

C-4-based process for preparing MMA with return and recycling of methacrolein

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Field of the invention

The present invention describes an improved process based on C-4 raw materials for producing methacrylates, in particular for preparing methacrylic acid and methyl methacrylate (MMA). The C4 raw materials in this case are in particular isobutene or tert-butyl alcohol. In addition, a wide range of embodiments for the efficient preparation of these products are presented.

The present invention relates in particular to a process for preparing methacrylic acid and methyl methacrylate by gas-phase oxidation of isobutene. In a second gas-phase oxidation step, methacrolein is converted to methacrylic acid and unconverted methacrolein is removed from methacrylic acid. This methacrolein is evaporated in an evaporation apparatus in the presence of various gases and steam and is mixed in gaseous form together with the process gas of the first oxidation stage in which methacrolein is prepared. In this way, the recycled methacrolein can be resupplied to the process and to the catalytic partial oxidation.

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Prior art

Methyl methacrylate (MMA) is used in large amounts to prepare polymers and together with other copolymerizable compounds in copolymers. In addition, methyl methacrylate is an important synthesis unit for a variety of specialty esters based on methacrylic acid (MAA) which are produced by transesterification with the appropriate alcohol.

There is consequently a great interest in very simple, economic and environmentally friendly processes for preparing this important chemical product.

The preparation of MMA is based on three possible raw material groups. One of these is C3 units, another one is C4 units, and C2 units.

C3 units are the first commercially significant group. Here, MMA is predominantly prepared proceeding from hydrogen cyanide and acetone via the acetone cyanohydrin (ACH) formed as central intermediate. This process has the disadvantage that very large amounts of ammonium sulfate are obtained, the workup of which is associated with very high costs. Further processes which use a raw material basis other than ACH are described in the relevant patent literature and in the meantime have been realized on a production scale.

Nowadays, the use as C-4-based raw materials of isobutylene or tert-butanol as reactants for methacrylate preparation is of increasing significance. These are converted over a plurality of

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process stages into the desired methacrylic acid derivatives. As a third alternative, methyl tert-butyl ether (MTBE), which is converted to isobutene by elimination of methanol, may also be used.

5 In this C4-based process, isobutylene or tert-butanol is generally oxidized to methacrolein in a first stage, this methacrolein then being reacted with oxygen to give methacrylic acid. The methacrylic acid obtained is then converted to MMA with methanol. More details on this process are given, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Methacrylic Acid and Derivatives, DOI: 10.1002/14356007.a16_441.pub2 and
 10 in Trends and Future of Monomer-MMA Technologies, SUMITOMO KAGAKU 2004- II. Further details on MMA and methacrylic acid preparation processes in general and specifically on the multistage gas-phase process proceeding from C4 units are described in Krill and Rühling et al. "Many paths lead to methacrylic acid methyl ester", WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, doi.org/10.1002/ciuz.201900869.

15 In general, the C4 route starts from the steam cracking product IBEN or alternatively also TBA, which is oxidized to MAL in the first step by means of gas-phase oxidation. In a further, second gas-phase oxidation stage, the methacrolein (MAL) obtained as intermediate is oxidized to MAA. The gaseous reaction products are cooled down in a downstream quenching step and to a very great extent condensed. It is characteristic of the process that the second reaction stage does not involve
 20 complete conversion with respect to MAL and that unconverted MAL is recovered in an absorption and desorption unit (recycle MAL) in order to subsequently feed it back as a feed for the second reaction stage.

Isobutylene or tert-butanol can be reacted with atmospheric oxygen in the gas phase over a
 25 heterogeneous catalyst to give methacrolein (MAL) and then converted to MMA by means of an oxidative esterification reaction of MAL using methanol. This process is described, inter alia, in US 5,969,178 and US 7,012,039. This process is also described in the article by SUMITOMO (cf. supra), with reference being explicitly made to the disadvantages of this process, which are in particular a high energy requirement which is caused inter alia by the unpressurized mode of
 30 operation. In this process, the problem of an evaporation of MAL is avoided since the process takes place in the liquid phase, hence MAL does not need to be transferred into the gaseous state and the problem of mixing with critical oxygen-containing gases is thus circumvented. A solution for optimizing the two-stage isobutene gas phase process with MAA as intermediate stage cannot be derived from this.

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The relatively unsatisfactory yield, caused in particular by high losses in the oxidation steps and hence the accompanying CO₂ formation, is also a problem in all of these processes. A formation of byproducts which further accompanies this and necessitates complex process steps for isolating the product additionally has to be pointed out. For instance, all processes proceeding

from isobutylene or equivalent C-4-based raw materials such as TBA or MTBE achieve selectivities of 80% to 90% per process stage in the gas-phase oxidation over a heterogeneous catalyst system. Thus, an overall yield of at most 65% to 70% is achieved. Naturally, the gas-phase process proceeds at moderate pressures of between 1 to 2 bar absolute and generates a process gas in which the product component is present only at about 4% to 6% by volume. The isolation of the product of value from the inert gas ballast is correspondingly energy intensive and consumes large amounts of cooling energy and steam for multistage distillative workup steps.

Overall, therefore, the following three routes for C4-based MMA preparation are well known:

Process A, "tandem C4 direct oxidation process", without intermediate isolation of methacrolein: Here, in a first step, methacrolein is prepared from isobutene and is oxidized in a process step 2 to methacrylic acid, before, in a process step 3, MMA is obtained by esterification of methacrylic acid with methanol. This process is also referred to in the literature as the "tandem process", since the process gas from the first stage is oxidized directly to methacrylic acid without isolating the methacrolein intermediate.

Process B, "separate C4 direct oxidation": Here, similarly to process A, methacrolein is prepared in a first process step from isobutene and is isolated and purified in liquid form in a separate process step, before being evaporated and oxidized to methacrylic acid in a process step 3, and lastly is converted to MMA by esterification in a process step 4.

Process C, "direct metha process", or direct oxidative esterification process: Here too, in a first process step, methacrolein is prepared in the gas phase over a catalyst I from isobutene and is likewise first isolated and intermediately purified in a process step 2, before being directly oxidatively esterified to MMA in a process step 3. Process step 3 is conducted in the liquid phase over a suspended catalyst II. Thus, the combination of a gas phase step and a process step in the liquid phase is the essential difference in this process compared to processes A and B, in which both partial oxidations are conducted over different catalysts, each in the gas phase.

All described processes according to the prior art are well documented, such as in (i) IHS Chemical Process Economics Program, Review 2015-05, R.J. Chang, Syed Naqvi or (ii) Vapor Phase Catalytic Oxidation of Isobutene to Methacrylic Acid, Stud. Sci. Catal. 1981, 7, 755-767. It is common to processes A and B that methacrylic acid is the main product, which may optionally be converted to methyl methacrylate in an esterification reaction with methanol. In general, an active Brønsted acidic catalyst is used for this last esterification step. It is possible to use a dissolved strong acid in the homogeneous variant. Preferred acids are sulfuric acid, methanesulfonic acid, or acids having a similar pKa. In another variant, ion exchangers with immobilized acid functions can be used.

Method C, the "direct metha process", proceeds as already described in the first two steps in a similar manner to process B, with the intermediate isolation of liquid methacrolein. In this case,

MMA is directly obtained from methacrolein in the liquid-phase oxidation and an intermediate step of methacrylic acid production is not needed.

Processes A and B therefore have the feature that when passing through the second oxidation stage only a partial conversion of the MAL contained in the gas mixture takes place. Besides carbon monoxide and carbon dioxide, a large number of further reaction products are formed, namely inter alia formaldehyde, acetic acid, acetone, acetaldehyde and acrolein. In the subsequent processing steps, unconverted MAL has to be isolated from the desired product methacrylic acid. Typically, this separation task is performed by at least one distillation or extraction step. MAL itself is absorbed from the process gas and processed further, purified to some degree, and isolated by a desorption process and optionally at least one distillation operation. The absorption and desorption are optionally followed by a further distillation. As a result of the presence of volatile but condensable components in addition to acrolein, according to the separation complexity, crude methacrolein is obtained with some organic by-product constituents, usually an MAL mixture having an MAL concentration of > 70% by weight. That means that the crude methacrolein mixture obtained in liquid form by removal of methacrylic acid can contain not only a few trace components such as methacrylic acid, acetic acid, terephthalic acid and stabilizers, but also certain amounts of components having similar or lower boiling points compared to MAL. There are various methods for reintroducing the liquid recycled methacrolein into the main gas system, in particular upstream of the second reaction stage. The step of evaporation of the crude methacrolein and the mixing with other gases and steam, inter alia the addition of oxygen-containing gases and in particular the mixing and recycling into the process, is a complex and critical operation which is not satisfactorily achieved in the prior art. Some of these secondary components have critical flash points and influence the explosion properties of the resulting mixtures with oxygen-containing gases. The process of reintroducing the recycled methacrolein into the main process, for example upstream of the second reaction stage, is a particularly safety-critical step in the overall process. Numerous proposals have already been made in the prior art for solving this problem by various processes in order to return incompletely converted methacrolein into the process. However, this prior art is not satisfactory in particular with regard to the safety-related aspects in the recycling of the removed, unconverted methacrolein after the second oxidation stage, its conditioning and evaporation and also mixing with inert gases and oxygen-containing gases and furthermore the adjustment necessary with steam in order to create optimal conditions for the second partial gas-phase oxidation step.

In all of these processes, there are the following difficulties concerning safety-related aspects which have to be optimized in particular during removal and isolation of the crude methacrolein fraction and also its evaporation and adjustment with gases:

1) Methacrolein is often isolated in liquid form after removal of the methacrylic acid. It must then be brought into gas form by evaporation and introduced into a gas reaction system. The liquid

recycling methacrolein reacts sensitively at the temperatures present, where above a specific temperature and within a specific residence time polymerization, dimerization and other associated undesired effects may occur. It is therefore necessary to find a route in which, for a given input of energy required for evaporation, the liquid recycling methacrolein is kept at a concentration at which the residence time can be kept so short that polymerization can be minimized or prevented entirely.

2) Recycled methacrolein may contain not only a few trace constituents such as methacrylic acid, acetic acid, terephthalic acid and stabilizers, but also certain amounts of components with similar or lower boiling point. In addition, terephthalic acid and often-used stabilizers are a catalyst poison for the catalyst of the second stage insofar as they lead to increased coking and covering of the catalysts in long-term operation. This in turn has negative effects on the performance and service life of the catalyst. It is therefore necessary, prior to the reintroduction of recycled methacrolein upstream of the reaction into the gas reaction system of the second stage, to remove the terephthalic acid and stabilizers, for example hydroquinone (HQ), as far as possible. Further substantial problems, arising as a result of components which have higher boiling points than methacrolein, are observable deposition on and covering of many plant parts and pipelines which are used in the region of evaporation and return, in particular in long-term operation. The problems resulting from this lead to operational disruptions and costly and inconvenient downtimes for removing these residues. Here too, a considerable need for improvement is an object of the present invention.

3) Based on the catalyst state, the two temperature-controlled reaction zones have different temperature levels. The gas stream leaving the first reaction zone has to be cooled before entering the second reaction zone. This is the case since, in the processes customary according to the prior art, the salt bath temperature of the first stage, which can be considered as a direct indicator for the reaction temperature, is 30°C to 100°C higher than the salt bath temperature of the corresponding second stage. In general, the hotter process gas of the first stage is cooled by mixing with a colder oxygen-containing gas stream containing recycled methacrolein. This procedure enables the oxygen content of the feed gas for the second stage to be increased and at the same time enables recycled methacrolein to be fed back to the process. In terms of safe operation, this process reacts very sensitively to all physical parameters and the stoichiometry and also to the residence time and the quality of the mixture. Otherwise, the relatively high oxygen concentration and a certain residence time within a zone with a relatively high temperature would increase the risk of a "postcombustion effect". Postcombustion is the phenomenon known for some temperature-sensitive substrates such as methacrolein in the form of gas mixtures. The corresponding substances have a tendency to be decomposed into smaller fragments. These could in turn lead to a spontaneous pressure and/or temperature rise which is problematic in terms of safety.

4) Last but not least, methacrolein cannot be completely converted in the second reaction zone. At conversion rates of 70% to 85%, a reasonable and good selectivity can be achieved. However, at higher conversion rates, the selectivity begins to fall considerably. In order to achieve a high yield of methacrylic acid, methacrolein has to be recycled. The recycling consists of (i) chilling and
5 quenching the process gas in thermostatically controlled, condensed process liquid and (ii) absorbing, desorbing and optionally distilling the methacrolein in downstream apparatus units. The following reintroduction of methacrolein involves the evaporation of a certain quality of the recycled methacrolein, and it is necessary to mix the evaporated crude methacrolein with oxygen-containing gases such as recycled gas, air and optional steam. In some cases an explosive gas
10 mixture can form during this recycling step due to local regions with a high temperature or excessively high fuel concentrations above the lower explosion limit. Especially in the case of long-term, continuous operation in which some plant parts and pipelines exhibit precipitation, soiling and deposits of byproducts and polymeric materials, incorrect distribution can be observed which in combination with excessively high oxygen concentrations leads to critical safety
15 conditions. Lastly, this also leads to overpressure relief via safety vents or in the worst case even to a local explosion or, depending on the severity of the disruption, to deflagration.

A new method for increasing process safety on an industrial scale while optimizing the yield therefore has to take into account each of these four discussed aspects.

20 Thus, for example, in USA 7,799,946 and GB 2 004 886, the recycled methacrolein is first led through a quenching column (quenching with process medium) in which the heavy constituents, including methacrylic acid, are condensed. The methacrolein-containing gas is absorbed in a subsequent column and is lastly desorbed and stripped from the absorbed liquid in order to obtain
25 a methacrolein-containing gas mixture which can be led into the second reactor. Here, this gas mixture is a non-explosive gas having a sufficiently low oxygen concentration. Nevertheless, even with this approach the oxygen is not sufficient to adequately and optimally supply the reaction of the second stage. Here, an additional oxygen-containing gas has to be supplied again prior to the reaction in the second stage.

30 EP 3 007 69 describes a special sparger construction at the introduction point of a methacrolein-containing recycling gas stream and the mixing of this stream with the reaction gas of the first stage. This is done in order to prevent the above-described postcombustion effects which lead to the decomposition of the methacrolein. EP 3 007 69 further describes a method for mixing the
35 relatively hot process gas of the first stage with the relatively cold methacrolein-containing recycling gas stream. This is done by spray injection of a gas stream, optionally mixed with air, inert gas and recirculated methacrolein, via a special arrangement of atomizers or nozzles. As a result of this injection, the relatively hot gas, which for example has a temperature of between 350°C and 400°C, is cooled to a resulting temperature of between 200°C and 240°C. In this
40 approach, the methacrolein-containing gas mixture would contain, at a relatively high

methacrolein concentration, an oxygen-rich concentration of up to 13 mol%. An explosive gas is consequently formed. Even if the gas mixture were cooled sufficiently below the ignition temperature by the spray injection, local hotspots having a temperature above the ignition point cannot be ruled out. Hotspots are formed and observed in the sparger as a result of tar-like deposits and problematic polymerized residues. A critical zone for local deposits of such residues can lead to the soiling and blockage of certain parts of the pipes and of the sparger region. While the described implementation of this concept in terms of apparatus is suitable in principle, it is susceptible to soiling in particular in continuous permanent operation, which makes regular shutdown necessary in order to remove these contaminants, which are sometimes tar-like and sometimes pulverulent. The contaminants can be removed pyrolytically by burning, by manual removal or by rinsing with suitable media. Complete cleaning of the apparatus can often be achieved only after deinstalling the sparger mechanism, which requires multiple days of plant downtime. The soiling in pipelines and in particular at the outlet nozzles upstream of and within the sparger region leads to incorrect distribution of the methacrolein-containing outlet gas and generates local gas mixtures which are flammable; in this respect operation cannot be considered to be safe in particular after two or more weeks of operation.

In US 3,876,693 and US 3,147,084, in each case the first reaction gas is cooled by a reactor equipped with an additional heat exchanger. This is done in order to further lower the temperature of the reaction gas of the first reactor. The topic of the safe reintroduction of recycled methacrolein and oxygen is not dealt with. However, here too, the byproducts, in particular TPA, could desublime in the heat exchanger pipes and block these at least to some extent. The heat exchange efficiency and the reaction run time are thus reduced. Furthermore, the reactor architecture would be quite complex and the production and maintenance costs of such an apparatus-based solution are accordingly high.

In a further proposal, EP 2 158 954, a specific method for recycling the unconverted methacrolein is described. A specific apparatus for evaporating the methacrolein is described in which a liquid methacrolein-containing stream is delivered to a packed column and the resulting MAL-containing gas stream is fed directly to the oxidation reactor. Higher-boiling components are discharged at the bottom, so that contaminants in this apparatus are substantially avoided. The problems of gas blending, in particular with oxygen-containing gases, in order to adjust the oxygen content upstream of the second partial oxidation reactor, and in particular the problems of returning to a relatively high pressure region of the reactors, are not satisfactorily solved. The bottom temperature of the apparatus can lead to further problems in continuous operation, since terephthalic acid and polymeric deposits can form in the medium. As a result of the circulation mode of the bottoms, a not inconsiderable portion of the heavy-boiling components is returned to the workup process, which is associated with a higher energy consumption. The composition of the resulting MAL-containing gas stream is essentially determined by the pressure and bottom temperature of the arrangement and of the apparatus.

In summary, it can be said that these prior art processes constitute a considerable technical challenge from the point of view of a process regime which is efficient in terms of safety. When evaporating the so-called recycling methacrolein, i.e. methacrolein which is not converted in the second oxidation stage, and injecting same between the two oxidation reactors, the process is operating in what is known as the "lean" range. This lean range is very close to the explosion limit of the mixture. The lean range of the mixture is defined by a relatively low concentration of volatile compounds in the gas mixture, which in particular also includes methacrolein. In principle, for the present substance composition, work is carried out below 2.5% by volume, preferably below 2.2% by volume, based on the sum of organic compounds. In principle, the gas mixture becomes less critical, the lower the proportion of organic constituents, the lower the oxygen content in the gas and the lower the residence time and thermal loading of the gas mixture. Less critical here means a procedure in which the described problems of decomposition in the context of postcombustion can be avoided.

If this critical mixture is fed with the process gas to the first reactor stage, for example at temperatures usually above 300°C, tar-like deposits and problematic compositions of the feed gas upstream of the second oxidation reactor often arise. This problem is described in a large number of prior art documents with corresponding proposed solutions. However, all of these solutions share the feature that they can only be implemented through complex and expensive measures. In addition, many of the problems cannot be sufficiently compensated, in particular in continuous operation.

At this point it can thus be stated that to date no process based on C4 raw material has been described in which the critical step of removal and conversion of unconverted methacrolein in the process gas has been described sufficiently safe for long-term operation. There is therefore a considerable need for improvement here.

Objects

An object of the present invention was the optimization of C4-based processes for preparing methacrylic acid or MMA, especially those processes with methacrylic acid as an intermediate or end product. The intention is to obtain high yields from the process with at the same time a long service life of the catalysts used, in particular in the second oxidation stage. Moreover, it should be possible to conduct the optimized process at non-critical concentrations of oxygen and volatiles, and/or at a non-critical temperature.

A further object was that of optimizing the process in such a way that it can be operated with longer process times between individual refitting or cleaning downtimes. This relates in particular

to the exchange of device parts in the so-called sparger section between the two oxidation stages. This concerns the region of the plant in which MAL, containing various byproducts and residual reactants together with oxygen, steam and nitrogen, is provided in gas form for the reaction in the second oxidation stage.

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In summary, it was therefore in particular an object of the present invention to provide an improved C4-based process for preparing methacrylic acid as end product or intermediate, which can be operated with fewer maintenance-related operational interruptions, and overall higher productivity and efficiency, and also overall improved operational safety. Such a process should in particular effectively avoid the deposition of soiling in the region of the evaporation of the recycle MAL and also of the downstream sparger section.

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These objects in particular concern a process which involves the two-stage catalytic gas-phase oxidation of isobutene. To this end, the formation of critical gas mixtures under critical reaction conditions is to be avoided in all process steps in the simplest possible way. This in particular also relates to the avoidance of the formation of polymers and high-boiling components in the sparger section. Such deposits would otherwise lead to increased risks in operation and/or to increased maintenance- and cleaning-related operational interruptions.

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Further objects not explicitly mentioned may become apparent from the description or the examples and from the overall context of the application, especially with respect to the prior art.

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Solution

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The stated objects have been achieved by the provision of a novel process for preparing methacrylic acid and/or methacrylic esters. This novel process comprises the following process steps:

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(a) conversion of isobutene, tert-butanol or a mixture containing isobutene and/or tert-butanol in a first catalytic gas-phase oxidation step to give a reaction product mainly containing methacrolein

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(b) conversion of the reaction product mainly containing methacrolein from process step (a) in a second catalytic gas-phase oxidation step to give a gaseous reaction product consisting predominantly of methacrylic acid and unconverted methacrolein

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(c) removal, preliminary purification and condensation of a portion of the unconverted methacrolein accumulating in the gaseous reaction product in process step (b) to form a liquid recycle methacrolein fraction

(d) transfer of the recycle methacrolein fraction into a gaseous stream

and

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(e) conversion of this gaseous recycle methacrolein stream in a catalytic oxidation step

The process according to the invention is in particular characterized in that process step (d) comprises the process aspects of:

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i) uniform distribution of the liquid recycle methacrolein fraction obtained in step c) in the form of droplets on the surface of a packing to obtain a liquid film

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ii) contacting of the liquid film obtained in step (i) with a gas stream containing 3% to 21% by volume of oxygen and having a temperature which is 10 to 150°C higher than the temperature of the liquid methacrolein, to obtain a gas mixture containing recycle methacrolein

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iii) optional mixing of the gas stream obtained according to (ii) with additional steam and

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iv) mixing of the resulting gas stream, containing methacrolein, oxygen, steam, nitrogen and other organic compounds having 1 to 6 carbon atoms, with the reaction product of the first oxidation stage (a)

The oxidation steps described in steps (a) and (b) preferably involve a catalytic gas-phase oxidation conducted in the presence of an oxygen-containing gas mixture and steam. This is particularly preferably conducted over a heterogeneous catalyst in a tubular reactor.

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For step (c) it is particularly preferable when at least 80% of the methacrylic acid formed is removed from the unconverted methacrolein. Particularly preferably, the removal and preliminary purification according to step (c) are implemented by the following aspects (i) to (iii):

(i) quenching the reaction mixture to obtain a process gas and a process liquid,
 35 (ii) removing at least a portion of the byproducts from the process liquid by crystallization and
 (iii) sequentially conducting absorption and desorption steps to obtain a liquid recycle methacrolein fraction and a nitrogen-, oxygen- and steam-containing recycle gas phase.

In this case it is possible according to the invention, although less preferred, for none of or only individual aspects from among these to be implemented.

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The liquid recycle methacrolein fraction obtained in step (c) optimally contains 65% to 99% by weight of methacrolein, 0% to 5% by weight of methacrylic acid, 0% to 5% by weight of water, up to 5000 ppm of stabilizers, terephthalic acid, nonvolatile compounds, 0.5% to 10% by weight of acetone and a total of 0% to 5% by weight of acetic acid, acetaldehyde and acrolein. This liquid fraction, mainly containing methacrolein and in particular heavy volatile fractions, such as acetic acid and methacrylic acid, in a preferred embodiment also contains trace amounts of stabilizers, such as hydroquinone or derivatives thereof, or N oxides such as Tempol or other inhibitors described in the prior art and mixtures of these. Thus, the evaporation section can be supplied with inhibitors in order to prevent deposits. On the other hand, however, in the region of evaporation and the pipelines to the sparger, suitable drainage points are preferably installed in order to clean the equipment continuously or discontinuously at predetermined intervals and to remove liquid or solid residues or residues present in suspension form. Therefore, the equipment can be kept residue-free in the course of operation and deposits can be very largely avoided.

For process step (d) it is in turn preferable when the recycle methacrolein fraction is sprayed and distributed by means of one or more nozzles in the presence of one or more gas streams with differing oxygen contents. This particularly preferably forms droplets having an average diameter of between 100 and 1000 μm . In addition, a first gas stream is preferably supplied having an oxygen content of less than 9% by volume and optionally a second gas stream is supplied having an oxygen content of greater than 9% by volume. In a preferred embodiment, the two gas streams, which differ in different oxygen contents and have resulting different nitrogen contents, can either be supplied separately to the evaporation apparatus or be mixed and combined beforehand to form a uniform gas mixture. The gas stream having an oxygen content of greater than 9% by volume is in the simplest case compressed air. The optional gas stream having an oxygen content of less than 9% by volume originates from the workup section and contains recycled gas which in the absorption has been very substantially freed of volatile organic constituents, especially methacrolein. Of course, this recycled gas stream still contains carbon monoxide and carbon dioxide components.

The equipment is operated at this point at atmospheric pressure or low positive pressures of up to 2 bar. The temperature and pressures should be selected here so as not to fall below the dew point of methacrolein and also water in the resulting gas mixture. Thus only small amounts of the more highly volatile constituents condense with certain amounts of water and acetic acid, which can in turn be removed via drainage points as described above.

There are also various preferred embodiments for step (e). For example, in step (e)(i), at least 50% of the recycle methacrolein droplets, having droplet sizes of less than 500 μm , can preferably be distributed on the packing.

In step (e) in turn, the gas stream containing 3% to 21% by volume of oxygen is preferably obtained by mixing returned process gas obtained in step (a) and/or step (b) and additional air.

This returned oxygen-containing gas has been freed of volatile organic components in an absorption step and has optionally been treated in a catalytic postcombustion in order also to remove traces of organic components, or to convert these into inert oxidation products such as carbon monoxide and carbon dioxide. In a preferred embodiment, such a recycled gas should have an oxygen content of less than 9% by volume and be compressed before being returned to the methacrolein evaporator. According to the invention, the return and use of this gas stream as inert gas in the evaporator is carried out in steps e(i) and e(ii).

The mixing of crude methacrolein, fresh air and recycled gas, and the addition of steam, is effected in the evaporation and mixing apparatus such that the resulting gas stream PG8 comprises a concentration of C1 to C6 components of less than or equal to 2% by volume. These components are present in proportions in the crude methacrolein, for example traces and in some cases significant amounts of acetone, acetaldehyde, acrolein and similar components. It is fundamental and important for safe operation of this plant part that the resulting gas mixture produced is adjusted to the lean region and the sum of the organic components does not amount to more than 2% by volume. The ratio of fuel to total gas and the likewise important oxygen-to-fuel ratio are defined thereby. Otherwise, the presence of higher concentration of these volatile constituents would lead to the formation of ignitable mixtures or would lead to mixtures in which the flash points of individual components can be considered critical.

The resulting gas stream PG8 typically has a concentration of oxygen of > 9% by volume. This resulting gas mixture is set in the region of the evaporation and mixing at temperatures far below 200°, preferably below 100°. It is not until the region of the sparger section that this recycle methacrolein-oxygen gas is heated further by the process gas of the first oxidation stage before it exits the sparger tips. The resulting gas stream PG3, formed by contacting PG8 with PG2, has an oxygen content of less than 9% by volume. PG3 must meet essential conditions in order to be used as a feed gas for the second partial oxidation.

The resulting gas stream PG3, formed by contacting PG8 with PG2, has an oxygen content of between 6.5% and 8.7% by volume and at the same time the molar stoichiometry of oxygen to the sum total of C-1 to C-6 components is between 1.4 and 3.0. A range of 2.0 to 2.9 has proven to be a particularly preferred and safe range for the stoichiometry of said components. Likewise essential for a safe operation is the concentration of the methacrolein in the gas stream PG3. Typically the concentration of methacrolein in the gas steam PG3 prior to entry onto the catalyst bed is between 2.5% by volume and 5% by volume, with a particularly preferred range between 3.0% by volume to 4.6% by volume.

To the applicant's surprise, it has been found that both the oxygen-to-fuel ratio and the methacrolein concentration in PG3 have considerable relevance for the selectivity and conversion

of the second partial oxidation and additionally have a significant effect on the service life of the modified heteropolyacid catalysts used.

5 Especially within the preferred concentration range of 3.0% to 4.6% by volume, and with a molar ratio of oxygen to C1-C6 components of 2.0 to 2.9, optimal selectivities are achieved. If higher oxygen ratios are set, the selectivities of the conversion of methacrolein to methacrylic acid decrease, with little effect on the catalyst service life. If, in turn, excessively low oxygen excesses are set, the catalyst service life is impaired. The catalyst service life can be assessed according to how greatly the salt bath temperature of the second stage has to be raised in order to achieve an
10 approximately equal conversion in the second reaction stage. Typically, the conversion in the second reaction stage is set to a methacrolein conversion (for a single pass through the catalyst bed) of between 65% and 85%, preferably of between 70% and 80%. The gas velocity, expressed as gas hourly space velocity (GHSV) also has an influence on the overall target performance of the system. It is customary to work with GHSV values of from 500 to 1500 (1/sec), preferably in
15 the range of a GHSV from 700 to 1300.

For step (e)(iv), it has proven to be advantageous and hence preferable when the gas mixture obtained in said step is introduced to the gas mixture resulting in step (a) by means of a gas sparger in such a way that the temperature at the exit point of the gas sparger is below 250°C.
20 The sparger is designed in a technically advantageous manner such that the gas mixture conditioned with oxygen-containing gases and steam has a temperature gradient within the conduits and feeds. In principle, a relatively low evaporation temperature is set in the region of the methacrolein evaporation. They should, however, be high enough to ensure the complete evaporation of MAL and to avoid falling below the dew point. On the other hand, they should
25 however be low enough that no polymeric deposits can form. Depending on the selected pressure, this is possible at temperatures between 50°C and 150°C, with temperatures of less than 100°C being preferred. The sparger can be designed so that the resulting MAL mixture with oxygen-containing gases and inert gases is guided into the reactor region with one or more central pipelines and then a multiplicity of pipes is supplied with the gas mixture. In industrial
30 reactors, it is a preferred embodiment when a plurality of nozzles and outlet pipes are connected to the sparger main pipes. In a preferred embodiment, these outlet pipes or nozzles are arranged along the sparger at equidistant spacings but differ in the free pipe diameter or length in order to ensure the most uniform possible gas distribution. In principle, it is very preferable when the free pipe diameter of the outlets furthest removed from the main conduit is greater than the pipe
35 diameter of the outlets in the vicinity of the main conduit. Such an embodiment is illustrated schematically in figure 4.

An essential feature of the apparatus for distributing the recycle MAL gas is a different temperature of the gas emerging from the sparger, in particular at the location where it is mixed with the process gas of the first reactor stage. Here, the principle applies that the temperature of
40 the gas at outlets further removed from the main pipe is higher for example than at outlets which

are closer to the main pipe. In principle, the sparger and the configuration of the outlets should be designed such that the gas temperature at the outermost outlet points does not exceed a temperature of 260°C. The design is preferably such that the maximum temperature at the outermost outlet point is less than or equal to 240°C. Naturally, in view of the presence of traces of higher-boiling components, there is also a lower limit in terms of the temperatures to be observed, in particular taking into account the problem caused by terephthalic acid ("TPA"). TPA sublimates/desublimates at temperatures of between 180°C and 220°C, meaning that this has to be taken into account when designing the sparger. If these temperatures are fallen below, deposits and resulting operational disruptions occur.

As is known to those skilled in the art, the mixing can be effected in countercurrent or in cocurrent, both variants being conceivable in principle. A preferred embodiment is mixing the various gas streams in countercurrent.

It is further advantageous and preferable to remove from the process liquid obtained in step (d) and (e) the high-boiling contaminants present and to discharge them.

In addition, it is favourable to subject the methacrylic acid obtained in step (b) and/or in step (e) to a purification step. This is particularly preferably conducted such that pure methacrylic acid having a purity of greater than 99% by weight is obtained.

The methacrylic acid can additionally — independently of its purity — be purified and subsequently subjected to an esterification step, for example with methanol to give MMA.

The process according to the invention in particular has the following advantages compared to the processes known from the prior art:

1) The process is surprisingly energy saving, in particular since no additional energy has to be provided for the evaporation of the recycling MAL.

2) A polymerization, in particular of the MAL, can be prevented surprisingly efficiently. This is realized in particular since at the critical points liquids can only form very briefly, if at all, for example in the form of droplets or liquid films.

3) Surprisingly, no special apparatuses for introducing gaseous or liquid streams are needed since the reaction system is operated at relatively low pressures.

4) There are few critical points in the production apparatus at which potentially critical mixing processes occur. This is possible as a result of the fact that the recycling MAL is first mixed with the oxygen and then led directly into the sparger.

5) The process according to the invention is also particularly efficient in terms of intermediate cooling, since in particular the reaction gas of the first stage is cooled in the sparger with relatively large amounts of cooler gas in an efficient and desired manner.

6) The process according to the invention enables significant advantages over the prior art as concerns the raw material efficiency and the selectivity and overall yield achieved.

In particular, precise monitoring and adjustment of the oxygen-to-methacrolein ratio (molar) within a range from 2.0 to 2.6 and an oxygen content in the overall gas of less than 9% by volume and greater than 7% by volume results in an optimal compromise between high selectivity and long service life of the catalyst used in the second catalyst stage. Overall, lower specific costs for C4 feedstocks such as isobutene or MTBE result and the specific catalyst utilization is also increased, it being possible to express the latter as amount of methacrylic acid per ton of catalyst. The amount of by-products such as acrolein, acetic acid and carbon monoxide, which are expensive to dispose of, is visibly reduced by the present process.

Besides the described process according to the invention, the present invention also provides a corresponding production apparatus for the preparation of methacrylic acid and/or methacrylic esters. Such a production apparatus comprises at least the following apparatuses:

- (a) at least one supply apparatus for at least one C4 compound
- (b) a first reactor, containing a first oxidation catalyst
- (c) a second reactor, containing a second oxidation catalyst
- (d) at least one separation apparatus
- and
- (e) at least one evaporation apparatus

The production apparatus is furthermore characterized by the following aspects:

- (1) The evaporation apparatus (e) is equipped with a packing and optionally with at least one drainage valve below the packing for the removal of liquids.
- (2) The evaporation apparatus (e) is connected to at least one supply apparatus for liquid methacrolein via at least one distribution apparatus.
- (3) The evaporation apparatus (e) is connected via an inlet to at least one supply apparatus for air and at least one supply apparatus for oxygen-depleted gas mixtures.
- (4) Said evaporation apparatus is connected to the second reactor (c) via a gas conduit.
- (5) The gas conduit leads into the second reactor (c) via an inlet comprising a gas sparger.
- (6) Optionally, the gas conduit is additionally connected to at least one supply device for steam.

To this end, a design of the production apparatus is preferred in which the separation apparatus (d) comprises at least one quenching step, at least one crystallization step and at least one absorption/desorption step.

Independently of this, the distribution apparatus of aspect (2) preferably comprises a plurality of nozzles.

Other embodiments in which, inside the evaporation apparatus, the inlets for air and for gases depleted in oxygen are arranged above the distribution apparatus, and the packing is arranged below the distribution apparatus, have proven to be particularly advantageous.

- 5 Lastly, the present invention also provides for the use of a production apparatus according to the description above for the preparation of methacrylic acid and/or methacrylic esters, preferably of MMA.

10 **List of reference symbols**

Figure 1 depicts a schematic process flow diagram. While the depiction is in accordance with the invention and serves to illustrate same, the depiction is not suitable for restricting the invention in
15 any way.

- F1: Air
- F2: Recycle gas
- F3: Isobutene and/or tert-butanol gas stream
- 20 F4: Steam
- F5: Methanol
- R1: Reactor for 1st stage
- R2: Reactor for 2nd stage
- R3: Esterification reactor
- 25 G1: Gas sparger
- G2: MAL evaporator
- SU1: Quenching
- SU2: Crystallization
- SU3: Absorption
- 30 SU4: Desorption
- SU5: Extraction
- SU6: Methacrylic acid purification
- SU7: MMA purification
- OU: Offgas unit
- 35 WS: Solid waste
- WG: Waste gas stream
- DP1: Drainage 1
- DP2: Drainage 2
- PG: Process gas
- 40 PS: Process stream

Figure 2 illustrates a specific embodiment of the invention by way of example

- (1) Reactor for 1st stage
- (2) Reactor for 2nd stage
- 5 (3) Gas sparger
- (4) Quenching/quench column
- (5) Crystallization
- (6) Absorption column
- (7) Desorption column
- 10 (8) Condenser
- (9) Methacrolein evaporator

Figure 3 illustrates a specific embodiment of the MAL evaporator by way of example

- 15 (102) Region with nozzles
- (103) Free space between packing and nozzles
- (104) Main packing
- (105) Lower packing

20

Figure 4 illustrates a specific embodiment of the gas sparger by way of example

- (108) Sparger: inlet to main conduit
- 25 (109) Sparger: middle section
- (110) Sparger: end section
- (111) Sparger: outlet pipe

30 The identification of process streams PS1 to PS10 and process gases PG1 to PG7 will be apparent from the context of figures 1 to 4 and from the description of the example further below.

Example 1

35 In a set-up corresponding to figure 1, a process gas feed (PG1), containing isobutene (F3) as starting material, air (F1), a recycling gas stream (F2) containing oxygen and inert gases, and steam (F4), is led into a reactor (R1). The streams have an overall molar ratio of isobutene to oxygen to water of 1:2:1.5. The temperature in the reactor was kept at 350°C and the pressure at the reactor inlet was kept at 1.2 bar positive pressure. This resulted in a gas hourly space velocity

40 (GHSV) of 1.000 h⁻¹. The reaction was conducted in a tube bundle reactor using a molybdenum

oxide-based catalyst produced in accordance with US 2007/0010394. The resulting process gas (PG2) was obtained with a temperature of 343°C. This process gas had the following composition: 4.8% by volume of methacrolein, 0.74 mol% of CO, 0.21 mol% of methacrylic acid, 0.21 mol% of acetic acid, 0.12 mol% of acetone, 0.21 mol% of acetaldehyde, 0.04 mol% of acrolein, 0.03 mol% of formaldehyde, 0.03 mol% of acrylic acid, 250 ppm of isobutene and 3.5% by volume of oxygen. The isobutene conversion rate was 99.6%, and the yield of methacrolein was 79.6%.

In the next step, the process gas (PG2) was contacted and mixed with the additional process gas (PG6) at a (PG6) to (PG2) volume flow ratio of 1 to 0.8. The mixing was effected by a gas sparger (G1). The additional process gas (PG6) is partially recycled methacrolein which, after evaporation in the MAL evaporator (G2) and mixing with further circulated recycle gas (no name), air (F1) and steam (F4), has a temperature of 80°C. The process gas (PG6) has the following composition: 1.41 mol% of organic constituents, containing 1.2 mol% of methacrolein, 0.03 mol% of methacrylic acid, 0.09 mol% of acetone, 0.05 mol% of acetaldehyde, 0.04 mol% of acrolein, and 17 mol% of oxygen and 13 mol% of water. The process gas (PG3) resulting during this mixing and contacting with reactor gas (PG2) has a temperature of 245°C and a molar ratio of methacrolein to oxygen to water of 1 to 2.5 to 4.1. In total, the process gas (PG3) contains 4.38 mol% of organic constituents which are predominantly made up of the following: 3.44 mol% of methacrolein, 0.31 mol% of CO, 0.12 mol% of methacrylic acid, 0.12 mol% of acetic acid, 0.15 mol% of acetone, 0.15 mol% of acetaldehyde, 0.06 mol% of acrolein, 0.02 mol% of formaldehyde and 0.01 mol% of acrylic acid. This process gas (PG3) was then led through a second reactor (R2). The reactor (R2) is partly filled with a catalyst which is a mixture containing phosphomolybdate. The catalyst was produced in accordance with US 2007/0010394, and the reaction was effected at initially 292°C (salt temperature) and with a throughflow rate of 1.000 h⁻¹ (GHSV). The conversion of the methacrolein in reactor R2 was approximately 78%, the selectivity for methacrylic acid was on average 85% in the operating period (fluctuation range of the various operating measurements and gas analyses +/- 1%).

For sustaining conversion over the entire operating time of several thousand hours, the salt bath temperature of the reactors is increased slightly at regular intervals. In order to keep the conversion constant, the temperature is increased by around 1°C per month, the end temperature after reaching 7000 hours of operation being 302°C. The reaction gas (PG4) present downstream of reactor R2 has the following composition: 0.7% by volume of methacrolein, 1 mol% of CO, 2.28 mol% of methacrylic acid, 0.31 mol% of acetic acid, 0.12 mol% of acetone, 0.21 mol% of acetaldehyde, 0.04 mol% of acrolein, 0.03 mol% of formaldehyde, 0.03 mol% of acrylic acid and 6.5% by volume of oxygen. The gas temperature of the methacrylic acid- and MAL-containing process gas (PG4) is approximately 306°C and is lowered to 230°C by means of a gas cooler, before the process gas is cooled down to 80°C in the quench column (SU1). At the bottom of the quench column, mainly methacrylic acid, acetic acid, TPA and acrylic acid and other components which are higher boiling relative to methacrolein are absorbed or condensed together with a portion of the process water.

The methacrolein-containing reaction gas is cooled down to a temperature of less than 30°C inside the quench column (SU1). In the quench column (SU1) a gas mixture (PG5) is formed therefrom and is cooled further down to 13°C with a plurality of external coolers. The majority of the methacrylic acid and of the water is condensed in the quench column. The quench liquid (PS1) formed in the process is collected at the bottom of the column and contains 35% by weight of methacrylic acid, 0.2% of methacrolein, 1000 ppm of TPA (terephthalic acid) and water. The liquid is cooled down to 13°C before being led into a TPA crystallization (SU2). In this crystallization (SU2), oversaturated TPA crystallizes out and the liquid is filtered through a TPA filtration unit. TPA is then withdrawn as waste solid (WS). The filtrate is in turn led to the methacrolein recovery column (SU4), now largely free from TPA.

The gas mixture (PG5) from the quench column (SU1) is then led into the bottom of the methacrolein absorption column (SU3). In this absorption column (SU3), a portion of the process stream (PS3) is used as absorber medium for the methacrolein. The process stream (PS3) originates from the downstream desorption (SU4) and is cooled down to 17°C before being introduced into the top of the column of the methacrolein absorption column. The majority of the methacrolein in the gas mixture (PG5) is absorbed by process stream (PS3), operated in countercurrent mode, to form the liquid process stream PS2. The gas mixture exiting via the top of the absorption column SU3, which comprises the majority of the unabsorbed or condensed gas phase of the MAL absorption column, is washed and then heated in a plurality of demisters and via the heat from the combustion system to 300°C to form the process gas (PG7). Lastly, process gas PG7 is led into a combustion system (OU, offgas unit), fitted with a standard Pt-Pd combustion catalyst, and all organic constituents are combusted there. The combustion system is operated regeneratively, that is to say that the waste heat from the reaction is used to preheat the inlet gases. A portion of the exiting waste gas from the combustion system is compressed in a waste gas compressor and recycled into the oxidation reaction system. This gas phase is referred to below as recycle gas (F2). The remaining portion is released into the atmosphere as waste gas (WG).

The process stream (PS2) from the bottom of the methacrolein absorption column (SU3) and the liquid phase from the TPA filtration are each led into the MAL recovery column (SU4) in order to recover unconverted methacrolein there. This column is operated under a reduced pressure of 350 mbar absolute. The temperature of the liquid in the bottom is approximately 80°C, and the temperature of the gas phase at the top of the column is approximately 40°C; this corresponds to the vapour temperature upstream of the condenser. A portion of the liquid from the bottoms (PS3) is, as described above, reused as absorber medium. The remainder of the bottoms (PS3), which contains 33% by weight of methacrylic acid, 80 ppm of methacrolein and 250 ppm of TPA, is conveyed on into the methacrylic acid workup system. The majority of the methacrolein in the gas phase is distilled off via the top of the column, cooled to 30°C, and obtained as a methacrolein-containing liquid. A portion of the liquid from the condenser is led back into the column as reflux. The other portion of the liquid phase (PS4) is led into the methacrolein evaporator (G2) as recycling stream.

The methacrolein recycling stream (PS4) contains 85% by weight of methacrolein, 5% by weight of acetone, 3% by weight of acrolein and 0.5% by weight of methacrylic acid, and also inhibitors. Before it is led into the methacrolein evaporator (G2), the recycling stream is cooled down to 3°C for intermediate storage. The methacrolein recycling stream (PS4) is then pumped into a liquid distributor equipped with an atomizer system. Droplets which are sprayed onto the packing in the methacrolein evaporator (G2) are generated here. This produces a homogeneous, uniform surface distribution for rapid, complete evaporation. The supplied air (F1) and the recycled gas (F2) are cooled down after compression to 90°C. The resulting composition of the gas phase after mixing F2 and F1 subsequently contains 15% by volume of oxygen. The compressed gas mixture is then led into the top of the methacrolein evaporator (G2). The evaporation is effected at a pressure of 1.2 bar positive pressure, and a resulting oxygen-containing gas is obtained with a temperature of 80°C, which is above the dew point of MAL at the selected pressure. It is important during the evaporation that the evaporation is effected close to or above the dew point of the organic mixture. This ensures the required complete evaporation of as many of the organic constituents as possible. It is possible during the evaporation operation that a portion of the organic constituents having a boiling point higher than methacrolein — such as the inhibitors, methacrylic acid or terephthalic acid — pass over into the gas phase incompletely or only in traces. Therefore, the methacrolein evaporator is regularly cleaned with water and this is withdrawn from a drainage point (DP1) from the bottom of the methacrolein evaporator (G2) and from a later second drainage point (DP2). The methacrolein phase (PG6) thus cleaned is lastly led into the gas distribution apparatus, the sparger (G1). Methacrolein, acrolein, acetone and other low-boiling components are evaporated and led as a gas phase at high velocity into the sparger (G1), optionally with additional steam (F4). The sparger guides and distributes the gas mixture directly below the outlet zone of the first reactor (R1). During the direct contact of the gas distribution apparatus and of the pipeline arrangement connected thereto with the hot reaction gas (PG2) of the first reaction zone, the gaseous recycle methacrolein stream (PG6) is combined with the reaction gas (PG2) to form a resulting gas stream (PG3) having a temperature of 238°C. This temperature measurement relates to the mixing temperature close to the outer outlet pipe of the sparger section.

The operation and the results of production operation were continuously evaluated and checked in order to assess conversion, and selectivity in particular of the second reaction stage.

The continuous evaluation of productivity and selectivity was ended after 7000 hours of operation; the results are presented in table 1. Over the entire time period, constant high selectivities of the order of 84% to 85% can be achieved; the decrease in catalyst activity, which can be assessed by means of the salt bath temperature increase, is moderate to low. The catalyst is still fully active even after 7000 hours of operation, can reach a degree of conversion of 78% and has sufficient reserves for continued operation. No shutdowns due to critical plant conditions are needed, and postcombustion phenomena or spontaneous pressure increases in critical plant parts, which

potentially lead to broaching of the safety apparatuses such as for example the bursting disks, are not observed.

Example 2

5

An isobutene oxidation was conducted in analogy to example 1 but with a modified composition of the recycled methacrolein-containing gas mixture (PG6). The streams F1, F2, F4 and PS4 were adapted such that the process gas (PG6) has the following composition: 1.40 mol% of methacrolein, 0.03 mol% of methacrylic acid, 0.09 mol% of acetone, 0.05 mol % of acetaldehyde, 10 0.04 mol% of acrolein, 17.1 mol% of oxygen and 13.5 mol% of water. As in example 1, the process gas PG6 is led into the sparger (G1) at a temperature of 80°C and mixed with process gas (PG2) to form a process gas (PG3) with a temperature of 240°C, which, however, has a ratio of methacrolein, oxygen and water of 1/2.8/4.1 and contains a total of 4.44 mol% of organic constituents. The organic constituents are made up as follows: 3.31 mol% of methacrolein, 0.30 15 mol% of CO, 0.12 mol% of methacrylic acid, 0.12 mol% of acetic acid, 0.15 mol% of acetone, 0.15 mol% of acetaldehyde, 0.06 mol% of acrolein, 0.02 mol% of formaldehyde and 0.01 mol% of acrylic acid.

The continuous evaluation of productivity and selectivity was again ended after 7000 hours of operation; the results are likewise presented in table 1. Here too, over the entire time period, 20 constant high selectivities of the order of 83% can be achieved, these being slightly lower than in example 1. The decrease in catalyst activity, which can be assessed by means of the salt bath temperature increase, is once again moderate to low. The catalyst is still fully active even after 7000 hours of operation, can reach a degree of conversion of 77% to 80% and has sufficient reserves for continued operation. In contrast to example 1, pressure increase events cannot be 25 reliably excluded by the higher oxygen concentration. These point to the presence of postcombustion phenomena which can potentially lead to broaching of the safety apparatuses such as for example the bursting disks. It can therefore not be excluded that the entire service life of the catalyst can be exhausted using the depicted mode of operation.

30

Example 3

An isobutene oxidation was conducted in analogy to example 1, but with a modified composition of the recycled methacrolein-containing gas mixture (PG6). The streams F1, F2, F4 and PS4 are adapted such that the process gas (PG6) has the following composition: 1.40 mol% of 35 methacrolein, 0.03 mol% of methacrylic acid, 0.09 mol% of acetone, 0.05 mol % of acetaldehyde, 0.04 mol% of acrolein, 10 mol% of oxygen and 13.5 mol% of water. As in example 1, the process gas PG6 is led into the sparger (G1) at a temperature of 80°C and mixed with process gas (PG2) to form a process gas (PG3) with a temperature of 240°C, which, however, has a ratio of methacrolein, oxygen and water of 1/2/4.1 and contains a total of 4.44 mol% of organic 40 constituents. The organic constituents are made up as follows: 3.31 mol% of methacrolein and

0.30 mol% of CO, 0.12 mol% of methacrylic acid, 0.12 mol% of acetic acid, 0.15 mol% of acetone, 0.15 mol% of acetaldehyde, 0.06 mol% of acrolein, 0.02 mol% of formaldehyde and 0.01 mol% of acrylic acid.

The continuous evaluation of productivity and selectivity was again ended after 7000 hours of operation; the results are likewise presented in table 1. Over the entire time period, the methacrylic acid selectivity after the second oxidation stage has dropped markedly from 84.6% (after 1000 hours of operation) to 81.8% (after 7000 hours of operation). In contrast to example 2, safe operation can be ensured at all times by the low oxygen concentration; pressure increase events can be reliably excluded. Overall, however, the low oxygen concentration has the result that the service life of the catalyst demonstrated in example 1 according to the invention cannot be exhausted in this example, either.

Table 1: Results

	Example 1			Example 2			Example 3		
O ₂ /MAL (mol/mol) in PG3	2.5			2.8			2		
O ₂ /fuel (mol/mol) in PG3	1.94			2.2			1.57		
O ₂ conc. (mol%) in PG3	8.5%			9.5%			6.8%		
Hours of operation (h)	1000	3000	7000	1000	3000	7000	1000	3000	7000
Methacrylic acid selectivity after the second oxidation stage	84.6%	84.3%	84.5%	83.2%	83.4%	82.9%	84.6%	83.4%	81.8%
Operating behaviour	No critical plant shutdowns (safe operating point)			Pressure increase not reliably excluded (postcombustion phenomenon)			No critical plant shutdowns but a visible effect on catalyst performance over longer operating time		

Example 4

The relevance of the composition of the process gas PG3 to safety can be demonstrated using explosibility tests. For this, the gas mixtures PG3 listed in table 1 (corresponding to examples 1 to

- 3), were investigated in terms of their flammability. The test was conducted in an electrically heated explosion sphere having a volume of 10 L at a temperature of 240°C and a pressure of 2.18 bara; the measurements were performed in accordance with the standard DIN EN 1839 "Determination of the explosion limits of gases and vapours" following the "bomb method" specified therein. The maximum variance of the gas metering was maintained at a value of 0.1% by volume (absolute) for all metered components. The test results are presented in table 2.
- As a comparison of the pressure achievable within the first 60 seconds after ignition shows, at an oxygen concentration of 9.5 mol% (according to example 2, comparative example) a pressure of just under 6 bar can be achieved, which is indicative of the presence of a deflagration reaction.
- When using lower oxygen concentrations of 8.5 mol% (analogous to example 1, example according to the invention) and 6.8 mol% (analogous to example 3, comparative example), the pressure remains virtually unchanged within the first 60 seconds with respect to the starting pressure, which shows that these operating parameters ensure safe plant operation.
- Table 2: Results of the explosibility tests (test conditions: temperature = 240°C, pressure = 2.18 bara)

	Example 1	Example 2	Example 3
O ₂ conc. (mol%)	8.5%	9.5%	6.8%
Organic constituents (mol%)	4.38	4.31	4.31
MAL (mol%)	3.41	3.41	3.41
Max. pressure within the first 60 s after ignition (bara)	2.217	5.989	2.206

Claims

1. Process for preparing methacrylic acid and/or methacrylic esters, comprising the process steps
- (a) conversion of isobutene, tert-butanol or a mixture containing isobutene and/or tert-butanol in a
5 first catalytic gas-phase oxidation step to give a reaction product mainly containing methacrolein,
- (b) conversion of the reaction product mainly containing methacrolein from process step (a) in a second catalytic gas-phase oxidation step to give a gaseous reaction product consisting predominantly of methacrylic acid and unconverted methacrolein,
- 10 (c) removal, preliminary purification and condensation of a portion of the unconverted methacrolein accumulating in the gaseous reaction product in process step (b) to form a liquid recycle methacrolein fraction,
- (d) transfer of the recycle methacrolein fraction into a gaseous stream and
- (e) conversion of this gaseous recycle methacrolein stream in a catalytic oxidation step,
15 characterized in that process step (d) comprises the process aspects of
- i) uniform distribution of the liquid recycle methacrolein fraction obtained in step c) in the form of droplets on the surface of a packing to obtain a liquid film,
- ii) contacting of the liquid film obtained in step (i) with a gas stream containing 3% to 21% by
20 volume of oxygen and having a temperature which is 10 to 150°C higher than the temperature of the liquid methacrolein, to obtain a gas mixture containing recycle methacrolein,
- iii) optional mixing of the gas stream obtained according to (ii) with additional steam and
- iv) mixing of the resulting gas stream, containing methacrolein, oxygen, steam, nitrogen and other organic compounds having 1 to 6 carbon atoms, with the reaction product of the first oxidation stage (a).
25
2. Process according to Claim 1, characterized in that the oxidation steps described in steps (a) and (b) involve a catalytic gas-phase oxidation conducted over a heterogeneous catalyst in the presence of an oxygen-containing gas mixture and steam in a tubular reactor.
30
3. Process according to Claim 1 or 2, characterized in that in step (c) at least 80% of the methacrylic acid formed is removed from the unconverted methacrolein.
4. Process according to at least one of Claims 1 to 3, characterized in that the removal and
35 preliminary purification according to step (c) is implemented by
- (i) quenching the reaction mixture to obtain a process gas and a process liquid,
- (ii) removing at least a portion of the byproducts from the process liquid by crystallization and
- (iii) sequentially conducting absorption and desorption steps to obtain a liquid recycle methacrolein fraction and a nitrogen-, oxygen- and steam-containing recycle gas phase.
40

5. Process according to Claim 1, characterized in that mixing of crude methacrolein, fresh air and recycled gas, and the addition of steam, is effected in the evaporation and mixing apparatus according to the features 1(a) to 1(e) such that
 - a. the resulting gas stream PG8 comprises a concentration of C1 to C6 components of less than or equal to 2% by volume
 - b. the resulting gas stream PG8 has a concentration of oxygen of > 9% by volume
 - c. the resulting gas stream PG3, formed by contacting PG8 with PG2, has an oxygen content of less than 9% by volume.
6. Process according to Claim 5, characterized in that resulting gas stream PG3, formed by contacting PG8 with PG2, has an oxygen content of between 6.5% and 8.7% by volume and at the same time the molar stoichiometry of oxygen to the sum total of C-1 to C-6 components is between 1.4 and 2.8.
7. Process according to at least one of Claims 1 to 6, characterized in that in process step (d) the recycle methacrolein fraction is sprayed and distributed by means of one or more nozzles in the presence of one or more gas streams with differing oxygen contents, wherein the droplets formed have an average diameter of between 100 and 1000 μm and one gas stream has an oxygen content of less than 10% by volume and optionally another gas stream has an oxygen content of greater than 10% by volume.
8. Process according to at least one of Claims 1 to 7, characterized in that the liquid recycle methacrolein fraction obtained in step (c) contains 65% to 99% by weight of methacrolein, 0% to 5% by weight of methacrylic acid, 0% to 5% by weight of water, up to 5000 ppm of stabilizers, terephthalic acid, nonvolatile compounds, 0.5% to 10% by weight of acetone and a total of 0% to 5% by weight of acetic acid, acetaldehyde and acrolein.
9. Process according to at least one of Claims 1 to 8, characterized in that, in step (e)(i), at least 50% of the recycle methacrolein droplets, having droplet sizes of less than 500 μm , are distributed on the packing.
10. Process according to at least one of Claims 1 to 9, characterized in that the high-boiling contaminants present in the process liquid obtained in step (d) and (e) are removed and discharged.
11. Process according to at least one of Claims 1 to 10, characterized in that the gas stream containing 3% to 21% by volume of oxygen which is used in step (e)(ii) is obtained by mixing returned process gas obtained in step (a) and/or step (b) and additional air.

12. Process according to at least one of Claims 1 to 11, characterized in that the gas mixture obtained in step (e)(iv) is introduced to the gas mixture resulting in step (a) by means of a gas sparger in such a way that the temperature at the exit point of the gas sparger is below 250°C.
- 5 13. Process according to at least one of Claims 1 to 12, characterized in that the methacrylic acid obtained in step (b) and/or in step (e) is subjected to a purification step to obtain pure methacrylic acid having a purity of greater than 99% by weight.
- 10 14. Process according to at least one of Claims 1 to 13, characterized in that the methacrylic acid is purified and then subjected to an esterification step.
15. Production apparatus for the preparation of methacrylic acid and/or methacrylic esters, comprising
- (a) at least one supply apparatus for at least one C4 compound,
- 15 (b) a first reactor, containing a first oxidation catalyst,
- (c) a second reactor, containing a second oxidation catalyst,
- (d) at least one separation apparatus and
- (e) at least one evaporation apparatus,
- characterized in that
- 20 (1) the evaporation apparatus (e) is equipped with a packing and optionally with at least one drainage valve below the packing for the removal of liquids,
- (2) the evaporation apparatus (e) is connected to at least one supply apparatus for liquid methacrolein via at least one distribution apparatus,
- (3) the evaporation apparatus (e) is connected via an inlet to at least one supply apparatus for air
- 25 and at least one supply apparatus for oxygen-depleted gas mixtures,
- (4) said evaporation apparatus is connected to the second reactor (c) via a gas conduit,
- (5) the gas conduit leads into the second reactor (c) via an inlet comprising a gas sparger and
- (6) optionally, the gas conduit is additionally connected to at least one supply device for steam.
- 30 16. Production apparatus according to Claim 15, characterized in that the separation apparatus (d) comprises at least one quenching step, at least one crystallization step and at least one absorption/desorption step.
- 35 17. Production apparatus according to Claim 15 or 16, characterized in that the distribution apparatus comprises a plurality of nozzles.
18. Production apparatus according to at least one of Claims 15 to 17, characterized in that, inside the evaporation apparatus, the inlets for air and for gases depleted in oxygen are arranged above the distribution apparatus, and the packing is arranged below the distribution apparatus.

19. Use of a production apparatus according to at least one of Claims 15 to 18 for the preparation of methacrylic acid and/or methacrylic esters, preferably of MMA.