

DESCRIPTION

CRYSTALLIZATION APPARATUS AND METHOD FOR OPERATING THE SAME

TECHNICAL FIELD

[0001]

The present invention relates to a crystallization apparatus and a method for operating the same.

The present application claims the priority of Japanese Patent Application No. 2007-064,938 filed at the Japan Patent Office on March 14, 2007, the contents of which are hereby incorporated herein by reference.

BACKGROUND ART

[0002]

When a refining operation is carried out using a crystallization apparatus, properties of the obtained crystal, in particular, liquid permeability of the crystal, is very important because this property dominates solid-liquid separability in subsequent steps. Consequently, in the refining step using the crystallization apparatus, it is required to constantly maintain higher liquid permeability of the crystal.

[0003]

As factors dominating the liquid permeability of the crystal, the average particle size and the particle size distribution of the crystal can be listed. Namely, it is important to obtain a crystal that has the average particle size as large as possible and the particle size distribution that does not distribute in a smaller region. It is said that, in general, an amount of heat for cooling affects the particle size and rapid cooling generates many

crystal particles with small particle sizes. Therefore, an operational condition is controlled while the amount of heat for cooling is controlled in the crystallization apparatus.

[0004]

As a method for controlling the amount of heat for cooling}, (1) a method for controlling the temperature of the fluid to be treated (slurry), which is the fluid to be cooled, in the apparatus or (2) a method for controlling the value calculated from the operating state of the cooler can be listed. As the method (2), for example, in the case of a stirred-tank crystallization apparatus equipped with a cooling jacket, a value calculated from a difference in a cooling medium temperature between inlet and outlet of the cooling jacket, a flow rate of the cooling medium in the cooling jacket, and a specific heat of the cooling medium is used.

[0005]

In Patent Document 1 below, a method for producing refined (meth)acrylic acid is described, in which (meth)acrylic acid is crystallized from a solution obtained by adding methanol, ethanol, propanol or butanol as the second component to crude (meth)acrylic acid, and the resultant deposited crystal and the mother liquor are separated.

[0006]

Further, in Patent Document 2 below, a method is described, in which, in the case of depositing crystal by a cooling crystallization method in which heat exchange is carried out through a heating surface of a cooler using the cooler equipped with an external circulation device or a jacket device, an operating condition of a crystallization apparatus is changed, the cooler is changed, or a reclaim treatment condition of the cooler is changed taking account of the fact that cooling capacity is lowered as crystal (scale) grows on the heating surface.

[0007]

However, in conventional methods, there has been a case where liquid permeability of the obtained crystal was considerably deteriorated, though the operating condition of the crystallization apparatus was controlled on the basis of a certain management criteria. In particular, this problem was prominent in the case of the crystallization step carried out with the purpose of removing impurities such as aldehydes from crude methacrylic acid obtained by performing an usual refining measure such as extraction or distillation on a product obtained by a gas-phase catalytic oxidation of isobutylene, tertiary butyl alcohol, methacrolein, or isobutyl aldehyde with molecular oxygen in one step or two steps.

[0008]

In the case of controlling the amount of heat for cooling in a conventional crystallization apparatus, it was difficult in the method of the Patent Document 1 to understand the extent of the substantial amount of heat for cooling because temperature of the fluid to be treated (slurry) in the tank was merely controlled and the surface temperature of the heating surface inside the tank, in particular, the surface temperature of a scale in the case that crystal (scale) was generated on the heating surface was not detected fundamentally.

Further, in the method of the Patent Document 2, only the workload done by the cooler was understood, however, the amount of heat practically removed from the fluid to be treated (slurry) could not be understood.

Patent Document 1: Japanese Patent No. 3,559,523

Patent Document 2: Japanese Patent Application Laid-Open No. 2003-126,607

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0009]

The present invention has been completed in view of the above-mentioned circumstances, and it is a subject of the present invention to provide a crystallization apparatus with which crystal having excellent liquid permeability can be obtained stably and a method for operating the apparatus.

MEANS FOR SOLVING THE PROBLEM

[0010]

The present inventors have diligently researched in order to solve the above-mentioned problem and have found that crystal having excellent liquid permeability can be stably obtained by calculating the value of the amount of heat that is practically removed from a fluid to be treated (slurry) taking account of the amount of heat to be released from a crystallization apparatus into the environment and carrying out crystallization operation while controlling the foregoing value of the amount of heat, when controlling an amount of heat for cooling of the crystallization apparatus, and thus they have completed the present invention.

[0011]

The present invention provides a method for operating a crystallization apparatus in the process of crystallization to carry out heat exchange of a fluid to be treated using a cooler, which comprises controlling a cooling condition for the fluid to be treated in such a way that a substantial amount of heat for cooling Q_r defined by the following equation (1) becomes fixed,

$$Q_r = Q_a - Q_{atm} \quad \cdots(1)$$

wherein Q_a represents an amount of heat for cooling in the cooler and Q_{atm} represents an amount of heat to be released into the environment.

[0012]

Further, the present invention provides a crystallization apparatus which comprises a cooler for carrying out heat exchange of a fluid to be treated; and a means for controlling a cooling condition for the fluid to be treated in such a way that a substantial amount of heat for cooling Q_r defined by the following equation (1) becomes fixed,

$$Q_r = Q_a - Q_{atm} \quad \cdots(1)$$

wherein Q_a represents an amount of heat for cooling in the cooler and Q_{atm} represents an amount of heat to be released into the environment.

EFFECT OF THE INVENTION

[0013]

According to the method for operating the crystallization apparatus of the present invention, crystal having excellent liquid permeability can be obtained stably. Further, according to the crystallization apparatus of the present invention, crystal having excellent liquid permeability can be obtained stably.

BEST MODE FOR CARRYING OUT THE INVENTION

[0014]

The crystallization apparatus in the present invention may be the one that is equipped with a cooler carrying out heat exchange through a heating surface and can cool a fluid to be treated supplied to the cooler to a predetermined temperature, and publicly known crystallization apparatuses can be properly used as the crystallization apparatus. For example, an apparatus described in "Handbook of Chemical Engineering, 6th Edition", pp. 505-520, Maruzen, Tokyo (1999) (in Japanese) can be used. In particular, a stirred-tank crystallization apparatus that is equipped with a stirred tank and a cooler having a cooling

jacket for bringing a cooling medium into contact with a peripheral surface of the stirred tank from outside, and cools the inside of the stirred tank by heat exchange using the peripheral surface of the stirred tank as a heating surface (hereinafter, expressed as a stirred-tank crystallization apparatus having a cooling jacket) is preferable.

[0015]

The fluid to be treated in the present invention is not particularly limited as long as it contains the compound to be refined by crystallization operation. For example, the present invention is suitable for a step in which the fluid to be treated is crude (meth)acrylic acid, and refined (meth)acrylic acid is obtained by carrying out the crystallization operation on the crude (meth)acrylic acid. In the present description, (meth)acrylic acid means at least one compound of acrylic acid and methacrylic acid, and crude (meth)acrylic acid means at least one compound of crude methacrylic acid and crude acrylic acid.

[0016]

As the fluid to be treated in the present invention, crude methacrylic acid to be obtained by separating methacrylic acid, which is obtained as a by-product in ACH method, by extraction or distillation can be suitably used.

Further, it is preferable to use, as the fluid to be treated in the present invention, the crude methacrylic acid which is obtained by extracting methacrylic acid from an aqueous solution obtained by absorbing a reactant gas to be obtained by a gas-phase catalytic oxidation of isobutylene, tertiary butyl alcohol, methacrolein, or isobutyl aldehyde with molecular oxygen in one step or two steps using an organic solvent, and removing the organic solvent and a nonvolatile matter by distillation, and to apply the present invention to the crystallization operation for removing impurities such as aldehydes from the crude methacrylic acid.

[0017]

In order to carry out the crystallization operation according to the method of the present invention, first, the fluid to be treated is supplied to the cooler of the crystallization apparatus. The supplying means is not particularly limited and a publicly known supplying means can be properly used.

[0018]

Next, the crystallization operation that deposits crystal by carrying out heat exchange of the fluid to be treated supplied to the cooler is carried out. The crystallization operation may be either batch type or continuous type, however, the operation of crystallizing crystal continuously from the fluid to be treated can be carried out stably according to the method of the present invention, so, in particular, the continuous type is suitable.

[0019]

The cooling temperature at which the fluid to be treated is subjected to heat exchange in the cooler may be a crystallization temperature at which crystal of a target compound in the fluid to be treated starts to crystallize or below. For example, in the case that the fluid to be treated is crude (meth)acrylic acid, the cooling temperature is preferably set in the range of from -10 to 10°C in point of operability.

[0020]

A component for adjusting the crystallization temperature may be added to the fluid to be treated, if necessary. For example, in the case of using the crude methacrylic acid as the fluid to be treated, the crystallization temperature can be lowered by adding a polar organic substance, as the second component, that does not form a solid solution with (meth)acrylic acid. As concrete examples of the polar organic substance, methanol, ethanol, propanol, and butanol can be listed. The amount of the second component to be added is preferably in the range of from 1 to 35% by mass. For example, in the case of using the crude methacrylic acid as the fluid to be treated, it is preferable to fix the amount

of addition of the second component so as to make the crystallization temperature fall in the range of from -10 to 10°C while the melting point of methacrylic acid is 15°C .

[0021]

When the crystallization operation is carried out, a substantial amount of heat for cooling Q_r which represents an amount of heat to be removed from the fluid to be treated in the cooler is calculated taking account of the amount of heat to be released from the cooler into the environment (amount of heat to be released into the environment Q_{atm}), and a cooling condition of the fluid to be treated is controlled while the substantial amount of heat for cooling Q_r is controlled to a fixed value.

[0022]

In the present invention, the substantial amount of heat for cooling Q_r is defined by the following equation (1).

$$Q_r = Q_a - Q_{\text{atm}} \quad \text{.....(1)}$$

(In the above equation, Q_r represents a substantial amount of heat for cooling (unit: W), Q_a represents an apparent amount of heat for cooling (unit: W), and Q_{atm} represents an amount of heat to be released into the environment (unit: W) calculated by the following equation (2).)

$$Q_{\text{atm}} = UA \times (T_{\text{atm}} - T_e) \quad \text{.....(2)}$$

(In the above equation, UA represents heat release coefficient (unit: W/K), T_{atm} represents environmental temperature (unit: $^{\circ}\text{C}$), and T_e represents a representative temperature of the apparatus (unit: $^{\circ}\text{C}$), respectively.)

[0023]

The apparent amount of heat for cooling in the equation (1) is a value representing energy to be consumed in the cooler during the crystallization operation, and can be calculated from operating state of the cooler. For example, in the case of a stirred-tank

crystallization apparatus having a cooling jacket, the apparent amount of heat for cooling Q_a (unit: W) is calculated from the following equation (3),

$$Q_a = \rho \cdot C_p \cdot v \cdot t \quad \cdots(3)$$

wherein t represents a difference in a cooling medium temperature between inlet and outlet of the cooling jacket (unit: °C), ρ represents density of the cooling medium (unit: kg/m³), v represents a flow rate of the cooling medium in the cooling jacket (unit: m³/s), and C_p represents specific heat of the cooling medium (unit: J/(kg · K)).

[0024]

The heat release coefficient UA in the equation (2) is a characteristic value of an apparatus, and can be easily obtained from operation records of a crystallization apparatus or by a measuring test to be carried out separately. As the measuring test, for example, in the case of a stirred-tank crystallization apparatus having a cooling jacket, heat exchange with a cooling medium is carried out while a certain amount of a fluid such as water is accommodated in the stirred tank, and temperature of the fluid in the tank is measured with time. Then, the heat release coefficient UA (unit: W/K) can be obtained from the temperature change curve in the tank, the amount, density, and specific heat of the fluid in the tank, the circulating amount, density, and specific heat of the cooling medium, the temperature of the cooling medium at the inlet and outlet of the cooling jacket, the environmental temperature at the site of the crystallization apparatus, and the representative temperature of the apparatus. Concretely, the amount of heat to be released into the environment Q_{atm} is calculated from the amount of heat used for temperature change of the fluid in the tank and the difference in the amount of heat corresponding to the variation of the cooling medium temperature in the cooling jacket, and UA can be calculated from the equation (2).

[0025]

The environmental temperature (T_{atm}) in the equation (2) represents environmental temperature at the site where the crystallization apparatus is set. Concretely, the temperature measured near the crystallization apparatus (unit: °C) is used, and the temperature measured at a position as near to the crystallization apparatus as possible is preferable.

[0026]

The representative temperature of the apparatus (T_e) in the equation (2) is a standard temperature at the time of calculating the amount of heat to be released into the environment Q_{atm} based on the difference between the environmental temperature (T_{atm}) and the standard temperature. Strictly speaking, the representative temperature of the apparatus (T_e) is preferably the temperature of the cooler at the interface of the cooler and the outside environment, however, the temperature changing in connection with this may be available, and the measuring point of the representative temperature of the apparatus (T_e) can be properly selected in accordance with the crystallization apparatus to be used. For example, the temperature of the fluid to be treated, the temperature of the cooling medium circulating in the cooler, the surface temperature of the cooler, or the like can be used.

[0027]

In the equation (1), the substantial amount of heat for cooling Q_r , which is corrected by taking account of the amount of heat to be released from the cooler into the environment, can be obtained by subtracting the amount of heat to be released into the environment Q_{atm} from the apparent amount of heat for cooling Q_a . When the environmental temperature (T_{atm}) is higher than the representative temperature of the apparatus (T_e), Q_r is corrected to be smaller than Q_a because heat flows into the cooler of the crystallization apparatus. On the other hand, when the environmental temperature (T_{atm}) is lower than the representative

temperature of the apparatus (T_e), Q_r is corrected to be larger than Q_a because heat flows out of the cooler of the crystallization apparatus.

[0028]

The substantial amount of heat for cooling Q_r thus corrected corresponds to the amount of heat to be substantially removed from the fluid to be treated, namely, to the amount of heat to be substantially used for depositing crystal. Consequently, the cooling state of the fluid to be treated can be maintained stably by operating the crystallization apparatus while controlling the cooling condition so as to cause the substantial amount of heat for cooling Q_r to be kept within a fixed range. As a result, depositing state of the crystal can be stabilized and the crystal having excellent liquid permeability can be stably obtained.

[0029]

Concretely, the fluctuation range of the substantial amount of heat for cooling Q_r during the crystallization operation is preferably controlled within the range of from -15% to $+15\%$ with respect to an operation target value of the substantial amount of heat for cooling Q_r , more preferably within the range of from -10% to $+10\%$, and furthermore preferably within the range of from -5% to $+5\%$.

[0030]

The operation target value of the substantial amount of heat for cooling Q_r is preferably set in such a way that a desired average particle size and particle size distribution of the crystal can be obtained.

The cooling condition to be used for controlling the substantial amount of heat for cooling Q_r may be a parameter that can affect the substantial amount of heat for cooling Q_r among operation conditions of the crystallization apparatus, and the one that is most appropriate to the subject system may be properly selected. As the preferable parameter, the inlet or outlet temperature of the cooling medium, the arithmetic mean or logarithmic

mean of the inlet temperature and the outlet temperature, or the like can be listed.

[0031]

In the crystallization apparatus of the present invention, the means for acquiring the substantial amount of heat for cooling Q_r and the means for controlling the cooling condition while controlling the value of the substantial amount of heat for cooling Q_r are not particularly limited. For example, Q_r may be calculated from operating state of the crystallization apparatus using an electronic calculator and the like and then operation condition of the crystallization apparatus may be changed manually, or Q_r may be automatically calculated and displayed by DCS (Distributed Control System) or computer and then operation condition of the crystallization apparatus may be changed manually or under automatic control such as PID control.

[0032]

For example, when the substantial amount of heat for cooling Q_r is larger than the operation target value, the fluid to be treated can be judged to show a tendency to be somewhat super cooled in the cooler. In this case, the value of the substantial amount of heat for cooling Q_r can be reduced by changing the operation condition such as raising the inlet temperature of the cooling medium, decreasing the circulating amount of the cooling medium, or increasing the feed rate of the raw material to the crystallization tank.

[0033]

When the substantial amount of heat for cooling Q_r is smaller than the operation target value, the fluid to be treated can be judged to show a tendency to be somewhat insufficiently cooled in the cooler, and the substantial amount of heat for cooling Q_r can be increased by changing the operation condition conversely to that mentioned above.

[0034]

The fluid to be treated thus subjected to the crystallization operation is subjected to

solid-liquid separation after discharged from the crystallization apparatus to be separated into a crystal and mother liquor. As a result, a refined crystal can be obtained. For example, when crude (meth)acrylic acid is used as the fluid to be treated, the crystal of refined (meth)acrylic acid can be obtained, and the mother liquor contains the second component optionally added to the fluid to be treated, concentrated impurities, and (meth)acrylic acid that has not deposited.

[0035]

The method for separating the crystal and the mother liquor is not particularly limited as long as it can separate solid and liquid, and for example, a publicly known solid-liquid separation method such as filtration method or centrifugation method can be used.

[0036]

As a concrete example of the separation apparatus, for example, KCP apparatus described in C. Shimizu, "Refining of organic compounds by Kureha Continuous Crystal Refining Apparatus", Chemical Engineering, vol. 27, No. 3 (1982), pp.49 can be listed. The type of the separation operation may be either batch type or continuous type.

[0037]

According to the present invention, a crystal having excellent liquid permeability can be obtained stably even if the environmental temperature changed largely during operation because the crystallization operation is carried out while controlling the substantial amount of heat for cooling Q_r in which the amount of heat to be released from the cooler into the environment is taken into account. Further, the quality of the crystal is also stabilized in a continuous operation over a long period of time.

[0038]

The present invention is suitable for the crystallization operation of crude (meth)acrylic acid which is particularly susceptible to the environmental temperature. Namely, the

melting point of acrylic acid is 12°C and the melting point of methacrylic acid is 15°C, and as mentioned above, the crystallization temperature of the crude (meth)acrylic acid after the aforementioned second component has been added to the crude (meth)acrylic acid is preferably in the range of from - 10 to 10°C. When the melting point and the crystallization temperature are close to the environmental temperature, as in this case, the crystallization operation is quite susceptible to the environmental temperature. For example, when the crystallization temperature is 8°C and the environmental temperature is 20°C, the substantial amount of heat for cooling Q_r becomes smaller than the apparent amount of heat for cooling Q_a and hence the cooling is liable to be insufficient, and when the environmental temperature is 0°C, the substantial amount of heat for cooling Q_r becomes larger than the apparent amount of heat for cooling Q_a and hence the cooling is liable to be super cooling. Under these circumstances, in particular, when the cooling state is liable to be changed largely from insufficient cooling to super cooling by the environmental temperature, the method of the present invention that enables to control the operation condition taking account of the amount of heat to be released from the cooler into the environment has a large effect on the quality stabilization.

EXAMPLES

[0039]

In the next place, examples of the present invention will be explained, however, the scope of the present invention is not limited to these examples.

In the following examples and comparative examples, the stirred-tank crystallization apparatus having a cooling jacket was used as the crystallization apparatus. As the cooling medium, 40% by mass ethylene glycol aqueous solution (specific heat: 1.1) was used. The heat release coefficient (UA) of the crystallization apparatus was calculated to be 490 W/K.

after a measurement test was carried out. The apparent amount of heat for cooling} Q_a was calculated from the feed rate of the cooling medium to the cooling jacket, the difference in a cooling medium temperature between inlet and outlet of the cooling jacket, and the specific heat of the cooling medium. The environmental temperature (T_{atm}) was measured providing a thermocouple near the apparatus. The cooling medium temperature at the inlet of the cooling jacket was defined as the representative temperature of the apparatus (T_e).

[0040]

The property of the obtained crystal was evaluated by the liquid permeability speed (K, unit: m/hr) which is obtained by the following method.

(Calculation method of liquid permeability speed)

- (1) A glass tube having inside diameter of 3 cm and length of 1 m is stood vertically and a wire mesh is set at the bottom.
- (2) A slurry (composed of crystal and mother liquor) obtained from the outlet of the crystallization apparatus is poured into the glass tube to the height of 50 cm.
- (3) Put a mark on the glass tube at a position of the upper surface of the crystal layer (H1) when the crystal in the glass tube has subsided and has become stable.
- (4) Put marks on the glass tube at positions 2.5 cm (H3) and 5 cm (H2) above H1, respectively.
- (5) Measure the time (T) to be taken for the liquid surface to fall down from H2 to H1.

During the measurement, the mother liquor of the slurry may be supplemented from the upper portion of the glass tube, if necessary.

- (6) During the measurement, put a mark on the glass tube at a position of the upper surface of the crystal layer (H) when the liquid surface becomes the height of H3 above H1.
- (7) Calculate a liquid permeability speed (K) using equation (4) from the data obtained.

$$K = H \cdot \ln (H_2/H_1)/T \cdot 3600 \quad \dots(4)$$

In the equation (4), each parameter represents the following.

K [unit: m/hr] : liquid permeability speed

H [unit: m] : height of the crystal layer

H₁ [unit: m] : height of the upper surface of the crystal layer at the start of the measurement

H₂ [unit: m] : height of the liquid surface at the start of the measurement

H₃ [unit: m] : middle height of the liquid surface

T [unit: second] : time taken for the measurement

Here, H, H₁, and H₂ are the heights from the wire mesh at the bottom.

[0041]

Preparation Example 1

Methacrolein was catalytically oxidized in a gas-phase with molecular oxygen and the obtained product gas was condensed, then extracted, and then distilled to obtain crude (meth)acrylic acid A. The obtained crude (meth)acrylic acid A was analyzed with gas chromatography, and as a result, the impurities shown in Table 1 were included.

[0042]

Table 1

Impurities	Content
Acetic acid	0.0040
Propionic acid	0.0255
Maleic acid	0.1720
Citraconic acid	0.0530
Tolualdehyde	0.0330

[0043]

Example 1

To a crystallization apparatus, the crude (meth)acrylic acid A obtained in the aforementioned Preparation Example 1 was supplied with the feed rate of 1,800 kg/hr, and at the same time, methanol was supplied with the feed rate of 90 kg/hr, and the mixed solution of them was cooled while stirred in a stirred tank to deposit crystal, and a slurry containing the resultant crystal was discharged from the stirred tank. This operation was continuously carried out for 180 days.

During the operation, a cooling medium temperature at the inlet of a cooling jacket was adjusted in such a way that a substantial amount of heat for cooling (Q_r) of the crystallization apparatus becomes 29 kW. The adjustment of the cooling medium temperature and measurement and calculation of each parameter were carried out continuously every 3 seconds using DCS. Measurements of a liquid permeability speed (K) were carried out in two cases, namely, a case (No.1) where an environmental temperature is relatively high and a case (No.2) where an environmental temperature is relatively low. These results are shown in Table 2 in addition to other operation conditions. The values of the parameters other than the liquid permeability speed (K) are average values over the period of 3 hours both before and after the measurement of the liquid permeability speed (total 6 hours) (hereinafter, the same condition will be applied).

[0044]

Table 2

Experiment No.	Temperature in stirred tank	Environmental temperature T_{atm}	Representative temperature of apparatus T_e	Apparent amount of heat for cooling Q_a	Substantial amount of heat for cooling Q_r	Liquid permeability speed K
	[°C]	[°C]	[°C]	[kW]	[kW]	[m/hr]
No. 1	5.4	24.7	- 1.6	41.9	29.0	8.9
No. 2	5.3	1.6	1.1	30.0	29.8	9.0

[0045]

From the results of Table 2, it was found that the liquid permeability speed (K) in each case of No. 1 and No. 2 was excellent, and hence the crystal having excellent liquid permeability could be stably obtained even though the environmental temperature changes largely during the operation. Further, comparing No. 1 with No. 2, the fluctuation range of the substantial amount of heat for cooling (Q_r) responding to the temperature lowering was suppressed to such a small value of + 2.8% with respect to the operation target value (29.0 kW), and was recognized to be properly controlled without any problems.

[0046]

Comparative Example 1

The same procedure as in Example 1 was carried out in the long range continuous operation of the crystallization apparatus except that the substantial amount of heat for cooling (Q_r) was not controlled and the cooling medium temperature at the inlet of a cooling jacket was adjusted in such a way that the temperature in the stirred tank was kept at 5.3°C. The obtained results of the liquid permeability speed (K) and other operation conditions are shown in Table 3.

[0047]

Table 3

Experiment No.	Temperature in stirred tank	Environmental temperature T_{atm}	Representative temperature of apparatus T_e	Apparent amount of heat for cooling Q_a	Substantial amount of heat for cooling Q_r	Liquid permeability speed K
	[°C]	[°C]	[°C]	[kW]	[kW]	[m/hr]
No. 3	5.3	24.9	- 1.5	41.3	28.4	8.8
No. 4	5.3	1.7	0.6	34.1	33.6	6.5

[0048]

From the results of Table 3, in the case of No. 4 where the environmental temperature was lowered, liquid permeability of the crystal was deteriorated. The fluctuation range of the substantial amount of heat for cooling (Q_r) in the case of No. 4 is + 18.3% with respect to the substantial amount of heat for cooling (Q_r) in the case of No. 3 where liquid permeability was excellent, and it is presumed that inside of the tank be in a supercooled state.

[0049]

Comparative Example 2

The same procedure as in Example 1 was carried out in the long range continuous operation of the crystallization apparatus except that the substantial amount of heat for cooling (Q_r) was not controlled and the cooling medium temperature at the inlet of a cooling jacket was adjusted in such a way that the apparent amount of heat for cooling Q_a was kept at 42 kW. The obtained results of the liquid permeability speed (K) and other operation conditions are shown in Table 4.

[0050]

Table 4

Experiment No.	Temperature in stirred tank	Environmental temperature T_{atm}	Representative temperature of apparatus T_e	Apparent amount of heat for cooling Q_a	Substantial amount of heat for cooling Q_r	Liquid permeability speed K
	[°C]	[°C]	[°C]	[kW]	[kW]	[m/hr]
No. 5	5.4	25.5	- 1.7	42.1	28.8	8.5
No. 6	5.1	2.8	- 2.0	42.0	39.6	5.2

[0051]

From the results of Table 4, in the case of No. 6 where the environmental temperature was lowered, liquid permeability of the crystal was deteriorated. The fluctuation range of the substantial amount of heat for cooling (Q_r) in the case of No. 6 is + 37.5% with respect to the substantial amount of heat for cooling (Q_r) in the case of No. 5 where liquid permeability was excellent, and it is presumed that inside of the tank be in a supercooled state.

[0052]

(Production Example: solid-liquid separation of slurry)

In the Example 1, a slurry to be discharged from the stirred tank was continuously introduced into a solid-liquid separation apparatus, KCP apparatus (trade name, manufactured by Kureha Engineering Co., Ltd.), and separated into refined (meth)acrylic acid and a mother liquor (methacrylic acid solution containing methanol). The obtained refined (meth)acrylic acid was analyzed with gas chromatography, and as a result, the contents of the impurities are shown in Table 5 and it was recognized that the purity of the crystal was high.

[0053]

Table 5

Impurities	Content[% by mass]	
	No. 1	No. 2
Acetic acid	0.0001	0.0001
Propionic acid	0.0015	0.0016
Maleic acid	Not detected	Not detected
Citraconic acid	Not detected	Not detected
Tolualdehyde	Not detected	Not detected

INDUSTRIAL APPLICABILITY

[0054]

According to the present invention, crystal having excellent liquid permeability can be obtained stably, and hence refining operation using a crystallization apparatus can be carried out while maintaining solid-liquid separability in high degree.

What is claimed is:

1. A method for operating a crystallization apparatus at the time of carrying out heat exchange of a fluid to be treated using a cooler, the method comprising:

controlling a cooling condition for the fluid to be treated in such a way that a substantial amount of heat for cooling Q_r defined by the following equation (1) becomes fixed,

$$Q_r = Q_a - Q_{atm} \quad \cdots(1)$$

wherein Q_a represents an amount of heat for cooling in the cooler and Q_{atm} represents an amount of heat to be released into the environment.

2. The method for operating the crystallization apparatus according to claim 1, wherein the control of the cooling condition is a control of the temperature of a cooling medium.

3. The method for operating the crystallization apparatus according to claim 1, wherein the control of the cooling condition is a control of the flow rate of a cooling medium.

4. The method for operating the crystallization apparatus according to any one of claims 1 to 3, wherein the fluid to be treated is methacrylic acid.

5. A crystallization apparatus, comprising:

a cooler for carrying out heat exchange of a fluid to be treated; and

a means for controlling a cooling condition for the fluid to be treated in such a way that a substantial amount of heat for cooling Q_r defined by the following equation (1) becomes fixed,

$$Q_r = Q_a - Q_{atm} \quad \cdots(1)$$

wherein Q_a represents an amount of heat for cooling in the cooler and Q_{atm} represents an amount of heat to be released into the environment.