

[DESCRIPTION]

[TITLE OF INVENTION]

METHOD OF PRODUCING HIGH QUALITY ϵ -CAPROLACTAM

5

[Technical Field]

[0001]

The present invention relates to a method of producing ϵ -caprolactam, and in particular, relates to a method of obtaining high quality ϵ -caprolactam with a good yield
10 from a crude ϵ -caprolactam containing impurities which is obtained by Beckmann rearrangement of cyclohexanone oxime.

Priority is claimed on Japanese Patent Application No. 2011-287373, filed December 28, 2011, the content of which is incorporated herein by reference.

15 [Background Art]

[0002]

ϵ -caprolactam is an important compound as a production intermediate of nylon-6, and various production methods thereof have been known. For example, it is produced in large quantities by Beckmann rearrangement of cyclohexanone oxime in the
20 presence of an acidic medium such as fuming sulfuric acid. However, this method has a problem of producing a large amount of ammonium sulfate as a by-product with a small added value.

[0003]

As a method of improving this situation, a method of producing ϵ -caprolactam
25 by a vapor phase Beckmann rearrangement reaction using a solid catalyst has been

known. As a solid catalyst used in the vapor phase Beckmann rearrangement reaction, boric acid-based catalysts, silica-alumina catalysts, solid phosphoric acid catalysts, composite metal oxide catalysts, zeolite-based catalysts or the like have been proposed. However, since the ϵ -caprolactam obtained by this method contains a variety of
5 impurities, it is usually purified by various methods such as crystallization, extraction, distillation, and hydrogenation.

[0004]

In Patent Document 1, a method has been disclosed in which ϵ -caprolactam is crystallized by pouring and mixing together a molten crude ϵ -caprolactam and a cooled
10 organic solvent, and the resultant is subjected to solid-liquid separation to produce a purified ϵ -caprolactam. In addition, as a method of increasing the recovery rate of ϵ -caprolactam, the effect of further conducting several times of crystallization from the mother liquid after crystallization has also been mentioned.

15 [Citation List]

[Patent Document]

[0005]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication
No. 2002-3472

20 [Summary of Invention]

[Technical Problem]

[0006]

As a method of crystallizing ϵ -caprolactam by pouring and mixing together a
25 molten crude ϵ -caprolactam and a cooled organic solvent and further crystallizing the

mother liquid after crystallization which is generated at the time of solid-liquid separation of the resultant, the so-called "evaporation-crystallization" has been known in which crystals of the desired product dissolved in the mother liquid are precipitated by evaporating a solvent from the mother liquid for concentration and increasing the supersaturation degree of the desired product. In the evaporation-crystallization, while it is possible to cool the mother liquid by vaporization heat and to thereby suppress the energy for cooling, the deposition of crystals (that is, scaling) onto the heat transfer surface, the inner wall surface of the crystallization tank, and internals such as the baffle and stirring blade that are disposed inside the crystallization tank is likely to occur. For this reason, in the case of further carrying out evaporation-crystallization from the mother liquid after crystallization to recover the crystals, not only the crystals that should have been obtained causes scaling and the recovery rate is unlikely to increase as a result, but also a continuous and stable operation is difficult for a prolonged period of time.

Therefore, there has been a demand for a method of suppressing the scaling in evaporation-crystallization.

[0007]

The present invention has been made in view of the above circumstances, with an object of providing a method of producing ϵ -caprolactam which is capable of obtaining high quality ϵ -caprolactam with a good yield by evaporation-crystallization from a crude ϵ -caprolactam containing impurities which is obtained by Beckmann rearrangement of cyclohexanone oxime.

[Solution to Problem]

[0008]

In order to solve the above problems, the present invention provides a method of

producing ϵ -caprolactam including:

a purification step in which a crude ϵ -caprolactam obtained by Beckmann rearrangement of cyclohexanone oxime is mixed with an organic solvent to obtain a mixed solution, ϵ -caprolactam is crystallized from the solution, and the aforementioned ϵ -caprolactam and a dropwise-crystallization-recovered-mother liquid are obtained by a solid-liquid separation; and

a recovering step in which an evaporation-crystallization-mother liquid containing the dropwise-crystallization-recovered-mother liquid is subjected to an evaporation-crystallization, followed by a solid-liquid separation to obtain a recovered ϵ -caprolactam and an evaporation-crystallization-recovered-mother liquid; wherein

the method includes

preparing a mixed liquid formed by mixing the dropwise-crystallization-recovered-mother liquid with at least part of the evaporation-crystallization-recovered-mother liquid, at least part of the evaporation-crystallization-mother liquid which is extracted from a tank for conducting evaporation-crystallization, or both of them, prior to the recovering step; and supplying the mixed liquid to the tank and mixing with the evaporation-crystallization-mother liquid retained in the tank.

[0009]

According to this method, since it should be by mixing and diluting the dropwise-crystallization-recovered-mother liquid with the evaporation-crystallization-recovered-mother liquid and/or evaporation-crystallization-mother liquid in advance, it becomes possible to suppress the rapid precipitation of crystals that causes scaling when the dropwise-crystallization-recovered-mother liquid is introduced into the tank for conducting evaporation-crystallization. Therefore, the method of producing ϵ -caprolactam is capable of increasing the recovery rate of ϵ -caprolactam and improving

the productivity by continuous operation.

[0010]

In the present invention, it is desirable to supply the mixed liquid to the liquid phase in the tank for conducting evaporation-crystallization.

5 [0011]

According to this method, it is configured such that crystallization is carried out after mixing the mixed liquid introduced into the tank for conducting evaporation-crystallization with the evaporation-crystallization-mother liquid retained in the tank. Therefore, it becomes possible to easily control the crystallization and to prevent scaling.

10 [0012]

In the present invention, in the recovering step, it is desirable to supply the mixed liquid toward a circumferential direction of the tank.

[0013]

According to this method, a stirring blade for stirring the inside of the tank is not required, and it is possible to eliminate the scaling to the stirring blade.

[0014]

In the present invention, it is desirable to heat at least part of an internal wall of the tank for conducting the evaporation-crystallization to a temperature higher than an operation temperature of the evaporation-crystallization.

20 [0015]

In the present invention, it is desirable that a solvent evaporation load be 100 kg/m²/h to 2,000 kg/m²/h per area of a liquid level in the evaporation-crystallization.

[0016]

In the present invention, it is desirable that an operation-supersaturation degree be 0.1 kg/m³ to 20 kg/m³ in the evaporation-crystallization.

25

[0017]

In the present invention, it is desirable that an operation-pressure be 10 torr to 500 torr in the evaporation-crystallization.

[0018]

5 In the present invention, it is desirable that a crystallization temperature be 0°C to 60°C in the evaporation-crystallization.

[0019]

In the present invention, in the recovering step, it is desirable that part of the evaporation-crystallization-mother liquid be taken out of the tank and the part of the
10 evaporation-crystallization-mother liquid be resupplied to the tank to thereby recycle the evaporation-crystallization-mother liquid outside the tank; and that

an amount of the evaporation-crystallization-mother liquid taken out of the tank be 10 to 10,000 times the amount of the solvent evaporated from the evaporation-crystallization-mother liquid in the evaporation-crystallization.

15 [0020]

In the present invention, it is desirable that the crude ϵ -caprolactam be obtained by vapor phase Beckmann rearrangement using a solid catalyst and cyclohexanone oxime as a raw material.

[0021]

20 In the present invention, it is desirable that in the purification step, ϵ -caprolactam be crystallized by supplying and mixing together the crude ϵ -caprolactam in a liquid state with a cooled aliphatic hydrocarbon solvent or a mixed solvent containing a cooled aliphatic hydrocarbon and a small amount of organic solvent having a polarity higher than that of the aliphatic hydrocarbon, into the tank at a temperature lower than
25 that of the crude ϵ -caprolactam in a liquid state.

[0022]

In the present invention, it is desirable that the crude ϵ -caprolactam in a liquid state be a molten crude ϵ -caprolactam, a mixed solution of a molten crude ϵ -caprolactam and an aliphatic hydrocarbon solvent, or a mixed solution of molten-crude ϵ -caprolactam and a mixed solvent containing an aliphatic hydrocarbon and a small amount of organic solvent having a polarity higher than that of the aliphatic hydrocarbon.

[0023]

In other words, the present invention relates to the aspects described below.

[1] A method of producing high quality ϵ -caprolactam including:

a purification step in which a crude ϵ -caprolactam obtained by Beckmann rearrangement of cyclohexanone oxime is mixed with an organic solvent to obtain a mixed solution, ϵ -caprolactam is crystallized from the mixed solution, and a high quality ϵ -caprolactam and a dropwise-crystallization-recovered-mother liquid are obtained by a solid-liquid separation; and

a recovering step in which an evaporation-crystallization-mother liquid containing the dropwise-crystallization-recovered-mother liquid is subjected to evaporation to crystallize ϵ -caprolactam, followed by a solid-liquid separation to obtain a recovered ϵ -caprolactam and an evaporation-crystallization-recovered-mother liquid; wherein,

the method includes

preparing a mixed liquid formed by mixing the dropwise-crystallization-recovered-mother liquid with at least part of the evaporation-crystallization-recovered-mother liquid, at least part of the evaporation-crystallization-mother liquid which is extracted from a tank for conducting evaporation-crystallization, or both of at least part of the evaporation-crystallization-recovered-mother liquid and at least part of the

evaporation-crystallization-mother liquid, prior to the recovering step; and

supplying the mixed liquid to the tank and mixing with the evaporation-crystallization-mother liquid retained in the tank.

[2] The method of producing high quality ϵ -caprolactam according to [1], further

5 including adding the recovered ϵ -caprolactam to the crude ϵ -caprolactam.

[3] The method of producing high quality ϵ -caprolactam according to [1] or [2], wherein

a vapor phase and a liquid phase are provided in the tank for conducting the evaporation-crystallization, and the mixed liquid is supplied to the liquid phase.

[4] The method of producing high quality ϵ -caprolactam according to [3], wherein

10 supplying the mixed liquid to the tank in the recovering step includes supplying the mixed liquid toward a circumferential direction of the tank.

[5] The method of producing high quality ϵ -caprolactam according to any one of [1] to

[4], wherein at least part of an internal wall of the tank for conducting the evaporation-crystallization is heated to a temperature 20 to 60°C higher than an operation temperature

15 of the evaporation-crystallization.

[6] The method of producing high quality ϵ -caprolactam according to any one of [1] to

[5], wherein a solvent evaporation load is 100 kg/m²/h to 2,000 kg/m²/h per area of a liquid level in the evaporation-crystallization.

[7] The method of producing high quality ϵ -caprolactam according to any one of [1] to

20 [6], wherein an operation-supersaturation degree is 0.1 kg/m³ to 20 kg/m³ in the evaporation-crystallization.

[8] The method of producing high quality ϵ -caprolactam according to any one of [1] to

[7], wherein an operation-pressure is 10 torr to 500 torr in the evaporation-crystallization.

[9] The method of producing high quality ϵ -caprolactam according to any one of [1] to

25 [8], wherein a crystallization temperature is 0°C to 60°C in the evaporation-

crystallization.

[10] The method of producing high quality ϵ -caprolactam according to any one of [1] to [9], wherein

the recovering step further includes taking out part of the evaporation-
5 crystallization-mother liquid in the tank and resupplying the part of the evaporation-
crystallization-mother liquid to the tank to thereby recycle the evaporation-
crystallization-mother liquid outside the tank; and

an amount of the evaporation-crystallization-mother liquid taken out of the tank
is 10 to 10,000 times the amount of the solvent evaporated from the evaporation-
10 crystallization-mother liquid in the evaporation-crystallization.

[11] The method of producing high quality ϵ -caprolactam according to any one of [1] to [10], wherein

the crude ϵ -caprolactam is obtained by vapor phase Beckmann rearrangement
using a solid catalyst and cyclohexanone oxime as a raw material.

15 [12] The method of producing high quality ϵ -caprolactam according to any one of [1] to [11], wherein,

in the purification step, ϵ -caprolactam is crystallized by supplying and mixing
together the crude ϵ -caprolactam in a liquid state with a cooled aliphatic hydrocarbon or a
mixed solvent containing a cooled aliphatic hydrocarbon and an organic solvent having a
20 polarity higher than that of the aliphatic hydrocarbon, into the tank at a temperature 40 to
80 °C lower than the temperature of a crystallization temperature.

[13] The method of producing high quality ϵ -caprolactam according to any one of [1] to [12], wherein

the crude ϵ -caprolactam in a liquid state is a molten crude ϵ -caprolactam, a
25 mixed solution of a molten crude ϵ -caprolactam and an aliphatic hydrocarbon, or a mixed

solution of molten-crude ϵ -caprolactam and a mixed solvent containing an aliphatic hydrocarbon and an organic solvent having a polarity higher than that of the aliphatic hydrocarbon.

5 [Advantageous Effects of Invention]

[0024]

According to the present invention, it is possible to suppress scaling in the evaporation-crystallization, and it becomes possible to stably obtain a high quality ϵ -caprolactam, with a good yield, from a crude ϵ -caprolactam containing impurities which
10 is obtained by Beckmann rearrangement of cyclohexanone oxime.

[Brief Description of Drawings]

[0025]

FIG. 1 is a flow diagram showing a case of carrying out a production method
15 according to an embodiment of the present invention in a continuous process.

FIG. 2 is a flow diagram of a step including a solid-liquid separator and crystallization tank according to an embodiment of the present invention.

FIG. 3A is a part of a cross-sectional view of a crystallization tank according to an embodiment of the present invention in the horizontal direction.

20 FIG. 3B is a part of a cross-sectional view of a crystallization tank according to another embodiment of the present invention in the horizontal direction.

[Description of Embodiments]

[0026]

25 A method of producing high quality ϵ -caprolactam according to an embodiment

of the present invention includes:

a purification step in which a crude ϵ -caprolactam obtained by Beckmann rearrangement of cyclohexanone oxime is mixed with an organic solvent to obtain a mixed solution, ϵ -caprolactam is crystallized from the mixed solution, and a high quality ϵ -caprolactam and a dropwise -crystallization-recovered-mother liquid are obtained by a solid-liquid separation; and

a recovering step in which an evaporation-crystallization-mother liquid containing the dropwise-crystallization-recovered-mother liquid is subjected to evaporation to crystallize ϵ -caprolactam, followed by a solid-liquid separation to obtain a recovered ϵ -caprolactam and an evaporation-crystallization-recovered-mother liquid; wherein

the method further includes

preparing a mixed liquid formed by mixing the dropwise-crystallization-recovered-mother liquid with at least part of the evaporation-crystallization-recovered-mother liquid, at least part of the evaporation-crystallization-mother liquid which is extracted from a tank for conducting evaporation-crystallization, or both of at least part of the evaporation-crystallization-recovered-mother liquid and at least part of the evaporation-crystallization-mother liquid, prior to the recovering step; and

supplying the mixed liquid to the tank and mixing with the evaporation-crystallization-mother liquid retained in the tank.

[0027]

It should be noted that in the present description, the term “dropwise-crystallization-recovered-mother liquid” refers to a liquid phase fraction generated as a result of the crystallization of ϵ -caprolactam and the solid-liquid separation in the purification step.

The term "evaporation-crystallization-recovered-mother liquid" refers to a liquid phase fraction generated as a result of conducting the evaporation-crystallization and solid-liquid separation in the recovering step. In the description that follows, the "evaporation-crystallization-recovered-mother liquid" is sometimes referred to as a
5 "recycle liquid".

The term "high quality ϵ -caprolactam" refers to a ϵ -caprolactam in which the content of cyclohexanone oxime and basic compounds such as MTHI and OHP is equal to or less than a certain concentration. More specifically, it means an ϵ -caprolactam in which the concentration of cyclohexanone oxime contained in the ϵ -caprolactam is, with
10 respect to the ϵ -caprolactam, less than 10 ppm; the concentration of 1,2,3,4,6,7,8,9-octahydrophenazine is less than 10 ppm; and the concentration of 3-N-methyl-4,5,6,7-tetrahydrobenzimidazole is less than 25 ppm.

The term "evaporation-crystallization-mother liquid" is a liquid which is subjected to the evaporation-crystallization in the recovering step as a whole, and refers
15 to a liquid retained in a tank for conducting evaporation-crystallization (a crystallization tank 7 described later). In the evaporation-crystallization-mother liquid, the dropwise-crystallization-recovered-mother liquid generated in the purification step which is a step previous to the recovering step, and the evaporation-crystallization-recovered-mother liquid generated in the recovering step to be recycled are contained.

20 [0028]

In addition, in the present description, the term "crude ϵ -caprolactam" refers to a mixture including a high quality ϵ -caprolactam which is a target product obtained in the production process of ϵ -caprolactam and impurities (i.e., reaction solvents, unreacted raw materials, side reaction products, and the like). In the following description, as the
25 crude ϵ -caprolactam (hereinafter, sometimes referred to as "crude lactam"), a reaction

mixture obtained by the vapor phase Beckmann rearrangement of cyclohexanone oxime using a zeolite-based catalyst such as silica-alumina, metallosilicate, and silicalite (solid catalyst) is illustrated as an example, but the crude lactam to which the present invention can be applied is not limited thereto.

5 [0029]

FIG. 1 is a flow diagram showing an example of a case of carrying out a production method according to an embodiment of the present invention in a continuous process. The flow diagram described in FIG. 1 includes a crystallization tank 1, a solid-liquid separator 2, a crystallization tank 3, a solid-liquid separator 4, a crystal washing
10 machine 5, a dissolution tank 6, a crystallization tank 7, a solid-liquid separator 8, and a cooling facility 9.

Descriptions will be given below in order.

[0030]

(Purification step)

15 First, in the dissolution tank 6, a molten crude lactam is mixed with an organic solvent to prepare a mixed solution of molten crude lactam and organic solvent.

In the crude lactam, although it is not always the case depending on the production process, in addition to methanol used as the solvent and unreacted cyclohexanone oxime, a variety of by-products such as cyclohexanone, cyclohexenone,
20 n-hexanitrile, 5-hexenitrile, methyl lactam, 1,3,4,5-tetrahydroazepin-2-one, 1,5,6,7-tetrahydroazepin-2-one, 1,2,3,4,6,7,8,9-octahydrophenazine (hereinafter, sometimes referred to as OHP) and amines including 3-N-methyl-4,5,6,7-tetrahydrobenzimidazole (hereinafter, sometimes referred to as MTHI) are contained in some cases.

[0031]

25 For example, in the crude lactam obtained by the vapor phase Beckmann

rearrangement process, typically, with respect to ϵ -caprolactam, the concentration of cyclohexanone oxime is 10 ppm or more; the concentration of 1,2,3,4,6,7,8,9-octahydrophenazine is 10 ppm or more; the concentration of 3-N-methyl-4,5,6,7-tetrahydrobenzimidazole is 25 ppm or more; and the concentration of 1,3,4,5-tetrahydroazepin-2-one, 1,5,6,7-tetrahydroazepin-2-one, and the structural isomers thereof (hereinafter, referred to as caprenolactams) is 25 ppm or more in some cases, but among these impurities except for caprolactams, it is possible to remove and purify all together in a single pass by applying the crystallization method of the present invention.

[0032]

It should be noted that the crude lactam obtained by the vapor phase Beckmann rearrangement reaction using a zeolite-based catalyst contains solvents such as methanol, various by-products having a low boiling point and various by-products having a high boiling point. Accordingly, for the purpose of increasing the crystallization efficiency, it is preferable to carry out a preliminary distillation or the like for removing some or all of these solvents and by-products as needed, prior to dissolution in the dissolution tank 6.

[0033]

As an organic solvent used in the dissolution tank 6, in order to increase the recovery rate by causing a large amount of lactam not to remain in the solution after crystallization, aliphatic hydrocarbons of low polarity are recommended.

[0034]

Examples of the aliphatic hydrocarbons include linear aliphatic hydrocarbons of 6 to 12 carbon atoms, branched aliphatic hydrocarbons of 6 to 12 carbon atoms, and alicyclic hydrocarbons of 6 to 12 carbon atoms. Specific examples thereof include linear aliphatic hydrocarbons such as n-hexane, n-heptane, n-octane, n-nonane and n-decane; branched aliphatic hydrocarbons such as methyl hexane, isooctane and

neohexane; alicyclic hydrocarbons such as methylcyclopentane, cyclohexane and methylcyclohexane; and a mixture of aliphatic hydrocarbons such as petroleum benzene (mixture of hexane, isohexane or the like prescribed in JIS K 8594).

As the aliphatic hydrocarbons, aliphatic hydrocarbons having a boiling point which is equal to or more than the melting point of ϵ -caprolactam (69°C) and is also less than the boiling point of ϵ -caprolactam (267°C). Specific examples thereof include n-heptane, isooctane, and petroleum benzene.

Further, as the aliphatic hydrocarbons, aliphatic hydrocarbons having a boiling point which is equal to or more than the melting point of ϵ -caprolactam and is also equal to or less than about 150°C are more preferred, and specific examples thereof include cyclohexane.

[0035]

These may be used alone, or in combination of two or more types of aliphatic hydrocarbons, or may be used as a mixed solvent with an organic solvent having a higher polarity which can be mixed with them uniformly. In other words, as the mixed solvent, as long as the impurities can be removed which is the objective of the present invention, a mixed solvent prepared by mixing, with the aliphatic hydrocarbons described above, aromatic hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as trichlene; ethers such as propyl ether and isopropyl ether; esters such as ethyl acetate and isopropyl acetate; and alcohols such as ethanol and isopropanol and having a boiling point which is equal to or more than the melting point of ϵ -caprolactam and is also less than the boiling point of ϵ -caprolactam, can be used; and preferably, a mixed solvent having a boiling point which is equal to or more than the melting point of ϵ -caprolactam and is also equal to or less than about 150°C can be used.

[0036]

Among these solvents, a combination of solvents having a low polarity with similar boiling points is recommended. In this case, since there is little change in the solubility of ϵ -caprolactam and little effect on the crystallization efficiency even when there is a change in the solvent composition in a continuous operation, the control of solvent concentration becomes easy. As combinations of such solvents, a combination of linear hydrocarbons and alicyclic hydrocarbons is preferred, and in particular, a combination of *n*-heptane and cyclohexane is preferred.

[0037]

It should be noted that the crystallization at a later stage may be carried out by using only a molten crude lactam without mixing a molten crude lactam and an organic solvent in the dissolution tank 6 as described above. However, it is preferable to carry out the crystallization by using a solution obtained by mixing a molten crude lactam and an organic solvent in the dissolution tank 6 because lactam crystals with low oxime content can be obtained.

[0038]

The mixed solution prepared in the dissolution tank 6 is supplied to the crystallization tank 1. In the crystallization tank 1, crystallization is carried out by supplying, in parallel, the mixed solution prepared in the dissolution tank 6 as described above and an organic solvent cooled by the cooling facility 9 (hereinafter, sometimes referred to as "cold solvent").

[0039]

As the cold solvent, the same organic solvent as the organic solvent used for mixing with the crude lactam in the dissolution tank 6 as described above can be cooled and used suitably. It should be noted that the organic solvent used for mixing with the crude lactam and the cold solvent may be solvents of different types, unless the solvents

exhibit a high solubility of ϵ -caprolactam (that is, solvents of high polarity).

More specifically, for example, a crude ϵ -caprolactam in a liquid state which is prepared in the dissolution tank 6 (that is, a molten crude lactam, or a mixed solution of a melted crude lactam and an organic solvent; and specific examples thereof include a
5 molten crude lactam, a mixed solution of a molten crude lactam and an aliphatic hydrocarbon, and a mixed solution obtained by mixing a molten crude lactam with a mixed solvent of an aliphatic hydrocarbon and an organic solvent having higher polarity than the aliphatic hydrocarbon) and

a cooled aliphatic hydrocarbon solvent, or a mixed solvent obtained by mixing a
10 cooled aliphatic hydrocarbon and an organic solvent having higher polarity than the aliphatic hydrocarbon, are supplied together and mixed inside the tank at a temperature lower than that of the ϵ -caprolactam in a liquid state, thereby carrying out the crystallization.

In addition, it is also possible to recycle the liquid phase obtained in the
15 purification step after the solid-liquid separation, the liquid phase after the washing of crystals, and the recovered lactam obtained in the recovering step, to thereby supply to the dissolution tank 6.

[0040]

The amount and temperature of the cold solvent supplied to the crystallization
20 tank 1 is specified in accordance with the crystallization temperature which is determined in advance in order to achieve the intended crystal recovery rate. That is, for the cold solvent to be supplied, the capacity to remove heat is required, so that the amount of heat equivalent to the difference between the temperature of the crude lactam supplied to the crystallization tank 1 (molten crude lactam or a mixed solution of molten crude lactam
25 and an organic solvent) and the crystallization temperature, and the crystallization heat of

crystals to be deposited can be cancel out. Therefore, the amount and temperature of cold solvent is specified such that the sensible heat of the cold solvent cancels out these amounts of heat.

It should be noted that the phrase "low (lower) temperature" used herein describes that the solvent has a temperature lower than the crystallization temperature, preferably by 20°C to 100°C, and more preferably by 40°C to 80°C.

[0041]

The amount of the solvent to be used during crystallization is from about 1/2 times to about 5 times, and preferably from about 1 times to about 4 times, the mass of the crude lactam used for purification. Even if the solvent is used in an amount exceeding the above range, the crystallization effect that matches the amount used cannot be achieved, while the cost required for the solvent recovery increases. On the other hand, it may not be possible to recover the crystals of sufficient quality when the amount of solvent is less than the above range.

[0042]

The crystallization temperature is from about 10°C to less than the melting point of lactam (68°C), preferably from about 30°C to about 60°C, and more preferably from about 40°C to about 60°C. In order to achieve both the intended crystal recovery rate and the reduction in the necessary amount of heat removal (that is, reduction of operational energy of the steps), it is preferable to set the crystallization temperature close to the upper limit temperature that enables the setting of predetermined crystal recovery rate by taking into consideration the lactam solubility of the liquid phase at the crystallization temperature. Further, such crystallization temperature is preferred since impurities are easily separated.

[0043]

Furthermore, in order not to cause scaling on the outer wall of the crystallization tank, it is preferable to set the temperature of the outer wall of the crystallization tank to the same temperature as, or slightly higher than, the temperature of the crystallization tank so that the crystallization products do not re-dissolve excessively. Specifically, by
5 setting the outer wall temperature to a temperature which is a few degrees Celsius higher than the crystallization temperature, more specifically, a temperature which is higher than the crystallization temperature of lactam by about 5°C or less, and more preferably by about 1°C or less, it is possible to suppress the generation of scaling onto the tank wall. Alternatively, the outer wall of the crystallization tank may be configured as a heat
10 insulating structure.

[0044]

In the crystallization tank 1, the crude ϵ -caprolactam in a liquid state (molten crude lactam or a mixed solution of molten crude lactam with an organic solvent) is mixed together with the cold solvent in a continuous manner at a constant rate (combined
15 supplying and mixing) and held at a predetermined crystallization temperature while causing crystal deposition.

[0045]

In this case, even if the ratios of the crude lactam and solvent used in the crystallization are the same, a crystallization method is preferred in which part of the solvent to be used as the cold solvent is added to the crude lactam in advance to prepare a
20 diluted solution as described above, and then the solution is cooled in a range so that crystals are not deposited, while the residual cold solvent is poured together to carry out the crystallization treatment. As a result, as compared with a method that does not use a diluted solution in advance, the content of certain impurities remaining in the obtained
25 crystals, in particular, cyclohexane oxime can be reduced.

[0046]

In the crystallization tank 1, by securing the time required for crystallization (that is, by giving the aging time), it is possible to stabilize the concentration of a slurry in which the crystals deposited by crystallization are dispersed.

5 The time for such stabilization of slurry concentration is preferably at least 5 minutes.

[0047]

In the case of employing a step of carrying out crystallization by a continuous system in the crystallization tank 1, in order to extend the average residence time in the crystallization tank 1, it is necessary to increase the capacity of the crystallization tank 1. For this reason, an appropriate time is selected from the viewpoints of crystal quality and economy. Since between 5 minutes and 60 minutes is sufficient as the time required for the stabilization of the slurry concentration, it is preferable to control the time within such a range, and the time of 20 minutes to 40 minutes is more preferred.

15 [0048]

In the slurry containing the crystals of ϵ -caprolactam obtained in the crystallization tank 1, by using the solid-liquid separator 2 such as a liquid cyclone, it is also possible to separate the crystals contained in the slurry by sedimentation, separate part of the liquid phase containing fine crystals, and then the remainder of the liquid phase containing relatively large crystals is crystallized once again. More specifically, it is also possible to introduce the remainder of the liquid phase into the crystallization tank 3, and to supply a cold solvent once again to the remainder to cool the remainder, thereby crystallizing lactams.

In this case, it is possible to increase the yield (amount of deposition), as compared with the case where ϵ -caprolactam is recovered by being crystallized only in

the crystallization tank 1 without using the solid-liquid separator 2 and the crystallization tank 3.

[0049]

In this case, since the yield of crystallization in the crystallization tank 1 can be reduced, it is possible that impurities are hardly contained in the crystals obtained in the crystallization tank 1.

In addition, because the cold solvent is added once again in the crystallization tank 3, it is possible to reduce the impurity concentration of the solution to be the target of crystallization, and thus it is effective in improving the quality of the crystals of ϵ -caprolactam obtained in the crystallization tank 3.

[0050]

In the solid-liquid separator 2, the amount of organic solvent removed from within the slurry is not particularly limited, but is typically from 10% to 70% of the liquid phase, and the amount thereof is determined depending on the crystal quality.

The crystallization method in the crystallization tank 3 is the same as that in the crystallization tank 1, and, for example, the temperature of the crystallization tank may be held, and the cold solvent may be poured and mixed together. It should be noted that the crystallization in the crystallization tank 3 is carried out in a temperature range of about 30°C to 60°C, but the crystallization temperature is set to be lower than the temperature condition in the crystallization tank 1.

[0051]

The slurries obtained in the crystallization tank 1 and in the crystallization tank 3 are introduced into the solid-liquid separator 4. In the solid-liquid separator 4, by conducting solid-liquid separation, it is possible to separate the introduced slurries into a solid phase containing the ϵ -caprolactam crystals and a liquid phase containing impurities.

In this case, steps from the crystallization tank 1 up to the solid-liquid separator 4 are operated while holding the temperature so as not to lower the slurry temperature, but if necessary, it is possible to include a heating function or a cooling function.

[0052]

5 The solid-liquid separation can be carried out by using a filter used in a typical crystallization process, such as filtration under reduced pressure and pressure filtration, but in order to conduct filtration in a continuous manner, it is preferable to use a centrifugal filter, a continuous scraping-type centrifugal filter, a centrifugal decanter, or the like. In particular, in the continuous scraping-type centrifugal filter, centrifugal
10 decanter, and the like, crystals can be rinsed in a continuous manner, and it is possible to wash the liquid phase containing the impurities deposited onto the crystals and to further improve the crystal quality, which is therefore preferred.

[0053]

 The crystals of ϵ -caprolactam (solid phase) separated by the solid-liquid
15 separator 4 are supplied to, and washed by a crystal washing machine 5 that washes the crystals. As a result, the impurities adhered onto the crystal surface can be removed, and it is possible to obtain ϵ -caprolactam crystals of even higher purity (high quality ϵ -caprolactam), as compared with the ϵ -caprolactam crystals that are not washed.

Although the crystals of ϵ -caprolactam (solid phase) separated by the solid-liquid
20 separator 4 are preferably supplied to, and washed by, the crystal washing machine 5 for washing the crystals, the crystal washing machine 5 may be omitted as long as the ϵ -caprolactam crystals of satisfactory purity can be obtained by solid-liquid separation alone.

[0054]

25 The organic solvent used for washing is preferably a solvent having a low

solubility of ϵ -caprolactam, and the hydrocarbons of low polarity as described above can be used.

More specifically, it is preferable to use the same solvent as the solvent supplied to the dissolution tank and crystallization tanks.

5 [0055]

It should be noted that as an embodiment of the present invention, a case is described where the solid-liquid separator 4 and the crystal washing machine 5 are provided as separate apparatuses, although the same apparatus may have the functions of both the solid-liquid separator 4 and the crystal washing machine 5 (that is, a solid-liquid
10 separator may have a crystal washing unit).

[0056]

In addition, in order to obtain a ϵ -caprolactam of even higher purity (high quality ϵ -caprolactam), the solid-liquid separation by the solid-liquid separator 4 and the crystal washing by the crystal washing machine 5 may be repeated several times, and a
15 step of adding a crystal washing solvent between the cycles of solid-liquid separation and crystal washing, thereby conducting repulp washing of the crystals may be further added.

[0057]

Further, each step from the dissolution of crude lactam in the dissolution tank 6 to the washing of crystals in the crystal washing machine 5 may be carried out by a
20 continuous system, or may be carried out by a batch system (batch-wise), but is preferably carried out by a continuous system since the production efficiency can be enhanced.

[0058]

The liquid phase containing the organic solvent separated by the solid-liquid
25 separator 4, and the liquid phase containing the organic solvent discharged from the

crystal washing machine 5 may be partially used as an organic solvent for dissolving the crude lactam in the dissolution tank 6.

[0059]

(Recovering step)

5 Of the liquid phases discharged from the solid-liquid separator 2, solid liquid separator 4, and crystal washing machine 5, for the liquid phase that is not used in the dissolution tank 6, it is possible to increase the recovery yield of crystals easily by re-crystallizing the liquid phase and to thereby recover the crystals. It goes without saying that known methods other than crystallization, such as distillation, extraction, chemical
10 treatments, and activated carbon treatments, may be combined to recover crystals. By adopting a method in which the recovered crystals are recycled to the purification step described above, it is possible to efficiently recover high quality crystals of ϵ -caprolactam from the crude lactam.

[0060]

15 More specifically, the liquid phase that is not used in the dissolution tank 6 (dropwise-crystallization-recovered-mother liquid) is introduced into the crystallization tank 7. For the crystallization method in the crystallization tank 7, evaporation-crystallization under reduced pressure is adopted. From the viewpoint of energy conservation, it is preferable to evaporate the solvent to some extent from the dropwise-
20 crystallization-recovered-mother liquid using a multiple effect evaporator or the like, prior to evaporation-crystallization.

[0061]

 In the case of evaporation-crystallization, since the solvent is separated by evaporation, although not illustrated, because the organic solvent discharged from the
25 crystallization tank 7 is a purified organic solvent from which impurities are removed,

this can be reused as a cold solvent supplied to the crystallization tank 1, a solvent used in the crystallization tank 3, or a washing solvent employed in the crystal washing machine 5, or the like.

[0062]

5 The slurry following the crystallization treatment is introduced into a solid-liquid separator 8, and is separated into the crystals of ϵ -caprolactam as a solid phase (recovered lactam) and the liquid phase in which impurities are concentrated. The recovered lactam discharged from the solid-liquid separator 8 is introduced into the dissolution tank 6 and reused.

10 [0063]

On the other hand, the liquid phase discharged from the solid-liquid separator 8 is subjected to a distillation treatment in a solvent recovering step which is not shown, and the organic solvent is recovered while impurities are separated as residues.

Although not shown, by recovering the ϵ -caprolactam in the liquid phase discharged from the solid-liquid separator 8, the ϵ -caprolactam yield further improves. For the recovery method, known methods such as crystallization, distillation, extraction, chemical treatments and activated carbon treatments may be combined for recovery. By adopting a method of recycling the recovered ϵ -caprolactam to the purification step described above, it is possible to efficiently recover high quality crystals of ϵ -caprolactam from the crude lactam.

15
20

[0064]

It should be noted that when a mixed solvent with different boiling points is used, the composition of the recovered solvent varies, but it is preferable to mix the recovered solvents, including the solvent recovering step and reuse after adjusting the concentration.

25

[0065]

The recovered solvent may be recycled as a solvent used in the crystallization tank 1 and the like, and the emissions from the present process are only the residues in the solvent recovering step, which makes it a manufacturing process with extremely few wastes.

[0066]

Next, the recovering step will be described in more detail with reference to FIG. 2, FIG. 3A and FIG. 3B.

[0067]

FIG. 2 is a flow diagram of a step including the crystallization tank 7 and solid-liquid separator 8 according to an embodiment of the present invention.

The dropwise-crystallization-recovered-mother liquid introduced into the crystallization tank 7 is cooled to an extent to be crystallized in the crystallization tank 1 in the previous stage, and is subjected to solid-liquid separation in the solid-liquid separator 4 shown in FIG. 1 while being kept cooled, and is thus a highly concentrated solution that is almost saturated. For this reason, when the dropwise-crystallization-recovered-mother liquid of such a high concentration is introduced into the crystallization tank 7 which is under a reduced-pressure environment, solvents are evaporated from the dropwise-crystallization-recovered-mother liquid to reach saturation immediately, thereby depositing the crystals. When such a rapid crystal deposition is conducted, it may become a cause of scaling inside the crystallization tank 7, which is likely to result in the occurrence of defects, such as a decline in the crystal recovery rate and the failure in the continuous operation due to the blockage of lines or the like.

[0068]

Accordingly, in the crystallization tank 7 according to an embodiment of the

present invention, scaling within the crystallization tank 7 is suppressed by the following configuration.

[0069]

First, the inside of the crystallization tank 7 includes a portion where the slurry
5 containing the crystals deposited as a result of crystallization (evaporation-crystallization-mother liquid) is retained (liquid phase 7a) and a space above the liquid phase 7a (vapor phase 7b).

The crystallization tank 7 has a circular shape in cross-sectional view in the horizontal direction, and the diameter of the vapor phase 7b is larger than the diameter of
10 the liquid phase 7a. The liquid phase 7a and vapor phase 7b have a jacket structure, and are heated by supplying a heating medium to a jacket portion. That is, by having the above structure, at least part of an internal wall of the crystallization tank 7 is heated to a temperature higher than the operation temperature of the evaporation-crystallization. For this reason, the scaling of ϵ -caprolactam on the internal wall is suppressed.

15 It should be noted that as the "temperature higher than the operation temperature of the evaporation-crystallization", for example, a temperature higher than the operation temperature of the evaporation-crystallization by 0°C to 100°C is preferred, and a temperature 20°C to 60°C higher than the operation temperature of the evaporation-crystallization is more preferred.

20 [0070]

In the crystallization tank 7, an external circulation line 15 is provided for circulating at least a portion of the evaporation-crystallization-mother liquid outside the crystallization tank 7, by extracting at least a portion of the evaporation-crystallization-mother liquid inside the crystallization tank 7 and introducing into the crystallization tank
25 7 once again. By the circulation of the evaporation-crystallization-mother liquid via the

external circulation line 15, the dropwise-crystallization-recovered-mother liquid is diluted, while the concentration of the evaporation-crystallization-mother liquid is made to be uniform, thereby suppressing the scaling.

[0071]

5 In the following description, the circulation of the evaporation-crystallization-mother liquid using the external circulation line 15 is sometimes referred to as “external circulation”. In addition, the evaporation-crystallization-mother liquid flowing inside the external circulation line 15 is sometimes referred to as an “externally circulating slurry”.

10 [0072]

Of the liquid phases discharged from the solid-liquid separator 2, solid-liquid separator 4, and crystal washing machine 5 shown in FIG. 1, the liquid phase that is not used in the dissolution tank 6 (dropwise-crystallization-recovered-mother liquid) is introduced into the external circulation line 15 via a pipe 11, and is introduced into the
15 crystallization tank 7 together with the externally circulating slurry that flows inside the external circulation line 15. The pipe 11 is connected to a suction side of a pump 14a in the external circulation line 15, and the dropwise-crystallization-recovered-mother liquid is combined with the externally circulating slurry and mixed in the pump 14a before being supplied to the crystallization tank 7.

20 [0073]

In the external circulation line 15, a heat exchanger 17 for heating the slurry flowing inside is disposed. A mixed liquid of the externally circulating slurry that flows inside the external circulation line 15 and the dropwise-crystallization-recovered-mother liquid introduced into the external circulation line 15 via the pipe 11 is preheated by the
25 heat exchanger 17, and is then introduced in the transverse direction with respect to the

crystallization tank 7 (direction that intersects with the gravity direction).

[0074]

Each of FIG. 3A and FIG. 3B is a cross-sectional view of the crystallization tank 7 in the horizontal direction at a height position to which the external circulation line 15 according to an embodiment of the present invention is connected.

As shown in FIG. 3A, in the inside of the crystallization tank 7, the external circulation line 15 is connected to the crystallization tank 7 so that a front end 15a of the external circulation line 15 is not directed toward a direction of the center 7x of the crystallization tank 7 (toward the circumferential direction of the crystallization tank 7), or, as shown in FIG. 3B, is connected to the crystallization tank 7 while being directed toward the side surface direction of the crystallization tank 7 (tangential direction of the outer periphery of the crystallization tank 7). In the case of the configuration shown in FIG. 3B, a tip portion corresponding to the front end 15a as shown in FIG. 3A in the inside of the crystallization tank 7 may not be needed.

[0075]

By means of this configuration, when the mixed liquid of the externally circulating slurry that flows inside the external circulation line 15 and the dropwise-crystallization-recovered-mother liquid introduced into the external circulation line 15 via the pipe 11 is introduced into the crystallization tank 7, the evaporation-crystallization-mother liquid which is retained inside the crystallization tank 7 forms a flow in the circumferential direction (indicated by a curved arrow in the drawing). By this flow, it is possible to stir the evaporation-crystallization-mother liquid inside the crystallization tank 7, and it is also possible to efficiently dilute the mixed liquid of the externally circulating slurry that flows inside the external circulation line 15 and the dropwise-crystallization-recovered-mother liquid that has been introduced into the

external circulation line 15 via the pipe 11, with the evaporation-crystallization-mother liquid inside the crystallization tank 7. Therefore, in the crystallization tank 7 shown in FIG. 3A and FIG. 3B, a stirring blade for stirring the interior is no longer required, and it is possible to eliminate the scaling onto the stirring blade, and the scaling onto other parts in the crystallization tank 7 can also be reduced.

[0076]

Note that when the mixed liquid of the externally circulating slurry that flows inside the external circulation line 15 and the dropwise-crystallization-recovered-mother liquid that has been introduced into the external circulation line 15 via the pipe 11 is introduced into the liquid phase 7a, the direction of the front end 15a of the external circulation line 15 may be directed toward a direction of the center 7x of the crystallization tank 7. In addition, it does not matter if the direction of the front end 15a is directed toward the longitudinal direction (gravity direction) with respect to the crystallization tank 7.

[0077]

Further, although it is also possible to use as a configuration in which the mixed liquid of the externally circulating slurry that flows inside the external circulation line 15 and the dropwise-crystallization-recovered-mother liquid that has been introduced into the external circulation line 15 via the pipe 11 is introduced into the vapor phase 7b of the crystallization tank 7 and then falls down inside the crystallization tank 7 from the vapor phase 7b to the liquid phase 7a, in order to suppress the scaling at the front end of the external circulation line 15, it is more preferable that the above mixed liquid be introduced to the liquid phase 7a as described above.

[0078]

In FIG. 2, to the bottom portion of the crystallization tank 7, a pipe 12 for

driving out the evaporation-crystallization-mother liquid obtained inside the crystallization tank 7 and introducing into the solid-liquid separator 8 is connected. A pump 14b for driving out liquids is provided in the middle of the pipe 12 and is feeding the evaporation-crystallization-mother liquid to the downstream side. In the solid-liquid separator 8, the fed evaporation-crystallization-mother liquid is subjected to solid-liquid separation to obtain the recovered lactam and the liquid phase.

[0079]

Further, at least a portion of the liquid phase generated in the solid-liquid separator 8 (evaporation-crystallization-recovered-mother liquid: that is, a recycle liquid) is introduced into the external circulation line 15 via a pipe 16, and then introduced into the crystallization tank 7 once again and reused. The pipe 16 is connected to the suction side of the pump 14a in the external circulation line 15, and the evaporation-crystallization-recovered-mother liquid is combined with the externally circulating slurry and the dropwise-crystallization-recovered-mother liquid and mixed in the pump 14a before being supplied to the crystallization tank 7.

[0080]

In such a configuration, inside the external circulation line 15, the dropwise-crystallization-recovered-mother liquid introduced into the crystallization tank 7 from the pipe 11, the evaporation-crystallization-mother liquid circulated via the external circulation line 15 (externally circulating slurry) and the recycle liquid to be reused via the pipe 16 are mixed. As a result, the dropwise-crystallization-recovered-mother liquid introduced into the crystallization tank 7 forms a mixed liquid which is diluted with the evaporation-crystallization-mother liquid and the recycle liquid, thereby reducing the possibility that crystals are deposited immediately upon introduction of the dropwise-crystallization-recovered-mother liquid of high concentration into the crystallization tank

7.

[0081]

It should be noted that, as the pump 14a shown in FIG. 2, it is preferable that a pump for feeding the dropwise-crystallization-recovered-mother liquid be provided further on the downstream side than the position to which the pipe 11 and the pipe 16 are connected in the external circulation line 15. In the case of such an arrangement, the dropwise-crystallization-recovered-mother liquid, the evaporation-crystallization-mother liquid, and the recycle liquid are mixed when passing through the pump 14a, and are introduced into the crystallization tank 7 as a uniform slurry (mixed liquid). In the case of a non-uniform slurry, for example, crystals are sometimes deposited immediately upon introduction of a concentrated slurry into the crystallization tank 7, which may cause scaling. For this reason, by introducing a uniform slurry, it is possible to suppress such scaling.

[0082]

It should be noted that as the operating conditions of the crystallization tank 7, the solvent evaporation load in the crystallization tank 7 is preferably 100 kg/m²/h to 2,000 kg/m²/h per area of a liquid level.

The slurry concentration of the evaporation-crystallization-mother liquid which is retained in the liquid phase 7a inside the crystallization tank 7 is preferably 10% by mass or more and 40% by mass or less.

The operation-supersaturation degree of evaporation-crystallization is preferably 0.1 kg/m³ or more and 20 kg/m³ or less.

The operation-pressure of evaporation-crystallization is preferably 10 torr (1.3 kPa) or more and 500 torr (66.7 kPa) or less.

The crystallization temperature of evaporation-crystallization is preferably 0°C

or more and 60°C or less.

The amount of the evaporation-crystallization-mother liquid circulated via the external circulation line 15 is preferably 10 to 10,000 times the amount of the solvent evaporated from the evaporation-crystallization-mother liquid in the evaporation-
5 crystallization. As a result, the supersaturation degree of the evaporation-crystallization-mother liquid reduces, thereby making it difficult to cause scaling. In addition, since it becomes possible to obtain large crystals by crystallization and the surface area is reduced, the amount of impurities adhered onto the obtained crystals can also be reduced.

10 [0083]

In the crystallization tank 7 according to an embodiment of the present invention, by adopting the configuration as described above, it becomes possible to suppress the scaling inside the crystallization tank 7 and to thereby improve the productivity and crystal recovery rate.

15 [0084]

The recovered ϵ -caprolactam obtained in this manner is added to the aforementioned crude ϵ -caprolactam, and purified together with the crude lactam in the purification step described above. The high quality ϵ -caprolactam obtained in the purification step (purified lactam) is preferably controlled in such a manner that the
20 contents of the cyclohexanone oxime contained and the basic compounds, such as MTHI and OHP, are equal to or less than a certain concentration. More specifically, it is preferable to control the operating conditions of the crystal washing machine 5 in such a manner that, with respect to ϵ -caprolactam, the concentration of the cyclohexanone oxime contained in the purified lactam is less than 10 ppm; the concentration of
25 1,2,3,4,6,7,8,9-octahydrophenazine is less than 10 ppm; and the concentration of 3-N-

methyl-4,5,6,7-tetrahydrobenzimidazole is less than 25 ppm.

[0085]

The degree of processing of the crude lactam is controlled by the above impurity content indicators. The degree of impurity removal by the crystallization treatment may be adjusted depending on the crystallization conditions such as the type of solvent to be used, the amount of solvent, and the crystallization temperature, and thus may be confirmed by a preliminary experiment.

[0086]

It is desirable that each crystallization treatment be carried out under the crystallization treatment conditions so that a purified lactam of satisfactory quality is obtained by a single treatment, but when a high level of purification is needed, it is recommended to carry out several times of crystallization treatments.

[0087]

In addition, as for the caprenolactams that are difficult to remove by crystallization, it is possible to remove the ϵ -caprolactam obtained in the crystal washing machine 5 by bringing into contact with hydrogen in the presence of a hydrogenation catalyst to hydrogenate the caprenolactams, followed by washing or the like. It is usually possible to control the content of caprenolactams to less than 25 ppm by such a treatment.

The method of producing ϵ -caprolactam according to an embodiment of the present invention is carried out in the manner described above.

[0088]

According to the method of producing a high quality ϵ -caprolactam having the configuration as described above, it is possible to suppress scaling in the evaporation-crystallization, and it is possible to obtain a high quality ϵ -caprolactam, with a good yield,

from the crude ϵ -caprolactam containing impurities which is obtained by the Beckmann rearrangement of cyclohexanone oxime.

[0089]

It should be noted that in an embodiment of the present invention, it is

5 configured in such a manner that the pipe 11 and the pipe 16 are connected to the external circulation line 15, and the dropwise-crystallization-recovered-mother liquid is mixed, in the external circulation line 15, with both of part of the evaporation-crystallization-mother liquid (that is, the externally circulating slurry) and part of the evaporation-crystallization-recovered-mother liquid (that is, the recycle liquid), but the
10 configuration is not limited thereto.

[0090]

As another embodiment, it may be configured in such a manner that only the pipe 11 is connected to the external circulation line 15, the dropwise-crystallization-recovered-mother liquid and the externally circulating slurry are mixed inside the

15 external circulation line 15 and are supplied to the crystallization tank 7, and the recycle liquid is supplied into the crystallization tank 7 by connecting the pipe 16 to the crystallization tank 7.

[0091]

Alternatively, as yet another embodiment, it may be configured in such a

20 manner that after connecting the pipe 11 and the pipe 16 without connecting the pipe 11 and the pipe 16 to the external circulation line 15, the pipes after the joining are connected to the crystallization tank 7. In this case, by connecting the pipe 11 and the pipe 16, the dropwise-crystallization-recovered-mother liquid and the recycle liquid are mixed inside the pipe following the joining and are supplied to the crystallization tank 7.
25 In this case, it is preferable to place a pump for feeding the mixed liquid of the dropwise-

crystallization-recovered-mother liquid and the recycle liquid further on the downstream side than the position to which the pipe 11 and the pipe 16 are connected, since the mixed liquid is introduced into the crystallization tank 7 as a uniform slurry.

[0092]

5 In the pipe 16 in the another embodiment and the pipe following the joining of the pipe 11 and the pipe 16 in the yet another embodiment, it is preferable to provide the same heat exchange as the heat exchanger 17 provided in the external circulation line 15 and to supply the mixed solution to the crystallization tank 7 after preheating.

[0093]

10 Preferred embodiments according to the present invention have been described above with reference to the accompanying drawings. However, it goes without saying that the present invention is not limited to these embodiments. Various shapes, combinations, and the like for the respective constituting elements described in the abovementioned embodiments is merely an example, and various changes and
15 modifications, as based on the design requirements or the like, are possible without departing from the spirit and scope of the present invention.

[Examples]

[0094]

20 The present invention will be described below based on Examples. However, the present invention is not limited to these Examples.

[0095]

(Example 1)

(Purification step)

25 Using a high-silica type zeolite catalyst, a vapor phase Beckmann rearrangement

reaction of cyclohexanone oxime was carried out at 380°C in the presence of methanol to obtain a reaction product. The impurities having a lower boiling point than that of ϵ -caprolactam and the impurities having a higher boiling point than that of ϵ -caprolactam were removed from the reaction product by distillation, thereby obtaining a crude ϵ -caprolactam.

[0096]

Subsequently, the crude ϵ -caprolactam was heated to 75°C, and the obtained molten material and a mixed solvent of n-heptane: cyclohexanone = 3:1 (weight ratio) which was cooled to 5°C were poured at the same time and also in a continuous manner into a crystallization tank in which the jacket temperature was kept at 56°C. The crystallization temperature was 55°C, and the average residence time was 30 minutes.

[0097]

A slurry obtained in the crystallization tank was fed to a centrifugal decanter (solid-liquid separator) which had been kept at 55°C and subjected to solid-liquid separation, and then the above mixed solvent which was kept at about 50°C was sprayed onto the obtained crystals for continuous washing, thereby obtaining ϵ -caprolactam crystals of high quality. In addition, a solution obtained by mixing a liquid phase separated in the centrifugal decanter and the mixed solvent used for washing the crystals was obtained as a dropwise-crystallization-recovered-mother liquid.

[0098]

(Recovering step)

Subsequently, to a crystallization tank for carrying out evaporation-crystallization in the recovering step, the above dropwise-crystallization-recovered-mother liquid was supplied, and evaporation-crystallization was carried out by mixing a slurry retained in the crystallization tank and an evaporation-crystallization-recovered-

mother liquid described below to form an evaporation-crystallization-mother liquid.

[0099]

In the evaporation-crystallization, a portion of the evaporation-crystallization-mother liquid was extracted from the crystallization tank, and supplied once again to the crystallization tank via a pipe which was provided outside the crystallization tank, thereby forming a flow of liquid that circulated outside the crystallization tank (that is, externally circulating liquid). It was configured in such a manner that the evaporation-crystallization-mother liquid inside the crystallization tank was stirred by the flow of the liquid, and no stirring device was provided inside the crystallization tank.

[0100]

Further, a liquid phase (evaporation-crystallization-recovered-mother liquid: that is, a recycle liquid) obtained by extracting the evaporation-crystallization-mother liquid in which the crystals of ϵ -caprolactam were deposited from the crystallization tank through evaporation-crystallization, followed by solid-liquid separation was recycled by being supplied once again to the crystallization tank.

[0101]

It should be noted that the dropwise-crystallization-recovered-mother liquid, the externally circulating liquid and the recycle liquid were mixed in advance to form a mixed liquid prior to being fed into the crystallization tank, and the mixed liquid was fed directly into the evaporation-crystallization-mother liquid retained inside the crystallization tank via a supply nozzle provided toward the circumferential direction of the crystallization tank. The supply rate of the dropwise-crystallization-recovered-mother liquid was $0.5 \text{ m}^3/\text{h}$, the circulation rate of the externally circulating liquid was $9.6 \text{ m}^3/\text{h}$, and the supply rate of the recycle liquid was $1.0 \text{ m}^3/\text{h}$.

[0102]

The operation temperature of evaporation-crystallization was set to 39°C, the residence time of the evaporation-crystallization-mother liquid in the crystallization tank was set to 266 seconds, and the operation-pressure was set to 90 torr (12.0 kPa). As a result, a continuous operation of 5 days was achieved.

5 [0103]

(Comparative Example 1)

The purification step was carried out in the same manner as in Example 1.

In the recovering step, when supplying the dropwise-crystallization-recovered-mother liquid, the externally circulating liquid, and the recycle liquid to the crystallization tank, each of these liquids was supplied separately into the evaporation-crystallization-mother liquid retained in the crystallization tank via a supply nozzle provided toward the center of the crystallization tank. The supply rate of the dropwise-crystallization-recovered-mother liquid was 0.5 m³/h, the circulation rate of the externally circulating liquid was 9.6 m³/h, and the supply rate of the recycle liquid was 1.0 m³/h.

[0104]

The operation temperature of evaporation-crystallization was set to 39°C, the residence time of the evaporation-crystallization-mother liquid in the crystallization tank was set to 266 seconds, and the operation-pressure was set to 140 torr (18.7 kPa). As a result, an operation of few days was possible.

[0105]

However, when the operation-pressure was set to 110 torr (14.7 kPa), scaling onto the internal wall of the crystallization tank or onto a pipe for extracting the evaporation-crystallization-mother liquid from the crystallization tank was increased, and the operation became impossible in the space of a few hours.

[0106]

(Comparative Example 2)

The purification step was carried out in the same manner as in Example 1.

In the recovering step, by providing a stirring device inside the crystallization
5 tank, the evaporation-crystallization-mother liquid was stirred without externally
circulating the evaporation-crystallization-mother liquid.

[0107]

In addition, each of the dropwise-crystallization-recovered-mother liquid and the
recycle liquid was supplied separately to a vapor phase inside the crystallization tank.

10 The supply rate of the dropwise-crystallization-recovered-mother liquid was $0.5 \text{ m}^3/\text{h}$,
and the supply rate of the recycle liquid was $1.0 \text{ m}^3/\text{h}$.

[0108]

The operation temperature of evaporation-crystallization was set to 39°C , the
residence time of the evaporation-crystallization-mother liquid in the crystallization tank
15 was set to 266 seconds, and the operation-pressure was set to 300 torr (40.0 kPa). As a
result, a large amount of scales was deposited onto the line supplying raw materials to the
vapor phase inside the crystallization tank, the internal wall of the crystallization tank,
and the pipe for extracting the evaporation-crystallization-mother liquid from the
crystallization tank, and the operation became impossible in the space of a few hours.

20 [0109]

From these results, according to the production method of the present invention,
it became apparent that the occurrence of scaling was unlikely even when the operation-
pressure was lowered in the evaporation-crystallization, and the continuous operation
was possible in a favorable manner, thereby confirming the usefulness thereof.

[Industrial Applicability]

[0110]

According to the present invention, it is possible to suppress scaling in the evaporation-crystallization, and it becomes possible to stably obtain a high quality ϵ -caprolactam, with a good yield, from a crude ϵ -caprolactam containing impurities which is obtained by Beckmann rearrangement of cyclohexanone oxime, and it is therefore extremely useful industrially.

[Reference Signs List]

10 [0111]

1: Crystallization tank, 2: Solid-liquid separator, 3: Crystallization tank, 4: Solid-liquid separator, 5: Crystal washing machine, 6: Dissolution tank, 7: Crystallization tank, 8: Solid-liquid separator, 9: Cooling facility, 11: Pipe, 12: Pipe, 13: Pipe, 14a, 14b: Pump, 15: External circulation line, 15a: Front end of pipe, 16: Pipe, 17: Heat exchanger

15

[CLAIMS]

[Claim 1]

A method of producing high quality ϵ -caprolactam comprising:

5 a purification step in which a crude ϵ -caprolactam obtained by Beckmann rearrangement of cyclohexanone oxime is mixed with an organic solvent to obtain a mixed solution, ϵ -caprolactam is crystallized from the mixed solution, and a high quality ϵ -caprolactam and a dropwise-crystallization-recovered-mother liquid are obtained by a solid-liquid separation; and

10 a recovering step in which an evaporation-crystallization-mother liquid containing the dropwise-crystallization-recovered-mother liquid is subjected to evaporation to crystallize ϵ -caprolactam, followed by a solid-liquid separation to obtain a recovered ϵ -caprolactam and an evaporation-crystallization-recovered-mother liquid; wherein

15 the method further comprises preparing a mixed liquid formed by mixing the dropwise-crystallization-recovered-mother liquid with at least part of the evaporation-crystallization-recovered-mother liquid, at least part of the evaporation-crystallization-mother liquid which is extracted from a tank for conducting evaporation-crystallization, or both of at least part of the evaporation-crystallization-recovered-mother liquid and at least part of the evaporation-crystallization-mother liquid, prior to the recovering step; and

supplying the mixed liquid to the tank to mix with the evaporation-crystallization-mother liquid retained in the tank.

[Claim 2]

The method of producing high quality ϵ -caprolactam according to Claim 1, further comprising adding the recovered ϵ -caprolactam to the crude ϵ -caprolactam.

5 [Claim 3]

The method of producing high quality ϵ -caprolactam according to Claim 1, wherein

a vapor phase and a liquid phase are provided in the tank for conducting evaporation-crystallization, and the mixed liquid is supplied to the liquid phase.

10

[Claim 4]

The method of producing high quality ϵ -caprolactam according to Claim 3, wherein

supplying the mixed liquid to the tank in the recovering step comprises

15 supplying the mixed liquid toward a circumferential direction of the tank.

[Claim 5]

The method of producing high quality ϵ -caprolactam according to Claim 1, wherein at least part of an internal wall of the tank for conducting the evaporation-crystallization is heated to a temperature 20 to 60°C higher than an operation temperature of the evaporation-crystallization.

20

[Claim 6]

The method of producing high quality ϵ -caprolactam according to Claim 1,

25 wherein a solvent evaporation load is 100 kg/m²/h to 2,000 kg/m²/h per area of a liquid

level in the evaporation-crystallization.

[Claim 7]

The method of producing high quality ϵ -caprolactam according to Claim 1,
5 wherein an operation-supersaturation degree is 0.1 kg/m^3 to 20 kg/m^3 in the evaporation-crystallization.

[Claim 8]

The method of producing high quality ϵ -caprolactam according to Claim 1,
10 wherein an operation-pressure is 10 torr to 500 torr in the evaporation-crystallization.

[Claim 9]

The method of producing high quality ϵ -caprolactam according to Claim 1,
wherein a crystallization temperature is 0°C to 60°C in the evaporation-crystallization.
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[Claim 10]

The method of producing high quality ϵ -caprolactam according to Claim 1,
wherein

the recovering step further comprises taking out part of the evaporation-
20 crystallization-mother liquid in the tank and resupplying the part of the evaporation-crystallization-mother liquid to the tank to thereby recycle the evaporation-crystallization-mother liquid outside the tank; and

an amount of the evaporation-crystallization-mother liquid taken out of the tank
is 10 to 10,000 times the amount of the solvent evaporated from the evaporation-
25 crystallization-mother liquid in evaporation-crystallization.

[Claim 11]

The method of producing high quality ϵ -caprolactam according to Claim 1,
wherein

the crude ϵ -caprolactam is obtained by vapor phase Beckmann rearrangement
5 using a solid catalyst and cyclohexanone oxime as a raw material.

[Claim 12]

The method of producing high quality ϵ -caprolactam according to Claim 1,
wherein,

10 in the purification step, ϵ -caprolactam is crystallized by supplying and mixing
together the crude ϵ -caprolactam in a liquid state with a cooled aliphatic hydrocarbon or a
mixed solvent containing a cooled aliphatic hydrocarbon and an organic solvent having a
polarity higher than that of the aliphatic hydrocarbon, into the tank at a temperature 40 to
80 °C lower than the temperature of a crystallization temperature.

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[Claim 13]

The method of producing high quality ϵ -caprolactam according to Claim 12,
wherein

the crude ϵ -caprolactam in a liquid state is a molten crude ϵ -caprolactam, a
20 mixed solution of a molten crude ϵ -caprolactam and an aliphatic hydrocarbon, or a mixed
solution of molten-crude ϵ -caprolactam and a mixed solvent containing an aliphatic
hydrocarbon and an organic solvent having a polarity higher than that of the aliphatic
hydrocarbon.