

Process for removing a small-molecule contaminant from a chlorine compound stream

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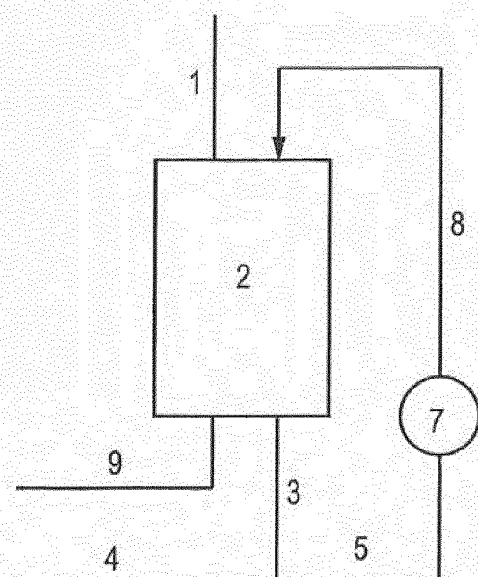


Fig.1

(57) Abstract: The invention pertains to a process for removing a small-molecule contaminant from a chlorine-compound stream, the process comprising an adsorption sequence comprising the steps of - contacting a chlorine compound stream comprising a small-molecule contaminant with an adsorbent for the small-molecule contaminant, the chlorine compound being chlorine or chloromethane, said chlorine compound stream being in the liquid phase, and - withdrawing a purified chlorine compound stream from which small-molecule contaminant has been removed from the adsorbent, and (ii) a desorption sequence comprising the steps of - contacting the adsorbent containing small-molecule contaminant with a chlorine compound stream in the gaseous phase, and - withdrawing a chlorine compound stream comprising small molecule contaminant in the gaseous phase from the adsorbent, wherein the chlorine compound stream used in the desorption sequence is derived from the purified chlorine compound stream obtained in the adsorption section. The chlorine compound stream preferably is a chlorine stream or a monochloromethane stream. The small-molecule contaminant preferably is water. The process according to the invention allows the use of less equipment and gas streams, is flexible and avoids the introduction of additional contaminants.

Process for removing a small-molecule contaminant from a chlorine compound stream

- 5 The present invention pertains to a process for removing a small-molecule contaminant from a chlorine compound stream, in particular a chlorine stream or a chloromethane stream.

In the manufacture of chlorine and chloromethane, product streams are often
10 formed which contain small-molecule contaminants, i.e. contaminants which have a molecular size which is below the molecular size of the chlorine compound. Examples of small-molecule contaminants are water, O₂, H₂, N₂, CO₂, CH₃OH, CH₄, HCl, and CO. These contaminants are to be removed from the chlorine compound stream. Preferably, the small-molecule contaminant
15 according to the present invention is water.

Processes for removing small-molecule contaminants from chlorine streams and chloromethane streams are known in the art.

DE-A-19955142 describes a process for removing water from a continuously
20 obtained liquid mixture comprising 1,2-dichloromethane, HCl, and water, by passing the stream over a molecular sieve at a temperature below 60°C and a pressure of 1.5 bar, to effect adsorptive drying. The adsorbent may be regenerated by contacting it with nitrogen or air. DD-B-209182 describes a regeneration process using a nitrogen gas at different temperatures.

25 US 5,269,834 discloses a process for treating liquid chlorine to remove inert gases therefrom, such as H₂, N₂, O₂, CO₂, and CO. The chlorine is contacted in the liquid phase with a molecular sieve, which acts as adsorbent. The adsorbent is periodically regenerated by heating, vacuum evacuating the column in which the sieve is present, and purging the molecular sieve with a gas to flush out
30 impurities, followed by a further vacuum evaporation of the column. Because of corrosion problems, a disadvantage of the process according to US 5,269,834 is that the system includes a storage tank which stores, under pressure, the

liquid chlorine that needs to be purified. Another disadvantage of the system according to US 5,269,834 is that it is a batch system. Additionally, a chlorine containing waste stream is generated during the regeneration process. This waste stream needs to be processed in the plant and will typically be converted
5 to bleach. This means that the overall process results in a lower yield of the desired purified chlorine and a significant amount of the undesired byproduct bleach, especially if chlorine gas is used for the regeneration. A further disadvantage is that in case contaminated chlorine is used for regeneration, the regeneration will be less efficient, meaning that higher temperatures will need to
10 be applied to remove the impurities from the column. This in turn makes that the column will need to be made of more expensive materials.

In the industrial manufacture of chlorine and chloromethane there is need for an efficient process for removing small-molecule contaminants from a chlorine-
15 compound stream which process does not generate additional waste streams, and can be used without the need for additional equipment. The present invention provides such a process.

The present invention pertains to a process for removing a small-molecule
20 contaminant from a chlorine-compound stream, the process comprising an adsorption sequence comprising the steps of

- contacting a chlorine compound stream comprising a small-molecule contaminant with an adsorbent for the small-molecule contaminant, the chlorine compound being chlorine or chloromethane, and
- 25 - withdrawing a purified chlorine compound stream from which small-molecule contaminant has been removed from the adsorbent,

and a desorption sequence comprising the steps of

- contacting the adsorbent containing small-molecule contaminant with a chlorine compound stream in the gaseous phase, and
- 30 withdrawing a chlorine compound stream comprising small molecule contaminant in the gaseous phase from the adsorbent,

wherein the chlorine compound stream used in the desorption sequence is derived from the purified chlorine compound stream obtained in the adsorption sequence.

5 In the process according to the invention small-molecule contaminants are adsorbed from the chlorine-compound stream when the chlorine compound stream is in the liquid phase using an adsorbent. The adsorbent is regenerated by contacting the adsorbent onto which small-molecule contaminants have been adsorbed with a chlorine compound stream in the gaseous phase,
10 wherein the chlorine compound stream is derived from the stream resulting from the purified chlorine compound stream obtained in the adsorption sequence. In other words, the adsorbent is regenerated using part of the product stream. In contrast with earlier processes there thus is no separate regeneration gas. This means that less equipment and gas streams are required. It also means that the
15 process has a high flexibility, because the amount of regeneration gas required can be easily varied. Further, the use of separate regeneration gases is always accompanied by the risk of introducing additional contaminants which can cross over to the product stream. This risk is also prevented in the process according to the invention. Further advantages of the process according to the invention
20 and specific embodiments will become clear from the further specification.

The present invention will be discussed in more detail below.

In the following, reference may be made to the following Figures. The Figures
25 are intended to illustrate various aspects of the present invention. However, the invention is not to be considered limited thereto or thereby.

Figure 1 illustrates a first embodiment of the process according to the invention.

Figure 2 illustrates a second embodiment of the process according to the invention.

30 Figure 3 illustrates a third embodiment of the process according to the invention.

Figure 4 illustrates a fourth embodiment of the process according to the invention.

Figures 5, 6, and 7 provide the results of technical experiments.

- 5 In the process according to the invention, the starting material is a chlorine compound stream which is a chlorine stream or a chloromethane stream. The chlorine stream, if used, generally comprises at least 95 wt.% of chlorine, in particular at least 98 wt.% of chlorine, more in particular at least 99 wt.% of chlorine. It further comprises small-molecule contaminants, such as one or more of water, O₂, H₂, N₂, CO₂, CH₃OH, CH₄, HCl, and CO. In particular, water
10 may be present as small-molecule contaminant, e.g., in an amount of 5-2000 ppm, depending on origin, temperature, and pressure of the chlorine stream, in particular 20-1000 ppm, more in particular 50-500 ppm. In one embodiment, oxygen is present in the chlorine stream, whether or not in
15 combination with water in the ranges indicated above. Oxygen may, e.g., be present in an amount of 10-7500 ppm, depending on origin, temperature, and pressure of the chlorine stream. In one embodiment, the chlorine stream comprises water, oxygen, or water and oxygen in the ranges stipulated above.
- 20 There are of course four types of chloromethane, namely monochloromethane, dichloromethane, trichloromethane, and tetrachloromethane. Unless specified otherwise, the term chloromethane as used in the present specification encompasses all compounds, and mixtures thereof. The chloromethane stream, if used, generally comprises at least 95 wt.% of
25 chloromethane, in particular at least 98 wt.% of chloromethane, more in particular at least 99 wt.% of chloromethane. It further comprises small-molecule contaminants, such as one or more of water, O₂, H₂, N₂, CO₂, CH₃OH, CH₄, HCl, and CO. In particular, water may be present as small-molecule contaminant, e.g., in an amount of 5-3000 ppm, depending on origin,
30 temperature, and pressure of the chloromethane stream, in particular 20-2000 ppm, more in particular 100-2000 ppm.

The present invention is of particular relevancy to monochloromethane streams. In one embodiment, the chlorine compound stream is a monochloromethane stream, which generally comprises at least 95 wt.% of monochloromethane, in particular at least 98 wt.% of monochloromethane, more in particular at least 99
5 wt.% of monochloromethane, in combination with the small-molecule contaminants specified above.

Small-molecule contaminants which can be removed by the process according to the invention include water, O₂, H₂, N₂, CO₂, CH₃OH, CH₄, HCl, and CO. The
10 process according to the invention is of particular interest for removing water from water-containing chlorine compound streams. This process can also be indicated as a drying process.

In the first step of the process according to the invention, the chlorine
15 compound stream comprising a small-molecule contaminant is contacted in the liquid phase with an adsorbent for the small-molecule contaminant.

The contacting takes place in the liquid phase. This means that temperature and pressure have to be selected such that the chlorine compound stream is
20 liquid.

Where water is present, it is preferred to select the temperature and pressure in such a way that the formation of hydrates is avoided, while ensuring that the chlorine compound stream is in the liquid phase. Chlorine hydrate is a solid crystal the formation of which can interfere with the adsorption of water by the
25 adsorbent. It can also lead to clogging of the equipment, and result in a corrosion issue. Condensation temperature, i.e., the maximum temperature at which the composition is liquid, is dependent on pressure. With increasing pressure, the condensation temperature increases. The temperature at which hydrate formation takes place is not dependent on pressure. In consequence, at
30 higher pressures, the difference between the condensation temperature and the hydration temperature increases, making for a wider temperature range at which the invention can be employed.

It is within the scope of the skilled person to determine temperature and pressure combinations at which the chlorine compound is liquid and, where applicable, the formation of hydrates is avoided.

5 Where the chlorine compound is chlorine and the chlorine compound stream comprises water, suitable conditions include, for example, a pressure in the range of 8.44 to 20 bar, in combination with a temperature of 28.3 to 60°C. A pressure of at least 9 bar, in particular at least 10 bar may be preferred.

Where the chlorine compound is chlorine and the chlorine compound stream
10 does not comprise water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, in combination with a temperature of -50 to 60°C.

Within the context of the present specification, the term "comprises water" means that the chlorine compound stream comprises at least 1 ppm of water. Conversely, the wording "does not comprise water" means that the chlorine
15 compound stream comprises less than 1 ppm of water.

Where the chlorine compound is monochloromethane and the chlorine compound stream comprises water, suitable conditions include, for example, a
20 pressure in the range of 5 to 20 bar, in combination with a temperature of 21 to 60°C.

Where the chlorine compound is monochloromethane and the chlorine compound stream does not comprise water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, in combination with a
25 temperature of -40 to 60°C.

Where the chlorine compound is dichloromethane and the chlorine compound stream comprises water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature
of 1.6 to 60°C.

30 Where the chlorine compound is dichloromethane and the chlorine compound stream does not comprise water, suitable conditions include, for example, a

pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature of -40 to 60°C.

Where the chlorine compound is trichloromethane and the chlorine compound stream comprises water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature of 1.6 to 60°C.

Where the chlorine compound is trichloromethane and the chlorine compound stream does not comprise water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature of -40 to 60°C.

Where the chlorine compound is tetrachloromethane and the chlorine compound stream comprises water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature of 1.45 to 60°C.

Where the chlorine compound is tetrachloromethane and the chlorine compound stream does not comprise water, suitable conditions include, for example, a pressure in the range of 0.5 to 20 bar, preferably 1-5 bar, in combination with a temperature of -20 to 60°C.

The liquid chlorine compound stream is contacted with an adsorbent for the small-molecule contaminant.

The adsorbent is selected such that it has high affinity for the small-molecule adsorbent to be removed, but only limited affinity for the chlorine compound. In one embodiment, the adsorbent is a porous material, in particular a porous inorganic material, the pore size of which is such that the small-molecule contaminant can enter the pores while the chlorine compound cannot. Examples of suitable adsorbents are molecular sieves, such as zeolites. The selection of the adsorbent depends on the nature of the chlorine compound and on the nature of the contaminant. It is within the scope of the skilled person to select a suitable adsorbent, where necessary using routine experimentation.

For example, preferred adsorbents for the removal of small-molecule contaminants from chlorine streams include molecular sieves 3Å, 4Å, and 5Å. Further adsorbents that may be suitable include calcium chloride, calcium sulphate, silica, magnesium perchlorate hydrate, magnesium sulphate, potassium carbonate, and sodium sulphate.

Where the contaminant is one or more of water, oxygen, nitrogen, carbon monoxide, and carbon dioxide, molecular sieves 3Å, 4Å, and 5Å are all suitable. Where the contaminants are larger, such as methanol, methane, or hydrochloric acid, molecular sieves of type 4Å or 5Å may be more suitable.

Of course, the adsorbent can be combined with materials known in the art to form a composition suitable for practical use. Suitable materials which can be combined with the adsorbent include binders, to bond the adsorbent particles together to form larger particles. Combinations of different types of adsorbent can also be used in this context. The adsorbent can, e.g., be present in the form of particles with a diameter of 0.5-10 mm, in particular 1-5 mm, although other sizes may also be suitable.

The reactor containing the adsorbent can have any form conventionally used in the art. The use of an adsorption column, wherein the adsorbent is present in a column with the feed being provided to one end of the column and the product being withdrawn from the other end of the column is considered preferred. Other embodiments include, e.g., fluidized bed adsorption and moving bed adsorption. These are considered less suitable here.

The purified chlorine compound stream resulting from the adsorbent has a reduced concentration of small molecule contaminants as compared to the chlorine compound stream before it is contacted with the adsorbent. In one embodiment, the amount of small-molecule contaminant present in the stream resulting from the adsorbent is at most 20% of the amount present in the chlorine compound stream before it is contacted with the adsorbent. Preferably, the amount of small-molecule contaminant present in the stream resulting from

the adsorbent is at most 10% of the amount present in the chlorine compound stream before it is contacted with the adsorbent, more in particular at most 5%.

5 Where the small-molecule contaminant is water and the chlorine compound stream is a chlorine stream, it is preferred for the chlorine product stream to have a water content below 50 ppm more in particular below 20 ppm.

Where the small-molecule contaminant is water and the chlorine compound stream is a monochloromethane stream, it is preferred for the monochloromethane product stream to have a water content below 100 ppm.

10 Where the small-molecule contaminant is water and the chlorine compound stream is a dichloromethane stream, a trichloromethane stream, or a tetrachloromethane stream, it is preferred for the product stream to have a water content below 100 ppm.

15 During the adsorption step, at some point in time the adsorbent will be saturated with small molecule contaminant. This can be seen from the fact that the concentration of small molecule contaminant in the product will start to increase (breakthrough). At or before the point where the amount of contaminant in the product becomes higher than the desired amount, the adsorbent will be
20 regenerated.

It is a feature of the present invention that the adsorbent is regenerated by contacting it with a gaseous chlorine compound stream which is derived from the purified chlorine compound stream resulting from the adsorbent. By using part of the product to regenerate the adsorbent, it is not necessary to introduce
25 new streams into the system, which makes for a process which is efficient both in the use of apparatus and in the use of resources. Regeneration with the purified product stream is also more efficient than regeneration with the unpurified feed stream, leading to less waste generation.

30 Of course, for a meaningful process, not all of the purified chlorine compound stream resulting from the adsorbent is used to regenerate the adsorbent. In general, the amount used to regenerate the adsorbent is at most 40% of the

purified chlorine compound stream resulting from the adsorbent, in particular at most 35%, even more in particular at most 25%, still more in particular at most 15%. To obtain efficient regeneration it may be preferred to use at least 2% of the purified chlorine compound stream to regenerate the adsorbent, e.g., at
5 least 5%, in particular at least 10%.

As indicated above, part of the liquid purified chlorine compound stream is converted to the gaseous phase to be used for regeneration of the adsorbent. Conversion to the gaseous phase can be carried out by increasing the
10 temperature and/or decreasing the pressure, as will be evident to the skilled person. In one embodiment, the part of the liquid purified chlorine compound stream to be used in regenerating the adsorbent is converted to the gaseous phase by increasing its temperature to a value of at least 50°C, more in particular at least 80°C, e.g. in the range of 90-120°C. In one embodiment this is
15 done without the pressure being changed. Of course it is also possible to provide a gaseous chlorine compound stream by increasing temperature and at the same time increasing pressure, as long as the temperature increase is sufficient to ensure that a gaseous phase is obtained.

20 In the regeneration step, the adsorbent is contacted with a chlorine compound stream in the gaseous phase. This leads to desorption of the small-molecule contaminant from the adsorbent, and incorporation thereof in the gaseous chlorine compound stream, which is then withdrawn from the adsorbent. The temperature and pressure in the desorption step are not critical, as long as the
25 chlorine compound stream is in the gaseous form. Suitable temperatures include a temperature in the range of 20-150°C, in particular 50-150°C, more in particular 80-120°C. Suitable pressures include a pressure in the range of 8.44-15 bar in case Where the chlorine compound is chlorine; a pressure in the range of 5.1-15 bar in case the chlorine compound is monochloromethane; and
30 a pressure in the range of 1-5 bar in case of other chlorine compounds.

Temperature regulation can be carried out in a manner known in the art, applying external or internal heating or cooling as desired.

Preferably, in the process according to the present invention, no vacuum is applied during the desorption step. In this way, the formation of a low pressure chlorine compound containing waste stream is prevented, avoiding the significant costs associated with recompression and/or compression of this stream.

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In one embodiment of the invention, the process for removing a small-molecule contaminant from a chlorine-compound stream comprises:

10

(i) an adsorption sequence comprising the steps of

- contacting a chlorine compound stream comprising a small-molecule contaminant with an adsorbent for the small-molecule contaminant, the chlorine compound being chlorine or chloromethane, said chlorine compound stream being in the liquid phase, and
- withdrawing a purified chlorine compound stream from which small-molecule contaminant has been removed from the adsorbent,

15

20 and

(ii) a desorption sequence comprising the steps of

- contacting the adsorbent containing small-molecule contaminant with a chlorine compound stream in the gaseous phase, and
- withdrawing a chlorine compound stream comprising small molecule contaminant in the gaseous phase from the adsorbent, wherein the chlorine compound stream used in the desorption sequence is derived from the purified chlorine compound stream obtained in the adsorption section.

25

30

and wherein the desorption sequence is carried out at a pressure which is at least such that upon cooling to 0°C (at that same pressure), a liquid would be formed.

In this way, the chlorine compound stream can be retrieved. The pressure preferably lies within the range of 8.44-15 bar for Cl₂, within the range of 5.1-15 bar for CH₃Cl and for other chlorine compounds according to the present invention it lies within the range of 1-5 bar. Preferably, the desorption sequence is carried out at a pressure which is at least such that upon cooling to 15°C (at that same pressure), and most preferably at 30°C (at that same pressure), a liquid will be formed.

In another embodiment of the present invention, all process steps are carried out at substantially the same pressure, i.e. no specific measures are carried out to ensure pressure difference between the various process steps. In a process carried out in this manner, heaters and coolers are used to convert the various streams from the gaseous to liquid phase and vice versa, rather than compressors and decompressors, which are more cost-intensive apparatus. In practice still some pressure drop will occur over the columns. This pressure drop can be compensated for by installing a pump after the chlorine drying column to increase the pressure of the outgoing chlorine compound stream.

The process according to the invention is illustrated by Figure 1, without being limited thereto or thereby.

25

In Figure 1, in the adsorption sequence, a liquid chlorine compound stream (1) is provided to a reactor (2) comprising an adsorbent. Purified stream (3) is removed from the adsorbent, and withdrawn through line (4). When the adsorbent is to be regenerated, liquid compound stream (1) is discontinued and part of the purified stream (3) is provided through line (5) to a evaporator (7) where the liquid stream is converted to a gaseous stream (8) by increasing the temperature and/or decreasing the pressure. Gaseous chlorine compound

30

stream (8) is provided to the adsorbent, to remove small-molecule contaminants therefrom. A gaseous chlorine compound stream comprising small molecule contaminant (9) is then withdrawn from the adsorbent.

In Figure 1, the liquid chlorine compound stream (1) processed in the adsorption stage and the gaseous stream (8) used in the desorption stage enter the reactor at the same side (concurrent adsorption/regeneration). The process according to the invention is by no means limited to this. In fact, it may be preferred for the adsorption/regeneration to be carried out countercurrently, wherein the chlorine compound stream which is used in the desorption sequence is provided to the reactor at the location where the purified chlorine compound stream is withdrawn from the reactor. This embodiment is presented in Figure 2. In Figure 2 it is also illustrated that the gaseous chlorine compound stream comprising small molecule contaminants (2) withdrawn from the adsorbent in the regeneration step is provided to a condenser (111) to form a liquid stream (112), which is combined with the liquid chlorine compound stream (1). Condenser (111) also yields a gaseous waste stream (113) which contains most small-molecule contaminants, and optionally a liquid aqueous stream (114).

Where the small-molecule contaminant is or comprises water, it can be removed through gaseous waste stream (113) and/or through a liquid aqueous stream (114). Where the chlorine compound stream does not comprise water, a liquid aqueous stream (114) will not be formed.

In one embodiment of the present invention, the process according to the invention is integrated in a two-step process for effecting removal of small-molecule contaminants, in particular water, from chlorine compound streams. In this embodiment, the invention pertains to a process comprising the following steps:

- subjecting a gaseous chlorine compound stream comprising small-molecule contaminants to a condensation step, to form a liquid chlorine compound stream comprising small-molecule contaminants and one or more of a liquid water fraction and a gaseous fraction comprising small contaminants,

- separating the liquid chlorine compound stream from the one or more of the liquid water fraction and a gaseous fraction comprising small contaminants, and providing the chlorine compound stream comprising small-molecule contaminant to the process as discussed above.

5

The presence of a preceding condensation step opens up the possibility of recycling the chlorine compound stream used to regenerate the adsorbent. In a preferred embodiment of this process, at least part of the chlorine compound stream comprising small-molecule contaminant that is withdrawn in the gaseous
10 phase from the adsorbent in the desorption step is provided to the condensation step.

Which fractions are formed in the condensation step depends on the composition of the gaseous chlorine compound stream entering the
15 condensation step. Where water is present in the gaseous chlorine compound stream, a liquid fraction can be formed. Other small-molecule contaminants are in general too volatile to form a liquid fraction. Their presence will result in the formation of a gaseous fraction.

20 This embodiment is illustrated by Figure 3, without being limited thereto or thereby.

In Figure 3, a starting gaseous chlorine compound stream comprising small-molecule contaminants (10) is provided to a condenser (11). In the condenser
25 (11), pressure is increased and/or temperature is decreased, to form a liquid chlorine compound stream, which is withdrawn through line (1). Where the starting gaseous chlorine compound stream comprises water as small molecule contaminant, a liquid water fraction may be formed, which is withdrawn through line (12). The liquid chlorine compound stream and the water fraction form
30 separate phases.

Where the starting gaseous chlorine compound stream comprises volatile small molecule contaminants, a gaseous small molecule contaminant fraction can be formed, which is withdrawn through line (13).

In the adsorption sequence, the liquid chlorine compound stream (1) is provided to a reactor (2) comprising an adsorbent. Purified stream (3) is removed from the adsorbent, and withdrawn through line (4). When the adsorbent is to be regenerated, liquid compound stream (1) is discontinued and part of the purified stream (3) is provided through line (5) to an evaporator (7) where the liquid stream is converted to a gaseous stream (8) by increasing the temperature and/or decreasing the pressure. Gaseous chlorine compound stream (8) is provided to the adsorbent. A gaseous chlorine compound stream comprising small molecule contaminant (9) is then withdrawn from the adsorbent, and recycled to condenser (11), in the figure by being combined with gaseous chlorine compound stream comprising small-molecule contaminants (10).

15

In one embodiment, the process according to the invention is carried out using at least two reactors, at least one of which is operated in adsorption mode while at least a further reactor is operated in desorption mode.

An attractive way to carry out the invention is illustrated in Figure 4. In Figure 4, two reactors (21) (22) comprising adsorbent are present, one of which is operated in adsorption mode, while the other is operated in desorption mode. Both reactors are connected to feed line (1) through lines (111) and (112), respectively, but only the line connected to the unit operating in adsorption mode is open. The feed line connected to the unit operating in desorption mode is closed. In the following, the process will be described with unit (21) operating in adsorption mode and unit (22) operating in desorption mode. The feed stream (111) provides liquid chlorine compound stream to adsorption reactor (21). The purified product is removed through line (31). Part of the product is withdrawn through line (41). Another part of the product is provided to evaporator (71), and converted to the gaseous phase. The gaseous stream (81) thus obtained is provided to reactor (22), and results in desorption of small

molecule contaminant from the adsorbent, and formation of a gaseous chlorine compound stream (91) comprising small molecule contaminant. Stream (91) can be recycled to condenser (11). Once the adsorbent in reactor (21) is saturated, and the adsorbent in reactor (22) has been regenerated, reactor (21) switches from adsorption mode to desorption mode, and reactor (22) switches from desorption mode to adsorption mode. Feedstream (111) to reactor (21) is closed, and feedstream (112) to reactor (22) is opened. Purified product is withdrawn from reactor (22) through line (32). Part of the product is withdrawn through line (42). Another part of the product is provided to evaporator (72), and converted to the gaseous phase. The gaseous stream (82) thus obtained is provided to reactor (21), and results in desorption of small molecule contaminant from the adsorbent, and formation of a gaseous chlorine compound stream (92) comprising small molecule contaminant. Stream (92) can be recycled to condenser (11).

Operating the process according to the invention in this way makes it possible to operate the process in a continuous fashion. In this embodiment it is also easy to switch the reactor between adsorption and desorption modes, which makes the process suitable for coping with varying contaminant levels. The total number of units, the number of units operating in adsorption mode, and the number of units operating in desorption mode can be varied at will. It is also possible to provide a reactor with a number of adsorbent beds, wherein at least one bed is operating in adsorption mode while at least one bed is operating in desorption mode.

As will be evident to the skilled person, various elements of the present invention can be combined at will. For example, the preferred embodiments of various steps can be combined with each other.

The invention will be illustrated by the following examples, without being limited thereto or thereby.

Example 1: Water removal from a chlorine stream – computer model example

A chlorine stream with a chlorine content of 99 wt.% and a water content of 1 wt.% is provided through line (10) to an operation as presented in Figure 4. The feed has a pressure of 8.5 bar (or higher) and a temperature of 100°C. The pressure is maintained during the entire operation. In the condenser (11) the temperature is reduced to 28-30°C, depending on the pressure. A liquid water fraction is formed, and removed through line (12). A liquid chlorine stream is formed which contains about 300 ppm water. The stream is provided through line (111) to reactor (21), operating in adsorbent mode. The reactor contains an adsorbent, more specifically a 3Å molecular sieve, and is at a temperature of 28-30°C. The product withdrawn from the reactor through line (31) has a temperature of 28-30°C, is at a pressure of 8.5 bar or higher, and has a water content of less than 10 ppm. The major fraction of the product (85%) is withdrawn from the process through line (41). A minor fraction (15%) is provided to evaporator (71) through line (51). In evaporator (71) the temperature of the fraction is increased to a value of 100°C, with the pressure being maintained at a value of at least 8.5 bar. The gaseous fraction is provided through line (81) to reactor (22), where it is contacted with an adsorbent being regenerated. The gaseous effluent withdrawn from reactor (22) through line (91) is chlorine with a water content of up to a number of 70 wt.% at a pressure of at least 8.5 bar 8 bar and a temperature of somewhat below 100°C. This stream is provided to condenser (11).

Once the adsorbent in reactor (21) is saturated and the adsorbent in reactor (22) has been regenerated, reactor (21) will be operated in regeneration/desorption mode, while reactor (22) will be operating in adsorption mode. This means the product from condenser (11) is provided through line (112) to reactor (22), operating in adsorption mode. The rest of the process will be analogous to what has been described above.

Example 2: Water removal from a monochloromethane (MCM) stream – computer model example

A MCM stream with a MCM content of 80 wt.% and a water content of 20 wt.% is provided through line (10) to an operation as presented in Figure 4. The feed has a pressure of 5 bar and a temperature of 100°C. The pressure of 5 bar is maintained during the entire operation. In the condenser (11) the temperature is reduced to 20-30°C. A liquid water fraction is formed, and removed through line (12). A liquid MCM stream is formed which contains about 2000 ppm water. The stream is provided through line (111) to reactor (21), operating in absorbent mode. The reactor contains an adsorbent, more specifically a molecular sieve, e.g., molecular sieve 3Å and is at a temperature of 20-30°C. The product withdrawn from the reactor through line (31) has a temperature of 20-30°C, is at a pressure of 5 bar, and has a water content of less than 10 ppm. The major fraction of the product (65%) is withdrawn from the process through line (41). A minor fraction (35%) is provided to evaporator (71) through line (51). In evaporator (71) the temperature of the fraction is increased to a value of 100°C, with the pressure being maintained at 5 bar. The gaseous fraction is provided through line (81) to reactor (22), where it is contacted with an adsorbent being regenerated. The gaseous effluent withdrawn from reactor (22) through line (91) is MCM with about 5700 ppm water at a pressure of 5 bar and a temperature of 100°C. This stream is provided to condenser (11).

Once the absorbent in reactor (21) is saturated and the absorbent in reactor (22) has been regenerated, reactor (21) will be operated in regeneration/desorption mode, while reactor (22) will be operated in absorption mode. This means the product from condenser (11) is provided through line (112) to reactor (22), operating in absorption mode. The rest of the process will be analogous to what has been described above.

Example 3: Water removal from a dichloromethane (DCM) stream – technical example

3 g/s of a liquid DCM stream containing 1500 ppm water at room temperature
5 was provided to the bottom of a borosilicate glass column with a diameter of
31mm and height of 800mm packed with 385g of dry 3Å molecular sieves. Prior
to use the column was purged with nitrogen overnight to achieve complete
desorption prior to the first adsorption cycle. Adsorption was carried out until the
outlet water concentration reached 15% of the inlet concentration. After that
10 desorption was carried out from the top of the column with 0.95 g/s dry DCM for
the same duration as the adsorption. During desorption the inlet vapor
temperature and external heating temperature of the column were maintained at
100°C. After desorption the column was immediately used for a second
adsorption step. This was followed by a second desorption step and a third
15 adsorption step.

Figure 5 shows the adsorption breakthrough curves for the three adsorption
cycles, indicated as, respectively, CSS A1, CSS A2, and CSS A3. From the
adsorption breakthrough results it can be seen that the behavior of the bed is
20 the same for all three cases, proving that the column is regenerated completely
under the experimental conditions applied.

Figure 6 shows the water outlet concentrations during the desorption steps D1
and D2. It can be seen that the desorption steps give substantially the same
results.

25 Figure 7 shows the temperature and loading profiles during cyclic operation.
The switch from adsorption to desorption cycle and vice versa is at the dashed
vertical lines. It can be seen that the adsorption and desorption profile of the
various cycles are quite similar. This means that the regeneration process is
effective, and that a stable process is obtained.

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This example shows the effect of the process according to the invention for
water removal from DCM. It will be appreciated by the skilled person from these

results that analogous results will be obtained for chlorine and MCM. For these compounds it is more difficult to carry out experiments in view of required high-pressure equipment and HSE regulations. DCM serves as a model compound for chlorine and MCM. Equivalent considerations apply to trichloromethane and

5 tetrachloromethane.

CLAIMS

1. Process for removing a small-molecule contaminant from a chlorine-compound stream, the process comprising
- 5 (i) an adsorption sequence comprising the steps of
- contacting a chlorine compound stream comprising a small-molecule contaminant with an adsorbent for the small-molecule contaminant, the chlorine compound being chlorine or chloromethane, said chlorine compound stream being in the
 - 10 liquid phase, and
 - withdrawing a purified chlorine compound stream from which small-molecule contaminant has been removed from the adsorbent,
- and
- 15 (ii) a desorption sequence comprising the steps of
- contacting the adsorbent containing small-molecule contaminant with a chlorine compound stream in the gaseous phase, and
 - withdrawing a chlorine compound stream comprising small molecule contaminant in the gaseous phase from the adsorbent,
 - 20 wherein the chlorine compound stream used in the desorption sequence is derived from the purified chlorine compound stream obtained in the adsorption section.
2. Process according to claim 1, wherein the chlorine compound stream is a
- 25 chlorine stream.
3. Process according to claim 1, wherein the chlorine compound stream is a chloromethane stream, in particular a monochloromethane stream.
- 30 4. Process according to any one of the preceding claims, wherein the small-molecule contaminant is selected from the group of one or more of water, O₂, H₂, N₂, CO₂, and CO, in particular water.

5. Process according to any one of the preceding claims wherein the step of contacting a chlorine compound stream comprising a small-molecule contaminant in the liquid phase with an adsorbent for the small-molecule contaminant takes place at a temperature which is above the hydrate formation temperature and below the condensation temperature of the chlorine compound stream.
6. Process according to any one of the preceding claims, wherein the adsorbent is a porous material, in particular a porous inorganic material, e.g., a molecular sieve, such as a zeolite.
7. Process according to any one of the preceding claims, wherein the adsorbent comprises a molecular sieve 3Å, 4Å, and/or 5Å.
8. Process according to any one of the preceding claims, wherein all process steps are carried out at substantially the same pressure.
9. Process according to any one of the preceding claims, additionally comprising the steps of
- subjecting a gaseous chlorine compound stream comprising small-molecule contaminants to a condensation step to form a liquid chlorine compound stream comprising small-molecule contaminants and one or more of a liquid water fraction and a gaseous fraction comprising small contaminants,
 - separating the liquid chlorine compound stream from the one or more of the liquid water fraction and a gaseous fraction comprising small contaminants,
- and
- providing the chlorine compound stream comprising small-molecule contaminant to a process for removing a small-molecule

- contaminant from a chlorine-compound stream, the process comprising
- an adsorption sequence comprising the steps of
- contacting a chlorine compound stream comprising a small-molecule contaminant in the liquid phase with an adsorbent for the small-molecule contaminant, the chlorine compound being chlorine or chloromethane, and
 - withdrawing a purified chlorine compound stream from which small-molecule contaminant has been removed from the adsorbent, and a desorption sequence comprising the steps of
 - contacting the adsorbent containing small-molecule contaminant with a chlorine compound stream in the gaseous phase, and
 - withdrawing a chlorine compound stream comprising small molecule contaminant in the gaseous phase from the adsorbent,
- wherein the chlorine compound stream used in the desorption sequence is derived from the purified chlorine compound stream obtained in the adsorption section.
10. Process according to claim 9, wherein at least part of the chlorine compound stream comprising small-molecule contaminant that is withdrawn in the gaseous phase from the adsorbent in the desorption step is provided to the condensation step.
11. Process according to any one of the preceding claims, wherein the process is carried out using at least two reactors, at least one of which is operated in adsorption mode while at least a further reactor is operated in desorption mode.

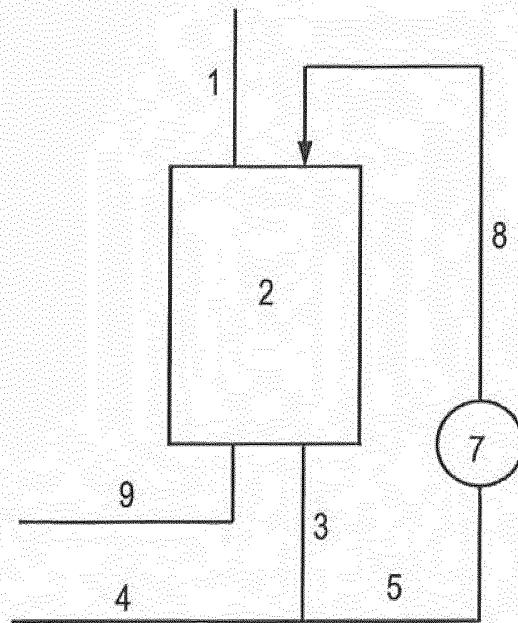


Fig.1

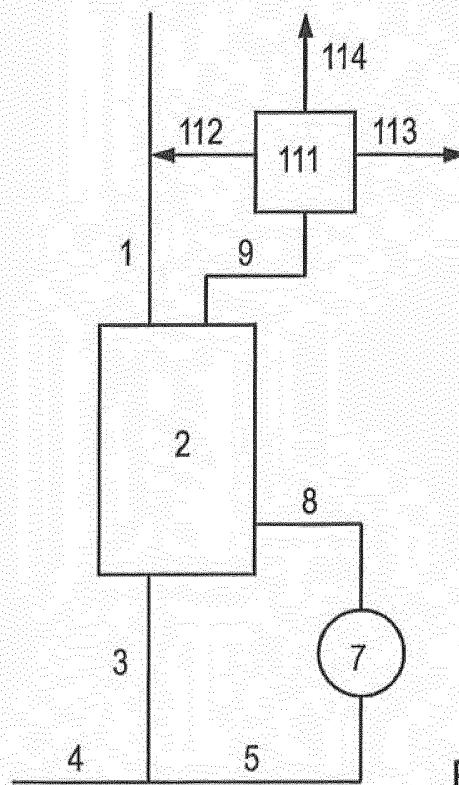


Fig.2

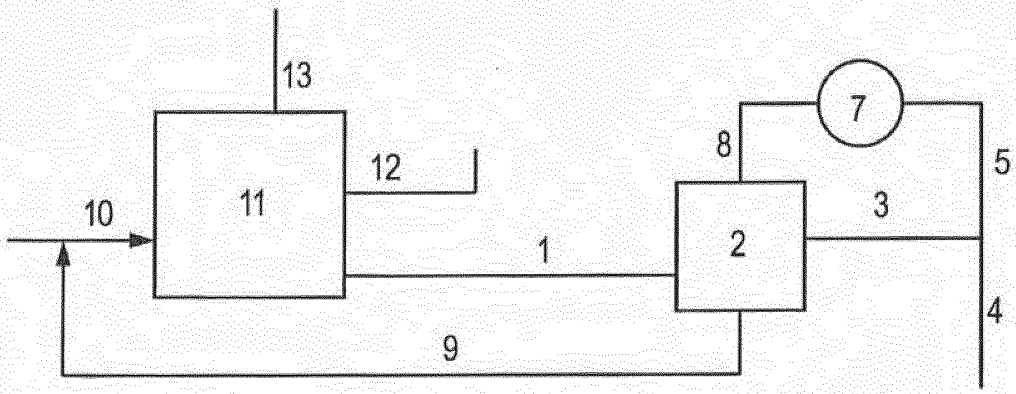


Fig.3

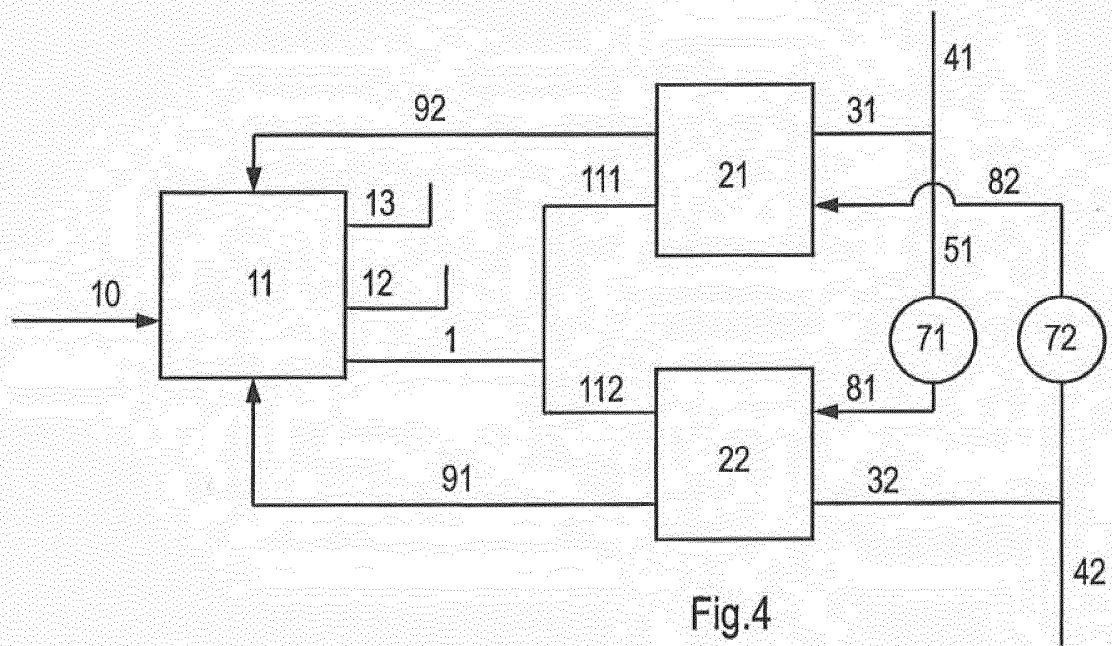


Fig.4

Figure 5 - Adsorption breakthrough curves for three adsorption cycles

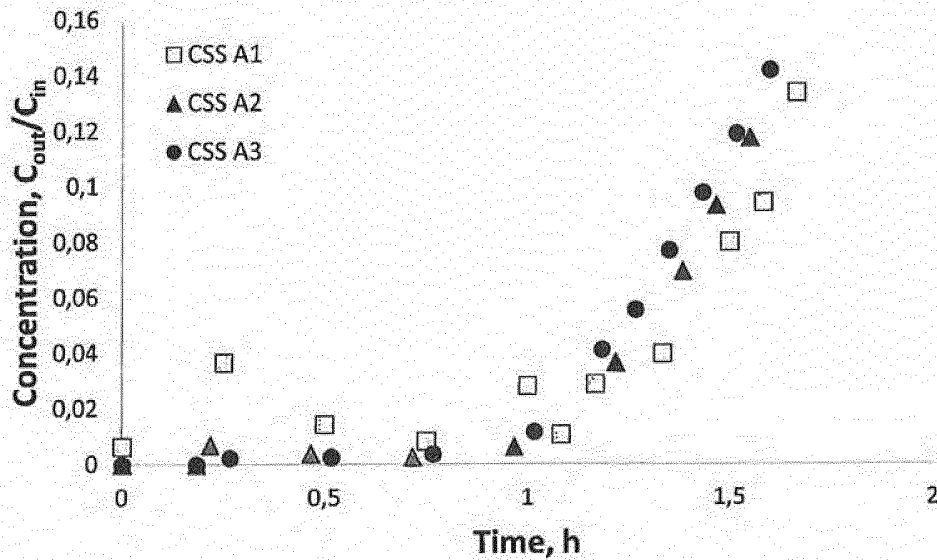


Figure 6 – Water desorption curves for two desorption cycles

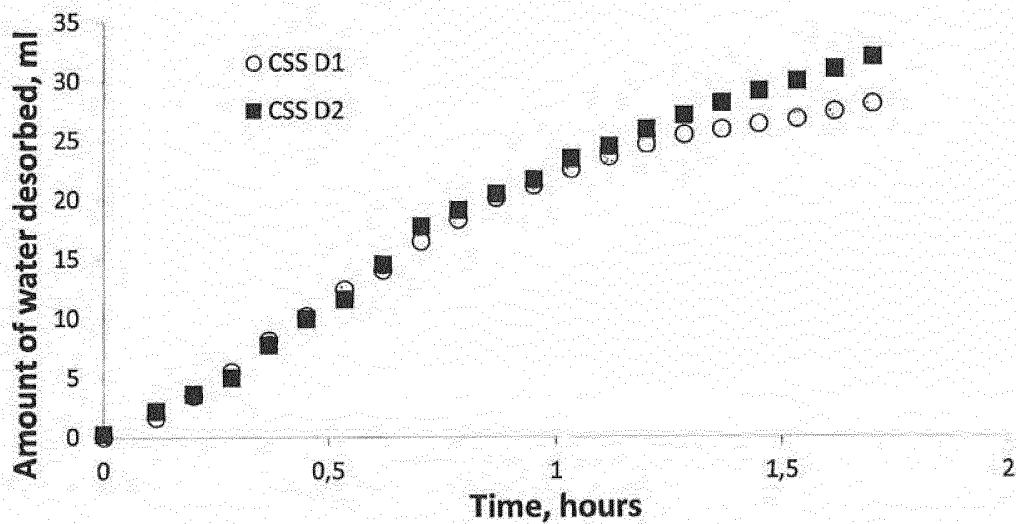
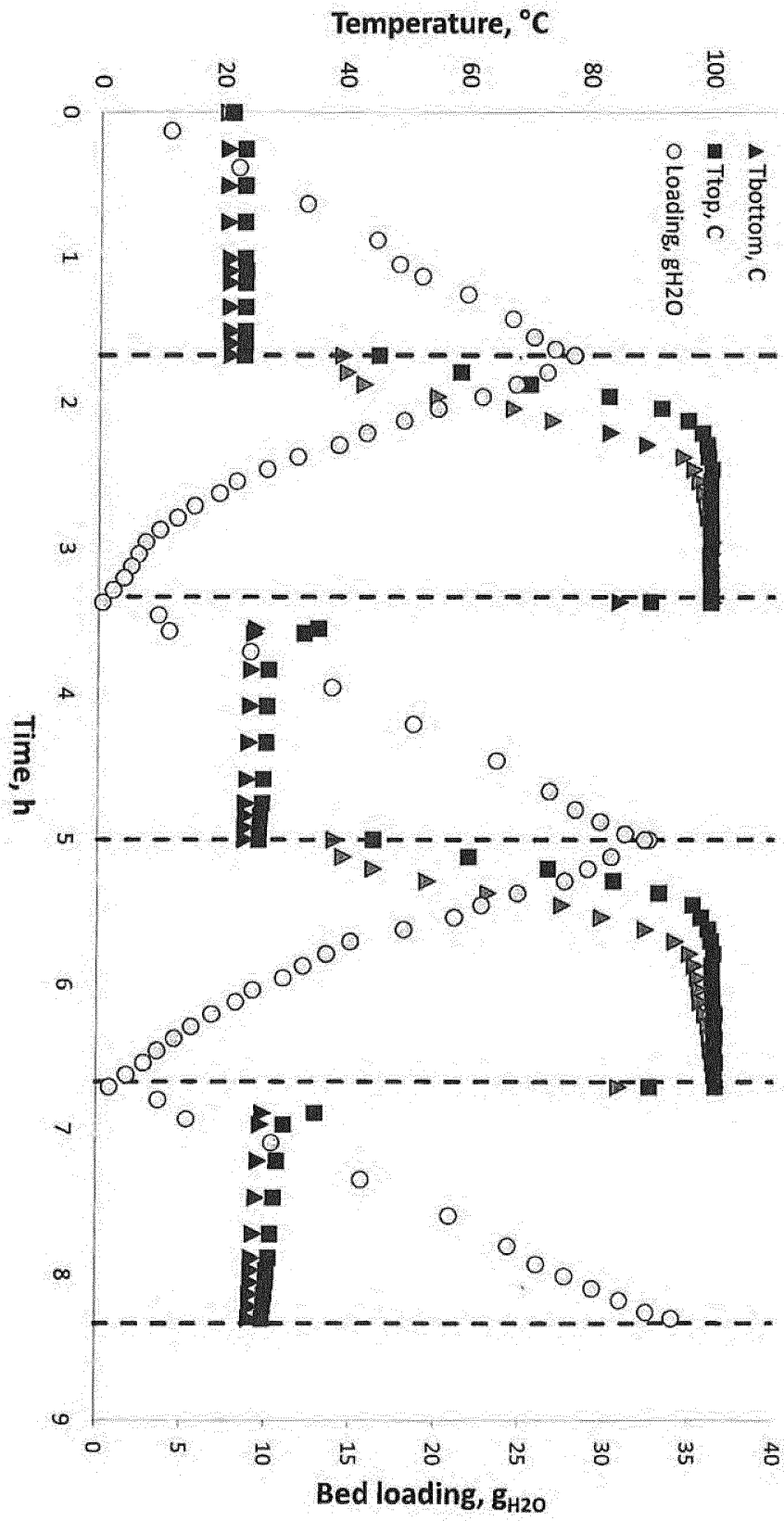


Figure 7 – Temperature and loading profiles during cyclic operation



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/075871

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D53/04 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 269 834 A (DOTSON RONALD L [US] ET AL) 14 December 1993 (1993-12-14) cited in the application column 4, line 59 - column 5, line 25 column 5, line 60 - column 6, line 26 figure 1	1-11
Y	DE 199 55 142 A1 (KRUPP UHDE GMBH [DE]) 31 May 2001 (2001-05-31) cited in the application column 1, line 42 - column 2, line 32; figure	1-11
Y	EP 0 262 849 A2 (ICI PLC [GB]) 6 April 1988 (1988-04-06) column 6, line 30 - line 51; figure 2	1-11
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
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Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">21 January 2016</div>	Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">04/02/2016</div>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <div style="text-align: center; font-size: 1.2em;">Fourgeaud, Damien</div>	

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International application No
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