

Process for preparing methylmercaptopropionaldehyde

The invention provides a process for preparing methylmercaptopropionaldehyde (MMP) from gaseous acrolein (AC) and methyl mercaptan (MC). The present invention provides, more particularly, a process for preparing methylmercaptopropionaldehyde from gaseous acrolein and methyl mercaptan, which is characterized in that, in one process step, simultaneously,
5 (a) gaseous acrolein is absorbed from a mixture at least comprising one compound from the group consisting of the hemithioacetal of methylmercaptopropionaldehyde, methylmercaptopropionaldehyde and methyl mercaptan, (b) in this mixture, acrolein is reacted with methyl mercaptan and/or the hemithioacetal of methylmercaptopropionaldehyde to give
10 methylmercaptopropionaldehyde and (c) impurities and by-products are removed from this mixture.

MMP formation from methyl mercaptan and a gas mixture comprising acrolein is known from the prior art.

DE 2627430 describes, for example, a two-stage process wherein, in the first stage, the AC
15 is absorbed from a gas mixture in MMP and, in a second stage, the AC dissolved in MMP reacts with MC at temperatures between 10 and 50°C in the presence of a catalyst. A great economic disadvantage of this separation in two stages is the necessity of MMP recycling at -10°C in order to completely absorb AC in MMP. The MMP yield based on the MMP introduced into the absorption column in the example described is 99%. At the same time,
20 preferably 0.1 to 0.2% hemithioacetal is established in the reaction mixture. At hemithioacetal concentrations below 0.1%, AC is lost due to incomplete conversion, whereas at hemithioacetal concentrations above 1% the yield of the MMP reaction worsens. The gas mixture formed during the catalytic oxidation of propylene is absorbed from the acrylic acid present in a solvent such as, for example, tri-n-butyl phosphate (FR 7718136), a mixture of
25 biphenyl and diphenyl ether (FR 1393175) or water (FR 1393175), and, after performance of this process step, freed of water in a condenser at -5-0°C. This condensation step too leads to higher capital and operating costs.

According to NL-A 68/09647, it is also possible first to contact MC with MMP in the reaction zone and to contact the mixture thus obtained with the AC-containing gas. However, an
30 additional step is needed here for treatment of the aqueous phase (extraction), and only an MMP yield of 91% based on the AC used is achieved.

WO 9429254 describes the continuous preparation of MMP from an acrolein-containing gas mixture and MC in a "gas/liquid" reaction zone, in which uncondensable gases are additionally separated from the AC process. Hemithioacetal formation is prevented by the equimolar addition of MC and AC, monitored preferably by periodic use of gas chromatography. According to the description, it should thus be possible to increase the MMP formation rate by a factor of 3-10. The limitation of the AC mass transfer is minimized by turbulent conditions in the reaction system.

In all documents described above, MC worked up by distillation is used. This is evident from the fact that the principle secondary components from the MC reaction, such as dimethyl sulphide and dimethyl disulphide, are present neither in the MMP product nor in the MMP offgas (WO 9429254 and US 4319047). MC is usually synthesized in the gas phase at temperatures between 300 and 500°C and at pressures between 1 and 25 bara. One process is described, for example, in EP 850922. The product mixture of the synthesis comprises, as well as the desired MC, the water formed in the reaction and, as by-products, dimethyl sulphide, dimethyl ether, small amounts of polysulphides, and unconverted methanol, excess hydrogen sulphide, and the gases which are inert for the purposes of the reaction: nitrogen, carbon monoxide, carbon dioxide and hydrogen. The separation of the product gas mixture into its components serves for recovery of methyl mercaptan and dimethyl sulphide, for discharge of water and inert gas components, and for recycling of unconsumed methanol and hydrogen sulphide into the synthesis reactor. This gives rise, for example, to pure MC with an MC content of up to 99.6% by weight (EP 0850923 and DE 1768826). Disadvantages of this distillative workup of the complex reaction mixture are, in addition to the high capital and operating costs, the unavoidable formation of residues which have to be disposed of and the associated loss of materials of value.

DE 10359636 describes a process which avoids the high distillation complexity to obtain pure methyl mercaptan and nevertheless uses the methyl mercaptan obtained in the catalytic reaction of H₂S with methanol, without losses, for the further conversion to MMP with liquid AC. Based on the crude MC used, the isolated yield is virtually quantitative, i.e. > 99.9%. This is achieved by distillative removal of the constituents from the MC synthesis still present in the MMP reaction mixture, and preferably by the supply of an inert entraining agent, for example nitrogen. The process is not described for the use of AC-containing gases.

US 3529940 discloses that reaction temperatures in the MMP synthesis can be controlled by dividing the exothermicity of hemithioacetal formation as intermediate and, after subsequent

addition of liquid AC, the MMP reaction enthalpy of the MMP reaction into 2 zones. However, the process is likewise not described for the use of AC-containing gases.

It is therefore an object of the present invention, in a minimum number of process steps, to prepare MMP of maximum purity and maximum yield, based on the amounts of AC and MC used, from AC-containing gas without separate water condensation and from crude MC (MC > 87% by weight, dimethyl sulphide 1.5–5% by weight, dimethyl disulphide 0.2–1% by weight, dimethyl ether 0–3% by weight, water ~0-2% by weight and methanol ~0-2% by weight).

This object is achieved by a process for preparing methylmercaptopropionaldehyde from gaseous acrolein and methyl mercaptan, characterized in that, in one process step, simultaneously, (a) gaseous acrolein is absorbed from a mixture at least comprising one compound from the group consisting of the hemithioacetal of methylmercaptopropionaldehyde, methylmercaptopropionaldehyde and methyl mercaptan, (b) in this mixture, acrolein is reacted with methyl mercaptan and/or the hemithioacetal of methylmercaptopropionaldehyde to give methylmercaptopropionaldehyde and (c) impurities and by-products are removed from this mixture. In the reaction of acrolein with methyl mercaptan and/or hemithioacetal, it can be assumed that hemithioacetal does not react directly with acrolein but first decomposes to acrolein and methyl mercaptan (equilibrium) and the methyl mercaptan thus released then reacts with acrolein to give MMP.

In an advantageous embodiment, the process step is performed in a reactive absorber. The reactive absorber is characterized in that, in only one vessel or in only one stage, gaseous AC is absorbed in a mixture of principally MMP, MC and hemithioacetal, AC reacts directly or via the hemithioacetal intermediate with MC to give MMP, and low-boiling secondary components (including dimethyl sulphide, acetaldehyde, water and dimethyl disulphide) are stripped, with minimization of the offgas losses of reactants and target product.

In an advantageous embodiment, the impurities removed comprise at least one compound from the group consisting of dimethyl sulphide, acetaldehyde, water, dimethyl disulphide, methanol, carbon dioxide, propane, propene, hydrogen sulphide and dimethyl ether.

It is unnecessary to remove water from the product in order to achieve MMP yields based on the AC used close to 100%. In a preferred embodiment, water is not removed additionally from the methylmercaptopropionaldehyde obtained.

In the present invention, MMP is produced from the chemical reaction between AC and MC. The AC required for this reaction forms through partial oxidation of propylene in a gas phase reaction in a shell-and-tube reactor. After leaving the reactor, the AC-containing gas is freed in the quench column of excess water, unwanted by-products, for example acetic acid, formaldehyde, allyl alcohol, and principally acrylic acid. A small proportion of acetaldehyde is also separated out at this point. In the subsequent step, AC is absorbed from the gas phase in a mixture of MMP and hemithioacetal and reacts in the same vessel with MC or hemithioacetal.

In a preferred embodiment, the MC required for the reaction is metered continuously, in liquid or gaseous form, into an MMP feed stream to the reactive absorber.

The present invention is a considerable simplification with respect to the above-described prior art, since the reactive absorber used additionally functions as a stripping column and thus, in addition to the low-boiling substances from the AC-containing gas, also removes low-boiling secondary components from the reaction between hydrogen sulphide and methanol, for example dimethyl sulphide. It is thus ensured that MC with low purity (MC > 87% by weight, dimethyl sulphide 1.5-5% by weight, dimethyl disulphide 0.2-1% by weight, dimethyl ether 0-3% by weight, water ~0-2% by weight and methanol ~0-2% by weight) can also be used and hence a complex purification, as described, for example, in EP 0850923 and DE 1768826, can be dispensed with. It is preferred that the methyl mercaptan used contains 1.5-5% by weight of dimethyl sulphide and 0-3% by weight of dimethyl ether.

The present invention is described in detail hereinafter by a flow diagram (Figure 1).

Acrolein is prepared in a catalytic gas phase reaction in the shell-and-tube reactor (A). At the inlet of the reactor, propylene (1) is mixed with air (2) and an inert gas stream (3) composed of nitrogen and small amounts of carbon dioxide and water vapour. The dilution of the reaction gas is necessary in order to avoid the risk of an explosive mixture and to minimize temperature peaks in the catalyst bed. The temperature of the gas mixture is about 130-200°C.

In addition to acrolein and water, by-products such as principally acrylic acid, acetic acid, formaldehyde, acetaldehyde, carbon dioxide and carbon monoxide are also formed in the shell-and-tube reactor (A). The reaction gas enters what is called the quench column (B) in the lower region, in which the temperature of the gas mixture is cooled rapidly by intensive contact with water. A majority of the water vapour in the gas mixture is condensed. In this

region of the column, a large proportion of the by-products, principally acrylic acid and acetic acid, is likewise retained and leaves the column (B) via the bottom. This liquid is circulated by means of a "pumparound" system and is thus used as the cooling medium to quench the AC reaction gas. On the way to the top of the column, the reaction gas is contacted in counterflow to a water stream, which brings about a further reduction in the by-product content in the reaction gas. This water stream forms from the condensation by further cooling of the reaction gas to $< 20^{\circ}\text{C}$ (1.2–2.5 bara) in the upper region of the column (B) (upper pumparound). The liquid stream leaving the column (B) can be pumped to the top of a stripping column (D) in which the majority of the dissolved acrolein can be recovered. The stripping medium (5) used may be inert gases. The remaining liquid (4) can finally be sent to a thermal incineration for disposal.

From the top of the quench column (B), the AC-rich gas (11) enters the reactive absorber (C) in the standard case via a jet pump (12). This has the advantage that polymerization of AC can be avoided, an optimal pressure regime in the reactive absorber (C) is more readily possible and the upstream AC process can be conducted at lower pressures. In an alternative embodiment, the AC can also be fed directly into the lower section of the reactive absorber.

In the reactive absorber (C), AC is first absorbed in a mixture of principally MMP, free MC, hemithioacetal and water (12, 13, 14) and then reacts with MC or hemithioacetal in the presence of a homogeneous catalyst to form further MMP. In contrast to the prior art, there is no need either to avoid hemithioacetal formation from MC and MMP (WO 9429254) nor for MC to be present completely in the form of the hemithioacetal before the reaction with AC (US 3529940) in order to obtain quantitative MMP yields based on the AC used. It is advantageous that the mixture forms the hemithioacetal of methylmercaptopropionaldehyde by addition of methyl mercaptan onto methylmercaptopropionaldehyde in a concentration between 0.1 and 10% by weight, preferably between 1 and 10% by weight.

In an advantageous embodiment, the ratio between MC and AC in the liquid phase of the reactive absorber is adjusted with the aid of an inline near infrared (NIR) measurement (accuracy ± 0.0005 mol/mol). It is advantageous that the ratio between methyl mercaptan and acrolein in the mixture is adjusted to a value between 0.95 and 1.1 mol/mol, preferably between 1.00 and 1.01 mol/mol, more preferably between 1.004 and 1.009 mol/mol, and especially preferably to 1.005 mol/mol.

In a preferred embodiment, the input concentration of the gaseous acrolein (11) in the mixture is detected with the aid of an inline Fourier transform infrared (FTIR) measurement in order to adjust the feed rate, i.e. in order to be able to adjust the MC metering (6) at a very early stage. These inline measurements have the advantage that it is possible to react immediately to changes in the system and hence to keep the offgas losses of reactant and product low and the MMP product quality continuously at a high level.

The MMP reaction proceeds principally on the internals and in the bottom of the column (C). The internals used may, for example, be structured packings, random packings or trays. The pressure at the top of the column (C) is in the range from 1 to 2.5 bara, preferably from 1.2 to 1.6 bara. A pump circulates a portion of the MMP from the column bottom through two heat exchangers connected in series in order to reduce the temperature of this stream. In the first stage, cooling is effected with "cooling tower water (CTW)" to ~35°C, and then with "chilled water (CW)" to 0-20°C, preferably 5-10°C. A large portion of the MMP thus cooled enters at the top of the reactive absorber (C) (14) and functions as absorption/reaction medium. A further portion of the MMP is removed either after the first (preferred) or the second cooling step as product stream (7). A second pumparound, which in the standard case uses MMP from the bottom of the column (C), enters as absorption/reaction medium (13) in the middle region of the column (C). The temperature of this stream is in the range of 20–50°C, preferably 30-40°C. A third pumparound (12) in a particularly preferred embodiment enters the column below (13). Liquid and/or gaseous MC (6) is preferably added to this stream, but can also be supplied at any other point, preferably in the lower region of the column, into one of the other pumparounds.

The temperatures in the lower part of the column can be controlled by the heat exchanger in stream (12). The temperature in this part of the column is in the range of 20°C to 90°C, preferably 40°C to 75°C. The low temperatures at the top of column (C) help to minimize AC, MC and MMP losses. However, excessively low temperatures cause the retention of unwanted components such as dimethyl sulphide (DMS) and acetaldehyde (AA). These components are by-products of the MC or AC reaction and have to be substantially removed before MMP can be used, for example, in methionine or MHA production. In the standard case of the invention, these by-products are substantially stripped in the reactive absorber (C) and are present in the offgas (8) which leaves the column (C) at the top and is then supplied to a thermal incineration.

In an advantageous embodiment, the impurities and by-products are removed from the mixture by stripping at 0.3 to 5 bara, preferably at 1 to 2 bara, and at 5 to 70°C, preferably at 5 to 20°C.

In an advantageous embodiment, the process step is performed in the presence of a homogeneous and/or heterogeneous catalyst (9). This catalyst is preferably dimethylbenzylamine (DMBA) and/or triethanolamine. It is additionally advantageous that the concentration of the catalyst in the mixture is in the range from 50 to 500 ppmw, preferably in the range from 130 to 150 ppmw.

To regulate the pH and the associated better storage stability of the MMP produced, it is advantageous to continuously supply to the mixture at least one compound from the group consisting of inorganic and organic acids, preferably acetic acid and tartaric acid, and inorganic and organic bases, preferably triethanolamine.

These substances form, for example in a mixture with DMBA, what is called the catalyst/stabilizer mixture which is supplied continuously to the reactive absorber (C). In principle, other acids and bases are also possible. EP 1408029 mentions, by way of example, inorganic oxo acids, for example sulphuric and phosphoric acid, hydrogen halides, for example hydrogen fluoride, bromide and chloride. Also suitable are organic acids, for example aliphatic monocarboxylic acids (e.g. formic acid, propionic acid, octanoic acid, acrylic acid, trichloroacetic acid, trifluoroacetic acid), aliphatic polycarboxylic acids (oxalic acid, succinic acid, adipic acid), aromatic monocarboxylic acids (phenylacetic acid, benzoic acid, cinnamic acid, furoic acid, thiophenecarboxylic acid) and aromatic polycarboxylic acids (phthalic acid, monoesters of sulphuric acid, sulphonic acid).

Examples of basic substances are inorganic bases (ammonia, sodium hydroxide, potassium hydroxide, ammonium carbonate, sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium acetate, sodium acetate, potassium acetate) and nitrogen-containing organic bases (piperidine, triethylamine, pyridine, quinoline, urotropin, N,N-dimethylaniline).

The present invention has the advantages that

- the absorption of AC from a gas, the MMP reaction using crude MC and the stripping of low boilers, for example DMS, DMDS, DME, methanol, CO₂, H₂S, water, propene,

propane, acetaldehyde, is possible in only one process step, for example in a reactive absorber,

- losses of MC, AC and MMP can be minimized,
 - the MC/AC stoichiometry can be monitored by using an NIR and FTIR,
- 5 ▪ a separate water condensation from the AC-containing gas can be dispensed with, and
- probability of polymer formation can be minimized.

The working examples which follow are intended to illustrate the advantageous aspects of the present invention.

1) Standard case

- 10 The AC-containing gas stream (11) entering the reactive absorber (C) has the following composition (Table 1):

Table 1:

Composition AC process gas (% by vol.)	
CO ₂	0.651
O ₂	5.112
Argon	0.625
N ₂	85.147
H ₂ O	1.331
Propene	0.162
Propane	0.030
CO	0.354
Acetaldehyde	0.143
Acrolein	6.430
Allyl alcohol	0.003
Allyl acrylate	0.001
Acetic acid	0.011
Acrylic acid	0.000

- 15 In order to show the additional stripping effect on low boilers such as dimethyl sulphide and acetaldehyde, methyl mercaptan (6) in the composition below (Table 2) was introduced into the reactive absorber (C).

Table 2:

MC composition (% by wt.)	
H ₂ S	0.212
H ₂ O	0.860
Dimethyl ether	0.068
Methanol	0.410
Methyl mercaptan	95.981
Dimethyl sulphide	1.830
Dimethyl disulphide	0.650

For instance, the majority of dimethyl sulphide and acetaldehyde is present in the offgas (8), while only a very low proportion remains in the MMP product (7). The MC, AC and MMP

5 losses are kept very low (Tables 3 and 4).

Table 3:

MMP composition (% by wt.)	
Methyl mercaptan	0.443
Acetaldehyde	0.043
Dimethyl sulphide	0.043
Acrolein	0.015
Methanol	0.126
H ₂ O	2.415
Dimethyl disulphide	0.212
Allyl alcohol	0.025
Allyl acrylate	0.015
Dimethylbenzylamine	0.016
MMP	96.500
Acrylic acid	0.000
Acetic acid	0.148
Dimethyl ether	0.000

Table 4:

Offgas composition (% by wt.)	
CO ₂	1.064
H ₂ S	0.000
Water	0.341
Propene	0.254
Propane	0.049
Dimethyl ether	0.034
Methanol	0.016
Acetaldehyde	0.223
Methyl mercaptan	0.356
Acrolein	0.000
Dimethyl sulphide	0.216
Allyl alcohol	0.000
Acetic acid	0.014
Dimethyl disulphide	0.021
Allyl acrylate	0.000
MMP	0.150
O ₂	6.079
CO	0.368
N ₂	89.891
Argon	0.926

MMP product (7) was additionally distilled at 200°C and at 30 mbara for 25 minutes in order to determine the residue concentration. Surprisingly, at 0.20–0.25% by weight, it was actually below the residue concentration of 0.30–0.40% by weight of an MMP sample which originates from an MMP process using liquid AC (US 3529940). The evolution of the residue in the course of storage for up to 32 days in the present invention, at 0.03% by weight per day, was also lower than in a process using liquid AC (0.05% by weight per day).

In order to ensure the MMP quality for a downstream methionine process, no separate water condensation from the AC-containing gas (11), as described in DE 2627430, is thus necessary. A certain water content may even have a positive influence on the MMP formation rate since water has a higher degree of dissociation of the basic amine catalyst used up to a certain concentration. All by-product components in the MMP (7) are also within the specification for the downstream methionine process in spite of the use of the above-described crude MC (6). The sufficient stripping effect of the reactive absorber (C) was thus confirmed. The MC, AC and MMP losses in the offgas (8) are sufficiently low to be able to run the process economically. For very exact establishment of the MC/AC stoichiometry of 1.004–1.009, an NIR measuring unit in particular is suitable. Inline measurements allow a rapid reaction to a change in the process, for example an adjustment of the feed streams

(AC and/or MC), and hence a constant MMP quality. In addition, reactant and product losses via the offgas (8) are minimized. The input concentration of the AC gas can be effected via an online GC measurement, or else preferably via an inline FTIR measurement.

2) Influence of the MC feed point in the reactive absorber (C)

- 5 In the case of feeding of MC directly into the column (C), a great influence on the reaction system is discernible. The increased amount of MC which has to be absorbed in the column as a result, in conjunction with exothermic hemithioacetal formation, results in a distinct increase in the temperature profile in the reactive absorber (C). This effect leads additionally to increased MC and AC losses in the offgas (8) (Table 5).

10 Table 5: Offgas losses (8) with different MC feed points

	Standard	MC metering directly into column
Offgas (8) - Top [% by vol.]		
MC	0.111	0.608
AC	0.030	0.281
MMP	0.040	0.057

Claims

1. Process for preparing methylmercaptopropionaldehyde from gaseous acrolein and methyl mercaptan, characterized in that, in one process step, simultaneously,
 - 5 (a) gaseous acrolein is absorbed from a mixture at least comprising one compound from the group consisting of the hemithioacetal of methylmercaptopropionaldehyde, methylmercaptopropionaldehyde and methyl mercaptan,
 - (b) in this mixture, acrolein is reacted with methyl mercaptan and/or the
10 hemithioacetal of methylmercaptopropionaldehyde to give methylmercaptopropionaldehyde and
 - (c) impurities and by-products are removed from this mixture.
2. Process according to Claim 1, characterized in that the process step is performed in a reactive absorber.
- 15 3. Process according to at least one of Claims 1 and 2, characterized in that the mixture comprises the hemithioacetal of methylmercaptopropionaldehyde, formed by addition of methyl mercaptan onto methylmercaptopropionaldehyde in a concentration between 0.1 and 10% by weight, preferably between 1 and 10% by weight.
- 20 4. Process according to at least one of Claims 1 to 3, characterized in that the impurities and by-products are removed from the mixture by stripping at 0.3 to 5 bara, preferably at 1 to 2 bara, and at 5 to 70°C, preferably at 5 to 20°C.
5. Process according to at least one of Claims 1 to 4, characterized in that the impurities removed comprise at least one compound from the group consisting of dimethyl sulphide, acetaldehyde, water, dimethyl disulphide, methanol, carbon dioxide,
25 propane, propene, hydrogen sulphide and dimethyl ether.
6. Process according to at least one of Claims 1 to 5, characterized in that methyl mercaptan is supplied to the mixture continuously in liquid and/or gaseous form.

7. Process according to at least one of Claims 1 to 6, characterized in that the process step is performed in the presence of a homogeneous and/or heterogeneous catalyst.
8. Process according to Claim 7, characterized in that the catalyst is dimethylbenzylamine and/or triethanolamine.
- 5 9. Process according to at least one of Claims 7 and 8, characterized in that the concentration of the catalyst in the mixture is in the range from 50 to 500 ppmw, preferably in the range from 130 to 150 ppmw.
- 10 10. Process according to at least one of Claims 1 to 9, characterized in that the ratio between methyl mercaptan and acrolein in the mixture is adjusted to a value between 0.95 and 1.1 mol/mol, preferably between 1.00 and 1.01 mol/mol, more preferably between 1.004 and 1.009 mol/mol, and especially preferably to 1.005 mol/mol.
11. Process according to Claim 10, characterized in that the ratio between methyl mercaptan and acrolein in the mixture is adjusted with the aid of an inline near infrared (NIR) measurement.
- 15 12. Process according to at least one of Claims 1 to 11, characterized in that the input concentration of the gaseous acrolein in the mixture is detected with the aid of an inline Fourier transform infrared (FTIR) measurement in order to adjust the feed rate.
- 20 13. Process according to at least one Claims 1 to 12, characterized in that at least one compound from the group consisting of inorganic and organic acids, preferably acetic acid and tartaric acid, and inorganic and organic bases, preferably triethanolamine, is supplied continuously to the mixture.
14. Process according to at least one of Claims 1 to 13, characterized in that the methyl mercaptan used contains 1.5-5% by weight of dimethyl sulphide and 0-3% by weight of dimethyl ether.
- 25 15. Process according to at least one of Claims 1 to 14, characterized in that water is not removed additionally from the methylmercaptopropionaldehyde obtained.