

---

## ESTERIFICATION OF (METH)ACRYLIC ACID

---

The present invention relates to a process for preparing an alkyl (meth)acrylate by  
10 continuous reaction of a (meth)acrylic acid-containing aqueous solution obtained  
directly from the gas-phase oxidation with an alkanol.

The term "(meth)acrylic acid" used in this application refers to both acrylic acid  
and methacrylic acid.

15

Methacrylic acid is obtainable, inter alia, by gas-phase oxidation of 1-butene,  
isobutene, isobutyraldehyde, isobutyric acid, MTBE and/or methacrolein with  
oxygen or oxygen-containing gases in the presence of catalysts such as multimetal  
oxides which comprise the elements molybdenum and vanadium in oxidic form.  
20 Preference is given to starting from methacrolein. The oxidation is carried out at  
elevated temperatures and also, owing to the high heat of reaction, preferably with  
dilution of the reactants with inert gases such as N<sub>2</sub>, CO<sub>2</sub> and/or hydrocarbons  
and/or water vapor. However, this process gives not pure methacrylic acid, but a  
reaction mixture comprising, apart from methacrylic acid, unreacted starting  
25 material such as methacrolein, water vapor, inert diluent gas (eg. nitrogen) and  
by-products (eg. carbon oxides), lower aldehydes such as formaldehyde, high-  
boiling constituents such as citraconic acid and also acids such as acetic acid,  
acrylic acid, formic acid and/or propionic acid, in particular acetic acid (cf. for  
example EP-A 0 253 409 and DE-A 19 62 431).

However, other conceivable starting compounds are those from which the starting material, eg. methacrolein, is first formed as an intermediate in the gas-phase oxidation. Examples which may be mentioned are the methyl ether of tert-butanol (MTBE). To prepare methacrolein, it is also possible to condense formaldehyde and propionaldehyde and to obtain methacrolein by subsequent distillation. Such a process is described in EP-B 0 058 927. The methacrolein obtained in this way can then be reacted in a conventional manner by catalytic gas-phase oxidation to form methacrylic acid. Such a reaction is described, inter alia, in EP-B 0 297 445.

10

Acrylic acid can, inter alia, be obtained analogously starting from the corresponding C<sub>3</sub> compounds, in particular propene and/or acrolein.

In general, the reaction mixture obtained in a process as described above for the preparation of (meth)acrylic acid is first subjected to a condensation step, giving a (meth)acrylic acid-containing aqueous solution.

The esterification of (meth)acrylic acid with an alkanol such as methanol to give an alkyl (meth)acrylate such as methyl (meth)acrylate and water is an equilibrium reaction which is increasingly shifted to the side of the starting materials with increasing water content. It is known that such equilibrium reactions can be shifted to the product side by use of an excess of one or the starting components (usually the alkanol) or by removing the reaction products (water and alkyl (meth)acrylate) from the esterification mixture. Furthermore, it is known that the esterification can be considerably accelerated by addition of suitable acids.

25

Thus, in JP-A 7 301 369, a mixture of methacrylic acid is esterified with an excess of alkanol (molar excess: 1.2-5.0) in the presence of an acid catalyst.



Furthermore, numerous esterification processes in which an aqueous methacrylic acid solution is used are known. In these processes, the methacrylic acid is generally separated from the water by extraction and subsequently esterified with an alkanol. Methacrylic acid and water cannot be separated by distillation owing  
5 to the formation of an azeotrope of these two components.

Thus, DE-A 29 07 602 describes a process for preparing alkyl (meth)acrylates from dilute aqueous methacrylic acid solutions, in which the methacrylic acid is separated from the water by extraction with an inert high-boiling solvent and  
10 subsequent distillation and is then esterified with an alkanol in the presence of an acid catalyst.

These processes all have the disadvantage of an additional separation problem which is caused by the introduction of the extractant and makes a series of  
15 separation steps necessary for obtaining (meth)acrylic acid or the (meth)acrylic ester without residues of the extractant.

Furthermore, US-A 43 31 813 describes the catalytic preparation of methyl methacrylate from an aqueous solution of isobutyric acid and methanol in the gas  
20 phase at  $410^{\circ}\text{C}$  and a pressure of  $1 \times 10^5 \text{ Pa}$ .

The direct esterification of an aqueous methacrylic acid solution is described in DE-A 31 46 191. According to this document, an esterification mixture comprising an aqueous methacrylic acid solution (methacrylic acid content: 5-  
25 60% by weight) is reacted continuously with an alkanol in the presence of sulfuric acid or an organic sulfonic acid to give the corresponding ester and the latter is subsequently distilled off.



4-

It is an object of the present invention to provide a further improved process for preparing an alkyl (meth)acrylate by continuous reaction of a (meth)acrylic acid-containing aqueous solution obtained directly from the gas-phase oxidation of (meth)acrolein, which process makes it possible to convert aqueous (meth)acrylic acid solutions having a water content of up to 90% by weight in the presence of various secondary components such as unreacted starting material such as (meth)acrolein (up to about 1% by weight), acetic acid (up to about 10% by weight), formic acid (up to about 1.5% by weight) and high-boiling constituents into the corresponding alkyl (meth)acrylate by reaction with a suitable alkanol.

Furthermore, the process of the present invention should be able to be carried out in an energetically more favorable manner than the processes known hitherto.

We have found that this object is achieved by the process of the present invention.

The present invention accordingly provides a process for preparing an alkyl (meth)acrylate by continuous reaction of a (meth)acrylic acid-containing aqueous solution obtained directly from the gas-phase oxidation with a linear or branched alkanol having from 1 to 6 carbon atoms or a mixture of two or more thereof in the presence of an esterification catalyst, wherein the alkanol is introduced in gaseous form into the (meth)acrylic acid-containing aqueous solution.

As already mentioned above, according to the process of the present invention a (meth)acrylic acid-containing aqueous solution obtained directly from the gas-phase oxidation of, for example, (meth)acrolein is reacted. Such aqueous solutions generally have a (meth)acrylic acid content of from about 10 to about 90% by weight, preferably from about 40 to about 90% by weight and more preferably from about 50 to about 90% by weight. The water content of these solutions is accordingly generally from about 10 to about 90% by weight, preferably from about 10 to about 60% by weight and more preferably from about 10 to about 50% by weight. The most important secondary constituents are unreacted starting

material such as (meth)acrolein up to a content of about 1% by weight, acetic acid up to a content of about 10% by weight and formic acid up to a content of 1.5% by weight and also high-boiling constituents, where the abovementioned percentages add up to 100% by weight.

5

In the process of the present invention, it is particularly surprising that the presence of unreacted starting material such as (meth)acrolein, ie. an aldehyde having a C-C double bond as a further reactive group, does not lead to the formation of residues in the reaction mixture under the selected reaction conditions, although it is known that, for example, aldehydes tend to form resin in the presence of acids.

Furthermore, the (meth)acrylic acid-containing aqueous solution used can further comprise a small amount, ie. up to about 1% by weight, of relatively nonvolatile constituents such as polymerization inhibitors. During the course of the reaction, these relatively nonvolatile constituents accumulate in the reaction mixture and can be removed, for example, by continuously taking off part of the bottoms. The bottoms can, if desired, in turn be worked up by conventional methods, in particular distillation processes. The volatile constituents, eg. water, (meth)acrylic acid and alkyl (meth)acrylate, present in the bottoms which have been taken off can be returned to the reaction after separating off the low-boiling constituents.

To prepare the (meth)acrylic acid-containing aqueous solution reacted in the present process, the gaseous products obtained from the gas-phase oxidation can, in one embodiment, be taken up in water, as a rule giving solutions having a relatively high water content of generally more than 50% by weight.

In a further embodiment, the gaseous products obtained from the gas-phase oxidation can be condensed by cooling, directly giving (meth)acrylic acid-

containing aqueous solutions having a relatively low water content of generally up to 50% by weight.

The catalyst used is sulfuric acid or a sulfonic acid, eg. benzenesulfonic acid, 5 toluenesulfonic acid or methanesulfonic acid, with preference being given to p-toluenesulfonic acid. The proportion of catalyst in the reaction mixture is calculated such that it is present in a concentration of from about 0.5 to 2 mol/l, preferably from about 1 to 1.5 mol/l, of reaction mixture. Although the major part, or even all, of the catalyst added is constantly regenerated within the reaction, 10 further relatively small amounts of catalyst can be metered in discontinuously or continuously during the reaction.

In the process of the present invention, the (meth)acrylic acid-containing aqueous solution, if desired together with small amounts of catalyst, is fed continuously to 15 a reaction apparatus, with the amount of reaction mixture present in the steady state being from 5 to 200% by weight, preferably from 50 to 150% by weight, based on the (meth)acrylic acid-containing aqueous solution fed in per hour.

Simultaneously with the abovementioned aqueous solution, a linear or branched 20 alkanol having from 1 to 6 carbon atoms is continuously added as gas to the reaction mixture in an at least equimolar amount, if desired in an excess of up to 4 times the stoichiometric amount, based on the amount of (meth)acrylic acid fed in. The preferred molar ratio of (meth)acrylic acid to alkanol is about 1:1.2 to 2.0. In the process of the present invention, the alkanol used is preferably methanol, 25 ethanol, isopropanol, n-propanol, isobutanol, tert-butanol or n-butanol, more preferably n-butanol, tert-butanol or methanol. The alkanol used can also contain a small amount of water. Of course, it is also possible to use mixtures of two or more alkanols.

When feeding in the alkanol, the feed conditions, ie. in particular temperature and pressure, are set such that the alkanol is fed in gaseous form to the reaction mixture. This makes it possible to significantly reduce the total energy consumption of the esterification and the subsequent vaporization of the product, possibly together with water, compared to addition of the alkanol in liquid form.

The reaction mixture is held at the boiling point under atmospheric or subatmospheric pressure and at from about 70 to about 170°C. In general, pressures of from about  $6 \times 10^3$  to  $2 \times 10^5$  Pa are required for this. The reaction mixture forms the bottoms of a distillation unit, where part of the bottoms is, when nonvolatile residues accumulate, as defined above, removed, purified and, if desired, recirculated.

The bottoms obtained in the process of the present invention are heated by means of a suitable heating apparatus and kept boiling to such an extent that the amount of reaction mixture remains approximately constant. The bottom of the distillation unit is preferably configured as a forced circulation-depressurization vaporizer or convection vaporizer in order to ensure good mixing of the reaction mixture without mechanical interference.

20

The distillate comprising an alkyl (meth)acrylate leaving the bottom of the unit is preferably taken off via a distillation column. This distillate comprises a mixture of the alkyl (meth)acrylate-water azeotrope and the alkanol used. For methyl methacrylate, the methyl methacrylate-water azeotrope at atmospheric pressure has the composition 86% by weight of methyl methacrylate and 14% by weight of water. The distillation is preferably carried out in such a way that (meth)acrylic acid which is generally likewise present in the feed to the distillation is separated from the distillate. This is, in particular, achieved when a part of the alkyl (meth)acrylate is returned to the distillation. Thus, the azeotrope is free of (meth)acrylic acid when it is separated off.

30

According to the present invention it has furthermore proven to be advantageous that the azeotrope is present as one phase when being separated off. The azeotrope is no more present as "one phase" if the azeotrope is separated into a methyl(meth)acrylate phase and a water phase. Furthermore, it has proven especially advantageous according to the present invention that the azeotrope is present as one phase as well as being free of (meth)acrylic acid when it is separated off.

- 10 It is in particular preferred that the azeotrope is present as one phase inside the column, thus achieving an especially good separation.

If the separation is carried out by means of a distillation column, it is in particular preferred that the azeotrope is present in the upper part of the column as one phase or free of (meth)acrylic acid or preferably present as one phase and free of (meth)acrylic acid. In this regard, it has been found that temperatures of from 50 to 100, preferably from 60 to 80 and more preferably from 65 to 75 °C in the head part are particularly suitable. Furthermore, it is advantageous that the separation is carried out at normal pressure, preferably in a range of  $\pm 300$  mbar, preferably  $\pm$  20 200 mbar, around normal pressure.

According to the present invention, the azeotrope is regarded as being free of (meth)acrylic acid if the azeotrope contains less than 10, preferably less than 1 and more preferably less than 0.1 weight-% (meth)acrylic acid.

25

After condensation, the distillate is separated into an upper organic phase comprising the alkyl (meth)acrylate and a lower water layer comprising the alkanol by means of a suitable apparatus. This separation can be carried out in one or more stages.

A part, generally the major part, of the organic phase is preferably returned to a column, part thereof preferably into the upper section of the column, whereby the separation performance is improved in order to obtain the alkyl (meth)acrylate in  
5 higher purity.

The organic phase can, apart from the alkyl (meth)acrylate as main product, further comprise high- and low-boiling constituents which can be separated from one another in a known manner by a plurality of distillation stages. The  
10 methacrylic acid-containing aqueous solution used frequently contains a small amount of isobutyric acid and especially acetic acid. This is esterified together with the methacrylic acid and can be separated from the corresponding ester mixture by distillation, for which a distillation column having an appropriately large number of theoretical plates is required.

15

The aqueous phase of the distillate comprises, apart from water, the main amount of the unreacted alkanol and, depending on the solubility, secondary constituents such as acetone or further aldehydes or ketones, as well as acetic and formic acids. Of course, the alkanol can be separated from the aqueous phase by conventional  
20 methods, for example fractional distillation, and be returned to the reaction in gaseous form.

According to the present invention, however, it is preferred that a part of the alkanol contained in the aqueous phase is withdrawn from the aqueous phase.  
25 This withdrawal is preferably carried out by distillative separation of the alkanol from the aqueous phase. For this purpose it is preferred to use a distillation column. According to the present invention it is preferred to withdraw at least a third, preferably at least the half, and more preferably at least 2/3 of the alkanol contained in the aqueous phase from the aqueous phase. Normally, the aqueous  
30 phase comprises 1 to 30, preferably 5 to 20, and even more preferably 10 to 15

weight-% of alkanol, preferably methanol, 0.1 to 10, preferably 1 to 7 and even more preferably 2 to 5 weight-% of the alkyl(meth)acrylic ester, preferably methyl(meth)acrylate, and up to 100 weight-% of aqueous phase of water.

- 5 For the distillative separation of alkanol and in particular for the distillative separation of methanol, it has proven particularly advantageous according to the invention that the aqueous phase is kept at a temperature of from 90 to 130, preferably from 95 to 120 and more preferably from 100 to 115 °C. In the upper part of the distillation column a temperature in the range of 60 to 90, preferably 65  
10 to 85, and more preferably of 70 to 80 °C has proven to be suitable.

Furthermore, it has proven particularly advantageous that the distillative separation of the alkanol is carried out at a pressure of from 1 to 3, preferably 1.1 to 3, and more preferably 1.2 to 1.4 bar.

15

- The alkanol withdrawn from the aqueous phase may be introduced into the (meth)acrylic acid containing aqueous solution. It may be introduced in the form of the liquid alkanol as well as in the form of the gaseous alkanol, it being preferred to introduce the alkanol in its gaseous form into the (meth)acrylic acid-  
20 containing aqueous solution.

Both the withdrawal of the alkanol from the aqueous phase as well as the introduction of the alkanol in the (meth)acrylic acid-containing aqueous solution may be carried out continuously or discontinuously, preferably continuously.

25

- The withdrawal of the alkanol from the aqueous phase and the introduction of the alkanol in the (meth)acrylic-containing aqueous solution have the advantage that the non-reacted alkanol contained in the aqueous phase can be introduced to the reaction in the (meth)acrylic acid-containing aqueous solution. Thus, the alkanol  
30 may be used in an economical manner, thus saving resources.

To prevent polymerization, a polymerization inhibitor such as hydroquinone, phenothiazine or hydroquinone monomethyl ether can be added, preferably at the top of the distillation apparatus. This gradually gets into the distillation bottoms and is removed during work-up of the latter.

5

The present invention is illustrated by the examples below.

Examples 1 to 5 which are according to the present invention were carried out in a unit for the continuous esterification of (meth)acrylic acid with methanol. This  
10 comprised a metering-in section, ie. a reservoir for the (meth)acrylic acid-containing aqueous solution, plus a feed facility for gaseous methanol, a reaction section having a reaction volume of from 500 to 1,000 ml, a packed column having a length of 100 cm and a nominal width of 5 cm as distillation unit and a phase-separation stage.

15

At the beginning, a reaction mixture comprising the methacrylic acid-containing aqueous solution obtained directly from the gas-phase oxidation of methacrolein, methanol and p-toluenesulfonic acid as catalyst were placed in the reaction section and brought to the operating conditions. Subsequently, gaseous methanol and the  
20 methacrylic acid-containing aqueous solution were continuously metered in at such a rate that the volume of the bottoms remained constant. Methyl methacrylate formed during the reaction was taken off at the top of the distillation unit as an azeotrope with water and was separated into an organic and an aqueous phase in a phase separator. Part of the organic phase was returned as runback to  
25 the top of the distillation column in order to prevent methacrylic acid from distilling off. Phenothiazine as stabilizer was metered into the runback stream in order to avoid polymerization in the distillation column.

The operating conditions and mass flows which were used in the Examples 1 to 5 which were according to the present invention and the methacrylic acid concentrations used in the examples are shown in Table 1 below.

- 5 The composition of the methacrylic acid-containing aqueous solutions used as feed are shown in Table 2.

**Table 1 – Operating conditions and mass flows**

The table below shows the operating conditions and mass flows for various methacrylic acid concentrations:

| Ex. No. | Temperature<br>at the<br>bottom<br>[°C] | Pressure<br>[mbar] | Reaction<br>volume<br>[ml] | MAA conc.<br>[mol/l] | MAA<br>feed<br>[g/h] | MEOH<br>feed<br>[g/h] | Molar ratio<br>MeOH/MAA | Flowback<br>[g/h] | Yield of<br>MMA<br>[g/h] | Yield<br>[% of theory] |
|---------|-----------------------------------------|--------------------|----------------------------|----------------------|----------------------|-----------------------|-------------------------|-------------------|--------------------------|------------------------|
| 1       | 101                                     | 1013               | 500                        | 1                    | 635                  | 356                   | 2.2:1                   | 1500              | 514                      | 99.4                   |
| 2       | 105                                     | 1013               | 600                        | 1                    | 421                  | 158                   | 2:1                     | 1600              | 244                      | 99.7                   |
| 3       | 103                                     | 1013               | 800                        | 1                    | 500                  | 112                   | 2:1                     | 2200              | 173                      | 99.2                   |
| 4       | 103                                     | 1013               | 900                        | 1                    | 600                  | 90                    | 2:1                     | 3000              | 135                      | 96.4                   |
| 5       | 105                                     | 1013               | 1000                       | 1                    | 534                  | 41                    | 2:1                     | 3000              | 57                       | 91.5                   |

5

10 **Table 2 – Composition of the (meth)acrylic acid-containing aqueous solutions**

Composition of the MAA feed streams:

| Ex. No. | Methacrylic acid<br>[% by wt.] | Water<br>[% by wt.] | Acetic acid<br>[% by wt.] | Acrylic acid<br>[% by wt.] | Formic acid<br>[% by wt.] | Methacrolein<br>[% by wt.] | Phenylacetylene<br>[% by wt.] | Propionic acid<br>[% by wt.] |
|---------|--------------------------------|---------------------|---------------------------|----------------------------|---------------------------|----------------------------|-------------------------------|------------------------------|
| 1       | 70.0                           | 20.8                | 6.0                       | 0.2                        | 1.5                       | 0.5                        | 0.5                           | 0.5                          |
| 2       | 50.0                           | 49.5                | 0.4                       | 0.1                        | 0.0                       | 0.0                        | 0.0                           | 0.0                          |
| 3       | 30.0                           | 69.6                | 0.3                       | 0.1                        | 0.0                       | 0.0                        | 0.0                           | 0.0                          |
| 4       | 20.0                           | 79.7                | 0.2                       | 0.1                        | 0.0                       | 0.0                        | 0.0                           | 0.0                          |
| 5       | 10.0                           | 89.8                | 0.1                       | 0.1                        | 0.0                       | 0.0                        | 0.0                           | 0.0                          |

Examples 6 to 12 relating to the continuous esterification of aqueous methacrylic acid were carried out in a mini-plant consisting of a metering-insection (a reservoir for the starting materials and the stabilizer solution), a reaction section (reactor with convection vaporizer), a distillation section and a settler-stage. At the beginning, one liter of the reaction solution was introduced into the reaction vessel and heated to operating temperature (95 to 110 °C). In the reactor aqueous methacrylic solution (liquid) and water-containing methanol (gaseous) were metered. Additionally, a stabilizer (phenotiazine) and a catalyst (p-toluenesulfonic acid) were added. Methyl methacrylate formed during the reaction was withdrawn at the top of the distillation column as an azeotrope with water as well as excess methanol. The condensate of the distillation was separated into an aqueous and an organic phase in a phase separator by adding water. Part of the organic phase was returned as run-back to the top of the distillation column. Part of the bottom of the reaction section was sometimes removed because of the secondary reactions.

The aqueous phase was fed into a distillation column in which at a bottom temperature of 100 to 115 °C and a head temperature of 60 to 80 °C at 1.3 bar the distillation was carried out. The overhead product contained besides methanol 2 to 12 % of water.

The operating conditions and the results of the analysis obtained in the examples according to the present invention can be taken from the enclosed Tables 3a to 3c. In the following Tables the operation and the results of the analysis are comprised for different bottom temperatures, MAA : MeOH-ratios and return flows.

Table 3a

| Feed   |               |                |               |                            | Measure Points        |                |                           |                            |
|--------|---------------|----------------|---------------|----------------------------|-----------------------|----------------|---------------------------|----------------------------|
| Ex.No. | MAA<br>[ml/h] | MeOH<br>[ml/h] | MMA<br>[ml/h] | H <sub>2</sub> O<br>[ml/h] | Return flow<br>[ml/h] | Bottom<br>[°C] | Head of<br>column<br>[°C] | After<br>condenser<br>[°C] |
| 6      | 600           | 450            | 140           | 750                        | 790                   | 104            | 71                        | 24                         |
| 7      | 603           | 429            | 148           | 760                        | 800                   | 105            | 71                        | 24                         |
| 8      | 600           | 439            | 155           | 775                        | 818                   | 105            | 71                        | 24                         |
| 9      | 600           | 420            | 141           | 750                        | 604                   | 103            | 71                        | 24                         |
| 10     | 605           | 426            | 143           | 761                        | 630                   | 103            | 71                        | 25                         |
| 11     | 623           | 428            | 140           | 760                        | 600                   | 107            | 71                        | 24                         |
| 12     | 588           | 481            | 146           | 748                        | 1522                  | 115            | 71                        | 24                         |

**Table 3b**

| Analysis of the organic head product |            |            |            |            |            |
|--------------------------------------|------------|------------|------------|------------|------------|
| Ex.No.                               | MeOH       | MeAc       | MMA        | MAA        | Water      |
|                                      | [% by wt.] | [% by wt.] | [% by wt.] | [% by wt.] | [% by wt.] |
| 6                                    | 2,12       | 0,39       | 96,04      | 0,00       | 1,45       |
| 7                                    | 0,86       | 0,28       | 97,43      | 0,00       | 1,44       |
| 8                                    | 1,44       | 0,25       | 96,87      | 0,00       | 1,44       |
| 9                                    | 0,40       | 0,25       | 97,92      | 0,00       | 1,43       |
| 10                                   | 1,32       | 0,24       | 97,07      | 0,00       | 1,38       |
| 11                                   | 1,60       | 0,23       | 96,71      | 0,00       | 1,45       |
| 12                                   | 2,02       | 0,46       | 95,94      | 0,00       | 1,58       |

**Table 3c**

| Analysis of the aqueous head product |                    |                    |                   |                   |                     |
|--------------------------------------|--------------------|--------------------|-------------------|-------------------|---------------------|
| Ex.No.                               | MeOH<br>[% by wt.] | MeAc<br>[% by wt.] | MMA<br>[% by wt.] | MAA<br>[% by wt.] | Water<br>[% by wt.] |
| 6                                    | 11,12              | 0,06               | 1,60              | 0,01              | 87,21               |
| 7                                    | 10,43              | 0,04               | 1,62              | 0,00              | 87,91               |
| 8                                    | 9,31               | 0,04               | 1,66              | 0,01              | 88,99               |
| 9                                    | 9,54               | 0,04               | 1,63              | 0,01              | 88,79               |
| 10                                   | 10,02              | 0,03               | 1,63              | traces            | 88,32               |
| 11                                   | 10,82              | 0,04               | 1,73              | 0,00              | 87,41               |
| 12                                   | 11,15              | 0,08               | 1,74              | 0,01              | 87,03               |

The abbreviations in Table 3a to 3c mean:

- MAA-feed: solution of methacrylic acid in 15 weight-% water
- MeOH-feed: gaseous metering of methanol with 10 weight-% water
- 5 - H<sub>2</sub>O: feed of water into the settler stage in order to improve the phase separation of the condensate.



### Claims

5

We claim:

- 10 1. A process for preparing an alkyl (meth)acrylate by continuous reaction of a (meth)acrylic acid-containing aqueous solution obtained directly from the gas-phase oxidation with a linear or branched alkanol having from 1 to 6 carbon atoms or a mixture of two or more thereof in the presence of an esterification catalyst, wherein the alkanol is introduced in gaseous form into the (meth)acrylic acid-containing aqueous solution.
- 15 2. A process as claimed in claim 1, wherein the alkanol is selected from the group consisting of methanol, butanol, tert-butanol and mixtures of two or more thereof.
- 20 3. A process as claimed in claim 1 or 2, wherein the esterification catalyst is p-toluenesulfonic acid.
4. A process as claimed in any of claims 1 to 3, wherein the alkyl (meth)acrylate is, in a separation stage, separated off as distillate comprising the azeotrope of the alkyl (meth)acrylate with water.
- 25 5. A process as claimed in claim 4, wherein the azeotrope is present as one phase or free of (meth)acrylic acid or is present as one phase and free of (meth)acrylic acid.



6. A process as claimed in claims 4 or 5, wherein the distillate is separated into an organic and an aqueous phase.
- 5 7. A process as claimed in claim 6, wherein at least a part of the organic phase is returned to the separation stage.
8. A process as claimed in claim 6, wherein from the aqueous phase at least a part of the therein contained alkanol is withdrawn.
- 10 9. A process as claimed in claim 8, wherein the alkanol is introduced into the (meth)acrylic acid-containing aqueous solution.
- 15 10. A process as claimed in any of claims 1 to 9, wherein the reaction is carried out in a convection vaporizer.