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(54) **Title:** PROCESS FOR PRODUCING A GAS STREAM DEPLETED OF HYDROGEN SULPHIDE AND OF MERCAPTANS

(57) **Abstract:** The invention provides a process for producing a gas stream depleted of H_2S and of RSH from a feed gas stream comprising H_2S and RSH, the process comprising the steps of : (a) contacting the feed gas stream with absorbing liquid in a H_2S removal zone to obtain a gas stream depleted of H_2S; (b) contacting the gas stream obtained in step (a) with aqueous scrubbing solution comprising $CUSO_4$ in a RSH removal zone to obtain a mixture comprising Cu-alkylsulphide products and the gas stream depleted of H_2S and depleted of RSH.

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PROCESS FOR PRODUCING A GAS STREAM DEPLETED OF HYDROGEN SULPHIDE AND OF MERCAPTANS

The invention relates to a process for producing a gas stream depleted of hydrogen sulphide (H_2S) and of mercaptans (RSH).

Producing a gas stream depleted of H_2S and of RSH involves the removal of these compounds. Removal of H_2S and of RSH from gas streams comprising these compounds has always been of considerable importance in the past and is even more so today in view of continuously tightening environmental regulations.

Numerous natural gas wells produce what is called "sour gas", i.e. natural gas comprising H_2S, often in combination with RSH. The total amount of sulphur compounds is generally too high, making 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.

Removal of RSH from a gas stream, generally more difficult compared to removal of H_2S, is of importance because RSH, due to their odorous nature, can be detected at parts per million concentration levels. Thus, it is desirable in cases where the gas stream is intended for domestic use, to have concentrations of RSH lowered to e.g. less than 5, or even less than 2 ppmv.

RSH removal is also important in cases where the gas stream is a carrier gas stream, for example an inert gas

or a hydrocarbonaceous gas that has been used to strip a RSH comprising reactor bed and is loaded with RSH. The removal of RSH from such a loaded gas stream is necessary to be able to use the gas stream again as stripping gas.

Another situation where RSH removal is important is in the event that the depleted gas stream is to be further processed. For example, natural gas can be used for the generation of synthesis gas, typically in a gasifier unit. The thus-formed synthesis gas is generally converted to hydrocarbons in a catalytic process, known in the art as a Fischer-Tropsch process. If mercaptans are present in the natural gas stream, they will react to form H_2S in the gasifier, resulting in a synthesis gas stream comprising H_2S. The H_2S may bind irreversibly on catalysts and cause sulphur poisoning. This results in a deactivated catalyst, which severely hampers the catalytic process. Hence, in cases where the process involves a catalytic step, removal of mercaptans to very low levels, as low as less than 2 ppmv or even in the ppbv range, is required.

Generally, a total concentration of sulphur compounds of less than 30 ppmv is desired. Sales gas specifications often mention total sulphur concentrations lower than 10 ppmv, or even as low as less than 4 ppmv.

Processes for producing a gas stream depleted of H_2S and of RSH from a gas stream comprising both these compounds are known in the art. Generally, the known processes are based on physical and/or chemical absorption, solid bed adsorption and/or chemical reaction. However, a number of disadvantages exist in the known processes. Physical absorption processes generally suffer from the fact that large reactors are needed to achieve the desired low concentrations of RSH. 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, see for example US 4,311,680. Large solid beds take relatively large amounts of time for regeneration and disproportionately large amounts of regeneration gas are needed. Chemical processes in general are able to remove H_2S, but they suffer from the fact that they do not effectively remove RSH and often produce large amounts of waste, see for example EP 229,587.

A special problem exist in the event that the feed gas stream comprises relatively high amounts of H_2S as well as a RSH and optionally carbon dioxide. Processes aimed at producing a gas stream depleted of H_2S and of RSH from such feed gas streams are known in the art.

For example, in US 4,957,715 a process is described in which H_2S, alkyl-substituted RSH and carbon dioxide are removed from a gas stream by using an adsorbent in a first step to remove H_2S and part of the RSH, followed by washing treatment in a second step to remove carbon dioxide and a further part of the RSH. A disadvantage of the process described in US 4,957,715 is that large amounts of adsorbents are required, especially when the amount of sulphur compounds in the feed gas is high.

In US 5,700,438 a process is described to remove H_2S and RSH from gas streams by contacting the stream with copper compounds. This, however, is an expensive and laborious process because a hindered amine-copper complex is needed. Moreover, carbon dioxide present in the feed gas stream will not be removed.

In US 5,424,051 a process is described in which carbon dioxide, RSH and H_2S are removed by first removing

carbon dioxide by means of an adsorbent and removing in a second step remaining carbon dioxide, H_2S and RSH by means of alkaline scrubbing. This process is expensive and laborious and moreover, considerably waste of spent alkaline scrubbing liquid is produced.

In US 4,311,680 a process is described for the removal of H_2S and RSH by using an iron oxide fixed bed, followed by regeneration of the absorbent by reaction with hydrogen peroxide. Such a process needs large amounts of adsorbents, while regeneration is expensive and laborious.

In EP 0,986,432 a process is described for the removal of sulphur contaminants using an aqueous solution of $CuSO_4$. Although the removal of H_2S is shown, there is no mention of the removal of RSH. In general, RSH are more difficult to remove compared to H_2S. Furthermore, in the process described in EP 0,986,432 carbon dioxide is not removed.

In US 5,147,620 a process is described for the removal of H_2S using an aqueous solution of $CuNO_3$. A disadvantage of the process described in US 5,147,620 is that the formation of NO_2 takes place. This compound is corrosive, toxic and moreover is an environmental pollutant. Its formation is therefore unwanted.

In view of the difficulties encountered in the known processes, there is a need in the art for a simple and versatile process for producing a gas stream depleted of H_2S and of RSH, especially from a feed gas stream comprising relatively high amounts of these contaminants, without the operational problems of known processes and without the production of unwanted waste compounds.

To this end, the invention provides a process for producing a gas stream depleted of H_2S and of RSH from a feed gas stream comprising H_2S and RSH, the process comprising the steps of:

(a) contacting the feed gas stream with absorbing liquid in a H_2S removal zone to obtain a gas stream depleted of H_2S;

(b) contacting the gas stream obtained in step (a) with aqueous scrubbing solution comprising $CuSO_4$ in a RSH removal zone to obtain a mixture comprising Cu-alkylsulphide products and the gas stream depleted of H_2S and depleted of RSH.

The process according to the invention enables the production of a gas stream depleted of H_2S and of RSH wherein the concentration of H_2S is suitably below 10 ppmv and wherein the concentration of RSH is suitably below 10 ppmv.

In step (a) of the process according to the invention, H_2S is transferred from the feed gas stream to the absorbing liquid to obtain a gas stream depleted of H_2S.

Any feed gas stream comprising H_2S and RSH can be processed. Suitably, the feed gas stream comprises natural or associated gas, but also other gas streams can be processed, for instance hydrogen-comprising refinery streams, e.g. obtained after a desulphurisation reaction. Natural gas is a general term that is applied to mixtures of light hydrocarbons and optionally other 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. Other compounds that may be present in natural gas in varying amounts include H_2S, aliphatic and/or aromatic RSH, sulphides, disulphides, especially carbon disulphide (CS_2), thiophenes and carbon dioxide.

The process according to the invention is especially suitable for feed gas streams comprising besides H_2S also significant amounts of carbon dioxide, as both compounds are efficiently removed in the liquid absorption process in step (a).

Suitably the total feed gas stream comprises in the range of from 0.05 to 20 vol% H_2S, from 1 ppmv to 1 vol% RSH and from 0 to 40 vol% carbon dioxide, preferably from 0.1 to 5 vol% H_2S, from 20 ppmv to 1 vol% RSH and from 0 to 30 vol% carbon dioxide, based on the total feed gas stream. In a special embodiment of the invention, the total gas stream comprises H_2S in an amount between 0.15 and 1.0 vol%.

Even feed gas streams having a relatively high amount of RSH compared to H_2S, typically having a ratio of RSH (expressed as ppmv) to H_2S (expressed as vol%) is high, typically at least 50, preferably at least 100, more preferably at least 200, still more preferably above 250, can be processed. Due to this high ratio the gas stream obtained in step (a) will have a relatively high content of RSH. The process according to the invention enables the removal of these RSH without problems in step (b).

The absorbing liquid is any liquid capable of removing H_2S from the feed gas stream. Suitable absorbing

liquids are chemical solvents, physical solvents or mixtures thereof.

Suitable chemical solvents are primary, secondary and/or tertiary amines, especially amines that are derived of ethanolamine, especially monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) or mixtures thereof. A preferred chemical solvent is a secondary or tertiary amine, preferably an amine compound derived from ethanol amine, more especially DIPA, DEA, MMEA (monomethyl-ethanolamine), MDEA, or DEMEA (diethyl-monoethanolamine), preferably DIPA or MDEA. It is believed that these chemical solvents react with acidic compounds such as H_2S, thereby removing H_2S from the feed gas stream.

The absorbing liquid may also comprise a so-called activator compound. The addition of an activator compound to an absorbing liquid system is believed to result in an improved removal of acidic compounds. Suitable activator compounds are piperazine, methyl-ethanolamine, or (2-aminoethyl)ethanolamine, especially piperazine.

Preferably, the absorbing liquid comprises MDEA and piperazine.

Suitable physical solvents are sulfolane (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 preferred physical solvent is sulfolane. It is believed that H_2S is taken up in the physical solvent and thereby removed from the feed gas stream. An advantage of using an absorbing liquid comprising a physical solvent is that in addition to

removal of H_2S, removal of aromatic compounds from the feed gas stream is also achieved. Examples of aromatic compounds are benzene, toluene and xylene, known collectively as BTEX or BTX. Aromatic compounds are carcinogenic and their emission must therefore be below certain levels. It is therefore desirable to reduce the concentration of aromatic compounds, especially BTX compounds, in the gas stream. However, it is an advantage of the process according to the invention that the presence of aromatic compounds does not hinder the removal of RSH in step (b). Therefore, even feed gas stream comprising aromatic compounds such as BTX can be processed.

The absorption liquid in step (a) may also be a mixed system comprising a chemical and a physical liquid. Absorption liquids comprising both chemical and physical solvents are especially preferred because they show good absorption capacity and good selectivity for H_2S against moderate investment costs and operational costs. In addition, in the event that the feed gas stream comprises carbon dioxide, carbon dioxide will also be removed in the mixed absorption liquid to a large extent, resulting in a gas stream depleted of H_2S and of carbon dioxide. Another advantage of mixed systems is that they perform well at high pressures, especially between 20 and 90 bara. Hence, in the case that the feed gas stream is pressurised, for example if the feed gas stream is a natural gas stream obtained at high pressure, no depressurising step is needed. Yet another advantage is that the use of a combined physical/chemical absorbing liquid, rather than an aqueous chemical absorbing liquid only, also results in the possibility of flashing any carbon dioxide at relatively high pressures (i.e. between

5 and 15 bara). This reduces re-compression requirements, e.g. for re-injection.

A preferred absorbing liquid system comprises water, sulfolane and a secondary or tertiary amine, preferably an amine compound derived from ethanol amine, more especially DIPA, DEA, MMEA (monomethyl-ethanolamine), MDEA, or DEMEA (diethyl-monoethanolamine), preferably DIPA or MDEA. The amount of water is preferably between 20 and 45 parts by weight, the amount of sulfolane is preferably between 20 and 35 parts by weight and the amount of amine is preferably between 40 and 55 parts by weight, the amounts of water, sulfolane and amine together being 100 parts by weight. The preferred ranges result in optimum carbon dioxide removal in most cases.

Another preferred absorbing liquid comprises in the range of from 15 to 45 parts by weight, preferably from 15 to 40 parts by weight of water, from 15 to 40 parts by weight of sulfolane, from 30 to 60 parts by weight of a secondary or tertiary amine derived from ethanol amine, and from 0 to 15 wt%, preferably from 0.5 to 10 wt% of an activator compound, preferably piperazine, all parts by weight based on total solution and the added amounts of water, sulfolane, amine and optionally activator together being 100 parts by weight. This preferred absorbing liquid enables removal of carbon dioxide, hydrogen sulphide and/or COS from a gas stream comprising these compounds. This offers an advantage over a process that does not enable removal of carbon dioxide. When compared with the same absorbing liquid without the addition of a primary or secondary amine compound, especially a secondary amine compound, one or more of the following advantages are obtained: the carbon dioxide absorption rate is faster, the loading amount is higher, the

solvent/gas ratio is lower, the design of the plant is smaller and the regeneration heat requirement is lower (resulting is less cooling capacity). When compared with an absorbing liquid comprising aqueous amines, especially DMEA and piperazine, the addition of sulfolane enables the production of a gas stream comprising carbon dioxide having intermediate pressures, e.g. pressures between 3 and 15 bara, preferably between 5 and 10 bara.

It is an advantage of the invention that step (a) can be adjusted to enable producing a gas stream depleted of hydrogen sulphide and of RSH from feed gas streams further comprising other compounds, in particular selected from the group of carbon dioxide, aromatic compounds and other sulphur contaminants. The process offers a choice whether or not to remove compounds other than hydrogen sulphide and RSH, for example other sulphur-containing compounds or carbon dioxide or aromatic compounds, from the feed gas stream. Hence, different compositions of the gas stream obtained in step (a) can be achieved, suitably by adjusting the choice of absorbing liquid in step (a).

Suitably, step (a) is carried out at a temperature in the range of from 15 to 90 °C, preferably at a temperature of at least 20 °C, more preferably from 25 o 80 °C, still more preferably from 40 to 65 °C, and even still more preferably at about 55 °C. Step (a) is suitably carried out at a pressure between 10 and 150 bar, especially between 25 and 90 bara.

Step (a) is suitably carried out in a zone having from 5-80 contacting layers, such as valve trays, bubble cap trays, baffles and the like. Structured packing may also be applied. The amount of CO_2-removal can be optimised by regulating the solvent/feed gas ratio. A

suitable solvent/feed gas ratio is from 1.0 to 10 (w/w), preferably between 2 and 6.

The gas stream obtained in step (a) is depleted of H_2S, meaning that the concentration of H_2S in the gas stream obtained in step (a) is lower than the concentration of H_2S in the feed gas stream. It will be understood that the concentration of H_2S in the gas stream obtained in step (a) depends on the concentration of H_2S in the feed gas stream. Typically, the concentration of H_2S in the gas stream obtained in step (a) is in the range of from 80% to 0.0001%, preferably from 20% to 0.001%, more preferably from 10% to 0.0001% of the H_2S concentration in the feed gas stream. Suitably, the concentration of H_2S in the gas stream obtained in step (a) is less than 10 ppmv, preferably less than 5 ppmv.

It will be understood that the RSH concentration in the H_2S-depleted gas stream gas stream obtained after step (a) will depend on the RSH concentration in the feed gas stream. Suitably, RSH concentrations in the H_2S-depleted gas stream obtained after step (a) will be in the range of from 100 ppbv to 0.1 vol%.

In step (a), loaded absorbing liquid comprising H_2S and optionally CO_2 and/or C_3+ RSH and other sulphur compounds such as carbonyl sulphide is obtained. Step (a) will usually be carried out as a continuous process, which process also comprises the regeneration of the loaded absorbing liquid. Therefore, the H_2S removal zone preferably further comprise at least one regenerator wherein loaded absorbing liquid is regenerated by transferring at least part of the contaminants to a regeneration gas stream, typically at relatively low

pressure and high temperature. The loaded absorbing liquid may contain beside H_2S and optionally CO_2 and/or COS appreciable amounts of other compounds from the gas mixture to be purified, e.g. hydrocarbons, carbon monoxide, hydrogen etc. It may be advantageous to remove these (non-acid) compounds at least partially from the loaded solvent by flashing to a pressure which is higher that the sum of the partial pressures belonging to the CO_2 and optionally H_2S and/or COS. In this way only very small amounts of CO_2 and optionally H_2S and COS are released from the solvent together with the (non-acid) compounds. The loaded absorbing liquid may advantageously flashed in a second step to a pressure which is below the partial pressures of CO_2 and optionally H_2S and COS at the prevailing temperature, i.e. to a pressure usually between 1 and 5 bara. Usually the flash is carried out at a pressure between 1 and 15 bara, preferably between 1 and 10 bara, more preferably ambient pressure. Flashing at atmospheric pressure is preferred. In the gas set free during the flashing large amounts of the carbon dioxide and optionally H_2S and/or COS are present. The temperature in the last flashing operation is suitably in the range of from 50 to 120 °C, preferably between 60 and 90 °C.

Preferably, the loaded absorbing liquid obtained in step (a), optionally after flashing as described above, is regenerated. The regeneration is suitably carried out by heating in a regenerator at a relatively high temperature, suitably in the range of from 70 to 150 °C. The heating is preferably carried out with steam or hot oil. Preferably, the temperature increase is done in a stepwise mode. Suitably, regeneration is carried out at a pressure in the range of from 1 to 2 bara.

After regeneration, regenerated absorbing liquid is obtained and a loaded regeneration gas stream loaded with contaminants such as hydrogen sulphide, C_3+ RSH and/or optionally carbon dioxide and carbonyl sulphide. Preferably, regenerated absorbing liquid is used again in the absorption stage of step (a) for H_2S removal. Suitably the regenerated absorbing liquid is heat exchanged with loaded absorbing liquid to use the heat elsewhere. Suitably, sulphur compounds are removed from the loaded regeneration gas stream in a sulphur recovery unit, for example via the Claus process.

In step (b) of the process according to the invention, RSH are removed from the gas stream obtained in step (a) by contacting the gas stream depleted of H_2S obtained in step (a) with aqueous scrubbing solution comprising $CuSO_4$ in a RSH removal zone, thereby obtaining a mixture comprising Cu-sulphide products and the gas stream depleted of H_2S and depleted of RSH.

Reference herein to RSH is to aliphatic RSH, especially C_1-C_6 RSH, more especially C_1-C_4 RSH, aromatic RSH, especially phenyl mercaptan, or mixtures of aliphatic and aromatic RSH. The invention especially relates to the removal of methyl RSH, which is considered to be one of the most difficult RSH to be removed by means of conventional liquid absorption technologies, ethyl mercaptan, normal- and iso-propyl mercaptan and butyl mercaptan isomers.

It is believed that RSH react with CuSO4 in step (b) mainly, but not limited to:

$$2\ RSH + CuSO_4 \rightarrow R\text{-}S\text{-}Cu\text{-}S\text{-}R + H_2SO_4 \qquad (1)$$

If any H_2S is still present in the gas stream, it is believed that at least part of it will be converted to CuS according to:

$$H_2S + CuSO_4 \rightarrow CuS + H_2SO_4 \quad (2)$$

Reference herein to Cu-sulphide products is to products comprising Cu-mono-sulphide or Cu-disulphide compounds or both, typically comprising R-S-Cu-S-R and optionally CuS.

The concentration of $CuSO_4$ in the aqueous scrubbing solution is chosen such that a sufficient amount of $CuSO_4$ is dissolved, but that no or little precipitation of $CuSO_4$ takes place. Preferably, the concentration of $CuSO_4$ in the aqueous scrubbing solution in step (b) is in the range of from 0.1 wt% to saturation, preferably from 1 wt% to saturation, based on the total scrubbing solution. Optionally, the aqueous scrubbing solution further comprises an acidic compound, preferably H_2SO_4.

Suitably, step (a) and step (b) take place in gas/liquid contactors. Suitable gas/liquid contactors are described for example in Perry's Chemical Engineers' Handbook, 7th edition, section 14 (1997) and include spargers.

In step (b) the gas stream obtained in step (a) is preferably sparged into the aqueous scrubbing solution comprising $CuSO_4$. This ensures an optimum contact between the gas stream and the scrubbing solution.

Preferably, the process according to the invention comprises the additional step (step (c)) of removing at least part of the Cu-sulphide products from the mixture obtained in step (b). This can for example be achieved through filtration or preferably via a density separation

step. Optionally, at least part of the Cu-sulphide products thus removed can then converted to CuO in a roasting zone according to:

$$x\ R\text{-}S\text{-}Cu\text{-}S\text{-}R + y\ O_2 \rightarrow x\ CuO + 2x\ SO_2 + z\ CO_2 \quad (3a)$$

$$2cCuS + 3\ O_2 \rightarrow 2\ CuO + 2\ SO_2 \quad (3b)$$

Preferred operating temperatures of the roasting zone are above 150 °C. Preferably, the operating pressure of the roasting zone is in the range of from 1 bara to 5 bara.

Suitably, at least part of the CuO thus formed can then be converted to $CuSO_4$ in a $CuSO_4$ regeneration zone according to:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \quad (4)$$

Suitably, ambient temperatures and pressures are used in the $CuSO_4$ regeneration zone.

Preferably, at least part of the $CuSO_4$ formed from CuO is led to the RSH removal zone and used in step (b). Optionally, excess H_2O is evaporated and removed from the $CuSO_4$ regeneration zone.

As an alternative to roasting, at least part of the Cu-sulphides formed are removed from the process, and for example sent to a copper smelter, and fresh $CuSO_4$ is added to the RSH removal zone.

The process according to the invention may be carried out in a continuous mode, preferably using a continuous regeneration process of the absorbing liquid and a continuous regeneration process of the $CuSO_4$.

The gas stream depleted of H_2S and of RSH obtained in step (b) can be processed further in known manners. For example, the gas stream can be subjected to catalytic or non-catalytic combustion, to generate electricity, heat or power, or can be used as a feed gas for a chemical reaction or for residential use. In the event that the feed gas stream comprises natural gas, the gas stream obtained in step (b) can also be converted to liquefied natural gas (LNG).

The invention will now be illustrated by the following, non-limiting examples.

Example 1 (comparative).

A feed gas stream having a composition as shown in table 1, column A, was contacted with an absorbing liquid comprising sulfolane, MDEA and water in an absorber unit at a temperature of 45 °C and a pressure of 60 bar g. The composition of the gas stream leaving the absorber unit is shown in table 1, column B.

Example 2 (comparative).

A feed gas stream having a composition as shown in table 1, column A, was contacted with an absorbing liquid comprising MDEA and piperazine in an absorber unit at a temperature of 45 °C and a pressure of 60 bar g. The composition of the gas stream leaving the absorber unit is shown in table 1, column C.

Example 3 (according to the invention).

A feed gas stream having a composition as shown in table 1, column A, was contacted with an absorbing liquid comprising sulfolane, MDEA and water at a temperature of 45 °C and a pressure of 60 bar g. The composition of the gas stream leaving the absorber unit is shown in table 1, column B. The gas stream leaving the absorber unit was sparged into a solution comprising 10 wt% (based on total

solution) of $CuSO_4$ in water. The concentration RSH in the gas stream leaving the $CuSO_4$ solution, measured using gas chromatography, was below 2 ppmv.

Example 4 (according to the invention).

A feed gas stream having a composition as shown in table 1, column A, was contacted with an absorbing liquid comprising sulfolane, MDEA and water at a temperature of 45 °C and a pressure of 60 bar g. The composition of the gas stream leaving the absorber unit is shown in table 1, column B. The gas stream leaving the absorber unit was sparged into a solution comprising 10 wt% (based on total solution) of $CuSO_4$ and 10 wt% (based on total solution) of H_2SO_4 in water. The concentration RSH in the gas stream leaving the $CuSO_4$ solution, measured using gas chromatography, was below 2 ppmv.

Table 1: concentrations of components in mol%. Total BTX and total RSH in ppmv.

	A	B	C
H_2O	0.010	0.223	0.201
CO_2	2.118	0.002	0.000
H_2S	0.432	0.000	0.000
CH_3SH	0.004	0.000	0.003
C_2H_5SH	0.011	0.001	0.001
i-C_3H_7SH	0.001	0.000	0.001
N_2	3.715	3.831	3.811
C_1	84.622	86.814	86.715
C_2	5.387	5.499	5.529
C_3	1.777	1.798	1.823
iC_4	0.619	0.622	0.634
nC_4	0.654	0.652	0.670
iC_5	0.184	0.182	0.189
nC_5	0.159	0.156	0.163
C_6	0.135	0.129	0.138
C_7	0.058	0.053	0.058
C_8	0.019	0.017	0.019
Benzene	0.042	0.011	0.029
Toluene	0.019	0.005	0.015
Total BTX (ppmv)	610	151	439
Total RSH (ppmv)	165	12	73

From the examples it is evident that the process according to the invention enables producing a gas stream depleted of RSH and of H_2S having a concentration of RSH below 2 ppmv and of H_2S in the ppbv range. The

comparative processes result in gas streams having an RSH concentration above 10 ppmv.

C L A I M S

1. A process for producing a gas stream depleted of H_2S and of RSH from a feed gas stream comprising H_2S and RSH, the process comprising the steps of:

(a) contacting the feed gas stream with absorbing liquid in a H_2S removal zone to obtain a gas stream depleted of H_2S;

(b) contacting the gas stream obtained in step (a) with aqueous scrubbing solution comprising $CuSO_4$ in a RSH removal zone to obtain a mixture comprising Cu-alkylsulphide products and the gas stream depleted of H_2S and depleted of RSH.

2. A process according to claim 1, further comprising the step of

(c) separating at least part of the Cu-sulphide products from the RSH removal zone.

3. A process according to claim 2, further comprising the steps of:

(d) converting at least part of the Cu-sulphide products separated in step (c) to CuO in a roasting zone;

(e) converting at least part of the CuO products obtained in step (d) to $CuSO_4$ in a $CuSO_4$ regeneration zone.

4. A process according to any one of claims 1 to 3, wherein the absorbing liquid in step (a) comprises a chemical solvent and a physical solvent.

5. A process according to any one of claims 1 to 4, wherein the absorbing liquid in step (a) further comprises water.

6. A process according to any one of claims 1 to 5, wherein the concentration of $CuSO_4$ in the fresh aqueous scrubbing solution in step (b) is in the range of from 0.1 wt% to saturation, preferably from 1 wt% to saturation, based on the total scrubbing solution.

7. A process according to any one of claims 1 to 6, wherein the aqueous scrubbing solution further comprises H_2SO_4.

8. A process according to any one of claims 1 to 7, wherein step (b) is performed by sparging the gas into the aqueous scrubbing solution comprising $CuSO_4$.

9. A process according to any one of claims 1 to 8, wherein the feed gas stream comprises natural gas.

10. A process according to any one of claims 1 to 9, wherein the concentration of RSH in the feed gas stream is in the range of from 1 ppmv to 1 vol%, based on the feed gas stream.

11. A process according to any one of claims 1 to 10, wherein the absorbing liquid in step (a) comprises one or more solvents selected from the group of monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA).

12. A process according to any one of claims 1 to 11, wherein the absorbing liquid in step (a) comprises one or more compounds selected from the group of sulfolane, aliphatic acid amides, N-methylpyrrolidone, N-alkylated pyrrolidones and the corresponding piperidones, methanol, ethanol and dialkylethers of polyethylene glycols.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/064241

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/52 B01D53/14

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 practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 52 088584 A (TAIKISHA KK) 25 July 1977 (1977-07-25) abstract	

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 September 2006	06/10/2006

Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
PCT/EP2006/064241

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