

METHOD FOR PRODUCING ACRYLIC ACID

The present invention relates to a method for producing acrylic acid in which acrylic acid is separated from an
5 acrylic acid-containing aqueous solution obtained by catalytic vapor phase oxidation of propylene and/or acrolein while preventing polymerization.

Acrylic acid has currently been produced by catalytic vapor phase oxidation of propylene and/or acrolein in the
10 industrial scale. Since catalytic oxidation is conducted with a solid catalyst in the presence of molecular state oxygen and water vapor, the oxidation product is usually obtained in the form of an acrylic acid-containing aqueous solution.

15 The acrylic acid-containing aqueous solution contains many by-products, other than acrylic acid, such as acetic acid, formic acid, formaldehyde, furfural, acrolein, acetaldehyde, propionic acid, maleic acid, benzaldehyde, protoanemonin and the like.

20 In order to recover acrylic acid from such acrylic acid-containing aqueous solution, it is necessary to first remove water from the acrylic acid-containing aqueous solution.

As the method for removing water from the acrylic
25 acid-containing aqueous solution, the following methods

have been known.

- (1) Solvent extraction methods using a solvent such as a ketone, an acetic acid ester, a butyric acid ester, an aromatic hydrocarbon or the like (for example, Publication of Examined Japanese Patent Application No. Sho 46-18728, Publication of Examined Japanese Patent Application No. Sho 49-34966, Publication of Unexamined Japanese Patent Application No. Sho 48-62712, Publication of Unexamined Japanese Patent Application No. Sho 49-5915 and the like).
- (2) Dehydration methods by azeotropic distillation using a solvent which boils azeotropically with water such as toluene, methyl isobutyl ketone and the like (for example, Publication of Unexamined Japanese Patent Application No. Sho 49-7216, Publication of Examined Japanese Patent Application No. Sho 63-10691, Publication of Unexamined Japanese Patent Application No. Hei 3-181440, Publication of Examined Japanese Patent Application No. Sho 41-11247 and the like).

In recent years, the dehydration method by azeotropic distillation has become the main current because of economic grounds and also of the fact that the concentration of acrylic acid in the acrylic acid-containing aqueous solution is remarkably increased up to 40 to 70% by weight and the concentration of water is remarkably decreased due to improvement in the performance of catalysts for catalytic

vapor phase oxidation of propylene and/or acrolein and in the conditions for oxidation.

Since, however, acrylic acid has a property of easily polymerizing by the action of heat, light, peroxides,
5 impurities such as aldehydes and so on, a large amount of polymers is produced when the acrylic acid-containing aqueous solution which contains many by-products is subjected to dehydration through azeotropic distillation by feeding directly to an azeotropic dehydration column. It
10 is known that these polymers causes not only decrease in heat-transfer performance by adhering onto a heat surface of a reboiler for distillation column but also blockade of a distillation column leading to the situation including unwilling stop of operation. Therefore, prevention of the
15 polymerization is very important from the industrial viewpoint.

As a means for preventing polymerization of acrylic acid, it has conventionally been proposed and conducted to add polymerization inhibitors to the acrylic acid-
20 containing solution. As representative polymerization inhibitors are known phenols such as hydroquinone, hydroquinone monomethyl ether and the like, amines such as phenothiazine, diphenylamine and the like, copper salts such as copper dibutyldithiocarbamate and the like, manganese
25 salts such as manganese acetate and the like, nitro compounds,

nitroso compounds and so on. These polymerization inhibitors have been used independently or in combination with themselves or in combination with a molecular state oxygen-containing gas.

5 In addition, since the presence of impurities such as aldehydes has recently been deemed to be a problem in the case of producing a water absorptive resin and a polymeric coagulant in which the polymerization of acrylic acid is affected greatly by impurities, there have been proposed
10 methodes for purifying acrylic acid as follows;

 (1) a method for purifying acrylic acid in which an aromatic amine, an aliphatic amine, or another amine such as an amide, an imine, an imide, a polyamine or the like is added to a crude aldehyde-containing acrylic acid and the mixture is
15 distilled to remove aldehydes from acrylic acid (Publication of Examined Japanese Patent Application No. Sho 48-31087).

 (2) a method for preventing polymerization of acrylic acid and/or a method for decomposing aldehydes contained in acrylic acid in which at least one compound selected from
20 the group consisting of ammonia, methylamine, ethylamine, dimethylamine, diethylamine and salts thereof are added to acrylic acid obtained by catalytic vapor phase oxidation of propylene and/or acrolein (Publication of Unexamined Japanese Patent Application No. Sho 50-50314).

25 (3) a method for purifying acrylic acid in which acrylic

acid obtained by catalytic vapor phase oxidation of propylene and/or acrolein is treated with a molecular sieve having an adsorbed hydrazine compound or an amine compound to decompose and remove aldehydes contained in acrylic acid
5 (Publication of Unexamined Japanese Patent Application No. Sho 56-18934).

(4) a method for purifying acrylic acid in which a primary amine and/or a salt thereof and, in addition, at least one organic sulfonic acid and/or a salt thereof are added to
10 acrylic acid containing aldehydes, and acrylic acid is separated from the mixture by distillation (Publication of Unexamined Japanese Patent Application No. Hei 7-149687).

(5) a method for producing acrylic acid in which, in the evaporative purification of acrylic acid with addition of
15 a de-aldehyde agent after azeotropic dehydration of an oxidation product containing acrylic acid obtained by catalytic vapor phase oxidation of propylene and/or acrolein, at least one amine selected from aliphatic amines, heterocyclic amines and aromatic monoamines and a de-
20 aldehyde agent are added to the solution after azeotropic dehydration (Publication of Unexamined Japanese Patent Application No. Hei 9-208515).

These methods are designed to obtain acrylic acid containing less amount of aldehydes by distillation of a
25 solution after adding an amine in order to remove a small

amount of aldehydes contained in acrylic acid, or relate to a treatment of aldehyde-containing acrylic acid with a molecular sieve having an adsorbed amine compound.

Problems arise, however, that polymerization is liable to
5 occur in a distillation column and a tarry substance is produced during the distillation of aldehyde-containing acrylic acid with addition of amines.

In addition, the life of molecular sieve shortens when the treatment is conducted with a molecular sieve having an
10 adsorbed amine compound.

An object of the present invention is to provide a method for producing acrylic acid which comprises subjecting an acrylic acid-containing aqueous solution obtained by
15 catalytic vapor phase oxidation of propylene and/or acrolein to azeotropic dehydration to separate acrylic acid; the method enable to prevent polymerization in separation of acrylic acid, reduce adherence of polymers either to an azeotropic dehydration column for removing water from the
20 acrylic acid-containing aqueous solution or to a low-boiling separation column for removing impurities such as acetic acid or the like contained in the obtained acrylic acid or to a high-boiling separation column for removing high-boiling impurities such as maleic acid or the like, and
25 obtain stably acrylic acid as the commercial product without

stopping operation for a long period.

Under such circumstances, the present inventors have conducted an extensive research on a method for producing acrylic acid which comprises subjecting an acrylic acid-
5 containing aqueous solution obtained by catalytic vapor phase oxidation of propylene and/or acrolein to azeotropic dehydration to separate acrylic acid; the method enable to reduce polymeric substance adhered in an azeotropic dehydration column or a distillation column for removing
10 impurities contained in acrylic acid. As the result, they have found the fact that the above problem can be solved by once evaporating the acrylic acid-containing aqueous solution and then feeding the obtained acrylic acid-containing vapor to an azeotropic dehydration column to
15 effect azeotropic dehydration, not feeding the acrylic acid-containing aqueous solution directly to an azeotropic dehydration column.

Thus, the present invention provides a method for producing acrylic acid which comprises subjecting an acrylic
20 acid-containing aqueous solution obtained by catalytic vapor phase oxidation of propylene and/or acrolein to azeotropic dehydration to separate acrylic acid, in which the acrylic acid-containing aqueous solution is subjected to evaporation before azeotropic dehydration and the
25 obtained acrylic acid-containing vapor is subjected to

azeotropic dehydration.

An acrylic acid-containing aqueous solution obtained by catalytic vapor phase oxidation of propylene and/or
5 acrolein used in the present invention, may be either one obtained by the single step oxidation or the two step oxidation of propylene, or further one obtained by the system wherein raw exhaust gas is directly circulated to a oxidation reactor or circulated to a oxidation reactor after burning
10 itself.

When propylene and/or acrolein is subjected to catalytic vapor phase oxidation by molecular state oxygen in the presence of water vapor and a solid catalyst, various aldehydes and various organic acids are produced in addition
15 to acrylic acid and water. The composition of the acrylic acid-containing aqueous solution depends on the kind of the catalyst used and reaction conditions, but usually includes about 40 to 70% by weight of acrylic acid, 20 to 56% by weight of water and 2 to 10% by weight of acetic acid.

20 The present invention is characterized in that the acrylic acid-containing aqueous solution is first subjected to evaporation with an evaporator and the obtained acrylic acid-containing vapor is subjected to azeotropic dehydration, and not subjecting the solution directly to
25 azeotropic dehydration as seen in the conventional method.

The type of the evaporator used in the present invention is not particularly limited but usually includes those of wet wall column system and of forced circulation system. The pressure for evaporation operation is not particularly
5 limited but it is preferred to operate at a pressure somewhat higher than the operating pressure in the azeotropic dehydration column, because it is necessary to feed the generated vapor to the subsequent azeotropic dehydration column. The evaporator may either be single-stage or
10 multi-stage. It is preferred to use a multi-stage evaporator in order to increase recovery of acrylic acid. The rate of evaporation is preferably at least 90%. It is desirable to recover acrylic acid by feeding the bottom residue in the evaporator to an acrylic acid recovering step
15 such as dimer-degradation or the like.

In the operation for evaporation, it is preferred to add conventionally known polymerization inhibitors for acrylic acid including phenols such as hydroquinone, hydroquinone monomethyl ether and the like, amines such as
20 phenothiazine, diphenylamine and the like, copper salts such as copper dibutyldithiocarbamate and the like, manganese salts such as manganese acetate and the like, nitro compounds, nitroso compounds and so on, and further to blow a gas containing molecular state oxygen.

25 In addition, in order to enhance the effect of the

present invention, it is preferred to add at least one compound selected from the group consisting of ammonia, primary amines, secondary amines, hydrazines, urea or salts thereof to the acrylic acid-containing aqueous solution
5 before the acrylic acid-containing aqueous solution is evaporated. Addition of triethylenetetramine is particularly preferred. The primary amines and secondary amines include aliphatic amines such as ethanolamine, diethanolamine, diethylamine, hexamethylenediamine,
10 octylamine, triethylenetetramine, diethylenetriamine, propylamine, hexylamine, triethylenepentamine, tetraethylenepentamine, ethylenediamine and the like; alicyclic amines such as cyclohexylamine, cyclopentylamine and the like; and aromatic amines such as phenylenediamine
15 and the like. The hydrazines include hydrazine, phenylhydrazine and the like.

When at least one compound selected from the group consisting of ammonia, primary amines, secondary amines, hydrazines, urea or salts thereof are added to the acrylic
20 acid-containing aqueous solution, these compounds are added in an amount of about 10 to 1,000 ppm to the acrylic acid-containing aqueous solution. The temperature for addition is usually within a range of about 10 to 100°C and preferably about 30 to 80°C. Further, the duration of
25 contact is not particularly limited and usually about 5 to

150 minutes. The site of addition is not particularly limited and preferably the addition is in the bottom liquid in the absorption tower for a gas produced by catalytic vapor phase oxidation of propylene and/or acrolein, or in a tank
5 for the acrylic acid-containing aqueous solution. The means for mixing may be one which allows sufficient mixing of the additives and the acrylic acid-containing aqueous solution and includes, for example, static mixer, line mixer, stirring machine, storage tank for acrylic acid-containing
10 aqueous solution having a pump circulation line and the like.

Then, the obtained vapor of the acrylic acid-containing aqueous solution is fed to an azeotropic dehydration column in order to remove mainly water. The method for the treatment in the azeotropic dehydration column is not
15 particularly limited and may be a conventional method used in the production of acrylic acid. For example, the azeotropic dehydration is carried out with toluene, methyl isobutyl ketone, xylene, ethylbenzene, heptane or a mixture thereof under a vacuum of about 100 to 200 mmHg. By treating
20 in such azeotropic dehydration column, the water content of a solution at the bottom of the azeotropic dehydration column usually becomes to 1,000 ppm or lower. On the other hand, water, acetic acid, azeotropic agent and low-boiling aldehydes are distilled out from the top of the azeotropic
25 dehydration column. It is preferred that water and the

azeotropic agent are not mutually soluble. The aqueous phase of the distillate is withdrawn to outside of the system and the oily phase is returned to the azeotropic dehydration column as a reflux.

5 The bottom liquid withdrawn from the azeotropic dehydration column is then fed to a low-boiling separation column at which low-boiling substances such as water, acetic acid, azeotropic agent are removed. Acrylic acid as the commercial product is obtained from the bottom liquid in the
10 low-boiling separation column after a further purification by distillation, if necessary. On the other hand, the distillate from the low-boiling separation column containing acrylic acid, azeotropic agent and acetic acid is further distilled to separate acetic acid and the
15 remaining acrylic acid and azeotropic agent are fed back to preceding step such as the azeotropic dehydration column, low-boiling separation column or the like as an acrylic acid containing solution for recovery.

 According to the conventional method in which acrylic
20 acid-containing aqueous solution is directly fed to an azeotropic dehydration column for azeotropic dehydration, formation of polymers and tarry substances in the recovering region and in the reboiler of an azeotropic dehydration column are remarkable. Therefore, a stable operation for
25 a long period is difficult. On the other hand, when an

evaporation of acrylic acid-containing aqueous solution is conducted before an azeotropic dehydration as in the present invention, adhering substance in the azeotropic dehydration column is remarkably reduced. Also, frequency
5 of removing polymers adhered on complicated structures such as packed tower, sieve tray, heating surface of a reboiler as a heat supplying apparatus and the like is decreased. In addition, the evaporating apparatus has a simpler structure and is costless as compared with the distilling apparatus.
10 Therefore, two series of evaporators may be placed for alternative use when polymeric substance adhered on the wall of the apparatus. In this case, the resting evaporation apparatus can be easily cleaned by washing with alkali or water jet washing. Furthermore, adhering substance in the
15 low-boiling separation column for distilling the bottom liquid from the azeotropic dehydration column and in the high-boiling separation column can also be decreased. Therefore, the method has a great advantage for use in the industrial field.

20

EXAMPLES

The present invention will now be described in more detail with reference of Examples, which should not be construed as a limitation upon the scope of the present
25 invention.

Example 1

Into a 2 m² wet-wall type evaporator was fed an acrylic acid-containing aqueous solution, obtained by two-step catalytic vapor phase oxidation of propylene, and containing
5 55% by weight of acrylic acid, 41% by weight of water, 3% by weight of acetic acid, and each several tens ppm to several thousands ppm of acrolein, formaldehyde, furfural, acetaldehyde, propionic acid, maleic acid, benzaldehyde, protoanemonin and so on as impurities, at a rate of 50 kg/hr,
10 and heated with a saturated steam at 1.1 kg/cm². The generated vapor was fed to an azeotropic dehydration column. The system was designed such that the bottom liquid from the wet-wall type evaporator was circulated back to the evaporator with a pump except a part of the bottom liquid,
15 which was withdrawn to outside with a pump. The air was supplied to the bottom of the evaporator at a rate of 0.3% by volume based on the boiled up vapor. Polymerization inhibitors were supplied to the evaporator so that the concentrations of hydroquinone and the concentration of
20 copper dibutyldithiocarbamate were about 2,000 ppm and 100 ppm, respectively.

The azeotropic dehydration column used was made of stainless steel, had an inside diameter of 200 mm, packed with OP cascade mini-ring (manufactured by Dodwell & Company
25 Ltd.) for a length of 5 m in the concentrating zone and 2

m in the recovering zone in the column, and equipped with a 2 m² reboiler at the bottom of the column and a 4 m² condenser at the top of the column, with the outlet of the condenser being connected to a vacuum adjusting apparatus. The
5 azeotropic agent was toluene, which was supplied from the reflux line so that the concentration of toluene in the bottom liquid was 17% by weight. The reboiler was heated with a saturated steam at 1.1 kg/cm² and adjustment of heating was controlled by the amount of steam. The distillate
10 condensed by the condenser at the top of the column was phase-separated by standing in a decanter. The total amount of azeotropic agent phase was returned and an aqueous phase was withdrawn to outside of the system. The bottom liquid was withdrawn by a pump so that the liquid level was kept
15 constant and used as a material for low-boiling separation column described later. In the azeotropic dehydration column, the pressure at the top of the column was controlled at 150 mm Hg. From the top of the column, phenothiazine and copper dibutyldithiocarbamate as the polymerization
20 inhibitors were supplied so that the concentration thereof in the bottom liquid were about 200 ppm and 100 ppm, respectively. In addition the air was supplied to the reboiler at a rate of 0.3% by volume based on the boiled up vapor.

25 The operation of the evaporator and azeotropic

dehydration column was continued in this manner for 23 days. The temperature at the top of the azeotropic dehydration column as this time was about 45°C and the temperature at the bottom was about 80°C. The amount of the aqueous phase
5 withdrawn from the decanter was 21 kg/hr and the aqueous phase had a composition containing 95% by weight of water, 4% by weight of acetic acid and 0.1% by weight of acrylic acid. The amount of the liquid withdrawn from the bottom of the azeotropic dehydration column was 31 kg/hr and the
10 liquid contained 0.05% by weight of water, 2% by weight of acetic acid, 80% by weight of acrylic acid, 17% by weight of toluene, polymerization inhibitors and so on. The amount of the bottom liquid withdrawn from the evaporator was 3 kg/hr and the bottom liquid contained 10% by weight of water,
15 70% by weight of acrylic acid (including dimer), 4% by weight of acetic acid and high-boiling substances such as polymerization inhibitors. After continuously operating for 23 days, the operation of the evaporator and the azeotropic dehydration column was stopped and they were
20 dismantled for inspection. Only a small amount of polymeric substance adhered at the inside surface of the evaporator and only a slight amount of black tarry substance adhered at the recovering zone.

The polymeric substance at each part was vacuum-dried
25 at about 80°C for 2 hours and measured the dry weight. The

results of the measurement are shown in Table 1.

Then, the liquid withdrawn from the bottom of the azeotropic dehydration column was fed to the low-boiling separation column at a feeding rate of 300 g/hr to distillate
5 and separate the low-boiling substance. The low-boiling separation column was a glass cylinder having an inside diameter of 30 mm, equipped with a 2 liter flask as a reboiler at the bottom and a condenser at the top of the column, with the outlet of the condenser being connected to a vacuum
10 adjusting apparatus. The concentrating zone and the recovering zone of the low-boiling separation column were packed with stainless Dickson packing for a length of 15 cm and 60 cm, respectively. After supplying the distillate condensed in the condenser at the top of the column with
15 polymerization inhibitors diluted with toluene so that the concentrations of phenothiazine and copper dibutyldithiocarbamate were about 200 ppm and 33 ppm, respectively, a part of the distillate was used as the reflux for the low-boiling separation column and the rest of the
20 distillate was withdrawn to outside of the system. Heating of the flask acting as the reboiler was carried out with an oil bath and the amount of the distillate was adjusted by the temperature of the oil bath. The air was supplied to the bottom of the flask at a rate of 0.3% by volume based
25 on the boiled up vapor. The liquid level in the flask was

kept constant by withdrawing the bottom liquid from the flask by a pump. The operation of the low-boiling separation column was continued for 23 days controlling the pressure at the top of the column at 70 mmHg, the reflux ratio at 4, 5 the temperature at the top of the column at about 63°C and the temperature at the bottom of the column at about 82°C. The amount of the withdrawn distillate was 100 g/hr and the distillate had a composition containing 6% by weight of acetic acid, 40% by weight of acrylic acid and 54% by weight 10 of toluene. The amount of the liquid withdrawn from the bottom of the low-boiling separation column was 200 g/hr and the liquid contained 98% by weight of acrylic acid, several ppm of toluene, 200 ppm of acetic acid, high-boiling substance, polymerization inhibitors and so on. After 15 continuously operating for 23 days, the operation of the low-boiling separation column was stopped and it was dismantled for inspection. The weight of Dickson packing as the packing in the concentrating zone was increased by 0.35 g. The weight of the packing in the recovering zone 20 was also increased by 0.35 g. Further, the weight of the flask as the reboiler was increased by 0.10 g. However, no visible production of polymer was observed at any zone.

Then, the liquid withdrawn from the bottom of the low-boiling separation column was fed to the high-boiling 25 separation at a feeding rate of 400 g/hr to recover acrylic

acid for the commercial product. The high-boiling separation column was a glass cylinder having an inside diameter of 30 mm, equipped with a 2 liter flask as a reboiler at the bottom and a condenser at the top of the column, with
5 the outlet of the condenser being connected to a vacuum adjusting apparatus. The concentrating zone and the recovering zone of the high-boiling separation column were packed with stainless Dickson packing for a length of 30 cm and 10 cm, respectively. The distillate condensed in the
10 condenser at the top of the column was supplied with phenothiazine so that the concentration was about 200 ppm. A part of the distillate was used as the reflux for the high-boiling separation column and the rest of the distillate was withdrawn as the product. Heating of the
15 flask and the blowing of the air were carried out in the same manner as in the low-boiling separation column. The liquid level in the flask was kept constant by withdrawing the bottom liquid from the flask by a pump. The operation of the high-boiling separation column was continued for 10 days
20 controlling the pressure at the top of the column at 75 mmHg, the reflux ratio at 1, the temperature at the top of the column at about 79°C and the temperature at the bottom of the column at about 88°C.

The amount of the withdrawn distillate as the product
25 from the high-boiling separation column was 350 g/hr and the

distillate had a composition containing 99% by weight or more of acrylic acid, 0.1% or less of water, 300 ppm or less of acetic acid and, in addition, 100 ppm or less of aldehydes. The amount of the liquid withdrawn from the bottom of the
5 column was 50 g/hr and the liquid contained high-boiling substance, polymerization inhibitors and so on, in addition to acrylic acid. After continuously operating for 10 days, the operation of the high-boiling separation column was stopped and it was dismantled for inspection. The weight
10 of Dickson packing as the packing in the concentrating zone was increased by 0.15 g. The weight of the packing in the recovering zone was also increased by 0.10 g. Further, the weight of the flask as the reboiler was increased by 0.13 g. However, no visible production of polymer was observed
15 at any zone.

Example 2

The separation of acrylic acid was carried out in the same manner as in Example 1, except that 500 ppm of triethylenetetramine was added to the acrylic acid-
20 containing aqueous solution.

The results are shown in Table 1.

Example 3

The separation of acrylic acid was carried out in the same manner as in Example 1, except that 500 ppm of
25 diethylenetriamine was added to the acrylic acid-containing

aqueous solution.

The results are shown in Table 1.

Comparative Example 1

The separation of acrylic acid was carried out in the same manner as in Example 1, except that the acrylic acid-containing solution was directly fed to the azeotropic dehydration column in the liquid form without passing through the evaporator.

The results are shown in Table 1.

10

Table 1

		Example 1	Example 2	Example 3	Comparative Example 1
Amount of polymer adhered in azeotropic dehydration column (g)	• Reboiler	0.80	0.29	0.48	3.60
	• Recovering zone	64.4	54.2	55.9	146.9
	• Concentrating zone	0.00	0.00	0.00	0.00
Amount of polymer adhered in low-boiling separation column (g)	• Bottom	0.10	0.05	0.06	0.35
	• Recovering zone	0.35	0.11	0.17	1.04
	• Concentrating zone	0.35	0.11	0.11	1.04
Amount of polymer adhered in high-boiling separation column (g)	• Bottom	0.13	0.03	0.05	0.40
	• Recovering zone	0.10	0.05	0.05	0.25
	• Concentrating zone	0.15	0.05	0.08	0.55



CLAIMS

1. A method for producing acrylic acid which comprises
subjecting an acrylic acid-containing aqueous solution
obtained by catalytic vapor phase oxidation of propylene
5 and/or acrolein to azeotropic dehydration to separate
acrylic acid, in which the acrylic acid-containing aqueous
solution is subjected to evaporation before azeotropic
dehydration and the obtained acrylic acid-containing vapor
is subjected to azeotropic dehydration.
- 10 2. The method for producing acrylic acid according to
claim 1, wherein at least one compound selected from the
group consisting of ammonia, primary and secondary amines,
hydrazines, urea or salts thereof are added to the acrylic
acid-containing aqueous solution.
- 15 3. The method for producing acrylic acid according to
claim 2, wherein the amine is triethylenetetramine.
4. The method for producing acrylic acid according to
claim 2, wherein the amine is diethylenetriamine.

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ABSTRACT

METHOD FOR PRODUCING ACRYLIC ACID

The present invention provides a method for producing
5 acrylic acid which comprises subjecting an acrylic acid-
containing aqueous solution obtained by catalytic vapor
phase oxidation of propylene and/or acrolein to azeotropic
dehydration to separate acrylic acid, in which the acrylic
acid-containing aqueous solution is subjected to
10 evaporation before azeotropic dehydration and the obtained
acrylic acid-containing vapor is subjected to azeotropic
dehydration.

According to the method of the present invention, it can
be reduced polymers adhered in an azeotropic dehydration
15 column, a low-boiling separation column or a high-boiling
separation column in the production plant of acrylic acid,
therefore the production plant can be operated for a long
time without stopping operation.



CLAIMS

1. A method for producing acrylic acid which comprises subjecting an acrylic acid-containing aqueous solution obtained by catalytic vapor phase oxidation of propylene and/or acrolein to azeotropic dehydration to separate acrylic acid, in which at least one compound selected from the group consisting of primary and secondary amines are added to the acrylic acid-containing aqueous solution before the acrylic acid-containing aqueous solution is evaporated, the acrylic acid-containing aqueous solution is subjected to evaporation before said azeotropic dehydration whereby the obtained acrylic acid-containing vapor is subjected to said azeotropic dehydration.

2. The method for producing acrylic acid according to claim 1, wherein said at least one compound selected from the group consisting of primary and secondary amines is triethylenetetramine.

3. The method for producing acrylic acid according to claim 1, wherein said at least one compound selected from the group consisting of primary and secondary amines is diethylenetriamine.

