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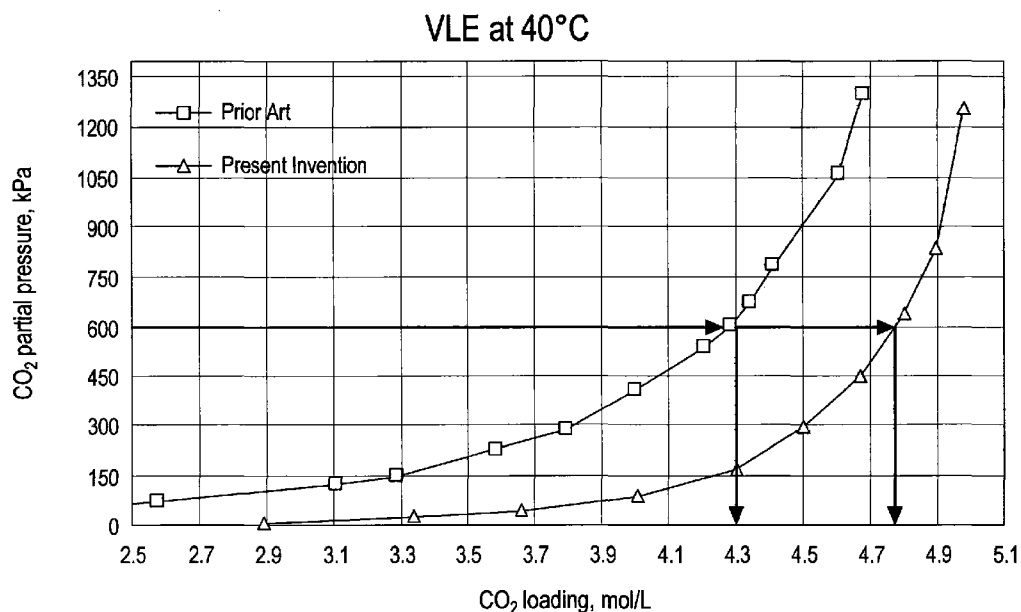


Figure 2

(57) Abstract: The present invention relates to an absorption solvent and, more particularly, to an absorption solvent for removing carbon dioxide from a gaseous mixture having high carbon dioxide partial pressure.

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Title: Solvent And Process For Removing Carbon Dioxide From A Gaseous Mixture Having High Carbon Dioxide Partial Pressures

Description of Invention

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FIELD OF TECHNOLOGY

The present invention relates to an absorption solvent and, more particularly, to an absorption solvent for removing carbon dioxide from a gaseous mixture
10 having high carbon dioxide partial pressure.

BACKGROUND OF THE INVENTION

The purification of gaseous mixtures, and in particular the purification of
15 hydrocarbon gaseous mixtures such as natural gas, which consists primarily of methane, or of synthesis gas, in order to remove contaminants and impurities from them is a common operation in industry. These impurities and contaminants are in particular the "acidic gases" such as for example carbon dioxide (CO₂) and hydrogen sulphide (H₂S); water, and certain hydrocarbons.

20

Generally, a solvent has its own advantages and disadvantages, for instance, properties such as loading capacity, kinetics, regeneration energy, selectivity, stability, corrosivity, etc. determine the operational performance of a solvent. This disclosure is directed to an improved solvent with unexpected properties.

25

SUMMARY OF THE INVENTION

The present invention relates to a solvent composition for partially or completely removing carbon dioxide gas from a feed gas stream by washing
30 the gaseous stream with a solution containing a combination of chemical solvents. The present invention further relates to a process carried out in the

presence of an alkanolamine compound in an amount of from 10 to 65 wt.% (or 20 to 50 wt.%), a selective activator (otherwise referred to as a polyamine) to promote the reaction kinetics in an amount of from 3 to 25 wt.%, the balance being water and unavoidable impurities. Additionally, the present disclosure
5 relates to an absorbent liquid to be used in a purification process for the removal of acid gases.

Representative features of the present invention are set out in the following clauses, which stand alone or may be combined, in any combination, with one
10 or more features disclosed in the text and/or figures of the specification.

The present invention is now described with reference to the following clauses:

1. A solvent for removing gases from a gaseous mixture comprising:
15 a polyamine present in an amount from 3% to 25% by weight;
a sterically hindered alkanolamine present in an amount from 10% to 65% by weight;
the balance being water and unavoidable impurities.
- 20 2. The solvent of clause 1, wherein the polyamine is present in an amount from 5% to 15% by weight.
3. The solvent of clause 1 or clause 2, wherein the polyamine is present in an amount of: 5% by weight ($\pm 10\%$); or, 10% by weight ($\pm 10\%$); or, 15% by
25 weight ($\pm 10\%$).
4. The solvent of any one of clauses 1 to 3, wherein the sterically hindered alkanolamine is present in an amount of: from 20% to 50% by weight; or, from 30% to 40% by weight.

30

5. The solvent of any one of clauses 1 to 4, wherein the sterically hindered alkanolamine is present in an amount of: 45% by weight ($\pm 10\%$); or, 40% by weight ($\pm 10\%$); or, 30% by weight ($\pm 10\%$); or, 25% by weight ($\pm 10\%$).

5 6. The solvent of any one of clauses 1 to 5, wherein the polyamine is: 2-piperazine-1-ethylamine (otherwise known as 2-piperazin-1-ylethanamine, amino ethyl piperazine or AEP); and/or, 1-(2-hydroxyethyl)piperazine; and/or, piperazine; and/or, 1,4-diaminocyclohexane; and/or, 4-aminopiperidine; and/or, 4-amino-1-piperidineethanol; and/or, 3-dimethylamino-1-propylamine; and/or, *N*-methylamino-1-propylamine; and/or, 3-diethylamino-1-propylamine; and/or, *N*-ethylamino-1-propylamine; optionally, wherein:
10 the polyamine is 2-piperazine-1-ethylamine.

7. The solvent of any one of clauses 1 to 6, wherein the sterically hindered alkanolamine is: 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD); and/or, 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD); and/or, 2-amino-2-methyl-1-propanol; and/or, 2-amino-2-methyl-1,3-propanediol (otherwise known as AMPD); and/or, 2-methylamino-2-ethyl-1,3-propanediol (otherwise known as MAEPD); and/or, 2-methylamino-2-hydroxymethyl-1,3-propanediol (otherwise known as MAHPD); and/or, 2-methylamino-2-methyl-1,3-propanediol (otherwise known as MAMPD); optionally, wherein:

the sterically hindered alkanolamine is: 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD); and/or, 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD).
25

8. The solvent of any one of clauses 1 to 7, wherein the polyamine is 2-piperazine-1-ethylamine (otherwise known as amino ethyl piperazine or AEP) and the sterically hindered alkanolamine is 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD).
30

9. The solvent of any one of clauses 1 to 8, wherein the polyamine is 2-piperazine-1-ethylamine (otherwise known as amino ethyl piperazine or AEP) and the sterically hindered alkanolamine is 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD).

5

10. A process for removal of acid gases from a gaseous mixture comprising the steps of:

obtaining a solvent, the solvent comprising: a polyamine present in an amount from 3% to 25% by weight; a sterically hindered alkanolamine present
10 in an amount from 10% to 65% by weight; the balance being water and unavoidable impurities; optionally, the solvent having a temperature of from 30°C to 65°C; and

applying the solvent to a gaseous mixture comprising one or more gases selected from the group consisting of: carbon dioxide, mercaptans,
15 hydrogen sulphide, and carbonyl sulphide.

11. The process of clause 10, wherein the solvent is a solvent according to any one of clauses 1 to 9.

20 12. The process of clause 10 or clause 11, further comprising the step of: heating the gas absorbed solvent to a temperature of from 65°C to 110°C.

13. The process of any one of clauses 10 to 12, further comprising the step
25 of:

loading the solvent into a regeneration column with at least carbon dioxide/acid gas at a regeneration pressure of from 0 bar to 5 bar and at a temperature of from 75°C to 130°C.

30 14. The process of any one of clauses 10 to 13, further comprising the step of:

heating the solvent to a temperature of from 105°C to 130°C.

15. The process of any one of clauses 10 to 14, wherein the gaseous mixture comprises one or more gases present at less than 4 ppm.

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16. The process of any one of clauses 10 to 15, further comprising the step of:

a. reducing the concentration of carbon dioxide in the gaseous mixture to less than 100 ppm by volume; and/or,

10 b. reducing the concentration of H₂S in the treated gaseous mixture to less than 2 ppm by volume and reducing the concentration of carbon dioxide in the treated gaseous mixture to less than 50 ppm by volume; and/or,

c. reducing the concentration of mercaptans in the treated gaseous mixture to less than 5 ppm by volume.

15

17. The process of any one of clauses 10 to 16, further comprising the step of:

reducing a concentration of carbon dioxide in the gaseous mixture to less than 10 ppm.

20

18. The process of any one of clauses 10 to 17, wherein the gaseous mixture is a synthesis gas obtained from a process selected from the group consisting of: a coal gasification process, a steam reforming process, and a direct reduced iron process; each synthesis gas comprising one or more of
25 carbon monoxide, carbon dioxide, hydrogen sulfide, carbonyl sulfide, hydrogen, nitrogen, and methane.

19. The process of any one of clauses 10 to 18, wherein the gaseous mixture is natural gas comprising methane.

30

BRIEF DESCRIPTION OF THE DRAWINGS

The features, nature, and advantages of the present disclosure will become more apparent from the detailed description set forth below when taken in
5 conjunction with the figures.

Figure 1 illustrates a graph showing vapor liquid equilibrium (VLE) relationship between partial pressure of CO₂ in the vapor phase and the loading (i.e. concentration) of CO₂ in a solvent at 40°C.

10

Figure 2 is a graphical representation illustrating vapor liquid equilibrium (VLE) data at 40°C of an absorbent solution (i.e. a solvent) of the present invention and an absorbent solution (i.e. a solvent) of the prior art, according to the present disclosure.

15

DETAILED DESCRIPTION OF THE INVENTION

The following description and examples illustrate various embodiments of the present disclosure in detail. Those of skill in the art will recognize that there
20 are numerous variations and modifications of this disclosure that are encompassed by its scope. Accordingly, the description of the disclosed embodiments should not be deemed to limit the scope of the present disclosure.

25 Some examples of this disclosure, illustrating all its features, will now be discussed in detail. The words "comprising," "having," "containing," and "including," and other forms thereof, are intended to be equivalent in meaning and be open ended in that an item or items following any one of these words is not meant to be an exhaustive listing of such item or items, or meant to be
30 limited to only the listed item or items.

It must also be noted that as used herein and in the appended claims, the singular forms "a," "an", and "the" include plural references unless the context clearly dictates otherwise.

- 5 Examples of the present disclosure will be described more fully hereinafter with reference to the accompanying figures in which examples are shown. Examples of the claims may, however, be embodied in many different forms and should not be construed as limited to the examples set forth herein. The examples set forth herein are non-limiting examples and are merely examples
10 among other possible examples.

Definitions

- Unless defined otherwise, all technical and scientific terms used herein have
15 the same meaning as is commonly understood by one of ordinary skill in the art. All patents, applications, published applications and other publications referenced herein are incorporated by reference in their entirety unless stated otherwise. In the event that there is a plurality of definitions for a term herein, those in this section prevail unless stated otherwise.

20

- As used herein, "polyamine" refers to a compound with 2 or more nitrogen atoms. In some examples, "polyamine" refers to a compound with three nitrogen atoms: one primary nitrogen atom, one secondary nitrogen atom and one tertiary nitrogen atom. Examples of "polyamines" include: 2-piperazine-1-ethylamine (otherwise known as 2-piperazin-1-ylethanamine, amino ethyl
25 piperazine, 1-(2-aminoethyl)piperazine or AEP); 1-(2-hydroxyethyl)piperazine; piperazine; 1,4-diaminocyclohexane; 4-aminopiperidine; 4-amino-1-piperidineethanol; 3-dimethylamino-1-propylamine; *N*-methylamino-1-propylamine; 3-diethylamino-1-propylamine; and, *N*-ethylamino-1-propylamine.
- 30 In the solvents of the presently claimed invention, the "polyamine" acts as an "activator" or "amine promoter", meaning it acts faster to remove gases than

the other compound(s) present in the solvent and therefore improves the kinetics of the CO₂ absorption of the solvent as a whole.

Some of the example “polyamines” described above are set out in Table 1.

Table 1: Examples of “polyamines”

Name	Abbreviation	Formula	MW/ g mol ⁻¹	CAS#	Synonyms
2-piperazine-1-ethylamine	AEP	C ₆ H ₁₅ N ₃	129.21	140-31-8	2-piperazin-1-ylethanamine; amino ethyl piperazine; 1-(2-aminoethyl)piperazine
1-(2-hydroxyethyl)piperazine	HEP	C ₆ H ₁₄ N ₂ O	130.19	103-76-4	2-piperazinoethanol; piperazine-1-ethanol
piperazine	PZ	C ₄ H ₁₀ N ₂	86.14	110-85-0	1,4-diazacyclohexane; 1,4-piperazine; hexahydropyrazine; pyrazine hexahydride
1,4-diaminocyclohexane	DACH	C ₆ H ₁₄ N ₂	114.19	2615-25-0	1,4-cyclohexanediamine; 1,4-cyclohexylenediamine; cyclohexane-1,4-diamine; hexahydro-1,4-phenylenediamine
4-amino piperidine	4-AP	C ₅ H ₁₂ N ₂	100.17	13035-19-3	
4-amino-1-piperidineethanol	4-A-1PE	C ₇ H ₁₆ N ₂ O	144.22	89850-72-6	2-(4-amino-1-piperidinyl)ethanol; 2-(4-aminopiperidin-1-yl)ethanol; 2-(4-aminopiperidin-1-yl)ethan-1-ol; 2-(4-amino-piperidin-1-yl)-ethanol
3-dimethylamino-1-propylamine	DMAPA	C ₅ H ₁₄ N ₂	102.18	109-55-7	3-aminopropyl(dimethylamine; 1-Amino-3-(dimethylamino)propane; (3-aminopropyl)dimethylamine; γ-(dimethylamino)propylamine
N-methylamino propylamine	MMAPA	C ₄ H ₁₂ N ₂	88.15	6291-84-5	
3-diethylamino propylamine	DEAPA	C ₇ H ₁₈ N ₂	130.23	104-78-9	N,N-diethyl-1,3-propanediamine; N,N'-diethyl-1,3-diaminopropane; N,N'-diethyltrimethylenediamine
N-ethylamino propylamine	MEAPA	C ₅ H ₁₄ N ₂	102.18	10563-23-2	1,3-propanediamine, N-ethyl-; 1-amino-3-(ethylamino)propane; N-Ethyl-1,3-propanediamine

As used herein, “sterically hindered alkanolamine” refers to a compound with at least one amine group and at least one hydroxyl group, wherein the amine group is bonded to a carbon atom, which carbon atom is itself bonded to three other carbon atoms (i.e. the carbon atom to which the at least one amine group is bonded is itself sterically hindered). In some examples, the amine group is a primary amine or a secondary amine. Examples of “sterically hindered alkanolamines” include: 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD); 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD); 2-amino-2-methyl-1,3-propanediol (otherwise known as AMPD); 2-methylamino-2-ethyl-1,3-propanediol (otherwise known as MAEPD); 2-methylamino-2-hydroxymethyl-1,3-propanediol (otherwise known as MAHPD); and, 2-methylamino-2-methyl-1,3-propanediol (otherwise known as MAMPD).

Some of the example “sterically hindered alkanolamine” described above are set out in Table 2.

Table 2: Examples of “sterically hindered alkanolamines”

Name	Abbreviation	Formula	MW	CAS#	Synonyms
2-amino-2-ethyl-1,3-propanediol	AEPD	C ₅ H ₁₃ NO ₂	119.16	115-70-8	2-amino-1,3-dihydroxy-2-ethylpropane; 1,3-propanediol, 2-amino-2-ethyl-; 2-amino-2-ethylpropane-1,3-diol
2-amino-2-hydroxymethyl-1,3-propanediol	AHPD	C ₄ H ₁₁ NO ₃	121.14	77-86-1	Tris(hydroxymethyl)aminomethane; 1,3-propanediol, 2-amino-2- (hydroxymethyl)-; 2-amino-2-(hydroxymethyl)propan-1,3-diol; Trimethylol Aminomethane
2-amino-2-methyl-1,3-propanediol	AMPD	C ₄ H ₁₁ NO ₂	105.14	115-69-5	1,3-propanediol, 2-amino-2-methyl-; 2-amino-2-methylpropane-1,3-diol; aminomethyl propanediol
2-methylamino-2-ethyl-1,3-propanediol	MAEPD	C ₆ H ₁₅ NO ₂	133.19	27646-82-8	1,3-propanediol, 2-ethyl-2-(methylamino)-; 2-ethyl-2-(methylamino)-1,3-propanediol;
2-methylamino-2-hydroxymethyl-1,3-propanediol	MAHPD	C ₅ H ₁₃ NO ₃	135.16	74178-02-2	1,3-propanediol, 2-(hydroxymethyl)-2-(methylamino)-; 2-(Hydroxymethyl)-2-(methylamino)-1,3-propanediol
2-methylamino-2-methyl-1,3-propanediol	MAMPD	C ₅ H ₁₃ NO ₂	119.16		1,3-propanediol, 2-methyl-2-(methylamino)-; 2-methyl-2-(methylamino)-1,3-propanediol; 2-methyl-2-(methylamino)propane-1,3-diol

As used herein, “unavoidable impurities” refers to components present in a mixture in small amounts which have no bearing on the function of the overall mixture. Unavoidable impurities are generally inert and non-reactive. In some examples, “small amounts” refers to less than 5% by weight, or less than 4%
5 by weight, or less than 3% by weight, or less than 2% by weight, or less than 1% by weight, or less than 0.5% by weight.

Where a range of values is provided, it is understood that the upper and lower limit, and each intervening value between the upper and lower limit of the
10 range is encompassed within the examples.

Removing carbon dioxide from a gas stream

This disclosure relates to a process for removing carbon dioxide from a gas
15 stream by washing the gas stream with an aqueous solution containing, a sterically hindered alkanolamine (for example, 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) and/or 2-amino-2-ethyl-1,3-propanediol (AEPD)), a polyamine (sometimes referred to as “an activator” in this specification) (for example, 2-piperazine-1-ethylamine and/or piperazine) as an aqueous
20 solution.

Solvent characteristics play a role in both equipment size and process energy requirements when undertaking carbon dioxide capture. In certain circumstances, the following factors can be considered when choosing a
25 solvent:

- Cyclic capacity (the difference between CO₂ concentration in the solvent leaving an absorber and that leaving a reboiler in a carbon dioxide capture system): a solvent having a high or higher cyclic capacity is desirable since higher cyclic capacity results in a lower reboiler duty,
30 reduced electrical consumption in pumps, and potential downsizing of equipment, which can result in lower investment costs;

- Evaporative losses: a carbon capture solvent will have high operational evaporative losses if it exhibits a high vapor pressure. Traditionally, gas treatment processes incorporate a water wash section at the top of the absorber column to mitigate against evaporative losses. The use of a solvent possessing a low vapor pressure is desirable, leading to the reduction in the size of, or even the need for a water wash section.

These properties, namely, CO₂ cyclic capacity and vapor pressure, play a significant role in the process design and operation of a gas treating (e.g. a carbon capture) process plant. Generally, absorption solutions with high CO₂ loading capacities and low vapor pressures offer low operating cost for a gas treatment processing plant.

The solvents described herein includes a sterically hindered alkanolamine, capable of achieving a high CO₂ loading capacity. One specific improvement in the performance of the acid gas cleaning system, relative to prior art utilising aqueous solvents containing 2-amino-2-methyl propanol, relates to the solubility of the amine salts at high CO₂ solvent loadings. Solutions containing 2-amino-2-methyl propanol (AMP) at concentrations greater than 25 wt.% tend to precipitate out of solution as a bicarbonate salt, owing to the relative insolubility of the salts, when loaded with high levels of CO₂. However, the present inventors discovered that the solubility of the bicarbonate salts of 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD) and 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD) in aqueous solution are much greater than in the case of 2-amino-2-methyl propanol solvent mixtures and thus, solutions containing 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD) and/or 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD) were found to offer higher capacity CO₂ loading without precipitation. Without wishing to be bound by theory, it is believed that this higher capacity CO₂ loading without precipitation is due to the solubility of amine bicarbonate salts in the reaction system.

Whilst the present inventors made this discovery (the solubility of the bicarbonate salts of AHPD and AEPD in aqueous solution are much greater than in the case of 2-amino-2-methyl propanol solvent mixtures) with AHPD and AEPD, it is believed that this discovery also applies to other “sterically hindered alkanolamines”, including: 2-amino-2-methyl-1,3-propanediol (otherwise known as AMPD); 2-methylamino-2-ethyl-1,3-propanediol (otherwise known as MAEPD); 2-methylamino-2-hydroxymethyl-1,3-propanediol (otherwise known as MAHPD); and, 2-methylamino-2-methyl-1,3-propanediol (otherwise known as MAMPD).

The solvent described herein includes a sterically hindered alkanolamine for high CO₂ loading capacity. To improve the performance of an acid gas cleaning system in comparison with prior art *N*-methyl diethanolamine (MDEA), which results in relatively low carbon dioxide loading capacity. Significantly higher carbon dioxide loading is observed in aqueous solutions containing 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD) and/or 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD) than the prior art solvent technology containing MDEA.

20

To improve the kinetics of the acid gas cleaning system and deep removal of the acid gas cleaning system such as carbon dioxide, a polyamine (which can be referred to as an “amine activator”) (e.g. 2-piperazine-1-ethylamine (otherwise known as AEP)) may be utilised in an aqueous solvent system containing at least one sterically hindered alkanolamine. Other examples of suitable “polyamines” to be included in the solvents of the present invention include: 1-(2-hydroxyethyl)piperazine; piperazine; 1,4-diaminocyclohexane; 4-aminopiperidine; 4-amino-1-piperidineethanol; 3-dimethylamino-1-propylamine; *N*-methylamino-1-propylamine; 3-diethylamino-1-propylamine; and, *N*-ethylamino-1-propylamine.

30

A mixture for absorbing the gases disclosed herein from a gas stream includes; at least one sterically hindered alkanolamine (for example 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-ethyl-1,3-propanediol). This mixture demonstrates an absorption capacity and selectivity suitable for acid
5 gas absorption. Furthermore, the performance of this mixture is beneficial at a relatively high partial pressure of CO₂, such as between 1 bar and 50 bar. The liquid/gas ratio of the solvent system disclosed herein may be manipulated, for example at high pressures and/or deep carbon dioxide removal.

10 The addition of a suitable activator compound (otherwise referred to as a polyamine), for example in relatively smaller amounts than the sterically hindered alkanolamine, allows for more carbon dioxide to be flashed at relatively high pressure as compared to similar, aqueous chemical absorbents known in the art. For example, the addition of AEP results in improved kinetics
15 of the system as compared to systems currently known in the art, thereby resulting in an improvement in the liquid/gas ratio and reduction in the vapor pressure of the solvent system. Further, a deep removal of carbon dioxide may be obtained.

20 The present disclosure therefore provides a process for removing carbon dioxide, and optionally hydrogen sulphide, from a gas stream by washing the gas stream with an aqueous solution comprising: a sterically hindered alkanolamine (for example, 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-ethyl-1,3-propanediol); and a polyamine (otherwise referred to as
25 an amine activator) (for example, 2-piperazine-1-ethylamine); in an aqueous solution.

The gases to be treated in the process disclosed herein may be a synthesis gas, obtained by, for example, (catalytic) partial oxidation and/or by steam
30 methane reformation of hydrocarbons, for example methane, natural or associated gas, Naphtha, diesel and liquid residual fractions, gases originating

from coal/biomass gasification, coke oven gases, refinery gases, hydrogen and hydrogen containing gases, and synthesis gas or natural gas. The process may be carried out at a temperature of from 15°C to 90°C. Alternatively, the process may be carried out at from 25°C to 80°C.

- 5 Alternatively, the process may be carried out from 40°C to 65°C. The process may also be carried out at a pressure of from 10 bar to 150 bar. Alternatively, the process may be carried out at a pressure of from 15 bar to 90 bar.

The disclosed process may be carried out continuously through regeneration of a loaded solvent. Contact of the gas mixture with the absorbent solvent may be done through any means known in the art. For example, contact of the gas mixture with the absorbent solvent may be carried out in an absorption column having valve trays, bubble cab trays, baffles, and the like, and structured/random packing may also be applied. Changing the solvent/gas ratio may optimize the amount of CO₂ removed. The solvent/gas ratio may be from 1.0 to 10.0 (w/w). The loaded solvent may contain, besides CO₂ and optionally H₂S, appreciable amounts of other compounds from the gas mixture to be purified, such as hydrocarbons, carbon monoxide, hydrogen, and other potential pollutants. These (non-acid) compounds may be removed from the loaded solvent by flashing to a pressure higher than the sum of the partial pressure belonging to the CO₂ and optional H₂S. In this scenario, small amounts of CO₂ and optionally H₂S will be released from the solvent with the (non-acid) compounds. The loaded solvent may also be flashed in a second step to a pressure below the partial pressures of CO₂ and optionally H₂S at the prevailing temperature. This flashing may be carried out at a pressure of from 1 bar to 15 bar. Alternatively, this flashing may be carried out at from 1 bar to 10 bar. Alternatively, the flashing may occur at ambient pressure. After flashing, the loaded solvent may be regenerated at a relatively high temperature and at a pressure of from 1 bar to 5 bar. Alternatively, regeneration of the loaded solvent may occur at from 1 bar to 3 bar. The regeneration may be carried out by heating, in a regeneration column, at a

temperature of from 70°C to 150°C. The heating may be carried out with steam or hot oil. The lean absorbent solvent may be used again in the absorption stage. The lean solvent may be heat exchanged with the loaded solvent.

5

Additionally, the solvent of the presently claimed invention may be able to remove H₂S, carbonyl sulphide (COS) and mercaptans from the purification process and may be able to make the aforementioned gas useful for other applications not disclosed herein.

10

In some embodiments, at least one sterically hindered amine (otherwise referred to as a sterically hindered alkanolamine) such as 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-ethyl-1,3-propanediol is present at from 20 wt.% to 65 wt.% (or to 45 wt.%), and an amine activator (otherwise referred to as a polyamine) such as 2-piperazine-1-ethylamine and/or piperazine is present at from 3 wt.% to 25 wt.%, the balance being water (for example, demineralised water) and unavoidable impurities.

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In some embodiments, at least one sterically hindered amine such as 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-ethyl-1,3-propanediol is present at from 30 wt.% to 45 wt.%, and an amine activator (otherwise referred to as a polyamine) such as 2-piperazine-1-ethylamine and/or piperazine is present at from 5 wt.% to 15 wt.%, the balance being water and unavoidable impurities.

25

In an example, the solvent may have a composition of 40 wt.% 2-amino-2-hydroxymethyl-1,3-propanediol and/or 40 wt.% 2-amino-2-ethyl-1,3-propanediol, and 5 wt.% 2-piperazine-1-ethylamine, the balance being demineralised water and unavoidable impurities.

30

EXAMPLES

Example 1:

Table 3: Prior art and present invention for CO₂ loading (mol of CO₂ per litre of solvent solution)

Solvent Components in Weight % (the balance being demineralised water)	CO ₂ Loading, mol/L (CO ₂ partial pressure @5 bar, 40C)
Prior Art (45% MDEA + 5%PZ)	4.02
Present Invention (45% AEPD + 5% AEP)	4.70
Prior Art (45% AMP +5% PZ)	N/A (Precipitation occurs)
Prior Art (45% AMP +5% AEP)	N/A (Precipitation occurs)
40% AEPD + 10% AEP	4.73
10% AHPD	0.99
10% AEPD	0.92
20% AHPD	1.93
20% AEPD	1.82
10% AHPD + 10%AEP	2.00
10% AEPD + 10%AEP	1.98
30% AEPD + 15%AEP	3.97
30% AHPD + 15%AEP	4.18
25% AEPD + 15%AEP + 10% MDEA	3.82
30% AEPD + 10%AEP + 10% MDEA	4.08
30% AHPD + 10%AEP + 10% MDEA	3.97
30% AEPD + 5%AEP + 15% MDEA	4.00
30% AHPD + 15%AEP + 5% MDEA	4.02
30% AEPD + 15%AEP + 5% MDEA	4.20

MDEA = *N*-methyl-diethanolamine

PZ = piperazine

AEPD = 2-amino-2-ethyl-1,3-propanediol

10 AEP = 2-piperazine-1-ethylamine

AHPD = 2-amino-2-hydroxymethyl-1,3-propanediol

AMP = 2-amino-2-methyl propanol

Prior Art (45% MDEA + 5% PZ) offers a CO₂ loading capacity in comparison with present invention (45% AEPD + 5% AEP).

- 5 Prior Art (45% AMP +5% PZ) and/or (45% AMP + 5% AEP) on CO₂ loading results in a precipitate out of solution as a bicarbonate salt, owing to the relative insolubility of the salts, when loaded with high levels of CO₂. The solubility of the bicarbonate salts of the solvents of the present Invention (45% AEPD + 5% AEP) does not precipitate out and offers significant high CO₂ loading. Therefore, the solvents of the presently claimed invention provide advantages.

Example 2:

- 15 The presence of 2-amino-2-ethyl-1,3-propanediol (AEPD) provides a relatively low vapor pressure and thus, minimises evaporative vapor solvent losses, when compared to at least a prior art solvent comprising 2-amino-2-methyl propanol.

20 **Table 4:** Vapor pressures of different compounds

Alkanolamine	Vapor Pressure, Pa at 20° C
2-amino-2-ethyl-1,3-propanediol (AEPD)	2.63E-04
2-amino-2-methyl propanol (AMP)	0.045

The values in Table 4 are given for the pure components, i.e. not in solution.

Example 3:

Figure 2 is a graphical representation of the Vapor Liquid Equilibrium data at 40°C of a prior art solvent and a solvent according to the presently claimed invention. From the graph of Figure 2, a solvent according to the presently claimed invention has a higher CO₂ loading compared to the prior art solvent.

For example, at a CO₂ partial pressure of 6 bar (600 kPa) the CO₂ loading with the:

- 10 a. Present Invention (45% AEPD + 5% AEP): 4.76 mol CO₂/L solvent
- b. Prior Art (45% MDEA + 5%PZ): 4.30 mol CO₂/L solvent

MDEA = *N*-methyl-diethanolamine

PZ = piperazine

15 AEPD = 2-amino-2-ethyl-1,3-propanediol

AEP = 2-piperazine-1-ethylamine

In a. and b., the balance is demineralised water.

20 The solvent according to the present invention (a.) has a significantly higher CO₂ loading as a CO₂ partial pressure of 6 bar (600 kPa), when compared to the prior art (b.). Therefore, a solvent according to the present invention provides advantages over the prior art.

25 *From Indian Patent Application Number 201811023872 (filed 26 June 2018), the disclosure of which is hereby incorporated by reference in its entirety:*

Figure 1 illustrates a graph showing vapor liquid equilibrium (VLE) relationship between partial pressure of CO₂ in the vapor phase and the loading (i.e. concentration) of CO₂ in a solvent at 40°C.

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Table 5: a table showing unloaded (no CO₂) solvent viscosity and CO₂ loaded solvent viscosity at 40 °C.

Solvent	Unloaded Viscosity, cP @40 C	CO2 loaded Viscosity, cP @40 C	
		CO2 loading, mol/L	Viscosity, cP
40% DEEA + 10%AEP	4.472	2.000	12.59
10% AHPD + 10%AEP	1.370	0.597	1.78
10% AEPD + 10%AEP	1.470	0.658	1.86
30% AEPD + 15%AEP	3.759	2.020	8.77
30% AHPD + 15%AEP	4.004	2.050	10.62

5

In Table 5, the components are given in weight %. The balance in each case is demineralised water.

DEEA = 2-(diethylamino)ethanol

10 AHPD = 2-amino-2-hydroxymethyl-1,3-propanediol

AEPD = 2-amino-2-ethyl-1,3-propanediol

AEP = 2-piperazine-1-ethylamine

A1. A solvent comprising:

15 a tertiary amine (for example, N-methyl-diethanolamine and/or 2-(diethylamino)ethanol), and/or,

a sterically hindered amine (or sterically hindered alkanolamine) (for example, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-methyl-1-propanol),

20 and/or,

a polyamine (for example, 2-piperazine-1-ethylamine and/or 1-(2-hydroxyethyl)piperazine), and/or,

a carbonate buffer (for example, potassium carbonate), and/or, water (for example, deionised water).

25

A2. A solvent according to clause A1, wherein the solvent comprises: an amino hindered alcohol (optionally, amino-2-methyl-1-propanol), a polyamine (optionally, amino ethyl piperazine) and water.

- 5 *From Indian Patent Application Number 201811024582 (filed 2 July 2018), the disclosure of which is hereby incorporated by reference in its entirety:*

An intensified solvent, in some embodiments, comprises: an alkanolamine, a reactive amine and a carbonate buffer. An intensified solvent, in some
10 embodiments, comprises: a tertiary amine (for example, *N*-methyl-diethanolamine and/or 2-(diethylamino)ethanol), and/or, a sterically hindered amine (or sterically hindered alkanolamine) (for example, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-methylamino-2-methyl propanol and/or 2-amino-2-methyl-1-propanol), and/or, a polyamine (for
15 example, 2-piperazine-1-ethylamine and/or 1-(2-hydroxyethyl)piperazine), and/or, a carbonate buffer (for example, potassium carbonate), and/or, water (for example, deionised water).

In an example of the invention, the solvent may be an intensified solvent.
20 Optionally, the intensified solvent comprises a tertiary amine, a sterically hindered amine (or sterically hindered alkanolamine), a polyamine, a salt and water. The use of an intensified solvent along with microwave radiation is typically applied to increase the absorption of the microwave radiation by the solvent. An intensified solvent optionally contains water, carbonates,
25 bicarbonates and carbamate salts. A rise in temperature may be observed. Without wishing to be bound by theory, the rise in temperature is caused by the interaction between solvent components and the microwave radiation, resulting in the rotation of dipoles of the solvent components and ionic conduction mechanisms.

30

Optionally, the tertiary amine in the intensified solvent is one or more of: *N*-methyl-diethanolamine (MDEA) or 2-(diethylamino)ethanol (DEA). Optionally, the sterically hindered amines (or sterically hindered alkanolamines) in the intensified solvent are one or more of: 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) or 2-amino-2-methyl-1-propanol (AMP). Optionally, the polyamine in the intensified solvent is one or more of: 2-piperazine-1-ethylamine (AEP) or 1-(2-hydroxyethyl)piperazine. Optionally, the salt in the intensified solvent is potassium carbonate. Optionally, water (for example, deionised water) is included in the solvent so that the solvent exhibits a single liquid phase.

B1. An intensified solvent comprising:

- a tertiary amine (for example, *N*-methyl-diethanolamine and/or 2-(diethylamino)ethanol), and/or,
- a sterically hindered amine (otherwise referred to as an alkanolamine) (for example, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-hydroxymethyl-1,3-propanediol and/or 2-amino-2-methyl-1-propanol), and/or,
- a polyamine (for example, 2-piperazine-1-ethylamine and/or 1-(2-hydroxyethyl)piperazine), and/or,
- a carbonate buffer (for example, potassium carbonate), and/or, water (for example, deionised water).

B2. The intensified solvent of clause B1, wherein the intensified solvent is a solvent comprising: an alkanolamine, a reactive amine and a carbonate buffer.

B3. The intensified solvent of clause B1 or clause B2, wherein the intensified solvent is free of monoethanolamine.

When used in this specification and claims, the terms "comprises" and "comprising" and variations thereof mean that the specified features, steps or

integers are included. The terms are not to be interpreted to exclude the presence of other features, steps or components.

5 The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

10

Although certain example embodiments of the invention have been described, the scope of the appended claims is not intended to be limited solely to these embodiments. The claims are to be construed literally, purposively, and/or to encompass equivalents.

15

Claims

1. A solvent for removing gases from a gaseous mixture comprising:
a polyamine present in an amount from 3% to 25% by weight;
5 a sterically hindered alkanolamine present in an amount from 10% to 65% by weight;
the balance being water and unavoidable impurities.
2. The solvent of claim 1, wherein the polyamine is present in an amount
10 from 5% to 15% by weight.
3. The solvent of claim 1 or claim 2, wherein the polyamine is present in
an amount of: 5% by weight ($\pm 10\%$); or, 10% by weight ($\pm 10\%$); or, 15% by
weight ($\pm 10\%$).
15
4. The solvent of any one of claims 1 to 3, wherein the sterically hindered
alkanolamine is present in an amount of: from 20% to 50% by weight; or, from
30% to 40% by weight.
- 20 5. The solvent of any one of claims 1 to 4, wherein the sterically hindered
alkanolamine is present in an amount of: 45% by weight ($\pm 10\%$); or, 40% by
weight ($\pm 10\%$); or, 30% by weight ($\pm 10\%$); or, 25% by weight ($\pm 10\%$).
- 25 6. The solvent of any one of claims 1 to 5, wherein the polyamine is: 2-
piperazine-1-ethylamine (otherwise known as 2-piperazin-1-ylethanamine,
amino ethyl piperazine or AEP); and/or, 1-(2-hydroxyethyl)piperazine; and/or,
piperazine; and/or, 1,4-diaminocyclohexane; and/or, 4-aminopiperidine;
and/or, 4-amino-1-piperidineethanol; and/or, 3-dimethylamino-1-propylamine;
and/or, *N*-methylamino-1-propylamine; and/or, 3-diethylamino-1-propylamine;
30 and/or, *N*-ethylamino-1-propylamine; optionally, wherein:
the polyamine is 2-piperazine-1-ethylamine.

7. The solvent of any one of claims 1 to 6, wherein the sterically hindered alkanolamine is: 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD); and/or, 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as
- 5 AHPD); and/or, 2-amino-2-methyl-1-propanol; and/or, 2-amino-2-methyl-1,3-propanediol (otherwise known as AMPD); and/or, 2-methylamino-2-ethyl-1,3-propanediol (otherwise known as MAEPD); and/or, 2-methylamino-2-hydroxymethyl-1,3-propanediol (otherwise known as MAHPD); and/or, 2-methylamino-2-methyl-1,3-propanediol (otherwise known as MAMPD);
- 10 optionally, wherein:
- the sterically hindered alkanolamine is: 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD); and/or, 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD).
- 15 8. The solvent of any one of claims 1 to 7, wherein the polyamine is 2-piperazine-1-ethylamine (otherwise known as amino ethyl piperazine or AEP) and the sterically hindered alkanolamine is 2-amino-2-hydroxymethyl-1,3-propanediol (otherwise known as AHPD).
- 20 9. The solvent of any one of claims 1 to 8, wherein the polyamine is 2-piperazine-1-ethylamine (otherwise known as amino ethyl piperazine or AEP) and the sterically hindered alkanolamine is 2-amino-2-ethyl-1,3-propanediol (otherwise known as AEPD).
- 25 10. A process for removal of acid gases from a gaseous mixture comprising the steps of:
- obtaining a solvent, the solvent comprising: a polyamine present in an amount from 3% to 25% by weight; a sterically hindered alkanolamine present in an amount from 10% to 65% by weight; the balance being water and
- 30 unavoidable impurities; optionally, the solvent having a temperature of from 30°C to 65°C; and

applying the solvent to a gaseous mixture comprising one or more gases selected from the group consisting of: carbon dioxide, mercaptans, hydrogen sulphide, and carbonyl sulphide.

- 5 11. The process of claim 10, wherein the solvent is a solvent according to any one of claims 1 to 9.
12. The process of claim 10 or claim 11, further comprising the step of:
heating the gas absorbed solvent to a temperature of from 65°C to
10 110°C.
13. The process of any one of claims 10 to 12, further comprising the step of:
loading the solvent into a regeneration column with at least carbon
15 dioxide/acid gas at a regeneration pressure of from 0 bar to 5 bar and at a temperature of from 75°C to 130°C.
14. The process of any one of claims 10 to 13, further comprising the step of:
20 heating the solvent to a temperature of from 105°C to 130°C.
15. The process of any one of claims 10 to 14, wherein the gaseous mixture comprises one or more gases present at less than 4 ppm.
- 25 16. The process of any one of claims 10 to 15, further comprising the step of:
a. reducing the concentration of carbon dioxide in the gaseous mixture to less than 100 ppm by volume; and/or,
b. reducing the concentration of H₂S in the treated gaseous mixture to
30 less than 2 ppm by volume and reducing the concentration of carbon dioxide in the treated gaseous mixture to less than 50 ppm by volume; and/or,

c. reducing the concentration of mercaptans in the treated gaseous mixture to less than 5 ppm by volume.

17. The process of any one of claims 10 to 16, further comprising the step
5 of:

reducing a concentration of carbon dioxide in the gaseous mixture to less than 10 ppm.

18. The process of any one of claims 10 to 17, wherein the gaseous
10 mixture is a synthesis gas obtained from a process selected from the group consisting of: a coal gasification process, a steam reforming process, and a direct reduced iron process; each synthesis gas comprising one or more of carbon monoxide, carbon dioxide, hydrogen sulfide, carbonyl sulfide, hydrogen, nitrogen, and methane.

15

19. The process of any one of claims 10 to 18, wherein the gaseous mixture is natural gas comprising methane.

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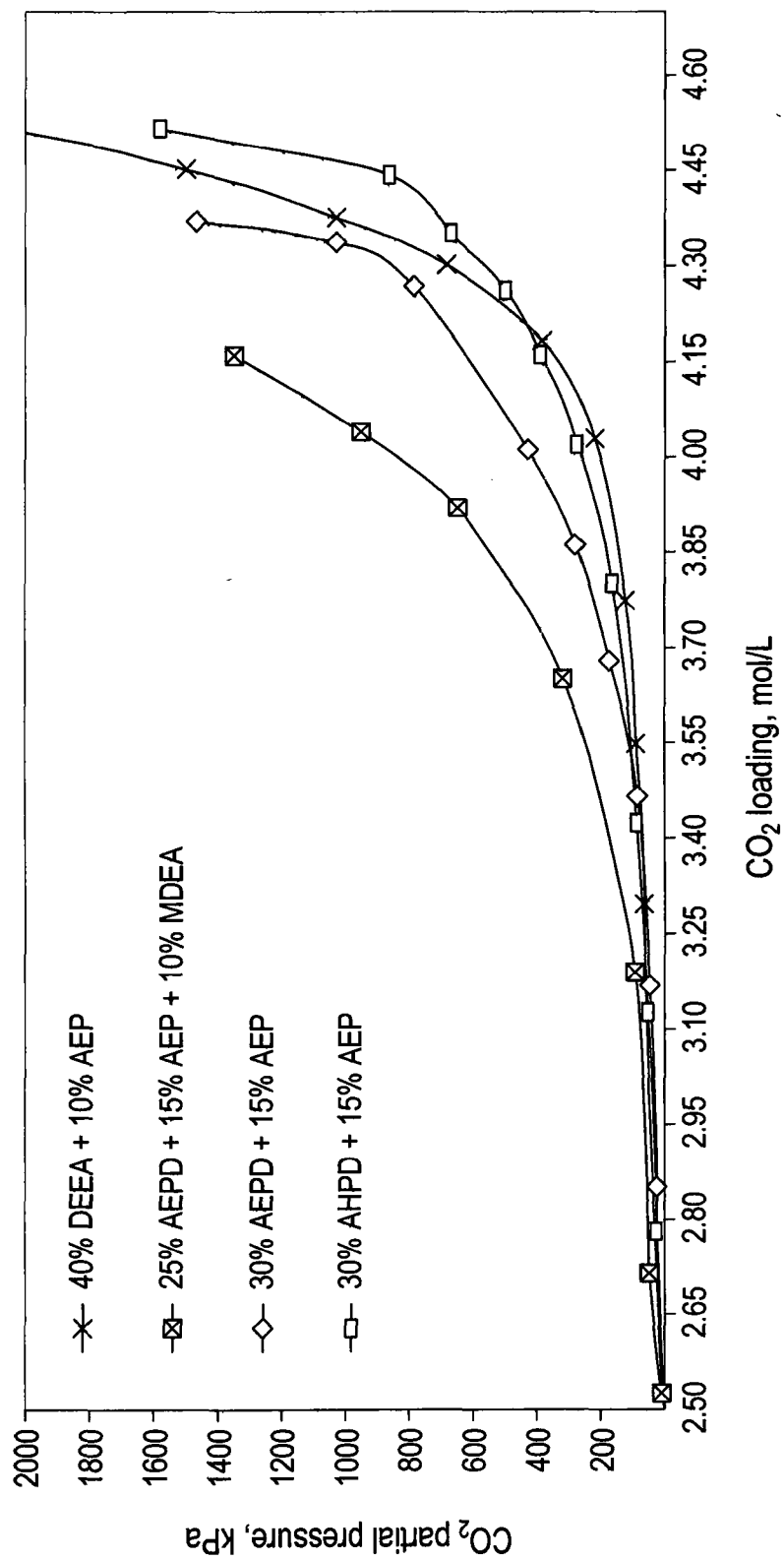
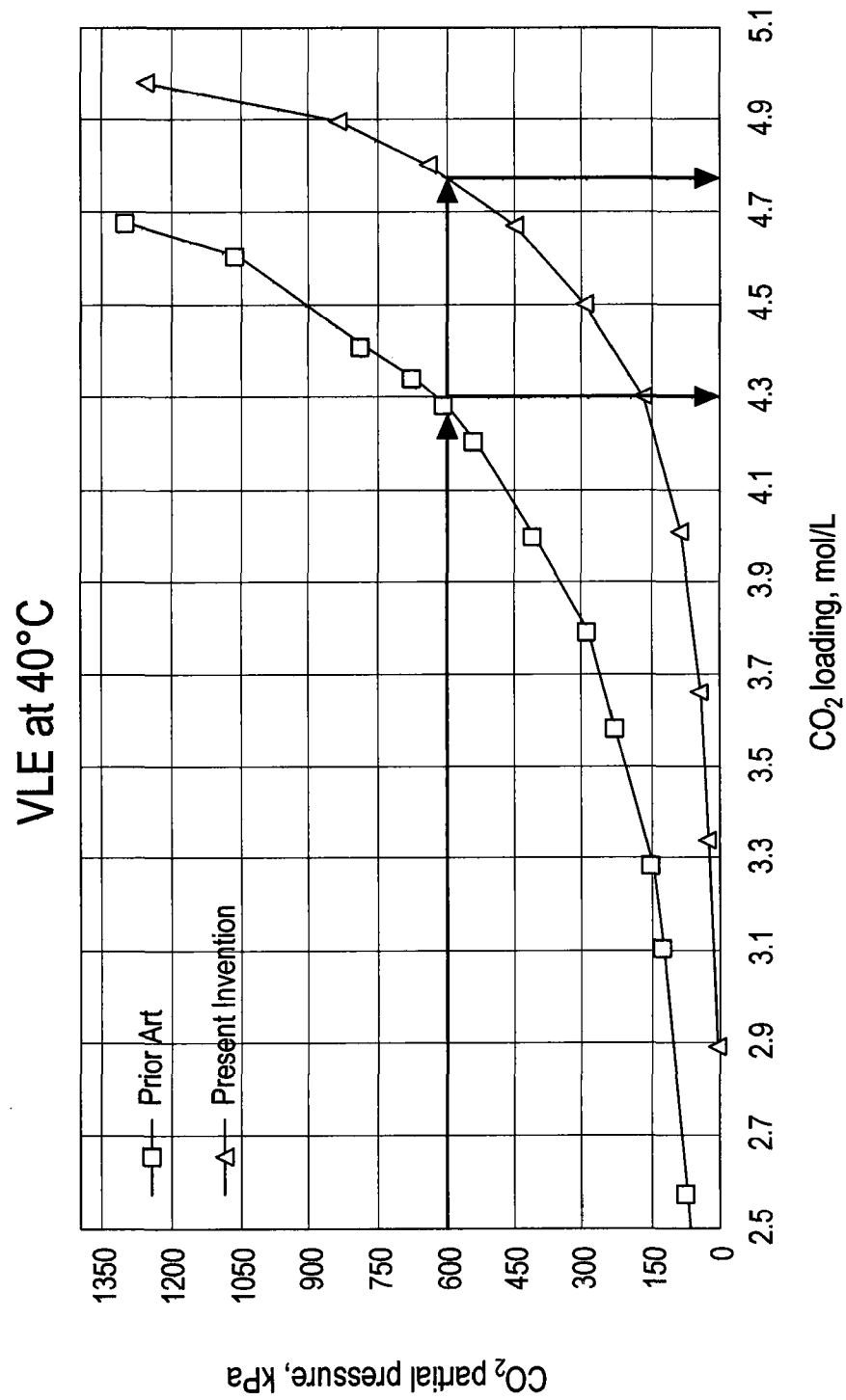


Figure 1

2/2

Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/051774

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D53/52 B01D53/62 B01D53/14 ADD.		
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 practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/118633 A2 (CARBON CLEAN SOLUTIONS PVT LTD) 7 August 2014 (2014-08-07) page 13, paragraph 3; claims 1, 12-13, 17, 22 page 15, paragraphs 2,4 -----	1-19
X	US 6 500 397 B1 (YOSHIDA KUNIHICO [JP] ET AL) 31 December 2002 (2002-12-31) column 6, lines 48-60; claim 2 -----	1,10
X	EP 0 558 019 A2 (KANSAI DENRYOKU KK) 1 September 1993 (1993-09-01) example 9 -----	1,10
A	WO 2016/057499 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 14 April 2016 (2016-04-14) page 27, lines 1-17 ----- -/--	1-19
☒ Further documents are listed in the continuation of Box C. ☒ 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 application or patent 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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 27 August 2019		Date of mailing of the international search report 02/09/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Artos Fernández, V

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2019/051774

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/099241 A2 (EXXONMOBIL RES & ENG CO [US]) 26 June 2014 (2014-06-26) figures 4-5 -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2019/051774

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014118633 A2	07-08-2014	EP 2950910 A2	09-12-2015
		US 2016193563 A1	07-07-2016
		WO 2014118633 A2	07-08-2014

US 6500397 B1	31-12-2002	KR 930017605 A	20-09-1993
		US 6036931 A	14-03-2000
		US 6500397 B1	31-12-2002

EP 0558019 A2	01-09-1993	DE 69306829 D1	06-02-1997
		DE 69306829 T2	15-05-1997
		DK 0558019 T3	14-04-1997
		EP 0558019 A2	01-09-1993

WO 2016057499 A1	14-04-2016	AR 102230 A1	15-02-2017
		BR 112017006616 A2	02-01-2018
		CA 2963598 A1	14-04-2016
		CN 107073387 A	18-08-2017
		EP 3204142 A1	16-08-2017
		JP 2017537771 A	21-12-2017
		KR 20170067782 A	16-06-2017
		RU 2017114425 A	25-10-2018
		US 2017239613 A1	24-08-2017
		WO 2016057499 A1	14-04-2016

WO 2014099241 A2	26-06-2014	CA 2895228 A1	26-06-2014
		CN 104870075 A	26-08-2015
		EP 2934724 A2	28-10-2015
		RU 2015126501 A	02-02-2017
		US 2014205525 A1	24-07-2014
		WO 2014099241 A2	26-06-2014
