% or over. It is important that acid or this strength be produced, as otherwise full conversion of the cellulose will not be obtained. If the temperature or conditions be such that acid of this strength is not formed, the difficulty may be remedied by slightly increasing the pressure within the converter as by introducing the HCl gas under pressure. The absorption of HCl gas

by the water or moisture raises the temperature of the mass and in order that such increase in temperature may not reduce the strength of the liquid hydrochloric acid by driving off the HCl gas therefrom, it is generally necessary to cool the mass, unless the pressure is high, which cooling may be done by circulating a cooling fluid in the jacket 10 as above described. In treatments which I have carried out, I find that after from 24 to 72 hours practically 100% of the cellulose will be converted. It is not necessary that the mass be continually agitated after it has once been thoroughly mixed and the water therein has absorbed sufficient HCl gas to produce liquid hydrochloric acid of 39% strength or over.

I understand that the action in converting the cellulose to glucose is a hydrolytic action, the cellulose taking up molecules of water and the HCl acting as a catalytic agent. Other halogen acids, such as hydrogen iodid, may be used, but it is important that the halogen acid be of the critical strength, which, as above explained, is 39% or over in the case of HCl, in order that the required yield may be obtained. Authorities give the critical strength of hydrofluoric acid as from 70% to 75% and the critical strength of hydrobromic acid as about 66% or over, while the critical strength of hydriodic acid is believed to be about 68% or over when used hot as above 60° C.

After the conversion is completed, the HCl gas in the converter may be withdrawn therefrom and stored for further use by suitable evacuating apparatus. There will then remain a small amount of liquid hydrochloric acid in the mass. By increasing the temperature and evacuating the converter, this may be largely removed, the liquid acid first giving off HCl gas until the strength of the acid has been reduced to about 20% and then hydrochloric acid of about this strength being distilled off. This may be saved and used to furnish part of the liquid acid for another batch. A suitable apparatus for accomplishing these objects is shown in my copending application Ser. No. 151175, filed Feb. 27, 1917.

By limiting the amount of water used in the treatment to an amount less than the weight of the sawdust and preferably to from $\frac{1}{3}$ to $\frac{1}{2}$ the weight of the wood material, not only is there much less liquid hydrochloric acid to be removed after the conversion, but the water present is below the amount which would render fluid any substantial part of the mass by forming a solution of the glucose or other soluble conversion product. If much of the mass is rendered fluid, it causes the material to ball up and so prevents all parts of the cellulose material from being efficiently acted upon and hence results in a loss or else an undue amount of time in bringing about the conversion.

After the small amount of acid present has been largely removed as above described, sufficient water may be added to make a glucose solution of the desired consistency and then the material removed from the converter through the bottom manhole and treated by a suitable fermentation process to produce alcohol. It is unnecessary to remove the unconverted lignin of the wood and the small amount of acid remaining in the mass does not necessarily interfere materially with the fermentation process.

I find that the converting action can be greatly hastened, if the temperature be increased slightly above room temperature. In order that such increase in temperature may not cause the strength of the acid to fall below the critical strength (39% if HCl be used), I increase the pressure within the converter. This may be done by charging the converter with the halogen acid gas under pressure. I have obtained excellent results by keeping the temperature at between 40° and 60° C. and the pressure of the HCl gas between 40 and 60 pounds per square inch. The greater the pressure, the quicker the desired or critical strength of acid is formed with the water or dilute acid already in the material. I prefer to use approximately saturated acid, which should be at least 39% if HCl is used, and the strength of saturated acid is of course different for different temperatures and pressures, so that for increases of temperature, as for example from 40° C. to 60° C., the pressure must be raised to maintain the acid to the critical strength. 50 to 100 lbs. pressure is generally sufficient. By using such increases in temperature and pressure, I have brought about substantially complete conversion of the cellulose in from $\frac{1}{2}$ to 2 hours. The higher the temperature used and the greater the strength of acid used, the shorter the time it takes to produce the desired conversion. If desired, the saturated acid of critical strength may be formed at substantially room temperature and then later the conversion hastened by increasing the temperature. Where the acid is brought up to critical strength by absorption of gas the heat produced by the absorption of the HCl gas may be used to accelerate the hydrolysis. In an actual trial, I found that sawdust, which stood in contact with hydrochloric acid of 42% strength, had reached the maximum conversion after standing for 1 hour at 40° to 45° C., and in one half hour at about 60° C.

If the treatment is such that the cellulose is not only converted to glucose, but the glucose has to some extent been reconverted to other materials, then the mass may be

boiled with water, or the solution heated to 110° C., to reconvert these materials to glucose or similar fermentable products. The amount of water used is preferably such as to form about 30% glucose solution after this final hydrolysis has taken place. This boiling with water may take place in the converter, the heat being applied by turning steam into the jacket or by turning steam directly into the material in the converter, or this step may be carried out in any other suitable apparatus. Following this step the batch may be further diluted, when it is ready for fermentation, although, if desired, the insoluble residue consisting mostly of lignin may be first separated from the dissolved glucose.

If in the beginning, the sawdust does not contain sufficient moisture or water, a sufficient amount of water or hydrochloric acid may be added. If desired, the wood may first be dried to remove the moisture therefrom and then dilute hydrochloric acid added until the desired amount of water is present in the mixture. The amount of water present should be at least 10% of the weight of the cellulose, as substantially this amount is necessary for the hydrolysis according to the formula

$$C_6H_{10}O_5+H_2O=C_6H_{12}O_6.$$

Besides wood, numerous other cellulose substances may be treated according to the invention, as for example, hydro-, hydrato- and oxycellulose, as well as cellulose which exists in combined form.

Instead of forming the acid of critical strength *in situ* in the material by admitting the halogen acid gas, the liquid acid of the desired hydrolyzing strength (for example, 39% to 40% strength if HCl is used) may be mixed with the cellulose containing material. In such case, however, the material should first be dried or treated so as to remove substantially all the water or moisture therefrom, as otherwise, such water or moisture would reduce the strength of the acid below the critical strength as soon as it became mixed with the material. Wood waste, sawdust, plant stalks, straw and the like usually contain from 5% to 35% of moisture. However, if the moisture in the cellulose material be so small and the strength of treating acid so great that when mixed the strength of the acid does not fall below the critical value, such drying or removing of moisture may be omitted.

Many other changes and modifications may also be made without departing from the spirit and scope of the invention in its broader aspects.

What I claim as new and desire to secure by Letters Patent, is:

1. The process of converting cellulosic material into sugar or sugars, which consists in treating the cellulosic material with hydrochloric acid of at least 39% strength, the amount of water present being below the amount required to render the resulting mass fluid.

2. The process of converting cellulose containing material, which comprises treating the same with hydrochloric acid of at least 39% strength, the total amount of water being less in weight than the weight of the material being treated.

3. The process of converting cellulose which consists in hydrolyzing the same with hydrochloric acid of at least 39% strength in an atmosphere of HCl gas, the amount of water present being below the amount which would render fluid any substantial part of the mass.

4. The process of converting cellulose, which consists in treating the cellulose-containing substance to make the moisture content thereof about one half part by weight of the cellulose to be converted, subjecting the so-treated mass to the action of hydrochloric acid gas in a closed container until all the materials present are saturated with the gas to form hydrochloric acid of at least 39% strength, and maintaining an excess of gas in the container while the mass in said container is kept at a temperature of at least as high as room temperature and at a pressure at least as great as atmospheric pressure for a period of time sufficient to convert the cellulose contained in the mass into glucose or sugars.

5. The process for converting cellulose, which consists in treating a comminuted cellulose-containing substance in such a way as to effect an equal distribution of moisture through the mass so that the water content thereof is less than the weight of the mass, subjecting the moist mass while the same is in a closed container to hydrochloric acid gas until the moisture and other constituents of the mass are saturated with the hydrochloric acid gas to form an acid of at least 39% strength, maintaining an excess of hydrochloric acid gas within the container while the mass within is maintained at a pressure at least as great as atmospheric and at a temperature of at least 15° C. until the hydrolysis of the cellulose in the mass is complete, eliminating the excess of hydrochloric acid, and then adding water to the mass within the container to dissolve the glucose present in the treated mass.

6. The herein described process for converting cellulose, which consists in treating a cellulose-containing substance in such a manner that the water present in the mass represents at least 10% of the cellulose to be converted, and not in such excess as would be sufficient when saturated with hydrogen chlorid gas to form a liquid solution at any one time of any more than a small portion

of the cellulose to be converted, allowing hydrogen chlorid gas to contact with the moist mass so as to saturate the moisture and other substances contained in the mass to form hydrochloric acid of at least 39% strength at a pressure at least as high as atmospheric and at room temperature, and maintaining an excess of hydrogen chlorid gas in contact with the mass while the whole is kept in a closed container at a temperature of at least 15° C. until the hydrolysis of the cellulose is completed.

7. The process of treating cellulose, which consists in hydrolyzing the same with hydrochloric acid of 39% strength or more, in an air-tight container containing an atmosphere of HCl gas without air, to prevent the strength of the hydrolyzing acid falling below the critical strength of 39%, the amount of water present being less than the weight of the material being treated and insufficient in amount to render fluid any substantial part of the mass whereby the tendency of the mass to ball up upon being agitated is substantially eliminated, and the HCl may be efficiently used and yet practical quantitative hydrolysis of the cellulose obtained.

8. The process of treating cellulose which consists in hydrolyzing the cellulose with a halogen acid of 39% strength or over and of critical strength in the presence of halogen acid gas under pressure greater than atmosphere, the amount of water present being less by weight than the dry weight of the material being treated.

9. The process of converting cellulose which consists in treating cellulose material with hydrochloric acid of 39% strength or more, the amount of water present being insufficient to render fluid any substantial part of the material, and then distilling off the hydrochloric acid before any substantial amount of water has been added to the converted glucose.

Signed at Decatur in the county of Adams and State of Indiana this 16th day of March A. D. 1917.

RUDOLPH A. KOCHER.