SUMMARY

The process of the present disclosure is simple and cost-efficient due to reduced energy consumption in the downstream purification steps (e. g. distillation) and the possibility to refrain from using additional decolorizing agents, e.g. oxidizing agents, and offers the possibility to achieve a high MSA yield and/or a highly pure MSA with low colorization.
The inventive process for manufacturing of methane sulfonic acid (MSA) thus overcomes at least some of the disadvantages known in the art.

The problem is solved by the features of the independent claims. Preferred examples of the present disclosure are provided by the dependent claims.
The disclosure therefore relates, in one example, to a process for the manufacturing of an alkanesulfonic acid by reaction (for example radical reaction, mainly or partially radical reaction) of an initiator composition with an alkane and sulfur trioxide comprising the steps:

i. Preparation of the initiator composition by reacting aqueous hydrogen peroxide with the components alkanesulfonic acid and/or H_2SO_4,
ii. Reaction of initiator composition from step i. with sulfur trioxide and alkane to form an alkanesulfonic acid, for example by partially, mainly or completely radical reaction,

Wherein alkane with a purity of at least 98.0 mol-% is used.

In an aspect, there is provided a process for the manufacturing of an alkanesulfonic acid by reaction of an initiator compo-sition with an alkane and sulfur trioxide comprising the steps:

i. Preparation of the initiator composition by reacting aqueous hydrogen peroxide with the components alkanesulfonic acid and/or H2SO4,
ii. Reaction of initiator composition from step i. with sulfur trioxide and alkane to form an alkanesulfonic acid,

wherein alkane with a purity of at least 98.0 mol-% is used, and wherein the alkanesulfonic acid is methanesulfonic acid and wherein the alkane is methane, and wherein the methane has a maximum content of hydrocarbons of 500 ppm.

In the inventive process, step ii. may comprise or consist of a radical reaction. Step ii. may partially or mainly run according to a radical mechanism.
In the inventive process, methane with a purity of at least 98.0 mol-% is used.
In a preferred example of the inventive process, methane with a purity of at least 98.5 mol-% is used.

In a further preferred example of the inventive process, methane with a purity of at least 99.0 mol-% or 99.5 mol-% or even 99.7 or 99.8 or 99.9 mol-% is used.

In an example of the inventive process, methane with a content of higher homologues of methane (including ethane, propane, butane and C5-C8 alkanes) of not more than 2.0 mol-% is used.

In an example of the inventive process, methane with a content of ethane of not more than 1.5 mol-% is used. In a preferred example this methane contains not more than 1.0 or 0.5 or 0.1 mol-% of ethane. Even more preferred is an ethane content of less than 0.05 or 0.01 mol-%. In an example of the inventive process, methane with a content of propane of not more than 1.0 mol-% is used. In a preferred example this methane contains not more than 0.5 or 0.1 mol-% of propane. Even more preferred is a propane content of less than 0.05 or 0.01 mol-% or 0.005 mol-%.

In an example of the inventive process, methane with a content of butanes (total of n- and iso butane) of not more than 1.0 mol-% is used. In a preferred example this methane contains not more than 0.5 or 0.1 mol-% of butanes. Even more preferred is a butane content of less than 0.05 or 0.01 mol-% or 0.005 mol-%.

The same limits as for butanes apply for the higher alkanes C5-C8.

The methane used for the inventive process generally has a maximum content of hydrocarbons of 500 ppm, preferably less than 400 ppm, less than 350 ppm, less than 300 ppm and more preferably less than 250 ppm or 200 ppm. The term "hydrocarbon" in the present disclosure comprises e.g. those hydrocarbons which are quoted in Ullmann's Enzyklopädie, "Natural Gas" (details see above), namely e.g. ethane, propane, n-butane, i-butane etc. The term hydrocarbon could furthermore comprise other, higher saturated and unsaturated, branched and non-branched hydrocarbons as e.g. ethylene, propylene, i-butylene etc.

The methane used for the inventive process generally has a maximum content of ethane of 300 ppm, preferably less than 200 ppm, more preferably less than 150 ppm.
Furthermore, the methane used for the inventive process generally has a maximum content of propane of 200 ppm, preferably less than 150 ppm, preferably less than 100 ppm, more preferably less than 80 ppm.

Furthermore, the methane used for the inventive process generally has a maximum content of butanes of 150 ppm, preferably less than 100 ppm, preferably less than 80 ppm, more preferably less than 50 ppm.

Furthermore, the methane used for the inventive process generally has a maximum content of higher alkanes C5-C8 of 100 ppm, preferably less than 80 ppm, more preferably less than 50 ppm.

The standard method to determine composition and purity of methane is gas chromatography. The contents of the compounds mentioned above (e.g. ethane, propane, butanes and C5-C8 alkanes, further H_2S and carbon dioxide) may thus be measured by gas chromatography.

The inventive process results in a product with a high purity.

In one example of the inventive process, after step iii. MSA with a purity of greater than 98,0 % by weight is obtained. Preferably, the inventive process yields MSA with a purity of greater than 99.0% by weight, more preferably greater than 99.5% or 99,8 % by weight.

Furthermore, the inventive process surprisingly provides a product with a low color number. None of the patents / patent applications dealing with the reaction of methane and SO3 points out any issues related to the color number of the MSA produced. The more surprised were the authors of this patent application to observe colorization of the MSA produced according to de

scriptions of the state of the art. Choosing different recipes with varying reaction conditions with regard to pressure, temperature and molar ratios of the reactants allowed to increase or decrease the content of side products in the MSA produced, e.g. of MSA anhydride, methylmethanesulfonic acid or methylbisulfate, but did not yield any improvement with regard to colorization of the MSA.

In one example of the inventive process, after the synthesis step ii. MSA yields of at least 80 mol-% are obtained. Preferably, the inventive process provides MSA yields above 83 mol-%. Even more preferably the process generates MSA yields higher than 85 mol-%, higher than 88 mol-% or 90 mol-%. In a further preferred example, the inventive process generates MSA yields of higher than 93 mol-%, higher than 95 mol-% or even higher than 98 mol-%.

After painstaking investigations, the authors identified certain impurities as root cause of the colorization and developed countermeasures to reduce the degree of colorization of the raw MSA.

A typical and general process layout includes the following steps:

i. Synthesis of a starter, for example radical starter
ii. Synthesis of MSA
iii. Purification of MSA

In one example of the inventive process, MSA with an HAZEN color number of < 400 HAZEN is obtained. In another example MSA with an HAZEN color number of < 300 HAZEN or 250 HAZEN is obtained. Preferably, the inventive process yields MSA with an HAZEN color number of < 200, more preferably < 150 or < 100 or even < 50 or < 10 HAZEN.

The color number is measured, unless mentioned otherwise, according to a standard procedure given in the literature, i. e. DIN EN ISO 6271 (platinum cobalt scale).

It is to be noted that the mentioned low color number is obtained from the inventive process without further process steps (except, optionally, distillation and/or crystallization). To be more precise, in the inventive process it is not necessary to add oxidizing compounds and/or bleaching agents at the end of the process, contrary to the disclosures of the prior art.

The synthesis of a raw MSA may for example be done in the following way:

a) Generating a starter solution (initiator solution, for example radical starter solution), for example by adding H_2O_2 to a solution containing MSA and/or Oleum and/or sulfuric acid and/or MSAA.
b) Inerting the whole system e.g. with N_2 or by evacuating the system and refilling it with N_2 and executing this procedure once or several times (optionally after step c))
c) Charging a reactor with the initiator solution and optionally additional MSA, H_2SO_4, Oleum, SO_3 or mixtures thereof basically free of water

d) Charging the same reactor with methane
e) Set the pressure to > 25 bar (30 – 150 bar, 50 – 100 bar)
f) Set the temperature to > 30°C (30 – 70°C, 45 – 65°C) (or alternatively exchange steps e) and f))
g) In a continuous mode of operation continuously remove the reaction product from the reactor and constantly replenish the reactor with methane, SO3 and starter solution (e. g. radical starter solution) to keep concentrations in the reactor constant (steady state).

Other options to carry out the synthesis can be found e.g. in WO 2015/071365 or in WO 2004/041399.

In an example of the disclosure the starter (e.g. a radical starter) can be formed in situ as part of step ii, e.g. by addition of H2O2 solution to the reactor itself or by addition into one of the pipelines feeding other liquid streams into the reactor.

In a preferred example the initiator composition in step a) further comprises sulfur trioxide.

In a preferred example the initiator composition in step a) further comprises a recycle stream from the bottom purge of the distillation of methanesulfonic acid mainly consisting of methane sulfonic acid and sulfuric acid.

In a preferred example the reaction (e. g. radical reaction) described in steps c) - f) comprises an initiation reaction and a propagation reaction.

In a preferred example the process comprises a step iii. for purification of methane sulfonic acid and optionally methane sulfonic acid anhydride obtained from the synthesis described in steps a) – g) or from alternative procedures described in the literature (e.g. WO 2015/071365 or WO 2004/041399).

In a preferred example the purification step iii. is a single step distillation or a multi step distillation.

In an example of the inventive process, the purification step iii. comprises at least two distillation steps.

In an example of the inventive process, the purification step iii. comprises a first distillation step at a temperature in the range of 30° to 220° C, preferably 100° to 200° C and a subsequent second distillation step at a temperature in the range of 150° to 220 °C, preferably 160° to 200 °C. The temperatures given are the temperatures at the bottom of the respective distillation columns.

In an example of the inventive process, the purification step iii. comprises a first distillation step at a pressure in the range of 5 to 1000 mbar, preferably 7 to 200 mbar and a subsequent second distillation step at a pressure in the range of 0.1 to 20 mbar, preferably 2 to 10 mbar. In an example of the inventive process, the purification step iii. is performed in at least two separate distillation columns, preferably in two or three separate distillation columns.

In an example of the disclosure, between step ii. and step iii. a step can be introduced to release the pressure used in step ii. before entering the purification step iii., e.g. a distillation. Such a step ("flash" or "flash unit") could be carried out in one or a sequence of normal vessels, in one or a sequence of pressure control valves with pressure release option, in one or a sequence of flash drums or any other set-up suitable for the purpose of pressure release from step ii. to step iii. A flash unit furthermore supports the removal of light boilers like unreacted methane from the product stream leaving step ii. prior to entering step iii. Thus, the purification step iii. has to handle lower amounts of light boilers than without a flash. These lights could be incinerated to generate heat or recycled into the process or used for other purposes. Reduction of the pressure between steps ii. and iii. in a flash is preferred.

In an example of the inventive process, in a first distillation step at a temperature of 30° to 220 °C (preferably 100° to 200 °C, more preferably 120° to 190 °C) and a pressure of 5 to 1000 mbar (preferably 7 to 200 mbar, more preferably 10 to 100 or 10 to 50 mbar), a large percentage of the methane and sulfur trioxide contained in the reaction mixture is removed, e.g. more than 80%, preferably more than 90% or 95% or even more than 98%. In a second distillation step at a temperature of 150°C to 220°C (preferably 160°C to 200°C) and a pressure of 0.1 to 20 mbar (preferably 2 to 10 mbar), mainly MSA and sulfuric acid are separated. MSA can be withdrawn at the head or the side discharge of the column, whereas e.g. sulfuric acid and methanedisulfonic acid remain in the sump.

In another example of the disclosure, at least a part of the bottom fraction of the MSA distillation in column 1 and/or in column 2 and/or additional downstream columns is not purged from the system but at least partially recycled to the synthesis step of the starter solution (e. g. radical starter solution) or to the synthesis step of the MSA synthesis with CH_4 and SO_3.

In a preferred example of the inventive process, the two-stage distillation process is performed in at least two separate distillation columns or alternative equipment meeting the same functionality, e.g. perform the first distillation step in a simple vessel under the conditions given above. This is preferable inter alia because a preferred example of the inventive process for the synthesis of MSA is a continuous process.

In an example of the inventive process, said distillation process comprising at least two distillation steps involves stripping of the distillation mixture with an inert gas in the first distillation stage, selected from the list consisting of nitrogen and argon.

In an example of the inventive process, the alkanesulfonic acid is withdrawn at the side discharge of the distillation column in the second distillation stage and also of the columns of potential further columns.

In an example of the inventive process, the process is a continuous process.
In a preferred example the purification step iii. for purification of MSA, and optionally MSA anhydride, obtained e.g. from steps a) - g) is a crystallization followed by a solid-liquid separation.

In a preferred example step i. is conducted in a reactor A, step ii. is conducted in a reactor B and step iii. is conducted in a column or set of columns C, and whereas reactor A, reactor B and column C are connected to conduct the process for the manufacturing of methane sulfonic acid continuously.

In a preferred example step iii. is conducted in a crystallization unit, where the mother liquor is recycled into the crystallization unit or into the reactor A or into the reactor B or drained.

In a preferred example an additional step iv., after methane sulfonic acid is obtained from step ii., methane sulfonic acid anhydride is provided for subsequent charging of reactor A with methane sulfonic acid anhydride.

In a preferred example the provision of methane sulfonic acid anhydride in step iv. for subsequent charging of reactor A, comprises a separated methane sulfonic acid anhydride manufacturing step after step iii. or a separation of methane sulfonic acid anhydride as side-component from step iii.

In a preferred example after step i., after the initiator composition is formed, the water content is in the range from 0 wt-% to 1 wt-% and the content of sulfuric acid is in the range from 0 wt-% and 20 wt-% or in the range from 0 wt-% and 15 wt-%, 0 wt-% and 10 wt-%, 0 wt-% and 5 wt-% or 0 wt-% and 2 wt-%.

In a preferred example after step ii., after methane sulfonic acid is formed, the content of sulfuric acid is in the range from 0 wt-% to 50 wt-%, or 0 wt-% to 40 wt-%, or 0 wt-% to 30 wt-%, or 0 wt-% to 20 wt-%, or 0 wt-% to 15 wt-%, or 0 wt-% to 10 wt-%, or 0 wt-% to 5 wt-%.

In a preferred example after step iii., after methane sulfonic acid is purified, the content of sulfuric acid is in the range from 0 ppm to 200 ppm, preferred 0 ppm to 100 ppm and most preferred 0 ppm to 50 ppm.

In a preferred example the temperature in step i. is in the range from -5°C to 25°C, the temperature is step ii. is in the range from 25°C and 80°C, and the temperature in step iii. in the bottom of the column is in the range from 30°C to 220°C.

In a preferred example the pressure in step i. is about 1013 mbar or beyond 1013 mbar, the pressure in step ii. is in the range from 10 bar to 150 bar, and the pressure in step iii. is in the range from 2 mbar to 1000 mbar.

In an example MSA anhydride is used as water scavenger, whereas methane sulfonic acid is manufactured preferably by radical reaction (or at least partially radical reaction), and whereas an initiator composition comprises aqueous hydrogen peroxide, methane sulfonic acid, optionally sulfur trioxide and sulfuric acid and methane sulfonic acid anhydride.

One example of the disclosure comprises the use of an initiator composition comprising methane sulfonic acid, methane sulfonic acid anhydride and aqueous hydrogen peroxide for the manufacturing of methane sulfonic acid, preferably by radical reaction (or at least partially radical reaction).

In an example of the disclosure, an initiator composition is used, whereas the initiator composition additionally comprises sulfuric acid and/or sulfur trioxide.

The disclosure further relates to MSA, whereas after purification in step iii. the methane sulfonic acid content is in the range from 99.5 wt-% to 100 wt-%.

Further objects of the present disclosure include methansulfonic acid, obtainable by the inventive process, and the use of a methanesulfonic acid, obtainable by the inventive process, e.g. for cleaning applications or in an electroplating process or as acidic catalyst e.g. in esterification reactions.

DETAILED DESCRIPTION OF THE INVENTION

In a first aspect the invention relates to a process for manufacturing of methane sulfonic acid (MSA) by reaction (for example radical reaction) of an initiator composition with methane and sulfur trioxide comprising the steps:

i. Preparation of the initiator composition by mixing aqueous hydrogen peroxide (H_2O_2) with the components methane sulfonic acid (MSA), optionally sulfur trioxide (SO_3) and optionally sulfuric acid (H2SO4) and optionally methane sulfonic acid anhydride (MSA anhydride or MSAA),
ii. Reaction of the initiator composition from step i. with sulfur trioxide and methane to form MSA (preferably by radical reaction), wherein methane with a purity of at least 98 mol-% is used.

It was found that reduction of the percentage of hydrocarbons as listed above (see ranges quoted from Ullmann's Enzyklopädie), e.g. ethane and/or propane and/or butanes and/or C5-C8 alkanes in the methane used as educt had positive effects both on the product (yield, purity, colour number) and the manufacturing process (lower energy consumption).