

Process for preparation of methacrylic acid and methacrylic acid ester

The invention relates to a process for preparation of methacrylic acid, a process for preparation of a methacrylic acid ester, and a process for treatment of an aqueous phase comprising at least one organic compound

Methacrylic acid (MAA) and methacrylic acid esters, such as methyl methacrylate (MMA) and butyl methacrylate are used in a wide variety of applications. The commercial production of methacrylic acid occurs, among other ways, by heterogeneously catalysed gas phase oxidation of isobutylene, tert-butanol, methacrolein or isobutyl aldehyde. The thus obtained, gaseous reaction phase is transformed into an aqueous methacrylic acid solution by cooling and condensing, optionally separated from low-boiling substances such as, for example, acetaldehyde, acetone, acetic acid, acrolein and methacrolein and then introduced into a solvent extraction column, in order to extract and separate methacrylic acid by means of suitable extraction agents, such as, for example, short-chain hydrocarbons. The separated methacrylic acid is further purified, for example by distillation, to separate high-boiling impurities, such as, for example, benzoic acid, maleic acid and terephthalic acid, in order to obtain a pure methacrylic acid. Such a known process is described for example in EP 0 710 643, US 4,618,709, US 4,956,493, EP 386 117 and US 5,248,819.

Such known processes generate large amounts of waste water at various process stages, of which the greatest amount is in the form of the aqueous phase remaining after the extraction of the methacrylic acid from the quench phase. The water comes mainly from added steam or water into the gas phase oxidation step, and from the use of water as quenching agent in the cooling and condensing step, as well as from the oxidation reaction itself. This waste water contains considerable amounts of organic compounds and cannot be re-used or safely disposed of without further treatment to remove at least partially these organic compounds. Such organic compounds generally include desirable products such as methacrylic acid, due to incomplete extraction into the organic extraction agent, as well as other byproducts of the oxidation step such as acrylic acid, acetic acid and propionic acid, which also have commercial value. The organic content in this waste water is generally too high to be compatible with water treatment processes such as biological treatment, for example activated sludge processes, without requiring significant dilution, considerable time and very

large treatment facilities, so that in commercial methacrylic acid production the waste water is often combusted, as described, for example, in US 4,618,709. Combustion of waste water is, however, both environmentally and economically unfavourable, requiring high energy input, leading to emissions which may require further treatment before release into the environment, and also leading to loss of potentially valuable organic compounds present in the waste water, as well as loss of the water itself.

It would thus be advantageous to be able to recover at least partially the organic compounds present in the waste water. It would also be advantageous to recover at least some of the water itself, either with an organics content which is sufficiently low for it to be subjected to a biological treatment and/or be discharged into the environment, for example without further treatment, or in a purity which is sufficient for the water to be re-usable, for example as industrial process water, or in the reaction itself, for example in the oxidation and/or quenching steps. CN 1903738 proposes the use of a membrane separator followed by a rectification tower for purifying waste water from acrylic acid production and recovering acrylic acid, toluene and acetic acid. A disadvantage of membrane filtration is that in general large amounts of water – often the waste water itself is used – are required to wash away the components which do not pass through the filter. This washing water with increased concentration of organic compounds must then itself be either further treated or combusted.

An object of the present invention is generally to overcome or avoid as far as possible the disadvantages of the prior art processes.

A further object is to increase the overall efficiency and/or yield of the methacrylic acid production process by recovering organic compounds from process waste water.

Another object of the present invention is to reduce as far as possible the contamination of waste water with organic compounds so that the water can be reused, subjected to a biological purification process, or discharged to the environment, optionally after a biological or other type of purification process, rather than being combusted together with the organic compounds.

A contribution to solving the above objects is made by a process for preparation of at least one of methacrylic acid and a methacrylic acid ester, comprising process steps:

- a1) gas phase oxidation of at least one C₄ compound to obtain a reaction phase comprising methacrylic acid;
- a2) quenching of the reaction phase to obtain a crude aqueous phase comprising methacrylic acid;
- a3) extraction of at least a part of the methacrylic acid from the crude aqueous phase comprising methacrylic acid into an organic solvent to obtain a crude organic phase comprising methacrylic acid and a first aqueous phase, wherein the first aqueous phase comprises components
 - i. at least 65 wt.%, preferably in the range of from 65 wt.% to 99.9 wt.%, more preferably in the range of from 70 wt.% to 99.8 wt.% water, yet more preferably in the range of from 75 wt.% to 99 wt.%, more preferably in the range of from 76 wt.% to 98.5 wt.%, more preferably in the range of from 77 wt.% to 98 wt.%, even more preferably in the range of from 78 wt.% to 97.5 wt.%, even more preferably in the range of from 79 wt.% to 95 wt.%, yet more preferably in the range of from 80 wt.% to 90 wt.% water, based on the total weight of the first aqueous phase, and
 - ii. not more than 35 wt.%, preferably in the range of from 0.1 wt.% to 35 wt.%, preferably in the range of from 0.2 wt.% to 30 wt.%, more preferably in the range of from 1 wt.% to 25 wt.%, yet more preferably in the range of from 1.5 wt.% to 24 wt.%, more preferably in the range of from 2 wt.% to 23 wt.%, even more preferably in the range of from 2.5 wt.% to 22 wt.%, even more preferably in the range of from 5 wt.% to 21 wt.%, yet more preferably in the range of from 10 wt.% to 20 wt.% of at least one organic compound other than the organic solvent used as extraction agent, based on the total weight of the first aqueous phase,wherein the sum of the weight amounts of i. and ii. is 100 wt.%;
- a4) separation and optionally purification of at least a part of the methacrylic acid from the crude organic phase comprising methacrylic acid;
- a5) optionally, esterification of at least a part of the methacrylic acid obtained in step a4);
- b) crystallisation of at least a part of the water from at least a part of the first aqueous phase obtained in process step a3) to form a crystallised aqueous phase as second aqueous phase and a mother liquor, wherein the mother liquor comprises at least one component ii.;
- c) at least partial separation of the crystallised aqueous phase from the mother liquor.

A contribution to solving the above objects is also made by a process for treatment of an aqueous phase comprising at least one organic compound, comprising process steps:

- a) provision of a first aqueous phase comprising components
 - i. at least 65 wt.%, preferably in the range of from 65 wt.% to 99.9 wt.%, more preferably in the range of from 70 wt.% to 99.8 wt.% water, yet more preferably in the range of from 75 wt.% to 99 wt.%, more preferably in the range of from 76 wt.% to 98.5 wt.%, more preferably in the range of from 77 wt.% to 98 wt.%, even more preferably in the range of from 78 wt.% to 97.5 wt.%, even more preferably in the range of from 79 wt.% to 95 wt.%, yet more preferably in the range of from 80 wt.% to 90 wt.% water, based on the total weight of the first aqueous phase, and
 - ii. not more than 35 wt.%, preferably in the range of from 0.1 wt.% to 35 wt.%, preferably in the range of from 0.2 wt.% to 30 wt.%, more preferably in the range of from 1 wt.% to 25 wt.%, yet more preferably in the range of from 1.5 wt.% to 24 wt.%, more preferably in the range of from 2 wt.% to 23 wt.%, even more preferably in the range of from 2.5 wt.% to 22 wt.%, even more preferably in the range of from 5 wt.% to 21 wt.%, yet more preferably in the range of from 10 wt.% to 20 wt.% of at least one organic compound, based on the total weight of the first aqueous phase,wherein the sum of the weight amounts of i. and ii. is 100 wt.%,
- b) crystallisation of at least a part of the water from at least a part of the first aqueous phase to form a crystallised aqueous phase as second aqueous phase and a mother liquor, wherein the mother liquor comprises at least one component ii.;
- c) at least partial separation of the crystallised aqueous phase from the mother liquor.

The C₄ compound which is subjected to gas phase oxidation in step a1) of the process according to the invention is preferably a C₄ compound selected from isobutylene, tert-butyl alcohol, isobutylaldehyde and methacrolein, or a mixture of two or more thereof. In a preferred aspect of the invention, the C₄ compound is derived from splitting of methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE).

The gas phase oxidation in step a1) of the process according to the invention preferably occurs in the presence of at least one oxidation catalyst. If the C₄ compound is isobutylene or

tert-butyl alcohol, the gas phase oxidation to obtain a methacrylic acid-comprising gas phase can occur in one step, whereby one step in this context is considered to mean that initial oxidation to methacrolein and further oxidation to methacrylic acid occur substantially in the same reaction area, in the presence of at least one catalyst. Alternatively, the gas phase oxidation in step a1) can occur in more than one step, preferably in two steps, preferably in two or more reaction areas separated from each other, whereby two or more catalysts are preferably present, each catalyst preferably being present in a separate reaction area from each other catalyst. In a two-step gas phase oxidation, the first step is preferably at least partial oxidation of the C₄ compound to methacrolein, followed by at least partial oxidation of methacrolein to methacrylic acid. Accordingly, for example, in a first reaction step, preferably at least one catalyst suitable for oxidation of at least one C₄ compound to methacrolein is present, and in a second reaction step, at least one catalyst suitable for oxidation of methacrolein to methacrylic acid is present.

Suitable reaction conditions for gas phase catalytic oxidation are, for example, temperatures of from about 250 °C to about 450 °C, preferably from about 250 °C to about 390 °C and pressures of from about 1 atm to about 5 atm. The space velocity can vary from about 100 to about 6000 hr⁻¹ (NTP) and preferably from about 500 to about 3000 hr⁻¹. Oxidation, for example gas phase catalytic oxidation, of C₄ feeds such as isobutylene to methacrolein and/or methacrylic acid, as well as catalysts therefor, are well known in the literature, for example from US 5,248,819, US 5,231,226, US 5,276,178, US 6,596,901, US 4,652,673, US 6,498,270, US 5,198,579, US 5,583,084.

Particularly preferred catalysts and processes suitable for oxidation of isobutylene or tert-butanol to methacrolein and/or methacrylic acid are described in EP 0 267 556, and particularly preferred catalysts and processes suitable for oxidation of methacrolein to methacrylic acid are described in EP 0 376 117. These documents are hereby introduced as reference and form part of the disclosure of the present invention.

The gas phase oxidation of methacrolein to methacrylic acid in the process according to the invention preferably occurs at temperatures of from about 250 to about 350 °C and below, at pressures from about 1 to about 3 atm, and at volume loads of from about 800 to about 1800 NI/l/h.

As oxidising agent, generally oxygen is used, for example, in the form of air, or in the form of pure oxygen or oxygen diluted with at least one gas which is inert under the reaction conditions, such as at least one of nitrogen, carbon monoxide and carbon dioxide, whereby air is preferred as oxidising agent and nitrogen and/or carbon dioxide are preferred as diluent gas. If carbon dioxide is used as diluent gas, this is preferably carbon dioxide recycled from a combustion, preferably a catalytic or thermal combustion of reaction gases and/or byproducts. The gas subjected to gas phase oxidation in step a1) of the process according to the invention preferably also comprises water, which is generally present in the form of water vapour. The oxygen, inert gas or gases and water can be introduced into the reaction phase or combined with the C₄ compound before or during or before and during the gas phase reaction.

In a preferred embodiment of the process according to the invention, a mixture comprising at least one C₄ compound, air or oxygen and recycled oxidation reactor exit gas, preferably reactor exit gas which has been combusted prior to recycling, is supplied to step a1). The reactor exit gas preferably comprises at least one unreacted C₄ compound, at least one carbon oxide, nitrogen and oxygen, as well as water, depending on the separation conditions and the presence of and action of a combustion step.

In a two-step gas phase oxidation according to the invention, a preferred volume ratio in the first step of C₄ compound : O₂ : H₂O : inert gas is generally 1 : 0.5 - 5 : 1 - 20 : 3 - 30, preferably 1 : 1 - 3 : 2 - 10 : 7 - 20. The volume ratio in the second step of methacrolein : O₂ : H₂O : inert gas is preferably 1 : 1 - 5 : 2 - 20 : 3 - 30, preferably 1 : 1 - 4 : 3 - 10 : 7 - 18.

In step a2) of the process according to the invention, the gas phase which comprises methacrylic acid is cooled and condensed – commonly known as quenching – to obtain a condensate in the form of a crude aqueous methacrylic acid-comprising solution. The condensation can occur by any means known to the skilled person and appearing suitable, for example by cooling the methacrylic acid-comprising gas phase to temperatures below the dew point of at least one of its components, in particular of at least one of water and methacrylic acid. Suitable methods of cooling are known to the skilled person, for example, cooling by means of at least one heat exchanger, or by quenching, for example by spraying the gas phase with a liquid, for example with water, an aqueous composition or an organic solvent, such as, for example, aromatic or aliphatic hydrocarbons, or a mixture of at least two

thereof, whereby preferred organic solvents have relatively low vapour pressure under the quenching conditions, such as heptane, toluene or xylene, whereby water is preferred as quench liquid according to the invention, and at least a portion of the condensate formed in the quenching step itself is even more preferred. Suitable quenching processes are known to the skilled person, for example from DE 21 36 396, EP 297 445, EP 297 788, JP 01193240, JP 01242547, JP 01006233, US 2001/0007043, US 6,596,901, US 4,956,493, US 4,618,709, US 5,248,819, whose disclosure concerning quenching of acrylic and methacrylic acids is hereby incorporated and forms part of the present disclosure. It is preferred according to the invention that the gas phase is cooled to temperatures between 40 and 80 °C and washed with water and/or condensate from the quenching step to obtain an aqueous solution comprising methacrylic acid, which can also comprise varying amounts of impurities such as acetic acid, maleic acid, fumaric acid, citraconic acid, acrylic acid and formic acid, as well as aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, acrolein, methacrolein, ketones and unreacted C₄ compound or compounds. These impurities, as well as water, need to be separated to the greatest extent possible from the methacrylic acid in order to obtain a high degree of purity of methacrylic acid.

The extraction of at least a part of the methacrylic acid from the crude aqueous methacrylic acid-comprising solution occurs in process step a3) by means of an organic extraction agent, for example at least one organic solvent, preferably at least one organic solvent which is substantially immiscible with water, such that an aqueous phase and an organic phase can be formed. Preferred organic solvents which can be used in step c) of the process according to the invention have a boiling point different to, preferably lower than, the boiling point of methacrylic acid. Preferably, in the process according to the invention, the organic extraction agent used in process step a3) has a boiling point of less than 161 °C measured at atmospheric pressure. The organic extraction agent can then in principle be separated from methacrylic acid, for example by distillation, preferably at least partially, preferably to a substantial extent in step a4) of the process according to the invention, where it is preferably at least partially removed as a low boiler at a higher level in the distillation apparatus than the pure methacrylic acid. The separated organic extraction agent or a part thereof can be conducted back to process step a3), optionally after at least one cooling and/or purification step. Preferred organic solvents for this step are in particular selected from alkanes and aromatic, preferably alkylaromatic, hydrocarbons, whereby at least one organic solvent selected from C₆-C₈ hydrocarbons is preferred, whereby heptane, toluene and xylene are

particularly preferred and heptane, preferably n-heptane is most preferred. The extraction can be carried out by any means known and appearing suitable to the skilled person, preferably by means of a countercurrent extraction, for example by means of a solvent extraction column, a pulsed fill or packing column, rotating extractors, a washing column, a phase separator or other device suitable for extraction of an aqueous phase with an organic solvent and separation of the organic phase from the aqueous phase. It is preferred according to the invention that at least a part, preferably at least 50 wt.%, preferably at least about 70 wt.%, preferably at least about 80 wt.%, more preferably at least about 90 wt.% of the methacrylic acid comprised in the aqueous methacrylic acid solution is extracted into the organic phase.

Two phases are thus obtained in step a3) of the process according to the invention: a crude organic phase comprising methacrylic acid, which is conducted to step a4) of the process according to the invention, and the first aqueous phase comprising components i. and ii. – water and at least one organic compound – in the amounts described above. Organic compounds which may be comprised as component ii. in the first aqueous phase are any organic compounds which are formed during the gas phase oxidation reaction, such as those mentioned above in connection with the crude aqueous phase obtained in the quenching step, as well as unreacted C₄ compounds and any methacrylic acid which has remained in the aqueous phase. While the first aqueous phase may comprise a small amount of the organic solvent used as extraction agent in process step a3), for example due to incomplete separation, this organic solvent is preferably not considered as an organic compound of component ii. according to the invention.

In step a4) of the process according to the invention, the crude organic phase comprising methacrylic acid obtained in step a3) is subjected to a separation, preferably a thermal separation process to separate at least a part of the methacrylic acid comprised therein from the organic solvent which was used as extraction agent in process step a3). If a thermal separation is used, this is preferably a distillation, whereby organic solvent used for the extraction in process step a3) preferably is removed as head product or at an upper level of a distillation column, while methacrylic acid or a methacrylic acid-rich phase is removed as bottom product or at a lower level of the distillation column than the extraction agent. It is also possible to use, for example, a fractionating or rectification column, so that impurities with boiling points higher than methacrylic acid remain in the bottom product and methacrylic

acid of higher purity can be removed at a level which is higher than the bottom of the column. If the organic solvent used for extraction has a higher boiling point than the boiling point of methacrylic acid, it is also possible to remove methacrylic acid phases at the top and/or higher levels of the column. A further purification of the thus-obtained methacrylic acid or methacrylic acid-rich phase can be by means of a further thermal process, such as distillation or rectification, or by other means such as by crystallisation. Intermediate steps may also be comprised in the process according to the invention, before or during process step a4), such as, for example, any one or more of stripping or distillation to separate low boilers or high boilers, filtration to remove solid impurities, crystallisation, washing and the like. The number of purification and other separation steps depends on the amount of contaminants and on the desired purity of the methacrylic acid end product. If the methacrylic acid is to be used as such, for example as a monomer or co-monomer for preparation of a methacrylic acid polymer, a higher purity may be preferred, in particular depending on the end application. If the methacrylic acid is to be esterified, a lower purity of methacrylic acid can be acceptable, for example if the ester end product can be purified more simply, more effectively or more efficiently than the methacrylic acid.

The esterification in process step a5) of at least a part of the thus obtained methacrylic acid can be carried out in any way known and appearing suitable to the skilled person, optionally in the presence of a polymerisation inhibitor to prevent polymerisation of methacrylic acid and/or methyl methacrylate. The means of carrying out the esterification in step a5) is not particularly limited. The esterification can be carried out, for example, as described in US 6,469,202, JP 1249743, EP 1 254 887, US 4,748,268, US 4,474,981, US 4,956,493 or US 4,464,229 whose disclosures concerning esterification of acrylic and methacrylic acids are hereby incorporated and form part of the present disclosure. A liquid phase esterification is preferred. If the esterification occurs by means of a direct reaction between methacrylic acid and an alcohol it is preferred that the reaction is catalysed by a suitable catalyst. Esterification catalysts are known to the skilled person and include, for example, heterogeneous or homogeneous catalysts such as solid state catalysts or liquid catalysts. The esterification catalyst is preferably an acidic ion exchange resin such as those described in US 6,469,292, JP 1249743, EP 1 254 887 or commercially available under the trade name names Amberlyst® (Rohm and Haas Corp.), Dowex®, (Dow Corp.) or Lewerit® (Lanxess AG), or an acid capable of catalysing esterification, such as sulphuric acid, H₂SO₄.

Methacrylate esters prepared in process step a5) according to the invention preferably have formula $[\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(=\text{O})\text{O}]_n\text{-R}$, and can be formed by esterification of methacrylic acid with an alcohol of formula $\text{R}(\text{OH})_m$, whereby

n and m represent an integer from 1 to 10, preferably from 1 to 6, more preferably from 1 to 5, more preferably from 1 to 4, more preferably from 1 to 3 and

R is selected from the group consisting of linear or branched, saturated or unsaturated, aliphatic or aromatic, ring or straight chain hydrocarbons and linear or branched, saturated or unsaturated, aliphatic or aromatic, ring or straight chain hetero-atom-comprising hydrocarbons, for example alkyls, hydroxyalkyls, aminoalkyls, other nitrogen- and/or oxygen-comprising residues, glycols, diols, triols, bisphenols, fatty acid residues, whereby R preferably represents methyl, ethyl, propyl, iso-propyl, butyl, in particular n-butyl, iso-butyl, hydroxyethyl, preferably 2-hydroxyethyl, and hydroxypropyl, preferably 2-hydroxypropyl or 3-hydroxypropyl, 2-ethylhexyl, isodecyl, cyclohexyl, isobornyl, benzyl, 3,3,5-trimethyl cyclohexyl, stearyl, dimethylaminoethyl, dimethylaminopropyl, 2-tert-butyl aminoethyl, ethyl triglycol, tetrahydrofurfuryl, butyl diglycol, methoxypolyethylene glycol-350, methoxypolyethylene glycol 500, methoxypolyethylene glycol 750, methoxypolyethylene glycol 1000, methoxypolyethylene glycol 2000, methoxypolyethylene glycol 5000, allyl, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol 200, polyethylene glycol 400, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, glycerol, diurethane, ethoxylated bisphenol A, ethoxylated bisphenol A with 10 ethylene oxide units; trimethylolpropane, an ethoxylated $\text{C}_{16}\text{-C}_{18}$ fatty alcohol such as, for example, with 25 ethylene oxide units, 2-trimethylammonium ethyl.

The methacrylic acid esters can also be prepared from methyl methacrylate by other methods known to the skilled person, for example by transesterification. In a further possible preparation of the hydroxyester derivatives, methacrylic acid according to the invention can be reacted in a ring-opening reaction with a corresponding oxygen-comprising ring, for example an epoxide, in particular ethylene oxide or propylene oxide.

Preferred methacrylic acid esters are alkyl methacrylates, in particular methyl, ethyl, propyl, iso-propyl, butyl, methacrylates, in particular methyl, n-butyl, iso-butyl, sec-butyl methacrylates, in particular methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, hydroxyester methacrylate derivatives, for example hydroxyethyl methacrylate, preferably 2-hydroxyethyl methacrylate, and hydroxypropyl methacrylate, preferably 2-hydroxypropyl

methacrylate or 3-hydroxypropyl methacrylate, and other methacrylate esters such as ethyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, benzyl methacrylate, 3,3,5-trimethyl cyclohexyl methacrylate, stearyl methacrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, 2-tert-butyl aminoethyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, butyl diglycol methacrylate, methoxypolyethylene glycol-350 methacrylate, methoxypolyethylene glycol 500 methacrylate, methoxypolyethylene glycol 750 methacrylate, methoxypolyethylene glycol 1000 methacrylate, methoxypolyethylene glycol 2000 methacrylate, methoxypolyethylene glycol 5000 methacrylate, allyl methacrylate, a methacrylic ester of an ethoxylated (optionally, for example, with 25 mol EO) C₁₆-C₁₈ fatty alcohol, 2-trimethylammonium ethyl methacrylate chloride; ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol 200 dimethacrylate, polyethylene glycol 400 dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, glycerol dimethacrylate, diurethane dimethacrylate, ethoxylated bisphenol A dimethacrylate, ethoxylated (optionally, for example, with 10 EO) bisphenol A dimethacrylate; trimethylolpropane trimethacrylate, whereby methyl methacrylate, butyl methacrylates and hydroxyester methacrylate derivatives are particularly preferred.

In process step b) of the process according to the invention, at least a part of the first aqueous phase is subjected to a crystallisation to obtain a crystallised aqueous phase, in which the water of this phase is present in crystallised form, and a mother liquor comprising at least one component ii.. The crystallisation in process step b) can occur by methods known to the skilled person for continuous or batchwise, preferably continuous crystallisation, such as dynamic or static crystallisation or a combination of the two, for example melt crystallisation, scratch cooling crystallisation, fractional crystallisation, layer crystallisation, suspension crystallisation, falling film crystallisation and the like, or any combination of two or more thereof, whereby suspension melt crystallisation is preferred, preferably in a continuous crystallisation process. In a preferred aspect of step b) of the process according to the invention, the crystallisation can occur in two stages, whereby in a first stage crystals form, for example on a cooled surface, and in a second stage these crystals are allowed to grow and increase in size. The two stages can take place in substantially the same area as each other, or each stage can take place in a separate area. If a suspension melt crystallisation is carried out in the process according to the invention, it is preferred that the crystallisation

occurs in at least one crystallisation and melting cycle. In a preferred aspect of a suspension melt crystallisation according to the invention, at least a part of the melted crystallised water is used to wash at least a part of the crystallised water. Suitable processes are described, for example, with reference to purification of acrylic acid and/or methacrylic acid, in WO 02/055469, WO 99/14181 WO 01/77056, US 5,504,247, whose disclosure concerning crystallisation, in particular suspension melt crystallisation as disclosed in WO 01/77056 and WO 02/055469, is hereby incorporated by reference and forms part of the present disclosure. If water forms a eutectic mixture with one or more components ii. in the first aqueous phase, in order to obtain water in the crystallised (second) aqueous phase which is as pure as possible water is preferably only crystallised out to around the eutectic point.

In step c) of the process according to the invention the crystallised aqueous phase as second aqueous phase is at least partially separated from the mother liquor. The separation can be carried out by any means known and appearing suitable to the skilled person, preferably by means of at least one of a filtration, a centrifugation, a phase separation or other solid-liquid separation means, preferably a filtration, a centrifugation or a phase separation, whereby a washing of the crystals may also be comprised, for example a washing with at least one of mother liquor, melted crystallised aqueous phase, and water. Such a wash-melt-type crystallisation and separation is described, for example in the references cited above with respect to process step b). In a preferred aspect of step c) of the process according to the invention, a phase separation, preferably in a wash column, for example a wash column of the type disclosed in WO 01/77056, is used whereby the crystallised phase floats on and/or in the mother liquor, and/or is collected and/or compacted, for example by means of a movable plate which moves upwards in the column and allows mother liquor to pass through while retaining the crystallised phase on the plate, for example a plate in the form of a filter, so that the crystallised phase can be removed at the top or at an upper level of the wash column, while the mother liquor passes through the plate and is removed at a lower level of the phase separator compared to the crystallised phase. It is also possible that the crystallised phase is separated at a lower level of a phase separator, for example depending on the relative densities of the crystallised aqueous phase and the mother liquor, or the device used for crystallisation and/or separation. In this aspect, at least a part of the crystallised phase can be melted, for example in a heat exchanger, and conducted back to the wash column as wash liquid to wash the crystallised phase present in the wash column, preferably in countercurrent flow. In another preferred embodiment of step c) of the process

according to the invention the separation is carried out by centrifugation. In this embodiment at least a part of the crystallised phase can be melted, for example in a heat exchanger, and conducted back to the centrifugation device as wash liquid to wash crystallised phase present in the centrifugation device. Since the mother liquor is depleted in water and comprises a greater proportion of organic components compared to the first aqueous phase, it is possible to incinerate the mother liquor obtained after the separation in process step c). Such an incineration has the advantage that this substantially organic phase, with reduced water content compared to the first aqueous phase, can act as a fuel, thus reducing the need to purchase fuel. This option could be preferred, for example, if fuel costs or associated requirements, such as ease and/or cost of transport are disadvantageous and/or the market value of one or more of the organic compounds of component ii. is low, in particular compared to the overall effort and expenditure required for their separation and/or purification.

In a preferred aspect of the process according to the invention, steps b) and c) are carried out continuously. The crystallisation step b) may take place in a crystallisation unit suitable for carrying out step b) of the process according to the invention, which is optionally connected to a separation unit suitable for carrying out step c) of the process according to the invention, such as a wash unit or a centrifugation device, as described above. The crystallisation unit may comprise one or two stages, corresponding to the possible two stages of process step b). In the crystallisation unit, or in the first stage of a crystallisation unit, the first aqueous phase is generally cooled so that water at least partially crystallises out. If crystals form at least partially on cooled surfaces of the crystallisation unit, these can be scraped off. The resulting slurry is then optionally conducted to the second stage of the crystallisation unit, if a second stage is comprised, where the slurry is preferably stirred while more crystals grow and/or crystal size increases. From the crystallisation unit the crystal/mother liquor slurry is then conducted to the separation unit, where the solid crystals are at least partially separated and optionally washed to at least partially remove impurities. At least a part of the optionally washed crystals can be melted, and at least a part of the melted part can be either conducted to, or treated in, a further process step, as described below in connection with process step f), or used as wash liquid, whereby it is possible that a first part of the melted crystallised phase is handled as described below in connection with process step f) and a further part of the melted crystallised phase is used as wash liquid for washing the crystals. It is also possible that at least a part of the crystals is supplied to the

crystallisation unit as crystallisation seed. A melting step may also be comprised. The melting step may be effected by means of a device which may be internal or external to at least one of the crystallisation unit and the wash unit. The crystallisation unit can be any crystallisation unit known to the skilled person and appearing suitable for crystallisation of water from an aqueous solution comprising organic components. Suitable crystallisation units, as well as crystallisation units incorporating wash and/or melt units are those commercially available from Sulzer Chemtech AG, Switzerland or Niro Process Technology B.V., The Netherlands. Examples of suitable crystallisation units, wash units and melting units, as well as combined crystallisation/wash/melt units are given in the literature cited above in connection with process step b). Centrifugation devices suitable for the process according to the invention are known to the skilled person.

Process steps b) and c) can, but do not necessarily result in complete crystallisation of water out of the first aqueous phase, so that the mother liquor can, or even generally does, comprise a certain amount of water. This is, for example, particularly the case if water forms a eutectic mixture with one or more of the components ii. of the first aqueous phase. In this case, in order to obtain water in the crystallised (second) aqueous phase which is as pure as possible, water is preferably only crystallised out to around the eutectic point, so that a proportion of water remains in the mother liquor. The proportion of water remaining in the mother liquor thus depends on the type and amount of the respective components ii. in the first aqueous phase with which water forms a eutectic mixture, and the respective eutectic point of water with this or these components ii.. In a further aspect of the process according to the invention, the process further comprises at least one of the process steps

- d) at least partial dewatering of the mother liquor separated in process step c) to obtain an at least partially dewatered mother liquor;
- e) separation of at least a part of at least one component ii. from the mother liquor obtained in process step c) or from the at least partially dewatered mother liquor obtained in process step d).

In a preferred aspect of the process according to the invention, at least a part of the water remaining in the mother liquor after the crystallisation is separated from the mother liquor in process step d). The dewatering in process step d) preferably occurs by means of an azeotropic distillation, preferably an azeotropic distillation using an entrainer. Any entrainer known to the skilled person and appearing suitable for the at least partial dewatering of the

mother liquor separated in process step c) can be considered. Particularly preferred entrainers according to the invention are linear or branched alkanes, especially heptane or hexane, cycloalkanes, especially cyclohexane, acetates, especially isobutyl acetate or ethyl acetate, aromatic compounds, especially toluene or benzene, or CS₂, CCl₄ or bromo methane.

The separation in process step e) is preferably a thermal separation process, preferably a distillation, fractionation or rectification, whereby at least a part of at least one component ii. is separated from the mother liquor or from the dewatered mother liquor. The mother liquor or the dewatered mother liquor can comprise, for example, in addition to at least one component ii. to be separated, extraction agent from step a3) of the process according to the invention, or other components ii.. If more than one component ii. is comprised in the mother liquor or the dewatered mother liquor, for example two or more components ii., it is possible that only one component ii. is separated in process step e), or that two or more components ii. are separated. The selection of distillation, fractionation or rectification as separation means can be easily made by the skilled person and depends on a number of factors, for example on the number and amount of other compounds in the mother liquor or the dewatered mother liquor from which the at least one component ii. is to be separated, as well as the respective boiling points of the one or more components ii. to be separated and of the components of the mother liquor or the dewatered mother liquor which are not intended to be separated, in particular the proximity of the boiling points of the other components of the mother liquor or the dewatered mother liquor to the boiling point of the at least one component ii. to be separated and, if more than one component ii. is to be separated, the proximity of the boiling points of the components ii. to be separated to each other. Another factor to consider is the desired purity of the at least one component ii. to be separated.

In a preferred embodiment of the process according to the invention, the process further comprises process step

f) melting of the crystallised aqueous phase to obtain a melted crystallised aqueous phase as third aqueous phase,

wherein the melted crystallised aqueous phase is subjected to at least one of being conducted to at least one biological purification treatment, being used as process water, and being conducted to at least one of process steps a1), a2).

The melting of the crystallised aqueous phase can occur by any means known to the skilled person and appearing suitable. In particular, the crystallised aqueous phase can be subjected to a temperature at which it melts, for example in a melting device or a heat exchanger. The melting in process step f) can correspond to the melting already mentioned in the description of process steps b) and c), and/or it can be a further melting. Thus, for example, a first melting might be carried out within the scope of process steps b) and c), for example in order to provide a wash liquid for washing the crystals. The wash liquid itself then preferably at least partially crystallises on the crystals as it contacts them. The thus washed and then separated crystals can be melted again to provide a wash liquid, in as many wash-melt cycles as are necessary to obtain a desired crystal purity. Once a desired purity has been obtained, the crystals can then be melted in step f) of the process according to the invention, and further conducted to at least one of biological purification treatment, being used as process water, and at least one of process steps a1) and a2).

If the third aqueous phase is subjected to at least one biological purification treatment this treatment is preferably at least one of an aerobic treatment and an anaerobic treatment. In one embodiment of a treatment having two or more stages, for example, a first anaerobic treatment can be followed by an aerobic treatment, a first aerobic treatment can be followed by an anaerobic treatment, or a sequence of aerobic and/or anaerobic treatments can be used, as for example in a sequential batch reactor.

The melted crystallised aqueous phase, or third aqueous phase, according to the invention is generally of sufficient purity to be usable directly as process water or as added water in process steps a1) or a2) of the process according to the invention. In particular, the crystallised aqueous phase or the melted crystallised aqueous phase preferably comprises less than 5000 ppm, preferably less than 4000 ppm, more preferably less than 3000 ppm, preferably in the range of from 1500 to 2500 ppm, more preferably in the range of from 1800 to 2200 ppm, most preferably not more than 2000 ppm, based on the total weight of the respective aqueous phase, of organic compound. It is possible to achieve lower amounts of impurities, for example less than about 500 ppm, or even less than 100 ppm and in the range of from 0 ppm to 100 ppm, in particular by employing a large number of wash-melt cycles in process step c) according to the invention. These lower amounts of impurities are, however, generally only obtained together with a reduced amount of water. A biological purification treatment can optionally be carried out before use as process water or as added water in

process steps a1) or a2). If the water of the melted crystallised aqueous phase is to be used for other purposes or discharged into the environment it can be preferred but is not always necessary that such use or discharge follows a biological purification.

The term "biological purification treatment" in the context of the present invention is intended to mean any treatment which increases the purity of water, for example by removing contaminants or impurities, preferably organic contaminants, by means of one or more biological organisms and/or microorganisms or biologically or biochemically active substances, for example substances derived from such organisms or microorganisms. The contaminants and impurities to be removed in this way are generally the organic compounds remaining in the third aqueous phase. The removal is effected by digestion or breaking down of some or all of the organic compounds. Increased purity of water is measured, for example, by a decrease in contaminants and/or impurities, and/or by a decrease in the water's biochemical oxygen demand (BOD) or chemical oxygen demand (COD), preferably to levels which mean the waste water can be reused, for example as industrial process water, in the process according to the invention, in particular in one or both of process steps a1) or a2), or discharged into the environment or into a water supply chain, depending on the purity achieved. Biological purification treatments are known to the skilled person and can be, for example, one or more of a so-called activated sludge treatment. Such treatments are conventional and well known to the person skilled in the art. The biological purification treatment can be carried out in one or more stages, and may be continuous or discontinuous.

If the separation in process step e) of the process according to the invention is a thermal separation, it may not always be possible, or, for example, economically or technically practical to separate components from each other, for example if two or more components have very similar boiling points. This may be particularly the case if the mother liquor or the dewatered mother liquor which is subjected to process step e) comprises a relatively large number of components, in particular if one or more components ii. have similar boiling points to the at least one component ii. which is to be separated in process step e), making a fine tuning of the separation for just one component ii. in process step e) more difficult. It can then be more appropriate or more practical to separate two or more components ii. in the further process step g), where such an adaptation for the specific separation requirements of the respective components ii. may be more easily achieved. Accordingly, in an aspect of the

process according to the invention, the at least one component ii. separated in process step e) can be a mixture of at least two components ii. and in a further process step

g) at least one component ii. is preferably at least partially separated from this mixture.

The separation in process step g) of the process according to the invention may comprise one or more separation steps, such as a thermal separation, as already discussed above for other separation steps in the process according to the invention, a chromatographic separation, a chemical separation, for example by preferential reaction of one component ii. to form a reaction product which is more easily separable from the one or more other components ii. or by reaction of two or more components ii. to form reaction products which are more easily separable from each other, or any other separation means known and appearing suitable to the skilled person.

In a preferred embodiment of the process according to the invention, the at least one organic compound of component ii., preferably the at least one component ii. which is at least partially separated in process step g), is at least one organic compound selected from carboxylic acids, aldehydes and ketones. Among these, it is preferred according to the invention that the at least one component ii., preferably the at least one component ii. which is at least partially separated in process step g), is at least one of acetic acid, acrylic acid, propionic acid and methacrylic acid.

If the at least one component ii. separated in at least one of process steps e) and g) is or comprises methacrylic acid, in a preferred embodiment of the process according to the invention at least a part of this methacrylic acid phase is added to the crude aqueous phase obtained in process step a2) and/or to the crude organic phase obtained in process step a3) . This embodiment can be preferred, for example if the methacrylic acid separated in one or more of process steps e) and g) is not of the purity desired for its end use. Addition to the crude aqueous phase might be preferred, for example, if the separated methacrylic has been separated together with one or more other components with boiling point lower than methacrylic acid. Addition to the crude organic phase can be preferred, for example, if the components other than methacrylic acid have higher boiling points than methacrylic acid, since such higher boilers can be separated in process step a4). While the relative proportions of methacrylic acid to other components, in particular to other components ii., can also play a role, the nature of the other components in the at least one component ii. separated in at least one of process steps e) and g) has greater weight in deciding to which

phase this methacrylic acid-comprising phase separated in at least one of process steps e), f) and j) is added. For example, if the methacrylic acid separated in at least one of process steps e) and g) is relatively pure, comprising, for example, not more than about 5 wt.%, preferably not more than about 4 wt.%, preferably not more than about 3 wt.%, preferably not more than about 2 wt.%, preferably in the range of from about 1 wt.% to about 2 wt.% of impurities or other components ii., it can be preferred to introduce this methacrylic acid into the optional purification step of process step a4).

In a further aspect of the process according to the invention, at least a part of the at least one component ii. separated in at least one of process steps e) and g) or comprised in the dewatered mother liquor obtained in process step d), or at least a part of the first aqueous phase obtained in process step a3), is subjected to a process step

h) esterification to obtain an ester phase comprising at least one ester.

This step can be preferred if the respective at least one component ii. is a carboxylic acid. The details of the esterification step are generally the same as those described above for process step a5) of the process according to the invention. An esterification of at least one component ii. separated in at least one of process steps e) and g), rather than or in addition to obtaining the respective at least one component ii. itself, can be preferred, depending, for example, on the obtainable purity of the separated respective component ii., on the market or further applications for the respective component ii. compared to its ester. An esterification of at least one component ii. comprised in the first aqueous phase obtained in process step a3) can be preferred, for example, if the first aqueous phase comprises only a small proportion of impurities and/or components ii. which are not intended to be separated, for example a total amount of impurities of less than about 6 wt.%, preferably less than about 5 wt.%, preferably less than about 4 wt.%, more preferably less than about 3 wt.%, based on the total weight of the first aqueous phase, of impurities and/or components ii. which are not intended to be separated, based on the total weight of the first aqueous phase, in particular impurities which can be, for example, more easily separated from an ester of a respective component ii. than from the component ii. itself.

Particularly preferred esters comprised in the ester phase according to the invention are based on a C₁ – C₄ carboxylic acid and a C₁ – C₄ alcohol, whereby esters based on a C₂ – C₄ carboxylic acid are preferred. Particularly preferred esters, in addition to the methacrylate

esters mentioned in connection with process steps a5), are methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, sec-butyl acetate, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, methyl propionate, ethyl propionate, n-propyl propionate, isopropyl propionate, n-butyl propionate, isobutyl propionate, sec-butyl propionate, of which the acetates and the acrylates are preferred.

It is possible according to the invention that the ester phase comprises at least two esters. This can be the case if the at least one component ii. separated in at least one of process steps e) and g), or at least a part of the first aqueous phase obtained in process step a3), comprises at least two components ii. which are capable of reacting to form an ester, in particular at least two carboxylic acids. This embodiment can be preferred if the at least two components ii. which are capable of reacting to form an ester are particularly difficult to separate, for example by thermal or other means, for example where their properties such as boiling point, solubility in a given solvent and/or volatility are very close, whereas their esters can be separated from each other with less difficulty.

If the ester phase comprises two or more esters, the process according to the invention preferably further comprises the process steps

- j) at least partial separation of at least one ester from the ester phase;
- k) optionally, purification of the at least one ester separated in process step j).

In general, in addition to the at least one ester, the ester phase can comprise solvent, for example water or at least one organic solvent suitable for an esterification reaction, or a mixture thereof, as well as unreacted component ii., and possibly also further ester or esters. The separation in process step j) may be by any separation means known to the skilled person and appearing suitable for separating the respective ester from the ester phase. Examples of suitable separation means are, for example, thermal separation, such as distillation, fractionation or rectification, separation means based on different solubility of the at least one ester compared to other components of the ester phase, solid-liquid separation means such as filtration, among others. If necessary or desired, for example, depending on the intended end application of the respective ester, a purification of the at least one ester separated in process step j) can also be carried out in process step k). The purification means depends on the ester, whereby, for example, purification by thermal means, by chromatographic means, by washing, or by crystallisation can all be considered.

In an embodiment of the process according to the invention, the process further comprises the step

aa1) splitting of methyl tert-butyl ether (MTBE) to obtain at least one C₄ compound and methanol,

wherein at least a part of the at least one C₄ compound is supplied as feed to the gas phase oxidation of at least one of process steps a1). MTBE is widely used as feedstock for isobutylene and splitting of MTBE is well known in the art. Splitting of MTBE can occur by any suitable means which are known to the skilled person. Suitable catalysts and reaction conditions are described, for example, in EP 1 149 814, WO 04/018393, WO 04/052809; Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A4, p. 488; V. Fattore, M. Massi Mauri, G. Oriani, G. Paret, Hydrocarbon Processing, August 1981, p. 101-106; Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A16, p. 543-550; A. Chauvel, G. Lefebvre, "Petrochemical Processes, Technical and Economic Characteristics", Vol. 1, Éditions Technip, Paris, 1989, p. 213 et seq.; US 5,336,841, US 4,570,026, and references cited therein. The disclosures of these references are hereby incorporated by reference and form part of the disclosure of the present invention.

The two main products of MTBE splitting are the C₄ compound isobutylene and methanol. The further C₄ compound tertiary-butanol can also be comprised in the splitting reaction product phase. Either or both of isobutylene and tertiary-butanol can be supplied as feed to process step a1) to make up the total C₄ compound content of the feed for this process step or in addition to further C₄ content from another source. One or more intermediate separation and/or purification steps are also possible between the splitting of MTBE and the supplying of the thus-obtained at least one C₄ compound to the gas phase oxidation in process step a1), for example, to separate as far as possible the at least one C₄ compound and methanol from each other and to remove any side products from the splitting which might adversely affect the gas phase oxidation. Separation and/or purification can be by any means known to the skilled person and appearing suitable. Suitable purification and separation processes are described, for example, in EP 1 149 814, WO 04/018393 and WO 04/052809. After separation of methanol, the splitting phase which comprises the C₄ compound isobutylene as main component can then be optionally purified and provided as feed to process step a1). Suitable purification methods are known to the person skilled in the art and preferably comprise at least one of distillation, extraction, adsorption, absorption, chromatography or

washing, preferably at least one of distillation and extraction, preferably at least one distillation and at least one extraction. Unreacted MTBE can be at least partially separated from the C₄ compound phase in this step. Separated MTBE can be optionally purified and at least partially recycled to the splitting reaction.

In a preferred embodiment of the process according to the invention, the methanol obtained in process step aa1) is supplied to process step h). In another aspect of the process according to the invention, the methanol obtained in process step aa1) can be supplied to process step a5). The methanol can optionally be purified, preferably by means of a thermal purification such as distillation, fractionation or rectification, crystallisation, extraction, column or washing, more preferably at least one distillation. An example of a purification of methanol is described in EP 1 254 887.

The invention also relates to a device for production of at least one of methacrylic acid and a methacrylic acid ester, comprising at least the following components in fluid-conducting communication with each other:

- A1) a gas phase oxidation unit,
- A2) a quench unit,
- A3) a first extraction unit,
- A4) a first separation unit,
- A5) optionally, a first esterification unit,
- B) a crystallisation unit for crystallisation of water from an aqueous phase,
- C) optionally, a second separation unit.

The term "in fluid-conducting communication" is understood here as meaning that the units are connected such that a fluid, which can be at least one of a liquid, a gas, a vapour, a supercritical fluid or any other fluid, can be conducted from one unit to at least one other unit. This can be achieved, for example by direct communication via tubes or pipes, for example made of a material which is resistant to the reagents and conditions prevailing, such as stainless steel or glass, or any other suitable material known to the skilled person, or indirectly by means of tank vehicles or a tank or reservoir arranged between units. If a gas is to be conducted and should remain in gaseous form, the means of conducting the gas is preferably maintained at a temperature above the dew point of the gas. If a liquid is to be

conducted, the means of conducting the liquid is preferably maintained at a temperature above the solidification and/or precipitation point of the liquid and/or components present in the liquid. This can be achieved by means of insulating and/or heating the means of conducting the respective gas or liquid. All reactors, columns, and other device components are preferably made from a material which is resistant to the reagents and conditions, such as temperature and pressure conditions in particular, to which they are subjected.

The gas phase oxidation unit A1) preferably comprises at least one reactor suitable for carrying out a gas phase reaction, in particular a pressure reactor, preferably at least one multitube reactor, formed for example as a tube and shell reactor, and/or at least one plate reactor and/or at least one fluidised bed reactor, whereby a multitube reactor is preferred. Particularly preferred is at least one multitube reactor in which oxidation catalyst is arranged in at least one tube, preferably wherein the tubes are packed or coated, preferably packed, with oxidation catalyst. Oxidation catalysts preferred according to the invention are those mentioned above in connection with the inventive process. The reactor materials should be resistant and preferably inert to the reagents and prevailing conditions inside the reactor. Suitable reactors are commercially available, for example from MAN DWE GmbH, Deggendorfer Werft, Germany, or from IHI Corporation, Japan, and form part of the general knowledge of the person skilled in the art.

In a two stage gas phase oxidation, the gas phase oxidation unit A1) can comprise at least two reaction zones, each comprising oxidation catalyst. The at least two reaction zones can be at least two reaction zones in a single reactor, or at least two reactors. The oxidation catalyst in a first reaction zone is preferably an oxidation catalyst for oxidation of at least one C₄ compound, preferably isobutylene and/or tert-butanol, to methacrolein, and the oxidation catalyst in a second reaction zone is preferably suitable for oxidation of methacrolein to methacrylic acid. Suitable catalysts are mentioned above in connection with the process according to the invention.

In a preferred aspect of the apparatus of the present invention, at least one supply for at least one source of oxidant, preferably oxygen, preferably air, and at least one supply for water and/or steam, are in fluid communication with the gas phase oxidation unit. If the gas phase oxidation unit comprises at least a first and a further oxidation area, the apparatus can comprise, for each oxidation area, at least one supply for at least one oxidant source and at

least one supply for water and/or steam. The apparatus can further comprise a supply for a diluent such as nitrogen, argon and/or carbon dioxide, preferably nitrogen or carbon dioxide, for example carbon dioxide-comprising recycle gas from a catalytic combustion unit (CCU) or a thermal combustion unit (TCU), preferably a CCU or a TCU downstream in the device according to the invention. The respective supplies should be made of a material which is resistant to the reagents and conditions prevailing, for example, stainless steel or glass. In a preferred design the oxygen, diluent and water are supplied to the C₄ flow before entry into the respective reactor, so that a pre-formed mixture enters the reactor.

Step a1) of the process according to the invention is preferably carried out in the gas phase oxidation unit A1).

In a preferred embodiment of the apparatus according to the invention, the quench unit A2) is an absorption unit in which the gaseous oxidation phase is condensed and/or absorbed to form a liquid phase. It is preferred that methacrylic acid present in the oxidation phase leaving the catalytic reaction zone is condensed in the quench unit A2) to form a solution, preferably an aqueous solution, comprising methacrylic acid as main oxidation product. Unreacted methacrolein can also be separated in the absorption unit A2) and, if desired, conducted back to the gas phase oxidation zone for further reaction. Quench units suitable for use in the apparatus according to the invention are known to the skilled person. Step a2) of the process according to the invention is preferably carried out in the quench unit A2).

In a preferred embodiment of the device according to the invention, the quench unit A2) is followed by a first extraction unit A3). The methacrylic acid-comprising aqueous solution formed in the quench unit A2) is conducted to the first extraction unit A3), where an organic solvent is provided, into which solvent methacrylic acid is preferably substantially extracted. The organic solvent is preferably substantially immiscible with water, so that an aqueous phase which is at least partially depleted in methacrylic acid, and a methacrylic acid-comprising organic phase are formed. Details regarding preferred organic solvents are given above in the description of process step a3). Process step a3) is preferably carried out in the first extraction unit. Any extraction unit known to the skilled person and appearing suitable for such an extraction of methacrylic acid can be considered for use as the first extraction unit A3).

The device according to the invention comprises first separation unit A4) downstream of the first extraction unit A3). If the device according to the invention is for production of methyl methacrylate, the first separation unit A4) is upstream of the first esterification unit A5), preferably between and in fluid communication with the first extraction unit A3) and the first esterification unit A5). The first separation unit A4) is preferably suitable for separation and preferably purification of methacrylic acid, in particular for separation of methacrylic acid from the extraction agent used in the first extraction unit A3), and preferably also allows separation of methacrylic acid from other components present in the crude organic phase exiting the first extraction unit A3) of the device according to the invention, corresponding to the crude organic phase of process step a3) of the process according to the invention. The first separation unit A4) is preferably a thermal separation unit, preferably comprising at least one of a distillation column, a fractionating column, a rectification column, and any other thermal separation means known to the skilled person and appearing suitable for the separation of process step a3) of the inventive process. It is possible that the first separation unit A4) comprises more than one separation stage.

An optional first purification unit for purification of methacrylic acid separated in the first separation unit may also be arranged downstream of the first separation unit. The optional first purification unit can be, for example, a thermal purification unit, such as a distillation column, a fractionation column, a rectification column or the like, a crystallisation unit, or any other device known to the skilled person and appearing suitable for purification of methacrylic acid.

It is possible for the device according to the invention to further comprise one or more additional components between any or all of the units or components mentioned, for example thermal or stripping means for separating high and/or low boiling components, means for solid/liquid separation, such as at least one filter and/or centrifuge, and/or cooling and/or heating units. In a preferred design, for example, a distillation column for low boilers and optionally also a filter are arranged downstream of the quench unit and upstream of the extraction unit. In a further preferred aspect of a two-stage gas phase oxidation unit, a quench unit is arranged between the two stages.

Unreacted methacrolein can be separated in any of the quench unit, the first extraction unit, the first separation unit, the first purification unit, or any of the above-mentioned further device components, and conducted back to the gas phase oxidation unit for further reaction.

A first esterification unit A5) can be arranged downstream of the first separation unit A4) or the optional first purification unit. The first esterification unit A5) is not particularly limited and can be any unit suitable for esterification to form a methacrylate ester, preferably methyl methacrylate, from methacrylic acid. It is preferably suitable for liquid phase esterification. The first esterification unit A5) preferably comprises an esterification catalyst, which can be a heterogeneous or homogeneous catalyst such as a solid state catalyst or a liquid catalyst, and is preferably an acidic ion exchange resin such as those described in US 6,469,292, JP 1249743, EP 1 254 887 or commercially available under the trade name names Amberlyst® (Rohm and Haas Corp.), Dowex®, (Dow Corp.) or Lewertit® (Lanxess AG), or an acid capable of catalysing esterification, such as sulphuric acid, H₂SO₄.

A second purification unit can be arranged downstream of the first esterification unit A5), for purification of the methacrylate ester produced therein. The optional second purification unit can be, for example, a thermal purification unit, such as a distillation column, a fractionation column, a rectification column or the like, a crystallisation unit, or any other device known to the skilled person and appearing suitable for purification of methacrylic ester, in particular methyl methacrylate.

The device according to the invention further comprises a crystallisation unit B). The crystallisation unit B) serves to separate at least a part of the water comprised in the first aqueous phase obtained in the first extraction unit A3) from at least a part of at least one organic compound, in particular at least one component ii. as described above, to obtain a second aqueous phase and an organic phase. Process step b) of the process according to the invention is preferably carried out in crystallisation unit B). The device according to the invention preferably further comprises a second separation unit C), which is preferably a crystal separation unit. Process step c) of the inventive process is preferably carried out in second separation unit C).

In the crystallisation unit B), the first aqueous solution obtained in the first extraction unit A3) is generally cooled so that water at least partially crystallises out. The resulting slurry may

then be conveyed, optionally via a residence unit T1) for crystal growth, as described above in connection with process steps b) and c), to a crystal separation unit C), for example a wash column or a centrifuge, where the solid crystals are at least partially separated from the mother liquor, and preferably washed to at least partially remove remaining impurities to the greatest extent possible. At least one melting device may also be comprised in at least one of the crystallisation unit B) and the second separation unit C), and may be internal or external to at least one thereof, preferably being in fluid- and/or solid-conducting communication with at least the crystal separation unit. At least a part of the optionally washed crystals is preferably melted in the at least one melting unit and at least a part of the melted part either passed to the next device component or used as wash liquid for the crystals in the crystal separation unit C), or both. It is also possible that at least a part of the crystals is supplied, by means of one or more conduits, from the crystal separation unit C) to the crystallisation unit B) and/or to the residence unit as crystallisation seed.

Any crystallisation units, residence units and crystal separation units known to the skilled person and appearing suitable for the above-described purposes can be used in the device according to the invention, whereby respective units allowing a continuous crystallisation and separation are preferred. The crystallisation unit can be any crystallisation unit known to the skilled person and appearing suitable for crystallisation of water from an aqueous solution comprising organic components, whereby suspension crystallisation units are preferred, and even more preferred are suspension crystallisation units equipped with a scraper for at least partially scraping crystals off of cooled surfaces on which they may form. The residence unit, if provided, is preferably in the form of a tank, preferably equipped with stirring means, and with at least one inlet in fluid- and/or solid-conducting communication with the crystallisation unit and at least one outlet in fluid- and/or solid-conducting communication with the crystal separation unit. The crystallisation unit B), optionally together with the residence unit T1), is preferably suitable for carrying out step b2a) of the process according to the invention. The crystal separation unit C) is preferably suitable for carrying out step c) of the process according to the invention, and is preferably a wash column or a centrifugation device. Suitable crystallisation units, as well as crystallisation units incorporating wash and/or melt units are, for example, suspension crystallisation units with downstream washing of the crystals in an hydraulic or mechanical wash column as described in the book "Melt Crystallisation Technology" by G.F. Arkenbout, Technomic Publishing Co. Inc., Lancaster-Basel (1995), pp. 265-288, in Chem. Ing. Techn. (72) (10/2000), 1231-1233. Generally, any

wash melt wash columns with forced transport, eg described in Chem. Ing. Techn. 57 (1985) No. 2, p. 91-102 and Chem. Ing. Techn. 63 (1991), No. 9, p. 881-891 and in WO 99/6348. Examples of suitable wash melt columns are described in EP 97405, US 4735781, WO 00/24491, EP 920894, EP 398437, EP 373720, EP 193226, EP 191194, WO 98/27240, EP 305316, US 4787985, and are commercially available, for example from the TNO Institute in Apeldoorn, Netherlands, from Niro Process Technology B.V., Hertogenbosch, NL, or from Sulzer Chemtech AG, Switzerland, TNO or Niro Process Technology B.V., The Netherlands. Further examples of suitable crystallisation units, wash units and melting units, as well as combined crystallisation/wash/melt units are also given in the literature cited above in connection with process step b2a). Centrifugation devices suitable as crystal separation units in the device according to the invention are known to the skilled person and are widely available from commercial sources.

At least one incinerator or combustion unit may be comprised in the device according to the invention, for example for incineration of the mother liquor obtained from the crystallisation unit and/or the crystal separation unit.

The device according to the invention can also further comprise a dewatering unit D). The device according to the invention can also comprise a third separation unit E). The dewatering unit is preferably suitable for carrying out process step d) of the inventive process and the third separating unit is preferably suitable for carrying out process step e) of the inventive process. Dewatering units which are known to the skilled person and appear suitable for at least partial dewatering of the mother liquor separated in the crystallisation unit and/or the crystal separation unit can be considered for use in the device according to the invention. Preferred dewatering units according to the invention are, for example, columns packed with a dehydration agent which does not react with at least one component ii., such as molecular sieves, and distillation units, in particular distillation units which are suitable for azeotropic distillation. The third separation unit E) is preferably a thermal separation unit. Thermal separation devices known to the skilled person and appearing suitable for carrying out the separation of process step e) can be considered for use in the device according to the invention, such as at least one of distillation, fractionation or rectification columns, or the like.

Further separation units may also be comprised in the device according to the invention. One example of a preferred further separation unit is a separation unit suitable for separating at least one component ii. from a mixture comprising at least two components ii. according to the invention, for example a mixture obtained in step e) of the process according to the invention. Such further separation units are preferably thermal separation units, preferably comprising at least one distillation column, fractionation column, rectification column, or the like.

The device according to the invention preferably comprises at least one conduit between the third separation unit E) and/or at least one further separation unit, and first extraction unit A3) and/or first separation unit A4), for conducting at least one of methacrylic acid and a methacrylic acid-comprising phase back to at least one of the first extraction unit A3) and the first separation unit A4).

The device according to the invention optionally comprises at least one second esterification unit H) for esterification of at least one component ii., preferably downstream of at least one of the crystallisation unit B), the second separation unit C) and the third separation unit E). Process step h) of the inventive process is preferably carried out in second esterification unit H). The details concerning the second esterification unit H) are the same as those mentioned above for the first esterification unit A5).

The device according to the invention can also comprise at least one ester separation unit J) for at least partial separation of one or more esters from each other, in particular for at least partial separation of at least one ester from the ester phase obtained in the at least one second esterification unit, corresponding to process step j) of the inventive process. Any device known to the skilled person and appearing suitable for separation of esters may be used as ester separation unit J). Thermal separation devices of the types already mentioned, as well as crystallisation devices, extraction devices, phase separation devices are preferred as ester separation unit in the device according to the invention.

At least one further purification unit K) may also be provided in the device according to the invention, for purification of the ester and/or esters obtained in the second esterification unit or separated in the at least one ester separation unit. Process step k) of the process according to the invention is preferably carried out in the at least one further purification unit

K). The details of this further purification unit correspond to those for the purification unit mentioned in connection with the first esterification unit.

In a preferred aspect of the device according to the invention, the device further comprises an MTBE splitting unit AA1) upstream of the gas phase oxidation unit A1). Splitting units and suitable catalysts for MTBE splitting are well known in the art and form part of the general knowledge of the skilled person, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A4, p. 488; V. Fattore, M. Massi Mauri, G. Oriani, G. Paret, Hydrocarbon Processing, August 1981, p. 101-106; Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A16, p. 543-550; A. Chauvel, G. Lefebvre, "Petrochemical Processes, Technical and Economic Characteristics", Vol. 1, Éditions Technip, Paris, 1989, p. 213 et seq.; US 5,336,841, US 4,570,026, and references cited therein.

An isobutylene separation unit S1) is preferably arranged between the MTBE splitting unit AA1) and the gas phase oxidation unit A1) and in fluid-conducting communication with each. The isobutylene separation unit S1) serves to separate an isobutylene phase and preferably also a methanol phase from the effluent of the second catalytic reaction zone, which effluent comprises isobutylene and methanol as principal components. The isobutylene separation unit S1) can be at least one of an extractor, a crystalliser, a column, a distillation device, a rectification device, a membrane, a pervaporation device, a phase separator and a wash device. The isobutylene separation unit S1) preferably comprises an outlet for an isobutylene phase and an outlet for a methanol phase. The outlet for an isobutylene phase is preferably connected to the gas phase oxidation unit A1), optionally via an intermediate unit such as a purification unit, a heat exchanger, and/or a pressuriser. The outlet for a methanol phase is preferably connected to at least one of the first esterification unit A4) and the second esterification unit H), optionally via an intermediate methanol purification unit. Any device known to the skilled person and appearing suitable for purification of methanol may be comprised as methanol purification unit. Examples of suitable purification units preferably comprise at least one distillation device, crystalliser, extractor, column or wash device, more preferably at least one distillation device. An example of a purification unit for methanol is described in EP 1 254 887.

The invention also relates to a process according to the invention, wherein the process takes place in a device according to the invention.

The invention is more closely illustrated by the following figure and non-limiting examples.

Fig. 1 shows schematically a preferred embodiment of the process according to the invention in the form of a flow diagram.

Fig. 2 shows schematically an embodiment of the device according to the invention

According to the embodiment of Fig. 2, a C_4 compound is introduced into gas phase oxidation unit A1 where it is oxidised in a one- or two-stage catalytic gas phase oxidation to methacrylic acid. Inlets into gas phase oxidation unit A1 for C_4 compound, oxygen, steam and inert diluent gas are not shown. The C_4 compound can be provided from an MTBE splitting unit AA1 (not shown), via an isobutylene separating unit S1 (not shown). The gaseous methacrylic acid phase obtained in gas phase oxidation unit A1 is conducted via line 1 to quench unit A2, where it is cooled and absorbed into water or an aqueous phase to form an aqueous methacrylic acid-comprising phase. An inlet for the quench liquid into quench unit A2 is not shown. The aqueous methacrylic acid phase is conducted via line 2 to first extraction unit A3, where it is extracted with an organic solvent as extraction agent to form an organic phase and an aqueous phase (the first aqueous phase of the process according to the invention). These two phases are separated in first extraction unit A3.

The organic phase from first extraction unit A3 is conducted via line 3 to first separation unit A4, where it is distilled to separate methacrylic acid and extraction agent. The extraction agent can be recycled via line 6 to first extraction unit A3. The methacrylic acid can be collected via line 5 and optionally purified in downstream purification unit or units (not shown), or it can be conducted via line 4 to first esterification unit A5, optionally via a purification (not shown). In first esterification unit A5, the methacrylic acid can be esterified, for example with methanol, for example methanol separated from an MTBE splitting phase in separating unit S1 (not shown), to form methyl methacrylate. It is also possible to esterify methacrylic acid in first esterification unit A5 with other alcohols as mentioned above. The ester produced in first esterification unit A5 is collected via line 7 and can be optionally polymerised in

polymerisation unit A6 (not shown), optionally with intermediate and/or downstream purification.

The aqueous phase separated in first extraction unit A3 is conducted to crystallisation unit B, where it is generally cooled so that water at least partially crystallises out. If crystals form at least partially on cooled surfaces of the crystallisation unit B, these can be scraped off. The resulting slurry is then optionally conducted to a residence unit T1 (not shown), where the slurry is preferably stirred while more crystals grow and/or crystal size increases. From the crystallisation unit B and/or the residence unit T1 the slurry of crystals and mother liquor is then conducted via line 9 to the crystal separation unit C, where the solid crystals are at least partially separated from the mother liquor and optionally washed to at least partially remove impurities. A part of the crystals may be conducted back from crystal separation unit C to crystallisation unit B and/or to residence unit T1 to act as crystal seed (conduit not shown). At least a part of the optionally washed crystals can be melted (melting device not shown) and at least a part of the melted part can be recycled, for example to gas phase oxidation unit A1 (conduit not shown), used as process water, used as wash liquid for washing the crystals in the crystal separation unit C, conducted to a biological purification unit (not shown) or discharged, via line 20. The mother liquor separated in crystal separation unit C can be conducted, optionally via a dewatering unit D (not shown), via line 10 to third separation unit E where at least one component ii. can be separated. If a mixture of components ii. is separated in third separation unit E, this mixture can be conducted to a further separation unit for separation of components ii. from each other (not shown). If methacrylic acid or a methacrylic acid-comprising phase is separated in third separation unit E, this methacrylic acid or methacrylic acid-comprising phase can be conducted via line 15 to first extraction unit A3 or via line 16 to first separation unit A4. At least a part of the at least one component ii. separated in third separation unit E can be collected via line 11 and optionally purified in a further purification unit (not shown). It is also possible that at least a part of the at least one component ii. separated in third separation unit E is conducted via line 14 to second esterification unit H. The mother liquor separated in crystal separation unit C may be conducted to second esterification unit H. In second esterification unit H at least one component ii. is esterified with an alcohol to form a corresponding ester. If the alcohol is methanol, this methanol can, for example, be introduced from MTBE splitter AA1 via separation unit S1, optionally with intermediate purification (not shown). If the ester phase obtained in second esterification unit H comprises more than one ester, at least one ester

can be separated in ester separation unit J. At least one ester can be purified in downstream ester purification unit K (not shown).

Example 1:

The example was carried out in a pilot plant according to Fig. 3 (Niro process pilot plant rented from GEA). An artificial first aqueous phase was mixed and stored in B-100. The first aqueous phase was fed into a scraped surface heat exchanger (crystallizer) where the first aqueous phase was cooled to -15 °C wherein ice crystals are formed at the cool surfaces. The ice crystal containing first aqueous phase is fed to a re-crystallizer where larger crystals are formed. The ice crystals were separated from the concentrated liquid in a piston type wash column. From the wash column pure water was withdrawn as the second aqueous phase. This stream of ice crystals was finally melted to gain the third aqueous phase of pure water. With an yield of 84 % the water was removed from the first aqueous phase, while gaining pure water with an concentration of 99,85 % water and minor concentrations of acetic acid (0,11 %) and ethanol (0,04 %). Next to the second aqueous phase the mother liquor was withdrawn from the wash column with an water concentration of 55,5 %. The mother liquor was fed into the distillation column K-200 where the mother liquor was dewatered by an entrainer. As an entrainer isobutyl acetate (BuOAC) was used. The distillation column was packed with random packing and was continuously operated at 350 mbar with a steam heated evaporator and a condenser operated with cooling water. A phase separation vessel was used as a distillation vessel while the light phase was used for the reflux and the heavy phase was withdrawn from the system. The dewatering worked very well as water free sump effluent (dewatered mother liquor) was gained with a water concentration lower than 0,01 %. Finally the water is withdrawn from the system via the heavy phase of the distillate phase separation vessel with an concentration of 0,02 % acetic acid and an concentration of 2 % acetone.

[wt. %]	ACA	AA	MAA	PRA	EtOH	ACK	High boiler	FOL	H ₂ O
First aqueous phase	7	0,7	0,6	0,1	0,04	0,3	5	1,2	85,01
third aqueous phase	0,11	0	0	0	0,04	0	0	0	99,85
Mother liquor	27,4	3,0	2,7	0,6	0,1	1,1	6,9	2,7	55,5
H ₂ O from S-210.	0,02	0	0	0	0	1,98	0	0	98,0
Dewatered mother liquor	63,07	7,3	6,81	1,62	0	0	21,2	0	0,004

ACA = Acetic acid

AA = Acrylic acid

MAA = Methacrylic acid

PRA = Propionic acid

EtAC = Ethyl acetate

EtOH = Ethanol

ACK = Acetone

FOL = Formaldehyde

Claims

1. A process for preparation of at least one of methacrylic acid and a methacrylic acid ester, comprising process steps:
 - a1) gas phase oxidation of at least one C₄ compound to obtain a reaction phase comprising methacrylic acid;
 - a2) quenching of the reaction phase to obtain a crude aqueous phase comprising methacrylic acid;
 - a3) extraction of at least a part of the methacrylic acid from the crude aqueous phase comprising methacrylic acid into an organic solvent to obtain a crude organic phase comprising methacrylic acid and a first aqueous phase, wherein the first aqueous phase comprises components
 - i. at least 65 wt.%, preferably in the range of from 65 wt.% to 99.9 wt.%, more preferably in the range of from 70 wt.% to 99.8 wt.% water, yet more preferably in the range of from 75 wt.% to 99 wt.%, more preferably in the range of from 76 wt.% to 98.5 wt.%, more preferably in the range of from 77 wt.% to 98 wt.%, even more preferably in the range of from 78 wt.% to 97.5 wt.%, even more preferably in the range of from 79 wt.% to 95 wt.%, yet more preferably in the range of from 80 wt.% to 90 wt.% water, based on the total weight of the first aqueous phase, and
 - ii. not more than 35 wt.%, preferably in the range of from 0.1 wt.% to 35 wt.%, preferably in the range of from 0.2 wt.% to 30 wt.%, more preferably in the range of from 1 wt.% to 25 wt.%, yet more preferably in the range of from 1.5 wt.% to 24 wt.%, more preferably in the range of from 2 wt.% to 23 wt.%, even more preferably in the range of from 2.5 wt.% to 22 wt.%, even more preferably in the range of from 5 wt.% to 21 wt.%, yet more preferably in the range of from 10 wt.% to 20 wt.% of at least one organic compound other than the organic solvent used as extraction agent, based on the total weight of the first aqueous phase,
- wherein the sum of the weight amounts of i. and ii. is 100 wt.%;

- a4) separation and optionally purification of at least a part of the methacrylic acid from the crude organic phase comprising methacrylic acid;
 - a5) optionally, esterification of at least a part of the methacrylic acid obtained in step a4);
 - b) crystallisation of at least a part of the water from at least a part of the first aqueous phase obtained in process step a3) to form a crystallised aqueous phase as second aqueous phase and a mother liquor, wherein the mother liquor comprises at least one component ii.;
 - c) at least partial separation of the crystallised aqueous phase from the mother liquor.
2. A process for treatment of an aqueous phase comprising at least one organic compound, comprising process steps:
- a) provision of a first aqueous phase comprising components
 - i. at least 65 wt.%, preferably in the range of from 65 wt.% to 99.9 wt.%, more preferably in the range of from 70 wt.% to 99.8 wt.% water, yet more preferably in the range of from 75 wt.% to 99 wt.%, more preferably in the range of from 76 wt.% to 98.5 wt.%, more preferably in the range of from 77 wt.% to 98 wt.%, even more preferably in the range of from 78 wt.% to 97.5 wt.%, even more preferably in the range of from 79 wt.% to 95 wt.%, yet more preferably in the range of from 80 wt.% to 90 wt.% water, based on the total weight of the first aqueous phase, and
 - ii. not more than 35 wt.%, preferably in the range of from 0.1 wt.% to 35 wt.%, preferably in the range of from 0.2 wt.% to 30 wt.%, more preferably in the range of from 1 wt.% to 25 wt.%, yet more preferably in the range of from 1.5 wt.% to 24 wt.%, more preferably in the range of from 2 wt.% to 23 wt.%, even more preferably in the range of from 2.5 wt.% to 22 wt.%, even more preferably in the range of from 5 wt.% to 21 wt.%, yet more preferably in the range of from 10 wt.% to 20 wt.% of at least one organic compound, based on the total weight of the first aqueous phase,
- wherein the sum of the weight amounts of i. and ii. is 100 wt.%,

- b) crystallisation of at least a part of the water from at least a part of the first aqueous phase to form a crystallised aqueous phase as second aqueous phase and a mother liquor, wherein the mother liquor comprises at least one component ii.;
 - c) at least partial separation of the crystallised aqueous phase from the mother liquor.
3. The process according to any one of the preceding claims, further comprising at least one of the process steps
- d) at least partial dewatering of the mother liquor separated in process step c) to obtain an at least partially dewatered mother liquor;
 - e) separation of at least a part of at least one component ii. from the mother liquor obtained in process step c) or from the at least partially dewatered mother liquor obtained in process step d).
4. The process according to any one of the preceding claims, further comprising process step
- f) melting of the crystallised aqueous phase to obtain a melted crystallised aqueous phase as third aqueous phase,
- wherein the melted crystallised aqueous phase is subjected to at least one of being conducted to at least one biological purification treatment, being used as process water, and being conducted to at least one of process steps a1) and a2).
5. The process according to claim 4, wherein the at least one biological purification treatment is at least one of an aerobic treatment and an anaerobic treatment.
6. The process according to any one of the preceding claims, wherein the crystallised aqueous phase or the melted crystallised aqueous phase comprises less than 5000 ppm, preferably less than 4000 ppm, more preferably less than 3000 ppm, preferably in the range of from 1500 to 2500 ppm, more preferably in the range of from 1800 to 2200 ppm, most preferably not more than 2000 ppm, based on the total weight of the respective aqueous phase, of organic compound.
7. The process according to any one of the preceding claims, wherein the at least one component ii. separated in process step e) is a mixture of at least two components ii. and wherein in a further process step

- g) at least one component ii. is at least partially separated from this mixture.
8. The process according to any one of the preceding claims, wherein the at least one organic compound of component ii. is at least one organic compound selected from carboxylic acids, aldehydes and ketones.
9. The process according to any one of the preceding claims, wherein the at least one component ii. is or comprises at least one of acetic acid, acrylic acid, propionic acid and methacrylic acid.
10. The process according to any one of the preceding claims, wherein the at least one component ii. separated in at least one of process steps e) and g) is or comprises methacrylic acid and at least a part of this methacrylic acid is added to at least one of the crude aqueous phase obtained in step a2) and the crude organic phase obtained in process step a3).
11. The process according to any one of the preceding claims, wherein at least a part of the at least one component ii. separated in at least one of process steps e) and g) or comprised in the dewatered mother liquor obtained in process step d), or at least a part of the first aqueous phase obtained in process step a3), is subjected to a process step
- h) esterification to obtain an ester phase comprising at least one ester.
12. The process according to claim 11, wherein the ester phase comprises at least two esters.
13. The process according to claim 11 or claim 12, further comprising the process steps
- j) at least partial separation of at least one ester from the ester phase;
- k) optionally, purification of the at least one ester separated in process step j).
14. The process according to any one of claims 11 to 13, wherein the at least one ester is based on a C₁ – C₄ carboxylic acid and a C₁ – C₄ alcohol.
15. The process according to any one of the preceding claims, further comprising the step aa1) splitting of methyl tert-butyl ether to obtain at least one C₄ compound and methanol,

wherein at least a part of the at least one C₄ compound is supplied as feed to the gas phase oxidation of at least one of process steps a1).

16. The process according to claim 15, wherein the methanol obtained in process step aa1) is supplied to process step h).
17. A device for production of at least one of methacrylic acid and a methacrylic acid ester, comprising at least the following components in fluid-conducting communication with each other:
 - A1) a gas phase oxidation unit,
 - A2) a quench unit,
 - A3) a first extraction unit,
 - A4) a first separation unit,
 - A5) optionally, a first esterification unit,
 - B) a crystallisation unit for crystallisation of water from an aqueous phase,
 - C) optionally, a second separation unit.