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(54) Benævnelse: **CARBONOPSAMLINGSOPLØSNINGSMIDLER OG FREMGANGSMÅDER TIL ANVENDELSE AF SÅDANNE OPLØSNINGSMIDLER**

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DESCRIPTION

Description

BACKGROUND

[0001] This disclosure relates to a method for the preparation of solvents and methods for treatment of industrial effluent gases, and, more specifically, this disclosure relates to solvents and process for using these solvents to aid in the removal of carbon dioxide (CO_2) from other sources such as power plants or industrial utility.

[0002] US 6 436 174 B1 relates to a process for removing acidic gas constituents such as CO_2 and H_2S from gases using an absorption medium, to the absorption medium itself and to its use.

SUMMARY

[0003] The present invention is set out in the claims.

[0004] In particular, the present invention provides a solvent for recovery of carbon dioxide from gaseous mixture, comprising:

1. (a) an alkanolamine selected from the group comprising N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) and having a weight percentage between 25 wt% and 40 wt%,
2. (b) piperazine amines, wherein the piperazine amine is N-aminoethylpiperazine (AEP) having a weight percentage between 10 wt% and 25 wt%,
3. (c) a carbonate buffer having a weight percentage between 0.15 wt% and 10 wt%,
4. (d) water, and
5. (e) a glycol having a weight percentage between 10 wt% and 20 wt%, or

a sulfolane having a weight percentage between 10 wt% and 20 wt%,
wherein the solvent contains less than 75% by weight of water and has a single liquid aqueous phase.

[0005] The present invention also provides a method for removing CO_2 from a stream, comprising the steps of:

1. (a) contacting the stream with the solvent of according to the present invention;

2. (b) allowing the solvent to absorb CO_2 at a particular temperature to form a CO_2-rich solvent;
3. (c) regenerating the solvent by heating the CO_2-rich solvent to greater than 80°C.

[0006] Any disclosure which does not fall within the scope of the claims is included for illustrative purposes.

[0007] This disclosure is directed towards a solvent (not necessarily in full accordance with the claims) for recovery of carbon dioxide from gaseous mixture having an alkanolamine, reactive amines acting as promoter or activators, and a carbonate buffer. One specific solvent contains less than about 75% by weight of dissolving medium water and glycol (e.g., polyethylene glycol) and has a single liquid phase. Another specific solvent contains less than about 75% by weight of dissolving medium water and glycol (e.g., polyethylene glycol) and has a single liquid phase. Another specific solvent contains less than about 75 %> by weight of dissolving medium water and sulfolane and has a single liquid phase.

[0008] Additional features of the disclosure will become apparent to those skilled in the art upon consideration of the following detailed description of illustrative embodiments exemplifying the best mode of carrying out the disclosure as presently perceived.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The detailed description particularly refers to the accompanying figures in which:

FIG. 1 is a schematic picture of the reaction; and

FIG. 2 is a perspective view of one illustrative embodiment.

FIG. 3 shows a viscosity plot of one exemplary solvent.

DEFINITIONS

[0010] As used herein, the term "solvent" can refer to a single solvent or a mixture of solvents.

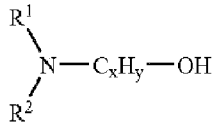
DETAILED DESCRIPTION

[0011] This disclosure includes several aspects and provides methods and solvents that, when

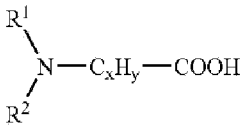
used alone or in combination, may significantly reduce or eliminate carbon dioxide (CO_2) emissions from industrial plants that burn solid fuels, particularly coal-fired power plants. This disclosure is directed to CO_2 capture/sequestration from flue gases CO_2 emissions should also be applicable to CO_2 capture from gas and oil fired boilers, combined cycle power plants, coal gasification, and hydrogen plants, biogas plants.

[0012] As shown in FIG. 1, the vapor and liquid phases are contact in a small cross-section. In treating the emissions, the absorption step involves removal of acid gases and other components from the gas phase by transport into the liquid phase. The gas-liquid interface separates the phases. An absorbing gas dissolves into the liquid at the interface, then diffuses across a thin layer of liquid (termed the diffusion layer) of one specific solvent. As it diffuses, the gas meets the reactive absorbent component in one specific solvent, reacts with it, and generates heat and reaction products such as carbonate. Reaction products can diffuse into the bulk liquid while the liberated heat of reaction heats the liquid. In one example, there is a mixture of tertiary amine/hindered amine, reactive amines (e.g., a polyamine activator), carbonate buffer, a dissolving medium of water and physical polyethylene glycol as to solvent system remain as a single liquid phase in removing acidic gases from gaseous mixture.

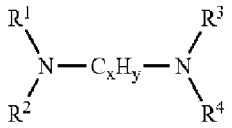
[0013] In embodiment, one specific solvent for absorbing CO_2 includes alkanolamines, which can be any one of compounds represented by following formulae (I) to (III) or a mixture thereof:



Nitrogen-containing compound (I)



Nitrogen-containing compound (II)



Nitrogen-containing compound (III)

in the formulae (I) to (III): x and y respectively satisfy relationship: 1 less than or equal to 5 and 2.less than or equal to 10; and R^1, R^2, R^3, and R^4 represent -- $C_iH_jO_kN_l$ (where i=0 to 10, j=1 to 21, k=0 to 5, and l=0 to 5).

[0014] In one illustrative solvent, reactive amines can be any one of nitrogen containing compounds represented by following formulae (IV) to (XIII) or mixture thereof. Reactive amines may be nitrogen-containing compound having a secondary nitrogen in a ring or a nitrogen-containing compound having a tertiary nitrogen in a ring.

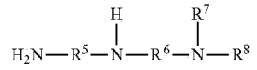
[0015] In another illustrative solvent, reactive amines can be a nitrogen-containing compound having secondary and tertiary nitrogen in a ring.

[0016] In another illustrative solvent, reactive amines can be a nitrogen-containing compound having a nitrogen in a substituent group branching from the ring.

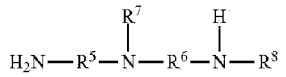
[0017] In another illustrative solvent, reactive amines can be nitrogen-containing compound may be a nitrogen-containing compound having a primary nitrogen in a substituent group branching from the ring.

[0018] In another illustrative solvent, reactive amines can be a nitrogen-containing compound having three nitrogen atoms or more in a molecule thereof.

[0019] In another illustrative solvent, reactive amines can be a nitrogen-containing compound having in a molecule thereof all of primary, secondary, and tertiary nitrogens.

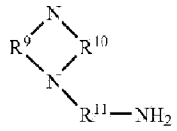


Nitrogen-containing compound (IV)



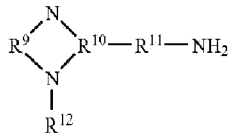
Nitrogen-containing compound (V)

in the formulae (IV) to (V): R^5 and R^6 represent -- $C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^7 and R^8 represent -- $C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



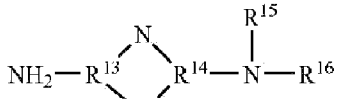
Nitrogen-containing compound (VI)

in the formula (VI): R^9 and R^{11} represent -- $C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R10 represents -- $C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



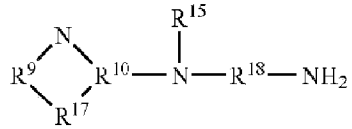
Nitrogen-containing compound (VII)

in the formula (VII): R^9 and R^{11} represent --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{10} and R^{12} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



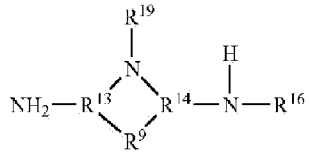
Nitrogen-containing compound (VIII)

in the formula (VIII): R^9 represents -- $C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{13}, R^{14}, R^{15} and R^{16} represent -- $C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



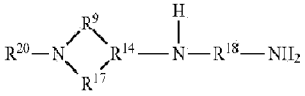
Nitrogen-containing compound (IX)

in the formula (IX): R9 and R18 represent --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R10, R15 and R17 represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



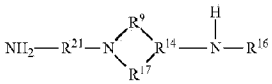
Nitrogen-containing compound (X)

in the formula (X): R^9 represents --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{13}, R^{14}, R^{16} and R^{19} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



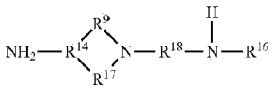
Nitrogen-containing compound (XI)

in the formula (XI): R^9 and R^{18} represent --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{14}, R^{17} and R^{20} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



Nitrogen-containing compound (XII)

in the formula (XII): R^9 and R^{21} represent --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{14}, R^{16} and R^{17} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),

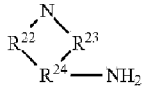


Nitrogen-containing compound (XIII)

in the formula (XIII): R^9 and R^{18} represent --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and

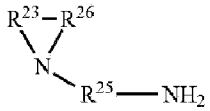
l=0 to 5); and R^{14}, R^{16} and R^{17} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5).

[0020] In one specific solvent, the second compound component may be any one of nitrogen-containing compounds represented by following formulae (XIV) to (XIX) or a mixture thereof:



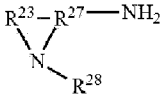
Nitrogen-containing compound (XIV)

in the formula (XIV): R^{22} represents --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{23} and R^{24} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



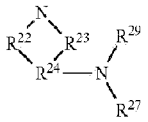
Nitrogen-containing compound (XV)

in the formula (XV): R^{25} represents --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R23 and R^{26} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



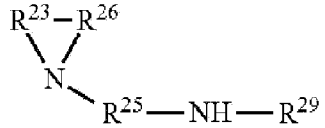
Nitrogen-containing compound (XVI)

in the formula (XVI): R^{23}, R^{27} and R^{28} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



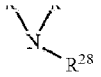
Nitrogen-containing compound (XVII)

in the formula (XVII): R^{22} represents --$C^iH^jO^kN^l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{23}, R^{24}, R^{27} and R^{29} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



Nitrogen-containing compound (XVIII)

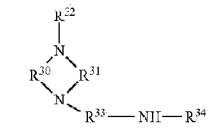
in the formula (XVIII): R^{25} represents --$C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5); and R^{23}, R^{26} and R^{29} represent --$C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5),



Nitrogen-containing compound (XIX)

in the formula (XIX): R^{23}, R^{27}, R^{28} and R^{29} represent $--C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5)

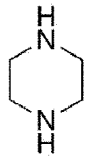
[0021] In one specific solvent, the reactive amine may be a nitrogen-containing compound represented by following formula (XX):



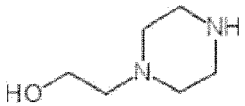
Nitrogen-containing compound (XX)

in the formula (XX): R^{30}, R^{32}, R^{33} and R^{34} represent $--C_iH_jO_kN_l$ (where i=1 to 10, j=0 to 26, k=0 to 5, and l=0 to 5), and R^{31} represents $--C_iH_jO_kN_l$ (where i=0 to 10, j=0 to 26, k=0 to 5, and l=0 to 5).

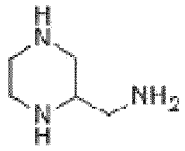
[0022] In one specific solvent, the reactive amine may be piperazine, N-2-Hydroethyl Piperazine, 2-aminomethyl piperazine or mixture thereof.



Piperazine



N-2-Hydroethyl Piperazine



2-aminomethyl piperazine

[0023] In one illustrative solvent, one of one specific solvent components can be represented by polyethylene glycol (PEG) represented by the following formulae (XXI) and / or physical pressure driven solvent or mixture thereof:

Polyethylene Glycol ($C_{2n}H_{4n+2}O_{n+1}$)

$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$

where, n=integer

Glycols suitable with specific embodiments include monoethylene glycol (EG), Diethylene Glycol (DEG), Triethylene Glycol, Tetraethylene Glycol, Methoxytriglycol (MTG). Other physical solvent used as a solvent component are Sulfolane, N-Methyl-2-Pyrrolidone (NMP).

[0024] In one specific solvent, alkanolamines may be contained in an amount in a range from equal to or larger than 10 wt % to equal to or less than 40 wt %, reactive amines may in an amount in a range from equal to or larger than 6 wt % to equal to or less than 40 wt %, and a total amount of the alkanolamine and reactive amines may be more than 20 wt % to equal to or less than 80 wt %.

[0025] In one specific solvent, the alkanolamine may be represented by the formula (I), where each of R^1 and R^2 is H.

[0026] In one specific solvent, the alkanolamine may be represented by the formula (I), where x is 2 to 4 and y is 4 to 8.

[0027] In one specific solvent, alkanolamines may be represented by the formula (I), where R^1 is H and R^2 is -CmHnOoNp (where m=1 to 5, n=1 to 11, o=0 to 5, and p=0 to 5).

[0028] In one specific solvent, the alkanolamine may be represented by the formula (I), where x is 2 to 4, y is 4 to 8, and R^2 is CH_3, C_2H_5, C_3H_7, or C_4H_9.

[0029] In one specific solvent, the alkanolamine may be represented by the formula (I), where R1 and R^2 represent -CmHnOoNp (where m=1 to 5, n=1 to 11, o=0 to 5, and p=0 to 5).

[0030] In one specific solvent, the alkanoamine may be represented by the formula (I), where x is 2, y is 4, R^1 is CH_3, and R^2 is C_2H_4OH.

[0031] An absorbent liquid for absorbing CO_2 or H_2S or both from gas according to certain embodiments includes a cyclic amine compound having one nitrogen in a ring. In one specific solvent, the cyclic amine having one nitrogen in a ring may be a cyclic amine having one nitrogen in a 5-membered ring, 6-membered ring, or 7-membered ring.

[0032] In one specific solvent, the cyclic amine having one nitrogen in a 5-membered ring, 6-membered ring, or 7-membered ring may be pyrrolidine (PR), piperidine (PZ), or hexamethyleneimine (HMI).

[0033] In one specific solvent, the cyclic amine compound having one nitrogen in a ring may be a nitrogen containing compound having a primary nitrogen in a substituent group branching from the ring.

[0034] In one specific solvent, the nitrogen-containing compound having a primary nitrogen in a substituent group branching from the ring may be aminomethylpiperidine or aminoethylpiperidine.

[0035] In one specific solvent, the cyclic amine compound having one nitrogen in a ring may be a nitrogen-containing compound having a hydroxyl group in a 5-membered ring, 6-membered ring, or 7-membered ring.

[0036] In one specific solvent, the nitrogen-containing compound having a hydroxyl group in a 5-membered ring, 6-membered ring, or 7-membered ring may be piperidinol (PDN).

[0037] An absorbent liquid includes a mixture of one specific solvent, and an alkanolamine. In one specific solvent, the alkanolamine may be monoethanolamine (MEA), ethylaminoethanol (EAE), triethanolamine, N-methyldiethanolamine (MDEA), diisopropanolamine, diglycolamine, or a mixture thereof.

[0038] A process for removing CO_2 or H_2S or both a includes an absorption tower that allows gas containing CO_2 or H_2S or both and an absorbent liquid to be in contact with each other to remove CO_2 or H_2S or both from the gas; and a regeneration tower that regenerates a solution which has absorbed the CO_2 or H_2S or both, the absorption tower reusing the solution regenerated at the regeneration tower by removing the CO_2 or H_2S or both from the solution.

[0039] In one embodiment, one specific solvent for recovery of carbon dioxide from gaseous mixture includes hindered amine, reactive amine, Polyethylene glycol, and a alkali carbonate buffer. The remaining solvent may be water.

[0040] Reactive amines may be a piperazine and its derivative such as piperazine, 2-aminomethyl piperazine, N-aminoethylpiperazine (in accordance with the claims), hydroxyethylpiperazine, 3-(3-pyrrolidyl)piperidine, 2-(3-pyrrolidyl)piperazine, 3-(3-piperidyl)-piperidine, 3-(2-piperazinyl)piperidine, or 2-(2-piperazinyl)piperazine, 2-aminomethyl piperazine. The reactive amine may be ethylenediamine, dimethyl ethylenediamine, pyrazolidine, imidazolidine, 2-(2-pyrrolidyl)-pyrrolidine, 2-(2-imidazolidyl) imidazolidine or mixture thereof. One example includes a solvent having hindered amine, mixture of active amine piperazine and N-2 Hydroethyl Piperazine, a carbonate buffer, polyethylene glycol, and water.

[0041] One embodiment may include a solvent with polyethylene glycol, any of a class of organic compounds belonging to the alcohol family; in the molecule of a glycol, two hydroxyl

(OH) groups are attached to different carbon atoms. The term is often applied to the simplest member of the class, ethylene glycol. Ethylene glycol, also called 1,2-ethanediol, molecular formula $HOCH_2CH_2OH$, is a colourless, oily liquid possessing a sweet taste and mild odor. It can be produced commercially from ethylene oxide, which is obtained from ethylene. Further, propylene glycol, also called 1,2-propanediol, resembles ethylene glycol in its physical properties. Other glycols include 1,3-butanediol, 1,4-butanediol, 2-ethyl-1,3-hexanediol, and 2-methyl-2-propyl-1,3-propanediol, methoxytriglycol and others and are suitable herewith.

[0042] One specific solvent may contain hindered or tertiary amines that act as high CO_2 loading carrier as the base solvent to increase the capacity of the CO_2 capture solvent. Hindered amine / tertiary amine may be N-methyldiethanolamine (MDEA), 2-(2-aminoethoxy)ethanol, Aminoethylethanolamine (AEEA), 2-amino-2methyl-1-proponal (AMP), 2-(ethyamino)-ethanol (EAE), 2-(methylamino)-ethanol (MAE), 2-(diethylamino)-ethanol (DEAE), diisopropanolamine (DIPA), methylaminopropylamine (MAPA), 3-aminopropanol (AP), 2,2-dimethyl-1,3-propanediamine (DMPDA), 3-amino-1-cyclohexylaminopropane (ACHP), diglycolamine (DGA), 1-amino-2-propanol (MIPA), 2-methyl-methanolamine (MMEA); Di ethyl ethanol amine (DEEA). MDEA and AMP are the only alkanol amines in accordance with the claims.

[0043] The solvent of the invention contains a carbonate buffer. The pH may range for a carbonate buffer may be between 8.0 and 9.0. Carbonate in one specific solvent increases the pH of one specific solvent. This high pH allows for increased carbon dioxide capture in the form of bicarbonate salts. The carbonate can be regenerated when one specific solvent is heated. In some instances percarbonate may contribute to the buffer system.

[0044] Suitable carbonate buffer salts are described herein. The amount of carbonate buffer salt used in the buffer system is an amount that is sufficient, when used with the remaining components, to raise salivary pH to a pH of about 7.8 or more, about 8.5 or more, and about 9 or more (e.g., about 9-11), irrespective of the starting pH.

[0045] In another embodiment, the carbonate salt is selected from the group consisting of sodium carbonate, potassium carbonate, calcium carbonate, ammonium carbonate, and magnesium carbonate. In yet another embodiment, the bicarbonate salt is selected from the group consisting of sodium bicarbonate, potassium bicarbonate, calcium bicarbonate, ammonium bicarbonate, and magnesium bicarbonate. In one embodiment, the binary buffer system comprises sodium carbonate and sodium bicarbonate. In another embodiment, the sodium bicarbonate is desiccant-coated sodium bicarbonate.

[0046] The amount of carbonate buffer and reactive amine piperazine in the solution is limited by the solubility of both components in water, thus resulting in solid solubility limit for aqueous solutions. At 25 °C, the solubility of potassium carbonate buffer in a CO_2 rich solution is 3.6 m and the solubility of piperazine in water is approximately 2 m. With the solid solubility limitation, the resulting lower concentration can result in slow reaction rate and low solution capacity. By

combining piperazine and carbonate buffer solubility in polyethylene glycol and aqueous solutions, the resultant solubility increases.

[0047] Reactive amines such as piperazine and CO_2 react, it undergoes equilibrium reaction to form piperazine carbamate and piperazine dicarbamate and some free and bound piperazine. Because of the addition of carbonate buffer salt; which react with free and bound piperazine in reacting more CO_2 to form piperazine carbamate and piperazine dicarbamate.

[0048] The ratio of equivalents of carbonate salt to equivalents of reactive amine can be between 0.3 - 3.0. The concentrations of the reactive amine and carbonate salt can be between 3.0 - 8.0 equivalents/Kg H_2O or 4.0 and 6.0 equivalents/Kg H_2O. The amount of piperazine and carbonate buffer salt can be adjusted based on the solubility in water and polyethylene glycol.

[0049] In one example, one specific solvent and method of use for the removal of CO_2 from flue gas, natural gas, hydrogen gas, synthesis gas, and other process and waste gas streams. One specific solvent may contain a carbonate buffer, a reactive amine, a hindered amine, and a polyethylene glycol, resulting in the solution pH between (10 - 13.5) in absence of CO_2. The reactive amine 6 wt% to 40 wt% with the total concentration limited by the solid solubility of the reactive amine in aqueous and polyethylene glycol solution or of the carbonate buffer salt from 0.15 wt% - 10 wt% with total concentration limited by the solid solubility in aqueous solution. This chemical solvent is designed to increase the rate of CO_2 removal to improve the efficiency of a removal process.

[0050] Piperazine is freely soluble in water and solubility in ethylene glycol up to about 20 wt%. Carbonate buffer salt solubility in water is 112 g/100 mL at 20 °C.

[0051] The temperature of the solution when contacting with the gaseous stream may be between approximately 30 °C - 125 °C. The rate constant for the reaction of CO_2 with the piperazine derivative (K_{PZ}) may be at least 25 m^3/mol-s at 25 °C, or at least 50 m^3/mol-s at 25 °C.

[0052] In one embodiment, one specific solvent has a reactive amine in concentration between about 6 wt% and 40 wt%.

[0053] In yet another embodiment, one specific solvent has a alkanolamine in a concentration between about 10wt% and 40 wt%.

[0054] In accordance with the claims, the solvent has a carbonate buffer with a concentration between about 0.15wt% - 10 wt%.

[0055] In yet another embodiment, one specific solvent has a solute concentration between about 2 wt% - 40 wt%.

[0056] In yet another embodiment, one specific solvent has a tertiary balance to keep one specific solvent or solvent system as a single liquid phase.

[0057] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 25 wt% and 40 wt% and is selected from group comprising N-methyldiethanolamine (MDEA), 2-amino-2methyl-1-proponal (AMP); the reactive amines have a weight percentage between 10 wt% and 25 wt% and is selected from group comprising piperazine, N aminoethylpiperazine (AEP); and the glycol has a weight percentage between 10 wt% and 25 wt%.

[0058] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 30 wt% and 40 wt% and is selected from group comprising N-methyldiethanolamine (MDEA), 2-amino-2methyl-1-proponal (AMP); the reactive amines have a weight percentage between 10 wt% and 18 wt% and is selected from group comprising piperazine, N aminoethylpiperazine (AEP); and the glycol has a weight percentage between 15 wt% and 20 wt%.

[0059] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 32 wt% and 35 wt% and is selected from group comprising N-methyldiethanolamine (MDEA), 2-amino-2methyl-1-proponal (AMP); the reactive amines have a weight percentage between 11 wt% and 15 wt% and is selected from group comprising piperazine, N aminoethylpiperazine (AEP); and the glycol has a weight percentage between 18 wt% and 20 wt%.

[0060] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 25 wt% and 40 wt%; the reactive amines have a weight percentage between 10 wt% and 25 wt%; and the glycol has a weight percentage between 10 wt% and 25 wt%.

[0061] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 30 wt% and 40 wt%; the reactive amines have a weight percentage between 10 wt% and 18 wt%; and the glycol has a weight percentage between 15 wt% and 20 wt%.

[0062] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 32 wt% and 35 wt%; the reactive amines have a weight percentage between 11 wt% and 15 wt%; and the glycol has a weight percentage between 18 wt% and 20 wt%.

[0063] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 25 wt% and 40 wt%; the reactive amines have a weight percentage between 10 wt% and 25 wt%; and the sulfolane has a weight percentage between 10 wt% and 25 wt%.

[0064] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 30 wt% and 40 wt%; the reactive amines have a weight percentage between 10 wt% and 18 wt%; and the sulfolane has a weight percentage between 15 wt% and 20 wt%.

[0065] In yet another embodiment, the solvent the alkanolamine has a weight percentage between 32 wt% and 35 wt%; the reactive amines have a weight percentage between 11 wt% and 15 wt%; and the sulfolane has a weight percentage between 18 wt% and 20 wt%.

[0066] In another embodiment, a method of removing CO_2 from a gaseous stream including: contacting a gaseous stream with a solution wherein the solution is formed by combining: alkanolamines, a reactive amine , an carbonate salt, poly ethylene glycol and water; whereby the contact removes CO_2 from the gaseous stream; and regenerating the solution. The concentrations may be limited by the solubility of the components at a temperature and contact of the exhaust gaseous stream with one specific solvent removes CO_2 from the gaseous stream; and regenerating the solution.

[0067] The regenerating may include heating CO_2-rich solution, which may occur at a temperature of approximately 90 °C - 130 °C, approximately 110 °C. An additive such as an antifoaming agent, an antioxidant, a corrosion inhibitor (e.g. vanadium oxide or a chromate), a flocculation aid, or a mixture of two or more additives may be included as part of the solution.

[0068] In another embodiment, the method of removing CO_2 from a gaseous stream may further include applying a water wash system, wherein the water wash system collects the volatile alkanolamine and reactive amine from treated gaseous stream. The regeneration of the solution may occur in a vacuum stripper column, and the solution may be returned to contact with the gaseous stream after regeneration.

[0069] Other components of a gaseous stream, such as COS may also be removed by the method of this disclosure. The gaseous stream may be from a coal-fired power plant, or it may be flue gas, natural gas, hydrogen gas, synthesis gas or a waste gas stream.

[0070] Fig. 2 is a schematic diagram of an apparatus for removing acidic gases especially CO_2. As shown in Fig. 2, gas is allowed to enter to an absorption tower 1 through a CO_2 - containing gas-feed. In a packed portion, the gas placed in the absorption tower 1 is brought into contact in a counter flow with a CO_2 absorbent liquid fed from 3, and CO_2 is absorb and removed from the gas by the absorbing liquid, and the resultant gas is discharge from the top as treated gas. The absorbent liquid fed to the absorption tower 1 absorb CO_2, and is led to heat exchanger and heated and led to a regeneration tower 4. In the regeneration tower 4, the absorbent liquid flows through a packed portion towards the lower portion of the tower. During this time, CO_2 is removed to regenerate the absorbent liquid. The regenerated absorbent liquid is led by a pump to the heat exchanger and fed back to the absorption tower 1 through an absorbent liquid feed inlet line 3.

[0071] On the other hand, in the upper portion of the regeneration tower 4, the CO_2 removed from the absorbent liquid is brought into contact with a reflux water, and cooled by a regeneration tower reflux condenser and, in a reflux drum, the CO_2 separated from the reflux

water formed by condensing water vapor accompanying the CO_2, and led to a CO_2 recovery step. The reflux water is fed by a reflux water pump to the regenerator tower 4. This embodiment briefly describes an overview of the CO_2 capture process description.

Illustrative Examples and Proposed Theory

[0072] Heat to produce steam to maintain driving force for CO_2, For the CO_2, to be transferred from the liquid to the gas phase there needs to be driving force on the basis of partial pressure. Thus, steam acts in such a way as to provide this driving force so that the mass transfer of CO_2 from the liquid to the gas phase is enhanced. This also has energy associated with it, which contributes to the overall reboiler duty. This can be obtained by finding out the amount of water associated with the pure CO_2 steam produced as this energy in the form of water is lost and needs to be provided by the reboiler. The stripping heat consists of the following:

$$Q_T = Q_{sens} + Q_{des} + Q_{strip}$$

Sensible heat of CO_2 rich solvent to raise the stripper temperature

[0073] One specific solvent loaded with CO_2 in the absorber may be heated up to stripper temperature for the regeneration of CO_2. One specific solvent stream can be pre-heated in the lean-rich cross heat exchanger and then additional heat may be used to maintain the temperature of one specific solvent in the stripper.

$$Q_{sens} = \frac{\delta C_P \Delta T}{(\alpha_{rich} - \alpha_{lean}) C_{amine}}$$

[0074] The contributing factors to the sensible heat are solvent flow, specific heat capacity of one specific solvent and the temperature increase. Thus, the only parameter that can be varied is one specific solvent flow which further depends on the concentration of one specific solvent and one specific solvent loadings. This can be decreased by circulating less solvent and maintaining the same CO_2 production rate. This is checked by means of comparing the Net Capacity of a solvent which is defined as the difference in the loading at the absorption and desorption conditions.

Heat of Desorption of CO_2

[0075] The CO_2 which is reversibly bound to one specific solvent needs to be regenerated.

The heat of desorption is equivalent to the heat of absorption.

Heat to produce steam to maintain driving force for CO_2

[0076] For the CO_2 to be transferred from the liquid to the gas phase there needs to be driving force in the basis of the partial pressure. Thus steam acts in such a way as to provide the driving force so that the mass transfer of CO_2 from the liquid to the gas phase is enhanced. This also has energy associated with it, which contributes to the overall reboiler duty. This can be obtained by finding out the amount of water associated with the pure CO_2 steam produced as this energy in the form of water is lost and needs to be provided by the rebuilder. The stripping heat consists of the following:

$$Q_{strip} = \frac{P_{H2O}^{sat}(T_{top,des})\chi_{H2O,freebasis}}{P_{CO2}^{*}(T_{top,des}.\alpha_{rich})}\Delta H_{H2O}^{vap}$$

Where

ΔH_{H2O}^{vap}

stands for heat of vaporization if water and

P_{CO2}^{*}

is the partial pressure of CO_2 that would be equilibrium with the rich solution at the bottom of the absorber. Thus, finding EXAMPLES

The disclosure will be further described in connection with the following examples, which are set forth for purposes of illustration only.

Table 1

		Sulfolane	**EG**	**NMP**	**DEG**	**Methoxytriglycol**
Molecular Weight	kg/kmol	120.2	62.1	99.1	106.1	164.2
Mass Cp	kJ/(kg*° C)	1.2319	2.4734	1.6181	2.3353	2.19
Dynamic Viscosity	cP	7.9380	9.5081	1.4516	15.3050	7.3000
Latent Heat of vaporization	kJ/kg	435.11	849.57	453.74	540.63	301.00
Boiling Point	Deg C	289.933	197.080	203.994	244.938	249.000

[0077] As the rate activator for the CO_2 absorption is piperazine and its derivative, the limitation with piperazine is its high volatility. It has highest reaction kinetics among its derivatives. It is white crystals which need more water to foam a clear solutions or need Polyethylene glycol to solubilize it. But because of the high volatility the loss of the piperazine is high and to minimize the volatility loss in the solvent, piperazine component is partly or completely replaced by rate activator such as N-2-hydroethyl piperazine whose vapor pressure is 99.7% less than piperazine.

Reactive Amine	Piperazine	N-2-HYDROETHYL Piperazine
Formula	$C_4H_{10}N_2$	$C_6H_{14}N_{20}$
Mol. Wt	84.16	130.19
State	SOLID	LIQUID
Appearances	WHITE CRYSTAL	LIGHT YELLOW
M.pt (deg C)	106	-10
B.pt (deg C)	146	246
Solubility (water)	SOLUBLE	SOLUBLE
Vapor pressure (mm Hg)	2.1 AT 20 °C	0.00492 AT 25°C
Acidity pKa	9.8	

Example 2

[0078] Below is the composition and characteristics of another exemplary solvent (not in accordance with the claims).

Density measurement

[0079] The densities of were measured using a 25 $\times 10^{-6} m^3$ (at 298 K) Gay-Lussac pycnometer. For each run, the pycnometer containing the solvent solution was put in a constant temperature bath. The bath temperature was controlled within ± 0.1 K of the desired temperature level using a circulator temperature controller. Once the solution reached the desired temperature, it was weighed to within ±0.0001 g with an analytical balance. Each reported density data is the average of at least three measurements.

Viscosity measurement

[0080] The viscosities of solutions were measured using Cannon Fenske Viscometer. For each viscosity measurement, the temperature was controlled within ±0.1 K of the desired level with a circulator temperature controller. The viscometers containing samples were immersed in a thermostatic bath and allowed to equilibrate to the set point temperature for at least 15 min. Later, the efflux time of samples was measured manually with a digital stopwatch having an accuracy of 0.01s. The efflux time is measured by allowing meniscus to pass between two specific marks. The kinematic viscosity was obtained by multiplying efflux time in seconds with the respective viscometer constant. The dynamic viscosity of the samples is calculated by multiplying the kinematic viscosity values with their corresponding density values. Each

viscosity data is the average of at least three measurements.

	Mass%	Mol%	Molarity (mol/lit)	Molality (mol/kg water)	Density Kg/m^3
MDEA	25	7.3	2.185	5.387	1055 at 40 °C
Ethylene Glycol	20	11.19	3.351	8.262	
Piperazine	15	6.05	1.811	4.465	
K_2CO_3	1	0.25	0.0734	0.186	
H_2O	39	75.21			

Density and viscosity of S1:

[0081]

Temp	viscosity	density
°C	m-Pa-sec	kg/m^3
30	10.16252	1065
40	6.962653	1055
50	4.170193	1048
60	2.777815	1040

[0082] FIG. 3 describes viscosity in mPa.sec and density in kg/m^3 (on Y-axis) w.r.t temperature °C (on X-axis) for the solvent Si. It is observed that viscosity and density decreases with the increase in temperature.

VLE of S_1

[0083] These measurements can determine the relationship between partial pressure of CO_2 and the subsequent loading of the solvent at different temperatures. This data can be used be used to do a first assessment of the solvent performance.

T=40 °C	
Loading	CO_2 PARTIAL pressure kPa
0.118545	0.068
0.167315	0.208

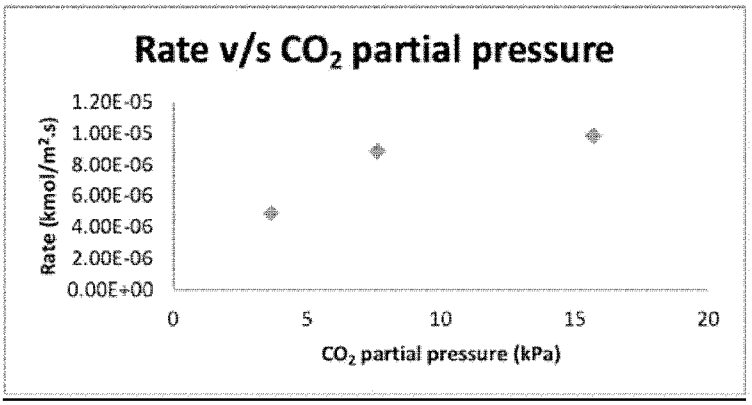
T=40 °C	
Loading	CO_2 PARTIAL pressure kPa
0.20191	0.420
0.231713	0.963
0.27593	2.388
0.315874	5.076
0.356194	8.245
0.395963	14.492
0.470479	33.408
0.496462	50.479
0.539315	78.051
0.575544	98.729
T = 50 °C	
Loading	CO_2 PARTIAL pressure kPa
0.067229	0.043
0.119626	0.159
0.189261	0.710
0.232958	1.701
0.287389	4.549
0.320698	7.513
0.379275	16.116
0.400526	24.539
0.484553	62.484
0.516075	76.269
0.528049	103.841

Kinetics Experiments Results

[0084]

	Mass%
MDEA	25
Ethylene Glycol	20
Piperazine	15
K_2CO_3	5

	Mass%
H_2O	35



T = 40 °C

Pressure	**Rate**
kPa	**kmol/m^2.s**
3.64	4.89E-06
7.62	8.82E-06
15.7	9.85E-06

[0085] Specific rate of absorption increases with CO_2 partial pressure.

Example 3

[0086] Below is the composition and characteristics of another exemplary solvent (not in accordance with the claims).

VLE data for solvent S2

(MDEA + PZ + Tetrahydrothiophenedioxide (SULFOLANE) + water (and K_2CO_3)) (48+2+10+40 wt%, respectively)

[0087]

T=313K		T=323K		T=333K	
p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}
2.07	0.108	26.88	0.263	41.28	0.249
28.95	0.362	82.71	0.474	192.63	0.464
53.76	0.493	261.78	0.708	343.84	0.636
93.05	0.633	506.91	0.868	616.88	0.754
254.35	0.790	677.88	0.946	855.13	0.894
496.29	0.934	856.09	1.020	1082.87	0.996
622.43	0.997	955.89	1.087	1127.33	1.062
756.84	1.032			1355.41	1.120
955.89	1.110				

VLE data for (MDEA + PZ + SULFOLANE + (H_2O and K_2CO_3)) (45+5+10+40 wt%, respectively)

[0088]

T=313K		T=323K		T=333K	
p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}
39.29	0.381	6.20	0.112	39.90	0.282
97.19	0.637	86.85	0.488	125.50	0.492
328.79	0.876	225.45	0.735	308.66	0.668
554.92	0.984	492.84	0.915	458.63	0.795
812.58	1.068	622.91	0.989	630.56	0.860
1046.34	1.132	851.53	1.044	834.36	0.954
		1022.51	1.079	1070.16	1.048
		1104.77	1.094	1334.16	1.157
		1292.37	1.137		

VLE data for (MDEA + PZ + SULFOLANE + water(and K_2CO_3)) (42+8+10+40wt%, respectively)

[0089]

T=313K		T=323K		T=333K	
p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}	p_{CO2}/kPa	α_{CO2}
1.24	0.236	5.38	0.321	16.80	0.264
16.18	0.503	49.49	0.567	65.72	0.455
94.38	0.750	101.33	0.671	174.93	0.615
192.78	0.855	145.10	0.738	326.32	0.805
223.33	0.895	274.27	0.848	497.35	0.898
465.28	1.004	332.93	0.860	670.47	0.936
599.69	1.082	545.93	0.973	833.25	0.997
777.53	1.144	779.60	1.075	1095.73	1.069
976.05	1.169	984.32	1.130	1164.45	1.091
1013.27	1.182				

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- US6436174B1 [0002]

PATENTKRAV

1. Opløsningsmiddel til genvinding af carbondioxid fra en gasformig blanding, hvilket opløsningsmiddel omfatter:

(a) en alkanolamin, der er valgt fra gruppen, som omfatter N-methyldiethanolamin (MDEA) og 2-amino-2-methyl-1-propanol (AMP), og udviser en vægtprocent mellem 25 vægt-% og 40 vægt-%,

(b) piperazinaminer, hvor piperazinaminen er N-aminoethylpiperazin (AEP) med en vægtprocent mellem 10 vægt-% og 25 vægt-%,

(c) en carbonatbuffer med en vægtprocent mellem 0,15 vægt-% og 10 vægt-%,

(d) vand og

(e) en glycol med en vægtprocent mellem 10 vægt-% og 20 vægt-% eller

en sulfolan med en vægtprocent mellem 10 vægt-% og 20 vægt-%,

hvor opløsningsmidlet indeholder mindre end 75 vægt-% vand og har en enkelt flydende vandig fase.

2. Opløsningsmiddel ifølge krav 1, hvor glycolen er polyethylenglycol.

3. Opløsningsmiddel ifølge krav 1, hvor glycolen er valgt fra gruppen bestående af monoethylenglycol (EG), diethylenglycol (DEG), triethylenglycol, tetraethylenglycol, methoxytriglycol (MTG).

4. Opløsningsmiddel ifølge krav 1 eller 2, hvor opløsningsmidlet indeholder mindre end 30 vægt-% vand.

5. Opløsningsmiddel ifølge krav 1, hvor

(a) alkanolaminen udviser en vægtprocent mellem 30 vægt-% og 40 vægt-%,

(b) piperazinaminerne udviser en vægtprocent mellem 10 vægt-% og 18 vægt-%,

(c) glycolen eller sulfolanen udviser en vægtprocent mellem 15 vægt-% og 20 vægt-%.

6. Opløsningsmiddel ifølge krav 1, hvor

(a) alkanolaminen udviser en vægtprocent mellem 32 vægt-% og 35 vægt-%,

(b) piperazinaminerne udviser en vægtprocent mellem 11 vægt-% og 15 vægt-%,

(c) polyethylenglycol udviser en vægtprocent mellem 18 vægt-% og 20 vægt-%.

7. Fremgangsmåde til fjernelse af CO_2 fra en strøm, hvilken fremgangsmåde omfatter følgende trin:

(a) strømmen bringes i kontakt med opløsningsmidlet ifølge et hvilket som helst af kravene 1 til 6;

(b) opløsningsmidlet tillades at absorbere CO_2 ved en bestemt temperatur til dannelse af et CO_2-rigt opløsningsmiddel;

(c) opløsningsmidlet regenereres ved opvarmning af det CO_2-rige opløsningsmiddel til mere end 80 °C.

8. Fremgangsmåde ifølge krav 7, hvor strømmen har en temperatur mellem 40 °C og 65 °C, og regenereringen sker under et tryk mellem 0,01 og 30 bar.

9. Fremgangsmåde ifølge krav 7, hvor

(a) alkanolaminen udviser en vægtprocent mellem 32 vægt-% og 35 vægt-%,

(b) piperazinaminer udviser en vægtprocent mellem 11 vægt-% og 15 vægt-%,

(c) glycolen eller sulfolanen udviser en vægtprocent mellem 18 vægt-% og 20 vægt-%.

DRAWINGS

Drawing

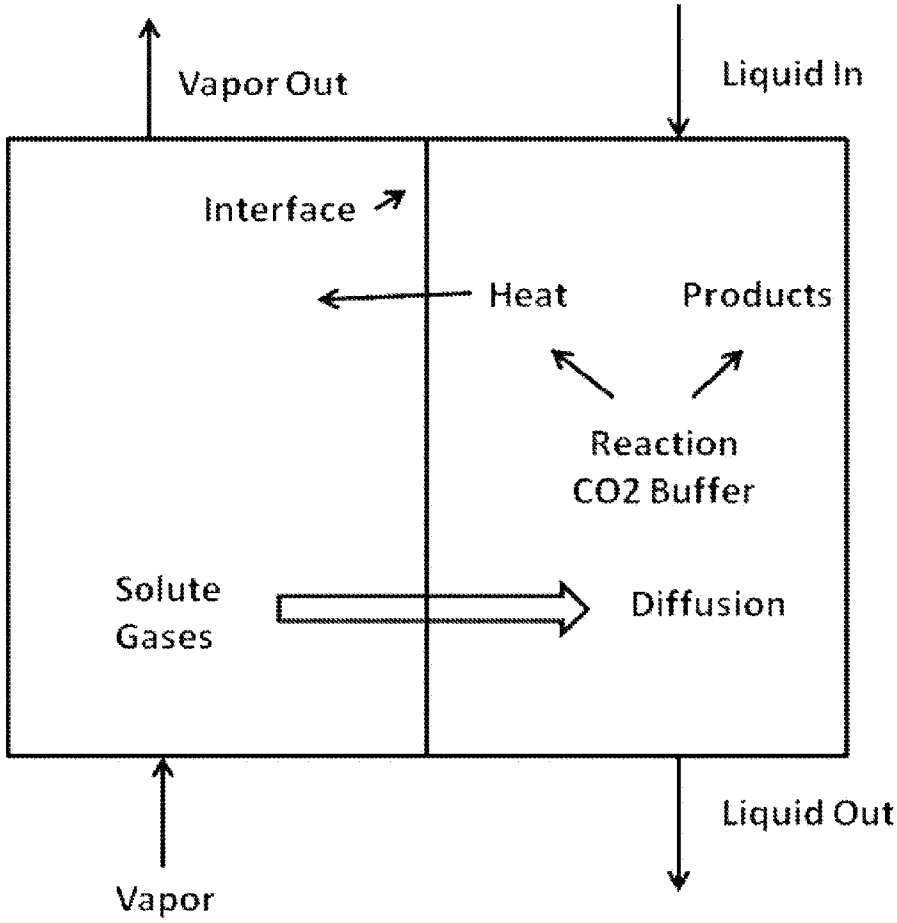
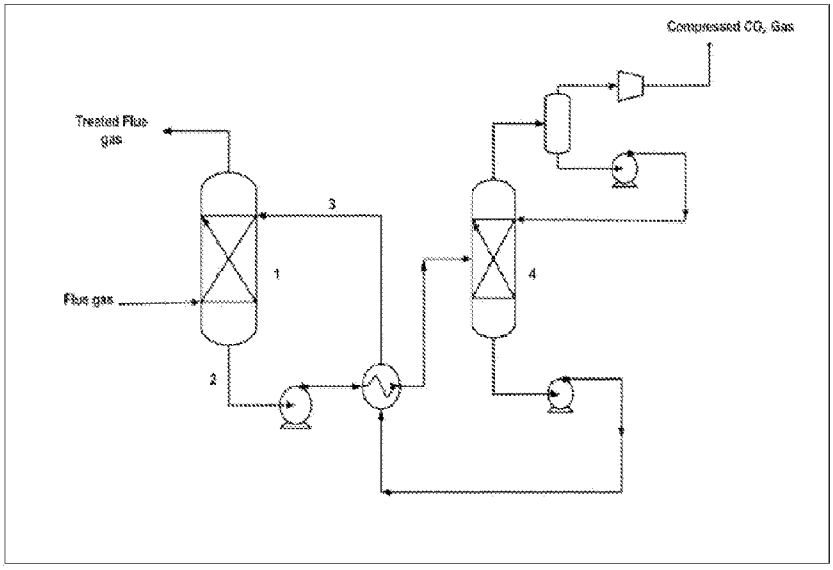


FIG. 1



Schematic diagram for CO_2 recovery

FIG. 2

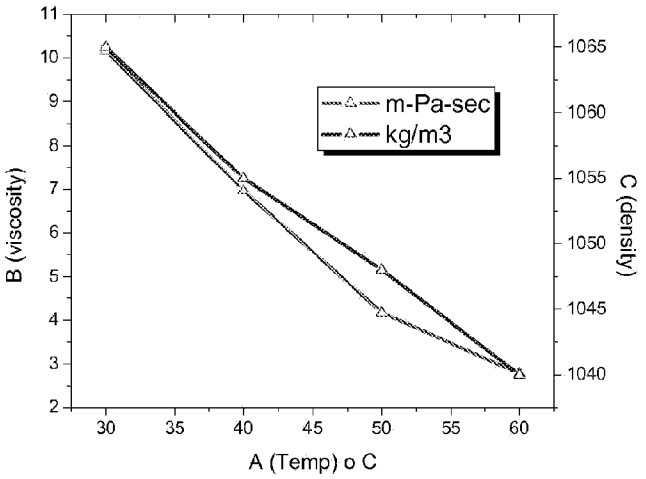


FIG. 3