

Description

Title of Invention: METHOD FOR PURIFYING ACETONITRILE

Technical Field

[0001]

The present invention relates to a method for purifying acetonitrile.

Background Art

[0002]

Currently, commonly commercially available acetonitrile is mainly prepared by collecting and purifying crude acetonitrile obtained as a by-product at the time of production of acrylonitrile or methacrylonitrile by a catalytic ammoxidation reaction of propylene or isobutene with ammonia and oxygen.

[0003]

Acetonitrile is used, for example, as a solvent for chemical reactions, in particular as a solvent for synthesis and purification of pharmaceutical intermediates, or as a moving bed solvent in high performance liquid chromatography. Recently, acetonitrile has also been used, for example, as a solvent for synthesis and purification of DNA, a solvent for synthesis of organic EL materials and as a cleaning solvent for electronic components; in such uses as

described above, acetonitrile has been required to be purified in a particularly high purity.

[0004]

The crude acetonitrile obtained by an ammoxidation reaction includes various impurities. As a method for purifying crude acetonitrile, there has hitherto been proposed a method in which crude acetonitrile and an alkali are mixed with each other.

[0005]

Patent Literature 1 discloses a method in which in purifying crude acetonitrile containing impurities, an alkali is added to the crude acetonitrile so as to be regulated to have the pH falling within a range from 10 to 13.5, and the thus treated crude acetonitrile is heat-treated, and then further treated with a formaldehyde pH-regulated solution to decompose acrylonitrile and hydrogen cyanide. Examples of the alkali to be added to the crude acetonitrile include sodium hydroxide, potassium hydroxide and ammonia.

[0006]

Patent Literature 2 discloses a dehydration purification method of acetonitrile in which an alkali is added to water-containing acetonitrile and stirred at 10°C to 50°C to separate and remove the aqueous phase. In the separated aqueous phase, hydrogen cyanide and acrylonitrile are included in addition to the alkali and water, and describes the possible use of the aqueous

phase as the alkali source in the purification step of acetonitrile described in Patent Literature 1.

[0007]

Patent Literature 3 discloses a method in which acetonitrile by-produced by ammoxidation reaction is treated with alkali at 60°C to decompose hydrogen cyanide and acrylonitrile, and then the acetonitrile is dehydrated in a dehydration column by further adding alkali. The alkali aqueous solution used for treating acetonitrile is collected, and recycled as the alkali source to be fed to the dehydration column.

Citation List

Patent Literature

[0008]

Patent Literature 1: Japanese Patent Laid-Open No. 48-81816

Patent Literature 2: Japanese Patent Laid-Open No. 55-153757

Patent Literature 3: Japanese Patent Laid-Open No. 2000-128847

Summary of Invention

Technical Problem

[0009]

In any one of the purification steps disclosed in foregoing Patent Literature 1, Patent Literature 2 and

Patent Literature 3, metal hydroxides such as sodium hydroxide and potassium hydroxide and/or ammonia is used as the alkali source. However, as a result of the investigation performed by the present inventors, it has been revealed that conventional techniques hydrolyze acetonitrile simultaneously when impurities are decomposed by using alkali. When acetonitrile is decomposed, the decomposed acetonitrile is converted into organic acids such as acetic acid, and thus offers a factor to reduce the production amount of high-purity acetonitrile. Additionally, the production of organic acids as described above decreases the pH, and also offers a problem that the decomposition of impurities require more alkali. The hydrolysis of acetonitrile is promoted by alkali, and hence the increase of the addition amount of alkali cannot be said to be a favorable method.

[0010]

In view of the problems involved in the conventional techniques, an object of the present invention is to provide a method for purifying acetonitrile, capable of improving the production amount of high-purity acetonitrile by suppressing the hydrolysis of acetonitrile when impurities are decomposed.

Solution to Problem

[0011]

The present inventors made a continuous diligent study in order to solve the above-described problems, and consequently have reached the present invention by discovering that the hydrolysis of acetonitrile is suppressed by feeding acetamide and/or acetic acid to the reaction vessel for decomposing impurities such as acrylonitrile and hydrogen cyanide contained in crude acetonitrile. Moreover, the present inventors paid attention to the acetamide and acetic acid produced in the purification process, made a study on the method for utilizing these products, and consequently have discovered that even when the alkali containing the acetamide and/or acetic acid is used, the hydrolysis of acetonitrile is suppressed.

[0012]

Specifically, the present invention is as follows.

[1]

A method for purifying acetonitrile, comprising:

obtaining a reaction solution by feeding crude acetonitrile obtained by an ammoxidation reaction and an alkali to a reaction vessel;

obtaining a distillate by distilling the reaction solution; and

feeding acetamide and/or acetic acid to the reaction vessel.

[2]

The method for purifying acetonitrile according to [1] above, further comprising a step wherein the reaction solution is introduced into a distillation column and high-boiling substance is removed, in the step of obtaining the distillate by distilling the reaction solution, thereafter the obtained distillate is fed to a dehydration column, and an alkali aqueous solution is then added to the dehydration column and an aqueous phase is separated.

[3]

The method for purifying acetonitrile according to [2] above, wherein the alkali fed to the reaction vessel comprises a part of the aqueous phase.

[4]

The method for purifying acetonitrile according to [2] or [3] above, further comprising adding, at 40°C or higher and 90°C or lower, the alkali aqueous solution to the dehydration column.

[5]

A method for producing high-purity acetonitrile, comprising purifying acetonitrile by using the method for purifying acetonitrile according to any one of [1] to [4] above.

Advantageous Effects of Invention

[0013]

According to the method for purifying acetonitrile of the present invention, the hydrolysis of acetonitrile in the reaction vessel for decomposing impurities is suppressed, and the production amount of high-purity acetonitrile can be improved.

Brief Description of Drawings

[0014]

[Figure 1] Figure 1 shows an example of a schematic diagram of an apparatus for producing acetonitrile according to an embodiment of the present invention.

[Figure 2] Figure 2 shows another example of a schematic diagram of an apparatus for producing acetonitrile according to an embodiment of the present invention.

Description of Embodiments

[0015]

Hereinafter, the mode for carrying out the present invention (hereinafter, simply referred to as the "present embodiment") will be described in detail. The following embodiment is an example for describing the present invention, and has no intention to limit the present invention to the following contents. The present invention can be implemented as appropriately modified within the scope of the gist thereof. In the drawings, the same reference sign is assigned to the same elements, and a duplicate description is omitted. Unless otherwise

specified, the vertical and horizontal positional relationships are based on the positional relationships shown in the drawings. The dimensional proportions of the apparatuses and members are not limited to the proportions shown in the drawings.

[0016]

The method for purifying acetonitrile in the present embodiment comprises: obtaining a reaction solution by feeding crude acetonitrile obtained by an ammoxidation reaction and an alkali to a reaction vessel; obtaining a distillate by distilling the reaction solution; and feeding acetamide and/or acetic acid to the reaction vessel.

[0017]

As shown in Figure 1, an example of the apparatus for purifying acetonitrile in the present embodiment has a concentration column 1 into which crude acetonitrile is introduced, and has a configuration in which a high-boiling separation column 3, a dehydration column 4, a low-boiling separation column 5 and a product column 6 are connected to the concentration column 1 in this order through the intermediary of a reaction vessel 2.

[0018]

Crude acetonitrile is obtained, for example, as a by-product at the time of production of acrylonitrile or methacrylonitrile from propylene, propane, isobutene or isobutane by catalytic ammoxidation reaction. In general,

crude acetonitrile is collected as a fraction other than the fraction containing as the main component acrylonitrile or methacrylonitrile, by performing extractive distillation of the products of an ammoxidation reaction. "Crude acetonitrile" as referred to herein means a fraction highest in the content of acetonitrile among the fractions obtained by performing extractive distillation of the products of an ammoxidation reaction. Crude acetonitrile is generally separated from the distillation column collecting most of acrylonitrile or methacrylonitrile, and usually contains 5 to 40% by mass of acetonitrile, 50 to 95% by mass of water, and additionally, many types of impurities such as hydrogen cyanide, allyl alcohol, oxazole, acrylonitrile, propionitrile, acetone, methacrylonitrile, cis- and trans-crotononitrile, acrylic acid, methyl acrylate, methacrylic acid, methyl methacrylate, acrolein, methacrolein and ammonia.

[0019]

Crude acetonitrile is transferred from a line 7 to a middle stage of a concentration column 1. The acetonitrile concentration column 1 is an upright distillation column, and has a not shown reboiler at the column bottom thereof and a not shown condenser at the column top thereof. While hydrogen cyanide is being removed from the column top portion (line 8) and water is being removed from the column bottom portion (line 9),

concentrated crude acetonitrile is withdrawn from the intermediate portion of the column (line 10).

Hereinafter, the withdrawn crude acetonitrile is also referred to as the "concentrated crude acetonitrile." A line 10 is provided with a not shown side-cut condenser, and the side-cut condenser is configured to condense the gaseous concentrated crude acetonitrile. The concentrated liquid crude acetonitrile flowing out from the side-cut condenser flows into a reaction vessel 2. The concentrated crude acetonitrile fed from concentration column 1 to the reaction vessel 2 usually has an acetonitrile concentration of 50 to 70% by mass, and additionally includes impurities such as 25 to 70% by mass of water, hydrogen cyanide, acrylonitrile and allyl alcohol.

[0020]

In the reaction vessel 2, the concentrated crude acetonitrile is treated with alkali to convert acrylonitrile or hydrogen cyanide contained as an impurity in the concentrated crude acetonitrile into a compound such as succinonitrile or a dimer. From the viewpoint of allowing the polymerization reaction to proceed sufficiently, the temperature of the reaction vessel 2 is preferably 50°C or higher and 80°C or lower, and the reaction is allowed to proceed more preferably at 60°C or higher and 75°C or lower for 3.0 hours or more and 15 hours or less, and furthermore preferably at 60°C

or higher and 75°C or lower for 4.0 hours or more and 10 hours or less.

[0021]

In the purification method in the present embodiment, acetamide and/or acetic acid can be added to the reaction vessel 2 from, for example, the line 11. At high temperatures, acetonitrile undergoes hydrolysis, and in particular, the hydrolysis is remarkable at a temperature of 50°C or higher. Accordingly, under the reaction conditions in the reaction vessel 2, acetonitrile is easily decomposed by hydrolysis into acetic acid and ammonia through acetamide, and thus usually the amount collected of acetonitrile is decreased. However, it has been found that when acetamide and/or acetic acid is fed to the reaction vessel 2, the hydrolysis of acetonitrile in the reaction vessel 2 is suppressed, and the amount collected of acetonitrile is improved. The concentration of acetamide and/or acetic acid to be fed to the reaction vessel 2 is not particularly limited; however, the concentration of acetamide and/or acetic acid concentration in the fed liquid in the line 11 or the like is preferably 0.50% by mass or more and 25% by mass or less, more preferably 1.0% by mass or more and 20% by mass or less, and furthermore preferably 3.0% by mass or more 15% by mass or less. In consideration of the flow-in amount from the concentration column 1 into the reaction vessel 2 and the liquid feed amount of the line

11 or the like, the concentration of acetamide and/or acetic acid in the reaction vessel 2 is preferably 0.050% by mass or more and 2.5% by mass or less, more preferably 0.25% by mass or more and 1.5% by mass or less and furthermore preferably 0.5% by mass or more and 1.5% by mass or less. Specifically, when the concentration of acetamide and/or acetic acid contained in the fed liquid of the line 11 or the like is 0.5% by mass or more, the suppression effect of the hydrolysis of acetonitrile tends to be remarkably exhibited. When the concentration is 25% by mass or less, not only the foregoing effect can be sufficiently ensured, but also the viscosity of the fed liquid can be reduced and a sufficient handleability tends to be ensured.

[0022]

The concentration of the acetamide and/or acetic acid fed from the line 11 can be regulated by regulating the temperature and the residence time of the alkali aqueous solution fed to the dehydration column 4.

[0023]

Acetonitrile is converted into acetamide under a basic condition, and further isolates ammonia to be successively hydrolyzed into acetic acid. A study made by the present inventor has revealed that the rate of the reaction converting acetonitrile into acetamide is slower than the rate of the reaction converting the acetamide into acetic acid. In other words, the reaction of

hydrolyzing acetonitrile into acetic acid involves the reaction of converting acetonitrile into acetamide as the rate-determining step.

[0024]

Acetamide and/or acetic acid has an effect to decrease the rate of the decomposition reaction of acetonitrile, and is considered to suppress the decomposition of acetonitrile. The industrial production of acetonitrile is performed in many cases as a continuous process, and the feeding of the starting materials to the reaction vessel and the withdrawing of the reaction mixture are regulated to be always in balance with each other. The residence of only particular components hardly occurs, and hence, for the purpose of decreasing the rate of the decomposition reaction of acetonitrile, it is necessary to feed acetamide and/or acetic acid. Alternatively, in the case where acetonitrile is produced by a discontinuous process, the decrease of the rate of the decomposition reaction of acetonitrile is considered to be a phenomenon occurring spontaneously, when the acetonitrile is decomposed into acetamide and acetic acid, and a certain amount of acetamide and/or acetic acid is produced. However, when acetonitrile is decomposed in the reaction vessel, acetic acid is produced to decrease the pH, and hence the decomposition of the impurities such as acrylonitrile and hydrogen cyanide is made slower. In order to prevent

such a decrease of pH, it is necessary to newly feed alkali to the reaction vessel; however, the decomposition reaction of acetonitrile is promoted by alkali, and hence the decomposition of acetonitrile further proceeds. Even in this case, the suppression effect of the decomposition of acetonitrile is enhanced by increasing the relative amount of acetamide and/or acetic acid, and hence the feeding of acetamide and/or acetic acid from outside the reaction system is effective.

[0025]

Accordingly, either in the case of a continuous process or in the case of a discontinuous process, by feeding acetamide and/or acetic acid to the reaction vessel, it is made possible to decompose impurities while the decomposition of acetonitrile is being suppressed.

[0026]

Acetic acid to be fed to the reaction vessel is not required to be present as pure acetic acid. Acetic acid either in a form of acetic acid ion or in a form of acetic acid salt (such as sodium acetate or potassium acetate) can suppress the decomposition of acetonitrile without causing any problem.

[0027]

The reaction solution in the reaction vessel 2 is transferred to a high-boiling separation column 3 through a line 12. Form the viewpoint of the separation of high-boiling substances, the high-boiling separation column 3

is preferably a reduced pressure distillation column. From the column top of the high-boiling separation column 3, acetonitrile is collected as an azeotropic composition mixture with water, or as a composition mixture close to the azeotropic composition mixture, and liquefied with a not-shown condenser. A part of the condensate is refluxed to the high-boiling separation column 3 through a not-shown line, and the rest of the condensate is transferred to the dehydration column 4 through a line 14. From a line 13 of the column bottom of the high-boiling separation column 3, compounds such as succinonitrile and the dimer, an alkali, acetic acid salt, allyl alcohol, propionitrile, water and a small amount of acetonitrile produced in the reaction vessel 2 are separated, and transferred to, for example, a wastewater treatment apparatus. At the column bottom, a not shown reboiler for giving heat necessary for distillation is installed, and supplies the heat necessary for distillation.

[0028]

The pressure in the high-boiling separation column 3 is, in terms of absolute pressure, preferably 80 mmHg or more and 760 mmHg or less, and more preferably 100 mmHg or more and 300 mmHg or less from the viewpoint of separating the high-boiling substances and also from the viewpoint of suppressing the decomposition of the substances produced in the reaction vessel 2 such as succinonitrile and the dimer. When the pressure is set

within the above-described range, the temperature of the column bottom portion is preferably 30°C or higher and 80°C or lower and more preferably 40°C or higher and 60°C or lower, and the temperature of the column top portion is preferably 20°C or higher and 70°C or lower and more preferably 30°C or higher and 50°C or lower.

[0029]

In the dehydration column 4, in addition to the distillate obtained from the column top of the high-boiling separation column 3, an alkali sufficient in amount to extract the water present in the distillate is added and mixed as an aqueous solution at 40°C or higher and 75°C or lower from a line 15. Then, an acetonitrile phase can be obtained from a line 17 by removing the aqueous phase extracted and separated at 10°C or higher and 50°C or lower over 0.10 hour or more and 3.0 hours or less from the column bottom of the dehydration column 4. The alkali aqueous solution is not particularly limited, but it is preferable to use an aqueous solution of sodium hydroxide and/or potassium hydroxide.

[0030]

As shown in Figure 2, another example of the schematic diagram of the purification apparatus of acetonitrile in the present embodiment is the same apparatus as shown in Figure 1 except that a part of the aqueous phase separated from the dehydration column 4 is circulated into the reaction vessel 2. In other words, a

part of the aqueous phase separated from the dehydration column 4 is fed from the line 11 to the reaction vessel 2. [0031]

In the purification method in the present embodiment, a part of the aqueous phase separated from the dehydration column 4 is circulated and can be used as an alkali source to be fed to the reaction vessel 2. The use of the aqueous phase separated from the dehydration column 4 makes it unnecessary to newly feed alkali from outside the reaction system, or makes it possible to reduce the feed rate of alkali from outside the reaction system, and thus contributes to the reduction of the feed rate of alkali in the whole purification step.

[0032]

Also in the dehydration column 4, acetonitrile is slightly decomposed to produce acetamide and/or acetic acid. In this case, from the viewpoint of controlling the production of acetamide and/or acetic acid in the dehydration column 4, it is preferable to warm beforehand the alkali aqueous solution to be fed to the dehydration column 4. The temperature of the alkali aqueous solution to be fed to the dehydration column 4 is preferably 40°C or higher and 90°C or lower, more preferably 45°C or higher and 75°C or lower and furthermore preferably 45°C or higher and 65°C or lower. The residence time in the dehydration column 4 is preferably 0.10 hour or more and 3.0 hours or less and more preferably 0.20 hour or more

and 2.8 hours or less. The aqueous phase extracted and separated from the dehydration column 4 contains alkali, acetamide and/or acetic acid, and hence the introduction of the aqueous phase into the reaction vessel 2 achieves the effect to suppress the hydrolysis of acetonitrile. On the other hand, the residence time in the reaction vessel 2 is 3.0 hours or more and 15 hours or less and more preferably 4.0 hours or more and 10 hours or less, and is longer as compared with the residence time in the dehydration column 4. Accordingly, the reaction vessel 2 offers a tendency for the decomposition of acetonitrile to proceed more easily as compared with the dehydration column 4. Even when the fraction of acetonitrile hydrolyzed in the dehydration column 4 is taken into account, the contribution of the suppression effect of the decomposition of acetonitrile in the reaction vessel 2 by feeding acetamide and/or acetic acid is large, and the yield of high-purity acetonitrile tends to be rather increased. Accordingly, the circulation of a part of the aqueous phase separated from the dehydration column 4 and the use of the part of the aqueous phase as the alkali source to be fed to the reaction vessel 2 are preferable from the viewpoint of simultaneously achieving both of the reduction of the feed rate of alkali in the whole purification step and the suppression of the decomposition of acetonitrile in the reaction vessel 2.

[0033]

The extraction temperature in the dehydration column 4 is preferably 5°C or higher and 40°C or lower and more preferably 10°C or higher and 35°C or lower, from the viewpoint of reducing the water content in the acetonitrile flowing out from the line 17 and suppressing the excessive hydrolysis of acetonitrile. In order to maintain the above-described extraction temperature, the liquid from the line 14 may be beforehand cooled and then fed to the dehydration column 4, or alternatively the main body of the dehydration column 4 may also be cooled. The extraction temperature as referred to herein means the temperature inside the dehydration column 4, more specifically, the temperature of the internal liquid located from the feed position of the column-top liquid of the high-boiling separation column 3 to the alkali feed position in the dehydration column 4.

[0034]

The amount used of the alkali in the dehydration column 4 is varied depending on the water content in the acetonitrile; however, the amount used of the alkali falls usually within a range of 10% by mass or more and 90% by mass or less, and preferably within a range of 30% by mass or more and 60% by mass or less, based on the water content in the acetonitrile. By the method for extracting water with an alkali, the water content in the acetonitrile is regulated to be preferably 10% by mass or less and more preferably 3% by mass or less.

[0035]

When at least a part of the column bottom liquid (aqueous phase) of the dehydration column 4 is transferred through the line 11 to the reaction vessel 2, the surplus fraction of the column bottom liquid of the dehydration column 4 is transferred through a line 16 to and processed in the waste water processing apparatus. The column bottom liquid of the dehydration column 4 mainly contains acetamide, acetic acid (inclusive of the alkali salts thereof), a small amount of acetonitrile and others, in addition to sodium hydroxide and/or potassium hydroxide as alkali, and water.

[0036]

The liquid transfer amount of the column bottom liquid of the dehydration column 4 to the reaction vessel 2 is preferably regulated in such a way that the amount of sodium hydroxide and/or potassium hydroxide per 1 mole of hydrogen cyanide in the liquid in the reaction vessel 2 is 1.0 mole or more and 3.5 moles or less, from the viewpoint of removing acrylonitrile and hydrogen cyanide from acetonitrile and from the viewpoint of suppressing the hydrolysis of acetonitrile. In this case, the pH of the mixed solution in the reaction vessel 2 is 12.0 ± 1.5 . Recycling of the column bottom liquid of the dehydration column 4 to the reaction vessel 2 can achieve the disuse or the amount reduction of the alkali to be added to the reaction vessel 2, and the reduction of the processing

amount of waste water in the column bottom liquid of the dehydration column 4. The recycling also offers an advantage that a small amount of acetonitrile contained in the column bottom liquid of the dehydration column 4 can be collected.

[0037]

The reduction of the decomposition amount of acetonitrile in the reaction vessel 2 increases the mass of the acetonitrile collected from the column top line 21 of the product column 6, which is the final distillation column. In the case where the mass of the produced high-purity acetonitrile is the same, the mass of the crude acetonitrile to be fed to the acetonitrile purification apparatus can be reduced, and accordingly the size reduction of the acetonitrile purification apparatus can be achieved. Additionally, because the amount of the decomposed acetonitrile is decreased, the amount of the waste water to be processed can be reduced, and the size of the waste water processing apparatus and the environmental load can be reduced.

[0038]

In order to separate and remove compounds lower in boiling point and compounds higher in boiling point than acetonitrile after the dehydration in the dehydration column 4, it is preferable to use two or more distillation columns. Specifically, first, low boiling-point compounds are separated and removed in the low-

boiling separation column 5 from the column top through a line 18, and the column bottom liquid in the low-boiling separation column 5 is transferred to the product column 6 through a line 19. Then, preferably, high boiling-point compounds are separated in the product column 6 from the column bottom thereof through a line 20, and purified acetonitrile is obtained from a line 21 of the column top.

[0039]

In the low-boiling separation column 5 and the product column 6, the reflux ratios and the withdrawn amounts of the low boiling-point compounds and the high boiling-point compounds can be appropriately determined so as to achieve the purification degree meeting the intended purpose. The reflux ratios of the low-boiling separation column 5 and the product column 6 are each preferably set at 1 or more and 50 or less, and more preferably set at 2 or more and 30 or less although the ratios depend on the intended purposes. The reflux ratio is defined as a value obtained by dividing the mass refluxed to the distillation column by the mass discharged to outside the distillation column. From the viewpoint of efficiently performing the separation and removal of the impurities by distillation, it is preferable to stably maintain the specified value of the reflux ratio during operation for the purpose of performing a purification to yield high-purity

acetonitrile. In each of the low-boiling separation column 5 and the product column 6, the lower limit of the pressure is set in such a way that the components to be separated in the distillation column concerned each exhibit an appropriate boiling point; thus, the lower limit of the pressure is, in terms of absolute pressure, preferably 0.05 MPa or more, more preferably 0.08 MPa or more and furthermore preferably 0.09 MPa or more. The upper limit of the pressure is, in terms of absolute pressure, preferably 0.27 MPa or less, more preferably 0.20 MPa or less and furthermore preferably 0.15 MPa or less. When the pressures are set within the preferable pressures, the column bottom temperature of each of the low-boiling separation column 5 and the product column 6 is preferably 80°C or more and 95°C or less, and more preferably 80°C or more and 88°C or less, and the column top temperature of each of the low-boiling separation column 5 and the product column 6 is preferably 70°C or more and 90°C or less, and more preferably 75°C or more and 85°C or less.

[0040]

Each of the low-boiling separation column 5 and the product column 6 is preferably a plate column or a packed column having a condenser at the column top and a reboiler at the column bottom. Examples of the plate column include a cross-current contact plate column having down comers and a counter-current contact plate

column having no down comers. As the opening of a tray, for example, a bubble cap-type opening, a porous plate-type opening and a valve-type opening can be used. The number of the stages of each of the distillation columns is not particularly limited as long as the number of stages is ten or more; the number of stages of each of the distillation columns is preferably 30 or more and 80 or less. As an example of the packed column, a column packed with an irregular packing material and/or a regular packing material as a packing material can be used. As the irregular packing material, for example, a Raschig ring, a Lessing ring, a Pall ring, a Berl saddle, an interlock saddle, a Tellerette packing, a Dixon ring or a McMahon packing can be used. As the regular packing material, a packing material having a network structure can be used. As the materials of these irregular and regular packing materials, for example, a porcelain material, a metallic material, a plastic material or a carbonaceous material can be used. The packed column can also increase the gas-liquid contact efficiency by installing a liquid redistribution plate at a position having an appropriate height.

[0041]

The pressure of the steam to be fed to the reboiler of each of the low-boiling separation column 5 and the product column 6 is set preferably at 1.0 MPaG or less and more preferably at 0.6 MPaG or less, from the

viewpoint of regulating the temperature difference from the liquid to be heated so as to be appropriate.

[0042]

As described above, in the present embodiment, the method for purifying acetonitrile preferably includes: a first step of obtaining a reaction solution by feeding crude acetonitrile obtained by an ammoxidation reaction, an alkali, and acetamide and/or acetic acid to a reaction vessel; and a second step of obtaining a distillate by distilling a mixed solution composed of the reaction solution and the acetamide and/or acetic acid.

[0043]

The method for producing high-purity acetonitrile in the present embodiment is a production method including the purification of acetonitrile by using the above-described purification method. In the method for producing high-purity acetonitrile, heretofore known methods can be used except the purification method of the present embodiment is used. Here, the "high purity" of the high-purity acetonitrile means the purity of 99.9% by mass or more.

Examples

[0044]

Hereinafter, the present invention is described in more detail with reference to Examples, but the present invention is not limited to these Examples.

[0045]

Gas chromatography was used for the measurement of the concentrations of acetonitrile, acrylonitrile, allyl alcohol, oxazole, propionitrile and acetamide, and the measurement conditions were as follows.

[0046]

The gas chromatograph HP-6890 manufactured by Hewlett-Packard Co. was used, and the column DB-624 manufactured by Agilent Technologies, Inc. was used. Specifically, the column was 60 m in length $\times$ 0.32 mm in inner diameter, and 5.0 μ m in wall thickness. As the detector, an FID was used, and as a carrier gas, helium was used.

[0047]

The column temperature conditions were as follows.

Initial temperature: 70°C

Initial time: 10 minutes

Temperature increase rate: 5.0°C/min

Intermediate temperature: 120°C

Post time: 10 min

Final temperature: 250°C

[0048]

The measurement of the concentration of hydrogen cyanide was performed by the silver nitrate titration method, the measurement of the concentration of ammonia was performed by ion chromatography, and the measurement

of the concentration of water was performed by the Karl-Fischer method.

[0049]

In the measurement of the concentration of acetic acid, in consideration of the probable conversion of a fraction of the acetic acid to alkali salts, the pH of the measurement sample was adjusted to pH 6 with sulfuric acid so as to dissociate the salts to yield acetic acid, and then the sample was analyzed by using the above-described gas chromatography.

[0050]

In the measurement of the concentration of sodium hydroxide, the concentration of the hydroxide ion was measured by neutralization titration with acetic acid, and the concentration of sodium hydroxide was derived from the concentration of the hydroxide ion. Moreover, the concentration of sodium ion was determined by ion chromatography, and the concentration of sodium hydroxide was derived from the concentration of sodium ion to confirm the above-described concentration of sodium hydroxide.

[0051]

In consideration of the susceptibility of the concentration of acetamide and the concentration of acetic acid to the temperature of the sample solution and the time required for analysis, analysis was performed in such a way that the sample solution was cooled after

sampling and at the same time, the analysis was performed quickly. These concentrations were sometimes presented as the total concentration of acetamide and acetic acid.
[0052]

The substances other than those described above were neither identified nor quantitatively determined, and the balance was assigned to these substances as other substances. In particular, in the reaction vessel 2, acrylonitrile and hydrogen cyanide react and polymerize to disappear independently or in a composite manner, and hence these products were counted as others.
[0053]

The analysis samples were obtained in necessary quantities from the nozzles installed in the specified lines in Figures 1 and 2 in such a way that the samples were deserved as the representative samples for the sampled sites, and the obtained samples were analyzed by the above-described methods.
[0054]

[Experimental Example 1]

In a mixer, 500 g of concentrated crude acetonitrile composed of 65% by mass of acetonitrile (MeCN) and 35% by mass of water, and 53.4 g of an alkali solution composed of water, sodium hydroxide and acetamide were charged to prepare a mixed solution. The mixed solution was maintained for 5 hours under stirring at 70°C. In the alkali solution, the concentration of sodium hydroxide

was 25% by mass and the concentration of acetamide was 1% by mass.

[0055]

The compositions of the respective solutions and the decomposition rate of acetonitrile (MeCN) are shown in Table 1. The decomposition rate of acetonitrile was specified as the value defined by the following formula.

Decomposition rate of acetonitrile (%) = (1 - mass of acetonitrile in reaction solution/mass of acetonitrile in concentrated crude acetonitrile) × 100

[0056]

[Table 1]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	313. 6	56.7	32.2	3.5
Ammonia	0.0	0.0	0.0	0.0	0.0	0.0	4.7	0.9	1.5	
Water	175.0	35.0	39. 5	74.0	214.5	38.8	209. 5	37.9	63.4	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	0.5	1.0	0.5	0.1	12.2	2.2	1.1	
Acetic acid	0.0	0.0	0.0	0.0	0.0	0.0				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0057]

[Experimental Example 2]

In the same manner as in Experimental Example 1, stirring was performed at 70°C for 5 hours except that the concentration of acetic acid in the alkali solution

was set at 3% by mass. The compositions of the respective solutions and the decomposition rate of acetonitrile are shown in Table 2.

[0058]

[Table 2]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	314. 5	56.8	32.4	3.2
Ammonia	0.0	0.0	0.0	0.0	0.0	0.0	4.4	0.8	1.4	
Water	175.0	35.0	38. 4	72.0	213.4	38.6	208. 8	37.7	63.3	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	0.0	0.0	0.0	0.0	12.4	2.2	1.1	
Acetic acid	0.0	0.0	1.6	3.0	1.6	0.3				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0059]

[Experimental Example 3]

In the same manner as in Experimental Example 1, stirring was performed at 70°C for 5 hours except that the concentrations of acetamide and acetic acid in the alkali solution were set at 5.0% by mass and 4.0% by mass, respectively. The compositions of the respective solutions and the decomposition rate of acetonitrile are shown in Table 3.

[0060]

[Table 3]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	317. 7	57.4	32.9	2.2
Ammonia	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.5	1.0	
Water	175.0	35.0	35. 2	66.0	210.2	38.0	207. 0	37.4	63.2	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	2.7	5.0	2.7	0.5	12.3	2.2	1.1	
Acetic acid	0.0	0.0	2.1	4.0	2.1	0.4				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0061]

[Experimental Example 4]

In the same manner as in Experimental Example 1, stirring was performed at 70°C for 5 hours except that the concentrations of acetamide and acetic acid in the alkali solution were set at 7.0% by mass and 8.0% by mass, respectively. The compositions of the respective solutions and the decomposition rate of acetonitrile are shown in Table 4.

[0062]

[Table 4]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	320. 9	58.0	33.5	1.3
Ammonia	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.3	0.5	
Water	175.0	35.0	32. 0	60.0	207.0	37.4	205. 3	37.1	63.0	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	3.7	7.0	3.7	0.7	12.2	2.2	1.1	
Acetic acid	0.0	0.0	4.3	8.0	4.3	0.8				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0063]

[Example 1]

By using the purification apparatus shown in Figure 2, the purification of acetonitrile was performed. Crude acetonitrile which contained acetonitrile, a by-product of the ammoxidation reaction of propylene, in a content of 15% by mass was fed from the line 7 to the acetonitrile concentration column 1. Hydrogen cyanide was separated and removed from the line 8, and a part of the water was separated and removed from the line 9. Vapor was withdrawn from the line 10 and condensed in the not shown condenser installed in the line 10 to yield concentrated crude acetonitrile which contained acetonitrile in a content of 65% by mass. The other composition components in the concentrated crude acetonitrile were 32% by mass of water, 1.1% by mass of

hydrogen cyanide, 360 ppm by mass of acrylonitrile, and 100 ppm by mass of ammonia; additionally, allyl alcohol, oxazole, propionitrile and the like were contained.

[0064]

To the reaction vessel 2, 2580 kg/h of the concentrated crude acetonitrile was fed through the line 10. To the reaction vessel 2, 230 kg/h of the below-described column bottom liquid of the dehydration column 4 was added from the line 11, and the resulting mixture was allowed to react at 73°C for 8 hours.

[0065]

To the high-boiling separation column 3, 2810 kg/h of the reaction solution in the reaction vessel 2 was transferred through the line 12. Into the reboiler installed at the column bottom, 2.8 t/h of a steam at 0.4 MPaG was made to flow and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 235 mmHg and 255mmHg, respectively; the column top temperature and the column bottom temperature were 41.5°C and 58.9°C, respectively. From the column bottom, 770 kg/h of a liquid which contained allyl alcohol, propionitrile, sodium hydroxide, water and others was withdrawn and subjected to waste water treatment. The vapor distilled from the column top was condensed in the condenser. Into the high-boiling separation column 3, 3940 kg/h of the condensate was refluxed, and 2040 kg/h of the distillate was fed from

the line 14, after being cooled with a not shown heat exchanger, to the lower portion of the dehydration column 4.

[0066]

From the line 15 in the upper portion of the dehydration column 4, 300 kg/h of a 48% by mass of sodium hydroxide aqueous solution at a temperature of 80°C was fed and brought into liquid-liquid contact with the distillate at a temperature of 7.1°C fed from the line 14. The dehydration column 4 was provided with a jacket on the outer circumference thereof, so as to have a structure allowing cooling thereof. From the column bottom of the dehydration column 4, the aqueous phase was withdrawn, 230 kg/h of the withdrawn aqueous phase was fed from the line 11 to the reaction vessel 2. The rest of the column bottom liquid was transferred from the line 16 to the not shown waste water processing apparatus and processed. The amount withdrawn from the line 16 was balanced at 260 kg/h. From the line 17, 1850kg/h of the acetonitrile phase at 25.9°C was withdrawn.

[0067]

The material balance of the reaction vessel 2 was sampled, and the obtained results are as shown in Table 5.

[0068]

[Table 5]

	Line 10		Line 11		Line 12			Decomposition rate of MeCN %
	kg/h	wt%	kg/h	wt%	kg/h	wt%	mol%	
Acetonitrile	1677.00	65.00	1.15	0.50	1649.62	58.71	40.87	1.7
Acrylonitrile	0.93	0.04	0.00	0.00	0.001	0.4ppm	0.00	
Ammonia	0.26	0.01	2.23	0.97	14.32	0.51	0.86	
Hydrogen cyanide	28.38	1.10	0.00	0.00	0.003	0.9ppm	0.00	
Water	825.60	32.00	142.98	62.17	956.06	34.02	53.96	
Sodium hydroxide	0.00	0.00	52.35	22.76	52.35	1.86	1.33	
Acetic acid and acetamide	0.00	0.00	31.27	13.59	60.49	2.15	1.02	
Others	47.83	1.85	0.02	0.01	77.16	2.75	1.96	
Total	2580	100	230	100	2810	100	100	

[0069]

[Example 2]

The operations were performed under the same conditions as in Example 1 except that the temperature of a 48% by mass of sodium hydroxide aqueous solution fed from the line 15 was set at 65°C. The material balance of the reaction vessel 2 was sampled, and the obtained results are as shown in Table 6.

[0070]

[Table 6]

	Line 10		Line 11		Line 12			Decomposition rate of MeCN %
	kg/h	wt%	kg/h	wt%	kg/h	wt%	mol%	
Acetonitrile	1677.00	65.00	1.04	0.45	1642.80	58.46	40.61	2.1
Acrylonitrile	0.93	0.04	0.00	0.00	0.001	0.5ppm	0.00	
Ammonia	0.26	0.01	1.96	0.85	16.82	0.60	1.00	
Hydrogen cyanide	28.38	1.10	0.00	0.00	0.003	0.9ppm	0.00	
Water	825.60	32.00	150.51	65.44	960.64	34.19	54.09	
Sodium hydroxide	0.00	0.00	52.69	22.91	52.69	1.88	1.34	
Acetic acid and acetamide	0.00	0.00	23.78	10.34	59.88	2.13	1.01	
Others	47.83	1.85	0.02	0.01	77.16	2.75	1.96	
Total	2580	100	230	100	2810	100	100	

[0071]

[Example 3]

The operations were performed under the same conditions as in Example 1 except that the temperature of a 48% by mass of sodium hydroxide aqueous solution fed from the line 15 was set at 45°C. The material balance of the reaction vessel 2 was sampled, and the obtained results are as shown in Table 7.

[0072]

[Table 7]

	Line 10		Line 11		Line 12			Decomposition rate of MeCN
	kg/h	wt%	kg/h	wt%	kg/h	wt%	mol%	%
Acetonitrile	1677.00	65.00	1.29	0.56	1633.81	58.14	40.28	2.7
Acrylonitrile	0.93	0.04	0.00	0.00	0.001	0.5ppm	0.00	
Ammonia	0.26	0.01	1.82	0.79	20.52	0.73	1.22	
Hydrogen cyanide	28.38	1.10	0.00	0.00	0.003	1.0ppm	0.00	
Water	825.60	32.00	159.32	69.27	965.40	34.36	54.21	
Sodium hydroxide	0.00	0.00	52.03	22.62	52.03	1.85	1.31	
Acetic acid and acetamide	0.00	0.00	15.50	6.74	61.06	2.17	1.03	
Others	47.83	1.85	0.05	0.02	77.18	2.75	1.95	
Total	2580	100	230	100	2810	100	100	

[0073]

[Example 4]

The acetonitrile phase withdrawn from the line 17 in Example 1 was fed to the low-boiling separation column 5. Into the reboiler of the low-boiling separation column 5, 2.6 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1172 MPa and 0.1181 MPa, respectively; the column top temperature and the column bottom temperature were 78.8°C and 86.4°C, respectively. The vapor distilled from the column top was condensed in the condenser. As the cooling medium for the condenser, water set at 28°C was used. Into the low-boiling separation column 5, 4150 kg/h of the condensate was refluxed, 300 kg/h of the condensate was withdrawn from the line 18, and thus

oxazole and low boiling-point substances were removed. The liquid in the line 18 was subjected to waste water treatment. To the product column 6, 1550 kg/h of the liquid withdrawn from the line 19 was fed.

[0074]

Into the reboiler of the product column 6, 1.6 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1100 MPa and 0.1112 MPa, respectively; the column top temperature and the column bottom temperature were 81.2°C and 82.2°C, respectively. From the line 20, 70 kg/h of a liquid which contained propionitrile and high boiling-point substances was withdrawn and subjected to waste water treatment. The vapor distilled from the column top was condensed in the condenser and made to flow down into the reflux drum. As the cooling medium for the condenser, water set at 28°C was used. Into the product column 6, 4380 kg/h of the condensate in the reflux drum was refluxed by using a pump, 1480 kg/h of the condensate was withdrawn from the line 21, and thus high-purity acetonitrile obtained by purification was obtained.

[0075]

The impurities in the high-purity acetonitrile were analyzed, and the results shown in Table 8 were obtained.

[0076]

[Table 8]

Acrylonitrile	(ppm)	1.2
Allyl alcohol	(ppm)	0.3
Oxazole	(ppm)	1.6
Ammonia	(ppm)	1.3
Hydrogen cyanide	(ppm)	0.8
Propionitrile	(ppm)	33

[0077]

[Example 5]

The operations were performed under the same conditions as in Example 4 except that the acetonitrile phase withdrawn from the line 17 in Example 2 was fed to the low-boiling separation column 5.

[0078]

From the line 21, 1484 kg/h of the high-purity acetonitrile obtained by purification was withdrawn. The impurities in the high-purity acetonitrile were analyzed, and the results shown in Table 9 were obtained.

[0079]

[Table 9]

Acrylonitrile	(ppm)	1.1
Allyl alcohol	(ppm)	0.2
Oxazole	(ppm)	1.4
Ammonia	(ppm)	0.7
Hydrogen cyanide	(ppm)	0.8
Propionitrile	(ppm)	36

[0080]

[Example 6]

The operations were performed under the same conditions as in Example 4 except that the acetonitrile phase withdrawn from the line 17 in Example 3 was fed to the low-boiling separation column 5.

[0081]

From the line 21, 1485 kg/h of the high-purity acetonitrile obtained by purification was withdrawn. The impurities in the high-purity acetonitrile were analyzed, and the results shown in Table 10 were obtained.

[0082]

[Table 10]

Acrylonitrile	(ppm)	1.2
Allyl alcohol	(ppm)	0.3
Oxazole	(ppm)	1.4
Ammonia	(ppm)	0.5
Hydrogen cyanide	(ppm)	0.7
Propionitrile	(ppm)	32

[0083]

[Comparative Experimental Example 1]

In a mixer, 500 g of concentrated crude acetonitrile composed of 65% by mass of acetonitrile and 35% by mass of water, and 53.4 g of an alkali solution composed of water and sodium hydroxide were charged to prepare a mixed solution. The mixed solution was maintained for 5 hours under stirring at 70°C. The compositions of the respective solutions and the decomposition rate of acetonitrile are shown in Table 11.

[0084]

[Table 11]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	313. 0	56.6	32.1	3.7
Ammonia	0.0	0.0	0.0	0.0	0.0	0.0	5.0	0.9	1.6	
Water	175.0	35.0	40. 1	75.0	215.1	38.9	209. 8	37.9	63.4	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	0.0	0.0	0.0	0.0	12.3	2.2	1.1	
Acetic acid	0.0	0.0	0.0	0.0	0.0	0.0				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0085]

[Comparative Experimental Example 2]

In a mixer, 500 g of concentrated crude acetonitrile composed of 65% by mass of acetonitrile and 35% by mass of water, and 53.4 g of an alkali solution composed of water, sodium hydroxide and ammonia were charged to prepare a mixed solution. The mixed solution was maintained for 5 hours under stirring at 70°C. The compositions of the respective solutions and the decomposition rate of acetonitrile are shown in Table 12.

[0086]

[Table 12]

	Concentrate d MeCN solution		Alkali solution		Mixed solution (calculated)		Reaction solution			Decompositio n rate of MeCN %
	g	wt%	g	wt%	g	wt%	g	wt%	mol%	
Acetonitril e	325.0	65.0	0.0	0.0	325.0	58.7	313. 1	56.6	32.1	3.7
Ammonia	0.0	0.0	0.5	1.0	0.5	0.1	5.5	1.0	1.8	
Water	175.0	35.0	39. 5	74.0	214.5	38.8	209. 3	37.8	63.2	
Sodium hydroxide	0.0	0.0	13. 4	25.0	13.4	2.4	13.4	2.4	1.8	
Acetamide	0.0	0.0	0.0	0.0	0.0	0.0	12.2	2.2	1.1	
Acetic acid	0.0	0.0	0.0	0.0	0.0	0.0				
Total	500.0	100.0	53. 4	100. 0	553.4	100.0	553. 4	100. 0	100. 0	

[0087]

[Comparative Example 1]

By using the purification apparatus shown in Figure 1, the purification of acetonitrile was performed. The column bottom liquid of the dehydration column 4 was wholly withdrawn from the line 16 and transferred to the waste water processing apparatus, and to the reaction vessel 2, a sodium hydroxide aqueous solution was added from the line 11. Acetonitrile was purified with the same apparatus as in Example 1 except for these.

[0088]

A liquid which contained crude acetonitrile, a by-product of the ammoxidation reaction of propylene, in a content of 15% by mass was fed from the line 7 to the acetonitrile concentration column 1. Hydrogen cyanide was separated and removed from the line 8, and a part of

the water was separated and removed from the line 9. Vapor was withdrawn from the line 10 and condensed in the not shown condenser installed in the line 10 to yield concentrated crude acetonitrile which contained acetonitrile in a content of 65% by mass. The other composition components in the concentrated crude acetonitrile were 32% by mass of water, 1.1% by mass of hydrogen cyanide, 360 ppm by mass of acrylonitrile, and 100 ppm by mass of ammonia; additionally, allyl alcohol, oxazole, propionitrile and the like were contained.

[0089]

To the reaction vessel 2, 2580 kg/h of the concentrated crude acetonitrile was fed through the line 10. To the reaction vessel 2, 180 kg/h of a 48% by mass of sodium hydroxide aqueous solution was added from the line 11, and the resulting mixture was allowed to react at 73°C for 8 hours.

[0090]

To the high-boiling separation column 3, 2760 kg/h of the reaction solution in the reaction vessel 2 was transferred through the line 12. Into the reboiler installed at the column bottom, 2.8 t/h of a steam at 0.4 MPaG was made to flow and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 235 mmHg and 255mmHg, respectively; the column top temperature and the column bottom temperature were 41.5°C and 58.9°C, respectively.

From the column bottom, 790 kg/h of a liquid which contained allyl alcohol, propionitrile, sodium hydroxide, water and others was withdrawn and subjected to waste water treatment. The vapor distilled from the column top was condensed in the condenser. Into the high-boiling separation column 3, 3940 kg/h of the condensate was refluxed, and 1970 kg/h of the distillate was fed from the line 14, after being cooled with a not shown heat exchanger, to the lower portion of the dehydration column 4.

[0091]

From the line 15 in the upper portion of the dehydration column 4, 300 kg/h of a 48% by mass of sodium hydroxide aqueous solution at a temperature of 50°C was fed and brought into liquid-liquid contact with the distillate at a temperature of 7.3°C fed from the line 14. The dehydration column 4 was provided with a jacket on the outer circumference thereof, so as to have a structure allowing cooling thereof. From the column bottom of the dehydration column 4, 475 kg/h of the aqueous phase was withdrawn, and transferred from the line 16 to the not shown waste water processing apparatus and processed. The temperature of the aqueous phase was 15.5°C.

[0092]

From the line 17, 1795 kg/h of the acetonitrile phase was withdrawn and fed to the low-boiling separation

column 5. The temperature of the acetonitrile phase was 25.7°C.

[0093]

The material balance of the reaction vessel 2 was sampled, and the obtained results are as shown in Table 13.

[0094]

[Table 13]

	Line 10		Line 11		Line 12			Decomposition rate of MeCN
	kg/h	wt%	kg/h	wt%	kg/h	wt%	mol%	%
Acetonitrile	1677.00	65.00	0.00	0.00	1619.98	58.70	41.31	3.4
Acrylonitrile	0.93	0.04	0.00	0.00	0.001	0.5ppm	0.00	
Ammonia	0.26	0.01	0.00	0.00	23.90	0.87	1.47	
Hydrogen cyanide	28.38	1.10	0.00	0.00	0.003	1ppm	0.00	
Water	825.60	32.00	93.60	52.00	894.17	32.40	51.93	
Sodium hydroxide	0.00	0.00	86.40	48.00	86.40	3.13	2.26	
Acetic acid and acetamide	0.00	0.00	0.00	0.00	58.41	2.12	1.02	
Others	47.83	1.85	0.00	0.00	77.14	2.79	2.02	
Total	2580	100	180	100	2760	100	100.00	

[0095]

[Comparative Example 2]

The acetonitrile phase withdrawn from the line 17 in Comparative Example 1 was fed to the low-boiling separation column 5. Into the reboiler of the low-boiling separation column 5, 2.5 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1172 MPa and

0.1181 MPa, respectively; the column top temperature and the column bottom temperature were 78.8°C and 86.4°C, respectively. The vapor distilled from the column top was condensed in the condenser. As the cooling medium for the condenser, water set at 28°C was used. Into the low-boiling separation column 5, 4150 kg/h of the condensate was refluxed, 300 kg/h of the condensate was withdrawn from the line 18, and thus oxazole and low boiling-point substances were removed. The liquid in the line 18 was subjected to waste water treatment. To the product column 6, 1495 kg/h of the liquid withdrawn from the line 19 was fed.

[0096]

Into the reboiler of the product column 6, 1.6 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1100 MPa and 0.1112 MPa, respectively; the column top temperature and the column bottom temperature were 81.2°C and 82.2°C, respectively. From the line 20, 70 kg/h of a liquid which contained propionitrile and high boiling-point substances was withdrawn and subjected to waste water treatment. The vapor distilled from the column top was condensed in the condenser and made to flow down into the reflux drum. As the cooling medium for the condenser, water set at 28°C was used. Into the product column 6, 4380 kg/h of the condensate in the reflux drum was

refluxed by using a pump, 1425 kg/h of the condensate was withdrawn from the line 21, and thus high-purity acetonitrile obtained by purification was obtained.

[0097]

The impurities in the high-purity acetonitrile were analyzed, and the results shown in Table 14 were obtained.

[0098]

[Table 14]

Acrylonitrile	(ppm)	1.2
Allyl alcohol	(ppm)	0.3
Oxazole	(ppm)	1.6
Ammonia	(ppm)	2.1
Hydrogen cyanide	(ppm)	0.8
Propionitrile	(ppm)	33

[0099]

[Example 7]

Purification of acetonitrile was performed by feeding crude acetonitrile which contained acetonitrile, a by-product of the ammoxidation reaction of propane, in a content of 12% by mass to the same apparatus as in Example 1.

[0100]

The crude acetonitrile was fed from the line 7 to the acetonitrile concentration column 1. Hydrogen cyanide was separated and removed from the line 8, and a part of water was separated from the line 9. Vapor was withdrawn from the line 10, condensed in the not shown condenser installed in the line 10 to yield concentrated

crude acetonitrile which contained acetonitrile in a content of 65% by mass. The other composition components in the concentrated crude acetonitrile were 32% by mass of water, 1.3% by mass of hydrogen cyanide, 350 ppm by mass of acrylonitrile, and 100 ppm by mass of ammonia; additionally, allyl alcohol, propionitrile and the like were contained.

[0101]

To the reaction vessel 2, 2580 kg/h of the concentrated crude acetonitrile was fed through the line 10. To the reaction vessel 2, 230 kg/h of the below-described column bottom liquid of the dehydration column 4 was added from the line 11, and the resulting mixture was allowed to react at 73°C for 8 hours.

[0102]

To the high-boiling separation column 3, 2810 kg/h of the reaction solution in the reaction vessel 2 was transferred through the line 12. Into the reboiler installed at the column bottom, 2.8 t/h of a steam at 0.4 MPaG was made to flow and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 235 mmHg and 255mmHg, respectively; the column top temperature and the column bottom temperature were 41.5°C and 58.9°C, respectively. From the column bottom, 770 kg/h of a liquid which contained allyl alcohol, propionitrile, sodium hydroxide, water and others was withdrawn and subjected to waste

water treatment. The vapor distilled from the column top was condensed in the condenser. Into the high-boiling separation column 3, 3940 kg/h of the condensate was refluxed, and 2040 kg/h of the distillate was fed from the line 14, after being cooled with a not shown heat exchanger, to the lower portion of the dehydration column 4.

[0103]

From the line 15 in the upper portion of the dehydration column 4, 300 kg/h of a 48% by mass of sodium hydroxide aqueous solution at a temperature of 50°C was fed and brought into liquid-liquid contact with the distillate at a temperature of 7.1°C fed from the line 14. The dehydration column 4 was provided with a jacket on the outer circumference thereof, so as to have a structure allowing cooling thereof. From the column bottom of the dehydration column 4, the aqueous phase was withdrawn, 230 kg/h of the withdrawn aqueous phase was fed from the line 11 to the reaction vessel 2. The rest of the column bottom liquid was transferred from the line 16 to the not shown waste water processing apparatus and processed. The amount withdrawn from the line 16 was balanced at 260 kg/h.

[0104]

From the line 17, 1850kg/h of the acetonitrile phase at 25.9°C was withdrawn. The material balance of the

reaction vessel 2 was sampled, and the obtained results are as shown in Table 15.

[0105]

[Table 15]

	Line 10		Line 11		Line 12			Decomposition rate of MeCN
	kg/h	wt%	kg/h	wt%	kg/h	wt%	mol%	%
Acetonitrile	1682.16	65.20	1.15	0.50	1644.59	58.53	40.62	2.3
Acrylonitrile	0.90	0.04	0.00	0.00	0.001	0.5ppm	0.00	
Ammonia	0.26	0.01	1.89	0.82	18.20	0.65	1.08	
Hydrogen cyanide	33.54	1.30	0.00	0.00	0.003	1ppm	0.00	
Water	825.60	32.00	153.53	66.75	962.13	34.24	54.12	
Sodium hydroxide	0.00	0.00	53.08	23.08	53.08	1.89	1.34	
Acetic acid and acetamide	0.00	0.00	20.33	8.84	59.99	2.13	1.01	
Others	37.54	1.46	0.02	0.01	72.00	2.56	1.82	
Total	2580	100	230	100	2810	100	100.00	

[0106]

[Example 8]

The acetonitrile phase withdrawn from the line 17 in Example 7 was fed to the low-boiling separation column 5. Into the reboiler of the low-boiling separation column 5, 2.6 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1172 MPa and 0.1181 MPa, respectively; the column top temperature and the column bottom temperature were 78.8°C and 86.4°C, respectively. The vapor distilled from the column top was condensed in the condenser. As the cooling medium for the condenser, water set at 28°C

was used. Into the low-boiling separation column 5, 4150 kg/h of the condensate was refluxed, 300 kg/h of the condensate was withdrawn from the line 18, and thus low boiling-point substances were removed. The liquid in the line 18 was subjected to waste water treatment. To the product column 6, 1550 kg/h of the liquid withdrawn from the line 19 was fed.

[0107]

Into the reboiler of the product column 6, 1.6 t/h of a steam at 0.4 MPaG was made to flow, and distillation was performed. The column top pressure and the column bottom pressure were, in terms of absolute pressure, 0.1100 MPa and 0.1112 MPa, respectively; the column top temperature and the column bottom temperature were 81.2°C and 82.2°C, respectively. From the line 20, 70 kg/h of a liquid which contained propionitrile and high boiling-point substances was withdrawn and subjected to waste water treatment. The vapor distilled from the column top was condensed in the condenser and made to flow down into the reflux drum. As the cooling medium for the condenser, water set at 28°C was used. Into the product column 6, 4380 kg/h of the condensate in the reflux drum was refluxed by using a pump, 1486 kg/h of the condensate was withdrawn from the line 21, and thus high-purity acetonitrile obtained by purification was obtained.

[0108]

The impurities in the high-purity acetonitrile were analyzed, and the results shown in Table 16 were obtained.

[0109]

[Table 16]

Acrylonitrile	(ppm)	0.9
Allyl alcohol	(ppm)	0.3
Oxazole	(ppm)	0.0
Ammonia	(ppm)	0.5
Hydrogen cyanide	(ppm)	0.7
Propionitrile	(ppm)	44

[0110]

As can be seen from the above-described results of Examples and Comparative Examples, in a process performing a purification to yield high-purity acetonitrile, by feeding acetamide and/or acetic acid to the reaction vessel 2, the recovery rate of acetonitrile can be improved without causing any change in the quality of the high-purity acetonitrile. As can also be seen from the same results as described above, by utilizing column bottom liquid of the dehydration column 4 as the alkali source of the reaction vessel 2, the amount used of alkali can be reduced.

[0111]

The present application is based on Japanese Patent Application (Japanese Patent Application No. 2012-192215) filed on August 31, 2012, and the contents thereof are incorporated herein by reference.

Industrial Applicability

[0112]

The method for purifying acetonitrile of the present invention is a process requiring small amount of waste water to be processed and small amounts used of the chemicals used for purification, and is a process being simple in purification equipment and also in process. The method of the present invention can efficiently perform a purification to yield high-purity acetonitrile usable in the applications such as a solvent for synthesis and purification of pharmaceutical intermediates, a solvent for synthesis and purification of DNA, a solvent for synthesis of organic EL materials, and a cleaning solvent for electronic components.

Reference Signs List

[0113]

- 1: Acetonitrile concentration column
- 2: Reaction vessel
- 3: High-boiling separation column
- 4: Dehydration column
- 5: Low-boiling separation column
- 6: Product column
- 7 to 21: Lines

Claims

[Claim 1]

A method for purifying acetonitrile, comprising:
obtaining a reaction solution by feeding crude acetonitrile obtained by an ammoxidation reaction and an alkali to a reaction vessel;
obtaining a distillate by distilling the reaction solution; and
feeding acetamide and/or acetic acid to the reaction vessel.

[Claim 2]

The method for purifying acetonitrile according to claim 1, further comprising a step wherein the reaction solution is introduced into a distillation column and high-boiling substance is removed, in the step of obtaining the distillate by distilling the reaction solution, thereafter the obtained distillate is fed to a dehydration column, and an alkali aqueous solution is then added to the dehydration column and an aqueous phase is separated.

[Claim 3]

The method for purifying acetonitrile according to claim 2, wherein the alkali fed to the reaction vessel comprises a part of the aqueous phase.

[Claim 4]

The method for purifying acetonitrile according to claim 2 or 3, further comprising adding, at 40°C or higher and 90°C or lower, the alkali aqueous solution to the dehydration column.

[Claim 5]

A method for producing high-purity acetonitrile, comprising purifying acetonitrile by using the method for purifying acetonitrile according to any one of claims 1 to 4.