

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.

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,

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

Crude acetonitrile, obtained as a by-product at the time of production of acrylonitrile or methacrylonitrile, includes: impurities such as allyl alcohol, oxazole, water, acetone, hydrocyanic acid, acrylonitrile, methacrylonitrile, propionitrile, cis- and trans-crotonitrile, acrylic acid, methyl acrylate, methacrylic acid, methyl methacrylate, acetic acid, acrolein, methacrolein, acetone and ammonia; and unanalyzable impurities.

[0003]

There have hitherto been proposed methods for 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.

Patent Literature 1 discloses a method for dehydrating acetonitrile in which an alkali is added to and mixed with aqueous acetonitrile in an amount sufficient to extract the water present in the aqueous acetonitrile, and then the separated aqueous phase is removed. Patent Literature 2 presents a description about an increase in production of acetonitrile, and discloses a method in which at the time of production of an unsaturated nitrile and acetonitrile by ammoxidation,

acetone or ethyl alcohol, or both of these are allowed to be present concomitantly in the reaction system.

Citation List

Patent Literature

[0004]

Patent Literature 1: Japanese Patent Laid-Open No. S55-153757

Patent Literature 2: Japanese Patent Laid-Open No. H03-246269

Summary of Invention

Technical Problem

[0005]

According to the method described in Patent Literature 1 or 2, although it is possible to produce high-purity acetonitrile, it is necessary to go through a plurality of processing steps in order to achieve a high purity, and hence many facilities are required. Consequently, the energy consumption required for purification (for example, the energies for generating the vapor for heating a distillation column, and the cooling water for the column top flow) is increased to significantly increase the cost. When a commonly-performed method for reducing the energy consumption such as a utilization of waste heat is simply applied to the purification process of acetonitrile, there occurs a

problem such that a disturbance such as a variation of the temperature or pressure occurs in an apparatus giving and receiving heat, to effect troubles such as the increase of the impurity concentration in the purification and the destabilization of the quality, and hence the obtained acetonitrile cannot be supplied to the users requiring high-purity acetonitrile. Accordingly, the present state of affairs is such that there has been desired a method small in energy consumption and capable of performing a purification to yield high-purity acetonitrile.

In view of such circumstances as described above, an object of the present invention is to provide a method capable of performing a purification to yield high-purity acetonitrile on the basis of a process small in energy consumption.

Solution to Problem

[0006]

The present inventors made a continuous diligent study in order to solve the above-described problems, and consequently have discovered that in the method for purifying, by using two or more distillation columns, crude acetonitrile collected in the process of producing acrylonitrile or methacrylonitrile by an ammoxidation method, the column top flow of a second distillation column can be utilized as a heat source for a reboiler

for a first distillation column. Thus, the present inventors have perfected the present invention by discovering that by utilizing this heat source, it is possible to provide a process small in the energy consumption used for the purification.

[0007]

Specifically, the present invention is as follows.

[1]

A method for purifying acetonitrile, including the steps of:

adding an alkali to water-containing acetonitrile produced by an ammoxidation reaction to react the alkali with the water-containing acetonitrile;

subsequently feeding a resulting reaction mixture to a first distillation column;

separating a mixture obtained by further mixing an alkali with a resulting distillate into an acetonitrile phase and an aqueous phase;

subsequently separating the aqueous phase; and

feeding the acetonitrile phase to a second distillation column,

wherein a distilled vapor from the second distillation column is used as a heat source for a reboiler of the first distillation column.

[2]

The method for purifying acetonitrile according to [1] above, wherein a part of the distilled vapor is fed

to the reboiler, and a rest of the distilled vapor is fed to a condenser connected to the second distillation column.

[3]

The method for purifying acetonitrile according to [1] or [2] above, wherein a feed rate of the distilled vapor to the reboiler is determined with reference to the reboiler pressure (on a distilled vapor side, gauge pressure) of the first distillation column and a column top pressure (gauge pressure) of the second distillation column.

[4]

The method for purifying acetonitrile according to [3] above, wherein the reboiler pressure of the first distillation column is set at a pressure equal to or less than 0.90 times the column top pressure of the second distillation column.

[5]

An apparatus for purifying acetonitrile, wherein a reaction vessel, a first distillation column, a dehydration column and a second distillation column are provided in this order;

after water-containing acetonitrile and an alkali are allowed to react with each other in the reaction vessel, a resulting reaction mixture is designed to flow into the first distillation column, a resulting distillate of the first distillation column is designed

to flow into the dehydration column, and a acetonitrile phase obtained in the dehydration column is designed to flow into the second distillation column; and

a distilled vapor of the second distillation column is used as a heat source for a reboiler of the first distillation column.

[6]

The apparatus for purifying acetonitrile according to [5] above, wherein a part of the distilled vapor is fed to the reboiler, and a rest of the distilled vapor is fed to a condenser connected to the second distillation column.

[7]

The apparatus for purifying acetonitrile according to [5] or [6] above, wherein a feed rate of the distilled vapor to the reboiler is determined with reference to a reboiler pressure (on a distilled vapor side, gauge pressure) of the first distillation column and a column top pressure (gauge pressure) of the second distillation column.

[8]

The apparatus for purifying acetonitrile according to [7] above, wherein the reboiler pressure of the first distillation column is equal to or less than 0.90 times the column top pressure of the second distillation column.

Advantageous Effects of Invention

[0008]

The method for purifying acetonitrile of the present invention enables to perform a purification to yield high-purity acetonitrile on the basis of a process small in energy consumption.

Brief Description of Drawings

[0009]

[Figure 1] Figure 1 shows an example of a schematic diagram of an apparatus for purifying acetonitrile in the present embodiment.

[Figure 2] Figure 2 shows a schematic diagram of an apparatus for feeding as a heat source at least a part of the vapor distilled from the column top of a product column to a reboiler of a high-boiling separation column.

[Figure 3] Figure 3 shows a schematic diagram of an apparatus for feeding as a heat source at least a part of the vapor distilled from the column top of a low-boiling separation column to the reboiler of the high-boiling separation column.

[Figure 4] Figure 4 shows a schematic diagram of an apparatus for feeding as a heat source at least a part of the column bottom liquid of the low-boiling separation column to the reboiler of the high-boiling separation column.

Description of Embodiments

[0010]

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.

[0011]

The method for purifying acetonitrile in the present embodiment includes the steps of: adding an alkali to water-containing acetonitrile produced by an ammoxidation reaction to react the alkali with the water-containing acetonitrile; subsequently feeding a resulting reaction mixture to a first distillation column; separating a mixture obtained by further mixing an alkali with a resulting distillate into an acetonitrile phase and an aqueous phase; and subsequently separating the aqueous phase and feeding the acetonitrile phase to a second

distillation column, wherein a distilled vapor from the second distillation column is used as a heat source for a reboiler of the first distillation column.

[0012]

The method for purifying acetonitrile in the present embodiment can be implemented, for example, by using the following apparatus for purifying acetonitrile.

An apparatus for purifying acetonitrile wherein: a reaction vessel, a first distillation column, a dehydration column and a second distillation column are provided in this order; after water-containing acetonitrile and an alkali are allowed to react with each other in the reaction vessel, the resulting reaction mixture is designed to flow into the first distillation column, the distillate of the first distillation column is designed to flow into the dehydration column, and the acetonitrile phase obtained in the dehydration column is designed to flow into the second distillation column; and the distilled vapor of the second distillation column is used as a heat source for the reboiler of the first distillation column.

[0013]

Figure 1 shows an example of a schematic diagram of an apparatus for purifying acetonitrile in the present embodiment. The apparatus shown in Figure 1 has a concentration column 1 into which crude acetonitrile is introduced, and 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.

[0014]

Crude acetonitrile is obtained 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, 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, propionitrile and ammonia.

[0015]

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 reboiler (not shown) at the column bottom thereof and a condenser (not shown) 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 gaseous acetonitrile (hereinafter, also referred to as the "concentrated acetonitrile") is withdrawn from the intermediate portion of the column (line 10). A line 10 is provided with a side-cut condenser (not shown), and the side-cut condenser is designed to condense the gaseous acetonitrile. The concentrated liquid acetonitrile flowing out from the side-cut condenser flows into a reaction vessel 2. The concentrated acetonitrile fed from concentration column 1 to the reaction vessel 2 usually has an acetonitrile concentration of 50 to 70% by mass, and includes in addition to acetonitrile other impurities such as 25 to 70% by mass of water, hydrogen cyanide and allyl alcohol.

[0016]

An alkali aqueous solution such as a sodium hydroxide aqueous solution or a potassium hydroxide aqueous solution is added to the reaction vessel 2 from a line 11 to convert acrylonitrile or hydrogen cyanide contained as an impurity in the concentrated acetonitrile into a polymer 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 20 to 80°C, and the reaction is allowed to proceed more preferably at 60 to 75°C for 1 to 15 hours and furthermore preferably at 60 to 75°C for 3 to 10 hours.

[0017]

The liquid flowing out from 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, polymers such as succinonitrile and the dimer, an alkali, 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 reboiler (not shown) for giving heat necessary for distillation is installed, and supplies the heat necessary for distillation. In the

high-boiling separation column 3, for the purpose of stably separating and removing allyl alcohol and propionitrile, the heat necessary for distillation is required to be constantly and stably supplied. The separation of allyl alcohol and propionitrile is particularly difficult, and allyl alcohol and propionitrile are preferably separated and removed as much as possible in the high-boiling separation column 3.

[0018]

The pressure in the high-boiling separation column 3 is, in terms of absolute pressure, preferably 80 to 300 mmHg and more preferably 100 to 250 mmHg from the viewpoint of separating the decomposition of high-boiling substances such as allyl alcohol and propionitrile 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 set within the above-described range, the temperature of the column bottom portion is preferably 45 to 65°C and more preferably 50 to 60°C, and the temperature of the column top portion is preferably 35 to 60°C and more preferably 40 to 50°C.

[0019]

An alkali sufficient in amount to extract the water present in the dehydration column 4 is added to and mixed in the dehydration column 4, in addition to the column top flow of the high-boiling separation column 3, then

the separated aqueous phase is removed from a line 16, and thus, the acetonitrile phase is obtained from a line 17. As the alkali, an aqueous solution or a solid of sodium hydroxide and/or potassium hydroxide is preferably used, and an aqueous solution of sodium hydroxide and/or potassium hydroxide is more preferably used.

[0020]

The extraction temperature in the dehydration column 4 is preferably 5°C to 60°C and more preferably 10°C to 35°C. 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.

[0021]

The amount used of the alkali is varied depending on the water content in the acetonitrile; usually, the amount used of the alkali falls usually within a range from 10 to 90% by mass and preferably within a range from 30 to 60% by mass in relation to 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 10% by mass or less and more preferably 3% by mass or less.

[0022]

In order to separate and remove compounds lower in boiling point and compounds higher in boiling point than acetonitrile after the dehydration, it is preferable to use two or more distillation columns. Specifically, preferably, first, low boiling-point compounds are separated and removed in the low-boiling separation column 5 from the column top through a line 18, the column bottom liquid in the low-boiling separation column 5 is transferred to the product column 6 through a line 19, then 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.

[0023]

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 to 50 and more preferably set at 2 to 30 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. The column top pressures of the low-boiling separation column 5 and the product column 6 are each set in the vicinity of normal pressure from the viewpoint of energy efficiency and impurity separation. The lower limit of each of the column top pressures is, in terms of absolute pressure, preferably 0.090 MPa or more, more preferably 0.095 MPa or more and furthermore preferably 0.100 MPa or more: the upper limit of each of the column top pressures is, in terms of absolute pressure, preferably 0.180 MPa or less, more preferably 0.150 MPa or less and furthermore preferably 0.130 MPa or less. When the column top pressures are set within the preferable range, the column bottom temperature of each of the low-boiling separation column 5 and the product column 6 is preferably 80 to 95°C and more preferably 80 to 88°C, and the column top temperature of each of the low-boiling separation column 5 and the product column 6 is preferably 70 to 90°C and more preferably 70 to 85°C.

[0024]

In the purification method in the present embodiment, at least a part of the vapor distilled from the column top of the product column 6 and/or the low-boiling

separation column 5 is fed as a heat source to the reboiler of the high-boiling separation column 3.

Figure 2 shows a schematic diagram of an apparatus for feeding as a heat source at least a part of the vapor distilled from the column top of the product column 6 to the reboiler 3b of the high-boiling separation column 3. In the example shown in Figure 2, the reboiler 3b is of a shell-tube type, and the distilled vapor from the column top of the product column 6 is fed to the shell side to heat the column bottom liquid of the high-boiling separation column 3 flowing through the tube side. In the high-boiling separation column 3, two reboilers (3a and 3b) are installed, the distilled vapor of the product column 6 is preferably introduced into the reboiler 3b, using the vapor concerned in a dedicated manner, of the high-boiling separation column 3, and another heat source is preferably supplied to the other reboiler 3a. The heat exchange with the column bottom liquid of the high-boiling separation column 3 occurs, and the vapor drain discharged from the reboiler of the high-boiling separation column 3 is made to pass through a heat exchanger such as a condenser, if necessary, cooled with water or the like, and then refluxed in and/or withdrawn into the product column 6.

[0025]

Figure 3 shows a schematic diagram of an apparatus for feeding as a heat source at least a part of the vapor

distilled from the column top of the low-boiling separation column 5 to the reboiler 3c of the high-boiling separation column 3. The apparatus shown in Figure 3 is the same as the example shown in Figure 2 except that the vapor distilled from the low-boiling separation column 5 is designed to be fed to the reboiler 3c of the high-boiling separation column 3, and hence, hereinafter, only the differences are described.

Depending on the design and the operation conditions such as the setting of the pressure inside the column, the column top temperature of the low-boiling separation column 5 is lower than the column top temperature of the product column 6 as the case may be; even in such a case, if the column top temperature of the low-boiling separation column 5 is higher than the column bottom temperature of the high-boiling separation column 3, the vapor distilled from the low-boiling separation column 5 can be used as a heat source. The column top vapor of the low-boiling separation column 5 contains low boiling-point components in high concentrations, and hence finds difficulty in being condensed in the reboiler 3c as the case may be as compared to the column top vapor of the product column 6, and hence it is a preferable aspect to set the reboiler temperature also in consideration of the composition of the column top flow.

[0026]

The preferable pressures and the preferable column top temperatures of the low-boiling separation column 5 and the product column 6 are described above; these affect the vapors distilled from these columns, and hence also from such viewpoints, there are preferable pressures and preferable column top temperatures. Specifically, for the purpose of utilizing the distilled vapor as a heat source, the temperature of the distilled vapor is required to be higher than the temperature of the column bottom liquid of the distillation column communicatively connected to the reboiler to which the distilled vapor is to be fed; accordingly, it is preferable to set the pressure of the distillation column also in consideration of realization of the intended column top temperature in accordance with such a viewpoint. Needless to say, the distilled vapor can also be used by decreasing the temperature of the column bottom liquid in the distillation column, and hence it is also useful to regulate the pressure of the distilled column to which the reboiler is connected. The situation in which the low-boiling separation column 5 and/or the product column 6 is operated under normal pressure or under a pressure close to normal pressure and the high-boiling separation column 3 effects reduced pressure distillation is a preferable aspect from the viewpoint of rendering the temperature of the distilled vapor higher than the

temperature of the column bottom liquid of the high-boiling separation column 3.

[0027]

As the reboilers (3b, 3c) through which distilled vapor is made for flow, idle apparatuses may be reused, or new reboilers may also be designed. In designing new reboilers, the new reboilers are designed according to the following approach.

First, from the flow rate of the distilled vapor and the enthalpy in the case of the total condensation of the vapor, the quantity of heat q capable of being supplied through the reboiler to the high-boiling separation column 3 is calculated. Successively, the heat transfer area is calculated in order to determine the size of the reboiler. The quantity of heat q is given by the product of the overall heat transfer coefficient U , the heat transfer area A and the temperature difference ΔT , namely $q = U \cdot A \cdot \Delta T$. As U , the actual value of the reboiler commonly used in chemical plants may be used, or may be estimated on the basis of a chemical engineering method. In the present embodiment, ΔT is the temperature difference between the temperature of the distilled vapor and the temperature of the column bottom liquid of the high-boiling separation column 3. ΔT is generated from the operation condition difference between the first distillation column and the second distillation column. The present embodiment takes as its object the

purification of the water-containing acetonitrile produced by the ammoxidation reaction, and hence the component proportions in the first distillation column and the second distillation column are not significantly varied. Accordingly, the conditions of the respective distillation columns are controlled so as to be approximately constant.

[0028]

In the purification of acetonitrile in the present embodiment, from the viewpoint of the separation of impurities and the energy efficiency, the temperature of the first distillation column and the temperature of the second distillation column are such that the column bottom temperature of the first distillation column is preferably 45 to 65°C and more preferably 50 to 60°C, and the column top temperature of the second distillation column is preferably 70 to 90°C and more preferably 70 to 85°C. Accordingly, ΔT is preferably 10 to 35°C and more preferably 15 to 25°C. Thus, the heat transfer area A is necessarily determined so as to fall within a specific range. The use of a reboiler having a heat transfer area A capable of covering the quantity of heat q necessary for distillation, with ΔT falling within a range from 10 to 35°C, enables a stable operation using the distilled vapor from the second distillation column as a heat source for the reboiler of the first distillation column.

[0029]

On the other hand, although the heat transfer area A takes a specified value when an idle apparatus is reused, the reboiler capable of covering the quantity of heat q necessary for distillation with ΔT falling within a range from 10 to 35°C enables a stable operation using the distilled vapor from the second distillation column as a heat source for the reboiler of the first distillation column.

[0030]

The use of at least a part of the vapor distilled from the low-boiling separation column 5 and/or the product column 6 as a heat source necessary for the distillation in the high-boiling separation column 3 is prevented from adversely affecting the precisions in the three columns concerned. The low-boiling separation column 5 and the product column 6 are each an apparatus for precisely distilling a liquid having an acetonitrile concentration of 95% by mass or more and 99% by mass or more. Examples of the adverse effect on the precision of the distillation include: a case where the disturbance in the low-boiling separation column 5 and/or the product column 6 providing the distilled vapor sometimes leads to the disturbance of the high-boiling separation column 3 using the distilled vapor; and a case where conversely the disturbance in the high-boiling separation column 3 sometimes possibly leads to the disturbance in the low-boiling separation column 5 and/or the product column 6.

Examples of the specific description of the mechanism of the transmission of the "disturbance" of a distillation column to another distillation column includes a case where a deviation (disturbance) from the intended value of the temperature and/or the pressure of the low-boiling separation column 5 and/or the product column 6 results in a variation of the amount of the vapor distilled from the distillation column thereof. Accordingly, the amount of the vapor fed as a heat source to the reboiler of the high-boiling separation column 3 is varied, and hence the variation of the quantity of heat supplied to the high-boiling separation column 3 is caused to occur in a chain-like manner. The occurrence of the variation of the reflux ratio or the like in the high-boiling separation column 3 results in an unstable distillation operation, and the precision of the distillation is adversely affected. The destabilization of the distillation in the high-boiling separation column 3 hinders sufficient separation and removal of allyl alcohol and propionitrile to fatally affect the quality of high-purity acetonitrile. Conversely, the disturbance of the temperature and/or pressure of the high-boiling separation column 3 causes a variation of the amount of the distilled vapor condensed in the shell side of the reboiler of the high-boiling separation column 3. The distilled vapor is condensed in the reboiler, and then introduced into the condenser of the low-boiling

separation column 5 and/or the product column 6 to be refluxed; accordingly, the variation of the condensed amount naturally causes the change of the reflux amount and the variation of the thermal load in the low-boiling separation column 5 and/or the product column 6. Consequently, the disturbance in the high-boiling separation column 3 is transmitted to the low-boiling separation column 5 and/or the product column 6, to adversely affect the stability of the column pressure. The low-boiling separation column 5 and the product column 6 are distillation columns for precisely distilling acetonitrile, and the disturbance of the distillation adversely affects the separation of the impurities in high-purity acetonitrile such as oxazole, hydrogen cyanide, water, ammonia, and other trace amounts of impurities.

[0031]

The disturbance of the distillation in the respective columns degrades the purity of the obtained acetonitrile, and hence the obtained acetonitrile loses the value as a product as the case may be. High-purity acetonitrile finds demands in applications as, in addition to an HPLC solvent, a solvent for synthesis and purification of DNA, a solvent for synthesis of organic EL materials, and a cleaning solvent for electronic components, and hence is desired to be high in purity as a product, and additionally, is desired to be free from

variation and constant in the concentrations of the impurities contained in trace amounts. From such a viewpoint as described above, the present inventors made a diligent study on the method for stabilizing the systems exchanging heat during the utilization of the distilled vapor of the distillation column.

[0032]

When the distilled vapor of the product column 6 is fed, to be used as a heat source, to the shell side of the reboiler 3b of the high-boiling separation column 3, from the viewpoint of the stability of the product column 6, it is preferable to stabilize the supplied quantity of heat in such a way that for the reboiler of the product column 6, the distilled vapor or the like of other distillation columns or the like is not used, but a certain flow rate of vapor from a utility feeding apparatus which is an apparatus solely generating and feeding vapor is made to flow through the reboiler of the product column 6. The pressure of the vapor fed from the utility feeding apparatus is preferably set at 1.0 MPaG or less and more preferably set at 0.6 MPaG or less, from the viewpoint of regulating the temperature difference from the body to be heated so as to be appropriate.

[0033]

The present inventors have discovered that the precision of the distillation purification can be maintained satisfactorily by regulating, so as to fall

within a specific range, the relation between the column top pressure of the distillation column feeding the distilled vapor and the pressure of the reboiler, through which the distilled vapor is made to flow, of the high-boiling separation column.

[0034]

The amount of the vapor distilled from the second distillation column (the low-boiling separation column 5 and the product column 6) and fed to the reboiler 3b of the first distillation column (the high-boiling separation column 3) is preferably determined with reference to the reboiler pressure (on the distilled vapor side, gauge pressure) of the first distillation column and the column top pressure (gauge pressure) of the second distillation column. In general, the gauge pressure represents a relative value of the pressure with reference to the atmospheric pressure taken to be zero, and hence when the distilled vapor is wholly condensed in the reboiler shell, the gauge pressure of the reboiler shell is zero. The gauge pressure of the reboiler shell can also be minus depending on the fluid temperature (the column bottom liquid temperature of the distillation column) of the reboiler tube side. From the viewpoint of stably performing continuous operation, a branch valve 6v is regulated in such a way that the pressure (gauge pressure) measured with a pressure gauge fixed to the shell side of the reboiler of the first distillation

column is preferably 0.90 or less times, more preferably 0.50 or less times and furthermore preferably 0.20 or less times the column top pressure (gauge pressure) of the second distillation column. The lower limit is not particularly limited; under the assumption of a case where the distilled vapor is wholly condensed, a realistic value of the lower limit is -0.1 or more times or zero or more times the column top pressure (gauge pressure) of the second distillation column. In below-described Examples, the column top pressure (gauge pressure) of the product column 6 is denoted by A and the shell pressure (gauge pressure) of the reboiler 3b is denoted by B, and the evaluation was performed in terms of the pressure ratio B/A.

[0035]

The fact that the ratio is small means that the difference is expanded. When the pressure difference is expanded, the flow of the vapor from the column top of the second distillation column to the reboiler of the first distillation column tends to be stabilized. When the flow of the vapor is stabilized, the supply of heat is stabilized, and the evaporation rate in the reboiler of the first distillation column is stabilized. Accordingly, the amount of the vapor ascending in the first distillation column is stabilized. The gas-liquid contact is repeated on the trays in the column, the vapor coming out from the column top is condensed in the

condenser and partially refluxed to the column. The stability of the gas-liquid contact is manifested in the pressure or the temperature in the column, and can be perceived, in particular, by observing the pressure variation. When the supply of the heat is stabilized, the variation of the pressure value of the first distillation column falls within $\pm 7\%$ of the median. Moreover, from the viewpoint of reducing the impurities in acetonitrile, the variation of the pressure value of the first distillation column is controlled so as to fall preferably within $\pm 5\%$ and more preferably within $\pm 3\%$. When the pressure variation is controlled so as to fall within $\pm 5\%$, the heat exchange between the vapor ascending and the liquid descending along the trays in the first distillation column occurs appropriately. Consequently, the impurities such as allyl alcohol and propionitrile to be separated in the first distillation column are concentrated in the column bottom and the amounts of the impurities distilled from the column top are remarkably reduced.

[0036]

The shell pressure of the reboiler 3b of the high-boiling separation column 3 depends on the condensation performance of the vapor in the shell, and the larger the heat transfer area of the reboiler 3b, the smaller the shell pressure tends to be. The heat transfer area of the reboiler 3b of the high-boiling separation column 3

is calculated by the above-described calculation to give an appropriate value and thus a new apparatus is preferably installed; an idle apparatus may also be reused. By regulating the feed rate of the distilled vapor with reference to the shell pressure of the reboiler 3b of the high-boiling separation column 3 and the column top pressure of the product column 6, the variation of the feed flow rate of the distilled vapor of the product column 6 to the reboiler 3b is suppressed, and consequently the heat supply rate in the reboiler 3b can be made constant, leading to the stabilization of the distillation purification of the high-boiling separation column 3. In other words, when the state of being uncondensed of the distilled vapor occurs sometimes and does not occur some other times, the pressure variation of the reboiler shell is caused, and the effect of the pressure variation is exerted to the product column 6, which is the feed source of the distilled vapor. Because stable condensation of the distilled vapor in the reboiler 3b and return of the mixture of the vapor and water with a predetermined gas/liquid ratio to the condenser of the product column 6 contribute to the stabilization of the whole system, the reboiler 3b pressure is adopted as an operation index for the stable condensation of the distilled vapor in the reboiler 3b. The reboiler pressure is appropriate as such an index because from the viewpoint of the flow of the fluid, the

reboiler pressure is required to be lower than the column top pressure of the product column 6 to feed the distilled vapor, and from the viewpoint of stable operation, the reboiler pressure is required to be stable in the pressure value.

[0037]

When the distilled vapor of the product column 6 is made to flow into the reboiler of the high-boiling separation column, the pressure relation between both columns affects the concentrations of allyl alcohol and propionitrile in the purified acetonitrile. Conceivably, the reasons for this are such that when the quantity of heat supplied to the high-boiling separation column 3 is unstable, the performance of the separation of allyl alcohol and propionitrile in the high-boiling separation column 3 is degraded, and due to the column pressure variation or the variation of the reflux amount in the product column 6, further the performance of the separation of propionitrile in the product column 6 is concomitantly degraded. Accordingly, the relation between the column top pressure of the product column 6 and the reboiler pressure of the high-boiling separation column 3 made to fall within the above-described preferable range facilitates the maintenance of the concentrations of allyl alcohol and propionitrile at low values.

[0038]

Also, similarly when the distilled vapor of the low-boiling separation column 5 is made to flow into the reboiler of the high-boiling separation column, the relation between the pressures of both columns affects the concentrations of allyl alcohol, propionitrile, oxazole and ammonia in the purified acetonitrile. As inferred by the present inventors, the reasons for this are such that on the basis of the same reasons as in the case of the product column 6, when the quantity of heat supplied to the high-boiling separation column 3 is unstable, the performance of the separation of allyl alcohol and propionitrile in the high-boiling separation column 3 is concomitantly degraded, and due to the column pressure variation or the variation of the reflux amount in the low-boiling separation column 5, the performance of the separation of oxazole, ammonia and the like in the low-boiling separation column 5 is concomitantly degraded. With respect to the pressure relation between both columns, a branch valve 5v is regulated in such a way that the pressure (gauge pressure) measured with a pressure gauge fixed to the shell side of the reboiler 3c of the high-boiling separation column 3 is preferably 0.90 or less times, more preferably 0.50 or less times and furthermore preferably 0.20 or less times the column top pressure (gauge pressure) of the low-boiling separation column 5. By regulating the relation between the column top pressure of the low-boiling separation column 5 and the

reboiler pressure of the high-boiling separation column 3 so as to fall within the above-described preferable range, the pressure in the high-boiling separation column is stabilized, and the variations of the pressure value of the first distillation column are regulated so as to fall within $\pm 7\%$, $\pm 5\%$ and $\pm 3\%$ of the median, respectively. Accordingly, a precise distillation in the first distillation column is enabled, and the concentrations of allyl alcohol, propionitrile, oxazole and ammonia in the purified acetonitrile are easily maintained at low values.

[0039]

The vapor drain produced in the reboiler 3b is stored in a vapor drain drum (not shown) installed, if necessary, and transferred to the condenser of the product column 6 by a pump (not shown). Preferably, in the gas phase section of the vapor drain drum, a vent line is installed if necessary, and the uncondensed gas is returned to the condenser of the product column 6. Into the condenser of the product column 6 flow the vapor drain, the uncondensed gas and the distilled vapor made to flow from the product column 6 through the branch valve 6v. As the coolant for the condenser of the product column 6, water set at 35°C or lower is used, and the condensation and cooling of the foregoing fluids are performed. The condensate flows downward into the reflux drum, a part of the condensate is returned to the product column 6, and the rest is withdrawn as the product

through the line 21. In the reflux drum, in order to withdraw the uncondensed gas, a vent line 21a is installed. Preferably, the uncondensed gas is guided into a scrubber, absorption treated with water and the like, and then released into the atmosphere.

[0040]

Similarly, the vapor drain produced in the reboiler 3c is stored in a vapor drain drum (not shown) installed, if necessary, and transferred to the condenser of the low-boiling separation column 5 by a pump (not shown). Preferably, in the gas phase section of the vapor drain drum, a vent line is installed if necessary, and the uncondensed gas is returned to the condenser of low-boiling separation column 5. Into the condenser of the low-boiling separation column 5 flow the vapor drain, the uncondensed gas and the distilled vapor made to flow from the low-boiling separation column 5 through the branch valve 5v. As the coolant for the condenser of the low-boiling separation column 5, water set at 35°C or lower is used, and the condensation and cooling of the foregoing fluids are performed. The condensate flows down into the reflux drum, a part of the condensate is returned to the low-boiling separation column 5, and the rest is withdrawn as the low boiling-point compounds through the line 18. In the reflux drum, in order to withdraw the uncondensed gas, a vent line 18a is installed. Preferably, the uncondensed gas is guided

into a scrubber, absorption treated with water and the like, and then released into the atmosphere.

[0041]

By using the vapor distilled from the low-boiling separation column 5 and/or the product column 6 as the heat source for the distillation in the high-boiling separation column 3, efficient use of energy is achieved as brought about by the reduction of the amount used of the vapor in the reboiler of the high-boiling separation column 3 and the reduction of the amount used of the cooling water in the condenser of the low-boiling separation column 5 and/or the product column 6, and additionally, the size reduction of the condenser of the low-boiling separation column 5 and/or the product column 6 can be achieved. The vapor distilled from the low-boiling separation column 5 and/or the product column 6 is made to flow into the dedicated reboiler, and then refluxed and withdrawn. By installing the dedicated reboiler, the respective columns can independently and stably supply heat to the high-boiling separation column 3, and the reflux to the low-boiling separation column 5 and/or the product column 6 can be performed without contamination. The reflux amount can also be stabilized, and the disturbance of the whole purification process of acetonitrile is hardly caused concomitantly.

[0042]

Each of the distillation columns 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 bubble-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 to 80. 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 or packing materials 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, for example, 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.

Examples

[0043]

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

For the measurement of the concentrations of the impurities in acetonitrile, gas chromatography was used and the measurement conditions were as follows.

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

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: 220°C

[0044]

[Comparative Example 1]

By using the purification apparatus shown Figure 1, the purification of acetonitrile was performed.

A liquid 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 condenser (not shown) installed in the line 10 to yield a liquid which contained acetonitrile in a content of 65% by mass. The other components were as follows: water: 32% by mass, hydrogen cyanide: 1.6% by mass, and the sum total of acrylonitrile, allyl alcohol, oxazole, propionitrile and others: 1.4% by mass.

The obtained liquid was fed through the line 10 to the reaction vessel 2. To the reaction vessel 2, a 48% by mass of sodium hydroxide aqueous solution was added from the line 11, and was allowed to react at 73°C for 8 hours.

To the high-boiling separation column 3, 2810 kg/h of the liquid 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 vapor 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. The

pressure variation in the high-boiling separation column was $\pm 1\%$ of the median taken as the above-described numerical value. 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 condensate was fed from the line 14 to the lower portion of the dehydration column 4.

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 was fed and brought into liquid-liquid contact with the water-containing crude acetonitrile fed from the line 14. From the line 16, the aqueous phase was withdrawn. From the line 17, 1850 kg/h of the acetonitrile phase was withdrawn and fed to the low-boiling separation column 5.

Into the reboiler of the low-boiling separation column 5, 2.6 t/h of a vapor 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 pressure variation in the low-boiling separation column was $\pm 1\%$ of

the median taken as the above-described numerical value. 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.

Into the reboiler of the product column 6, 1.6 t/h of a vapor 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. The pressure variation in the product column was $\pm 1\%$ of the median taken as the above-described numerical value. 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 purified acetonitrile was obtained.

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 1 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 2.

[0045]

[Table 1]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	2
Oxazole	(ppm)	1
Ammonia	(ppm)	0.5
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	45

[0046]

[Table 2]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	2.8
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	164
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.6
Amount of cooling water for condenser of product column	(t/h)	137

[0047]

[Example 1]

As shown in Figure 2, a reboiler 3b was added to the high-boiling separation column 3, and the distilled vapor

of the product column 6 was made to flow into the reboiler 3b so as to be used as a heat source. A vapor drain drum (not shown) for storing the vapor drain produced by the reboiler 3b, and a pump (not shown) to transfer a liquid into the condenser of product column 6 were installed. Acetonitrile was purified with the same apparatus as in Comparative Example 1 except for these.

In the initial stage, the valve 6v leading to the condenser of the product column 6 was fully opened. The valve 6v was gradually closed over one week, and consequently the supply of the heat to the reboiler 3b of the high-boiling separation column 3 was gradually increased. Concurrently, the amount of the vapor in the reboiler 3a of the high-boiling separation column 3 was gradually decreased. Finally, the valve 6v was perfectly closed. In this time, the column top pressure (represented by the gauge pressure "A") of the product column 6 was 0.0100 MPaG, the shell pressure of the reboiler 3b (represented by the gauge pressure "B") was 0.0002 MPaG, and the variation of each of A and B was $\pm 1\%$. The temperature of the distilled vapor of the product column 6 was 81.2°C, and the temperature of the column bottom liquid of the high-boiling separation column 3 was 58.9°C. The median of the pressure ratio B/A was 0.020, and the variation thereof was $\pm 3\%$. During the full open period of the valve 6v, no disturbance of the process was found, and no problem was found in the quality of the

obtained acetonitrile. After the perfect close of the valve 6v, the distilled vapor of the product column 6 was made to flow wholly into the reboiler 3b, and then the drain discharged from the reboiler 3b was made to flow down into a drum (not shown). The vapor drain in the drum was made to flow into the condenser of the product column by a pump (not shown).

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 3 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 4.

[0048]

[Table 3]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	2
Oxazole	(ppm)	1
Ammonia	(ppm)	0.3
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	46

[0049]

[Table 4]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	1.2
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	164
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.6
Amount of cooling water for condenser of product column	(t/h)	17

[0050]

[Example 2]

Acetonitrile was purified with the same apparatus as in Example 1 except that in addition to the distilled vapor of the product column 6, the distilled vapor of the low-boiling separation column 5 was further used as a heat source for the reboiler 3c of the high-boiling separation column 3. The flow of the distilled vapor of the low-boiling separation column 5 was as shown in Figure 3.

In the initial stage, the valve 5v leading to the condenser of the low-boiling separation column 5 was fully opened. During the full open period of the valve 5v, no disturbance of the process was found, and no problem was found in the quality of the obtained acetonitrile. The valve 5v was gradually closed over one week, and was finally closed by 10% (in a state of being opened by 90%). At this time, the column top pressure (represented by the gauge pressure "A") of the low-boiling separation column 5 was 0.0172 MPaG, and the column top temperature and the column bottom temperature of the low-boiling separation column 5 were 78.8°C and 86.4°C, respectively. The shell pressure (represented by the gauge pressure "B") of the reboiler 3c of the high-boiling separation column 3 was 0.0032 MPaG, and the column top temperature and the column bottom temperature of the high-boiling separation column 3 were 41.5°C and

58.9°C, respectively. The median of the pressure ratio B/A was 0.19. The variation of the column top pressure of the high-boiling separation column was $\pm 1\%$.

The column top pressure (represented by the gauge pressure "A'") of the product column 6 was 0.0100 MPaG, the shell pressure (represented by the gauge pressure "B'") of the reboiler 3b was 0.0002 MPaG, and the variation of each of A' and B' was $\pm 1\%$.

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 5 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 6.

[0051]

[Table 5]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	2
Oxazole	(ppm)	1
Ammonia	(ppm)	0.4
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	44

[0052]

[Table 6]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	0.6
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	121
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.6
Amount of cooling water for condenser of product column	(t/h)	17

[0053]

[Comparative Example 2]

Acetonitrile was purified with the same apparatus as in Comparative Example 1 except that as shown in Figure 4, a reboiler 3c was added to the high-boiling separation column 3, and the column bottom liquid of low-boiling separation column 5 was made to flow into the reboiler 3c so as to be used as a heat source.

In the initial stage, a bypass valve 51v for the additional reboiler 3c of the high-boiling separation column was fully opened. The bypass valve 51v was gradually closed, and the supply of the heat to the reboiler 3b of the high-boiling separation column 3 was gradually increased. Finally, the valve 51v was perfectly closed. In the meantime, the temperature variation and the pressure variation of each of the high-boiling separation column 3 and the low-boiling separation column 5 were $\pm 1\%$.

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 7 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 8, and the total amounts used of the reboiler vapor and the condenser cooling water were not different from the corresponding amounts in Comparative Example 1.

[0054]

[Table 7]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	2
Oxazole	(ppm)	1
Ammonia	(ppm)	0.5
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	47

[0055]

[Table 8]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	2.7
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	164
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.7
Amount of cooling water for condenser of product column	(t/h)	137

[0056]

[Example 3]

Acetonitrile was purified with the same apparatus as in Example 2 except that the valve 5v was finally closed by 50%. In the initial stage, the column top pressure (gauge pressure) of the low-boiling separation column 5 was 0.0172 MPaG, and the column top temperature and the column bottom temperature of the low-boiling separation column 5 were 78.8°C and 86.4°C, respectively. The shell pressure (gauge pressure) of the reboiler 3c of the high-boiling separation column 3 was 0.0168 MPaG, and the column top temperature and the column bottom temperature

of the high-boiling separation column 3 were 41.5°C and 58.9°C, respectively.

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 9 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 10.

[0057]

[Table 9]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	4
Oxazole	(ppm)	2
Ammonia	(ppm)	1.8
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	51

[0058]

[Table 10]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	0.4
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	107
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.6
Amount of cooling water for condenser of product column	(t/h)	17

[0059]

For a while from the start of the purification, the pressures of the low-boiling separation column 5 and the high-boiling separation column 3 were each maintained with $\pm 10\%$; however, after about one day from the start of

the purification, the shell pressure (gauge pressure) of the reboiler 3c of the high-boiling separation column 3 underwent hunting between 0.0071 MPaG and 0.0170 MPaG. Accordingly, the pressures of the high-boiling separation column 3 and the low-boiling separation column 5 also started to undergo hunting within a range of $\pm 20\%$.

The impurities in the acetonitrile purified after the start of the hunting were analyzed, and the results shown in Table 11 were obtained.

[0060]

[Table 11]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	66
Oxazole	(ppm)	19
Ammonia	(ppm)	3.3
Hydrogen cyanide	(ppm)	5
Propionitrile	(ppm)	372

[0061]

[Examples 4 to 9]

The valve 5v was gradually closed from the state of Example 2. The degree of closure (state of closure) of the valve 5v, and the column top pressure of the low-boiling separation column 5 and the shell pressure of the reboiler 3b of the high-boiling separation column in this case are shown in Table 12. The concentrations of the impurities in the valve 5v are also shown in Table 12.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 13.

[0062]

[Table 12]

Example	2	4	5	6	7	8	9
State of closure of 5v (%)	10	20	25	30	35	40	45
A: Column top pressure of low-boiling separation column (MPaG)	0.0172	0.0173	0.0172	0.0173	0.0173	0.0173	0.0173
Variation of A (%)	±1	±1	±2	±4	±4	±5	±9
B: Shell pressure of additional reboiler (MPaG)	0.0032	0.0045	0.0079	0.0089	0.0149	0.0156	0.0159
Variation of B (%)	±1	±2	±2	±6	±7	±7	±10
B/A	0.19	0.26	0.46	0.51	0.86	0.90	0.92
Variation of column top pressure of high-boiling separation column (%)	±1	±1	±2	±4	±4	±4	±9
Acrylonitrile (ppm)	1	1	1	1	1	1	1
Allyl alcohol (ppm)	2	3	5	22	24	25	48
Oxazole (ppm)	1	1	2	4	5	5	13
Ammonia (ppm)	0.5	0.5	0.6	1.1	1.3	2.4	2.6
Hydrogen cyanide (ppm)	2	2	2	2	2	3	4
Propionitrile (ppm)	47	50	55	108	110	111	202

[0063]

[Table 13]

Example	4	5	6	7	8	9
Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column (t/h)	0.6	0.6	0.5	0.5	0.5	0.4
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column (t/h)	2.6	2.6	2.6	2.6	2.6	2.6
Amount of cooling water for condenser of low-boiling separation column (t/h)	121	116	109	108	107	107
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column (t/h)	1.6	1.6	1.6	1.6	1.6	1.6
Amount of cooling water for condenser of product column (t/h)	17	17	17	17	17	17

[0064]

[Example 10]

Purification of acetonitrile was performed by feeding a liquid 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 2.

The liquid which contained acetonitrile in a content of 12% 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 water was separated from the line 9. Vapor was withdrawn from the line 10, condensed in the condenser (not shown) installed in the line 10 to yield a liquid which contained acetonitrile in a content of 64% by mass. The other components were as follows: water: 33% by mass, hydrogen cyanide: 1.7% by mass, and the sum total of acrylonitrile, propionitrile and others: 1.3% by mass.

The liquid obtained as described above was fed through the line 10 to the reaction vessel 2. To the reaction vessel 2, a 48% by mass of sodium hydroxide aqueous solution was added from the line 11, and was allowed to react at 73°C for 8 hours.

To the high-boiling separation column 3, 2810 kg/h of the liquid 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 vapor 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. The pressure variation in the high-boiling separation column was $\pm 1\%$ of the median taken as the above-described numerical value. 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 condensate was fed from the line 14 to the lower portion of the dehydration column 4.

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 was fed and brought into liquid-liquid contact with the water-containing crude acetonitrile fed from the line 14. From the line 16, the aqueous phase was withdrawn. From the line 17, 1850 kg/h of the acetonitrile phase was withdrawn and fed to the low-boiling separation column 5.

Into the reboiler of the low-boiling separation column 5, 2.6 t/h of a vapor 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 pressure variation in the low-boiling separation column was $\pm 1\%$ of the median taken as the above-described numerical value. 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.

Into the reboiler of the product column 6, 1.6 t/h of a vapor 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. The pressure variation in the product column was $\pm 1\%$ of the median taken as the above-described numerical value. 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 purified acetonitrile was obtained. The analysis results of the impurities in the purified acetonitrile are shown in Table 14. The amounts used of the reboiler vapor and the condenser cooling water were the same as in Comparative Example 1.

[0065]

[Table 14]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	2
Oxazole	(ppm)	0
Ammonia	(ppm)	0.5
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	47

[0066]

To the above-described process, the reboilers 3b and 3c as shown in Figures 2 and 3, respectively, were added.

The valve 6v is gradually closed, and consequently the supply of the heat to the reboiler 3b of the high-boiling separation column 3 was gradually increased. Finally, the valve 6v was perfectly closed. At this time, the column top pressure (represented by the gauge pressure "A") of the product column 6 was 0.0100 MPaG, the shell pressure (represented by the gauge pressure "B") of the reboilers 3b was 0.0020 MPaG, and the

pressure ratio B/A was 0.020. The variation of the column top pressure of the high-boiling separation column was $\pm 1\%$.

Successively, the valve 5v was gradually closed, and was finally closed by 35%. At this time, the column top pressure (represented by the gauge pressure "A'") of the low-boiling separation column 5 was 0.0172 MPaG, the shell pressure (represented by the gauge pressure "B'") of the reboiler 3c of the high-boiling separation column 3 was 0.0108 MPaG, and the median of the pressure ratio B'/A' was 0.63. The variation of the column top pressure of the high-boiling separation column was $\pm 1\%$.

The impurities in the purified acetonitrile were analyzed, and the results shown in Table 15 were obtained.

The amounts used of the reboiler vapor and the condenser cooling water were as shown in Table 16.

[0067]

[Table 15]

Acrylonitrile	(ppm)	1
Allyl alcohol	(ppm)	1
Oxazole	(ppm)	0
Ammonia	(ppm)	0.6
Hydrogen cyanide	(ppm)	2
Propionitrile	(ppm)	48

[0068]

[Table 16]

Amount of vapor (vapor at 0.4 MPaG) in reboiler of high-boiling separation column	(t/h)	0.6
Amount of vapor (vapor at 0.4 MPaG) in reboiler of low-boiling separation column	(t/h)	2.6
Amount of cooling water for condenser of low-boiling separation column	(t/h)	121
Amount of vapor (vapor at 0.4 MPaG) in reboiler of product column	(t/h)	1.6
Amount of cooling water for condenser of product column	(t/h)	17

[0069]

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 using as a heat source for the reboiler of the high-boiling separation column 3 the distilled vapor from the product column 6 and/or the low-boiling separation column 5, the energy consumption in the process can be remarkably reduced.

[0070]

The present application is based on Japanese Patent Application (Japanese Patent Application No. 2012-070086) filed at Japan Patent Office on March 26, 2012, and the contents thereof are incorporated herein by reference.

Industrial Applicability

[0071]

The present invention is a process small in the energy consumption for purification and simple both in purification facilities and in purification steps.

Therefore, while suppressing the cost increase to the minimum, the present invention can efficiently performing 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

[0072]

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

18a: Line

21a: Line

3a: Reboiler of high-boiling separation column

3b: Additional reboiler (for product column) of high-boiling separation column

3c: Additional reboiler (for low-boiling separation column) of high-boiling separation column

5v: Branch valve leading to low-boiling separation column condenser

6v: Branch valve leading to product column condenser

5lv: Bypass valve (for column bottom liquid of low-boiling separation column) for additional reboiler of high-boiling separation column

Claims

[Claim 1]

A method for purifying acetonitrile, comprising the steps of:

adding an alkali to water-containing acetonitrile produced by an ammoxidation reaction to react the alkali with the water-containing acetonitrile;

subsequently feeding a resulting reaction mixture to a first distillation column;

separating a mixture obtained by further mixing an alkali with a resulting distillate into an acetonitrile phase and an aqueous phase;

subsequently separating the aqueous phase; and

feeding the acetonitrile phase to a second distillation column,

wherein a distilled vapor from the second distillation column is used as a heat source for a reboiler of the first distillation column.

[Claim 2]

The method for purifying acetonitrile according to claim 1, wherein a part of the distilled vapor is fed to the reboiler, and a rest of the distilled vapor is fed to a condenser connected to the second distillation column.

[Claim 3]

The method for purifying acetonitrile according to claim 1 or 2, wherein a feed rate of the distilled vapor

to the reboiler is determined with reference to a reboiler pressure (on a distilled vapor side, gauge pressure) of the first distillation column and a column top pressure (gauge pressure) of the second distillation column.

[Claim 4]

The method for purifying acetonitrile according to claim 3, wherein the reboiler pressure of the first distillation column is set at a pressure equal to or less than 0.90 times the column top pressure of the second distillation column.

[Claim 5]

An apparatus for purifying acetonitrile, wherein a reaction vessel, a first distillation column, a dehydration column and a second distillation column are provided in this order;

after water-containing acetonitrile and an alkali are allowed to react with each other in the reaction vessel, a resulting reaction mixture is designed to flow into the first distillation column, a resulting distillate of the first distillation column is designed to flow into the dehydration column, and a acetonitrile phase obtained in the dehydration column is designed to flow into the second distillation column; and

a distilled vapor of the second distillation column is used as a heat source for a reboiler of the first distillation column.

[Claim 6]

The apparatus for purifying acetonitrile according to claim 5, wherein a part of the distilled vapor is fed to the reboiler, and a rest of the distilled vapor is fed to a condenser connected to the second distillation column.

[Claim 7]

The apparatus for purifying acetonitrile according to claim 5 or 6, wherein a feed rate of the distilled vapor to the reboiler is determined with reference to a reboiler pressure (on a distilled vapor side, gauge pressure) of the first distillation column and a column top pressure (gauge pressure) of the second distillation column.

[Claim 8]

The apparatus for purifying acetonitrile according to claim 7, wherein the reboiler pressure of the first distillation column is equal to or less than 0.90 times the column top pressure of the second distillation column.