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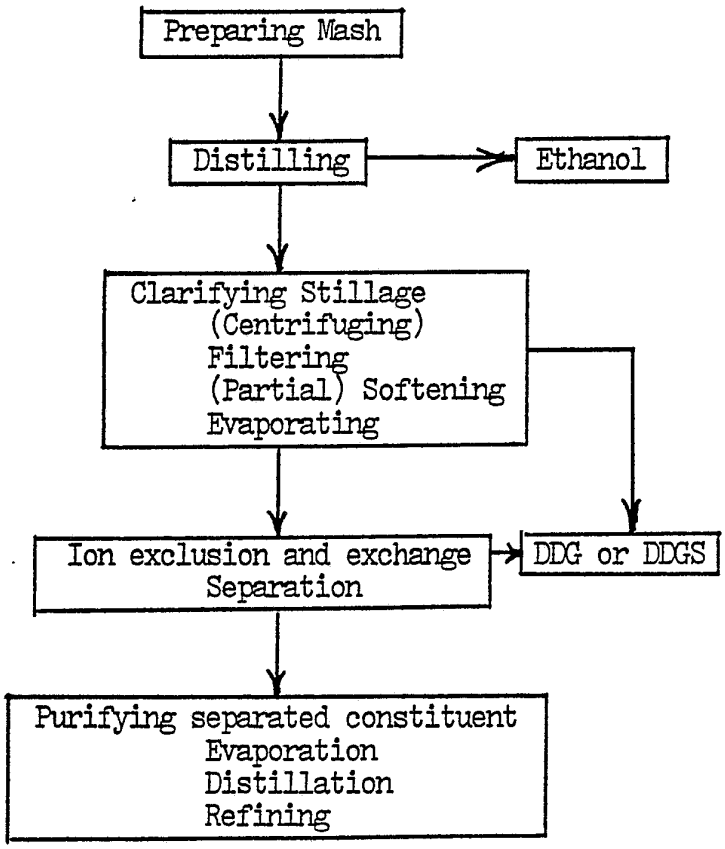
(54) Title: PROCESS AND APPARATUS FOR MANUFACTURING ETHANOL, GLYCEROL, SUCCINIC ACID AND FREE FLOWING DISTILLER'S DRY GRAIN AND SOLUBLES

(57) Abstract

This invention relates to processes and apparatus for the manufacture of ethanol, glycerol, succinic acid and a free flowing distiller's dry grain and solubles useful as an animal feed. In accordance with the processes disclosed, production of glycerol and succinic acid during a biomass fermentation and distillation process for producing ethanol is enhanced by selection of certain defined, favorable process variables such as immobilization of yeast cells, yeast cell concentration, pH and osmotic pressure. Glycerol and succinic acid is then recovered by processing the mash to clarify it and then separate by ion exclusion techniques then purifying the desired by-product constituents.



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PROCESS AND APPARATUS FOR MANUFACTURING ETHANOL, GLYCEROL, SUCCINIC ACID AND FREE FLOWING DISTILLER'S DRY GRAIN AND SOLUBLES

Field and Background of Invention

This invention relates to the manufacture of ethanol, glycerol, succinic acid and a free flowing distiller's dry grain and solubles useful as an animal feed.

The manufacture of all of the products named has been known heretofore, and all have commercial uses. Ethanol is used as a beverage, a chemical, and a fuel derived from renewable resources, and is typically manufactured by fermentation and distillation processes starting from biological materials such as grain or the like. Glycerol, while known to be produced as a by-product of ethanol fermentation and distillation processes, has been manufactured commercially by processes which have soap as the primary product or which synthesize glycerol from petrochemical feedstocks. Succinic acid is synthesized from maleic or acetic acid. Distiller's dry grain, characterized as with or without solubles, is conventionally produced as a by product of fermentation and distillation processes, and is usually sufficiently infused with sticky by products such as glycerol as to have poor flowing qualities and be difficult to handle.

The manufacture of ethanol is sufficiently well known that the interested reader is referred to the

available literature for descriptions of the basic processes. The manufacture of glycerol is, by way of example, discussed in Hildebrandt United States Patent 2,160,245; Wallerstein United States Patent 2,400,859; and Frankel United States Patent 2,772,207, to which the interested reader is referred. The manufacture of succinic acid and free flowing distiller's dry grain by processes such as those to be described hereinafter has not, insofar as is known to the present inventor, been described in any prior patent.

The processes and apparatus of the present invention contemplate the production of each or all of the products mentioned in a commercially feasible manner in a fermentation and distillation process.

Brief Description of Invention

More particularly, it is an object of this invention to produce glycerol as a valuable by-product of a fermentation process such as may produce ethanol. In realizing this object of the present invention, the efficiency of the known ethanol producing fermentation and distillation processes is essentially maintained, while an additional valuable product is derived.

Likewise, a further object of this invention is the manufacture of succinic acid as a by-product of a fermentation. In realizing this object of the invention, succinic acid is produced by an essentially natural biochemical process, starting from a biologically based material and without synthesis of the

type used heretofore.

Yet a further object of the invention is the manufacture of free flowing distiller's dry grain. Distiller's dry grain is a known by product of fermentation and distillation processes, useful as an animal feed. However, the handling of distiller's dry grain (known as DDG or DDGS depending upon the presence of solubles) has been made difficult heretofore by the presence of small quantities of glycerol and the like which render the product less flowable. In realizing this object of the present invention, DDG or DDGS becomes handleable using conventional procedures for free flowing dry materials, thus increasing the value of the by product.

Brief Description of Drawing

Some of the objects of the invention having been stated, other objects will appear as the description proceeds, when taken in connection with the accompanying drawing, in which a schematic representation of the flow of materials in the processes and apparatus of the present invention is shown.

Detailed Description of Invention

While the present invention will be described more fully hereinafter with reference to the accompanying drawing, in which a preferred embodiment of the present invention is shown, it is to be understood at the outset of the description which follows that persons of skill in the appropriate arts may modify the invention here

described while still achieving the favorable results of this invention. Accordingly, the description which follows is to be understood as being a broad, teaching disclosure directed to persons of skill in the appropriate arts, and not as limiting upon the present invention.

Referring now more particularly to the drawing accompanying this disclosure, the drawing represents certain steps and apparatus which, in the sequence disclosed hereinafter, accomplish the objects of this invention. Certain steps and apparatus, being well known to those having skill in the relevant arts, have not been shown but will be described for the reader.

It is known that the formation of ethanol in a fermentation process is growth associated and that the formation of glycerol and succinic acid is interrelated. In a typical batch fermentation process without the recycle of stillage, some 46.5 grams of ethanol, 3.5 grams of glycerol and 0.6 gram of succinic acid are formed per 100 grams of reducing sugar consumed. The present invention realizes the commercially feasible recovery of the glycerol and succinic acid constituents, resulting in the production of free flowing DDG and/or DDGS, and contemplates the enhancement of the production of the by products to be recovered by the adjustment of several process parameters. These process parameters and the result of operation in accordance with the present invention will be addressed hereinafter.

The first process parameter to be addressed relates to the form of yeast used in the fermentation process. It has been determined that a properly immobilized organism will enhance and increase production of glycerol and succinic acid. These results are achieved where the yeast is in a stable ionic and high density matrix, as illustrated in the following example.

Example 1

A mash prepared of ground whole corn was subjected to liquefaction at a pH of 6.3 to a dextrose equivalent (DE) of 20.3; to jet cooking for two minutes at 149 degrees Celsius; and to saccharification to DE 36 at pH 4.5. Immobilized yeast cells were prepared by mixing a 1.5 weight percent sodium alginate solution with the preferred ratio of hydrated yeast cells and sterilized sand. The resulting slurry was poured through a 12 mesh screen into an aqueous solution of 0.5 M $CaCl_2$ and 1.5 weight percent glucose at pH 4.6 and ambient temperature. On contact with the calcium chloride, the drops formed beads which, after 24 hours in a refrigerator at 4 degrees Celsius, gelatinized into firm beads with diameters of 2 - 4 mm. The mash was then fermented in two batches at 34 degrees Celsius with free and immobilized yeast cells at concentrations of 5.0 grams per liter. Fermentation was performed in a batch process with no recycling of stillage and adjustment of pH to 5.0 using NaOH. Comparing the two batches, yields were

as follows:

Yeast	Glycerol grams/100 grams	Succinic Acid Reducing Sugar (RS)
Free cells	3.38	0.67
Immobilized	4.09	0.87

Other process parameters which are contemplated as being subject to adjustment in accordance with this invention include yeast cell concentration and DE or carbohydrate concentration. As yeast cell concentration and carbohydrate concentration rise, production of glycerol and succinic acid are enhanced. These characteristics are illustrated in the following example.

Example 2

A mash was prepared from ground whole milo and fermentation started at pH 4.9 and DE 27 using free yeast cells and at a temperature of 33 degrees Celsius. Fermentation was performed in batch mode, without still-age recycle. Yields, related to yeast cell and carbohydrate concentration, were as follows:

Yeast cell concentration x 10^6ml	DE	Glycerol grams/100 grams RS	Succinic Acid
100	27	3.03	0.49
300	27	3.07	0.52
500	27	3.19	0.61
500	46	3.37	0.64
1,500	90	5.01	0.83

These results reflect enhanced glycerol and succinic acid production following from increased concentration of yeast cells and fermentable carbohydrates during fermentation.

Still other process variables which are contemplated by this invention as being optimized for the production of the desired by products while maintaining ethanol production include osmotic pressure during fermentation; concentration of dissolved carbon dioxide; pH; temperature; selection of the microorganism used; the mode of fermentation; and the formulation and preparation of fermentation media. More precisely, increased osmotic pressure from recycling stillage, increased solute concentration, and/or increased temperature increases production of glycerol and succinic acid, as does increased dissolved carbon dioxide. Yeast cells, as most microorganisms, are able to regulate its internal pH quite effectively within a range of mash pH of from about 3 to about 7, and thus the effect of process variations in pH may appear minimal. It has been determined, however, that production of glycerol and succinic acid is enhanced where an essentially constant pH is maintained during the first half of the fermentation step (when the bulk of glycerol and succinic acid are produced) by the addition of a suitable alkali such as sodium carbonate. The fermentation media, or mash, characteristics will affect the production of glycerol and succinic acid due to the interacting effects of the raw material itself, the concentration of any liquefying (metallo) enzyme, the ratio of fermentable sugars to nonsugars, the type of nonsugars present, and the nutritional requirements

of the particular fermentation microorganism chosen.

Proper selection of the parameters described above will result in enhanced production of glycerol and succinic acid as contemplated by this invention. The following examples include illustrations of variation in the various parameters and the effects on glycerol and succinic acid production of those variations.

Example 3

A mash prepared from ground whole corn was liquefied to DE 20.6 and subjected to jet cooking for 3 minutes at 152 degrees Celsius and partial saccharification. Batches of the mash were then fermented and distilled using process parameters as set forth in the following table, with yields as noted.

Process Parameter	Batch A	B	C	D
YCC	1.2	3.1	9.0	26.5
DE	33.2	56.3	78.7	78.7
Recycle	0	38.3	44.1	71.4
Temperature	30	34	35	35
pH	4.5	5.5	6.0	5.0
Head	atm.	1.7	2.3	1.2
Yeast type	free	immob.	immob.	immob.
Time	58	39	12	9
Yields grams/100 grams RS				
Ethanol	44.9	44.1	42.0	44.7
Glycerol	4.8	5.8	8.3	12.3
Succinic acid	0.6	0.7	1.1	1.4

In the table, YCC refers to yeast cell concentration in grams per liter with approximately 10^{10} cells per gram. DE refers to dextrose equivalent after saccharification. Recycle refers to the percentage of recycled stillage in

the mash being processed. Temperature is the temperature of fermentation in degrees Celsius. The reference to pH is to the value at which pH was maintained during the first half of the fermentation by the addition of sodium carbonate. The "Head" was head pressure in psig. Time is in hours for fermentation.

Considering the tabulated examples together, it is noted that production of glycerol and succinic acid was substantially enhanced with little adverse affect on ethanol production.

Example 4

A mash was prepared from clarified and pasteurized blackstrap molasses, and batches of the mash were then fermented and distilled using process parameters as set forth in the following table, with yields as noted.

Process Parameter	Batch A	B	C	D	E
YCC	1.0	3.0	18.2	32.0	20
RS	184	184	192	200	200
Recycle	0	24.7	43.0	37.9	48.4
Temperature	30	34	34	35	35
Head	atm.	0.9	1.8	2.1	1.2
Yeast type	free	free	immob.	immob.	immob.
Fermentation	batch	batch	batch	cont.	batch
Time	51	27	10	6	12
pH	4.5	5.0	6.0	5.5	5.0
Yields grams/100 grams RS					
Ethanol	48.3	47.8	43.9	46.4	45.1
Glycerol	3.7	4.3	8.4	5.1	10.9
Succinic acid	0.5	0.6	1.0	0.8	1.2

In the table, RS refers to reducing sugar concentration in grams per liter and "Fermentation" refers to a choice between batch and continuous processes, while the other

parameters are as identified above in the description of Example 3.

It will be observed that parameters may be found at which the production of glycerol and succinic acid drop below the maximized levels. However, the maximized levels of production of the by-products sought by the present invention is attained without significant impairment of ethanol production.

Example 5

In order to illustrate other processes without characterizing the additional processes as achieving optimal production of glycerol and succinic acid, a clarified wood hydrolyzate was prepared from yellow pine and processed by batch fermentation with pH held constant for 25 hours, without recycling of stillage and with parameters and yields as follows:

Process	Batch		
Parameter	A	B	C
YCC	15.0	40.0	40.0
RS	54.3	54.3	74.1
Temperature	31	33	34
Head	atm.	0.3	1.2
Yeast type	free	immob.	immob.
Fermentation	batch	batch	batch
Time	68	43	41
pH	5.0	5.5	5.0
Yields grams/100 grams RS			
Ethanol	29.4	34.5	40.4
Glycerol	3.4	3.9	6.9
Succinic acid	0.5	0.8	1.1

In accordance with this invention, a fermented mash prepared in accordance with any of the above examples is then further processed to yield pure glycerol

derived from natural sources (and thus of kosher purity) and/or succinic acid. As a result of the further processing, the end residue solids may be dried to yield DDG or DDGS which is free flowing and more readily handled than are the similar products of other prior processes, due to the removal of the glycerol.

Generally, the first further processing step is distillation of the fermentation to produce ethanol. Such distillation may be by use of a stripping column capable of handling a solids containing stream. The bottoms or stillage is then centrifuged and the thin stillage processed further in a clarification step, removing the dispersed solids to obtain a (sparkling) clear liquid. Clarification is preferably accomplished with (cross-flow) microfiltration systems containing ceramic or mineral membranes. In this process particles in the range of 0.1 - 10 microns, depending on the membrane selected are separated from the thin stillage. High and stable fluxes may be obtained through computer controlled backflushing and proper membrane selection. These new microfiltration membranes are known as such and are commercially available from known suppliers. Such known apparatus may be incorporated into the overall apparatus which practices the processes of this invention.

By way of more specific example, the processing of a chemical clarification process may proceed by taking up to 20 percent of the stillage and liming it to a pH

of 9.0 to 12.0 while at or near boiling. The remainder of the stillage is adjusted to a pH range of 4.5 to 7.5 with a suitable alkali at temperatures as high as practicable. The two portions are then mixed and a precipitate of salts forms, the separation of which is improved by the addition of polyelectrolytes, followed by centrifugation. Following microfiltration or chemical clarification is a (partial) softening step; mainly for the reduction of the divalent cation levels of calcium and magnesium. This will prevent the plugging and fouling of the downstream ion exclusion resin by salt deposits of divalent cations due to potential process upsets which would considerably reduce the operating temperature. As the stillage is clarified, it may be passed to and through an evaporator to remove as much water as possible and effect as high a solids concentration as is practicable. Due to proper clarification, the overall heat transfer coefficient involved will be considerably improved over thin stillage which has not been clarified, while the fouling of heat transfer surfaces will also be minimized. The clarified and concentrated stillage is passed to an ion exclusion apparatus such as that available from Illinois Water Treatment Company of Rockford, Illinois and which contains a suitable resin material such as IWT's SM-51-Na resin or the similar resin available from Dow Chemical as Dowex 50-WX8. As the material passes through the ion exclusion apparatus, glycerol is "retained"

while other ionic constituents are passed into an effluent stream. Recovery efficiencies are in the range of from about 80% to about 98%, and the purity of the glycerol recovered is in a range of from about 80% to about 90%. The apparatus may be a simple or multiple column system used as a pulsed bed or a simulated moving bed. Recycling may be used to maintain or increase product purity and/or recovery efficiency. Condensate from any evaporators used in the apparatus treated in a mixed bed ion exchange may serve as desorbent, with desorbent to recovered glycerol ratios in the range of from about 10 to about 25. Such a column is in ionic equilibrium and requires no regeneration. Effluent from a glycerol recovery ion exclusion apparatus may be passed through a comparable apparatus for recovery of succinic acid. The dilute succinic acid product is concentrated in an evaporator and purified through crystallization. The resulting by-product stream of the ion exclusion step, before or after succinic acid recovery, is ideal for use as a backset in the fermentation. It is a "clean" stream, which will increase osmotic pressure levels as well as reduce process water requirements.

The glycerol stream recovered from the ion exclusion apparatus and process may be further purified in a mixed bed ion exchanger and then concentrated and purified to any desired grade. Such concentration and purification may, for example, be accomplished by the

use of an energy efficient vacuum/steam multiple effect evaporator, and distillation and refining unit such as those available from G. Mazzoni SpA of Italy, with the more concentrated glycerol being deodorized, bleached, filtered and/or polished as desired.

As a final example, the production of glycerol and succinic acid without specific preparation of a stillage having enhanced levels of those constituents is believed valuable.

Example 6

Stillage from a facility for the production of ethanol from wet miller's biomass was centrifuged and the thin stillage subjected to microfiltration in a ceramic membrane unit. The clear permeate was partially softened and then concentrated through evaporation to 73 weight percent solids and fed to an IWT Adsep system consisting of a single three inch I.D. column with a bed height of 62.25 inches of IWT SM-51-Na resin. The concentrate was fed at a rate of 2 GPM/square foot, with 20% feed pulse at 1.442 liters/pulse. The glycerol containing effluent was passed through an IWT mixed bed ion exchange unit to improve purity; then adjusted to pH 7.0 using NaOH; then, using Mazzoni equipment, concentrated by evaporation to 85 weight percent glycerol; and distilled and refined to a CP/USP grade glycerol of high quality. Constituents in the material at stages in the process were as summarized in the following table showing weight distributions.

Constituent	Stillage	Clarified conc. stillage	Adsep effluent	Final product
Total solids	7.37	4.883	1.13	Trace
Protein	2.21	0.79	Trace	-----
Carbohydrates	1.19	0.73	0.03	-----
Fat	0.07	0.003	0.001	-----
Ash	0.84	0.61	0.05	-----
Lactic acid	1.42	1.29	0.02	Trace
Succinic acid	0.09	0.08	0.004	-----
Other	0.343	0.27	0.035	Trace
Glycerol	1.21	1.11	0.035	Trace
Water	92.63	3.18	5.27	0.004
Total	100.00	8.063	6.40	0.984
Percent Glycerol	1.21	13.77	15.47	99.59

In the drawing and specifications there has been set forth a preferred embodiment of the invention and, although specific terms are used, the description thus given uses terminology in a generic and descriptive sense only and not for purposes of limitation.

What is claimed is:

1. A process for manufacturing glycerol comprising the steps of:

preparing a fermented mash,

clarifying the fermented mash,

passing the clarified mash through an ion exclusion material for separating glycerol from other constituents of the clarified mash, and

purifying the separated glycerol.

2. A process for manufacturing succinic acid comprising the steps of:

clarifying stillage produced from the distillation of a fermented mash,

passing the clarified stillage through an ion exclusion material for separating succinic acid from other constituents of the clarified stillage, and

purifying the separated succinic acid.

3. A process for manufacturing succinic acid comprising the steps of:

preparing a fermented mash,

clarifying the fermented mash,

passing the clarified mash through an ion exclusion material for separating succinic acid from other constituents of the clarified mash, and

purifying the separated succinic acid.

4. A process for manufacturing glycerol and succinic acid comprising the steps of:

clarifying stillage produced from the distillation

of a fermented mash,

passing the clarified stillage through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified stillage, and

purifying the separated glycerol and succinic acid.

5. A process for manufacturing glycerol and succinic acid comprising the steps of:

preparing a fermented mash,

clarifying the fermented mash,

passing the clarified mash through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified mash, and

purifying the separated glycerol and succinic acid.

6. A process for manufacturing free flowing distiller's dry grain and solubles comprising the steps of:

clarifying stillage produced from the distillation of a fermented mash, and

passing the clarified stillage through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified stillage and thereby producing free flowing distiller's dry grain and solubles.

7. A process for manufacturing free flowing distiller's dry grain and solubles comprising the steps

of:

preparing a fermented mash,

clarifying the fermented mash, and

passing the clarified mash through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified mash thereby producing free flowing distiller's dry grain and solubles.

8. A process according to one of Claims 1 or 2 or 3 or 4 or 5 or 6 or 7 wherein the step of clarifying comprises adding alkali and thereby adjusting the pH to within a range of from about 4.5 to about 7.

9. A process according to Claim 8 wherein the step of clarifying further comprises centrifugally separating solids from liquid constituents.

10. A process according to Claim 8 wherein the step of clarifying further comprises passing the liquid constituents through a microfilter.

11. A process according to one of Claims 1 or 3 or 5 or 7 wherein the step of preparing a fermented mash comprises the steps of preparing a biomass mash, preparing immobilized yeast cells, and mixing the immobilized yeast cells with the biomass mash.

12. A process according to one of Claims 1 or 3 or 5 wherein the step of preparing a fermented mash comprises the steps of preparing a biomass mash and mixing with the mash yeast cells in a concentration in excess of 300 X 10^6 per milliliter.

13. A process according to one of Claims 1 or 3 or 5 or 7 wherein the step of preparing a fermented mash comprises the steps of preparing a biomass mash having a dextrose equivalent of at least about 30 and mixing yeast cells with the mash.

14. A process according to one of Claims 1 or 3 or 5 or 7 wherein the step of preparing a fermented mash comprises the steps of preparing a biomass mash having a reducing sugar concentration of at least about 200 grams/liter and mixing yeast cells with the mash.

15. A process according to one of Claims 1 or 3 or 5 or 7 wherein the step of preparing a fermented mash comprises the step of maintaining the pH of the mash substantially constant during the first half of the fermentation process.

16. A process for manufacturing ethanol, glycerol, succinic acid and free flowing distiller's dry grain and solubles comprising the steps of:

preparing a fermented mash having enhanced glycerol and succinic acid content,

distilling the fermented mash for producing ethanol and stillage,

clarifying the stillage produced from the distillation of the fermented mash,

passing the clarified stillage through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified stillage,

purifying the separated glycerol and succinic

acid, and

drying any stillage residue and thereby producing free flowing distiller's dry grain and solubles.

17. An apparatus for manufacturing glycerol comprising:

means for clarifying a liquid, fermented mash,

ion exclusion means for receiving clarified liquid and passing received liquid through a resin material for separating glycerol from other constituents of the clarified liquid, and

means for purifying the separated glycerol.

18. An apparatus for manufacturing glycerol comprising:

still means for receiving a fermented mash and for distilling the fermented mash and producing stillage,

clarification means for receiving stillage from said still means and for removing solids therefrom for clarifying the stillage,

ion exclusion means for receiving clarified stillage from said clarification means and for passing the clarified stillage through an ion exclusion material for separating glycerol from other constituents of the clarified stillage, and

means for purifying the separated glycerol.

19. An apparatus for manufacturing succinic acid comprising:

means for clarifying a liquid, fermented mash,

ion exclusion means for receiving clarified liquid and passing received liquid through a resin material for

separating succinic acid from other constituents of the clarified liquid, and

means for purifying the separated succinic acid.

20. An apparatus for manufacturing succinic acid comprising:

still means for receiving a fermented mash and for distilling the fermented mash and producing stillage,

clarification means for receiving stillage from said still means and for removing solids therefrom for clarifying the stillage,

ion exclusion means for receiving clarified stillage from said clarification means and for passing the clarified stillage through an ion exclusion material for separating succinic acid from other constituents of the clarified stillage, and

means for purifying the separated succinic acid.

21. An apparatus for manufacturing glycerol and succinic acid comprising:

means for clarifying a liquid, fermented mash,

ion exclusion means for receiving clarified liquid and passing received liquid through a resin material for separating glycerol and succinic acid from other constituents of the clarified liquid, and

means for purifying the separated glycerol and succinic acid.

22. An apparatus for manufacturing glycerol and succinic acid comprising:

still means for receiving a fermented mash and for

distilling the fermented mash and producing stillage,

clarification means for receiving stillage from said still means and for removing solids therefrom for clarifying the stillage,

ion exclusion means for receiving clarified stillage from said clarification means and for passing the clarified stillage through an ion exclusion material for separating glycerol and succinic acid from other constituents of the clarified stillage, and

means for purifying the separated glycerol and succinic acid.

23. An apparatus for manufacturing distiller's dry grain and solubles comprising:

means for clarifying a liquid, fermented mash,

ion exclusion means for receiving clarified liquid and passing received liquid through a resin material for separating glycerol from other constituents of the clarified liquid, and

means for drying the solid residue of the other constituents of the clarified liquid.

24. An apparatus for manufacturing distiller's dry grain and solubles comprising:

still means for receiving a fermented mash and for distilling the fermented mash and producing stillage,

clarification means for receiving stillage from said still means and for removing solids therefrom for clarifying the stillage,

ion exclusion means for receiving clarified

stillage from said clarification means and for passing the clarified stillage through an ion exclusion material for separating glycerol from other constituents of the clarified stillage, and

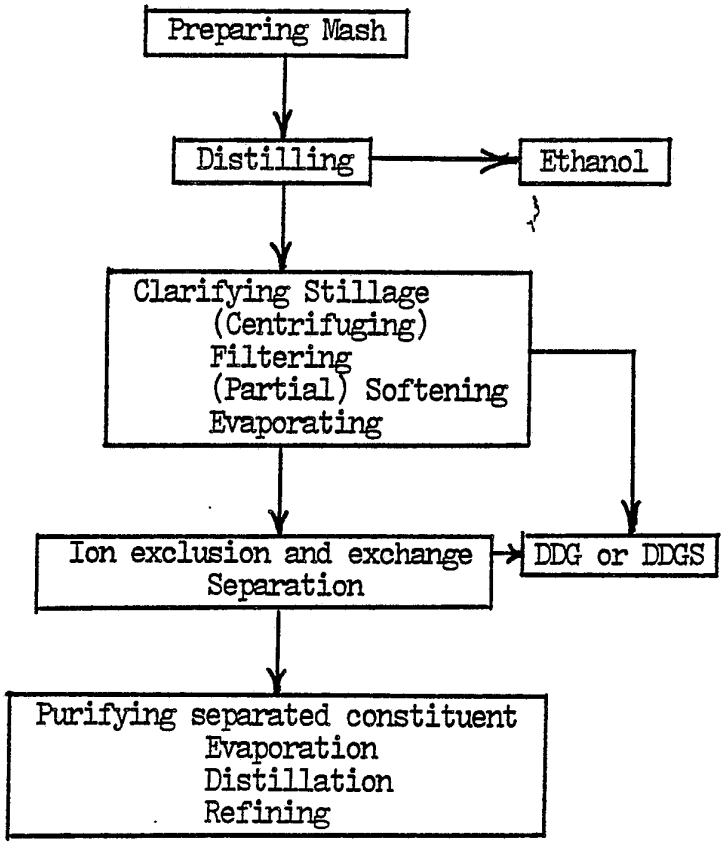
means for drying the solid residue of the other constituents of the clarified stillage.

25. Apparatus according to one of Claims 17 or 18 or 19 or 20 or 21 or 22 or 23 or 24 wherein said means for clarifying comprises centrifugal separating means for centrifugally separating solids from the liquid constituents of the stillage.

26. Apparatus according to one of Claims 17 or 18 or 19 or 20 or 21 or 2 or 23 or 24 wherein said means for clarifying comprises microporous filter means for filtering solids from the liquid constituents.

27. Apparatus according to one of Claims 17 or 18 or 19 or 20 or 21 or 22 wherein said means for purifying comprises an evaporator for removing water from the constituent to be purified.

28. Apparatus according to one of Claims 17 or 18 or 19 or 20 or 21 or 22 wherein said means for purifying comprises a still for distilling the constituent to be purified.


Preparing Mash
Distilling
Ethanol
Clarifying Stillage
(Centrifuging)
Filtering
(Partial) Softening
Evaporating
Ion exclusion and exchange
Separation
DDG or DDGS
Purifying separated constituent
Evaporation
Distillation
Refining

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/04529

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): C12P 7/44 7/20 7/06 C12F 3/10

U.S.C1. 435/145,159, 161, 302

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
US	435/145,159,161,163,302,813 422/255

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
O,X Y	B. Burris, "Recovery of Chemicals Such as Glycerol, Dextrose, and Amino Acids from Dilute Broths", presented to International Conference on Fuel, Alcohols and Chemicals from Biomass, Nov. 11-12, 1986, Miami Beach,Florida.	1,18-22 6-15,23-28
O,X Y	B. Burris, "Recovery of Glycerol from Stillbottoms," presented to International Conference on (Fuel) Alcohols and Chemicals from Biomass, Dec. 7-9, 1987, Montego Bay, Jamaica.	1,18-22 6-15,23-28
Y	US, A, 2,772,206 (Frankel et al.) 27 November 1956, see entire document.	1,8-15
Y	US, A, 2,772,207 (Frankel et al.) 27 November 1956, see entire document.	1,8-15

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21 MARCH 1989	20 APR 1989
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Timothy M. McMahon

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 48-58,191 (Idemitsu Ind. Co. Ltd.) 15 August 1973, see entire document.	2,3,8-15
A	US, A, 4,287,305 (Compere et al) 01 September 1981, see entire document.	

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers . because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

3. ☐ Claim numbers_____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.