

Method for the separation of sour gas

The invention pertains to a method for the separation of sour gas. The invention further pertains to an apparatus and
5 the solvent that are used in the method.

Sour gas, a gaseous mixture of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) is seen in the process industry and in particular in the petrochemical industry and in natural gas
10 exploration, as an unwanted component in the method of processing, because sour gas, and in particular hydrogen sulfide, compromise said processes or lead towards environmentally unfriendly exhaust fumes when said gas is
burned. In said burning process sulfur oxides and sulfuric
15 acid are produced out of hydrogen sulfide, which compounds can result in extensive corrosion problems when the conditions are below the acid dew point. Furthermore, the exhaust of gaseous sulphur compounds in any chemical form is a considerable burden for the environment.

20 For the above reasons sour gas is usually separated from a main stream, for instance from a natural gas stream, after which separation the main stream may further be processed. A known method for separating the sour gas from a main stream
25 uses a chemical absorption medium, or in other words, a solvent, in particular a solvent containing amine compounds is used.

A known method for processing sour gas into a sulfur end-
30 product is the Claus-process. This process is based on partial oxidation of hydrogen sulfide by oxygen and/or air in combination with consecutive catalyzed equilibrium reactions, leading to the end-products sulfur and water.

During these reactions a large amount of heat is released which heat is also necessary for a satisfyingly high reaction velocity. A prominent disadvantage of this process for sour gas treatment is that the efficiency of the process
5 is to a large extent dependent of the ratios $\text{H}_2\text{S}/\text{CO}_2$ of the gaseous mixture. At low ratios $\text{H}_2\text{S}/\text{CO}_2$, i.e. a large amount of CO_2 compared to H_2S , the relatively large inert mass of carbon dioxide is compromising the goal of a high temperature during the reactions. Furthermore the formation
10 of sulfur in said equilibrium reactions is compromised by having a small amount of H_2S , resulting in a further lowering of the efficiency of the process.

There are enrichment processes from the prior art to raise
15 the ratio $\text{H}_2\text{S}/\text{CO}_2$ in order to reduce the above mentioned disadvantages. These enrichment processes are usually performed in a sub-unit of the installation in which the sour gas is produced, and they entail a considerable burden, in the sense that the installation as a whole is made more
20 complex. Furthermore, these enrichment processes are not able to achieve a complete separation between carbon dioxide and hydrogen sulfide. Such a complete separation is however necessary to produce hydrogen sulfide and/or carbon dioxide in a suitable form for use as an industrial precursor.

25 It is an object of the invention to provide an efficient, simple and inexpensive method for the separation of sour gas, in which above-mentioned problems are solved partially, or completely.

30 To achieve said goal, a method is provided for the separation of a gaseous mixture that comprises as main ingredients H_2S and CO_2 , wherein the gaseous mixture is

contacted in a first device with a solvent comprising a weak Lewis-acid, wherein H_2S is absorbed in the solvent and the remaining CO_2 is abducted, and wherein the at least partially saturated solvent is regenerated subsequently, in at least
5 one second device wherein the released H_2S is abducted.

In this way, an efficient method is provided for the separation of sour gas, without the need of using Claus-units. In this process it is advantageous that the ratio
10 H_2S/CO_2 in the gaseous mixture does not, or only to a small extent, affect the efficiency of the process, because after absorption of H_2S in the solvent a pure CO_2 -gas stream is obtained and this gas stream does not have to be processed further.

15 Preferably the strength of the weak Lewis-acid is such that no Friedel-Craft reactions do occur with regard to the solvent. It is advantageous when the Lewis-acid has a strong affinity with H_2S and no or little affinity with CO_2 .

20 In a preferred embodiment of the method according to the invention the weak Lewis-acid comprises copper aluminium chloride ($Cu[AlCl_4]$) and more preferred even comprises the solvent monochlorobiphenyl (MCB). Although a combination of
25 both compounds is known as such from the Dutch patent no. 1002560, in which the combination is used for the separation of gases in a feed stream, the present invention is based on the discovery that using a combination of above compounds is extraordinarily efficient in separating sour gas. It has
30 been found that the use of the solvent according to the invention, makes a purity of end-products possible to such an extent that they can be readily used as an industrial precursor.

Preferably the solvent is contacted with the sour gas in counter-current fashion, which has the effect of improving the absorption of H_2S by the solvent. In addition, it is advantageous to maintain a pressure between 6 and 10 bar in
5 the first device at a temperature of approximately 50-70 degrees Celsius. As a large amount of heat is released during the absorption process which has the effect of delaying the absorption process, it is furthermore advantageous to cool the first device. The use of a wetted
10 wall reactor as heat exchanger, wherein the surface for heat exchange concomitantly serves as a surface for mass transfer in the absorption process, is preferred.

Also the regeneration process of the solvent in the second
15 device is preferably performed in a wetted wall reactor, wherein the solvent is led over the wetted wall, during which H_2S is stripped and subsequently abducted from the device. The pressure in the second device does not need a drastic lowering of pressure, such as for instance described
20 in the Dutch patent 1002560.

The construction of a wetted wall reactor will be further elucidated in the examples and figures below. Basically, the reactor consists of an inner space for the absorption
25 process or regeneration process, which comprises tubular spaces, and an outer space that surrounds the tubular spaces and is of importance for the heat exchange.

As it is advantageous to maintain a temperature in the
30 second device preferably between 140 and 150 degrees Celsius, the heat that is released in the first device during the absorption process, is according to a further preferred embodiment of the method of the invention,

transferred by means of a medium to the second device. In contrast to the absorption in the first device, it is advantageous to apply a higher temperature during the regeneration process, as it improves the velocity of the
5 regeneration process.

Besides it is remarked that it is not obvious to transfer heat from the first to the second device because the temperature in the second device is higher than in the first
10 device, as a consequence of the two different processes that are performed in them. Such a heat transfer was not applied or suggested before in the prior art.

It was found to be particular advantageous to use a medium
15 that comprises a condensable organic vapour, for transferring heat from the first to the second device. The term condensable means that the medium, dependent of the circumstances applied, can be in gas or liquid form in the method according to the invention. In general, the medium
20 will emit its heat during condensation and absorb its heat during evaporation.

In a further preferred embodiment of the method according to the invention, the medium is compressed before it is
25 transferred to the second device. For this goal a compressor is for example situated in the heat trajectory from the first to the second device. The compressor will densify the medium and concomitantly raise the temperature of it. As a consequence, the amount of heat absorbed in the first
30 device, is raised before it is used in the second device. Such a compression step improves the heat transfer from the first to the second device.

Preferably the medium is recycled from the second device back to the first device in order to cool the first device, wherein said medium is cooled during the recycle. In such manner, a closed cooling circuit is provided, in which the heat released during the absorption process is being used for the regeneration process of the solvent. The energy needed for compression of the medium in this circuit, is merely a fraction of the absorption heat or enthalpy, respectively the regeneration heat or enthalpy. As such, the method according to the invention is very advantageous with regard to energy consumption.

The use of the wetted wall reactor has an advantage during regeneration in that the solvent by virtue of dropping as a falling film within the tubular spaces, is able to desorb the H_2S -gas it contains, in a relatively easy way. In the tubular spaces, the gas ascends countercurrent to the solvent, and because of the spreading out of the solvent over the walls of the tubular spaces, the H_2S -gas can flow relatively freely in upwards direction in terms of rheology, before eventually exiting the tubular spaces.

In a further preferred embodiment of the method according to the invention, the regeneration process of the at least partially saturated solvent comprises further the stripping of the solvent by means of introducing at least a part of the abducted CO_2 from the first device. Preferably the introduction of CO_2 as a stripping gas occurs in a third device, more preferably a column. This process can be referred to as a post-regeneration. By leading a pure gas stream of CO_2 along the solvent which is coming from the second device, any traces of H_2S remaining in the solvent after regeneration in the second device, will be purged out

of the solvent, so that a regenerated solvent which is virtually H_2S -free, can be recycled to the first device. Such post-regeneration has the advantage that the first regeneration can be performed under atmospheric pressure and
5 that a usually applied, lowered pressure (known from the prior art) is not necessary.

In general, the use of CO_2 as stripping medium during regeneration is advantageous because no foreign stripping
10 gas such as nitrogen is necessary, which would have to be procured at financial expenses or had to be formed at the location using expensive apparatus and large amounts of energy.

15 The mixture of $\text{H}_2\text{S}/\text{CO}_2$ that originates from such a second regeneration step or post-regeneration, is subsequently recycled to the first device as well.

Preferably the abducted CO_2 from the first device is heated
20 before it is used for the regeneration process, and more preferably, the heating of the abducted CO_2 comprises heat exchange between regenerated solvent and the CO_2 to be used as stripping medium. The heat of the solvent coming from the second device, respectively the second regeneration step, is
25 hereby transferred to the CO_2 to be used as stripping medium.

In a further preferred embodiment of a method according to the invention, the at least partially saturated solvent is heated by the regenerated solvent before being regenerated
30 in the second device. As the absorption of H_2S preferably is performed at low temperature, the remaining heat of the regenerated solvent is advantageously transferred to the at least partially saturated solvent, so that the regeneration

process of the solvent profits from the heat transferred.
Preferably the exchange of heat between the regenerated
solvent on the one hand, and the at least partially
saturated solvent and the recycled CO₂ gas on the other hand,
5 is performed in the same heat exchanger.

The invention relates further to the use of the solvent
comprising copper aluminium chloride (Cu[AlCl₄]) and
monochlorobiphenyl (MCB) for the separation of a gaseous
10 mixture that comprises H₂S and CO₂ as main ingredients,
according to the method as described above. The invention
relates further to an apparatus for use in the method for
the separation of the gaseous mixture according to the
invention.

15

The invention will further be elucidated by appended figures
illustrating preferred embodiments of the invention,
wherein:

- 20 - Figure 1 shows a process scheme of a known method
 for separation of sour gas from a main stream
 using amine compounds;
- Figure 2 shows a process scheme of a method for
25 separation of sour gas according to the invention;
- Figure 3 shows schematically a wetted wall reactor
 which is used for absorbing H₂S-gas in the solvent
 according to the invention; and
- 30 - Figure 4 shows a detail of the wetted wall reactor
 of figure 3.

In figure 1 a process scheme 100 is shown of a known method for separating sour gas from a main stream 2. The main stream 2, which may be a natural gas stream, is led towards a sour gas absorption column 101, in which the main stream 2 is contacted with a solvent with amine compounds. The solvent is introduced at ambient temperature using a cooling device 105 at the top side of the column 101, and the solvent having absorbed sour gas, is abducted via conduit 4 from column 101. The purified main stream leaves via conduit 3 the system for further processing.

The conduit 4 is led through a heat exchanger 107 in which the heat of a conduit 6 is transferred to conduit 5. The stream in conduit 5 is a heated solvent which is enriched, i.e. at least partially saturated, and is introduced in a regenerator 102, in which the sour gas is stripped and abducted through conduit 8. Heat is conducted towards the regenerator 102 by a reboiler 103 so as to accelerate the regeneration process. The solvent is recycled through a conduit 6 via a pump 104, the heat exchanger 107 and cooler 105 eventually to the absorption column 101.

The separated sour gas is dried via conduit 8 in condensing device 106, and in column 9 the water is separated and recycled to the regenerator 102. On the top side of the column a pure sour gas stream is obtained in a conduit 1 subsequently.

The sour gas stream 1 is processed further in a known method by a sulphur processing unit 110, which consists of usually one or several Claus-units. By adding an oxidant 10 pure sulphur 12 is obtained with by-products comprising the condensate of the process 11 and the remaining gas 13. As

already indicated above, the ratio H_2S/CO_2 is of great importance for the functioning of the sulphur processing unit 110. Too large an amount of CO_2 can slow down the process or make it even completely impossible. In such cases
5 it may be possible to add an extra column in the system 100, in order to lower the CO_2 ratio in the sour gas stream 1. Such an additional step reduces the efficiency of the process and furthermore such a system may become highly expensive.

10 In figure 2 a process scheme 200 is shown for separating sour gas 1 according to the invention. Importantly, the depicted process is virtually insensitive to the ratio H_2S/CO_2 , so that an additional enrichment step which usually
15 is necessary in the known method may be left out.

The sour gas stream 1, i.e. a gaseous stream having main ingredients H_2S and CO_2 , is first led towards a compression and drying device 203 for the removal of all possibly
20 present water in said stream 1. The removal of said water can for instance be performed by cooling and by application of molecular sieves. It is of importance to remove water from stream 1, because water impedes the functioning of the solvent in the method. The stream 1 is preferably
25 pressurized to a pressure of about 6-10 bar. Water and other possible components different from hydrogen sulphide and carbon dioxide, are abducted via a conduit 30 from the gas stream 1.

30 The pure sour gas is led via a conduit 15 towards an absorption column 201, preferably a wetted wall reactor, in which solvent led through conduit 21 is contacted in counter current fashion with the stream 15. The solvent consists of

copper aluminium chloride ($\text{Cu [AlCl}_4\text{]})$ solved in monochlorobiphenyl (MCB). It was found that such a combination acts very well in the separation of sour gas because H_2S dissolves very well in the solvent and the solvent according to the invention does virtually absorb no CO_2 . The solvent absorbs the total amount of H_2S , so that a gas stream 22 that leaves the absorption column 201 at the top side consists of pure CO_2 .

The absorption process is preferably performed under a pressure between 6-10 bar and at a temperature of 50-70 degrees Celsius. As heat is released during the absorption process and too high a temperature slows down the absorption process - because of a lowered affinity of the solvent for H_2S at higher temperatures - , it is advantageous to cool the column 201. For this purpose a cooling conduit 32 is provided through which an organic vapour is led that absorbs the heat released during the absorption process, as well as leads the heat away so that the temperature in column 201 can be kept low. The complete cooling system will be discussed in more detail below.

At least partially saturated, or in other words, enriched solvent leaves the device 201 at the bottom side and the stream 16 is heated by a heat exchanger 204 from approximately 60°C to 120°C , after which the heated, rich stream 17 is brought in a flash tank 206 via a valve 205, in which any possible, small amount of dissolved CO_2 present in the solvent, is released and recycled via conduit 29 to the compression or drying device 203. The rich solvent is conducted from the flash tank 206 to a regenerator 202 via conduit 18.

In regenerator 202, the H₂S gas is subsequently stripped while supplying heat which originates from the absorption process of the gas in absorption column 201. The stripping is preferably performed at a temperature between 140-150°C under atmospheric pressure. For this goal, a heat exchange circuit is provided. In the heat exchange circuit the heat generated in absorption column 201 during the absorption process, is absorbed in a surrounding space (not shown) by means of an organic liquid that evaporates. The vapour formed is subsequently led through a conduit 31 and a compressor 214 (preferably a compressor of the displacement type) to a surrounding space (not shown) which heats the regenerator 202. In this surrounding space the medium condenses and emits at the same time its heat to the regenerator 202. In this way a very energy efficient process of absorption and regeneration is provided, in which the heat produced in one process is transferred to the other, while accelerating both processes. The pump or compressor 214 which is used in the process, requires an amount of energy which is relatively small when compared to the energy in terms of the heat of absorption and regeneration that is transferred.

The released H₂S gas is abducted via conduit 26 from regenerator 202 and cooled in cooling device 207. At this stage also small amounts of MCB will condense and this solvent is regained in an atmospheric column 208 and recycled via a conduit 27 to a second regenerator 209. The gas that is released at the top side of the atmospheric column 208 is pure H₂S-gas, which, because of its purity, is suitable as an industrial precursor, for instance in producing sulphur and numerous other products.

Also the solvent that is released at the bottom side of the regenerator 202 is led via a conduit 19 and a valve 210 towards a second regenerator 209, which operates also under atmospheric pressure. In this second regenerator 209 the last amount of remaining H₂S in the solvent is purged out of the solution by introducing a pure CO₂-stream 23 from the absorption column 201. The CO₂-stream 23 is first heated up to approximately 120°C, by a heat exchanger 204, and subsequently contacted with solvent exiting from conduits 19 and 27, in the regenerator 209. The contact with H₂S-free CO₂ releases the last remaining amounts of H₂S from the solvent, and the H₂S containing CO₂-gasstream 25 that is formed, is recycled to the compression and drying device 203. This secondary generation step secures that a virtually H₂S-free solvent is obtained. As the solvent still has a temperature of about 120°C, the solvent is led via conduit 20 and pump 212 through the heat exchanger 204, where the regenerated solvent 20 heats the rich solvent 16 and the CO₂-stream 23, before it is recycled back into the absorption column 201 via conduit 21.

The use of a second regeneration step in the second column 209 makes it possible to regenerate solvent under atmospheric pressure, as well as to a very high purity. The use of the already present, H₂S-free CO₂-gas, is very advantageous in this method. It will be clear that such a method of regenerating a solvent is very energy efficient when compared to, for instance, regeneration under vacuum circumstances. Also, the efficient exchange of heat between the several streams, for instance between the streams passing through the heat exchanger 204, contributes to the highly energy saving character of the described method.

In figure 3 a wetted wall reactor 300 is shown having at the bottom side an incoming current of sour gas 302, and at the top side an incoming current of solvent 304. Schematically shown is the middle part of the reactor 300 which is

5 provided with a multitude of tubular spaces 306, through which the solvent 304 drips down along the inner walls of the tubular spaces 306 while the sour gas 302 rises in upward direction and passes alongside the solvent 304, over a relatively large contact surface. In addition, the reactor
10 300 has a space outside the tubular spaces 306, a so-called surrounding mantle space 308, in which the medium for heat exchange flows. The medium enters as a condensed current of organic vapour 310, i.e. it is actually in its liquid phase. Examples of a suitable medium are hexane and toluene. The
15 condensed vapour 310 fills the mantle space 308 up to an indicated level 311, above which the compound makes a transition into a gas phase, and subsequently exits the mantle space 308 as organic vapour 312.

20 The heat that is formed during the absorption of H_2S from the sour gas 302 into the solvent 304, is transferred to the mantle space 308 and functions as a source of energy for the evaporation of the condensed vapour 310.

25 At the bottom side of the reactor, the so-called fat or enriched solvent 312 is collected in liquid form, and led via conduit 314 to a regeneration process, for instance in a second wetted wall reactor, which is not shown, but functions in a way analogous to what is explained above.

30 At the top side a gas stream 315 which is H_2S -free, leaves the reactor.

Tubular spaces are connected with each other and the outer wall 316 of the reactor, by connecting material 318 which allows for openings at the top and bottom side of the tubular spaces, while sealing the spaces between tubular spaces and as such delimiting the mantle space 308.

Finally in figure 4, a detail 400 is shown of the wetted wall reactor of figure 3. It concerns the left upper side of the reactor 300.

In figure 4, shown in more detail are the integrated outer wall 402 of the reactor, and the exit 404 for organic vapour 406 from the mantle space 408. Further are shown the tubular spaces 410, which are delimited by the inner walls 412, along which a film of solvent 414 flows downwards, while sour gas 416 ascends at the central inner side. The tubular spaces 410 are connected with each other and with the outer wall 402 by the connecting material 418, which material is positioned slightly below the endings at the upper side of the tubular spaces 410, so that the endings project slightly above the connecting material 418. As a consequence, a small reservoir 420 is formed during the introduction of solvent 414, before the solvent flows as a film along the inner walls 412 in downward direction. As such, an optimum surface of contact is achieved between the liquid phase of the solvent 414 on the one hand, and the gas phase of the sour gas 416 on the other hand.

Furthermore, the use of such a reactor for regeneration, in which saturated solvent flows along the inner walls in downward direction analogous to the description above, will achieve a satisfactory evaporation of the H_2S -gas from the solvent, because the current of H_2S -gas can flow away without

physical hindrance within the tubular spaces, while the solvent flows downward as a film.

The invention is not limited to the above described
5 embodiment, but includes other embodiments as well, which are covered by the wordings of the appended claims.

Claims

1. Method for separating a gaseous mixture that comprises
as main ingredients H_2S and CO_2 , wherein the gaseous
mixture is contacted in a first device with a solvent
comprising a weak Lewis-acid, wherein H_2S is absorbed in
the solvent and the remaining CO_2 is abducted, and
wherein the at least partially saturated solvent is
regenerated subsequently, in at least one second device
wherein the released H_2S is abducted.
2. Method according to claim 1, wherein the weak Lewis-
acid comprises copper aluminium chloride ($\text{Cu}[\text{AlCl}_4]$).
3. Method according to claim 1 or 2, wherein the solvent
comprises monochlorobiphenyl (MCB).
4. Method according to one of the claims 1, 2 or 3,
wherein the heat released in the first device during
the absorption process, is led towards the second
device by means of a medium.
5. Method according to claim 4, wherein the medium
comprises a condensable organic vapour.
6. Method according to claim 4 or 5, wherein said medium
is compressed before it is led towards the second
device.
7. Method according to claim 4, 5 or 6, wherein the medium
is recycled from the second device towards the first
device, for cooling of the first device, and wherein
the medium is cooled during the recycling.

8. Method according to one of the claims 1-7, wherein the process of regeneration of the at least partially saturated solvent further comprises the stripping of the solvent by means of introducing at least a part of the CO₂ abducted from the first device.
9. Method according to claim 8, wherein the CO₂ abducted from the first device, which is used for the stripping of solvent, is heated before it is introduced in the regeneration process.
10. Method according to claim 9, wherein the heating of the abducted CO₂ from the first device, comprises exchanging heat between regenerated solvent and said CO₂.
11. Method according to one of the claims 1-10, wherein the at least partially saturated solvent is heated by the regenerated solvent, before it is regenerated itself in the second device.
12. Apparatus for use in the method according to one of the preceding claims 1-11.
13. Use of the solvent comprising copper aluminium chloride (Cu[AlCl₄]) and monochlorobiphenyl (MCB) for separating a gaseous mixture that comprises as main ingredients H₂S and CO₂, according to a method of one of the preceding claims 1-11.