

Separation by rectification of (meth)acrylic acid from a mixture containing (meth)acrylic acid

- 5 The present invention relates to a novel process for the separation by rectification of (meth)acrylic acid from a mixture containing (meth)acrylic acid, in which the (meth)acrylic acid is taken from the rectification column above the point at which the liquid mixture containing the (meth)acrylic acid enters the rectification column.

(Meth)acrylic acid is used as an abbreviated designation for acrylic acid or methacrylic acid.

- 15 (Meth)acrylic acid, either as such or in the form of its esters, is of particular importance for preparing polymers for a wide variety of application areas, eg. use as adhesives.

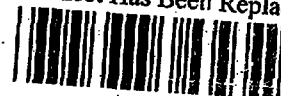
- (Meth)acrylic acid is obtainable, for example, by catalytic gas-phase oxidation of alkanes, alkanols, alkenes or alkenals containing 3 or 4 carbon atoms. (Meth)acrylic acid is particularly advantageously obtained, for example, by catalytic gas-phase oxidation of propene, acrolein, tert-butanol, iso-butene, iso-butane, iso-butyraldehyde or methacrolein.

- 25 However, other conceivable starting compounds are ones from which the actual C₃/C₄ starting compound is formed only as an intermediate during the gas-phase oxidation. An example which may be mentioned is the methyl ether of tert-butanol.

- 30 These starting gases, generally diluted with inert gases such as nitrogen, CO₂, saturated hydrocarbons and/or steam, are passed in admixture with oxygen at elevated temperatures (usually from 200 to 400°C) and, if desired, superatmospheric pressure over transition metal (eg. Mo, V, W and/or Fe-containing) mixed oxide catalysts and converted by oxidation into (meth)acrylic acid (cf. for example DE-A 4 405 059, EP-A 253 409, EP-A 92 097, DE-A 44 31 957 and DE-A 44 31 949).

- 40 However, owing to numerous parallel and subsequent reactions occurring during the course of the catalytic gas-phase oxidation and also owing to the inert diluent gases which are concomitantly used, the catalytic gas-phase oxidation does not give pure (meth)acrylic acid but a reaction mixture consisting essentially of (meth)acrylic acid, the inert diluent gases and by-products, from which the (meth)acrylic acid has to be separated.

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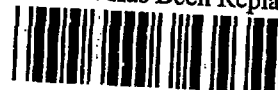
In addition to by-products which are comparatively simple to remove from (meth)acrylic acid and cause relatively little interference in the subsequent uses of the (meth)acrylic acid, eg. acetic acid, the reaction gas mixture also contains, in particular, lower aldehydes closely related to (meth)acrylic acid and therefore difficult to separate from (meth)acrylic acid, for example formaldehyde, acetaldehyde, acrolein, methacrolein, propionaldehyde, n-butyraldehyde, benzaldehyde, furfural and crotonaldehyde and in addition possibly maleic anhydride (based on the amount of (meth)acrylic acid present in the reaction gas mixture, the total amount of these secondary components which frequently interfere considerably in subsequent uses is generally $\leq 2\%$ by weight).

The (meth)acrylic acid is usually separated from the reaction gas mixture by extractive and rectificative separation processes, with, in the case of the latter, the (meth)acrylic acid generally being taken from the rectification column above the point at which the mixture containing the (meth)acrylic acid enters the rectification column (eg. at the top or via a lateral offtake).

DE-A 44 36 243 concerns, for example, a process for separating (meth)acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction gas mixture is conveyed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid, a rectification process is superimposed on the absorption process occurring naturally in the absorption column by withdrawing from the absorption column an amount of energy exceeding the natural dissipation of energy resulting from its contact with the surrounding atmosphere, and separating the (meth)acrylic acid from the liquid discharge from the absorption column (absorbate) containing (meth)acrylic acid and the absorption medium (absorbent) as main constituents and lower aldehydes and possibly maleic anhydride as secondary constituents by rectification via a lateral offtake (above the feed point into the rectification column). The (meth)acrylic acid obtainable in this way is referred to as raw (meth)acrylic acid. It generally has a purity $> 98\%$ by weight, with the impurities being, in particular, the lower aldehydes mentioned above and possibly maleic anhydride, while the separation of the (meth)acrylic acid from the high-boiling inert organic absorption liquid is essentially quantitative.

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According to DE-A 44 36 243, high-boiling inert hydrophobic organic liquids (absorbents) are all those liquids whose boiling point at atmospheric pressure is above the boiling point of (meth)acrylic acid and which comprise at least 70% by weight of 5 molecules which have no outward-acting polar groups and are thus, for example, not able to form hydrogen bonds.

DE-C 2 136 396 and DE-A 43 08 087 likewise disclose the separation of acrylic acid from the reaction gas mixture from the 10 catalytic gas-phase oxidation of propylene and/or acrolein by countercurrent absorption with a high-boiling inert hydrophobic organic liquid. The process is essentially carried out by conveying the reaction gas mixture through a conventional absorption column in countercurrent to the descending absorption liquid, 15 then, in a desorption column, largely removing the readily volatile secondary components which are simple to separate off from the liquid discharge from the absorption column composed essentially of acrylic acid, the absorption medium and secondary components by stripping with inert gas and subsequently treating the 20 liquid discharge from the desorption column containing acrylic acid and the absorbent as main constituents and lower aldehydes and possibly maleic anhydride as secondary constituents by rectification in a rectification column to separate off raw acrylic acid via the top.

25

EP-B 102 642, GB-PS 1 346 737 and DE-B 2 207 184 concern the rectificative separation of pure (meth)acrylic acid from raw (meth)acrylic acid which is aided by adding compounds containing an $-NH_2$ group to the raw (meth)acrylic acid. The primary amines 30 bind the aldehydes present as impurities to a high degree with formation of high-boiling compounds from which pure (meth)acrylic acid can be separated in high purity, eg. via the top in a rectification column.

35 A disadvantage of all rectificative separation processes in which (meth)acrylic acid is taken off from the rectification column above the point at which the mixture containing the (meth)acrylic acid enters the rectification column is that during the rectificative separation, even when using polymerization inhibitors such 40 as air, hydroquinone, hydroquinone monomethyl ether, para-nitrosophenol, para-methoxyphenol and/or phenothiazine, the rectification apparatus (particularly the vaporizer surface) relatively quickly becomes covered with a deposit, for which reason the usually continuous rectification has to be interrupted from time to 45 time for the purpose of removing the deposit formed. This is also the case when the starting mixture containing the (meth)acrylic



acid includes no lower aldehydes. However, the presence of the latter generally increases the deposit formation.

It is an object of the present invention to provide a novel process for the separation by rectification of (meth)acrylic acid from a mixture containing (meth)acrylic acid, in which process the (meth)acrylic acid is taken off from the rectification column above the point at which the liquid mixture containing the (meth)acrylic acid enters the rectification column and in which the deposit formation on the rectification apparatus (in particular on the vaporizer surface) is reduced.

We have found that this object is achieved by a process for the separation by rectification of (meth)acrylic acid from a mixture containing (meth)acrylic acid, in which process the (meth)acrylic acid is taken off from the rectification column above the point at which the liquid mixture containing the (meth)acrylic acid enters the rectification column, wherein the reflux liquid descending in the rectification column is taken from the rectification column at at least one position on the rectification column, oligomerized and/or polymerized (meth)acrylic acid present therein is removed and the reflux liquid is subsequently returned to the rectification column.

The above process procedure is the result of extensive research work in the course of which the following relationships were found.

Firstly, it was found that despite the presence of polymerization inhibitors, free-radical oligomerization and/or polymerization of the (meth)acrylic acid occurs to a certain extent along the rectification column. The (meth)acrylic acid oligomers and/or polymers thus formed have a higher boiling point than (meth)acrylic acid, for which reason they accumulate as far as the vaporizer in the case of rectifications in which the (meth)acrylic acid is taken off from the rectification column above the point at which the liquid mixture containing the (meth)acrylic acid enters the rectification column. Furthermore, it has been found that oligomers and/or polymers of (meth)acrylic acid have an increased molecular and/or colloidal solubility in (meth)acrylic acid. Since the reflux liquid descending in the rectification column becomes increasingly depleted of (meth)acrylic acid from the take-off point of the (meth)acrylic acid to the vaporizer, the molecular and/or colloidal solubility of the (meth)acrylic acid oligomers and/or polymers in the reflux liquid normally falls in the direction of the vaporizer. At the same time, the (meth)acrylic acid oligomers and/or polymers accumulate in this direction, as de-



scribed above, and increase their degree of polymerization until their solubility in the reflux liquid is exceeded and they precipitate as a deposit on the rectification apparatus and adhere to the latter by adsorption. The latter applies particularly to
5 the vaporizer surface on which a localized, particularly pronounced depletion of (meth)acrylic acid occurs as a result of the vaporization of the (meth)acrylic acid.

If the feed mixture supplied to the rectification column contains
10 aldehydes, resin formation attributable to the aldehydes occurs particularly in the lower part of the rectification column owing to the elevated temperatures prevailing there, and this likewise leads to deposit formation.

15 In accordance with the above explanations, it is easy to understand that taking off the reflux liquid descending in the rectification column at at least one point (the process step of the present invention can of course be used a plurality of times along the rectification column) of the rectification column and
20 subsequently removing oligomerized and/or polymerized (meth)acrylic acid present in the reflux liquid taken off and then returning the purified reflux liquid to the rectification column significantly reduces the deposit formation in the latter and thus increases the operating periods of the rectification column.

25 The process of the present invention is advantageously carried out in a rectification column comprising a stripping section and an enrichment section, ie. the feed mixture to be separated by rectification is preferably not fed in at the bottom, but at an
30 entry point located along the column. The part of the rectification column below this entry point is referred to as the stripping section and the part of the rectification column above this entry point is referred to as the enrichment section. In this case, the reflux liquid descending in the rectification column is
35 preferably taken from the latter immediately above the entry point of the feed mixture into the rectification column (ie. at the lower end of the enrichment section of the rectification column). The return then advantageously takes place immediately below the abovementioned entry point (ie. at the upper end of the
40 stripping section of the rectification column).

Possible methods of removing the oligomerized and/or polymerized (meth)acrylic acid from the reflux liquid taken from the rectification column are, in particular, ultrafiltration (nanofiltration)
45 tion) and/or ultracentrifugation. Both methods mentioned can also be used for the purposes of separation by rectification of pure (meth)acrylic acid from raw (meth)acrylic acid, since both the



geometric size and the density by mass of oligomerized and/or polymerized (meth)acrylic acid is sufficiently different from the corresponding property of the monomeric (meth)acrylic acid. The difference in the density by mass is caused, in particular, by

5 the increased space requirement of the electron cloud of an unsaturated double bond (for example, the density by mass of polymerized acrylic acid at 25°C and 1 atm is 1.54 g/cm³, while under the same conditions the density by mass of monomeric acrylic acid is 1.05 g/cm³; in the case of methacrylic acid, the change in the

10 density by mass under the conditions specified is from 1.45 g/cm³ to 1.01 g/cm³; (cf. for example Ullmann's Encyclopedia of Industrial Chemistry, fifth edition, 1992, VCH Verlagsgesellschaft, Weinheim, p. 169 and also D'ANS-LAX, Taschenbuch für Chemiker und Physiker, third edition, Springer Verlag, 1964,

15 Volume II, Organic Compounds). As a result of the higher density by mass, the colloidal oligomerized and/or polymerized (meth)-acrylic acid accumulates at the wall of the ultracentrifuge and can be continuously peeled from the latter. Of course, chromatographic methods can also be used for the separation. Another

20 generally applicable method of separation is to vaporize the volatile constituents of the reflux liquid taken off under reduced pressure and to return the vapor phase thus formed either as such or after condensation to the rectification column.

25 The separation according to the present invention of the oligomerized and/or polymerized (meth)acrylic acid from the reflux liquid taken from the rectification column can be realized in a particularly simple and efficient manner when the rectificative process concerns the separation of (meth)acrylic acid from a mixture containing (meth)acrylic acid and an inert hydrophobic

30 organic liquid having a boiling point higher than that of (meth)-acrylic acid as main constituents and also lower aldehydes as secondary constituents, as occurs, for example, in the separation of (meth)acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation in accordance with the methods described in DE-A 44 36 243, DE-C 2 136 396 and DE-A 4 308 087. In other words, when the feed mixture for the process of the present invention containing (meth)acrylic acid and an inert hydrophobic organic liquid having a boiling point higher than that of (meth)-

40 acrylic acid as main constituents and also lower aldehydes as secondary constituents has been obtained, for example, from the reaction gas mixtures from the catalytic gas-phase oxidation as liquid discharge from a countercurrent absorption with subsequent desorption by stripping as described in DE-C 2 136 396 or

45 DE-A 4 308 087, or as liquid discharge from a countercurrent absorption with superimposed rectification as described in DE-A 4 436 243. For the purposes of the present invention,

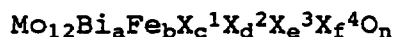


high-boiling inert hydrophobic organic liquids are liquids whose boiling point at atmospheric pressure is above the boiling point of (meth)acrylic acid and in which the solubility (% by weight, based on the weight of the solution) of (meth)acrylic acid
5 oligomers and/or polymers at 25°C and 1 atm is less than in pure (meth)acrylic acid.

In particular, they are those high-boiling organic liquids which comprise at least 70% by weight of molecules which contain no
10 outward-acting polar groups and are thus, for example, not able to form hydrogen bonds. In a narrower sense, the term here encompasses the high-boiling organic absorption liquids which are recommended in DE-C 2 136 396, DE-A 4 308 087 and DE-A 4 436 243. These are essentially liquids whose boiling point at atmospheric
15 pressure is above 160°C. Examples which may be mentioned are middle oil fractions from paraffin distillation, diphenyl ether, biphenyl, or mixtures of the abovementioned liquids such as a mixture of from 70 to 75% by weight of diphenyl ether and from 25 to 30% by weight of biphenyl. Another useful high-boiling hydro-
20 phobic organic absorption liquid is a mixture comprising a combination of from 70 to 75% by weight of diphenyl ether and from 25 to 30% by weight of biphenyl, plus, based on this combination, from 0.1 to 25% by weight of dimethyl o-phthalate.

25 In the case of methacrylic acid, the gas-phase catalytic oxidative preparation can here have been carried out, for example, starting from methacrolein which in turn can have been obtained by gas-phase catalytic oxidation of tert-butanol, iso-butane or iso-butene or by reacting formaldehyde with propionaldehyde as
30 described in EP-B 92 097 or EP-B 58 927. The gas-phase catalytic oxidation of tert-butanol, iso-butane or iso-butene is frequently carried out using a catalytically active composition of the general formula I

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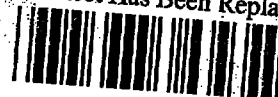


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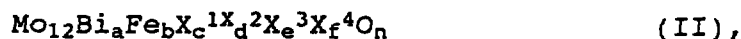
where the variables have the following meanings:

- X¹ is nickel and/or cobalt,
X² is thallium, an alkali metal and/or an alkaline earth metal,
40 X³ is phosphorus, arsenic, boron, antimony, tin, cerium, lead, niobium and/or tungsten,
X⁴ is silicon, aluminum, titanium and/or zirconium,
a is from 0.5 to 5,
b is from 0.01 to 3,
45 c is from 3 to 30,
d is from 0.02 to 2,
e is from 0 to 5,

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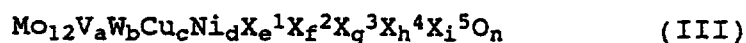
- f is from 0 to 10 and
n is an integer which is determined by the valence and amount of the elements in I which are different from oxygen,
- 5 at from 300 to 400°C and, apart from the particular temperature conditions, otherwise as per the conditions of DE-A 4 023 239. The methacrolein obtained in this way is generally used for the further oxidation without intermediate purification. The gas-phase catalytic oxidation of the methacrolein can here be carried
10 out, apart from the particular temperature conditions, as described in DE-A 4 132 263 at from 200 to 350°C or as described in DE-A 4 132 684 at from 250 to 400°C. In particular, the multimetal oxide catalysts described in DE-A 4 022 212 can be employed.
- 15 In the case of acrylic acid, the gas-phase catalytic oxidative preparation can have been carried out, for example, in one stage starting from acrolein or in two stages starting from propylene via acrolein. Suitable multimetal oxide catalysts for the catalytic gas-phase oxidation of propylene are, in particular, those
20 of the general formula II



where the variables have the following meanings:

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X¹ is nickel and/or cobalt,
X² is thallium, an alkali metal and/or an alkaline earth metal,
X³ is phosphorus, arsenic, boron, antimony, tin, cerium, lead, niobium and/or tungsten,
30 X⁴ is silicon, aluminum, titanium and/or zirconium,
a is from 0.5 to 5,
b is from 0.01 to 3,
c is from 3 to 10,
d is from 0,02 to 2,
35 e is from 0 to 5,
f is from 0 to 10 and
n is an integer which is determined by the valence and amount of the elements different from oxygen,

- 40 and for the catalytic gas-phase oxidation of acrolein in particular those of the general formula III



- 45 where the variables have the following meanings:

X¹ is one or more alkali metals,

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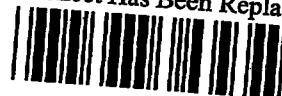
- X² is one or more alkaline earth metals,
X³ is chromium, manganese, cerium and/or niobium,
X⁴ is antimony and/or bismuth,
X⁵ is silicon, aluminum, titanium and/or zirconium,
5 a is from 1 to 6,
b is from 0.2 to 4,
c is from 0,5 to 6,
d is from 0.2 to 6,
e is from 0 to 2,
10 f is from 0 to 3,
g is from 0 to 5,
h is from 0 to 40,
i is from 0 to 40 and
n is an integer which is determined by the valence and amount
15 of the elements different from oxygen.

The reaction gases of the first oxidation stage are usually fed to the second oxidation stage without intermediate purification. The reaction conditions customarily used can be taken from, for
20 example, DE-A 4 431 957 and DE-A 4 431 949.

Such an abovedescribed mixture consisting essentially of (meth)-acrylic acid and an inert hydrophobic organic liquid having a boiling point higher than that of (meth)acrylic acid as main constituents and also lower aldehydes as secondary constituents generally contains from 5 to 25% by weight, usually from 5 to 15% by weight, of (meth)acrylic acid.
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The fact that the separation by rectification of (meth)acrylic acid via the top or via a lateral offtake of the rectification column is preferably carried out under reduced pressure (advantageously at a pressure at the top of ≤ 500 mbar, usually from 10 to 500 mbar, frequently from 10 to 200 mbar and preferably from 10 to 100 mbar; correspondingly, the bottom temperatures are generally from 100 to 230°C) and (meth)acrylic acid oligomers and/or polymers have a reduced molecular and/or colloidal solubility in the high-boiling inert hydrophobic organic liquids used opens up, in the case of the separation by rectification of (meth)acrylic acid from a mixture consisting essentially of (meth)acrylic acid
30 and an inert hydrophobic organic liquid having a boiling point higher than that of (meth)acrylic acid as main constituents and also lower aldehydes as secondary constituents, the following simple possibility for the separation according to the present invention of the oligomerized and/or polymerized (meth)acrylic
40 acid from the reflux liquid taken from the rectification column.
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The mixture comprising the (meth)acrylic acid to be separated off by rectification and the inert hydrophobic organic liquid having a boiling point higher than that of (meth)acrylic acid is here no longer fed directly to the rectification column consisting of a stripping section and an enrichment section. Rather, the feed mixture is first fed to a residence time vessel and only after a certain residence time in the latter (advantageously from 0.1 to 3 hours) fed to the rectification column, for example, via a bottom outlet (this feed point then defines stripping and enrichment sections).

In addition, the residence time vessel is, for example by fitting a tube for vapors on top, connected to the enrichment section of the rectification column (normally directly above the lowest theoretical plate of the enrichment section), which generates a corresponding vacuum in the residence time vessel located in between. Installation, for example, of a collection tray at the lower end of the enrichment section of the rectification column essentially suppresses the direct descent of the reflux liquid from the enrichment section of the rectification column into the stripping section of the rectification column, the reflux liquid is taken from the rectification column and, advantageously via an immersed inlet, fed to the residence time vessel. Furthermore, the residence time vessel is advantageously heated in such a way that the liquid mixture present therein is maintained at boiling point.

This means that the residence time vessel has the function of a vaporizer, with the vapor enriched in (meth)acrylic acid being fed to the enrichment section of the rectification column and the bottom liquid depleted of (meth)acrylic acid being fed to the stripping section of the rectification column. Accordingly, the residence time vessel can, for example, be configured as a vaporizer with convection circulation, as a vaporizer with forced circulation, as an expansion evaporator, as a thin-film evaporator (Sambay or Luva evaporator) or as a falling-film evaporator. Of course, the "residence time vaporizer" can have one or more stages.

The (meth)acrylic acid oligomers and/or polymers which have accumulated in solubilized form in the reflux liquid taken from the rectification column here precipitate in significant amounts from the bottom liquid of the "residence time vaporizer" enriched in the high-boiling hydrophobic organic solvent, so that the discharge of the "residence time vaporizer" which is fed to the stripping section of the rectification column comprises a reflux liquid depleted of (meth)acrylic acid oligomers and/or polymers



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from the enrichment section of the rectification column, which significantly reduces the deposit formation in the stripping section of the rectification column and thus makes possible an increased operating period of the latter. Of course, removal of the deposit formation occurring in the "residence time vaporizer" is also necessary from time to time. However, the operation of the rectification column can be maintained by switching over to another "residence time vaporizer".

- 10 A certain reduction of deposits in the stripping section of the rectification column also results from the vapor conveyed from the "residence time vaporizer" into the enrichment section of the rectification column being likewise enriched in lower aldehydes having comparable boiling points to (meth)acrylic acid, which re-
- 15 duces resin formation from the aldehydes in the stripping section. However, the reduction in deposit formation resulting therefrom is less pronounced.

- The process of the present invention is of course carried out in the presence of amounts which are customary per se of polymerization inhibitors customary per se. Phenothiazine is preferably used as polymerization inhibitor. The polymerization inhibitors are normally used in amounts of from 50 to 1000 ppm, based on the amount of (meth)acrylic acid (by weight). Furthermore, it is ad-
- 20 vantageous, owing to the action of atmospheric oxygen in inhibiting the polymerization of (meth)acrylic acid, to pass air through the rectification column during operation.

- Suitable rectification columns are all the usual types, ie. the rectification column can be, for example, a tray or packed column. Preference is given to using tray columns. Examples which may be mentioned are valve tray, bubble cap tray, tunnel tray, sieve tray and dualflow tray columns. Preference is given to using bubble cap trays. The dividing line between enrichment section and stripping section of the rectification column is advantageously about at the end of the first third of the distance between lowest and highest theoretical plates.
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- The process of the present invention can of course also be coupled with other methods of the prior art for suppressing deposit formation.
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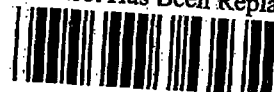


Examples

(The examples were carried out in the presence of 200 ppm (based on the weight of acrylic acid) of phenothiazine as polymerization inhibitor).

- a) A reaction gas mixture containing acrylic acid was produced by catalytic gas-phase oxidation of acrolein as described in Example B1 of DE-A 43 02 991. 2.1 standard m³/l of this reaction gas mixture were cooled to 170°C in a gas cooler by injection of a coolant mixture of 57.4% by weight of diphenyl ether, 20.7% by weight of biphenyl and 20% by weight of dimethyl o-phthalate.
- Subsequently, the proportion of the coolant which remained liquid was separated from the gas phase consisting of reaction gas and vaporized coolant in a separator. The gas phase at 170°C was introduced into a bubble cap tray column having 27 trays 80 mm in diameter at a point below the first tray and exposed to the countercurrent of 3 l/h of the absorption medium likewise composed of 57.4% by weight of diphenyl ether, 20.7% by weight of biphenyl and 20% by weight of dimethyl o-phthalate and introduced at the top of the column at a temperature of 45°C. The discharge from the absorption column is indirectly heated to 105°C in a heat exchanger and fed to the top of a desorption column which was configured as a bubble cap tray column having 20 trays. In the desorption column, components having boiling points lower than acrylic acid, for example acetic acid, were substantially removed from the mixture otherwise containing acrylic acid, lower aldehydes, absorption medium by stripping with nitrogen (400 l/h, countercurrent). The discharge of the desorption column comprised
- 84.5% by weight of absorption medium,
15 % by weight of acrylic acid and
- in particular lower aldehydes as secondary components.
- It was introduced at 25°C in an amount of 3 l/h into a rectification column through which air was passed and which comprised 20 bubble cap trays (diameter of the column: 80 mm) between the fifth and sixth tray. The rectification column was operated at a bottom temperature of 160°C and a bottom pressure of 130 mbar, and a pressure at the top of 80 mbar.

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Between the fifteenth and sixteenth trays (viewed from the vaporizer), 60 ml/h of acrylic acid having a purity of 99.3% by weight were continuously taken off via a lateral offtake. The gaseous top product was condensed, admixed with polymerization inhibitor and, apart from an amount of 5 ml/h, returned to the rectification column at a point above the uppermost bubble cap tray.

After an operating period of 165 hours, the operation of the rectification column had to be interrupted as a result of strong deposit formation in the stripping section of the rectification column.

b) As in a), but the discharge of the desorption column was first fed to a heatable round-bottom flask having a volume capacity of 500 ml, heated in the flask to 150°C and, at a residence time of 0.5 hours and a working volume of 250 ml fed via a bottom outlet of the round-bottom flask to the rectification column between the fifth and sixth trays (viewed from the vaporizer). After an operating period of 167 hours, the operation of the rectification column had to be interrupted. Essentially no deposit formation was found on the inner surface of the round-bottom residence time flask.

c) As in b), but the round-bottom residence time flask was connected via a tube for vapors to the enrichment section of the rectification column at a point immediately above the lowest bubble cap tray. The operating period of the rectification column until it had to be stopped was increased to 276 hours. There was moderate deposit formation on the inner surface of the round-bottom residence time flask.

d) As in c), but the descent of the reflux liquid from the enrichment section of the rectification column into the stripping section of the rectification column was suppressed by the lowest tray of the enrichment section being configured as a collection tray from which the reflux liquid was conveyed via an immersed feed line into the round-bottom residence time flask.

Even after an operating period of 820 hours, it was not necessary to stop operation of the rectification column. There was strong deposit formation on the inner surface of the round-bottom residence time flask.

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In the stationary state, the acrylic acid content in the round-bottom residence time flask was 5% by weight, based on the weight of the liquid therein.

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We claim:

A process for the separation by rectification of (meth)acrylic
5 acid from a mixture containing (meth)acrylic acid, in which pro-
cess the (meth)acrylic acid is taken off from the rectification
column above the point at which the liquid mixture containing the
(meth)acrylic acid enters the rectification column, wherein the
reflux liquid descending in the rectification column is taken
10 from the rectification column at at least one position on the
rectification column, oligomerized and/or polymerized (meth)-
acrylic acid present therein is removed and the reflux liquid is
subsequently returned to the rectification column.

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