Increasing the number of rectification trays to produce improved technical acrylic acid quality then leads to increased global load loss in the column, which turns into increased temperature loss in the column and worsening sensitivity to polymerization.

Moreover, acrylic acid has the particularity of easily forming Michael addition derivatives, such as 3-acryloxypropionic acid, also called acrylic acid dimer. These compounds are heavy products that reduce the recovery yield by consuming monomeric acrylic acid.

Like free-radical polymerization, this covalent reaction to form Michael derivatives is greatly favored by temperature. Consequently, the use of columns with a high number of rectification trays to meet the quality requirements of the acrylic acid leads to drawbacks in terms of product loss, which can only be compensated for in part by additional high-temperature cracking of the Michael derivatives to regenerate the acrylic acid monomer.

Accordingly, there is a substantial need to achieve separation while reducing the number of theoretical rectification trays, both to reduce the risk of polymerization and the formation of Michael addition derivative products, since both of these side effects are favored by a higher temperature.

What is more, the removal of light impurities (mainly water and acetic acid) in a solvent-free method such as described in document EP 2,066,613 requires a recycling loop between the 2 columns whose flow rate is large and inversely proportional to the efficacy of the finishing column. Therefore, increasing the recycling flow rate to compensate for insufficient efficacy leads to extra energy consumption.

In an aspect, there is provided a method for recovering purified (meth)acrylic acid, in the absence of organic solvent, from a gaseous reaction mixture comprising (meth)acrylic acid obtained by gaseous phase oxidation of a (meth)acrylic acid precursor, comprising at least the following steps:

a) subjecting the gaseous reaction mixture to a dehydration without using an azeotropic solvent in a first distillation column called a dehydration column having a top and a bottom, leading to a flow from the dehydration column top of which at least part is condensed and sent back to the dehydration column in the form of reflux, and to a flow from the dehydration column bottom of which at least part is sent back as reflux into a lower part of the dehydration column to form a recirculation loop;

b) sending at least in part the flow from the bottom of the dehydration column in part into a second distillation column called a finishing column having a top, a bottom, a top portion, a lower portion, a feed section, and a draw-off section, which separates a flow from the finishing column bottom containing

heavy compounds, and a flow from the finishing column top containing light compounds, of which at least part is sent back to the dehydration column;

wherein:i) the finishing column is equipped with a separating wall, the wall being connected with an upper dome of the finishing column in the top portion and not connected with the bottom of the finishing column in the lower portion, thereby separating the finishing column into two sections equipped with internal distillation elements that ensure gas-liquid contact, of which a lower space communicates with space at the bottom of the column, and of which a headspace is separated into two sealed areas, said finishing column being fed in said feed section from a single side of the separating wall, and

ii) a gaseous flow rich in light compounds and comprising water is extracted at the top of the feed section, then recycled, after condensation, at least in part in a recirculation loop at the bottom of the dehydration column, and

iii) a flow of purified (meth)acrylic acid extracted in gaseous form from the finishing column at a top of the section located opposite to the feed section, is drawn off after condensation to form a condensed flow, part of the condensed flow being sent back as liquid reflux at a top of the draw-off section.

In another aspect, there is provided a method for producing purified (meth)acrylic acid comprising the following steps:

A) subjecting at least one (meth)acrylic acid precursor to an oxidation in gaseous phase to form a gaseous reaction mixture comprising (meth)acrylic acid;

B) cooling the gaseous reaction mixture;

C) subjecting the cooled gaseous reaction mixture to the (meth)acrylic acid recovery method as defined above.

The inventors have discovered that using a column equipped with a separating wall and using it in specific conditions, like a finishing column in the method of document EP 2,066,613, overcomes the previously cited drawbacks by leading to a significant energy gain during the purification of the acrylic acid while producing a better quality of technical acrylic acid.

When a distillation column is equipped with a separating wall, the wall being connected with the upper dome of the column in the top portion, and not connected with the bottom of the column in the lower portion, the column includes two sections of which the lower space communicates with the space at the bottom of the column and of which the headspace is separated into two sealed areas.

When the finishing column has this configuration, the inventors have discovered that the light compounds and water contained in the feed flow of the finishing column are removed more effectively from the feed section, and can be recycled at the bottom of the dehydration

column in a lower flow rate recycling loop, while allowing the extraction of acrylic acid with improved purity at the top of the other section; and the flow of heavy products forming in the column's lower space is removed at the bottom of the finishing column.

CLAIMS

1. A method for recovering purified (meth)acrylic acid, in the absence of organic solvent, from a gaseous reaction mixture comprising (meth)acrylic acid obtained by gaseous phase oxidation of a (meth)acrylic acid precursor, comprising at least the following steps:

a) subjecting the gaseous reaction mixture to a dehydration without using an azeotropic solvent in a first distillation column called a dehydration column having a top and a bottom, leading to a flow from the dehydration column top of which at least part is condensed and sent back to the dehydration column in the form of reflux, and to a flow from the dehydration column bottom of which at least part is sent back as reflux into a lower part of the dehydration column to form a recirculation loop;

b) sending at least in part the flow from the bottom of the dehydration column into a second distillation column called a finishing column having a top, a bottom, a top portion, a lower portion, a feed section, and a draw-off section, which separates a flow from the finishing column bottom containing heavy compounds, and a flow from the finishing column top containing light compounds, of which at least part is sent back to the dehydration column;

wherein:

i) the finishing column is equipped with a separating wall, the wall being connected with an upper dome of the finishing column in the top portion and not connected with the bottom of the finishing column in the lower portion, thereby separating the finishing column into two sections equipped with internal distillation elements that ensure gas-liquid contact, of which a lower space communicates with space at the bottom of the column, and of which a headspace is separated into two sealed areas, said finishing column being fed in said feed section from a single side of the separating wall, and

ii) a gaseous flow rich in light compounds and comprising water is extracted at the top of the feed section, then recycled, after condensation, at least in part in a recirculation loop at the bottom of the dehydration column, and

iii) a flow of purified (meth)acrylic acid extracted in gaseous form from the finishing column at a top of a section located opposite to the feed section, is drawn off after condensation to form a condensed flow, part of the condensed flow being sent back as liquid reflux at a top of the draw-off section.

2. The method according to claim 1 wherein the (meth)acrylic acid precursor is acrolein, obtained by oxidation of propylene or oxydehydrogenation of propane.

3. The method according to claim 1 wherein the (meth)acrylic acid precursor is methacrolein obtained by oxidation of isobutylene and/or of tert-butanol or from oxydehydrogenation of butane and/or isobutane.

4. The method according to claim 1 wherein the (meth)acrylic acid precursor comprises carbon from a renewable source.

5. The method according to claim 1 wherein the finishing column is fed at a top at an upper tray of the feed section of the finishing column, and optionally, a portion of the gaseous flow that is extracted at the top of the feed section of the finishing column, is sent back after condensation into a feed flow of the finishing column.

6. The method according to claim 1 wherein the finishing column is fed at a point located lower than an upper tray of the feed section of the finishing column, and a portion of the gaseous flow that is extracted at a top of the feed section, is sent back after condensation as liquid reflux at the top of the feed section.

7. The method according to claim 1 wherein the feed section of the finishing column includes a number of theoretical trays inclusively between 5 and 20.

8. The method according to claim 1 wherein the draw-off section of the finishing column includes a number of theoretical trays inclusively between 2 and 20.

9. The method according to claim 1 wherein a lower space of the finishing column located under the separating wall is equipped with rectification elements representing between 1 and 5 theoretical trays.

10. The method according to claim 1 further comprising introducing into the finishing column a chemical processing agent aiming to reduce residual aldehyde content.

11. The method according to claim 10 wherein the chemical processing agent for aldehydes is chosen from the group consisting of:

- monoethanolamine, ethylene diamine, glycine, diethylenetriamine, dipropylenetriamine, ortho-, para-, and meta-phenylenediamine,
- aniline, ortho-, para-, and meta-methylaniline,
- hydrazine and its salts, hydrazine hydrate, hydrazine sulfate, hydrazine carboxylates, hydrazine hydrochloride, phenylhydrazine, 4-nitrophenylhydrazine, and 2,4-dinitrophenylhydrazine, aminoguanidine and its salts, aminoguanidine hydrogen carbonate, and
- carboxylic acid hydrazides and their salts, hydrazides of formic, acetic, propionic, butanoic, pentanoic, maleic acids, dihydrazides of adipic and succinic acids, urea or urea and hydrazine derivatives, semicarbazide and carbohydrazide and their salts;

alone or their mixtures in any proportions.

12. The method according to claim 10 wherein the chemical processing agent is introduced into a feed flow of the finishing column.

13. The method according to claim 10 wherein the chemical processing agent is introduced directly into the finishing column at a point located between the top and the bottom of the finishing column, lower than a tray where the column is fed.

14. The method according to claim 10 wherein a side draw of a gaseous flow comprising (meth)acrylic acid with intermediate quality is made from the draw-off section.

15. The method according to claim 1 further comprising an extra processing of purified (meth)acrylic acid by fractionated crystallization, or by distillation optionally in the presence of a compound reacting with residual aldehydes, leading to a polymer-grade (meth)acrylic acid quality.

16. A method for producing purified (meth)acrylic acid comprising the following steps:

A) subjecting at least one (meth)acrylic acid precursor to an oxidation in gaseous phase to form a gaseous reaction mixture comprising (meth)acrylic acid;

B) cooling the gaseous reaction mixture;

C) subjecting the cooled gaseous reaction mixture to the (meth)acrylic acid recovery method as defined according to claim 1.