

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Process for Producing Glutamic Acid from Fermentation Broth

WE, AJINOMOTO CO., INC., a Japanese Company, of 7, 1-chome, Takara-cho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing glutamic acid from microorganism-cultured broth containing glutamic acid (said broth being hereinafter referred to as "fermentation broth").

It is an object of the present invention to produce highly pure glutamic acid crystals in a good yield by a simple process involving easy operations on an industrial scale.

Fermentation broth usually contains, besides glutamic acid, other amino acids, organic acids, bacterial cells, remnant carbohydrates, ammonium ions and small amounts of inorganic ions. Therefore, when the pH of such a fermentation broth has been adjusted to the isoelectric point of glutamic acid, approximately 1.5 to 3.0 g. of glutamic acid per 100 g. of the mother liquor remain dissolved in the broth and so decrease the yield of glutamic acid crystals, obtained. The solubility of L-glutamic acid in pure water is 0.864 g./100 g. water at 25° C. On the other hand, when the fermentation broth is concentrated to increase the recovery of glutamic acid, the crystal habit of the glutamic acid being crystallised deteriorates remarkably and the purity of the crystals separated from the mother liquor is low.

To evade such defects, some methods have hitherto been employed which include such preliminary treatments before crystallising glutamic acid as (1) adding mineral acid to fermentation broth from which no glutamic acid (or only a part of the glutamic

acid) has been separated, heating the broth to decompose the impurities and removing the resulting solid matter or (2) contacting fermentation broth with various ion-exchange resins to increase the purity of the glutamic acid. The mineral acid treatment is, however, unfavourable if the glutamic acid is required in large amounts, due to the necessity of a reaction vessel with a high resistance to corrosion for the heating step and also because contamination of glutamic acid crystals with colouring matter results from the acid treatment. The ion-exchange treatment also is not advantageous as complicated processes are required and only a low concentration glutamic acid solution is obtained.

We have now found that coexisting zinc ions have no undesirable influences upon the crystallisation of glutamic acid as zinc glutamate is substantially insoluble in water in a certain pH range and that a high ratio of glutamic acid to impurities in the fermentation broth remarkably improves the crystal habit of glutamic acid crystals.

The present invention provides a process for producing glutamic acid from a microorganism-cultured broth, which comprises the steps of (i) treating a microorganism-cultured broth containing glutamic acid with a solution containing zinc glutamate and mineral acid to adjust the pH to between 2.5 and 4.0 and crystallising and separating out the glutamic acid, and (ii) adjusting the pH of the mother liquor, from which glutamic acid crystals have been separated, to a pH between 5.5 and 7.5 and crystallising and separating out the zinc glutamate.

In the first step of the present invention, fermentation broth is treated with a solution containing mineral acid and zinc glutamate to adjust the pH of the solution to between

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2.5 and 4.0. In this step, the glutamic acid derived from the zinc glutamate is useful for increasing the ratio of glutamic acid to impurities in the fermentation broth and the mineral acid serves to adjust the pH of said fermentation broth (its pH usually being 7-8) to the isoelectric point of glutamic acid. Zinc ions do not have any unfavourable influences upon glutamic acid crystallisation and their coexistence is not harmful. The zinc glutamate used in this first step may be prepared separately, but it is the most preferable to use the zinc glutamate which is obtained in a previous step (ii) of the process. Zinc glutamate crystals and mineral acid are preferably mixed well and dissolved to form a solution before they are added to the fermentation broth. This is to avoid partial crystallisation of glutamic acid at the decomposition pH of zinc glutamate, involving contamination of the crystallised glutamic acid by the zinc glutamate crystals, and deterioration of crystal habit of the glutamic acid crystals.

In the second step of the process, zinc glutamate is recovered from the mother liquor from which glutamic acid has been crystallised and separated in the first step and, for this purpose, the mother liquor is adjusted to a pH between 5.5 and 7.5. The solubility of zinc glutamate is, as described hereinafter, least in this pH range and the glutamic acid in a fermentation broth can now be recovered, according to the invention, to such a degree of recovery which could not easily be attained by any known methods. Alkali metal hydroxide, ammonia water and gaseous or liquid ammonia is preferably used for pH adjustment. When the amount of zinc ions (derived from the zinc glutamate added in the first step) in the mother liquor corresponds to that of glutamate in the mother liquor, no further pH adjustment is necessary. When insufficient zinc ions are present, additional zinc ions must be supplied, for example as a solution, or as crystals of a water-soluble zinc salt of an inorganic or organic acid or as a double zinc salt with such inorganic acid salts as ammonium or sodium sulphate. The pH adjustment and supply of zinc ions can be carried out in any order. Zinc glutamate is difficultly soluble in water in certain pH ranges and we have found that the variation in the amount of the glutamate remaining dissolved in the mother liquor compared with the pH in the second step of the present invention (using fermentation broth as starting material) is as follows:

TABLE

pH value	4.5	5.0	5.5	6.7	7.5	8.0
glutamic acid concentration	3.3	1.3	0.5	0.3	0.6	5.0

65 (g./dl.)

It is apparent from the Table, that zinc glutamate is substantially insoluble at pH 5.5-7.5, that almost all of it is recovered as crystals and a high recovery yield can be obtained in that pH range. The zinc glutamate recovered is used in the first step of a subsequent operation and, therefore, the glutamic acid originally present in fermentation broth can be recovered easily and substantially completely by the combination of the two steps.

As the crystals formed in both steps have a superior crystal habit, they can be separated by decanting or centrifuging, utilising the difference in specific gravity between bacterial cells and the crystals. By such a separation a highly pure glutamic acid can be produced in a high yield from fermentation broth according to the present invention, without previously removing bacterial cells which are difficult-to-filter. Moreover, the process of the present invention does not involve any troublesome steps, such as concentration and decomposition, and the crystallised glutamic acid is, at the most, only slightly coloured and highly pure. The following methods for example may be employed for the recovery or removal of the zinc ions remaining in the mother liquor from which zinc glutamate crystals have been separated in the second step: (1) adsorption and elution of zinc ions by an ion-exchange resin method, (2) crystallisation and separation of zinc ions in such forms of double salt as ammonium sulphate—zinc sulphate or sodium sulphate—zinc sulphate, (3) precipitation and separation of zinc ions as zinc hydroxide by adding alkali metal hydroxide or alkaline-earth metal hydroxide.

The following Examples illustrate the invention:

Example 1

24.5 kg. (wet) of zinc glutamate crystals obtained in the second step of a previous operation were mixed with 78.0 kg. of 30% sulphuric acid and the resulting solution was added to 514 litres (glutamic acid content: 34.2 kg.) of fermentation broth to adjust the pH to 3.2. The fermentation broth had been obtained by the process as described in British Patent Specification No. 873,448. The crystallised glutamic acid was separated from the mother liquor, still containing bacterial cells, by centrifuging, washed with an equal weight of water and dried to obtain 34.4 kg. of dried glutamic acid crystals of 97% purity. The glutamic acid mother liquor containing zinc ions was treated with 105 litres (zinc content: 6.35 kg.) of aqueous zinc sulphate solution and then adjusted to pH 6.4 with 45% aqueous sodium hydroxide. The crystallised zinc glutamate crystals were good and were separated by utilising the difference in

density between the crystals and the bacterial cells to obtain 24.5 kg. (wet) crystals, which was used in the glutamic acid crystallisation step (first step) of the next operation.

Example 2

The same procedure as in Example 1 was carried out with the exception that 39.8 litres of concentrated hydrochloric acid were used instead of 78.0 kg. of sulphuric acid to obtain 34.4 kg. of L-glutamic acid crystals of 97% purity.

Example 3

The pH of 34.8 kl. of fermentation broth which had been obtained by the process described in British Patent Specification No. 924,035 and contained 1.75 t. of glutamic acid was adjusted to 3.1 by adding a mixed solution of 1.99 t. of zinc glutamate (wet) obtained in the second step of a previous operation, 7.14 kl. of 20.4% sulphuric acid and 0.82 kl. of a mother liquor containing 0.4 t. of glutamic acid from which monosodium glutamate had been crystallised. Good granular glutamic acid was obtained in a yield of 1.98 t. (dried weight). Purity: 95%.

To the mother liquor from which the glutamic acid was recovered, there were added 580 litres of concentrated aqueous ammonia and 1.5 t. of zinc sulphate to adjust the pH to 6.5. Good zinc glutamate

crystals were obtained in a yield of 1.99 t. (wet) and were used in the first step of the following operation.

WHAT WE CLAIM IS:—

1. A process for producing glutamic acid from a microorganic-cultured broth, which comprises the steps of (i) treating a micro-organism-cultured broth containing glutamic acid with a solution containing zinc glutamate and mineral acid to adjust the pH to between 2.5 and 4.0, and crystallising and separating out the glutamic acid, and (ii) adjusting the pH of the mother liquor, from which glutamic acid crystals have been separated, to a pH between 5.5 and 7.5 and crystallising and separating out the zinc glutamate.

2. A process as claimed in claim 1, wherein the zinc glutamate added in step (i) is that obtained from a previous step (ii).

3. A process as claimed in claim 1, substantially as described with reference to any of the Examples.

4. Glutamic acid when produced by the process claimed in any of the preceding claims.

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