UNITED STATES PATENT OFFICE.

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PRODUCTION OF GLYCERIN BY FERMENTATION.

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To all whom it may concern:

Be it known that we, ALLEN THOMAS COCKING, a subject of the King of Great Britain and Ireland, and residing at "Carhampton House," Four Oaks, Sutton Coldfield, in the county of Warwick, England, and CECIL HERBERT LILLY, a subject of the King of Great Britain and Ireland, and residing at 29 Carlyle Road, Edgbaston, Birmingham, in the county of Warwick, England, have invented certain new and useful Improvements in the Production of Glycerin by Fermentation, of which the following is a specification.

This invention relates to the production of glycerin by fermentation.

It is known that sugars can be fermented with the production of alcohol and glycerin, and among the objects of the present invention are to obtain increased yields of glycerin, and to reduce the time factor of the fermentation.

It has hitherto been thought necessary to employ large additions of alkaline salts to the mash in order to obtain good yields of glycerin, and that within certain limits the greater the amount of alkaline salt added, the higher the yield, but we have found that alkaline additions are unnecessary and have substantial disadvantages.

The production of glycerin by fermentation in the presence of normal sulphites, as has been proposed, depends upon the fixation of an intermediate product of alcohol fermentation, viz, acetaldehyde, and upon the affinity of acetaldehyde for bisulphites.

Now although bisulphites are relatively strong antiseptics and cannot be used alone in large quantities so that it has been believed necessary to allow the bisulphite to be produced by the reaction and taken up at once by the acetaldehyde, we have discovered that they may be used in conjunction with normal sulphites producing a mixture which in solution is relatively non-antiseptic and neutral in reaction to litmus. The use of the mixed sulphites has substantial advantages, for example, the presence of the bisulphite anticipates the eventual splitting up of the normal sulphites in fermenting liquors, resulting in the fixation of the acetaldehyde at an earlier stage and consequently the saving of a portion of the sugar which with normal sulphites alone would pass completely through the various stages of fermentation to alcohol before sufficient bisulphite could be formed for fixing the intermediate product, acetaldehyde. Thus with normal sodium sulphite alone, the following reaction would take place:—

$$Na_2SO_3+CO_2+H_2O=NaHSO_3+NaHCO_3$$

the reaction with the salts mixed in equal proportions being

$$NaHSO_3+Na_2SO_3+CO_2+H_2O=2NaHSO_3+NaHCO_3.$$

Again in such fermentations the alkalinity resulting from the splitting up of the sodium sulphite can be reduced to a minimum, or may be entirely eliminated by adding bisulphite or increasing the proportion of bisulphite to normal sulphite in the subsequent additions, so as to neutralize the bicarbonate formed, thus, the reaction when using normal sulphite alone is as follows:—

$$\underset{252}{CO_2+H_2O+2Na_2SO_3}=\underset{168}{2NaHSO_3+2NaHCO_3}$$

the reaction with a mixture of the salts in molecular proportions being

$$\underset{230}{CO_2+H_2O+NaHSO_3+Na_2SO_3}=\underset{84}{2NaHSO_3+NaHCO_3}$$

showing that with the normal sulphite, 252 parts will produce 168 parts of bicarbonate, whereas with the mixed salts, 230 parts of the mixed sulphites produces only 84 parts of bicarbonate.

We find that most yeasts can be employed without special precautions being taken to acclimatize them to the special conditions.

We also find that for the same glycerin yields the fermentation period when using the mixed sulphites is considerably less than when normal sulphite alone is employed.

The invention consists in a process for the production of glycerin in larger quantities than heretofore in addition to acetaldehyde and alcohol by a yeast fermentation of a solution containing a fermentable sugar with such proportions of normal sulphite and bisulphite of an alkali metal as will produce a mixture of mash and salts which is approximately neutral to litmus.

The invention also consists in the produc-

tion of glycerin by the fermentation of fermentable sugars with yeast by the addition to the sugar solution of such mixtures of sodium sulphite and sodium bisulphite as do no inhibit fermentation.

The invention further consists in adding mixtures of sulphites (preferably in solution in water) in successive small proportions, until an amount has combined with the acetaldehyde corresponding to the yield of glycerin required, having regard to the other by-products which may be desired, or until the amount of sulphites practically required for the production of the corresponding theoretical yield of glycerin is reached. (The theoretical quantity of sulphite—calculated as Na_2SO_3—corresponds, we find, to 70% of the weight of the fermentable sugar; the theoretical yield of glycerin then amounting to 50% of the fermentable sugar; but the amount practically required may amount to 80%). It will, of course, be understood that the amount of normal sulfite added must eventually be sufficient to combine with the amount of aldehyde to be formed during the fermentation process.

The invention also consists in adding water solutions of sodium bisulphite as the fermentation proceeds, or increasing the proportion of sodium bisulphite in the mixture additions to maintain approximate neutrality to litmus.

In carrying the invention into effect according to one example, we take 15 gallons of an aqueous solution of molasses or sugar, containing 10.5% of total fermentable sugars and the yeast culture, and we add to this an aqueous solution containing 5 lbs. of a mixture of Na_2SO_3 and $NaHSO_3$ in equal proportions to produce a solution having the reaction neutral to litmus. After 18 hours of fermentation we add a further 2 lbs. of the mixed sulphites previously dissolved in a portion of the fermenting liquor, this operation being repeated with 1 lb. of the mixed salts added at 24 hours, and a further 1 lb. at 26 hours. 86% of the sugars present are in this case consumed in 120 hours from the commencement of the operation, and the yield of glycerin calculated on the sugar consumed amounts to about $35\frac{1}{2}$%, the average temperature throughout being 36° C.

In the above case the commercial sulphite mixture added contained the equivalent of 90% as Na_2SO_3, so that in all 9 lbs. of the mixed commercial sulphites containing actually 8.1 lbs. of mixed sulphites was added. At the end of the above period, the solution contained 0.9% of uncombined Na_2SO_3, and 1.5% of unfermented sugar, so that 6.8 lbs. of Na_2SO_3 had combined in the reaction, whilst 13.7 lbs. of sugar had been fermented. The calculated yield of glycerin on the sulphite combined is equivalent to 4.89 lbs. of glycerin on 13.7 lbs. of sugar consumed, or 35.6%. Actual analysis gave a figure of 35.5%. The ratio of sugar to sulphite added was 100:50, whilst the ratio of sugar consumed to sulphite combined was 100:49.6. The theoretical proportions for the maximum theoretical yield of glycerin, i. e. 50% on the sugar consumed, are 100:70. By our method it is unnecessary to add the sulphite in quantities exceeding to any great extent those theoretically required; nevertheless it is desirable to add up to about 10% in excess of the theoretical requirements, and the yields of glycerin and other products can be regulated as desired.

We further have found that it is better to dissolve the mixed salts to be added, in water instead of in a portion of the fermenting liquor as the time required for completion of the fermentation is thus reduced and injury to the cultures is avoided.

By increasing the total quantity of sulphites added, and continuing the fermentation, the yield of glycerin and acetaldehyde can be increased up to approximately 50% of glycerin expressed on the sugar consumed with the production of relatively less alcohol.

The avoidance of additions of sulphites in large excess has the advantage that the working up of the fermenting liquors is considerably facilitated.

A substantial advantage of this process is the freedom of choice it confers on the user in regard to the relative proportions of the principal products obtained, i. e., glycerin, acetaldehyde and alcohol. In some circumstances, e. g. it will be desirable to produce less glycerin and acetaldehyde and more alcohol.

In order to illustrate the flexibility of the process in this respect we give three further examples:

(*a*) Where the maximum glycerin yield is desired;

(*b*) Where a smaller yield of glycerin and a higher yield of alcohol is desired;

(*c*) Where a still smaller yield of glycerin and a still higher yield of alcohol is desired.

Example (a).

311 gallons of a solution of crude cane sugar equivalent to 788 lbs. of glucose (23.8% on solution) were sterilized and 40 lbs. of pressed yeast added. At intervals extending over a period of five days when the fermentation was most vigorous was added a solution in water of a mixture of sodium sulphite (95% Na_2SO_3) and sodium bisulphite (95% $NaHSO_3$) in equal parts by weight—which solution was neutral in reaction to litmus. At first 40 lb. quantities of the mixed salts in 16 gallons of water were added each time, but later 30 lb. quantities in the same volume of water were

added. In all, and extending over the period mentioned above, 176 gallons of water containing the mixed salts equivalent to 545 lbs. of Na_2SO_3 were added, and the fermentation was allowed to complete itself for a further four days at a temperature of 35° C. to 37° C.

Therefore 788 lbs. of sugar in 487 gallons of liquid is equivalent to an initial sugar concentration of 16.1%. After nine days 95% of the original sugar had been consumed while sulphite equivalent to 39 lbs. of Na_2SO_3 remained in the solution uncombined. Therefore 749 lbs. of sugar during fermentation had fixed a quantity of salts equivalent to 506 lbs. of Na_2SO_3. This quantity of Na_2SO_3 is equivalent to a production of 364 lbs. of glycerin or 48.6% of the weight of sugar consumed. Actually 336 lbs. of glycerin were found by analysis or 45% calculated on the weight of sugar consumed. The acetaldehyde produced in this case is equivalent to 23% of the sugar consumed, viz, 172.2 lbs. while the alcohol amounts only to 5% of the sugar consumed, viz, 37.4 lbs.

Example (b).

412 gallons of solution of crude cane sugar equivalent to 830 lbs. of glucose (20.1% on solution) were sterlized, and 40 lbs. of pressed yeast added. At intervals extending over a period of three days, when the fermentation was most vigorous was added a solution in water of a mixture of sodium sulphite (95%) and sodium bisulphite (95%) in equal parts by weight, which solution was neutral in reaction to litmus. At first 66 lbs. of the mixed salts in 24 gallons of water were added each time, but later this was reduced to 33 lbs. of mixed salts in the same volume of water per addition.

In all, and extending over the period mentioned above 232 gallons of water containing the mixed salts equivalent to 511 lbs. of Na_2SO_3 were added and the fermentation allowed to complete itself for a further three days at a temperature of 35° C. to 37° C.

Therefore 830 lbs. of sugar in 644 gallons of liquid is equivalent to an initial sugar concentration of 12.8%.

After a period of six days from the commencement of the fermentation 98.4% of the sugar had been consumed, while salts equivalent to 25 lbs. of Na_2SO_3 remained uncombined; therefore 816.7 lbs. of sugar had fixed a quantity of salts equivalent to 486 lbs. of Na_2SO_3. This quantity of Na_2SO_3 is equivalent to a production of 349.9 lbs. of glycerin of 41.6% on the sugar consumed. Actually 351 lbs. of glycerin were found by analysis or 43% calculated on the sugar consumed.

The acetaldehyde produced in this case is equivalent to 21% of the sugar consumed, or 171.5 lbs. while the alcohol amounts of 8% or 65.3 lbs. of the sugar consumed.

Example (c).

145 gallons of a solution of crude cane sugar equivalent to 288 lbs. of glucose (19.8% on solution) were sterilized and added to the culture remaining in the fermentation vat from a previous fermentation. At intervals extending over two days, when the fermentation was most vigorous, was added a solution in water of sodium sulphite (95% Na_2SO_3) and sodium bisulphite (95% $NaHSO_3$) in equal parts by weight, which solution was neutral in reaction to litmus. 12 lb. quantities of the mixed salts in 8 gallons of water were added each time, the total additions amounting to 76 gallons of water containing mixed salts equivalent to 93 lbs. of Na_2SO_3. At the end of four days at a temperature of 35° C. fermentation had ceased. 288 lbs. of sugar in 221 gallons of liquid is equivalent to an initial sugar concentration of 13%. When fermentation has ceased 97% of the sugar had been consumed, while no free sulphite remained in solution. Therefore 280 lbs. of sugar had fixed a quantity of salts equivalent to 93 lbs. of Na_2SO_3, equivalent to a production of 66.9 lbs. of glycerin or 23% on the sugar consumed. Actually 70.8 lbs. of glycerin were found by analysis, or 24.6% on the sugar consumed.

The acetaldehyde produced in this case is equivalent to 34.4 lbs. or 12.3% while the alcohol amounts to 72.8 lbs. or 26% on the sugar consumed.

It will be seen that the higher yields of glycerin require a longer time of fermentation.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process which consists in the fermentation by a yeast of a solution containing a fermentable sugar with such proportions of normal sulphite and bisulphite of an alkali metal as will produce a mixture of mash and salts which is approximately neutral to litmus.

2. A process which consists in the fermentation by a yeast of a solution containing a fermentable sugar with such proportions of sodium sulphite and sodium bisulphite as will produce a mixture of mash and salts which is approximately neutral to litmus.

3. In a process which consists in the fermentation by a yeast of a solution containing a fermentable sugar the addition in successive small portions of a mixture of normal sulphite and bisulphite of an alkali metal until an amount has combined with the acetaldehyde corresponding to the other by-products desired, the proportions of nor-

mal sulphite and bisulphite being such as to maintain the mash approximately neutral to litmus.

4. In a process consisting in the fermentation by a yeast of a solution containing a fermentable sugar the addition in successive small portions of a solution containing normal sulphite and bisulphite of an alkali metal in such proportions as will produce a mixture of mash and salts approximately neutral to litmus.

5. In a process consisting in the fermentation by a yeast of a solution containing a fermentable sugar the addition in successive small portions of a solution containing normal sulphite and bisulphite of sodium in such proportions as will produce a mixture of mash and salts approximately neutral to litmus.

6. A process which consists in the fermentation by yeast of a solution containing a fermentable sugar in the presence of a normal sulphite and bisulphite of an alkali metal in such proportions as will produce a solution approximately neutral to litmus including the step of adding an aqueous solution of the bisulphite of the alkali metal as the fermentation proceeds.

7. A process as claimed in claim 6 in which the addition of the bisulphite is made in a mixture of normal sulphite and bisulphite, the proportion of bisulphite in the mixture being increased for each addition and the total proportions of normal sulphite and bisulphite being such as will produce a mixture of mash and salts approximately neutral to litmus.

8. A process as claimed in claim 1 in which the sulphite and bisulphite are employed in equal proportions.

9. The process which consists in the addition to an aqueous solution of sugar and yeast of a mixture of equal parts of sodium sulphite and sodium bisulphite in the relative proportions 5 lbs. of mixture to 15 gallons of solution containing 10.5 per cent of the total fermentable sugars and yeast; the addition after an interval of a further quantity of dissolved mixed sulphites in the proportion of 2 lbs. for the quantities given above, the further addition of another quantity of mixed salts after another interval of fermentation in the proportion of 1 lb. for the above quantities and the still further addition of a quantity equal to the last quantity of mixed sulphite and bisulphite after a further period.

In testimony whereof we have signed our names to this specification.

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