Generally, distillation processes in a manufacturing process for MSA described so far mainly serve the purpose of removing water.

For the applications listed earlier the purified MSA needs to have a low content of sulfuric acid and a low content of methylmethanesulfonate. E.g. in eletroplating applications a low sulfuric acid content is important to avoid precipitation of metal sulfates on the metal substrate in the plating process. In chemical synthesis, e.g. in esterification reactions, sulfuric acid promotes corrosion whereas corrosion of MSA with a very low sulfuric acid content is reduced. Methylmethanesulfonate is carcinogenic. The content of methylmethanesulfonate in purified MSA therefore should be very low or zero, e.g. below 1000 ppm, to avoid handling of carcinogenic compounds or mixtures.

A distillation process for MSA generated in an anhydrous (water-free) environment has not been described so far. Typical low boilers in an anhydrous environment comprise e.g. methane, SO3, MSA anhydride, methylmethanesulfonate, and even MSA could be considered a low boiler in such an environment: MSA is light boiler compared to sulfuric acid, but it has a high boiling point itself. Typical high boilers comprise e.g. sulfuric acid, methionic acid and possibly polysulfuric acids generated by addition of SO3 to sulfuric acid and/or to MSA. One challenge for a distillation of such a feed is to separate MSA from high boilers, especially from sulfuric acid, with high MSA yields while at the same time avoiding or minimizing the formation of methylmethanesulfonate in the course of the distillation (additional methylmethanesulfonate might be introduced into the distillation step as side product from the MSA synthesis step when reacting methane and SO3. Methylmethanesulfonate formation in the synthesis step, i.e. prior to distillation, should be minimized as well but is not in the focus of this disclosure. However, it even emphasizes the need to reduce the formation of additional methylmethanesulfonate in the course of the distillation by thermal stress).
As a result of the different composition of MSA generated in an anhydrous environment the task for the purification step, namely for the distillation, is different from purification of MSA produced in an aqueous environment with typically a very low content of high boilers as sulfuric acid.

In other words, this disclosure needs to provide a solution to several problems at the same time. MSA needs to be separated from significant amounts of sulfuric acid to achieve low sulfate contents in the final product while at the same time avoiding or at least reducing the formation of methylmethanesulfonate. Another embodiment is that MSA purification achieves high MSA high yields. Yet another embodiment is that the separation of MSA and sulfuric acid requires significant amounts of energy. The overall consumption of energy should be kept to a minimum.
Yet another embodiment is that the formation of decomposition products as Methylmethanesulfonate needs to be avoided as carcinogenic byproducts are not wanted. In another embodiment their formation needs to be minimized to obtain high yields and don’t add further complexity to the purification steps.
Problems may therefore arise in the manufacture of alkanesulfonic acids from the correspond

ing alkane and sulfur trioxide, for example MSA from methane and sulfur trioxide, when the subsequent distillation is done in one step only (for example in one single distillation column), wherein the low-boiling components of the reaction mixture are removed at the column head and MSA is removed at a side discharge. High-boiling compounds as sulfuric acid remain at the bottom of the column and are removed from the process via bottom discharge (also called “ bottom purge” or just “purge”). In a process like this, to achieve a high separation performance and at the same time high MSA yields the temperatures in the sump and in the column packings must be relatively high, thus the formation of by-products as mentioned above is very likely, which may result in a reduced yield of the desired product and an increased amount of impurities.

Additional measures in such a set-up could be to either increase the purge, i.e. the amount of MSA removed from the system along with impurities. Depending on the impurity this means to either increase the low boiler purge stream at the upper part of a distillation column or to increase the high boiler purge stream in the lower part of a distillation column or both. However, this usually results in lower purification yields. Another option to achieve high MSA purities is by increasing the separation performance in the distillation step (more “theoretical plates”) which, however, increases both the pressure drop over the column (i.e. higher bottom temperatures and thus higher thermals stress on the product) and the residence time of the product in the column. Then the thermal stress on the product increases resulting in higher decomposition rates, and finally the energy demand increases as well.
Neither the set-up of a single column nor the standard measures to improve the performance of the purification are sufficient, neither for the product quality nor for the process economics, especially not for its yield and energy demand.

There is no disclosure in the art of a purification process (for example a distillation process) which could solve the problems mentioned above in the synthesis of an alkanesulfonic acid from the corresponding alkane and sulfur trioxide, e.g. MSA from methane and sulfur trioxide.

It was therefore an object of the present disclosure to provide a process for the production and/or purification of alkanesulfonic acids from sulfur trioxide and the corresponding alkane, in particular methanesulfonic acid from sulfur trioxide and methane, with high yield which avoids or at least reduces the generation of unwanted by-products, in particular in the distillation step, thus leading to MSA with a higher purity and/or greater yield. Another embodiment of the present disclosure is to provide a process where the amount of energy for the distillation is reduced.

The challenges listed above, the reduction of sulfuric acid in the resulting MSA despite high sulfuric acid concentrations in the distillation feed, along with the formation of decomposition products as methylmethanesulfonate with high temperatures, could now surprisingly be overcome by using a specific multi-step purification process, especially a two-step or a three-step distillation process. MSA with a high purity of > 99% and yields after distillation of > 80%, preferably of

> 85%, more preferably > 90% may be achieved. At the same time the formation of by-products could be minimized.
Furthermore, it was found that the energy input for distillation could be reduced.

Thus, in one aspect, the subject of the current disclosure is a process for preparing alkanesulfonic acids from sulfur trioxide and an alkane, wherein the produced raw alkane sulfonic acid is purified in a distillation process comprising at least two steps.
In another embodiment, the subject of the current disclosure is a process for purification of raw alkanesulfonic acids manufactured from sulfur trioxide and an alkane, wherein the raw alkane sulfonic acid is purified in a distillation process comprising at least two steps (as described in more detail below). In another embodiment, the invention relates to a process for purifying reaction mixtures comprising raw alkanesulfonic acids, preferably raw methanesulfonic acid, by subjecting the reaction mixture to at least two distillation steps.

In another aspect, there is provided an alkanesulfonic acid, preferably methanesulfonic acid, obtainable by the process as defined above.

In another aspect, there is provided the use of an alkanesulfonic acid, preferably methanesulfonic acid, obtainable by the process as defined above, for cleaning applications, for chemical synthesis or in an electro-plating process.

The process for preparing (raw) alkanesulfonic acids from sulfur trioxide and an alkane may be performed, for example, as described in BASF unpublished patent application no. EP 17173575.6. For example, the raw alkanesulfonic acid may be manufactured as follows: reaction of a radical initiator composition with methane and sulfur trioxide comprising the steps:

a) Preparation of the initiator composition by reacting aqueous hydrogen peroxide with the components methane sulfonic acid and methane sulfonic acid anhydride, and
b) Reaction of initiator composition from step a) with sulfur trioxide and methane to form methane sulfonic acid.

More specifically, one subject of the current disclosure is a process for preparing alkanesulfonic acids from sulfur trioxide and an alkane, wherein the produced raw alkane sulfonic acid is purified in a distillation process comprising at least two steps, and wherein a distillation set-up is used comprising (i) at least one distillation column with high separation performance (main distillation) and (ii) at least one additional distillation columns, either before and/or after the main distillation column, each with a separation performance not matching that of the main distillation column (pre-distillation and/or post-distillation, respectively).

The column with the high separation performance is characterized by a higher number of theoretical plates than the at least one additional distillation column.

In the context of this disclosure, the terms “high separation performance”, “high distillation performance” or “main distillation” refer to the number of theoretical plates of a column.

Generally spoken the more theoretical plates the better the separation performance. In other words, the more theoretical plates a column has, either the more complex product mixtures can be separated or alternatively product mixtures with compounds with very similar distillation behavior (e.g. boiling point) can be separated, and the less impurities remain in the main fraction. A theoretical plate can be technically realized e.g. by building a real plate into a column (fictive example: one theoretical plate corresponds to one real plate) or by increasing the height of the packing proportionally to the number of theoretical plates (fictive example: one theoretical plate corresponds to 50 cm height of the packing, two theoretical plates correspond to a height of 100

cm etc.). In the context of this disclosure the main fraction is the alkanesulfonic acid, particularly methanesulfonic acid.

In the following a purification set-up is described using methanesulfonic as example for an alkanesulfonic acid and methane as alkane, but the set-up could be used in the same way to purify alkanesulfonic acids with 1 to 4 carbon atoms in the chain and the corresponding C1 to C4 alkanes.
The liquid mixture entering the first purification apparatus (e. g. a distillation column) contains a high percentage of product (MSA), but also some unreacted methane and sulfur trioxide, along with sulfuric acid and other compounds such as methanesulfonic acid anhydride, methionic acid, methylbisulfate etc. This first purification step is typically realized in a distillation column. Alternatively it can be done in a reaction vessel or other devices as long as the reaction conditions given below can be met.

The inventive solution involves keeping the maximum temperatures in the distillation set-up low and the residence time of the alkanesulfonic acid, e.g. MSA, short while at the same time achieving a good purification effect for the alkanesulfonic acid. This is achieved with a distillation set-up which provides one distillation column with high separation performance (main distillation) and one or two additional distillation columns, either before and/or after the main distillation column, with a separation performance not matching that of the main distillation column (pre-distillation and/or post-distillation, respectively). The pressure drop in the main distillation column is the same or higher than the pressure drop in the other one or two columns, a higher pressure drop is preferred. This helps to keep the temperatures at the bottom of the columns low (the higher the pressure drop the higher will be the temperatures to partially evaporate the bottom mixture and the higher the respective thermal stress on this mixture, especially on MSA in the mixture). At the same time the residence times are reduced compared to a single-step distillation or compared to operating the additional columns at the same pressure drop as the main distillation column. The one to two additional columns are interconnected to the main distillation in a way that at least the liquid phases, but optionally also the gas phases are integral part of the product loops of the main distillation column. Prior to the distillation columns as such the raw-MSA stream coming from the synthesis step can be decompressed in an expansion or flash vessel. Such a flash vessel is considered part of the purification set-up.

Detailed description of the invention

In the following the invention is described in more detail. Schematic drawings of the inventive set-ups for the distillation can be found in figures 1 - 4.

Figure 1 shows a schematic drawing of an exemplary two-column set-up for the purification of alkanesulfonic acids by distillation according to the invention.
Figure 2 shows a schematic drawing of a two-column set-up for the purification of alkanesul

Claims

1. A process for preparing alkanesulfonic acids from sulfur trioxide and an alkane, wherein the produced raw alkane sulfonic acid is purified in a distillation process comprising at least two steps.
2. A process for preparing alkanesulfonic acids according to claim 1, wherein a distillation set-up is used comprising (i) one distillation column with high separation performance (main distillation) and (ii) at least one additional distillation column, either before and/or after the main distillation column, each with a separation performance not matching that of the main distillation column (pre-distillation and/or post-distillation, respectively).

3. A process according to claim 1 or 2, wherein the alkanesulfonic acid is methanesulfonic acid (MSA) and wherein the alkane is methane.

4. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps is operated at a temperature in the range of 130° C to 200° C, preferably 150° to 200° C, more preferably 170° to 195° C in all distillation columns.

5. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps is operated at a pressure in the range of 0.1 to 30 mbar, preferably 1 to 20 mbar, more preferably 3 to 15 mbar in all distillation columns.

6. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps is performed in at least two separate distillation columns.

7. Process according to any of the preceding claims, wherein said distillation process consists of two or three separate distillation columns.

8. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps is set up in a way that each distillation step can be realized in one column or in more than one column operated in parallel.

9. Process according to any of the preceding claims, wherein the first and/or a third distillation step is performed in a reaction vessel and the second distillation step is performed in a distillation column or a set of columns.

10. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps involves stripping of the distillation mixture with an inert gas in at least one of the distillation steps.

11. Process according to any of the preceding claims, wherein said distillation process comprising at least two distillation steps involves stripping of the distillation mixture with an inert gas

in the first distillation step, selected from the list consisting of nitrogen and argon.

12. Process according to any of the preceding claims, wherein the alkanesulfonic acid is withdrawn at the side discharge of the column where the product is separated with its final purity, namely of the first column in a two-column set-up and the third column of a three-column set-up.

13. Process according to any of the preceding claims, wherein the process is a continuous process.

14. Process according to any of the preceding claims, wherein the process is water-free.

15. Process according to any of the preceding claims, wherein the alkanesulfonic acid yield in the distillation is above 70 % by weight, preferably above 75 % by weight, more preferably above 80 % by weight.

16. Process according to any of the preceding claims, wherein at least a part of the bottom fraction of the MSA distillation is not purged from the system but at least partially recycled to the synthesis step of the radical starter solution or to the synthesis step of the MSA synthesis with CH_4 and SO_3.

17. Process to any of the preceding claims where the main distillation column is operated at a higher pressure drop than all of the other columns in the distillation set-up.

18. Process to any of the preceding claims, wherein the alkanesulfonic acid is methane sulfonic acid (MSA), and wherein the sulfate content of the purified MSA is less than 100 ppm and/or the MMS content is less than 1000 ppm, and/or the MSA yield in the distillation is above 80 wt-%.

19. Process according to any of the preceding claims, wherein the residence time in each distillation column is below 5h.

20. Process according to any of the preceding claims, wherein the ratio of the inner column diameter in the sump and the inner column diameter of the column directly above the sump for each column is in the range from 0.20 to 0.99.

21. Process according to any of the preceding claims, wherein the accumulation of peroxides in the column and/or in the product is prevented in the distillation by operating the distillation at temperatures in the range from 130°C to 200°C, at pressures in the range from 0.1 mbar to 30 mbar and with residence times at the bottom of each column < 5 h.

22. Process according to any of the preceding claims, wherein the raw-MSA generated in a synthesis step is sent to an expansion vessel prior to entering the distillation column.

23. Alkanesulfonic acid, preferably methanesulfonic acid, obtainable by the process of any of claims 1 to 22.

24. Use of an alkanesulfonic acid, preferably methanesulfonic acid, obtainable by the process

of any of claims 1 to 22, for cleaning applications, for chemical synthesis or in an electroplating process.