Summary

The present disclosure relates to an improved process for the production of alkanesulfonic acids from sulfur trioxide and an alkane with the help of an initiator. The disclosure provides a process especially for an improved process for the production of methanesulfonic acid by reacting methane with SO3 in the presence of an initiator.

In the context of the present disclosure, the terms “initiator” and “starter” may be used synonymously. Both terms refer to a compound which is able to initiate (i. e. start) a chemical reaction, in particular the reaction of an alkane with sulfur trioxide.

The initiator may selected from the group consisting of inorganic peroxoacids, salts of inorganic peroxoacids, organic peroxoacids, salts of organic peroxoacids, and mixtures thereof.
As mentioned, the initiator may be selected from inorganic or organic peroxoacids or salts thereof, as e.g. a peroxosulfuric acid comprising at least one peroxosulfuric acid of boron, silicon, phosphorus, carbon, nitrogen or sulfur. Consequently, typical initators may be Caro’s acid, Marshall’s acid, dimethylsulfonylperoxide, monomethylsulfonylperoxide etc
A preferred initiator is hydrogen peroxide.

The present disclosure relates, in particular, to a process for the production of alkanesulfonic acids from an alkane and SO3 with the help of an initiator, characterized in that the total energy consumption of the process is reduced by heat integration.

In an aspect, there is provided a process for the production of alkanesulfonic acids from an alkane and SO3 with the help of an initiator comprising a distillation step, wherein the total energy consumption of the process is reduced by heat integration, wherein the feed to the distillation step is heated by heat integration with the hot stream of purified alkanesulfonic acid, and/or the feed to the distillation is heated by heat integration with the hot distillation residue, and/or the feed to the distillation is first heated by heat integration with the hot purified alkanesulfonic acid and then by heat integration with the hot distillation residue, and/or the feed to the distillation is heated by heat integration with the hot stream from mixing the alkanesulfonic acid with water to yield an aqueous solution.

A further object of the present disclosure is also an alkanesulfonic acid, obtainable by the disclosed process.

The present disclosure also relates to a process for the production of alkanesulfonic acids from an alkane and SO3 with the help of an initiator, comprising the following steps

A synthesis of initiator and reaction of alkane with SO3 to form alkanesulfonic acid,
B quench to convert SO3 into a heavy boiler,
C removal of unreacted alkane by decompression (degassing),
D purification of alkanesulfonic acid by distillation,

D* pre-heating of feed to distillation by heat integration, and

E discarding of waste streams (purge).

The synthesis of the initiator (step A) may be performed in the same reactor as the following reaction of alkane with SO3. In another example of the disclosed process, the synthesis of the initiator in step A may be performed in a different reactor than the subsequent reaction of alkane with SO3 (in the presence of/ using the initator).

This process comprises a reaction step, in which the initiator is formed and the alkanesulfonic acid is formed (step A), preferably a quench step in which remaining SO3 is converted to a heavy boiler (step B), a decompression or degassing step (step C), and a distillation step for the purification of the alkanesulfonic acid (step D). One fraction of the bottom residue of the distillation is removed from the process (also called “purge”, step E) and optionally another fraction is recycled to the reaction.

The disclosed process is characterized in that the energy it contains is made use of internally rather than adding energy from an external energy source. Thus, heat is transferred from the hot streams, e.g. the streams leaving the distillation step, to cold streams, e.g. those entering the distillation step, by means of one or several heat exchangers thus significantly reducing the amount of additional energy which needs to be provided to the process compared to the prior art.

Another source of heat in the process is in the alkane, particularly in the methane, leaving step C when decompressing the system. This alkane, especially methane, can be incinerated and the heat generated in this way, in this case contained as a hot gas, be used directly for heat integration via a heat exchanger, or after transferring its heat to a heat transfer liquid in a heat exchanger and then from the heat transfer liquid into the cold process stream which needs to be heated up in another heat exchanger. Moreover, the heat of a further optional step downstream to the distillation, namely the formulation of the alkanesulfonic acid with water to yield an aqueous solution (step F), e.g. formulating methanesulfonic acid 100% (free of water) to an aqueous solution with an MSA content of 70 wt.-% by addition of water, can be used to pre-heat the feed to the distillation and in this manner contribute to reduce the demand of external, i.e. additional energy for heating and cooling the respective process streams. Another option to reduce the energy demand according to this disclosure is to operate the quench step adiabatically. By this means the energy demand required for heating and cooling the respective streams is significantly reduced.

In one example of the disclosed process, the feed to the distillation step is heated by heat integration with the hot stream of purified methanesulfonic acid from the distillation step. Heat integration is a method which in this disclosure is applied when there is the chance to save energy by heating up one stream or several streams and at the same time cooling down another stream or several streams. The heat transfer is realized through a heat exchanger, in which the cold stream is heated up by the hot stream while the hot stream itself is cooled down. If there

are several streams to be cooled down and heated up, for each combination of hot stream for heating and cold stream for cooling down a dedicated heat exchanger is used. In general, heat integration according to this disclosure works by transferring heat from any of the hot streams of step A to F to any of the cold streams of step A to F as long as the temperature levels are suitable for an effective heat transfer. Streams at suitable temperature levels have a temperature difference between the stream with the higher temperature level which needs to be cooled down and the stream with the lower temperature level which needs to be heated up of at least 5°C, preferred of at least 10°C and more preferred of at least 15°C. But it may also be sufficient if the temperature levels just have a difference as low as 2°C or 3°C or 4°C. There is no requirement for the maximum temperature difference of the streams at higher and lower temperature level, but based upon considerations of practicability and the integrity of the heat exchangers, e.g. regarding thermal stress and/or corrosivity of the process streams, the maximum temperature difference of the incoming stream at higher temperature level and the incoming stream at lower temperature level should be no more than 220°C, preferred no more than 200°C and most preferred no more than 180°C.

In a further example of the disclosed process, the feed to the distillation is heated by heat integration with the hot distillation residue leaving the bottom of the distillation column or set of distillation columns.

In another example of the disclosed process, the feed to the distillation step is heated by heat integration with the hot stream generated when mixing the alkanesulfonic acid with water to yield an aqueous solution (formulation step).

In a preferred example of the disclosed process, the feed to the distillation is heated by heat integration with the hot purified alkanesulfonic acid and the hot distillation residue in a sequence of heat transfer steps. More preferably, the feed to the distillation is first heated with hot purified alkanesulfonic acid and then, the feed is further heated with the hot bottom residue of the distillation step.

In another example of the disclosed process, the evaporators of the distillation are powered by steam and steam condensate coming from the evaporators of the distillation is used to heat the feed to the distillation.

In yet another example of the disclosed process, the energy released in the condensers of the distillation step is used to heat up the feed to the distillation.

In a preferred example of the disclosed process, the feed to the distillation is further heated to the distillation temperature after the heat integration steps described above powered by steam, by electrical power, by heating oil, by hot water (typically operated under elevated pressure to reduce or completely avoid evaporation of the water) or by other suitable energy sources.

Another example of the disclosed process, the feed to the distillation flows to the distillation applying a combination of all options named above to reduce the energy demand for heating or cooling of the system, respectively. This is to heat the feed to the distillation by heat integration with the hot streams from the purified product from distillation while still hot, with the hot distillation residue leaving the bottom of the distillation column, with the hot steam condensate from the evaporators of the distillation, with the hot cooling fluid from the condensers of the distillation and with the hot stream from the formulation step.

While heat integration with the different options named above helps to reduce energy consumption if just one of the options is applied, it is preferred to set-up the process applying at least two or all of the options to reduce the demand of external energy supply to the process for heating and cooling the respective streams.

It is particularly preferred if heat integration is realized in a sequence where the temperature of the streams used to heat the feed to the distillation column increases step by step, meaning that after operating the quench in adiabatic mode, heating of the feed to distillation is first done with the hot stream from the formulation step, followed by heating with the hot purified alkanesulfonic acid from distillation, followed by heating with the even hotter distillation residue leaving the bottom of the distillation column, and finally heating of the feed to distillation is done by providing external energy sources as e.g. steam or heating oil or hot water or other suitable energy sources.
Alternatively, the hot process streams used for the sequence of pre-heating can be switched.

In one example of the disclosure the feed to the distillation is pre-heated by a one-or-multistep of heat integration and/or external heating so that the difference between the feed temperature to the distillation and the operating temperature in the distillation column at the feeding point is less than 100°C, preferred less than 50°C and more preferred less than 30°C or even more preferred less than 10°C. The temperature difference between feed and distillation can also be designed to be less than 8°C, or less than 5°C, or less than 3°C or even less than 1°C.

In a further example of the disclosed process the feed to the distillation is heated above, below or exactly to the boiling point. Therefore, the feed can enter the column as a subcooled liquid, an overheated liquid, a boiling liquid or as a vapor. It is preferred, that the feed enters the column as a boiling liquid or as an overheated liquid (flash).

In one example of the disclosed process, each heat integration step is carried out in a dedicated heat exchanger or set of heat exchangers having the same functionality.

In a preferred example of the disclosed process, the heat exchangers installed for heat integration are made of a material selected, separately from each other, from the group consisting of silicon carbide (SiC, SSiC), Titanium, Tantalum, Gold, Hastelloy or glass-lined steel. More preferably, silicon carbide (SSiC) is used in at least one, preferably in all of the heat exchang-

ers. The heat exchangers may be e.g. of tube or tube bundle type, U-tube type, plate type or monolith type. In a preferred example, the heat exchangers are monoliths of pressureless sintered silicon carbide (SSiC). Sealings can e.g. be made of PFA or PTFE.

In a preferred example of the disclosed process, the heat in the heat integration step is transferred from the hot streams leaving the distillation to the cold feed directly without a heat transfer fluid in one apparatus.

In a further example of the disclosed process, the heat in the heat integration step is transferred from the hot streams leaving the distillation to the cold feed with the help of a heat transfer fluid. In this case the heat transfer fluid is first heated by the hot streams leaving the distillation and then releases the heat to the cold feed stream. Aliphatic and cyclic hydrocarbons as well as silicon oils can be used advantageously as heat transfer fluids.

In one example of the disclosed process, the quench step is operated isothermally.
In a preferred example of the disclosed process, the quench step is operated adiabatically.

In a further example of the disclosed process, remaining alkane from the synthesis of alkanesulfonic acids is incinerated to supply heat. The heat supplied by the incineration of methane can be used directly, i.e. as hot gas, or it can be used to generate steam or to heat up heat transfer fluids. The heat supplied by the incineration of methane can further be used to heat the feed to the distillation and/or to power the evaporators of the distillation.

Detailed description of the inventive process

This invention relates to an optimized process for the production of alkanesulfonic acids. In the following a detailed exemplary description of the process according to one embodiment of the present invention is given for the case that the alkane is methane and methanesulfonic acid (MSA) is formed in the reaction:

The schematic flow chart of one embodiment of the present invention is shown in Figure 1. A further embodiment of the inventive process is shown in Figure 3.
Figure 2 depicts an exemplary process for the production of MSA from methane and SO3 *without* heat integration.

MSA can be produced from sulfur trioxide and methane in the following steps:

A Reaction: Methanesulfonic acid (MSA) is formed from methane and SO_3 with a mixture of MSA and sulfuric acid as a solvent.

$$SO_3 + CH_4 \rightarrow CH_3\text{-}SO_3H \qquad -134\ kJ/mol \qquad (1)$$