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PROCESS AND DEVICE FOR THE SACCHARIFICATION OF CELLULOSE AND THE LIKE

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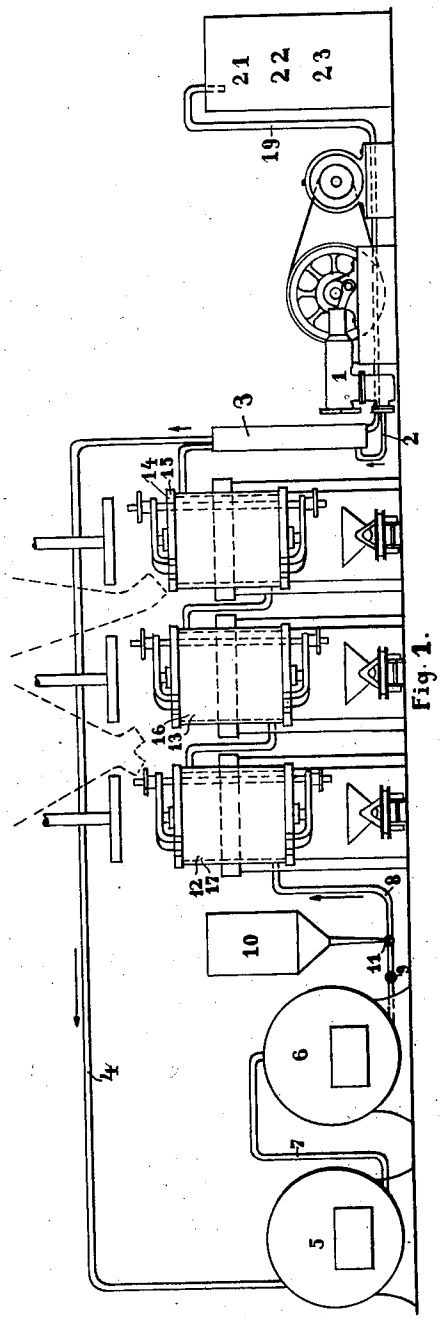


Fig. 1.

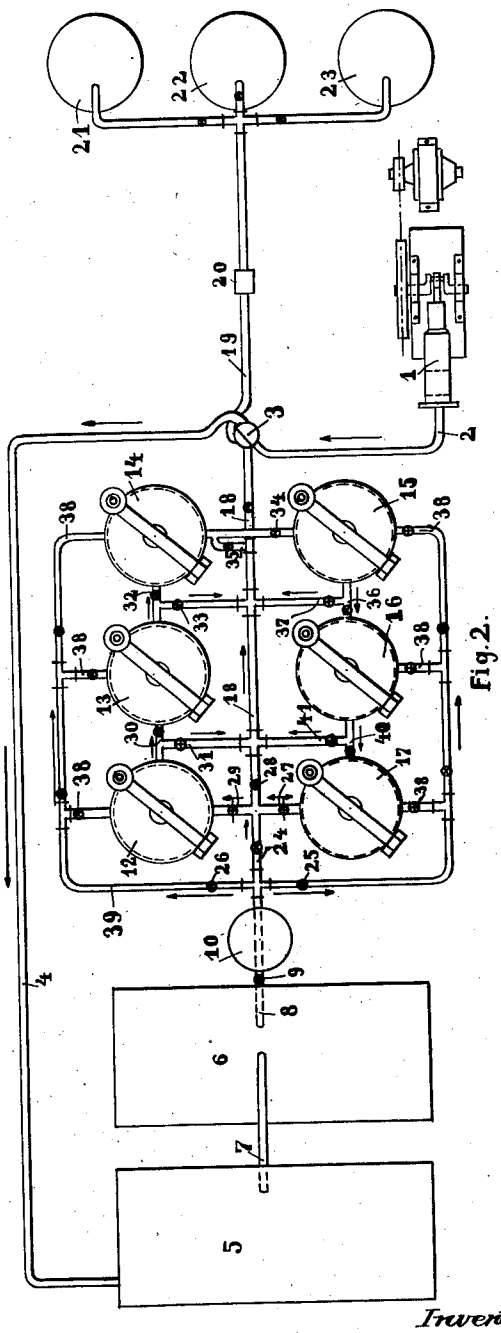


Fig. 2.

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PROCESS AND DEVICE FOR THE SACCHARIFICATION OF CELLULOSE AND THE LIKE

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The present invention relates to a process and device for the saccharification of cellulose and the like.

An economical solution of the problem of saccharifying cellulose involves high yields at low consumption of acid; the extraction of saccharine solutions of suitable concentration, composition, and fermentability; simplicity of procedure; and the recovery of the lignine residue in suitable form and its utilization.

Saccharification of cellulose resulting in high yields was hitherto possible only by means of concentrated acids. By applying the known saccharification processes employing diluted acids cellulose can be degradated quantitatively to grape sugar if the period of hydrolysis is long enough, but the grape sugar thus formed is exposed to continual decomposition so that the yield is poor.

The process forming the subject of the present invention eliminates these decomposition processes by pressing the diluted acid through the cellulose material at high pressures and temperatures so that the grape sugar forming is rapidly removed.

The decomposition of the grape sugar solution pressed out is prevented by neutralization, cooling, release of pressure etc.

The process of pressing the diluted acid through the cellulose material at high pressures and temperatures is referred to as percolation or percolating saccharification, and the reaction vessels are referred to as percolators.

By applying the process according to this invention a high and almost quantitative yield is obtained.

Owing to its bulk cellulose material requires large rooms and large quantities of acid so that the saccharine contents of the solutions obtained are quite low. For economic reasons a higher sugar concentration is often desired which can be obtained under the new process without affecting yield by reducing the size of the interstices in the cellulose material accessible to the acid and by exposing the material in this condition to percolating saccharification.

The reduction in the size of the hollow spaces can be brought about by pressing the cellulose material or by filling the interstices with solid, gaseous, foam-like substances or mixtures of gas and percolating liquid, which affords several advantages. For instance, if twice the ordinary quantity of cellulose material is stuffed into a percolator by pressing, the following superior features are evident when comparing this method with a process using no pressure:

(1) The saccharine solutions discharged show double concentration;

(2) The same equipment and the same amounts of acid produce twice the amount of sugar;

(3) The composition process is counteracted as the sugar formed is discharged from the percolator more rapidly than at present.

The cellulose material can be pressed in dry or wet condition. If wet pressing is preferred, it is advisable to make a paste of it by adding water and to place it into the percolator under pressure, the cellulose remaining then pressed within the percolator while the water runs off.

In the course of saccharification the amount of cellulose present in the percolator is reduced resulting in turn in a reduction of the speed at which sugar is being formed and also in a reduction in the concentration of the saccharine solution discharged.

In case of cellulose material containing incrusting matter the addition of fresh cellulose material or filling of the hollow spaces with air eliminates this drawback only partially, while a better method consists in working with several percolators under the counter-current process by letting the fresh acid enter first the most degradated material, then the semi-degradated and finally the newly added.

Danger to the sugar already formed is avoided by increasing the velocity of flow of the diluted acid.

Should this be impossible owing to the resistance of the pressed cellulose material, the temperature of reaction or the concentration of the acid (hydrogen ion concentration) is correspondingly reduced so that the speed at which sugar is formed and decom-

posed is lowered and thus the longer period of reaction compensated for.

As stated, it may be economically desirable to obtain a high concentration of sugar. For example, strong sugar solutions produce at alcoholic fermentation correspondingly strong alcohol concentrations whereby the cost of distillation is reduced.

The alcohol concentrations forming can be increased still more by employing an alcohol-containing sour liquid for the percolation, preferably and suitably a part of the fermented wort.

Accordingly, alcohol-containing sugar solutions are obtained first and afterward, after their fermentation, increased concentrations of alcohol.

The concentration of unstable sugar is replaced by concentration of stable alcohol.

This measure can be employed in all cases where the product of fermentation remains constant relative to the conditions of percolation.

As fermented wort usually contains small quantities of unattackable albuminous substances of high molecular weight and polymeric carbohydrates which can be decomposed and made useful by means of acid hydrolysis, the employment of fermented wort as percolating liquid is profitable also in this respect.

To work on the counter-current principle with several percolators offers special advantages also with regard to the effect and neutralization of the acid.

Cellulose material often possesses slightly neutralizing properties with the result that the acid becomes saturated in the percolator which was the last to be filled with fresh raw material and to be subjected to the action of the percolating liquid.

When using one battery the saturation of the acid is naturally restricted to the percolator through which it flows last so that the action of the acid is unhampered in the other percolators.

If the saturating effect of the cellulose material is insufficient to neutralize the acid in the last percolator, neutralization in the last percolator is brought about by suitable admixtures of a neutralizing character added to the cellulose material. This eliminates neutralization as a separate step in the process.

In addition to suitable concentration and neutral reaction of the sugar solutions obtained the fermentation of the sugar juices and the production of yeast require contents of soluble nitrogen-phosphor-potash and magnesium compounds. In the interest of an economical application of the process organic and inorganic compounds of the nitrogen, phosphorous, potassium and magnesium should be added to the cellulose material before percolation to suit requirements, the said compounds being absorbed during percolation by the saccharine solution formed so that the solutions discharged are adapted to fermentation without further preparation.

By employing neutralizing fertilizing substances (tricalcium phosphate, ammonium carbonate, ammoniac, potassium carbonate, magnesium oxide, etc.) fertilization and neutralization of the juices can be combined.

The admixture of organic nitrogen and phosphorus acid carriers (acrospires, lupines) offers special advantages in addition to the one mentioned by producing, through percolation, a favorable effect upon the degradation of the albuminous substances the dissolved constituent parts of which are removed from the system and thus protected against decomposition while the undissolved proteins are subjected to intensive acid hydrolysis and, on the other hand, by saccharifying and making useful through percolation the starch, cellulose and hemicellulose of the organic nitrogen and phosphorus acid carriers.

A satisfactory saccharification of a mixture of cellulose and starch was impossible by applying the usual starch and cellulose saccharification processes employing diluted acids, because saccharification of starch takes place many times more rapidly than that of the cellulose, and the sugar formed from starch decomposes during the intensive acid hydrolysis required for the cellulose. As percolation prevents the decomposition of the sugar, it is possible to saccharify cellulose mixed with other carbohydrates that can be readily hydrolized and to obtain a good yield from both.

Another feature of the invention of special importance for the problem of saccharification relates to the saccharification of cellulose material free from incrusting matter.

In case of material containing incrusting matter filling up with cellulose material during saccharification is possible only within certain limits on account of the residual incrusting matter, while, on the other hand, during the percolating saccharification of cellulose material not containing incrusting matter (cellulose dextrin) material of the same type may be added continually, as the percolating saccharification leaves no appreciable residue.

In such cases the pasty cellulose material free from incrusting matter is preferably mixed with acid at high temperatures and continually pressed into the percolator.

The charge of fresh cellulose material should be equal in quantity to the saccharine solutions discharged to keep the amount of cellulose within the percolator uniform. The employment of a battery of percolators can be dispensed with in this case.

For the purpose of saccharifying cellulose dextrin suitable filtering devices attached to

the discharge side of the percolator will retain the dispersed dextrin.

In place of a filter a suitable sieve may be used for fibrous cellulose material or for material containing incrusting matter.

Saccharine solutions obtained by percolation possess the property of increasing their contents of reducing and fermentable sugar by subsequent acid hydrolysis, which is probably due to the presence of cellubiosis. This subsequent hydrolysis of the sugar juices is preferably caused by retarding the complete neutralization and cooling, and the subsequent hydrolysis should be continued until the maximum of fermentable sugar has been reached. If complete neutralization happens to take place in the percolator through which the liquid has trickled last, secondary hydrolysis should precede it.

The flow of diluted acid through a battery of percolators requires a drop of pressure, i. e. pressure in one percolator must be lower than in the preceding one. If the operating pressure drops at any point in the battery to the steam pressure of the percolating liquid, evaporation sets in which may lead to the complete decomposition of the sugar formed and the cellulose left over.

To avoid such troubles either the operating pressure should be chosen from the start materially higher than the steam pressure of the percolating liquid or the steam pressure should be lowered by means of a suitable temperature drop in the direction of the flowing juices. Pressure above atmospheric can be produced only by pressure steam or compressed air.

The economy of the process is further enhanced by the recovery of the heat contained in the juices discharged. For this purpose freshly prepared acid (or cold water) is guided in counter-current towards these juices so as to effect simultaneously cooling of the juices and preheating of the acid (or water).

To reduce the cost of equipment acid is profitably added in a suitable manner to the already preheated pressure water immediately before it enters the percolator, whereby a considerable saving of acid-proof equipment and fittings is effected.

After saccharification is finished the percolators, aside from the lignine-like residue, contain the diluted and heated acid which can be pressed out of the percolator for further use without previous expansion. By rinsing with (pressure) water the last remnants of acid can be removed.

By the pressure release of the vessel a part of the heat contained in the percolator is saved in the form of steam while, on the other hand, lignine is caused to drop off semidry, which increases its adaptability for other uses.

The residues are to a large extent freed from the salts and resins of the original material by the percolating process and therefore particularly adapted for the production of ashless calorimetrically high grade coal and active carbon, which is another point in favor of the economy of the process.

To produce active carbon it is profitable to impregnate the residues while still in the percolators with metallic salts and to carbonize them after they are discharged.

The term "cellulose" and "cellulose material" cover wood, straw, peat, reed, leaves, moss etc.

The diluted acid solution used for percolation may consist of an organic or organic acids or acid salts or of mixtures of both substances.

One form of a device for applying the process described is shown in the drawing, in which

Figure 1 is a side view and Fig. 2 a top view. The fresh water or fermented wort is sucked up by the pump 1 and forced into the piping 2 provided with a heat exchanging vessel 3 which preheats the liquid while, on the other hand, it exercises a cooling effect upon the liquid circulating toward it, i. e., the subsequent saccharine solution. From the heat exchanging vessel 3 the piping 4 leads to the heater 5 where the liquid is heated to the desired high temperature and pressure. Behind the heater 5 is arranged a buffer vessel 6 connected with the heater 5 by the piping 7. From the buffer vessel 6 the piping 8 leads to the battery of percolators. Behind the buffer vessel 6 is a check valve 9 followed by the acid reservoir 10 connected with the piping 3 by an intermediate valve 11 adapted to regulate the amount of acid to be added. The piping 8 ends in a system of pipes leading to the percolators 12, 13, 14, 15, 16 and 17, whereupon it is continued as piping 18 and ends in the heat exchanging vessel 3. The piping 19 extends from the heat exchanging vessel and contains a flow regulating device consisting of a throttle valve 20. After passing this valve the acid or neutral saccharine solution enters the storage vessels 21, 22, 23 which can be opened and closed by the valves mentioned. The course of the acidified water through the battery of percolators can now be continually regulated by connecting the percolators either separately or in series, the acid entering always the most degradated percolator and being discharged at the freshly filled one. Let us assume that 4 percolators are working at a time and that they are to be continually connected clockwise. In this case the flow is as follows:

The acidified water flows through the piping 8 into the piping 24 whose valve is open while the valves 25 and 26 of the side piping are closed, as are the valves 27 and 28 of the other side pipings. The valve 29 of the

third side piping is open so that the acidified water flows through the pipings 8, 24 and 29 to the percolator 12. After piping 30 whose valve is open while the valve of the branch piping 31 is closed so that the liquid enters now the percolator 13. In the same way it flows through this percolator and enters the open piping 32 whose side piping 33 is closed. Through the piping 32 it flows into the percolator 14 and thence through the piping 34 into the percolator 15. The side piping 35 of the piping 34 is also closed by a valve. From the percolator 15 the liquid enters the piping 36 leading to the percolator 16, but as it is shut off here, the liquid enters the open side piping 37 and flows then through the piping 18 to the heat exchanging vessel 3 and the discharge piping 19. The speed of flow is being regulated by the throttle valve 20. The more active the acid is, the greater may be the speed of flow; and the more spent the acid is, the slower will have to be the speed. Each percolator is provided with supply pipes 38 ending in a ring main 39 to make it possible to feed the percolator from the ring main too. For example, to fill the percolator anew, it is disconnected and the acidified water flows through the pipings 8, 39, 38 to the percolator 13. The percolator 16 is then re-connected to the battery so that discharge takes place through the pipings 40, 41, 18. If the second percolator 13 is disconnected also, supply takes place through the ring main 39 and the arm 38 for the percolator 14 while the return flow is effected by means of the percolator 17 and the discharge pipings 27, 18.

I claim:—

1. The process of saccharification of cellulose material comprising, reducing the interstices in the cellulose material by pressure, percolating diluted acid through the compressed cellulose material while heating the same under pressure, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

2. The process of saccharification of cellulose material comprising, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

3. The process of saccharification of cellulose material comprising, percolating diluted acid according to the counterflow principle through the cellulose material while heating the same under pressure, decreasing the temperature of the diluted acid in progressive ratio when flowing through the gradually decomposed material, continually and rapidly removing the solution of sugar from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

4. The process of saccharification of cellulose material comprising, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, reducing the temperature of the diluted acid in progressive ratio when flowing through the gradually decomposed material, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

5. The process of saccharification of cellulose material comprising, admixing lime to the cellulose material, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, reducing the temperature of the diluted acid in progressive ratio when flowing through the gradually decomposed material, neutralizing the diluted acid by lime contained in the last traversed cellulose material, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

6. The process of saccharification of cellulose material comprising, admixing lime and calcium phosphate to the cellulose material, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, reducing the temperature of the diluted acid in progressive ratio when flowing through the gradually decomposed material, neutralizing the diluted acid by the lime combinations contained in the last traversed cellulose material, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

7. The process of saccharification of cellulose material comprising, working up the cellulose in the presence of organic nitrogen compounds, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, reducing the temperature of the diluted acid in progressive ratio when flowing through the gradually decomposed material, continually and rapidly removing the solu-

tion of sugar formed and the organic nitrogen compounds in solution from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

8. The process of saccharification of cellulose material comprising, working up the cellulose in the presence of starch, reducing the interstices of the cellulose material by pressure, percolating diluted acid according to the counterflow principle through the compressed cellulose material while heating the same under pressure, decreasing the temperature of the diluted acid in a progressive ratio when flowing through the gradually decomposed material, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

9. The process of saccharification of cellulose material comprising, reducing the interstices of the cellulose material by pressure, percolating with a mixture of diluted acid and thoroughly fermented flavoring according to the counterflow principle through the compressed cellulose material while heating the same under pressure, decreasing the temperature of the diluted acid in a progressive ratio when flowing through the gradually decomposed material, continually and rapidly removing the solution of sugar formed from the system, and reducing the temperature of the emerging sugar solution to prevent decomposition.

In witness whereof I have hereunto set my hand.

HEINRICH SCHOLLER.