

☒ Description : paged ...1... to paged ...11...☒ Claim(s) : paged ...12... to paged ...17...☐ Drawing(s) : paged to paged☒ Abstract : paged ...13... to paged ...17...

DATE OF RECEIPT

O.Z.0050/45272

Separation of (meth)acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of C₃/C₄ compounds

The present invention relates, in particular, to a novel process for the separation of acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by counter-current absorption using a high-boiling inert hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column countercurrently to the descending high-boiling inert hydrophobic organic liquid and acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing acrylic acid.

Due to its very reactive monoethylenically unsaturated bond and its acid function acrylic acid forms a valuable monomer for the preparation of polymers, *eg* for aqueous polymer dispersions suitable for use as adhesives. The same applies to methacrylic acid.

Acrylic acid is available, *inter alia*, by gas phase oxidation of propylene and/or acrolein with oxygen or gases containing oxygen in the presence of catalysts (*eg* multimetal oxides containing the elements molybdenum and vanadium in oxidic form) at elevated temperature and also due to the high heat of reaction preferably with dilution of the reactants with inert gases such as N₂, CO₂ and/or hydrocarbons and/or steam. In this process there is obtained however not pure acrylic acid, but a reaction gas mixture which contains, as secondary components apart from acrylic acid, substantially unconverted acrolein and/or propylene, steam (also formed as reaction product), carbon oxides, inert diluent gas (*eg* nitrogen), lower aldehydes such as formaldehyde, maleic anhydride and, in particular, acetic acid (*cf eg* EP-A 253,409 and DE-A 1,962,431), from which the acrylic acid must be subsequently separated. The isolation of methacrylic acid is similarly possible starting from C₄ compounds and is encumbered with similar problems.

DE-PS 2,136,396 and DE-A 4,308,087 disclose that it is possible to separate acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid.

The process is essentially carried out by passing the reaction mixture through a conventional absorption column countercurrently to the descending liquid absor-



bent, then, in a desorption column, substantially removing the readily volatile secondary components from the liquid effluent leaving the absorption column and substantially composed of acrylic acid, the absorbent, and secondary components by stripping, and subsequently rectifying the liquid effluent leaving the desorption
5 column for the purpose of separating substantially pure acrylic acid and also less readily volatile secondary components.

A disadvantage of this method is that the desorber off gas (the stripping gas used) entrains in normal operation of the desorption column at least one third of the
10 acrylic acid present in the liquid effluent leaving the absorption column and passed to the desorption column, for which reason the desorber off gas must be recycled to the absorption column (cf section 1 on page 7 of DE-A 2,136,396). In this way the prior process circulates a not inconsiderable amount of acrylic acid to be separated with no separating effect, which impairs the economical value of the
15 method used in the prior art to a considerable extent.

It is thus a particular object of the present invention to provide a process for the continuous separation of acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by effecting counter-
20 current absorption using a high-boiling inert hydrophobic organic liquid, which does not suffer from the drawbacks of the prior processes.

Simply omitting the desorption step provides no solution to the present problem, since the direct introduction of the liquid effluent from a conventional absorption
25 column into a rectifying column, would, particularly due to the fact that such a liquid effluent still contains quantities of secondary components (low-boilers) which boil, under standard pressure conditions, at temperatures which are below the boiling point of acrylic acid but are not very different from acrylic acid (liquid at 20°C and standard pressure (1 atm), exceed the separating capabilities of conventional
30 rectifying columns (for example, high base temperatures would be necessary in order to maintain the required temperatures for the number of separating stages and this would be unacceptable due to the high polymerization proneness of acrylic acid).

35 In order to achieve the desired object, we have found a process for the continuous separation of acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column countercurrently to the descending high-
40 boiling inert hydrophobic organic liquid and acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing



acrylic acid, wherein a rectifying process is superimposed on the absorption process occurring naturally in the absorption column by removing a quantity of energy from the absorption column which exceeds its natural energy loss resulting from contact with the ambient atmosphere.

5

Possible embodiments include both indirect cooling of the absorption column by means of cooled heat-transfer means (eg heat-transfer means comprising jackets, coils, tube bundles, double pipes, spirals, or panels) and/or direct cooling.

- 10 A particularly advantageous variant of an energy sink consist in withdrawing a portion of the descending liquid phase at a point along the absorption column, cooling it and subsequently recycling the cooled fluid to the absorption column.

Suitable absorption columns are all of the commonly used types. ie the absorption
15 column can be, eg, a valve tray column, a bubble-cap tray column, a column filled with a loose, irregular, packing, or a column filled with compact packs. Compact-packed columns are preferred, packed columns containing regular (well-ordered) compact-packs being particularly advantageous. Packed columns containing regular packs are known to the person skilled in the art and are described in, eg,
20 Chem.-Ing. Tech. 58 (1986) No. 1, pp 19-31 and Technische Rundschau Sulzer 2/1979 pp 49 et seq published by Gebrüder Sulzer Aktiengesellschaft, Winterthur, Switzerland. According to the invention, the use of sheet-metal or plate packs has been found to be advantageous. The use of Mellapak® column packs sold by Sulzer AG, eg those of type 250 Y or type 125 Y, is particularly advantageous.
25 Regular packs are particularly characterized by low pressure losses and guarantee small residence times, which is advantageous in view of the high polymerization proneness of acrylic acid.

The absorption column advantageously contains 5 to 20 theoretical separating
30 stages, depending on the concentration, in the gas mixture to be rectified, of by-products boiling at a temperature below the boiling point of acrylic acid under standard pressure conditions and liquid at 20°C under standard pressure conditions (low-boilers), particularly acetic acid and water. The reaction gas mixture withdrawn from the gas phase oxidation usually contains 1 to 10 wt% of
35 low-boilers, based on the acrylic acid present therein.

The absorbent is usually introduced at the top of the absorption column, whilst the gaseous reaction mixture normally enters at the bottom of the absorption column. If the energy sink required by the present invention is realized by withdrawing a
40 portion of the descending liquid phase at a point along the absorption column, cooling this portion and subsequently recycling the cooled portion to the absorption



column, this withdrawal is carried out advantageously at a point near the halfway mark of the absorption column, and recycling is usually carried out at a point slightly above the point of withdrawal.

- 5 Suitable high-boiling inert hydrophobic organic liquid absorbents are all those whose boiling temperature under standard pressure conditions is above the boiling temperature of acrylic acid and which to an extent of at least 70 wt% consist of molecules which contain no outwardly effective polar groups and thus, for example, are not capable of forming hydrogen bridges.

10

Thus suitable liquid absorbents are particularly all those recommended in DE-A 2,136,396 and DE-A 4,308,087. These are substantially liquids whose boiling point under standard pressure conditions is above 160 °C. The following may be mentioned by way of example only: middle oil fractions from the distillation of
15 paraffin, diphenylether, diphenyl, or mixtures of the aforementioned liquids such as a mixture of 70 to 75 wt% of diphenylether and 25 to 30 wt% of diphenyl. The use of a mixture comprising a blend of 70 to 75 wt% of diphenylether and 25 to 30 wt% of diphenyl, and also, based on this mixture, 0.1 to 25 wt% of *o*-dimethyl phthalate, is particularly advantageous.

20

In a manner suitable for these liquid absorbents the reaction gas mixture leaving the oxidation reactor and typically having a temperature of from 200 ° to 350 °C is advantageously cooled to a temperature of from 190 ° to 230 °C and preferably of from 200 ° to 210 °C prior to entering the absorption column. This cooling is
25 preferably effected by indirect heat exchange, for example in order to avoid formation of an aerosol as frequently occurs in the case of direct cooling with a liquid.

This indirect heat exchange is usually carried out in a shell-and-tube heat
30 exchanger. The coolant used can be for example boiling water (under pressures of up to 12 bar) or alternatively one of the possible liquid absorbents. It is important to ensure that when executing this cooling the temperature of the reaction gas mixture does not fall below its dew point. If the reaction gas mixture leaving the oxidation reactor already has a suitable absorption temperature, the indirect
35 cooling step is of course not necessary.

The introduction of the absorbent at the top of the column normally takes place in liquid form distributed over the entire cross-section of the packed column (sprinkling technique), the liquid absorbent usually having a temperature of from
40 50 ° to 100 °C and preferably from 50 ° to 70 °C.

This Sheet Has Been Replaced



The absorption column is usually operated under slightly elevated pressure. The operating pressure is preferably between 1 and 2 bar.

If the energy sink required by the present invention is realized by withdrawing a portion of the descending liquid phase at a point along the absorption column, cooling this portion and subsequently recycling the cooled liquid to the absorption column, the wall of the absorption column is itself normally in direct contact with the atmosphere surrounding it, which usually has room temperature. Possible wall materials are, theoretically, all suitable materials, such as ceramics or glass, but high-grade steel is preferred. As regards the selection of the wall material, properties such as corrosion resistance and mechanical resistance are of prime importance. Typical high-grade steel wall thicknesses are 4 to 20 mm.

The energy sink, operating pressure, and pressure loss of the column and the type of absorbent used are advantageously selected such that the bottom theoretical separating stage has a temperature of from 110° to 125°C and preferably from 115° to 120°C and the temperature at the top theoretical separating stage is 5° to 15°C, preferably 10°C, above the input temperature of the absorbent. This may be effected, for example, by withdrawing only a relatively small amount of liquid and recycling this in a highly cooled state, or by withdrawing a relatively large amount of liquid and cooling this only moderately. Such withdrawal of the descending liquid can be realized, for example, by the use of a covered flue structure, in which the flue, due to its cover, allows only the ascending steam/gas mixture to pass through it, whilst the flue base onto which the descending liquid runs has overflow tubes (preferably four overflow tubes disposed symmetrically around the flue located at the center). The liquid which has accumulated up to the overflow level can be withdrawn from the flue base in known manner.

The bottoms of the absorption column contain, in the process of the invention, the low-boilers, particularly acetic acid, impoverished extremely efficiently (usually containing only 0.1 to 1 wt%, based on the acrylic acid present, *ie* approximately one tenth of the original content), which makes it possible to work up the bottoms directly by fractional distillation in known manner, without having to go through the intermediate step of desorption, and to separate, during this phase, an acrylic acid having a purity of at least 99.7 wt%.

The process of the invention is preferably carried out continuously. The weight of high-boiling hydrophobic inert organic liquid fed to the top of the absorption column is usually four to eight times greater than the weight of acrylic acid fed in over an identical period via the reaction gas mixture to be purified.



The high-boiling organic liquid formed when executing the fractional separation of acrylic acid from the bottoms of the absorption column can, when the process of the invention is carried out continuously, be directly reused as absorbent and recycled to the top of the absorption column. In order to increase the operating times of the plant it may be recommendable to tap off a partial stream of this high-boiling organic liquid and to return it only after separation of virtually non-volatile impurities contained therein in higher concentrations.

In this embodiment of the process of the invention the polymerization inhibitor required, of course, in all process steps (except when cooling the reaction gas mixture to the absorption temperature), *eg*, phenothiazine, is advantageously added to the whole system at the top of the rectifying column used for separating the acrylic acid.

Another recommendation is to use a column containing regular packs for the fractional separation of acrylic acid from the bottoms of the absorption column and to withdraw acrylic acid through a side flue.

It is particularly advantageous to apply the process of the invention to reaction gas mixtures formed in the gas-phase catalyzed oxidative preparation of acrylic acid, such as are obtained, *eg*, by the process described in DE-A 4,220,859.

Theoretically, the steam/gas mixture emerging at the top of the absorption column in the process of the invention can be removed from the system.

Advantageously, however, a secondary column (which may, theoretically, be of the same type as is employed for the main column) will be mounted on the main column described above, where passage from one column to the other is possible only for the ascending steam/gas mixture, in which secondary column the ascending steam/gas mixture is caused to pass countercurrently to cold water fed to the top of said secondary column. The main purpose of the secondary column consists in condensing the components of the steam/gas mixture ascending in the secondary column and condensable at the temperature of the cold water fed thereto so that at the top of this column a mixture is removed which contains virtually only the inert diluent gases such as N_2 , etc co-used when executing the gas-phase catalyzed oxidative preparation of acrylic acid and also portions of the reaction gas mixture formed when the gas phase oxidation is effected by, *eg*, total combustion to produce carbon oxides.

Thus, theoretically, there is no need for the secondary column to contain more than



a single theoretical condensing step. However, the secondary column is preferably designed so as to include 2 to 4 theoretical condensing steps. The descending liquid accumulating at the bottom of the secondary column usually separates into a predominantly aqueous phase, which contains, in particular, considerable amounts of the mostly highly water-soluble by-products such as acetic acid boiling at a temperature below the boiling point of acrylic acid and into an organic phase comprising mainly absorbent and usually of greater specific gravity. When the process is carried out continuously, part of the aqueous phase and, with this, the low-boilers present therein, are advantageously separated and removed, whilst the remaining residual amount is cooled and recycled to the secondary column at the top of the secondary column instead of the fresh water introduced at the commencement of the process. Similarly, the cold water is cooled to the requisite temperature, *ie* usually to a temperature of from 5° to 30 °C and preferably from 5° to 25 °C and the aqueous phase removed following separation is withdrawn at such a rate that the amount of water present therein corresponds to the amount of steam removed by condensation, in the secondary column, from the steam/gas mixture ascending the main column. The organic phase coming from the base of the secondary column is normally recycled to the main column, preferably at the top thereof.

In the secondary column, condensation, absorption, and phase-deterioration processes overlap. Preferably the secondary column used is likewise a packed column containing regular packs.

The cold water is fed to the top of the secondary column at such a rate that it produces the desired condensing effect without causing flooding of the column. Thus this rate naturally depends on the input temperature used.

In practice the superposed arrangement of main column and secondary column will advantageously be realized by the use of a single column in which a lower section (corresponding to the main column) is separated from an upper section (corresponding to the secondary column) in such a manner that only the ascending steam/gas mixture can pass through to said upper section. This can be realized, *eg*, by the use of a flue structure having a covered flue and an impassable flue base. Thus the flue base serves as a collecting plate for the descending liquid phase coming from the upper section of the column, which phase separates, on this collecting plate, as described above, into a predominantly organic phase and a predominantly aqueous phase.

The object of the invention is achieved in a particularly preferred manner by providing a process for the separation of acrylic acid from the reaction gas mixture



formed in the catalytic gas phase oxidation of propene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column countercurrently to the descending high-boiling inert hydrophobic organic liquid and acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing acrylic acid wherein the reaction gas mixture exhibiting the necessary temperature is fed in below the bottom pack in a packed column equipped substantially throughout with regular packs and divided into two sections which are separated from each other by a junction which allows only the passage of the ascending steam/gas mixture, where the ascending reaction gas mixture fed to the lower section below the bottom pack (feed point 1) is passed countercurrently to the high-boiling hydrophobic organic absorbent fed in at a point above the top pack of the lower section (feed point 2), distributed over the entire cross-section of the column, and a portion of the descending liquid phase is withdrawn at a point along this section of the column and is cooled and returned to the packed column at a point between this point of withdrawal (point of withdrawal 1) and feed point 2 after having been cooled, the steam/gas mixture travelling up through said junction is passed passes up through the upper section of the packed column countercurrently to a stream of cold water which is fed to the column at a point above the top pack (feed point 3), distributed over the entire cross-section of the column, the junction being formed as a collecting point for the descending liquid phase from the upper section of the column, which liquid phase separates at this collecting point into a predominantly organic phase and a predominantly aqueous phase, and the organic phase accumulating at the collecting point is withdrawn from the collecting plate and returned to the lower section of the column, and the aqueous phase accumulating at the collecting point is also withdrawn (point of withdrawal 2), a portion of the withdrawn aqueous phase being separated off and removed such that the weight of water present in this portion is equal to the weight of steam removed by condensation from the steam/gas mixture ascending through said dividing junction, and the remainder of the withdrawn aqueous phase is cooled and recycled to the feed point 3 in the upper section of the column, whilst the gas phase which has not been liquefied by the cold water is withdrawn at the top of the column and removed and the liquid at the base of the column, mainly consisting of acrylic acid and the high-boiling hydrophobic organic absorbent, is transferred directly to a rectifying column where acrylic acid is fractionally separated from said bottoms in known manner.

Preferably the said rectifying column has more than 20 theoretical separating stages and is operated under reduced pressure. It is particularly advantageous to carry out the process at a head pressure of less than 100 mbar. It is particularly advantageous to effect the evaporation necessary when executing said rectifica-



tion by using a falling-film evaporator and thus carrying out the evaporating process under careful conditions.

Of course, the process of the invention can also be used for the separation of methacrylic acid from the reaction gas mixture coming from the catalytic gas phase oxidation of C_4 or masked C_4 starting compounds (eg butene, *tert*-butanol, ethers of *tert*-butanol, methacrolein etc, cf eg DEA 4,405,059) in a corresponding, advantageous manner. The main advantages of the process of the invention reside in the minimum total energy turnover and the particularly careful treatment of the very reactive unsaturated carboxylic acids, as a result of which the occurrence of uncontrolled reactions is minimized.

Example

In a process for the gas-phase catalyzed oxidative preparation of acrylic acid from propylene, in which N_2 was used as diluent, there was obtained a reaction gas mixture having a temperature of 277 °C and exhibiting the following composition:

13.50 wt%	of acrylic acid,
0.25 wt%	of by-products which boil under standard pressure conditions at a temperature higher than does acrylic acid (high-boilers),
5.35 wt%	of by-products which boil under standard pressure conditions at a lower temperature than does acrylic acid (low-boilers, eg H_2O , acrolein, formaldehyde, acetaldehyde and particularly acetic acid),
80.90 wt%	of residual gas (substantially N_2 , traces of carbon oxides and propylene).

At a rate of 220.2 kg/h, this reaction gas mixture was indirectly cooled in a shell-and-tube heat exchanger to a temperature of 204 °C. The coolant used was a mixture comprising 75 wt% of diphenylether and 25 wt% of diphenyl.

The cooled reaction gas mixture was subsequently passed into a packed column (internal diameter: 316 mm) having high-grade steel walls (wall thickness: 4 mm) and containing regular Mellapak packs sold by Sulzer AG, Winterthur, Switzerland, which column was in direct contact with the ambient atmosphere (25 °C) and was designed as follows:

On a supporting grate located above the feed point for the cooled reaction gas



mixture two of the aforementioned packs of type 125 Y and then sixteen of the aforementioned packs of type 250 Y (the diameter of the individual packs was 314 mm and their height was 210 mm) were directly stacked one above the other to form a first stack of packs. Below the supporting grate there was a structural unit having a length of 800 mm and designed to accept the bottoms. The feed point for the cooled reaction mixture (feed point 1) was located at the center the structural unit. 50 mm above the end of the first stack of packs there was provided a collecting plate for the descending liquid, which plate extended beyond the cross-section of the column and had a covered flue at the center to allow for the passage of the ascending steam/gas mixture (height: 400 mm; diameter: 106 mm), around which four overflow tubes (height: 300 mm; diameter: 43 mm) were mounted symmetrically.

From this collecting plate (point of withdrawal 1) there were continuously withdrawn 1700 kg/h of the liquid phase accumulating on this collecting plate and having a temperature of 59.9°C, which liquid phase was cooled to 42°C and directly recycled at this temperature to the packed column above the end of the second stack of packs.

The second stack of packs consisted of three regular packs of the same sort (type 250 Y) and directly stacked one above the other on a supporting grate situated above the transfer flue mounted on the collecting plate and separating the point of withdrawal 1 from the recycle point. Above the recycle point there were installed 13 further packs of type 250 C stacked one above the other (third stack of packs). At the end of this third stack of packs there was located the feed point for the absorbent (feed point 2). The absorbent used was a mixture of 57.4 wt% of diphenylether, 20.7 wt% of diphenyl, and 20 wt% of *o*-dimethyl phthalate. It was introduced at the feed point 2 at a temperature of 52°C and at a rate of 160.8 kg/h.

Directly above the feed point 2 there was a dividing flue unit, above which there were stacked five further regular packs of the same sort (type 250 Y) (fourth stack of packs). Directly above the end of the fourth stack of packs there was the feed point for the circulated cold water (feed point 3). 370 kg/h of aqueous phase were withdrawn from the collecting plate of the dividing flue unit (point of withdrawal 2) and 6.7 kg/h thereof were separated and removed. The residual amount was recycled to feed point 3. Its temperature of withdrawal was 40.5°C and it was cooled to 25°C prior to recycling. The withdrawn aqueous phase contained 6.9 wt% of acrylic acid (loss) and 93.1 wt% of water containing low-boilers. The top of the packed column was open. 181.8 g of gaseous compounds having a temperature of 26.6°C were given off through this opening. This off-gas consisted



of 2 wt% of steam, > 97.8 wt% of residual gas, < 0.1 wt% of acrylic acid and < 0.1 wt% of absorbent. The pressure at the top of the column was 1.15 bar, at feed point 1 1.24 bar. The organic phase accumulating at the point of withdrawal 2 was recycled to the enrichment column at feed point 2.

5 The withdrawal of the bottoms was effected at a rate of 192.5 kg/h, the temperature of the withdrawn bottoms being 118.4 °C. The composition of the bottoms was as follows: 15.2 wt% of acrylic acid, 84.35 wt% of absorbent, 0.29 wt% of components (maleic anhydride, phthalic anhydride etc) boiling at a temperature higher than the
10 boiling point of acrylic acid, and 0.16 wt% of low-boilers including H₂O.

The withdrawn bottoms were passed to a conventional rectifying column containing a regular pack (packed column containing regular packs) and were fractionally separated in known manner under reduced pressure. Acrylic acid was
15 isolated during this phase through a side flue in a purity > 99.7 wt%. At the top of the column there occurred small amounts of low-boilers and the bottoms were reused as absorbent. Phenothiazine used for the inhibition of polymerization was similarly introduced at the top of this rectifying column.

This Sheet Has Been Replaced



We Claim:

A process for the separation of (meth)acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by
5 countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column countercurrently to the descending high-boiling inert hydrophobic organic liquid and (meth)acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing (meth)acrylic acid, wherein
10 a rectifying process is superimposed on the absorption process occurring naturally in the absorption column by removing a quantity of energy from the absorption column which exceeds its natural energy loss resulting from contact with the ambient atmosphere.

This Sheet Has Been Replaced

Separation of (meth)acrylic acid from the reaction mixture formed in the catalytic gas phase oxidation of C_3/C_4 compounds

Abstract of the disclosure:

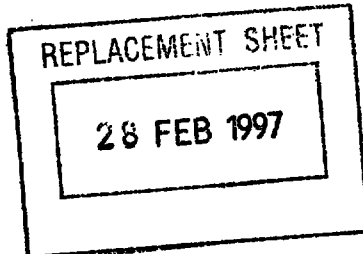
5

A process for the separation of (meth)acrylic acid from the reaction gas mixture formed in the catalytic gas phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column
10 countercurrently to the descending high-boiling inert hydrophobic organic liquid and (meth)acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing (meth)acrylic acid, wherein a rectifying process is superimposed on the absorption process occurring naturally in the absorption column by removing a quantity of energy from the absorption
15 column which exceeds its natural energy loss resulting from contact with the ambient atmosphere.

This Sheet Has Been Replaced



C 271013



REPLACEMENT SHEETS		SG
☒	Description	: paged 1... to paged 12.
☒	Claim(s)	: paged 13... to paged 14...
☐	Drawing(s)	: paged 15... to paged 16...
☒	Abstract	: paged 17... to paged 18...
DATE OF RECEIPT 28/2/97.....		

1

Separation of (meth)acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of C_3/C_4 compounds

The present invention relates, in particular, to a novel process for separating acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction gas mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid and the acrylic acid is subsequently separated by rectification from the acrylic acid-containing liquid discharge from the absorption column.

Owing to its very reactive monoethylenically unsaturated bond and its acid function, acrylic acid is a valuable monomer for preparing polymers, eg. for aqueous polymer dispersions suitable as adhesives. The same applies to methacrylic acid.

Acrylic acid is obtainable, inter alia, by gas-phase oxidation of propylene and/or acrolein with oxygen or oxygen-containing gases in the presence of catalysts (eg. multimetal oxides containing the elements molybdenum and vanadium in oxidic form) at elevated temperature and also, as a result of the high heat of reaction, preferably with dilution of the reactants with inert gases such as N_2 , CO_2 and/or hydrocarbons and/or steam. However, this process gives not pure acrylic acid, but a reaction gas mixture containing not only acrylic acid but also, as secondary components, mostly unreacted acrolein and/or propylene, water vapor (also formed as reaction product), carbon oxides, inert diluent gas (eg. nitrogen, lower aldehydes such as formaldehyde, maleic anhydride and, in particular, acetic acid (cf. for example EP-A 253 409 and DE-A 19 62 431), from which the acrylic acid subsequently has to be separated. Methacrylic acid can be obtained in a similar way from C_4 compounds, but this is encumbered by similar problems.

DE-C 21 36 396 and DE-A 43 08 087 disclose the separation of acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid.

Essentially, the process is carried out by passing the reaction mixture through a conventional absorption column in countercurrent to the descending absorption liquid, then

28 FEB 1997

2

stripping the liquid discharge from the absorption column, consisting essentially of acrylic acid, the absorption medium and secondary components, in a desorption column to substantially remove the high-volatility secondary components and subsequently treating the liquid discharge from the desorption column by rectification to separate off essentially pure acrylic acid and less volatile secondary components.

A disadvantage of this procedure is that the desorber off-gas (the used stripping gas) in normal operation of the desorption column carries out at least one third of the acrylic acid present in the liquid discharge from the absorption column which is fed to the desorption column, for which reason the desorber off-gas has to be recirculated to the absorption column (cf. Section 1 on p. 7 of DE-A 21 36 396). In this way, the process of the prior art circulates a not inconsiderable amount of the acrylic acid to be separated off without separation action, which has a considerable adverse effect on the economics of the procedure of the prior art.

It is an object of the present invention to provide a process for continuously separating acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of propylene and/or acrolein with countercurrent absorption using a high-boiling inert hydrophobic organic liquid which does not have the disadvantages of the processes of the prior art.

A simple elimination of the desorption step is ruled out as a solution to the problem, since direct introduction of the liquid discharge from a conventional absorption column into a rectification column would cause the conventional separation capacity of a rectification column to be exceeded, particularly because of the proportion of secondary components (low boilers) which at atmospheric pressure have lower boiling points than acrylic acid and are not very different from acrylic acid (liquid at 20°C and atmospheric pressure) still present in such a liquid discharge (eg. high bottom temperatures incompatible with the relatively high polymerization tendency of the acrylic acid would be necessary to cope thermally with the number of theoretical plates required).

We have found that this object is achieved by a process for continuously separating acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of propylene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction gas mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic

28 FEB 1997

organic liquid and the acrylic acid is subsequently separated by rectification from the acrylic acid-containing liquid discharge from the absorption column, wherein a rectification process is superimposed on the absorption process naturally occurring in the absorption column.

The latter can be realized in a simple manner by withdrawing from the absorption column an amount of energy exceeding the amount naturally given off as a result of contact with the surrounding atmosphere.

Possible embodiments are indirect cooling of the absorption column by means of cooled heat exchangers (eg. jacket, coil, tube-shell, double tube, spiral and plate heat exchangers) and/or direct cooling.

A particularly advantageous variant of an energy sink comprises taking off a part of the descending liquid phase along the absorption column, cooling it and subsequently returning the cooled liquid to the absorption column.

Suitable absorption columns are all the usual types, ie. the absorption column can be, for example, a valve tray, bubble cap or packed column. Preference is given to packed columns, with packed columns having ordered packing being particularly advantageous. Packed columns having ordered packing are known per se to those skilled in the art and described, for example, in Chem.-Ing. Tech. 58 (1986) No. 1, pp. 19-31 and in Technischen Rundschau Sulzer 2/1979, p. 49 ff. from Gebrüder Sulzer Aktiengesellschaft, Winterthur, Switzerland. According to the present invention, the use of metal sheet and plate packings has been found to be useful. Particularly advantageous is the use of Mellapak® column packings from Sulzer AG, eg. those of the type 250 Y or of the type 125 Y. Ordered packings have, in particular, a low pressure loss and ensure short residence times, which is advantageous in view of the high polymerization tendency of acrylic acid. The absorption column advantageously comprises, depending on the amount of by-products which are liquid at 20°C and atmospheric pressure and have boiling points at atmospheric pressure lower than that of acrylic acid (low boilers) present in the reaction gas mixture, in particular acetic acid and water, from 5 to 20 theoretical plates. The reaction gas mixture taken from the gas-phase oxidation usually contains from 1 to 10 % by weight of low boilers, based on the acrylic acid present therein.

28 FEB 1997

The ~~absorption medium~~ is usually introduced at the top of the absorption column, while the gaseous reaction mixture normally enters at the bottom end of the absorption column. If the energy sink required according to the present invention is provided by taking off a part of the descending liquid phase along the absorption column, cooling this part and subsequently returning the cooled liquid to the absorption column, this part of the liquid is advantageously taken off about half-way along the absorption column and is generally returned a little above the point at which it is taken off.

Suitable high-boiling inert hydrophobic organic absorption liquids are all those whose boiling point at atmospheric pressure is above the boiling point of acrylic acid and which comprise at least 70 % by weight of molecules containing no outward-acting polar groups and thus, for example, are not able to form hydrogen bonds.

Thus, suitable absorption liquids are, in particular, all those which are recommended in DE-A 21 36 396 and in DE-A 43 08 087. These are essentially liquids whose boiling point at atmospheric 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. Particularly advantageous is the use of 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.

In a manner matched to these absorption liquids, the reaction gas mixture leaving the oxidation reactor, which mixture is typically at from 200 to 350°C, is, prior to entering the absorption column, advantageously cooled to from 190 to 230°C, preferably from 200 to 210°C. This cooling is advantageously carried out by indirect heat exchange, eg. so as to avoid the aerosol formation which frequently occurs on direct cooling by means of a liquid.

This indirect heat exchange is generally carried out in a tube-shell heat exchanger. The cooling medium used can be, for example, boiling water (under pressures of up to 12 bar) or one of the possible absorption liquids. It is important that during this cooling the temperature does not drop below the dew point of the reaction gas mixture. If the reaction gas mixture leaving the

28 FEB 1997

oxidation reactor already has a suitable absorption temperature, the indirect cooling step is of course omitted.

The absorption medium is normally introduced at the top of the column in liquid form distributed across the cross section of the packed column (sprinkling on), with the absorption liquid generally being at from 50 to 100°C, preferably from 50 to 70°C.

The absorption column is generally operated at slightly above atmospheric pressure. Preferably, the working pressure is from one to two bar.

If the energy sink required according to the present invention is provided by taking off a part of the descending liquid phase along the absorption column, cooling this part and subsequently returning the cooled liquid to the absorption column, the wall of the absorption column itself is normally in direct contact with the surrounding atmosphere, which is usually at room temperature. Wall materials can in principle be any suitable materials, ie. for example ceramic or glass, but in particular stainless steel. Properties important in the selection of the wall material are, for example, corrosion resistance and mechanical strength. Typical stainless steel wall thicknesses are from 4 to 20 mm.

The energy sink, operating pressure, pressure loss of the column and the type of absorption medium used are advantageously selected in such a way that the lowest theoretical plate is at from 110 to 125°C, preferably from 115 to 120°C, and the uppermost theoretical plate is at a temperature which is from 5 to 15°C, preferably 10°C, above the temperature at which the absorption medium is introduced. This can be achieved, for example, by taking off only a relatively small amount of liquid and cooling it strongly before it is returned, or by taking off a relatively large amount of liquid and cooling it only moderately. Such a taking-off of descending liquid can be achieved, for example, by means of installation of a capped chimney which, as a result of the cap, lets through only the rising vapor/gas mixture, while the bottom of the chimney, onto which the descending liquid runs, has overflow tubes (preferably four overflow tubes symmetrically arranged around the centrally located chimney). The liquid which has run onto the chimney bottom up to the overflow level can be taken off in a manner known per se.

In the process of the present invention, the liquid from the bottom of the absorption column is extraordinarily efficiently depleted of the low boilers, in particular acetic acid (based on the acrylic acid present in the liquid, there is generally only

28 FEB 1997

6

from 0.1 to 1 % by weight still present, ie. about one tenth of the original content), which allows the liquid from the bottom to be directly worked up by rectification in a manner known per se without having to go through an intermediate desorption step so as to give an acrylic acid whose purity is at least 99.7 % by weight.

The process of the present invention is preferably carried out continuously. In such a continuous process, the amount of high-boiling hydrophobic inert organic liquid introduced at the top of the absorption column is generally from 4 to 8 times the weight of acrylic acid fed in over the same period of time via the reaction gas mixture to be worked up.

In a continuous embodiment of the process of the present invention, the high-boiling organic liquid obtained from the separation by rectification of the acrylic acid from the liquid from the bottom of the absorption column can be directly reused as absorption medium and returned to the top of the absorption column. To increase the operating times of the plant, it may be advisable to bleed off a substream of this high-boiling organic liquid and to return it only after removal of virtually non-volatile impurities which have accumulated therein.

In this embodiment of the process of the present invention, the polymerization inhibitor, eg. phenothiazine, which is self-evidently needed in all process steps (excluding the cooling of the reaction gas mixture to the absorption temperature), is added to the overall system, advantageously at the top of the rectification column which separates off the acrylic acid.

It is also recommended that a column having ordered packing be likewise used for the separation by rectification of the acrylic acid from the liquid from the bottom of the absorption column and acrylic acid be taken off via a side outlet.

The process of the present invention is particularly advantageously applied to reaction gas mixtures from the gas-phase catalytic oxidative preparation of acrylic acid, as are obtained, for example, according to DE-A 42 20 859.

For the purposes of the process of the present invention, the vapor/gas mixture leaving the top of the absorption column can in principle be discharged as waste.

28 FEB 1997

However, the abovedescribed main column advantageously has superposed on it a secondary column (suitable types of column are in principle the same ones as for the main column), with only the rising vapor/gas mixture being able to pass from one column into the other, and passing the rising vapor/gas mixture through this secondary column in countercurrent to the cold water introduced at the top of the latter. The main purpose of the secondary column is to condense the components of the vapor/gas mixture rising into the secondary column which are condensable at the temperature of the cold water introduced, so that the mixture discharged as waste at the top of the column consists essentially of only the inert diluent gases such as N_2 , etc., concomitantly used in the gas-phase catalytic oxidative preparation of acrylic acid and the reaction gas components formed in the gas-phase oxidation by, for example, total combustion to carbon oxides.

It is therefore sufficient in principle for the secondary column to comprise one theoretical condensation stage. However, the secondary column is preferably designed so that it comprises from 2 to 4 theoretical condensation stages. The descending liquid running onto the bottom of the secondary column generally separates into a predominantly aqueous phase which contains, in particular, considerable amounts of the mostly readily water-soluble by-products having boiling points lower than acrylic acid, for example acetic acid, and an organic phase consisting mainly of absorption medium, this organic phase generally having a higher specific gravity. In continuous operation, a part of the aqueous phase together with the low boilers present therein is advantageously separated off and discharged as waste, while the remaining aqueous phase is cooled and recirculated to the top of the secondary column in place of the fresh water introduced at the beginning of the process. Accordingly, the recirculated aqueous phase is normally cooled to the required cold water temperature, ie. generally to from 5 to 30°C, preferably to from 5 to 25°C, and the amount of aqueous phase discharged as waste is such that the amount of water present therein corresponds to the amount of water vapor condensed in the secondary column from the vapor/gas mixture rising from the main column. The organic phase from the bottom of the secondary column is normally returned to the main column, preferably via the top.

Condensation, absorption and phase separation processes are superimposed in the secondary column. Preferably, the secondary column is likewise a packed column having ordered packing.

28 FEB 1997

8

The amount of cold water introduced at the top of the secondary column is calculated so that, on the one hand, it has the desired condensation effect and, on the other hand, does not cause flooding of the column. This amount thus naturally depends on the introduction temperature selected.

In practice, the main and secondary columns in succession are advantageously constructed in the form of a single column in which a lower section (corresponds to the main column) is separated from an upper section (corresponds to the secondary column) in a way which allows only the rising vapor/gas mixture to pass through. This can be achieved, for example, by means of an installed chimney having a cap and an impermeable chimney bottom. The chimney bottom thus serves as collection tray for the descending liquid phase of the upper column section, with the liquid phase separating on this collection tray, as already described, into a predominantly organic phase and a predominantly aqueous phase.

A particularly preferred solution of the object of the present invention therefore provides a process for separating acrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of propene and/or acrolein by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction gas mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid and the acrylic acid is subsequently separated by rectification from the acrylic acid-containing liquid discharge from the absorption column, wherein the reaction gas mixture at the required temperature is introduced below the lowest packing element into a packed column fitted essentially right through with ordered packing and divided into two sections which are separated from one another by a connection which allows only the rising vapor/gas mixture to pass through, where, in the lower section, the rising reaction gas mixture fed in below the lowest packing element (feed point 1) is conveyed in countercurrent to high-boiling hydrophobic organic absorption medium introduced in distributed form across the column cross section above the uppermost packing element of the lower section (feed point 2) and a part of the descending liquid phase is taken off along this column section, cooled and returned in cooled form to the packed column in the region extending from this takeoff point (takeoff point 1) to the feed point 2, and in the upper section of the packed column the vapor/gas mixture rising through the appropriately permeable connection is conveyed in countercurrent to cold water introduced in distributed form across the column cross section above the uppermost packing

28 FEB 1997

element (feed point 3). The connection is configured as a collection point for the descending liquid phase of the upper column section, which liquid phase separates at this collection point into a predominantly organic phase and a predominantly aqueous phase, and the organic phase flowing onto the collection point is taken from the collection tray and returned to the lower column section and the aqueous phase flowing onto the collection point is likewise taken off (takeoff point 2). A part of the aqueous phase taken off is separated off and discharged as waste, this amount removed being such that the amount of water therein corresponds to the amount of water vapor condensed from the vapor/gas mixture rising through the dividing connection, the remaining aqueous phase taken off is cooled and recirculated to the feed point 3 in the upper column section. At the top of the column, the gas phase not liquified by the cold water is discharged as waste and the column bottoms consisting mainly of acrylic acid and the high-boiling hydrophobic organic absorption medium is transferred directly to a rectification column in which the acrylic acid is separated by rectification from this bottom liquid in a manner known per se.

The abovementioned rectification column preferably has more than 20 theoretical plates and is operated under reduced pressure. It is particularly advantageous to work at a pressure of less than 100 mbar at the top of the column. It is particularly useful to use a falling film evaporator for the vaporization required for the purposes of the rectification and thus to carry out the vaporization process gently.

Of course, the process of the present invention can also be employed for separating methacrylic acid from the reaction gas mixture from the catalytic gas-phase oxidation of C_4 or blocked C_4 starting compounds (eg. butene, tert-butenol, ethers of tert-butanol, methacrolein, etc., cf. for example DE-A 44 05 059) in a corresponding advantageous manner. The main advantages of the process of the present invention are based on the minimal total energy consumption and the particularly gentle treatment of the very reactive unsaturated carboxylic acids which reduces uncontrolled reactions.

Example

A process for the gas-phase catalytic oxidative preparation of acrylic acid from propylene, in which N_2 was used as diluent, gave a reaction gas mixture having a temperature of 277°C and the following composition:

28 FEB 1997

10

- 13.5 % by weight of acrylic acid,
- 0.25 % by weight of by-products having boiling points at atmospheric pressure above that of acrylic acid (high boilers),
- 5.35 % by weight of by-products having boiling points at atmospheric pressure below that of acrylic acid (low boilers, eg. H_2O , acrolein, formaldehyde, acetaldehyde and in particular acetic acid),
- 80.9 % by weight of residual gas (essentially N_2 , traces of carbon oxides and propylene).

220.2 kg/h of this reaction gas mixture were indirectly cooled to 204°C in a tube-shell heat exchanger. The cooling medium used was a mixture of 75 % by weight of diphenyl ether and 25 % by weight of biphenyl.

The cooled reaction gas mixture was subsequently introduced into a packed column (internal diameter: 316 mm) having a stainless steel wall (wall thickness: 4 mm) and fitted with ordered Mellapak packing from Sulzer AG, Winterthur, Switzerland, which column was in direct contact with the surrounding atmosphere (25°C) and was constructed as follows:

On a support grating located above the feed point of the cooled reaction gas mixture, first 2 of the abovementioned packing elements of the type 125 Y and subsequently 16 of the abovementioned packing elements of the type 250 Y (the diameter of the individual packing elements was 314 mm and the height was 210 mm) were stacked directly on top of one another as a first packing stack. Below the support grating there was a structural section having a length of 800 mm for accommodating the bottom liquid. The feed point for the cooled reaction mixture (feed point 1) was located in the middle of the structural section. 50 mm above the end of the first packing stack there was installed a collection tray for the descending liquid which went across the column cross section and was provided in the middle, for the purpose of allowing the rising vapor/gas mixture to pass through, with a capped chimney (height: 400 mm; diameter: 106 mm) around which four overflow tubes (height: 300 mm; diameter: 43 mm) were fitted symmetrically.

From this collection tray (takeoff point 1), 1700 kg/h of the liquid phase at 59.9°C flowing onto this collection tray were continuously taken off, cooled to 42°C and returned at this

28 FEB 1997

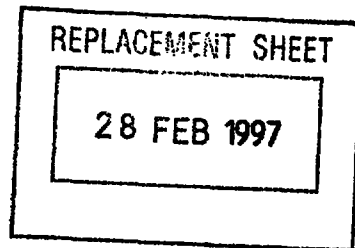
temperature to the packed column immediately above the end of the second packing stack.

The second packing stack consisted of three ordered packing elements of the same type (250 Y) stacked directly on top of one another and sitting on a support grating located above the chimney belonging to the collection tray, thus separating the takeoff point 1 from the return point. Above the return point, there were installed 13 further packing elements of the type 250 C stacked on top of one another (third packing stack). At the end of this third packing stack, there was located the feed point for the absorption medium (feed point 2). The absorption medium used was a mixture of 57.4 % by weight of diphenyl ether, 20.7 % by weight of biphenyl and 20 % by weight of dimethyl o-phthalate. It was introduced at the feed point 2 at 52°C and in an amount of 160.8 kg/h.

Immediately above the feed point 2 there was located an installed separation chimney above which there were fitted a further 5 ordered packing elements of the same type (250 Y) stacked on top of one another (fourth packing stack). Immediately above the end of the fourth packing stack there was located the feed point of the cold water circuit (feed point 3). 370 kg/h of aqueous phase were taken off from the collection tray of the installed separation chimney (takeoff point 2) and 6.7 kg/h of this were separated off and discharged as waste. The remaining amount was returned at the feed point 3. The takeoff temperature was 40.5°C and the aqueous phase was cooled to 25°C before return. The aqueous phase taken off contained 6.9 % by weight of acrylic acid (loss) and 93.1 % by weight of water and low boilers. The packed column was open at the top. 181.8 g of gaseous compounds were discharged at 26.6°C through this opening. This off-gas comprised 2 % by weight of water vapor, > 97.8 % by weight of residual gas, < 0.1 % by weight of acrylic acid and < 0.1 % by weight of absorption medium. The pressure at the top of the column was 1.15 bar, at the feed point 1 it was 1.24 bar. The organic phase flowing onto the takeoff point 2 was returned to the enrichment section at the feed point 2.

The amount of bottom liquid taken off was 192.5 kg/h, the associated takeoff temperature was 118.4°C. The composition of the bottom liquid was: 15.2 % by weight of acrylic acid, 84.35 % by weight of absorption medium, 0.29 % by weight of constituents having boiling points higher than that of acrylic acid (maleic anhydride, phthalic anhydride, etc.) and 0.16 % by weight of low boilers including H₂O.

The bottom liquid taken off was conveyed with ordered packing elements to a conventional rectification column (packed column having ordered packing) and fractionated by rectification under reduced pressure in a manner known per se. Acrylic acid was obtained in a purity of $> 99.7\%$ by weight via a side offtake. Small amounts of low boilers were obtained at the top of the column and the bottom liquid was reused as absorption medium. In a similar way, the phenothiazine used as polymerization inhibitor was introduced at the top of this rectification column.



THIS SHEET HAS BEEN
REPLACED

We claim:

A process for separating (meth)acrylic acid from the reaction gas mixture from catalytic gas-phase oxidation by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction gas mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid and the (meth)acrylic acid is subsequently separated by rectification from the (meth)acrylic acid-containing liquid discharge from the absorption column, wherein a rectification process is superimposed on the absorption process naturally occurring in the absorption column, by withdrawing from the absorption column an amount of energy exceeding the amount naturally given off as a result of contact with the surrounding atmosphere.

This Sheet Has Been Replaced



* C L M S *

REPLACEMENT SHEET

28 FEB 1997

THIS SHEET HAS BEEN
REPLACED

- 14 -

SEPARATION OF (METH)ACRYLIC ACID FROM THE REACTION GAS
MIXTURE FROM THE CATALYTIC GAS-PHASE OXIDATION OF
C₃/C₄ COMPOUNDS

Abstract

A process for separating (meth)acrylic acid from the reaction mixture from catalytic gas-phase oxidation by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid and the (meth)acrylic acid is subsequently separated by rectification from the (meth)acrylic acid-containing liquid discharge from the absorption column, in which a rectification process is superimposed on the absorption process naturally occurring in the absorption column by withdrawing from the absorption column an amount of energy exceeding the amount naturally given off as a result of contact with the surrounding atmosphere.

This Sheet Has Been Replaced



REPLACEMENT SHEET

28 FEB 1997



- 13 -

Claims

7607453-1 3805

REPLACEMENT SHEETS		SG
☐	Description	: paged to paged
☒	Claim(s)	: paged 13.. to paged 14..
☐	Drawing(s)	: paged to paged
☒	Abstract	: paged 15.. to paged 16..
DATE OF RECEIPT		3/2/99

REPLACEMENT SHEET

1. A process for the separation of (meth)acrylic acid from a reaction gas mixture formed by catalytic gas phase oxidation, by countercurrent absorption using a high-boiling inert, hydrophobic organic liquid, in which the reaction gas mixture is passed through an absorption column countercurrently to the descending high-boiling, inert, hydrophobic organic liquid and (meth)acrylic acid is subsequently fractionally separated from the liquid effluent leaving the absorption column and containing (meth)acrylic acid, wherein a rectifying process is superimposed on the absorption process occurring naturally in the absorption column by withdrawing a portion of the descending liquid phase at a point along the absorption column, cooling said withdrawn portion and subsequently recycling the cooled fluid to the absorption column at a point along the absorption column between the point of withdrawal and the feed point of the high-boiling hydrophobic absorbent.

2. The process as claimed in claim 1, wherein the withdrawal of the descending liquid phase is conducted at a point near the halfway mark of the absorption column and the liquid phase is recycled to the absorption column at a point slightly above the point of withdrawal.

3. The process as claimed in claim 1, wherein the bottom theoretical separating stage has a temperature of from 110°C. to 125°C. and the temperature at the top theoretical separating stage is 5° to 15°C. above the input temperature of the absorbent.

4. The process as claimed in claim 1, wherein the high-boiling, inert, hydrophobic organic liquid is a mixture of 70 to 75 wt.% of diphenylether and 25 to 30 wt.% of diphenyl.

5. The process as claimed in claim 1, wherein the high-boiling, inert, hydrophobic organic liquid is a mixture comprising a blend of 70 to 75 wt.% of diphenylether and 25 to

REPLACEMENT SHEET
03 FEB 1999



30 wt.% of diphenyl, and, based on this mixture, 0.1 to 25 wt.% of O-dimethylphthalate.

6. The process as claimed in claim 1, wherein said absorption column is a valve tray column, a bubble-cap tray column, a column filled with a loose, irregular, packing or a column filled with compact packs.

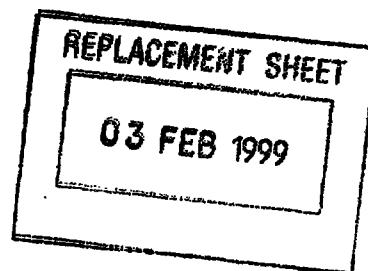
7. The process as claimed in claim 1, wherein the absorption column contains 5 to 20 theoretical separating stages.

8. The process as claimed in claim 1, wherein the reaction gas mixture entering the absorption column has a temperature of from 190° to 230°C.

9. The process of claim 8, wherein said temperature ranges from 200° to 210°C.

10. The process as claimed in claim 1, wherein the liquid absorbent entering the top of the absorption column has a temperature of from 50° to 100°C.

11. The process of claim 10, wherein said temperature ranges from 50° to 70°C.



- 15 -

SEPARATION OF (METH)ACRYLIC ACID FROM THE REACTION GAS
MIXTURE FROM THE CATALYTIC GAS-PHASE OXIDATION OF
C₃/C₄ COMPOUNDS

Abstract

A process for separating (meth)acrylic acid from the reaction mixture from catalytic gas-phase oxidation by countercurrent absorption using a high-boiling inert hydrophobic organic liquid, in which process the reaction mixture is passed through an absorption column in countercurrent to the descending high-boiling inert hydrophobic organic liquid and the (meth)acrylic acid is subsequently separated by rectification from the (meth)acrylic acid-containing liquid discharge from the absorption column, in which a rectification process is superimposed on the absorption process naturally occurring in the absorption column by withdrawing from the absorption column an amount of energy exceeding the amount naturally given off as a result of contact with the surrounding atmosphere.

