Title: A PROCESS FOR REGENERATION OF ADSORBENT BEDS

Abstract: The invention provides a process for the regeneration of at least one adsorbent bed, comprising at least the steps of: (a) contacting a first adsorbent bed (B1) with a gaseous stream (10) such that at least a portion of adsorbed species in said first adsorbent bed (B1) are released; (b) cooling a second adsorbent bed (B2); wherein a bypass (20) is provided around the second adsorbent bed (B2) and the gaseous stream (10), before contact with the first adsorbent bed (B1), is directed to at least one of (i) the second adsorbent bed (B2), and (ii) the bypass (20) around the second adsorbent bed (B2), wherein the proportion of gaseous stream (10) flowing through the bypass (20) is controlled.

Fig. 1
A PROCESS FOR REGENERATION OF ADSORBENT BEDS

The present invention relates to a process for the regeneration of adsorbent beds, especially a continuous process comprising removal of a particular species from a gaseous stream and subsequent regeneration of the adsorbent beds, particularly by temperature swing adsorption.

Adsorbent beds may be used for a variety of separation processes, for example, to dry a gaseous stream, to remove mercury from a produced gas stream or to remove sulphur compounds from a hydrocarbonaceous stream comprising said sulphur compounds.

The removal of sulphur-containing compounds from hydrocarbonaceous streams comprising such compounds has always been of considerable importance in the past and is even more so today in view of continuously tightening process requirements and environmental regulations. This holds not only for natural gas streams to be used for e.g. the preparation of synthesis gas or for residential use or to be transported as liquefied natural gas, but also for natural gas liquid streams, natural gas condensate streams as well as for crude oil derived refinery streams containing sulphur compounds.

Sulphur contaminants in hydrocarbon streams include hydrogen sulphide, carbonyl sulphide, mercaptans, sulphides, disulphides, thiophenes and aromatic mercaptans, which due to their odorous nature can be detected at parts per million concentration levels. Thus, it is desirable for users of such natural gas and refinery streams to have concentrations of total sulphur compounds lowered to e.g. less than 20 or 30 ppmv or
less than 50-75 mgS/Nm\(^3\), the amount of non-hydrogen sulphide compounds lowered to e.g. less than 5, or even less than 2 ppmv or less than 12 mgS/Nm\(^3\) or even less than 5 mgS/Nm\(^3\).

Numerous natural gas wells produce what is called "sour gas", i.e. natural gas containing hydrogen sulphide, mercaptans, sulphides and disulphides in concentrations that makes the natural gas unsuitable for direct use. Considerable effort has been spent to find effective and cost-efficient means to remove these undesired compounds. In addition, the natural gas may also contain varying amounts of carbon dioxide, which depending on the use of the natural gas often has to be removed at least partly.

Regenerable solid bed adsorption processes are very suitable for the removal of sulphur compounds such as methyl mercaptan, ethyl mercaptan, normal and isopropyl mercaptan and butyl mercaptan. However, the regeneration of the adsorption beds is often a considerable problem. Ageing of the adsorbents causes a gradual decrease in adsorption capacity. Several types of ageing exist: thermal cycling, hydrothermal ageing, and contamination, often caused by co-adsorption of species and coke formation on the surface of the adsorbent.

Adsorbent beds may also be used for removing water from a gaseous stream, such as a hydrocarbonaceous stream, prior to its further treatment, such as cooling and/or liquefying. Water may be present in a gaseous stream as a constituent from its source, or may become part of the gaseous stream due to one or more other treatments such as removal of one or more other constituents in the gaseous stream as mentioned hereinbefore. Natural gas may contain one or more
sulphur compounds, as well as varying amounts of carbon
dioxide, and such compounds, which together can form
'acid gas', can be removed from a gaseous stream by the
use of one or more amines, commonly in an 'acid gas
recovery unit' (AGRU). However, as a result, the treated
gaseous stream now has a relatively higher water
content, which must be reduced and/or removed before
cooling and/or liquefying the gaseous stream.
Regenerable adsorbent beds are suitable for the removal
of water from a gaseous stream.

However, the regeneration of an adsorbent bed by the
passage of a hot and dry regeneration gas at an
initially high temperature therethrough leads to cake-
formation of the adsorbent bed material, because the
first part of the adsorbent bed is heated too fast
compared to the later or furthest part of the adsorbent
bed, which is still relatively cool. This can condense
out the compound or compounds being desorbed, forming
undesired condensation and liquid in the adsorbent bed,
leading to deactivation of the adsorbent. Avoiding
caking requires a carefully controlled temperature
profile over time during regeneration.

Furthermore, regeneration at initially high
temperatures of an adsorbent bed previously loaded with
sulphur-compounds leads to coke-formation on the
adsorbent material. Coke formation occurs because the
sulphur-compounds have insufficient time to diffuse out
of the pores of the adsorbent before a temperature is
reached where they decompose and cause deactivation of
the adsorbent. Avoiding coking requires a carefully
controlled temperature profile over time during
regeneration.
The present invention provides a process for the regeneration of at least one adsorbent bed, comprising at least the steps of:

(a) contacting a first adsorbent bed (Bl) with a gaseous stream (10) such that at least a portion of adsorbed species in said first adsorbent bed (Bl) are released;
(b) cooling a second adsorbent bed (B2);
wherein a bypass (20) is provided around the second adsorbent bed (B2) and the gaseous stream (10), before contact with the first adsorbent bed (Bl), is directed to at least one of (i) the second adsorbent bed (B2), and (ii) the bypass (20) around the second adsorbent bed (B2), wherein the proportion of gaseous stream (10) flowing though the bypass (20) is controlled.

Embodiments and examples of the present invention will now be described by way of example only with reference to the accompanying non-limited drawing in which:

Figure 1 is a diagrammatic scheme for a process for the regeneration of at least one adsorbent bed according to one embodiment of the present invention.

For the purpose of this description, a single reference number be assigned to a line, as well as a stream carried in that line.

The present invention provides a process for the regeneration of at least one adsorbent bed by a gaseous stream, which is directed to at least another adsorbent bed and a by-pass, so that there is better control of the temperature of the gaseous stream prior to it contacting the adsorbent bed.

Figure 1 shows a process for the regeneration of a first adsorbent bed Bl with a gaseous stream 10 according to one embodiment of the present invention.
The gaseous stream 10 may be any suitable hydrocarbon stream, non-hydrocarbon stream, or mixture thereof able to assist with the desorption of the adsorbed species in the first adsorbent bed B1 as part of the regeneration. Suitable gaseous streams include natural gas, optionally treated.

The first adsorbent bed B1 may comprise one or more adsorbent beds, parts, areas, units, portions or stages, being in series, parallel or both. The present invention is not limited by the type or arrangement of the first adsorbent bed, or by the nature of the species, such as water or sulphur compounds, that can be adsorbed by the first adsorption bed.

The first adsorption bed B1 may comprise one or more adsorbents. One example comprises a zeolite dispersed in a binder, preferably a molecular sieve known in the art.

The adsorption of a species such as sulphur compounds or water by an adsorbent bed is known in the art. Such species can be constituents of a contaminated gaseous stream 30, which passes through an 'active' mode adsorbent bed such as the third adsorbent bed B3 shown in Figure 1. Such adsorption leads to a reduced-contaminant gaseous stream 40 which can then be passed for further treatment, including cooling and/or liquefaction such as to provide liquefied natural gas (LNG). Further discussion of suitable removal of sulphur compounds from hydrocarbons streams using absorbents is mentioned in our WO 2004/039926 Al.

Over time, the adsorbent in the third adsorbent bed B3 will become loaded or saturated, such that the third adsorbent bed B3 will need regeneration.

Regeneration of an adsorbent bed is a process known in the art. Further discussion of the regeneration of
loaded absorbents, including suitable operating parameters, is also mentioned in our WO 2004/039926 Al.

One regeneration process involves temperature-swing adsorption (TSA), in which a high-temperature gaseous stream is passed through the adsorbent bed once it is taken off-line from an active or adsorbent mode receiving a contaminated gaseous stream 30. The higher temperature during regeneration causes adsorbed species such as water to desorb from the adsorbent, and be carried with the gaseous stream out of the adsorbent bed as a post-desorption gaseous stream 10a. Treatment of a post-desorption gaseous stream 10a is known in the art and not further discussed herein.

Figure 1 shows a first adsorbent bed B1 intended to be regenerated according to an embodiment of the present invention. Hence, the first adsorbent bed B1 is shown in a "heating" mode. It is being heated as the higher temperature gaseous stream 10 passes therethrough in order to release at least a portion of adsorbed species in the first adsorbent bed B1.

The general operating parameters, such as pressure, flow rate, etc, for regenerating an absorbent bed are known in the art. The present invention may also comprise changing the pressure of one or more of the streams described herein to assist one or more of the processes described herein. The present invention may also involve one or more additional coolers, such as water and/or air coolers, to alter the temperature of a stream. The location and/or use of one or more additional coolers is known to the skilled person, and is not further described herein.

After an adsorbent bed has been regenerated, it has a high temperature (due to the passage of the higher
temperature gaseous stream 10 therethrough), such that following regeneration, the adsorbent bed requires a 'cooling' mode or period prior to reverting to the active or adsorption mode. Figure 1 shows a second adsorbent bed B2 in a cooling mode prior to reintroduction of a contaminated gaseous stream 30.

Typically, two or more adsorbent beds are aligned in a unit or apparatus to treat a contaminated gaseous stream 30. Figure 1 shows first, second and third adsorbent beds B1, B2 and B3 which may be in one or more discrete locations, or preferably aligned within a single adsorption unit 42. The adsorption unit 42 may be a 'dehydration unit' where the adsorbed species is water. The adsorption unit 42 may be a 'desulphurisation unit' where the adsorbed species is one or more sulphur compounds. The adsorption unit 42 may be a combination unit able to adsorb more than one species, such as water and sulphur compounds.

Where a single unit comprises at least two, preferably at least three adsorbent beds, a 'continuous' process for the treatment of a contaminated gaseous stream 30 can be carried out, based on simultaneously, at least one adsorbent bed being 'active' to treat the contaminated gaseous stream 30, at least one adsorbent bed being in a heating mode, and at least one adsorbent bed being a cooling mode.

In practice, single adsorption units comprise a plurality of adsorbent beds to allow for the continuous treatment of a contaminated gaseous stream 30 which can involve a number of adsorbent beds being off-line for heating and/or cooling. Multiple beds can be rotated in and out of the various modes of adsorption, heating and cooling.
Figure 1 shows a continuous process such that the first adsorbent bed B1, following step (a) contact with the gaseous stream 10 to desorb at least a portion of said species, is then step (b) cooled, and then step (c) operated to adsorb at least a portion of a contaminated gaseous stream 30 before returning again to step (a) contact with the gaseous stream 10 to desorb at least a portion of said species. Meanwhile, the second adsorbent bed B2, after step (b) cooling, is operated to undergo said step (c) and then step (a) and then step (b) .

Further meanwhile, the third adsorbent bed B3, after step (c), is operated to undergo said step (a) then step (b) then step (c) .

In this way, one of each said adsorbent bed B1, B2, B3 is continually at each of said three steps (a), (b) and (c) .

In the arrangement shown in Figure 1, the contaminated gas stream 30 is shown in bold line passing into the third adsorbent bed B3 in active mode .

Switching the passage of the contaminated gaseous stream 30 into either of the first adsorbent bed B1 (after its regeneration and cooling), and/or through the second adsorbent bed B2 (after completion of its cooling) can be carried out by using the feed lines 30a in a manner known in the art.

From the third adsorbent bed B3 is provided a reduced-contaminant gaseous stream 40, shown in Figure 1 in bold line. Similarly, passage of a reduced-contaminant gaseous stream 40 from one or both of the first and second adsorbent beds B1 and B2 can be carried out via lines 40a when required.

Once an adsorbent bed is regenerated, it is changed to a cooling mode prior to adsorption as described
above. Typically, cooling is assisted by the passage of the gaseous stream 10 therethrough, in order to cool the adsorbent bed as well as heat the gaseous stream 10 and therefore reduce the additional heating of the gaseous stream 10 required for it to be hot enough for the subsequent regeneration process.

Figure 1 shows the gaseous stream 10 passing through the cooling second adsorbent bed B2 prior to passage through a heater 24 such as a boiler, and then contacting the first adsorbent bed B1 as described above.

It is desired to be able to finely control the temperature regime, including ramp rate and distribution, in all parts of an adsorbent bed undergoing regeneration in order correctly regenerate all of the absorbent bed and avoid the problems mentioned hereinbefore (caking or coking). However, the heat adsorbed by the gaseous stream 10 by passage through the second adsorbent bed B2 cannot be controlled, as the heat adsorption is a simple heat exchange between the second adsorbent bed B2 and the regular flow of the gaseous stream 10 as required by the first adsorbent bed B1. The cooling second adsorbent bed B2 is not a controllable heat exchanger.

Similarly, subtle heating variation by known heaters 24 such as boilers, is also not possible at the required temperatures and flow rates of a gaseous stream. Thus, fine control of the temperature of the gaseous stream 10 prior to its passage into the first adsorbent bed B1 has hitherto not been possible. As a consequence, the first part of the first adsorbent bed B1 in contact with the gaseous stream 10 is usually heated more quickly than the further or later parts of the first adsorbent bed
This leads to a temperature differential across the first adsorbent bed Bl, which can cause uneven desorption and/or uneven carriage of the species desired to be carried out of the first adsorbent bed Bl as part of the regeneration process.

Uneven desorption and/or carriage can then lead to uneven heating and/or condensation and/or coking of a species in the first adsorbent bed Bl. For example, where the species is water, the condensation of liquid water can cause clay binder in a molecular sieve to dissolve, subsequently forming a solid cake during regeneration. Solid cake cannot subsequently then adsorb species during a subsequent active mode, and/or can lead to the formation of larger solid cakes causing flow disruption and/or unevenness of a contaminated gaseous stream therethrough. Furthermore, where the species is a sulphur compound such as methyl mercaptan, ethyl mercaptan, or propyl mercaptan, a fast heating rate can cause decomposition of the sulphur species on the adsorbent. Decomposition of sulphur species blocks pores in the adsorbent, impairing the ability of the adsorbent to remove species from the process stream during subsequent adsorption cycles. All of the above problems reduce the effectiveness of a regenerated adsorbent bed, especially on a large industrial scale. Continuing regeneration can lead to exasperating such problems.

The present invention provides a bypass 20 around the second adsorbent bed B2. Passage of the gaseous stream 10 or a fraction thereof through the bypass 20 can be controlled by a control system 22. The control system 22 may be located at any suitable location, at least a portion of which is associated with the bypass 20 as shown in Figure 1.
The proportion of the gaseous stream 10 directed to (i) the second adsorbent bed B2, and (ii) the bypass 20, is continuously variable, from the entire gaseous stream 10 flowing to (i) the second adsorbent bed B2, to, the entire gaseous stream 20 flowing to (ii) the bypass 20; and any proportion therebetween.

Preferably, the control system 22 can automatically vary the proportion of the gaseous stream flowing to at least one of (i) the second adsorbent bed B2 and (ii) the bypass 20, depending on, at least in part, the temperature detected in the first adsorbent bed B1 at one or more locations therein and/or at one or more inlets and outlets, compared to the temperature (s) sought in the first adsorbent bed B1 at the same locations.

By controlling the proportion of the gaseous stream 10 flowing through the bypass 20 and/or second adsorbent bed B2, the present invention is able to better control the temperature of the gaseous stream 10 downstream of the second adsorbent bed B2.

When it is the turn of the third adsorbent bed B3 to be regenerated, passage of the contaminated gaseous stream 30 can be switched via line 30a into the second adsorbent bed B2, and passage of the gaseous stream 10 can be switched to line 11 to pass through the first adsorbent bed B1 now in cooling mode. Figure 1 shows a bypass 11a around the first adsorbent bed B1 for the process of the present invention. The gaseous stream 10 can then contact the third adsorbent bed B3 though line 11b to provide a post-desorption gaseous stream 1c.

Similarly, when it is the turn of the second adsorbent bed B2 to be regenerated, passage of the contaminated gaseous stream 30 can be switched via line
30b into the first adsorbent bed B₁, and passage of the
gaseous stream 10 can be switched to line 12 to pass
through the third adsorbent bed B₃ now in cooling mode.
Figure 1 shows a bypass 12a around the third adsorbent
bed B₃ for the process of the present invention. The
gaseous stream 10 can then contact the second adsorbent
bed B₂ though line 12b to provide a post-desorption
gaseous stream 12c.

Preferably, the process of the present invention
comprises a heater 2₄ operable to further heat the
gaseous stream 10 downstream of the cooling adsorbent
bed and its bypass. Figure 1 shows a heater 2₄
downstream of the second adsorbent bed B₂ and its bypass 2₀.

Optionally, the present invention further includes a
bypass 3₂ around the heater 2₄. In this way, the gaseous
stream 10 can be directed to at least one of (i) the
heater 2₄, and (ii) the bypass 3₂ around the heater 2₄.
Preferably, the proportion of the gaseous stream 10
directed to (i) the heater 2₄, and (ii) the bypass 3₂
around the heater 2₄, is continuously variable, from the
entire gaseous stream 10 flowing to (i) the heater 2₄,
to, the entire gaseous stream flowing to (ii) the bypass
3₂ around the heater 2₄; and any proportion
therebetween.

More preferably, a control system 3₄ is provided to
automatically vary the proportion of gaseous stream 10
flowing to (i) the heater 2₄ and (ii) the bypass 3₂
around the heater 2₄, depending on, at least in part,
the temperature (s) detected in the first adsorbent bed
B₁ compared to the temperature (s) sought therein.

In this way, the temperature of the gaseous stream
10 contacting the first adsorbent bed B₁ can be
controlled, at least in part, by the relative proportion of the gaseous stream 10 directed to (i) the heater 24, and (ii) the bypass 32 around the heater 24.

The present invention provides a process wherein the temperature of a gaseous stream contacting an adsorbent bed, such the first adsorbent bed B1 undergoing regeneration, can be better controlled by the use of the passage of at least a portion, part or fraction of the gaseous stream through a bypass around an adsorbent bed undergoing cooling, such as the second adsorbent bed B2 shown in Figure 1.

The passage of the gaseous stream 10 in Figure 1 is shown in bold. By varying the proportion of the gaseous stream 10 passing through the bypass 20 in Figure 1, it is possible to better control the temperature of the gaseous stream 10 contacting the first adsorbent bed B1.

In one example, it may be desired to gradually increase the temperature of the gaseous stream 10 contacting the first adsorbent bed B1, and this may be achieved by relating a gradual increase in the proportion of the gaseous stream 10 directed through the second adsorbent bed B2, and corresponding decrease through the bypass 20 around the second adsorbent bed B2.

The present invention provides the ability to change the temperature in an adsorbent bed undergoing regeneration with a constant or regular or even rate of change, to avoid in particular any period and/or location during the heating of the adsorbent bed where the temperature increase is static or otherwise not increasing, and in particular where the dewpoint of the species being dissolved is greater than the temperature
of the gaseous stream at one or more locations in the adsorbent bed.

The person skilled in the art will understand that the present invention can be carried out in many various ways without departing from the scope of the appended claims.
CLAIMS

1. A process for the regeneration of at least one adsorbent bed, comprising at least the steps of:
   (a) contacting a first adsorbent bed (Bl) with a gaseous stream (10) such that at least a portion of adsorbed
   species in said first adsorbent bed (Bl) are released;
   (b) cooling a second adsorbent bed (B2);
   wherein a bypass (20) is provided around the second adsorbent bed (B2) and the gaseous stream (10), before
   contact with the first adsorbent bed (Bl), is directed
to at least one of (i) the second adsorbent bed (B2),
and (ii) the bypass (20) around the second adsorbent bed
(B2), wherein the proportion of gaseous stream (10)
flowing though the bypass (20) is controlled.

2. A process as claimed in claim 1, wherein the
   proportion of the gaseous stream (10) directed to (i)
   the second adsorbent bed (B2), and (ii) the bypass (20),
is continuously variable, from the entire gaseous stream
(10) flowing to (i) the second adsorbent bed (B2), to,
the entire gaseous stream (10) flowing to (ii) the
bypass (20); and any proportion therebetween.

3. A process as claimed in claim 1 or claim 2, wherein
   a control system (22) is provided to automatically vary
   the proportion of the gaseous stream flowing to at least
   one of (i) the second adsorbent bed and (ii) the bypass,
   depending on, at least in part, the temperature detected
   in the first adsorbent bed compared to the temperature
   sought.

4. A process as claimed in any preceding claim, wherein
   the temperature in the first adsorbent bed (Bl) during
   step (a) is controlled, at least in part, by the
relative proportion of gas directed to (i) the second adsorbent bed (B2), and (ii) the bypass (20).

5. A process as claimed in any preceding claim, wherein the temperature of the first adsorbent bed (B1) is gradually increased.

6. A process as claimed in any preceding claim, wherein the proportion of the gaseous stream (10) directed through (i) the second adsorbent bed (B2) is gradually increased.

7. A process as claimed in any preceding claim, wherein a third adsorbent bed (B3) is used, the process further comprising the step of (c) operating the third adsorbent bed (B3) to adsorb at least a portion of a contaminated gaseous stream (30).

8. A process step as claimed in claim 7, wherein step (c) comprises adsorbing sulphur containing compounds from a hydrocarbonaceous stream, especially a gaseous hydrocarbonaceous contaminated gas stream, comprising said sulphur compounds or wherein step (c) comprises adsorbing water from a hydrocarbonaceous stream, especially a gaseous hydrocarbonaceous contaminated gas stream, comprising water.

9. A process as claimed in claim 7 or 8, wherein the process is a continuous process such that the first adsorbent bed (B1) following step (a) contact with a gaseous stream (10) to desorb at least a portion of said species, is then step (b) cooled, and then step (c) operated to adsorb at least a portion of a contaminated gaseous stream (30) before step (a) contact with the gaseous stream (10) to desorb at least a portion of said species;
the second adsorbent bed (B2), after step (b) cooling, is operated to undergo said step (c) then step (a) and then step (b); the third adsorbent bed (B3), after step (c), is operated to undergo said step (a) then step (b) then step (C);
such that one of each said adsorbent bed (B1, B2, B3) is continually at each of said three steps (a), (b) and (C).

10. A process as claimed in any preceding claim, wherein upstream of the first adsorbent bed (B1), preferably downstream of the second adsorbent bed (B2), a heater (24) is provided operable to heat the gaseous stream (10).

11. A process as claimed in claim 10, wherein a bypass (32) is provided around said heater (24) and thus the gaseous stream (10), before contact with the first absorbent bed (B1), preferably after contact with one of (i) the second adsorbent bed (B2) and (ii) the bypass (20) around the second absorbent bed (B2), is directed to at least one of (i) the heater (24), and (ii) the bypass (32) around the heater (24), wherein a control system (34) is provided to automatically vary the proportion of gaseous stream (10) flowing to (i) the heater (24) and (ii) the bypass (32) around the heater (24), depending on, at least in part, the temperature detected in the first adsorbent bed (B1) compared to the temperature sought.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**
INV.  B01D53/04 B01J20/34

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)

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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 practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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**D** Further documents are listed in the continuation of Box C

X See patent family annex

* Special categories of cited documents

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"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search: 24 April 2009

Date of mailing of the international search report: 07/05/2009

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European Patent Office, P B 5818 Patentlaan 2
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