Title
Process for removing sulphur compounds including hydrogen sulphide and mercaptans from gas streams

International Patent Classification(s)
B01D 53/14 (2006.01) 53/04
B01D 53/04 (2006.01) A26060101AL12005100
C10L 3/10 (2006.01) \*9\*99999\*9\*999999
B01D 53/14 3/10
20060101AL12005100 20060101AL12005100

Application No: 2003298333
WIPO No: W004/847955

Priority Data
Number (31) 02258200.1
Date (32) 2002.11.28
Country (33) EP

Publication Date: 2004.06.10
Publication Journal Date: 2004.07.22

Applicant(s)
Shell Internationale Research Maatschappij B.V.

Inventor(s)
Van de Graaf, Jolinde Wachteld

Agent/Attorney
Spruson & Ferguson, Level 35 St Martins Tower 31 Market Street, Sydney, NSW, 2000

Related Art
US 3725531 A
GB 2275625 A
GB 2103645 A
Title: PROCESS FOR REMOVING SULPHUR COMPOUNDS INCLUDING HYDROGEN SULPHIDE AND MERCAPTONS FROM GAS STREAMS

Abstract: The invention concerns a process for the removal of hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide from a gas stream comprising hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide, by removing in a first step most of the hydrogen sulphide, part of the mercaptans and optionally part of the carbon dioxide and carbonyl sulphide by washing the gas stream with an aqueous washing solution comprising 10 to 40 wt% based on total solution of a physical solvent and 30 to 60 wt% based on total solution of an amine, which first removal step is followed by a second removal step in which mercaptans are removed by means of molecular sieve, in which process the amount of mercaptans which is removed by the aqueous washing stream is between 60 and 96 wt% (of total removed mercaptans in steps one and two) and the amount which is removed by the molecular sieve in step two is between 80 and 99 wt% (of total removed mercaptans in steps one and two).
PROCESS FOR REMOVING SULPHUR COMPOUNDS INCLUDING HYDROGEN SULPHIDE AND MERCAPTONS FROM GAS STREAMS

The present invention relates to a process for the removal of hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide from a gas stream containing these compounds.

The removal of sulphur-containing compounds from gas streams comprising such compounds has always been of considerable importance in the past and is even more so today in view of continuously tightening environmental regulations. This holds for combustion gases as obtained in the combustion of organic compounds as coal, as well as for natural gas streams to be used for e.g. the preparation of synthesis gas and for residential use or to be transported as liquid natural gas.

Sulphur contaminants in natural gas streams include hydrogen sulphide and mercaptans. Mercaptans, due to their odorous nature, can be detected at parts per million concentration levels. Thus, it is desirable for users of natural gas to have concentrations of mercaptans lowered to e.g. less than 5, or even less than 2 ppmv, and total concentration of sulphur compounds to e.g. less than 30 or, preferably, less than 20 ppmv, e.g. 15 or 10 ppmv. Sales gas specifications often mention total sulphur concentrations less than 4 ppmv.

Numerous natural gas wells produce what is called "sour gas", i.e. natural gas containing hydrogen sulphide, often in combination with mercaptans, the total amount of sulphur compounds being present 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 and carbonyl sulphide, which depending on the use of the natural gas often have to be removed at least partly.

A number of processes are known for the removal of sulphur compounds and optionally carbon dioxide and carbonyl sulphide from gas streams as natural gas. These processes are based on physical and/or chemical absorption, solid bed adsorption and/or chemical reaction. Physical and/or chemical absorption processes suffer from the fact that they frequently encounter difficulties in reaching the low concentration of the undesired sulphur compounds, unless (extremely) large reactors are used. Solid bed adsorption processes suffer from the fact that they are only able to adsorb limited amounts of undesired compounds, while regeneration is relatively cumbersome. Especially large solid beds take relatively large amounts of time for regeneration and disproportionately large amounts of regeneration gas is needed. Chemical processes in general are able to remove carbon dioxide and/or hydrogen sulphide without large difficulties, however, they suffer from the fact that they do not effectively remove mercaptans and often produce large amounts of wastes.

A special problem exist in processes in which hydrogen sulphide has to be removed in combination with a relatively high amount of mercaptans. Such processes have been described in the literature, in US 4,957,715 a process is described in which hydrogen sulphide, alkyl mercaptans and carbon dioxide are removed from a gas stream by using an adsorbent in a first step to remove hydrogen sulphide and part of the mercaptans, followed by
washing treatment in a second step to remove carbon
dioxide and a further part of the mercaptans. Such a
process, however, requires large amounts of [regenerable]
adsorbents, especially when the amount of sulphur
compounds in the feed gas is high. In US 5,700,438 a
process is described to remove hydrogen sulphide and
mercaptans from gas streams by contacting the stream with
copper compounds. This, however, is an expensive and
laborious process. In US 5,424,051 a process is described
in which carbon dioxide, mercaptans and hydrogen sulphide
are removed by first removing carbon dioxide by means of
an adsorbent and removing in a second step carbon
dioxide, hydrogen sulphide and mercaptans by means of
alkaline scrubbing. This process is expensive and
laborious. In US 4,311,680 a process is described for the
removal of hydrogen sulphide and mercaptans by using an
iron oxide fixed bed, followed by regeneration of the
adsorbent by reaction with hydrogen peroxide. Such a
process needs large amounts of adsorbents, while
regeneration is expensive and laborious.

It has now been found that sulphur compounds,
especially hydrogen sulphide in combination with
mercaptans, and optionally carbon dioxide and carbonyl
sulphide, may be removed from gas streams, especially
natural gas streams, by a combined process, in which in a
first step in a physical/chemical absorption process most
of the hydrogen sulphide, at least a part of the carbon
dioxide (if present) and a part of the mercaptans is
removed, while in a second step in a solid adsorption
step the remaining hydrogen sulphide and the remaining
mercaptans and other sulphur compounds are removed.

The above process uses the well-proven
physical/chemical absorption process. Such a process has
been described in for instance GB 2,103,645 and
GB 2,103,646, incorporated herein by reference.
Almost all hydrogen sulphide is removed in a very
efficient way. When necessary, also the carbon dioxide
which needs to be removed is removed in this part of the
process. As only part of the mercaptans has to be removed
in the first step, the process avoids the use of very
large and inefficient reactors. In the second step a
relatively small solid adsorption bed can be used to
remove the remaining part of the mercaptans. This is due
to the fact that almost all hydrogen sulphide has already
been removed in the first step together with part of the
mercaptans. Regeneration of such a bed is not very
laborious or cumbersome. Thus, the above combination of
sulphur removal processes results in an overall efficient
removal of hydrogen sulphide, mercaptans and optionally
part of the carbon dioxide and carbonyl sulphide, while
avoiding the disadvantages of only one technology or
other technologies. In addition, treating the
regeneration gas of the solid bed adsorber in a dedicated
absorber optimises the process. The laden solvent of the
dedicated absorber is then regenerated in the same
regenerator as is used for the main process.

It is observed that the use of a combined
physical/chemical absorbent rather than an aqueous
chemical absorbent only, also results in the possibility
of flashing any carbon dioxide at relatively high
pressures (i.e. between 5 and 15 baral). This reduces re-
compression requirements, e.g. for re-injection.

The present invention therefore provides a
a process for the removal of hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide from a gas stream comprising hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide, by removing in a first step most of the hydrogen sulphide, part of the mercaptans and optionally part or most of the carbon dioxide and carbonyl sulphide by washing the gas stream with an aqueous washing solution comprising 10 to 45 wt% based on total solution of water, 10 to 40 wt% based on total solution of a physical solvent and 20 to 60 wt% based on total solution of an amine, which first removal step is followed by a second removal step in which mercaptans are removed by means of molecular sieves, in which process the amount of mercaptans which is removed by the aqueous washing stream is between 85 and 93% (of total removed mercaptans in steps one and two), and the amount which is removed by the molecular sieves is between 15 and 7% (of total removed mercaptans in step one and two) and in which gas stream the ratio between the amount of mercaptans (expressed as ppmv) and the amount of hydrogen sulphide (expressed as vol%) is at least 50 and wherein the total gas stream comprises 0.05 to 20 vol% hydrogen sulphide, 10 to 1500 ppmv mercaptans and 0 to 40 vol% carbon dioxide.

The process is especially suitable for gas streams containing large amounts of hydrogen sulphide and, optionally large amounts of carbon dioxide, as both compounds are efficiently removed in the liquid adsorption process. The process is especially suitable when the ratio mercaptan/hydrogen sulphide is high, and the gas stream after the first step contains a relatively high amount of mercaptans. The process is able to deal with the common mercaptans (especially C₂₅-C₁₀ mercaptans, more especially C₁-C₄ mercaptans), also without any problems with methyl mercaptan, which is considered to be one of the most difficult mercaptans to be removed by means of adsorption technologies.

The feed gas for the process of the present invention may contain low as well as high amounts of sulphur compounds and carbon dioxide. Suitably the total feed gas stream comprises 0.05 to 20 vol% hydrogen sulphide, 10 to 1500 ppmv mercaptans and 0 to 40 vol% carbon dioxide, preferably 0.1 to 5 vol% hydrogen sulphide, 20 to 1000 ppmv mercaptans and 0 to 30 vol% carbon dioxide. In
a special embodiment of the invention, the total gas stream comprises hydrogen sulphide in an amount between 0.15 and 1.0 vol%. The presence of these amounts of H₂S hinders the removal of mercaptans, since H₂S is preferentially adsorbed. Therefore, a gas stream comprising hydrogen sulphide in an amount between 0.15 and 1.0 vol% is regarded as a very difficult gas stream to remove all mercaptans from.

The process according to the invention is especially suitable for the removal of mercaptans from gas feed streams in which the ratio of mercaptans (expressed as ppm) and the amount of hydrogen sulphide (expressed as vol%) is high. Due to this high ratio the gas stream after the first step will have a (relatively) high content of mercaptans. These mercaptans are adsorbed without problems in the second step. Thus, the process is preferably used for the purification of gas feed streams in which the ratio between the amount of mercaptans (expressed as ppm) and the amount of hydrogen sulphide (expressed as vol%) is at least 50, more preferably at least 100, more preferably at least 200, still more preferably above 250.

Very suitably the feed gas stream is natural or associated gas, but also other gas streams can be treated, for instance hydrogen containing refinery streams, e.g. obtained after desulphurisation reaction, and syngas streams. Natural gas is a general term that is applied to mixtures of light hydrocarbons and optionally inert gases (nitrogen, carbon dioxide, helium) derived from natural gas wells. The main component of natural gas is methane. Further, often ethane, propane and butane are present. In some cases (small) amounts of higher hydrocarbons may be present, often indicated as natural
gas liquids or condensates. When produced together with oil, the natural gas is usually called associated gas. Hydrogen sulphide, mercaptans, sulphides, disulphides, thiophenes and aromatic mercaptans may be present in natural gas in varying amounts.

The first step of the present invention appears to be very efficient to remove the hydrogen sulphide (and at least part of the carbon dioxide). By means of a washing process the feed gas stream is washed with a chemical solvent, an aqueous amine solution, and physical solvent. The use of aqueous amine solutions comprising a physical solvent for removing so-called acidic gases as hydrogen sulphide and optionally carbon dioxide and/or COS from a gas stream containing these compounds has been described long ago. See for instance A.L. Kohl and F.C. Riesenfeld, 1974, Gas Purification, 2nd edition, Gulf Publishing Co. Houston and R.N. Maddox, 1974, Gas and Liquid Sweetening, Campbell Petroleum Series.

On an industrial scale there are chiefly two categories of absorption solvents, depending on the mechanism to absorb the acidic components: chemical solvents and physical solvents. Each solvent has its own advantages and disadvantages as to features as loading capacity, kinetics, regenerability, selectivity, stability, corrosivity, heating/cooling requirements etc.

Chemical solvents which are useful in the process of the present invention are primary, secondary and/or tertiary amines derived alkanolamines, especially amines are derived from ethanamine, especially monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyl diethanolamine (MDEA) or mixtures thereof.
Physical solvents which are suitable in the process of the present invention are cyclo-tetramethylenesulfone and its derivatives, aliphatic acid amides, N-methylpyrrolidone, N-alkylated pyrrolidones and the corresponding piperidones, methanol, ethanol and mixtures of dialkylethers of polyethylene glycols or mixtures thereof.

The mixed systems show good absorption capacity and good selectivity against moderate investment costs and operational costs. They perform very well at high pressures, especially between 20 and 90 bars. Preferably in the hydrogen sulphide removal step between 90 and 100 wt% of the hydrogen sulphide based on total weight of hydrogen sulphide present in the gas stream is removed, preferably between 95 and 100 wt%, especially hydrogen sulphide is removed till a level of less than 10 ppmv, more especially to a level of less than 5 ppmv.

The preferred physical solvent is sulfolane. The preferred amine is a secondary or tertiary amine, preferably an amine compound derived from ethanol amine, more especially DIPA, DEA, MSEA (monomethyl-ethanolamine), NCEA, or DEHMA (diethyl-monomethanolamine), preferably DIPA or MSEA.

The aqueous washing solution comprises preferably 15 to 35 wt%, 20 to 40 wt% of a physical solvent and 40 to 55 wt% of an amine, based on total solution of water.

Very suitably the gas stream obtained in the first step is first cooled to a temperature between 5 and 45 °C, preferably between 10 and 35 °C, where after any condensate is separated from the gas stream, followed by the second step.

In addition, the gas stream obtained in the first step is cooled by at least 10 °C, preferably 20 °C.
Suitably the amount of mercaptans which is removed by the aqueous washing stream in the first step is between 70 and 93% (of removed mercaptans), preferably between 75 and 90%, and the amount which is removed by the mol sieves is between 30 and 74% (of removed mercaptans), preferably between 25 and 10%.

In the first removal step at least 90 wt% of the hydrogen sulphide is removed (based on total amount of hydrogen sulphide present in the gas stream), preferably 95 wt%, more preferably 98 wt%.

The amount of mercaptans in the gas stream which is treated in the second step is between suitably 5 and 60 ppmv, preferably between 10 and 50 ppmv.

Suitably the first step of the invention is carried out at a temperature of at least 20 °C, preferably between 25 and 90 °C, more preferably between 30 and 55 °C, at a pressure between 10 and 90 bars. In the second step preferably a crystalline molecular sieve is used, more preferably a sieve having an average pore diameter of 5 Ångström or more, especially between 6 and 13 Ångström. The second step is suitably carried out at a temperature of 25 °C and a pressure between 15 and 90 bars. The regeneration of the mol sieve beds may be done with suitable inert gases. It is preferred to use a hydrocarbon stream, especially a hydrocarbon stream which is obtained by a process according to the present invention. The regeneration gas containing the mercaptans of the second step is preferably reutilized with the starting gas stream. Preferably a dedicated absorber is used (similar to the absorber used in the main process).

The iodine solvent of the dedicated absorber is regenerated in the same regenerator as is used in the main process.
The process according to the present invention may be carried out in a continuous mode, preferably using a continuous regeneration process of the aqueous washing solution and two or more reactors comprising the mol sieves. In the regeneration process the pressure of the laden washing solution is released, usually in one or two steps, followed by temperature increase. Preferably, the temperature increase is done in a stepwise mode. When using two or more mol sieve reactors, at least one reactor will be in the adsorbing mode and at least one reactor will be in the desorption mode. Depending on the actual situation there may be a combination of two, three, four or even more reactors, one or more in adsorbing mode, the others in different stages of desorbing mode.

The second step of the present invention uses mol sieves. These mol sieves are commercially available.

Mol sieves comprise small zeolite particles dispersed in a binder, usually alumina. The zeolites comprise preferably zeolite type A or zeolite type X.

Especially suitable in the process of the present invention is the use of an adsorbent in step two comprising at least two beds containing mol sieves, one bed comprising 3 or 4 Å pore diameter mol sieves removing the water from the gas stream before it is treated in the second bed, the second bed containing mol sieves of 5 Å pore diameter or larger.

The mol sieves removing the water hardly adsorb any sulphur compounds. In general, the capacity of such mol sieves is higher than larger pore diameter mol sieves.

The amount of water to be removed in the small pore diameter mol sieves is preferably at least 60 wt% of the water present, preferably at least 90 wt%.
water is removed to a level of less than 1 wt% in the treated gas, preferably less than 0.01 ppmv.

The second and further beds suitably contain m1 sieve of 5 Å or more, to remove the sulphur compounds.

In a further preferred embodiment at least two beds are used containing the wide pore diameter m1 sieve, preferably one bed containing 5 Å m1 sieve, the other bed containing m1 sieve of pore diameter of 6 Å and larger, preferably 13 Å. The m1 sieve having the pore diameter of 5 Å removes hydrogen sulphide (if present), methyl mercaptan and some ethyl mercaptan, while the second bed removes the remainder of the ethyl mercaptan and the higher mercaptans. It will be appreciated that the above indicated beds can be applied in one single vessel, or may be spread over two or more vessels. The advantage of using more than one vessel is that each vessel may be used and regenerated under the most optimal conditions.

The laden solvent obtained in the process of the invention contains hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide and may also contain appreciable amounts of dissolved non-acid components from the gas mixture to be purified, e.g. hydrocarbons, carbon monoxide and/or hydrogen. Suitably, the laden solvent is regenerated in a regenerator at relatively low pressure and high temperature. A lean solvent is obtained and a gas stream comprising hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide. It may be advantageous to remove these non-acid components at least partially from the laden solvent by flashing to a pressure which is higher than the sum of the partial pressures belonging to the hydrogen sulphide and carbon dioxide present in the laden
solvent. In this way only small amounts of hydrogen sulphide and carbon dioxide are released from the solvent together with the non acid compounds. In a second step the laden solvent is flashed to a pressure which is below the sum of the partial pressures of the hydrogen sulphide and carbon dioxide present in the laden solvent at the prevailing temperature, i.e. to a pressure usually between 1 and 5 bara. Flashing at atmospheric pressure is preferred. The temperature in the last flashing operation is suitably in the range of from 50 to 120°C, preferably between 60 and 90°C.

The present invention will now be illustrated by way of the following Examples 1 to 4. It should be understood that the following examples do not limit the scope and generality of the claims.

**Examples 1 and 2: Comparison between low sulphur feed gas (comparative example) and high sulphur feed gas (according to the invention).**

Examples 1 and 2 represent the processing of feed gases which contain H₂S, CO₂ and organic sulphur using a combination of an acid gas removal unit, where the gases are contacted with an absorbing solvent, and a molsieve unit, where the gases exiting the acid gas removal unit are contacted with molsieves. In the acid gas removal unit, an absorbing solvent comprising 50 wt% of an amine, 35 wt% of sulfolane and 15 wt% of water is used.

Calculations have been done to design the acid gas removal unit for the following possible cases:

1. the CO₂ and H₂S specifications are both met, whichever is the more demanding. This case is called the RSH resulting case;
2. mercaptans are removed with the acid gas removal unit to the specification level, similar to the level that can be achieved after the molecular sieve unit (e.g. 3.5 ppmv), meaning that all mercaptan removal takes place in the acid gas removal unit and only dehydration is required in the molecular sieve unit. This case is referred to as the all RSH case;
3. Next a number of 'in between' cases are calculated, varying the % of mercaptan removal in the acid gas removal unit and in the molsieve unit.

In all the above cases the capital costs of the Sulfinol unit and the molecular sieve unit are calculated.

Two feed gases have been compared: a base feed, containing relatively low amounts of sulphur and a high sulphur feed. The feed gas compositions are given in Table 1.
Table 1: Feed compositions and conditions for the base feed and high sulphur feed

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Base Feed: Example 1</th>
<th>High Sulphur Feed: Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Bara 70</td>
<td>70</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>25</td>
</tr>
<tr>
<td>Flow</td>
<td>224 kg/s</td>
<td>224</td>
</tr>
<tr>
<td>Feed composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>mol% 3.51</td>
<td>3.49</td>
</tr>
<tr>
<td>C1</td>
<td>mol% 83.5</td>
<td>83.0</td>
</tr>
<tr>
<td>C2</td>
<td>mol% 5.46</td>
<td>5.43</td>
</tr>
<tr>
<td>C3</td>
<td>mol% 3.25</td>
<td>3.24</td>
</tr>
<tr>
<td>IC4</td>
<td>mol% 0.405</td>
<td>0.40</td>
</tr>
<tr>
<td>C4</td>
<td>mol% 0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>IC5</td>
<td>mol% 0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>C5+</td>
<td>mol% 0.34</td>
<td>0.35</td>
</tr>
<tr>
<td>CO₂</td>
<td>mol% 2.06</td>
<td>2.05</td>
</tr>
<tr>
<td>H₂S</td>
<td>mol% 0.56</td>
<td>1.11</td>
</tr>
<tr>
<td>CH₄S</td>
<td>mol% 0.0024</td>
<td>0.0048</td>
</tr>
<tr>
<td>C₂H₆S₃</td>
<td>mol% 0.0156</td>
<td>0.0310</td>
</tr>
<tr>
<td>C₄H₁₀S</td>
<td>mol% 0.0049</td>
<td>0.0097</td>
</tr>
<tr>
<td>C₅H₁₁S</td>
<td>mol% 0.0011</td>
<td>0.0022</td>
</tr>
<tr>
<td>H₂O</td>
<td>mol% 0.0690</td>
<td>0.0694</td>
</tr>
</tbody>
</table>

**Results**

Example 1:
For the base feed (low sulphur), when the acid gas removal unit is designed for the
required H₂S and CO₂ removal (RSH resulting), it also meets the mercaptan requirements,
so that extent that the molecular sieve configuration does not have to be adapted for
mercaptan removal in the base feed case. The molecular sieve line-up consists of a
regeneration reactor and two absorption reactors. Therefore there are no major step
changes in the costs of the combined units as illustrated in Figure 4.
Figure 4 Relative costs for the acid gas removal unit and Molecular sieve unit for the Base Case (basis total costs resulting RSH).

Example 2:

However, for the high sulphur feed a capital cost step change occurs when Sulfinol mercaptan removal is reduced even a little and mercaptan removal determines the molecular sieve design. A second step change may be expected as the Sulfinol unit design moves toward H2S and CO2 removal only and the mercaptan level left in the treated gas, is too large to be handled in one molecular sieve unit. Two parallel trains are required.

The study results are represented in Figure 5.

Figure 5 Relative costs for the Sulfinol and Molecular sieve unit for the High Sulphur Case (basis total costs resulting RSH).
Examples 1 and 2 illustrate that at high mercaptan levels in the feed gas an optimisation of the acid gas removal unit and the molecular sieve unit (when used for mercaptan removal) can result in a 10% capital cost saving. There is also a significant operating cost savings for the optimised system. Taking the optimum for individual processes will often not result in the optimum of the combined line-up, as is clearly shown in Figure 4 and 5. It is thus by no means straightforward or obvious, starting from two known individual steps, to achieve an optimum removal of mercaptans, H₂S and CO₂ at lowest capital cost.

Although the improvement margin is 10% when applied on the large investments involved this is a considerable effect. Significant reduction in absorbing solvent circulation rates result in reduced process energy requirements, which energy savings are only partially offset by increased molecular sieve energy requirements.

The operability of this process, and the processing flexibility has been proven in the NAM operated gas plant in Emmen, Holland, in the Shell operated Manistee plant and in the Golden Spike plant operated by ATCO.

**Examples 3 and 4: Comparison of different solvent compositions.**

In examples 3 and 4, a comparison is made between two types of solvent used to remove H₂S selectively from a feed gas. Selective removal of the H₂S is necessary to meet the CO₂ content set in the specifications. The comparison is based on the optimized acid gas removal-molecular sieve design (example 2 above) against the application of an absorbing solvent comprising an aqueous amine (MDEA), combined with molecular sieves for dehydration and mercaptan removal. The composition of the feed gas used in given in table 3.

**Table 3: Feed gas composition for solvent comparison case**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Base Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>bara</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>Flow</td>
<td>kg/s</td>
</tr>
<tr>
<td>Feed Composition</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>mol% 4.99</td>
</tr>
<tr>
<td>C₁</td>
<td>mol% 81.4</td>
</tr>
<tr>
<td>C₂</td>
<td>mol% 4.54</td>
</tr>
<tr>
<td>C₃</td>
<td>mol% 1.65</td>
</tr>
<tr>
<td>C₄</td>
<td>mol% 0.88</td>
</tr>
</tbody>
</table>
The results of the comparison are summarised in Table 4.

**Table 4**: Capital costs for \( \text{H}_2\text{S} \), \( \text{CO}_2 \), \( \text{COS} \) and mercapto removal for an aqueous MDEA line-up (comparative) and an optimised acid gas removal unit - molecular sieve unit line-up (according to the invention).

<table>
<thead>
<tr>
<th>Process</th>
<th>Comparative: Example 3</th>
<th>According to the Invention: Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent unit</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>Molecular sieve unit</td>
<td>66</td>
<td>29</td>
</tr>
<tr>
<td>Regeneration gas ex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular sieve unit</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>58</strong></td>
</tr>
</tbody>
</table>

The results show that the process according to the invention results in considerable capital expenditure savings compared to the comparative process leading to a substantial advantage over the prior art.

Modification and variations such as would be understood by a skilled person are deemed to be within the scope of the present invention.
The claims defining the invention are as follows:

1. A process for the removal of hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide from a gas stream comprising hydrogen sulphide, mercaptans and optionally carbon dioxide and carbonyl sulphide, by removing in a first step most of the hydrogen sulphide, part of the mercaptans and optionally part or most of the carbon dioxide and carbonyl sulphide by washing the gas stream with an aqueous washing solution comprising 10 to 45 wt% based on total solution of water, 10 to 60 wt% based on total solution of a physical solvent and 20 to 60 wt% based on total solution of an amine, which first removal step is followed by a second removal step in which mercaptans are removed by means of molecular sieves, in which process the amount of mercaptans which is removed by the aqueous washing stream is between 85 and 91% (of total removed mercaptans in steps one and two), and the amount which is removed by the molecular sieves is between 15 and 7% (of total removed mercaptans in step one and two) and in which gas stream the ratio between the amount of mercaptans (expressed as ppmv) and the amount of hydrogen sulphide (expressed as vol%) is at least 50 and wherein in the total gas stream comprises greater than 0.56 to 20 vol% hydrogen sulphide, 19 to 1500 ppmv mercaptans and 0 to 40 vol% carbon dioxide.

2. A process according to claim 1 wherein the total gas stream comprises greater than 0.56 to 5 vol% hydrogen sulphide, 20 to 1000 ppmv mercaptans and 0 to 30 vol% carbon dioxide.

3. A process according to claim 1 or 2, in which the total gas stream comprises hydrogen sulphide in an amount greater than 0.56 vol% to 1 vol%.

4. A process according to claim 1, in which the total gas stream comprises hydrogen sulphide in an amount between 0.6 vol% and 20 vol%.

5. A process according to any one of claims 1, 2 and 4, in which the total gas stream comprises hydrogen sulphide in an amount between 0.6 vol% and 5 vol%.

6. A process according to any one of claims 1, 2 and 4, in which the total gas stream comprises hydrogen sulphide in an amount between 0.6 vol% and 1 vol%.

7. A process according to claims 1 or 4, in which the total gas stream comprises hydrogen sulphide in an amount between 1.11 vol% and 20 vol%.

8. A process according to any one of claims 1, 2, 4, 5 and 7, in which the total gas stream comprises hydrogen sulphide in an amount between 1.11 vol% and 5 vol%.
9. A process according to any one of claims 1 to 8, in which the ratio between
the amount of mercaptans (expressed as ppmv) and the amount of hydrogen sulphide
(expressed as vol%) is at least 100, preferably at least 200.
10. A process according to any one of claims 1 to 9, in which the gas stream is
natural or associated gas.
11. A process according to any one of claims 1 to 10, in which the physical
solvent is sulfolane.
12. A process according to any one of claims 1 to 11, in which the amine is a
secondary or tertiary amine, preferably an amine compound derived from anilin amine
or a mixture thereof, more preferably DIPA, DEA, MDEA, MDEA, or DEMEA, most
preferably DIPA or MDEA or a mixture thereof.
13. A process according to any one of claims 1 to 12, in which the aqueous
washing solution comprises 20 to 30 wt% based on total solution of water, 20 to 35 wt%
of a physical solvent and 40 to 55 wt% of an amine.
14. A process according to any one of claims 1 to 13, in which the gas stream
obtained in the first step is cooled to a temperature between 5 and 45°C, preferably
between 10 and 35°C, where after any condensate is separated from the gas stream.
15. A process according to any one of the preceding claims, in which the first step
is carried out at a temperature of at least 20°C, preferably between 25 and 90°C, more
preferably between 30 and 55°C, at a pressure between 15 and 90 bar.
16. A process according to any one of the preceding claims, in which in the
second step a crystalline molecular sieve is used, preferably a sieve having an average
pore diameter of 5 angstrom or more, especially about 6 angstrom.
17. A process according to any one of the preceding claims, in which the second
step is carried out at a temperature of 25°C and a pressure between 15 and 90 bar.
18. A process according to any one of the preceding claims in which the
regeneration gas of the second step containing mercaptans is recombined with the starting gas
stream or is treated in a dedicated absorber.

Dated 18 April, 2008

Shell Internationale Research Maatschappij B.V.

Patent Attorney for the Applicant/Nominated Person
SPRUSON & FERGUSON