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(54) Titre : PROCEDE D'ELIMINATION DE DIOXYDE DE CARBONE DE MELANGES DE GAZ

(54) Title: PROCESS FOR REMOVING CARBON DIOXIDE FROM GAS MIXTURES

(57) **Abrégé/Abstract:**

The present invention relates to a process for removing carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution containing water, sulfolane and a secondary or tertiary amine derived from ethanolamine. More particularly the invention relates to the process described above, the process being carried out in the presence of a primary or secondary amine compound in an amount between 0.5 and 15 wt. % based on water, sulfolane and amine. The invention further relates to an absorbent liquid to be used in the above process.



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(54) Title: PROCESS FOR REMOVING CARBON DIOXIDE FROM GAS MIXTURES

(57) Abstract: The present invention relates to a process for removing carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution containing water, sulfolane and a secondary or tertiary amine derived from ethanolamine. More particularly the invention relates to the process described above, the process being carried out in the presence of a primary or secondary amine compound in an amount between 0.5 and 15 wt. % based on water, sulfolane and amine. The invention further relates to an absorbent liquid to be used in the above process.



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PROCESS FOR REMOVING CARBON DIOXIDE FROM GAS MIXTURES

The present invention relates to a process for removing carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution
5 containing water, sulfolane and a secondary or tertiary amine derived from ethanol amine. The invention further relates to an absorbent liquid to be used in the above process.

The use of organic solvents or aqueous solutions of
10 organic solvents for removing of so-called acidic gasses as carbon dioxide and optionally hydrogen sulphide 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,
15 Gulf Publishing Co. Houston and R.N. Maddox, 1974, Gas and Liquid Sweetening, Campbell Petroleum Series. Preferably a regenerable absorbent solvent is used in a continuous process.

On an industrial scale there are chiefly two
20 categories of absorbent 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,
25 stability, corrosivity, heat/cooling requirements etc.

Chemical solvents which have proved to be industrially useful are primary, secondary and/or tertiary amines derived alkanolamines. The most frequently used amines are derived from ethanolamine,

especially monoethanol amine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA).

Physical solvents which have proved to be industrially suitable 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.

A well-known commercial process uses an aqueous mixture of a chemical solvent, especially DIPA and/or MDEA, and a physical solvent, especially cyclotetramethylene-sulfone. Such 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 bara.

A further improvement of the above described mixed aqueous systems using both types of solvents is desired. In order to improve the liquid/gas ratio, especially at high pressures and/or deep carbon dioxide removal, it has now been found that the addition of primary or secondary amine compounds in relatively small amounts further improves the process. For instance, the addition of a few wt% of piperazine results in a clear improvement of the kinetics of the system, resulting in a lower liquid/gas ratio, which may result in a smaller design of the plant (absorber as well as regenerator). When using the same liquid/gas ratio an, often considerable, larger amount of carbon dioxide may be removed.

In addition, in the case of addition of suitable primary or secondary amine compounds in relatively small amounts more carbon dioxide may be flashed at a relatively high pressure when compared with similar,

aqueous chemical absorbents. This reduces re-compression requirements, e.g. for re-injection. This holds especially for the combination of DEA, TEA, DIPA and MDEA, especially DIPA and MDEA, and piperazine.

5 It has been described in the literature that the addition of e.g. piperazine to e.g. MDEA results in an improved acid gas removal. However, one particular disadvantage of such a combination is that carbamates may be formed, especially at high solvent loadings, which
10 carbamates are insoluble in aqueous solutions, see e.g. US 4,336,233. Thus, only limited amounts of primary or secondary amine compounds can be used in purely aqueous solutions. It is advised, therefore, not to use physical solvents in order to avoid the formation of the insoluble
15 carbamates. It has, however, now surprisingly been found that such limitations do not occur in water/tetramethylenesulfone mixtures as applied in the usual commercial applications. In addition, degradation and corrosivity of these mixtures are very acceptable.

20 The present invention, therefore, relates to a process for the removal of carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution containing between 15 and 45 parts by
25 weight based on total solution, preferably between 15 and 40 parts by weight, of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine,
30 the amounts of water, sulfolane and amine together being 100 parts by weight, the process being carried out in the presence of a primary or secondary amine compound in an

amount between 0.5 and 15 wt%, preferably between 0.5 and 10 wt%, based on water, sulfolane and amine.

When compared with a prior art process, i.e. the same process without the additional use of a primary or
5 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
10 regeneration heat requirement is lower (resulting is less cooling capacity). When compared with another prior art process, i.e. an absorbent containing aqueous amines, especially DMEA and piperazine, the addition of sulfolane results in the possibility to produce carbon dioxide at
15 intermediate pressures, e.g. pressures between 3 and 15 bara, preferably between 5 and 10 bara.

The gases to be treated in the process according to the present invention may be synthesis gas, obtained for instance by (catalytic) partial oxidation and/or by steam
20 methane reforming of hydrocarbons, e.g. methane, natural or associated gas, naphtha, diesel and liquid residual fractions, gases originating from coal gasification, coke oven gases, refinery gases, hydrogen and hydrogen containing gases, and is especially synthesis gas or
25 natural gas.

The amounts of acidic gaseous compounds may range from a few tenth of a percent up to 70 or even 80 vol% of the total gas stream. Suitably the amount of carbon dioxide is between 1 and 45 mol%, preferably between 5
30 and 25 mol%, the amount of hydrogen sulphide is between 0 and 25 mol%, preferably between 0 and 10 mol%, and the amount of COS is between 0 and 2 mol% (all % based on total gas stream).

In the aqueous absorbent in the present process 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 results in optimum carbon dioxide removal in most cases.

The amine derived from ethanol amine may be a single secondary or tertiary amine derived from ethanol amine or mixtures of secondary amines and/or tertiary amines.

Suitable amines are secondary amines derived from ethanol amine which ethanol amine may or may not be substituted at one or both carbon atoms. Preferably the ethanol amine is not substituted or substituted at one carbon atom. Suitable substituents are C₁₋₄ alkyl groups, preferably methyl or ethyl groups, more preferably methyl. The amine group is substituted by a C₁₋₄ alkyl group, which group is optionally substituted by a hydroxyl group. Preferred amine substituent groups are methyl, 2-(1-hydroxyethyl) and 1-(2-hydroxypropyl). Very suitable amines are DIPA, DEA or MMEA, preferably DIPA.

Another group of suitable amines are tertiary amines derived from ethanolamine which ethanolamine may or may not be substituted at one or both carbon atoms. Preferably the ethanolamine is not substituted or substituted at one carbon atom. Suitable substituents are C₁₋₄ alkyl groups, preferably methyl or ethyl groups, more preferably methyl. The second substituents may be chosen from the same group as the first substituent. The third substituent of the amine group is a C₁₋₄ alkyl group, which group is optionally substituted by a hydroxyl group. Preferred amine substituent groups are

methyl, 1-(2-hydroxyethyl) and 1-(2-hydroxypropyl). Very suitable amines are MDEA or DMEA, preferably MDEA.

5 The primary or secondary amine compound has suitably a pK_b (at 25 °C in water) below 5.5, preferably below 5, more preferably below 4.5. A lower pK_b results in improved process results in the form of increased CO_2 absorption.

10 The primary or secondary amine compound to be added to the absorption solution suitably reacts faster with carbon dioxide under the same conditions than the amine reacts with carbon dioxide. Preferably the primary or secondary amine compound reacts at least twice as fast with carbon dioxide then the amine reacts with carbon dioxide, the reaction velocity being defined as the
15 reaction velocity constant (at 25 °C). More preferably the primary or secondary amine compound reacts five times as fast as the amine, still more preferably reacting twenty times as fast as the amine. It is preferred to use in the case of a secondary amine a primary amine
20 compound, and in the case of a tertiary amine a primary or secondary amine. Very suitable compounds are piperazine, methyl ethanol amine, or (2-aminoethyl)-ethanol amine, especially piperazine.

25 The amount of primary or secondary amine compound will usually be between 0.5 and 15 wt% based on water, sulfolane and amine, preferably between 1 and 10 wt%, more preferably about 4 wt%.

30 The amount of primary or secondary amine compound is suitably at least 0.8 mol/l, especially between 1.0 mol/l and 3.0 mol/l, more especially between 1.0 mol and 3.0 mol/l, especially piperazine. For the specific combination of MDEA and piperazine a preferred embodiment

is the use of 0.7-0.9 mol/l of piperazine, especially 0.6-0.8 mol/l.

The process according to the present invention is suitably carried out at a temperature between 15 and 90 °C, preferably at a temperature of at least 20 °C, more preferably between 25 and 80 °C, still more preferably between 40 and 65 °C, and even still mote preferably at about 55 °C. The process is suitably carried out at a pressure between 10 and 150 bar, especially between 25 and 90 bara.

The invention will usually be carried out as a continuous process, which process also comprises the regeneration of the loaded solvent.

The contacting of the gas mixture with the absorbent solvent is well known in the art. It 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 CO₂ removal can be optimised by regulating the solvent/gas ratio. A suitable solvent/gas ratio is from 1.0 to 10 (w/w), preferably between 2 and 6. The loaded solvent may contain beside CO₂ and optionally H₂S 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 than the sum of the partial pressures belonging to the CO₂ and optionally H₂S and/or COS. In this way only very small amounts of CO₂ and optionally H₂S and COS are released from the solvent together with the (non-acid) compounds. The loaded solvent may advantageously be flashed in a second step to a pressure which is below the partial

pressures of CO₂ and optionally H₂S and COS at the prevailing temperature. Usually the flash is carried out at a pressure between 1 and 15 bara, preferably between 1 and 10 bara, more preferably ambient pressure. In the gas set free during the flashing large amounts of the carbon dioxide and optionally H₂S and/or COS are present.

The loaded solvent, optionally after flashing as described above is regenerated at a relatively high temperature suitably at a pressure between 1 and 2 bara. The regeneration is suitably carried out by heating in a regeneration column, suitably at a temperature between 70 and 150 °C. The heating is preferably carried out with steam or hot oil. The lean absorbent solvent will be used again in the absorption stage described before. Suitably the lean solvent is heat exchanged with the loaden solvent.

The invention further relates to an absorbent solvent containing between 15 and 45 parts by weight based on total solution, preferably between 15 and 40 parts by weight, of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine, the amounts of water, sulfolane and amine together being 100 parts by weight and a primary or secondary amine compound in an amount between 0.5 and 15 wt% based on water, sulfolane and amine. The preferred individual compounds of the absorbent solvent and the ranges in the solvent are similarly defined as in the way as has been done for the process as described above.

EXAMPLE

A stream of natural gas comprising 11.9 vol% carbon dioxide was washed with an absorbent solution comprising

35 wt% MDEA, 18 wt% sulfolane and 43 wt% water. A commercially available standard absorber was used. At a liquid/gas ratio of 4.4, the carbon dioxide was removed until a level of 3.1 vol%. Addition of 1 wt% piperazine resulted in a further reduction of the amount of carbon dioxide ((1.7 vol%). Addition of another 1 wt% piperazine resulted in a further reduction of carbon dioxide (1.3 vol%).

A similar experiment as described above was done at a liquid/gas ratio of 3.1 and using 2 wt% piperazine. This resulted in a carbon dioxide level 1.9 vol%.

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C L A I M S

1. Process for the removal of carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution containing between 15 and 45 parts by weight based on total solution of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine, the amounts of water, sulfolane and amine together being 100 parts by weight, the process being carried out in the presence of a primary or secondary amine compound in an amount between 0.5 and 15 wt% based on water, sulfolane and amine.
2. Process according to claim 1, in which the gas stream is natural gas or synthesis gas.
3. Process according to claim 1 or 2, in which the amount of carbon dioxide is between 1 and 45 mol%, preferably between 5 and 25 mol%, the amount of hydrogen sulphide is between 0 and 25 mol%, preferably between 0 and 10 mol%, and the amount of COS is between 0 and 2 mol% (all % based on total gas stream).
4. Process according to any of claims 1 to 3, in which the amount of water is between 20 and 45 parts by weight, the amount of sulfolane is between 20 and 35 parts by weight and the amount of amine is between 40 and 55 parts by weight, the amounts of water, sulfolane and amine together being 100 parts by weight.

5. Process according to any of claims 1 to 4, in which the secondary amine derived from ethanolamine is DIPA, DEA or MMEA, preferably DIPA.

6. Process according to any of claims 1 to 4, in which the tertiary amine derived from ethanolamine is MDEA or DEMEA, preferably MDEA.

7. Process according to any of claims 1 to 6, in which the primary or secondary amine compound has a pK_b (at 25 °C in water) below 5, preferably below 4.5.

8. Process according to any of claims 1 to 6, in which the primary or secondary amine compound reacts at least twice as fast with carbon dioxide then the amine reacts with carbon dioxide, the reaction velocity defined by the reaction velocity constant (at 25 °C), the primary or secondary amine compound preferably reacting five times as fast as the amine, more preferably reacting twenty times as fast as the amine.

9. Process according to any of claims 1 to 8, in which the primary or secondary amine compound is piperazine, methyl ethanol amine, or (2-aminoethyl)ethanol amine, especially piperazine.

10. Process according to any of claims 1 to 9, in which the amount of primary or secondary amine compound is between 2.5 and 10 wt%.

11. Process according to any of claims 1 to 10, in which the amount of primary or secondary amine compound is at least 0.8 mol/l, especially between 1.0 mol/l and 3.0 mol/l, more especially between 1.0 mol and 3.0 mol piperazine/l.

12. Process according to any of claims 1 to 11, in which the process is carried out at a temperature of at least 20 °C, preferably between 25 and 90 °C, more preferably

between 40 and 65 °C at a pressure between 25 and 90 bara.

13. Process according to any of claims 1 to 12, which process also comprises a regeneration of the loaded solvent.

14. Process according to any of claims 1 to 13, in which the process is carried out a pressure between 25 and 90 bara, in which process the loaded solvent is flashed off at a pressure between 1 and 15 bara, followed by regeneration at a pressure between 1 and 2 bara.

15. An absorbent liquid containing between 15 and 45 parts by weight based on total solution of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine, the amounts of water, sulfolane and amine together being 100 parts by weight and a primary or secondary amine compound in an amount between 0.5 and 15 wt% based on water, sulfolane and amine.

16. An absorbent liquid as defined in claim 15, the individual compounds further defined as in claims 4, 5, 6, 7, 8, 9, 10 or 11