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(54) Title: BLENDS OF THERMALLY DEGRADED AMINES FOR CO₂ CAPTURE

(57) Abstract: Compositions and methods related to the removal of acidic gas are described. In particular, the present disclosure relates to a composition and method for the removal of acidic gas from a gas mixture using an aqueous amine solvent comprising a thermal degradation product of an amine that is in equilibrium with the amine at high temperatures.



BLENDS OF THERMALLY DEGRADED AMINES FOR CO₂ CAPTURE

[0001] This application claims priority to U.S. Provisional Application No. 62/311,382, filed March 21, 2016, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This application relates to blends of amines for CO₂ capture from flue gases.

BACKGROUND

[0003] As concerns of global climate changes spark initiatives to reduce carbon dioxide emissions, its economic removal from gas streams is becoming increasingly important. Such carbon dioxide emissions may be produced by a variety of different processes, such as the gas stream produced by coal-fired power plants. The removal of CO₂ can be an expensive process, potentially increasing the cost of electricity by 50% or more. Therefore, technology improvements to reduce the costs associated with the removal of CO₂ are highly desirable. Removal by absorption/stripping is a commercially promising technology, as it is well suited to sequester carbon dioxide (CO₂).

[0004] The removal of CO₂ from fuel gas and flue gas by absorption/stripping with aqueous amines is a commercially practiced technology. The use of absorption and stripping processes with aqueous solvents such as alkanolamines and promoted potassium carbonate is a known, effective technology for the removal and capture of CO₂ from flue gas, natural gas, hydrogen, synthesis gas, and other gases. U.S. Pat. Nos. 4,477,419 and 4,152,217 describe aspects of this technology. The first generation of technology relating to alkanolamine absorption/stripping uses aqueous solutions of monoethanolamine (MEA). Advances in this technology have provided other alkanolamine solvents for CO₂ treating in various industries. Monoethanolamine (MEA), diethanolamine (DEA), and the hindered amine aminomethylpropanol (AMP) are used alone in an aqueous solution. Typical solvent blends include a methyldiethanolamine (MDEA) solution promoted by piperazine or other secondary amines. Also, potassium carbonate solvents are commonly promoted by DEA or other reactive amines.

[0005] Gas absorption is a process in which soluble components of a gas mixture are dissolved in a liquid. Stripping is essentially the inverse of absorption, as it involves the transfer of volatile components from a liquid mixture into a gas. In a typical CO₂

removal process, absorption is used to remove CO₂ from a combustion gas, and stripping is subsequently used to regenerate the solvent and capture the CO₂ contained in the solvent. Once CO₂ is removed from combustion gases and other gases, it can be captured and compressed for use in a number of applications, including sequestration, production of methanol, and tertiary oil recovery.

[0006] The conventional method of using absorption/stripping processes to remove CO₂ from gaseous streams is described in U.S. Pat. No. 4,384,875. In the absorption stage, the gas to be treated containing the CO₂ to be removed, is placed in contact, in an absorption column, with the chosen absorbent under conditions of pressure and temperature such that the absorbent solution removes virtually all the CO₂. The purified gas emerges at the top of the absorption column and, if necessary, it is then directed towards a scrubber employing sodium hydroxide, in which the last traces of CO₂ are removed. At the bottom of the absorption column, the absorbent solution containing CO₂ (also called “rich solvent”) is drawn off and subjected to a stripping process to free it of the CO₂ and regenerate its absorbent properties. Other methods of using absorption/stripping process to remove CO₂ from gaseous stream are described in U.S. Patent Application Publication No. 2011/0171093, U.S. Patent No. 7,938,887, and U.S. Provisional Patent Application Serial No. 61/585,865.

[0007] To effect the regeneration of the absorbent solution, the rich solvent drawn off from the bottom of the absorption column is introduced into the upper half of a stripping column, and the rich solvent is maintained at its boiling point under pressure in this column. The heat necessary for maintaining the boiling point is furnished by reboiling the absorbent solution contained in the stripping column. The reboiling process is effectuated by indirect heat exchange between part of the solution to be regenerated located in the lower half of the stripping column and a hot fluid at appropriate temperature, generally saturated water vapor. In the course of regeneration, the CO₂ contained in the rich solvent is released and stripped by the vapors of the absorbent solution. Vapor containing the stripped CO₂ emerges at the top of the stripping column and is passed through a condenser system which returns to the stripping column the liquid phase resulting from the condensation of the vapors of the absorbent solution. At the bottom of the stripping column, the hot regenerated absorbent solution (also called “lean solvent”) is

drawn off and recycled to the absorption column after having used part of the heat content of the solution to heat, by indirect heat exchange, the rich solvent to be regenerated, before its introduction into the stripping column.

[0008] In simple absorption/stripping as it is typically practiced in the field, aqueous rich solvent is regenerated at 100-160°C in a simple, countercurrent, reboiled stripper operated at a single pressure, which is usually 1-10 atm. The rich solvent feed is preheated by cross-exchange with hot lean solvent to within 5-30°C of the stripper bottoms. The overhead vapor is cooled to condense water, which is returned as reflux to the countercurrent stripper. When used for CO₂ sequestration and other applications, the product CO₂ is compressed to 100-150 atm.

[0009] Commercially used amines that are used by themselves in water as absorbers include monoethanolamine, diethanolamine, methyldiethanolamine, diglycolamine[®], diisopropanolamine, some hindered amines, and others. These amines are soluble or miscible with water at ambient temperature at high concentrations that are used in the process to maximize capacity and reduce sensible heat requirements. Other amines, including piperazine, are used in combination with methyldiethanolamine and other primary amines.

[0010] Aqueous monoethanolamine (MEA) with a concentration between 15–30 % has been previously used in similar applications such as CO₂ removal from natural gas and hydrogen, and is currently considered the state-of-the-art technology for CO₂ absorption/stripping because of its effectiveness for CO₂ capture and low cost of production. However, the low resistance to degradation, and low CO₂ capacity and CO₂ absorption rates of MEA lead to high capital and energy cost, as well as some environmental issues.

[0011] Diglycolamine[®] (abbreviated herein as DGA), also known as 2-(2-aminoethoxy)ethanol (AEE) — all these terms are used interchangeably herein — has been traditionally used as an alternative to MEA for many natural gas sweetening plants, due to its ability to partially remove COS, low volatility, and reversible thermal degradation pathway. AEE has been investigated for flue gas CO₂ capture in recent years. Although AEE has greater thermal stability than MEA, it still oxidatively degrades. The CO₂

capacity and absorption rate of 10 m AEE is even lower than 7 m MEA by about 20% for flue gas CO₂ capture.

SUMMARY

[0012] The present disclosure generally relates to the removal of acidic gases, including carbon dioxide, from flue gas or other gases through aqueous absorption and stripping processes. More particularly, in some embodiments, the present disclosure relates to methods and compositions for the removal of acidic gas from a gas mixture using an aqueous amine solvent blend.

[0013] Provided is an aqueous amine solvent comprising a blend of a primary alkanolamine and a tertiary alkanolamine.

[0014] Embodiments include the aqueous amine solvents wherein the primary alkanolamine comprises $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$ and the tertiary alkanolamine comprises $(\text{C}_1\text{-C}_2 \text{ alkyl})_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, wherein m and n are each independently 1, 2 or 3; wherein m and n are both 2 or are both 3.

[0015] In other embodiments, the primary and tertiary alkanolamines are each independently present in about 20 to about 40 % of the total alkanolamine content (such as each independently about 30 to 40 %) and the secondary amine is present in about 20 to 60 % (such as about 30 to 40 %) of the total alkanolamine content. In other embodiments, the total alkanolamines may be present in the aqueous solvent in from a lower limit of 3, 5, or 8 to an upper limit of 10, 15 or 20 molar amounts.

[0016] In other embodiments, the primary alkanolamine comprises 2-(2-aminoethoxy)ethanol (AEE) and the tertiary alkanolamine comprises dimethylaminoethoxyethanol (DMAEE); and wherein the aqueous amine solvent further comprises methylaminoethoxyethanol (MAEE); wherein AEE and DMAEE are each present in amounts from about 1200 to about 1300 mmol/kg of total aqueous solvent and MAEE is present in an amount from about 800 to about 900 mmol/kg of total aqueous solvent; and/or wherein AEE, MAEE and DMAEE are in thermal equilibrium; such as wherein the K_{eq} is from 0.4 to 1.0.

[0017] In other embodiments, the primary alkanolamine comprises monoethanolamine and the tertiary alkanolamine comprises dimethylethanolamine, diethylethanolamine, methyldiethanolamine, ethyldimethanolamine or triethanolamine; and

wherein the aqueous amine solvent further comprises methylethanolamine or ethylethanolamine when the tertiary amine comprises dimethylethanolamine, diethylethanolamine, methyldiethanolamine, or ethyldimethanolamine; and/or wherein the aqueous amine solvent further comprises diethanolamine when the tertiary alkanolamine comprises triethanolamine.

[0018] In another aspect, a method of amine scrubbing of an acidic gas comprising contacting the acidic gas with the aqueous amine solvent of any of the embodiments above is provided.

[0019] The method may comprise contacting a gaseous stream with the aqueous amine solvent; and wherein the gaseous stream comprises the acidic gas; and allowing the acidic gas to transfer from the gaseous stream to the solvent.

[0020] Embodiments of the method include the method of further comprising forming a purified gaseous stream and a rich solvent stream; and the method further comprising routing the rich solvent stream through a stripper; and/or the method comprising contacting the gaseous stream with the aqueous amine solvent in an absorber; forming a purified gaseous stream and a rich solvent stream; and routing the rich solvent stream through a stripper. The stripper may be selected from the group consisting of a simple stripper, a matrix stripper, a multistage flash stripper, an exchange stripper, a multipressure stripper, a flashing feed stripper, and a multistage stripper.

[0021] Any of the methods above may further comprise recycling a solvent stream exiting the stripper.

[0022] In any of the above methods, the gaseous stream may be selected from the group consisting of flue gas, a natural gas, a hydrogen gas, and a synthesis gas.

[0023] In any of the above methods, the acidic gas may be carbon dioxide.

[0024] Any of the methods above may comprise obtaining an aqueous amine solvent comprising a blend of a primary alkanolamine and a tertiary alkanolamine; exposing the aqueous amine solvent to a temperature of 120°C or higher for a time sufficient to allow the primary alkanolamine and the tertiary alkanolamine to interact to provide an amount of a secondary alkanolamine; such as wherein the primary alkanolamine, the secondary alkanolamine and the tertiary alkanolamine are in thermal equilibrium.

[0025] In any of the methods above, the carbon dioxide absorption rate using the aqueous amine solvent comprising the blend of a primary alkanolamine and a tertiary alkanolamine is increased compared to the carbon dioxide absorption rate of an aqueous amine solvent comprising either the primary alkanolamine or the tertiary alkanolamine alone.

[0026] In any of the methods above, the carbon dioxide capacity using the aqueous amine solvent comprising the blend of a primary alkanolamine and a tertiary alkanolamine is increased compared to the carbon dioxide capacity of an aqueous amine solvent comprising either the primary alkanolamine or the tertiary alkanolamine alone.

[0027] The features and advantages of the present invention will be readily apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] FIG. 1 shows a plot of the degradation of 5 m DGA and 5 m DMAEE with 0.2 mol H^+ /mole alkalinity at 150 °C, along with the formation of MAEE and QUAT for DMAEE degradation.

[0029] FIG. 2 shows a plot of the degradation of 7 m DGA with 0.3 mol CO_2 /mole alkalinity at 150 °C, compared to 5 m DGA with 0.4 mol CO_2 /mole alkalinity measured at the same temperature.

[0030] FIG. 3 shows a plot of the degradation of 5 m DGA/5 m DMAEE with 0.3 mol H^+ /mole alkalinity at 175 °C, along with the formation of MAEE.

[0031] FIG. 4 shows a plot of K_t for DGA/DMAEE/MAEE thermally degraded at 175 °C ($\alpha_H=0.3$).

[0032] FIG. 5 shows a plot of the degradation of 5 m DGA/5 m DMAEE with 0.4 mol CO_2 /mole alkalinity at 150 °C, along with the formation of MAEE and other minor products.

[0033] FIG. 6 shows a plot comparing the loss of effective amine for 5 m DGA/5 m DMAEE to 7 m MEA with 0.4 mol CO_2 /mole alkalinity at 150 °C.

[0034] FIG. 7 shows a plot of CO_2 cyclic capacity and average absorption rate (kg' avg) at 40 °C for DGA/MAE/DMAEE with variable concentration, compared to 7 m MEA, 10 m DGA, and 5 m PZ.

[0035] FIG. 8 shows a plot of CO₂ solubility in 1.75 m DGA/1.75 m MAE (as a proxy for MAEE)/3.50 m DMAEE at various temperatures.

DESCRIPTION

[0036] All patents cited herein are incorporated by reference.

[0037] The present disclosure generally relates to the removal of acidic gases, including carbon dioxide and hydrogen sulfide, from flue gas or other gases through aqueous absorption and stripping processes. More particularly, in some embodiments, the present disclosure relates to methods and compositions for the removal of acidic gas from a gas mixture using an aqueous amine solvent blend. It should be understood that aspects of the present disclosure may be combined, as applicable, without deviating from the spirit of the disclosure.

[0038] Using novel amines with desirable chemical and physical properties is a critical approach to reduce the cost and mitigate environmental issues. An ideal amine solvent would feature high CO₂ cyclic capacity, fast absorption rate, high resistance to degradation, low amine volatility, low viscosity, and high heat of CO₂ absorption. However, it is not likely to find a single solvent that has all the desired features. Primary amines, such as MEA and AEE, feature high heat of CO₂ absorption, but have disadvantages of low CO₂ cyclic capacity due to the high carbamate stability. Tertiary amines, which cannot form carbamates, show much higher CO₂ cyclic capacity than primary amines, but substantially lower CO₂ absorption rate and heat of CO₂ absorption. Secondary amines generally have fast CO₂ absorption rate, but moderate CO₂ cyclic capacity and heat of CO₂ absorption. Blending different solvents is one approach to combine desirable characteristics.

[0039] Thermal degradation of amine solvents is in general unfavorable, as it causes the loss of original amines, and some of the degradation products may cause environmental and health issues. However, some degradation products may have better properties than the original amine solvent for CO₂ capture.

[0040] Surprisingly, aqueous amine solvents comprising blends of primary alkanolamines and tertiary alkanolamines provide improved properties of the carbon dioxide absorption rate and/or capacity compared to an aqueous amine solvent comprising either the primary alkanolamine or the tertiary alkanolamine alone. Also surprisingly,

when primary alkanolamines are mixed with tertiary alkanolamines and heated, they may interact to form secondary alkanolamines. Without being bound to any particular hypothesis, the resulting three-way blends of primary alkanolamines, secondary alkanolamines and tertiary alkanolamines may provide aqueous solvents with improved properties for CO₂ capture.

[0041] Blends of primary and tertiary alkanolamines can degrade when heated to elevated temperatures such as from 120 to 175°C. The alkanolamines can be any amines that are useful in absorption and stripping process, so long as they can interact to provide a secondary alkanolamines. In some instances, the thermal degradation product(s) of the amine(s) are at equilibrium with the original amine(s) at temperatures of 120°C or higher. Preferably, the thermal degradation product of the amine can be any thermal degradation product that achieves equilibrium with the amine at high temperatures, such as those of 120°C or higher.

[0042] For example, the aqueous solvents may comprise solvents wherein the primary alkanolamine comprises H₂N(CH₂CH₂O)_mH and the tertiary alkanolamine comprises (C₁-C₂ alkyl)₂N(CH₂CH₂O)_nH, wherein m and n are each independently 1, 2 or 3. Preferred solvents are those wherein m and n are both 2 or are both 3.

[0043] In some instances, the primary alkanolamine comprises monoethanolamine and the tertiary alkanolamine comprises dimethylethanolamine, diethylethanolamine, methyldiethanolamine, ethyldimethanolamine or triethanolamine. After thermally-initiated interaction between the primary alkanolamines and the tertiary amine, the aqueous amine solvent may further comprise methylethanolamine or ethylethanolamine when the tertiary amine comprises dimethylethanolamine, diethylethanolamine, methyldiethanolamine, or ethyldimethanolamine. Alternatively, the aqueous amine solvent may further comprise diethanolamine when the tertiary alkanolamine comprises triethanolamine.

[0044] In a notable embodiment, the primary alkanolamine comprises 2-(2-aminoethoxy)ethanol (AEE) and the tertiary alkanolamine comprises dimethylaminoethoxyethanol (DMAEE). The method of thermal equilibration of primary and tertiary alkanolamines is illustrated herein using this blend as an example. The impact on properties useful for CO₂ capture is also demonstrated.

[0045] As a tertiary amine, DMAEE can increase the CO₂ cyclic capacity of AEE. At high temperature, the AEE/DMAEE blend reaches equilibrium with its major degradation product, methylaminoethoxyethanol (MAEE), a secondary amine. This equilibration provides an aqueous amine solvent further comprising methylaminoethoxyethanol (MAEE). The production of MAEE enhances the CO₂ absorption rate, while maintaining the CO₂ capacity of the original solvent. Due to the high cost of production, MAEE is not able to be directly used for CO₂ capture. Thermally degraded AEE/DMAEE was found to have a better performance for CO₂ capture than the original solvent and the benchmark solvent, 7 m MEA. The thermal degradation of AEE/DMAEE was evaluated at normal operating conditions to calculate the equilibrium constant for AEE/MAEE/DMAEE. The equilibration constant is indicative of the amounts of the three components when AEE, MAEE and DMAEE are in thermal equilibrium. The degraded AEE/DMAEE at equilibrium with variable compositions was evaluated for CO₂ cyclic capacity, CO₂ absorption rate, viscosity, and heat of CO₂ absorption.

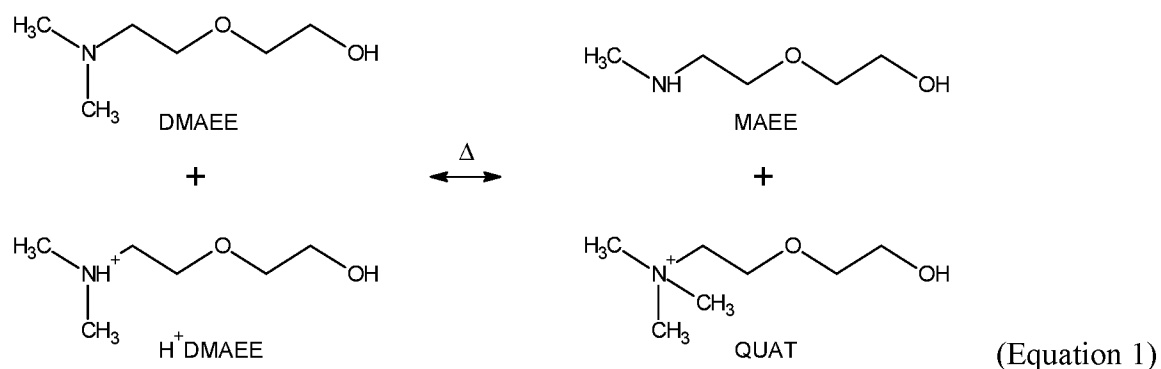
[0046] In some embodiments, the primary and tertiary alkanolamines are each independently present in about 20 to about 40 % of the total alkanolamine content (such as each independently about 30 to 40 %) and the secondary amine is present in about 20 to 60 % (such as about 30 to 40 %) of the total alkanolamine content. In other embodiments, the total alkanolamines may be present in the aqueous solvent in from a lower limit of 3, 5, or 8 to an upper limit of 10, 15 or 20 molar amounts.

[0047] Aqueous amine solvent blends were studied using the methods described in the Examples Section below.

Thermal Degradation of AEE and DMAEE in Acidified Solution

[0048] Degradation in solution acidified by sulfuric acid instead of CO₂, which has protonated amine but no amine carbamate, was performed to develop understanding of the mechanism for the initial degradation reaction between a free amine species and a protonated amine species. Figure 1 shows the degradation of 5 m DGA and 5 m DMAEE with 0.20 mol H⁺/mole alkalinity (added as H₂SO₄) at 150 °C, along with the formation of the degradation product for 5 m DMAEE. No degradation of DGA was observed at this condition for 2 weeks, indicating the good thermal stability of DGA. DMAEE appears to reach equilibrium with its two degradation products. The degradation products are

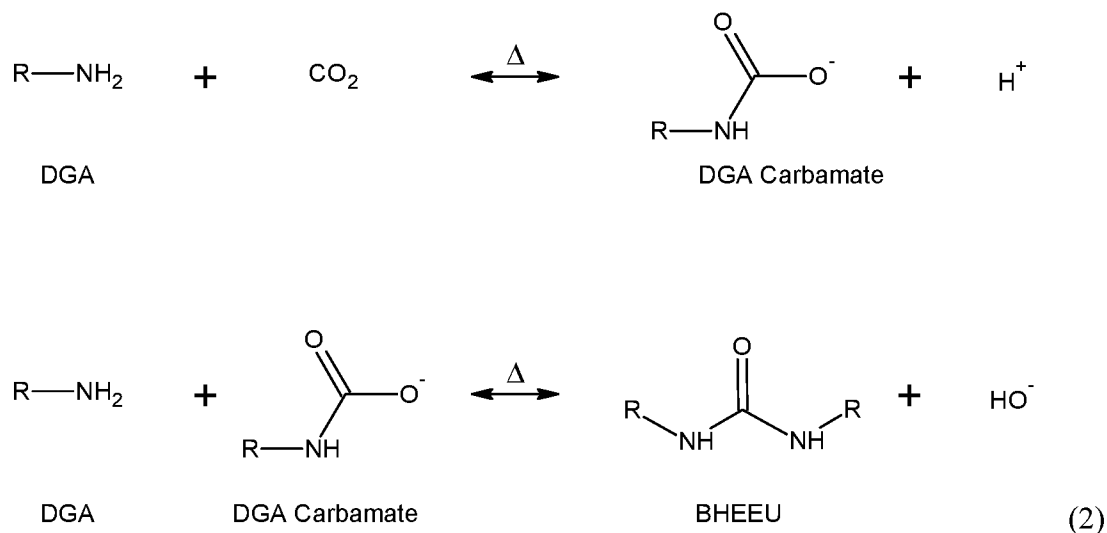
believed to be MAEE and 2-[2-(methylamino)ethoxy]ethanol, a quaternary amine (QUAT), based on their retention-time on the cation chromatograph and the proposed degradation mechanism. In Figure 1, the amount of parent amines DGA and DMAEE is according to the scale on the left axis, and the amount of degradation products MAEE and QUAT is according to the scale on the right axis. The degradation mechanism for DMAEE in acidified solutions should be similar to that of other tertiary amines. DMAEE attacks protonated DMAEE (H^+DMAEE), and reaches equilibrium with MAEE and QUAT (Equation 1).



Thermal Degradation of AEE in CO₂ Loaded Solution

[0049] Although the acid-loaded experiments are useful in understanding the initial degradation pathway of AEE, the degradation of AEE was also investigated in CO₂ loaded solutions to evaluate its thermal stability in a real CO₂ capture application with other side reactions caused by the formation of amine carbamate. Figure 2 shows the degradation of 7 m AEE with 0.3 mol CO₂/mole alkalinity at 150 °C, compared to 5 m AEE with 0.4 mol CO₂/mole alkalinity at the same temperature.

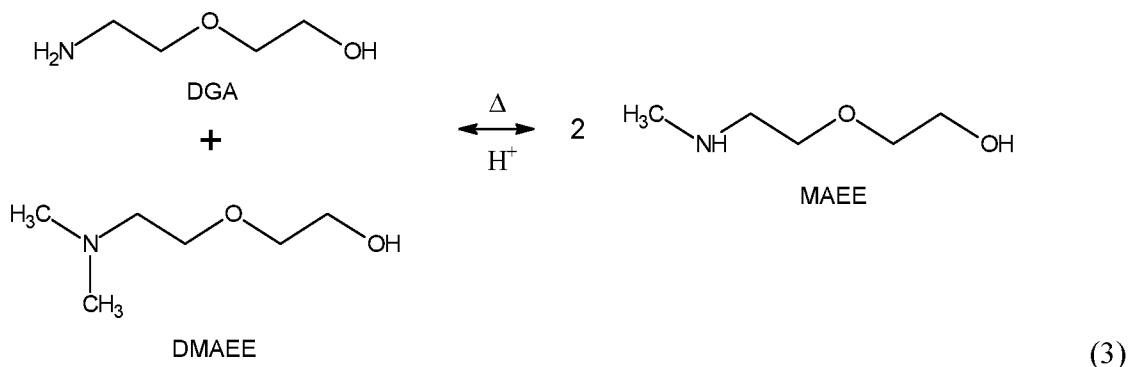
[0050] In both cases, AEE appears to reach equilibrium with the degradation products. Morpholine was identified as the only degradation product on cation chromatography for the degradation of 7m DGA with 0.3 mol CO₂/mole alkalinity at 150 °C. The production of morpholine only accounted for about 10 % of the DGA loss. The majority of the lost DGA was probably converted to N,N-bis(hydroxyethoxyethyl)urea (BHEEU), which is the predominant degradation product for CO₂ loaded DGA solution (Equation 2).



[0051] R in Equation 2 denotes HOCH₂CH₂OCH₂CH₂-.

Thermal Degradation of DGA/DMAEE in Acidified Solution

[0052] Thermal degradation of DGA/DMAEE with variable compositions was investigated in acidified solution up to 175 °C, above expected operating conditions, to accelerate degradation in order to more easily quantify the reactions occurring. Figure 3 shows the degradation of 5 m DGA/5 m DMAEE with 0.30 mol H⁺/mole alkalinity at 175 °C, along with the formation of the only degradation product, MAEE. Figure 3 shows that the original solution contained about 2000 to about 2100 mmol/kg of each of AEE and DMAEE, or AEE and DMAEE each comprising about 50 mole % of total amines. After thermal treatment for about 10 days, the resulting solution appeared to show that DGA and DMAEE appeared to reach equilibrium with MAEE (Equation 3), with no significant change in concentration of amines observed on heating for an additional 10 days. The thermally equilibrated solvent contained AEE and DMAEE each present in amounts from about 1200 to about 1300 mmol/kg of aqueous solvent (each comprising about 28 to about 33 mole % of total amines) and MAEE present in an amount from about 1600 to about 1700 mmol/kg of aqueous solvent (about 38 to about 33 mole % of total amines).



[0053] This S_N2 substitution reaction is commonly referred to as “arm switching”. Based on the initial degradation pathway shown in Equation 3, a second-order rate model was used to fit the degradation for DGA/DMAEE (Equation 4), where C_{DGA} , C_{DMAEE} , and C_{MAEE} are the concentration of amines; $k_{2,f,c}$ and $k_{2,r,c}$ are concentration-based second-order forward and reverse rate constants, respectively; t is the experimental time in seconds.

$$-\frac{dC_{DGA}}{dt} = -\frac{dC_{DMAEE}}{dt} = 2 * \frac{dC_{MAEE}}{dt} = k_{2,f,c} * C_{DGA} * C_{DMAEE} - k_{2,r,c} * (C_{MAEE})^2 \quad (4)$$

[0054] The lines in Fig. 3 indicate second-order reversible rate models fit the data.

[0055] Figure 4 shows the effect of initial DGA to DMAEE ratio on the interconversion of DGA, DMAEE, and MAEE (Equation 5) with 0.30 mol H^+ /mole alkalinity at 175 °C. The points in Figure 4 are experimental K_t ; Lines indicate second-order reversible rate models fit the data (Equation 5), wherein K_t is the ratio of products to reactants at time t .

$$K_t = \frac{[MAEE]^2}{[DGA] * [DMAEE]} \quad (5)$$

[0056] Of note are aqueous solvents wherein the mol ratio of tertiary amine to primary amine in the initial solvent is less than or equal to 1:1, such as from 1:1 to 1:5, or 1:1 to 1:3. K_t for 2.5 m DGA/7.5 m DMAEE (initial ratio of 1:3) and 5 m DGA/5 m DMAEE (initial ratio 1:1) tend toward a value of 1.7 at equilibrium (when $K_t = K_{eq}$, the equilibrium constant). When the mole amount of tertiary amine is greater than the mole amount of primary amine, the K_t may be different. K_t for 7.5 m DGA/2.5 m DMAEE (initial ratio of 3:1) tends toward a value of 1.1. Without being bound by hypothesis, the

lower K_{eq} in 7.5 m DGA/2.5 m DMAEE may result from the degradation of DGA to morpholine.

Degradation of DGA/DMAEE in CO₂-loaded solution

[0057] Figure 5 shows the degradation of 5 m DGA/5 m DMAEE (initial ratio about 1:1) with 0.4 mol CO₂/mole alkalinity at 150 °C, along with the formation of the degradation products. Solid lines and dashed line indicate second-order reversible rate models fit the data (Equation 4). Similar to that in acidified solution, DGA and DMAEE in CO₂ loaded solution also reach equilibrium with the major degradation product, MAEE (Equation 3). Two minor products, which were not identified in acidified solution, were present in the CO₂-loaded DGA/DMAEE. One of them was identified as 1-methylmorpholine (1M-Morph), and the other one was QUAT. BHEEU, as the major degradation product for DGA in CO₂ loaded solution, should also be present in the solution. In Figure 5, the amount of parent amines DGA and DMAEE is according to the scale on the left axis, and the amount of degradation products MAEE, QUAT and 1M-Morph is according to the scale on the right axis. The initial solvent comprised about 1900 to about 2100 of each of DGA and DMAEE. After equilibration for about 30 days, AEE and DMAEE are each present in amounts from about 1200 to about 1400 mmol/kg of aqueous solvent (each about 28-37 % of total amines) and MAEE is present in an amount from about 800 to about 900 mmol/kg of aqueous solvent (about 19-24 % of total amines). 1M-Morph was present in about 200 mmol/kg (about 5 % of total amines).

[0058] The second-order reversible rate model (Equation 4) under-predicted the loss of DGA and DMAEE, while over-predicting the production of MAEE, as a result of the formation of BHEEU, 1M-Morph and QAUT. K_{eq} for 5 m DGA/5 m DMAEE (Equation 4) in CO₂ loaded solutions was found to be from 0.4 to 1.0, depending on the CO₂ loading and temperature, which is significantly smaller than that in acidified solutions.

Loss of effective amine in degraded DGA/DMAEE

[0059] Figure 6 compares the loss of effective amine for 5 m DGA/5 m DMAEE (MAEE is considered an effective amine for CO₂ absorption) to 7 m MEA with 0.4 mol CO₂/mole alkalinity at 150 °C. The solid line indicates a first-order rate model fit the data. The sum of DGA, DMAEE, and MAEE decreased by 6% within one day and then maintained a constant value for the next 3 weeks. 1M-Morph and QAUT accounted for

about 35% of the loss of the effective amine, while BHEEU may account for the rest. Once equilibrium was reached, the total amine content available for scrubbing CO₂ remained generally constant. However, the degradation of MEA followed a first order rate model, and lost 60% of its initial amine within 2 weeks. This demonstrates that blends of amines as described herein maintain a higher level of effective amines than a commercial standard MEA for scrubbing CO₂.

CO₂ Cyclic Capacity and Absorption Rate

[0060] Based on the thermal degradation of DGA/DMAEE in CO₂ loaded solutions, a K_{eq} of 0.5 was chosen to evaluate the CO₂ cyclic capacity and absorption rate for DGA/DMAEE/MAEE. CO₂ equilibrium partial pressure (P_{CO₂*}) and absorption rate in DGA/DMAEE/MAEE with five different compositions were measured at 40 °C using a wetted wall column (WWC). Due to the lack of a commercial source for a large quantity of MAEE, 2-(methylamino)ethanol (MAE), which is a secondary amine with similar structure and pKa to MAEE, was used as a proxy for MAEE for evaluation.

[0061] The CO₂ cyclic capacity of a solvent (ΔC_{solv}) is defined as the difference in CO₂ concentration between the lean and rich solvents (Equation 6), wherein C_{lean} and C_{rich} are the CO₂ concentration of lean and rich solvents.

$$\Delta C_{solv} = \frac{C_{rich} - C_{lean}}{kg \text{ (amine+ water)}} = \frac{mol \text{ CO}_2}{kg} \quad (6)$$

[0062] For coal-fired flue gas, the normal operational lean and rich solvents correspond to P_{CO₂*} of 0.5 kPa and 5 kPa at 40 °C, respectively, in order to maintain enough driving force for CO₂ absorption throughout the absorber. ΔC_{solv} is normalized by the viscosity of the solvent to consider the effect of viscosity on the optimized heat exchanger cost (Equation 7), based on the observation that the heat transfer coefficient generally depends on solvent viscosity to about -0.35 power.

$$\Delta C_{\mu} = \Delta C_{solv} / (\mu_{mid} / \mu_{7 \text{ m MEA}})^{0.175} \quad (7)$$

μ_{mid} and $\mu_{7 \text{ m MEA}}$ are the viscosities of the studied amine and 7 m MEA, respectively, at mid-loading (P_{CO₂*} = 2.0 kPa) and 40 °C.

[0063] The term kg' is defined as the liquid film mass transfer coefficient on a partial pressure basis, and is calculated as the ratio of CO₂ flux to the liquid film partial pressure driving force. For each solvent, k_{g'} avg is calculated for an isothermal absorber at

40 °C for coal flue gas and 90% CO₂ removal (Equation 8), assuming a linear concentration profile and equilibrium curve in the absorber, and negligible gas film resistance.

$$k'_{g\text{ avg}} = \frac{Flux_{CO_2,LM}}{(P_{CO_2} - P_{CO_2}^*)_{LM}} = \frac{(Flux_{CO_2,top} - Flux_{CO_2,bottom}) / \ln(Flux_{CO_2,top} / Flux_{CO_2,bottom})}{(P_{CO_2,top} - P_{CO_2,lean}^*) - (P_{CO_2,bottom} - P_{CO_2,rich}^*) / \ln(\frac{P_{CO_2,top} - P_{CO_2,lean}^*}{P_{CO_2,bottom} - P_{CO_2,rich}^*})}$$

(8)

[0064] The P_{CO₂} at the bottom and top of the absorber are 12 and 1.2 kPa, the rich and lean P_{CO₂}^{*} are 5 and 0.5 kPa. Experimental values at 40 °C are used to interpolate k_g' that corresponds to P_{CO₂}^{*} at 5 and 0.5 kPa, which are then used to calculate the corresponding flux.

[0065] Figure 7 and Table 1 show the normalized CO₂ cyclic capacity (ΔC_μ) and average CO₂ absorption rate (k_g'_{avg}) at 40 °C for DGA/DMAEE/MAE at variable compositions, compared to 7 m MEA, 10 m DGA, and 5 m PZ. Labels indicate the concentrations of DGA, MAE, and DMAEE in solution in molal (m). 2.1 m DGA/4.9 m DMAEE shows a comparable ΔC_μ to 5 m PZ, which is substantially larger than that of 7 m MEA and 10 m DGA. All of the blends exhibited normalized CO₂ cyclic capacity from about 0.45 to about 0.55 mol CO₂/kg of solvent. However, the k_g'_{avg} of 2.1 m DGA/4.9 m DMAEE is slightly lower than 7 m MEA. Replacing some DGA and DMAEE with MAE increases the k_g'_{avg} significantly. k_g'_{avg} of the four DGA/DMAEE/MAE solvents tested in this work is 30-70% higher than that of 7 m MEA, but it is still much lower than that of 5 m PZ. Although 2.5 m DGA/2.5 m MAE/5.0 m DMAEE and 1.07 m DGA/1.93 m MAE/7 m DMAEE absorb CO₂ faster than the other DGA/MAE/DMAEE with total alkalinity of 7 m, as a result of the higher concentration of MAE, their ΔC_μ are smaller, due to higher viscosity.

Table 1

Properties of DGA/MAE/DMAEE solvents with variable concentration,
compared to 7 m MEA, 10 m DGA, and 5 m PZ.

Amine (m)			μ _{mid} (cP)	ΔC _{solv} (mol/kg)	ΔC _μ ^b (mol/kg)	k _g ' _{avg-40 °C} (10 ⁻⁶ mol/Pa*m ² *s)
DGA	MAE ^a	DMAEE				
2.50	2.50	5.00	7.3	0.56	0.47	0.66
1.07	1.93	7.00	8.1	0.57	0.47	0.75
1.75	1.75	3.50	5.4	0.56	0.50	0.61
0.75	1.35	4.90	5.1	0.59	0.52	0.57
2.10		4.90	5.1	0.56	0.50	0.41

10°		10.0	0.38	0.30	0.36
	7 m MEA	2.7	0.35	0.35	0.43
	5 m PZ	4.2	0.57	0.53	1.13

a: MAE was used as a proxy for MAEE

b: $\Delta C_{\mu} = \Delta C_{solv} / (\mu_{mid} / \mu_{7mMEA})^{0.175}$

CO₂ Solubility in 1.75 m DGA/1.75 m MAEE/3.50 m DMAEE at 20 – 160 °C

[0066] Figure 8 shows the vapor liquid equilibrium (VLE) of CO₂ in 1.75 m DGA/1.75 m MAE (as a proxy for MAEE)/3.50 m DMAEE at 20–160 °C. Solid points: WWC results; open points: total pressure results; lines: model prediction (Equation 9). CO₂ equilibrium partial pressure, $P_{CO_2}^*$ (Pa), was regressed using the following semi-empirical model (Equation 9) as a function of temperature, T (K), and CO₂ loading, α (mol CO₂/mol alkalinity), in the liquid phase.

$$\ln P_{CO_2}^* = 35 - 10212 \cdot \frac{1}{T} + 4777 \cdot \frac{\alpha}{T} \quad (9)$$

[0067] The heat of CO₂ absorption (ΔH_{abs}) for 1.75 m DGA/1.75 m MAE/3.50 m DMAEE can be extracted from the equilibrium data by applying the fundamental thermodynamic relationship to the semi-empirical model (Equation 10):

$$-\Delta H_{abs} = R \cdot \left(\frac{\partial \ln(P_{CO_2}^*)}{\partial (1/T)} \right)_{P,x} = -10212 + 4777 \cdot \alpha \quad (10)$$

[0068] ΔH_{abs} for 1.75 m DGA/1.75 m MAE/3.50 m DMAEE at CO₂ loading corresponding to a $P_{CO_2}^*$ of 1.5 kPa at 40 °C is 72 kJ/mol, which is comparable to 7 m MEA (71 kJ/mol), and higher than 5 m PZ (64 kJ/mol).

[0069] We have found that thermally degraded DGA/DMAEE is a superior solvent for CO₂ capture from flue gas. The blend was found to have a better performance for CO₂ capture than the original solvent blend. At high temperature, DGA/DMAEE reaches equilibrium with its major degradation product, methylaminoethoxyethanol (MAEE).

[0070] The production of MAEE enhances the CO₂ absorption rate, while maintaining the CO₂ capacity of the original solvent. The normalized CO₂ cyclic capacity of DGA/MAEE/DMAEE is substantially greater than that of 7 m MEA and 10 m DGA, and comparable to 5 m PZ. The average CO₂ absorption rate ($k_g'_{avg}$) of DGA/MAEE/DMAEE is 30-70% higher than 7 m MEA, although it is still much lower than 5 m PZ.

[0071] The heat of CO₂ absorption (ΔH_{abs}) for 1.75 m DGA/1.75 m MAEE/3.50 m DMAEE at CO₂ loading corresponding to a $P_{\text{CO}_2}^*$ of 1.5 kPa at 40 °C is 72 kJ/mol, which is comparable to 7 m MEA, and greater than 5 m PZ.

[0072] When starting with 5 m DGA/5 m DMAEE with 0.4 mol CO₂/mole alkalinity, the sum of DGA, DMAEE, and MAEE decreased by 6% within one day at 150 °C, and then maintained a constant value for the next 3 weeks. At the same condition, MEA lost 60% of its initial amine within 2 weeks.

[0073] The capital and energy cost for flue gas CO₂ capture using thermally degraded DGA/DMAEE is expected to be much lower than that using 7 m MEA, while still higher than that using 5 m PZ.

[0074] In some embodiments, a method can include contacting an acidic gas with an aqueous amine solvent. The aqueous amine solvent can include one or more amines, wherein a degradation product of at least one of the one or more amines is at equilibrium with the at least one of the one or more amines at temperatures of 120°C or higher. In certain aspects the aqueous amine solvent comprises DMAEE. The aqueous amine solvent can further include AEE. The thermal degradation product of the at least one of the one or more amines can be MAEE. In certain embodiments, the method can further comprise a stripper at a temperature of about 120°C to about 175°C. In certain aspects, the acidic gas can be carbon dioxide.

[0075] In still other embodiments, a method of amine scrubbing of an acidic gas can include obtaining an amine pre-solvent comprising a first amine; exposing the amine pre-solvent to a temperature of 120°C or higher for a time sufficient to allow a degradation product of the first amine to reach equilibrium with the first amine thereby yielding a final amine solvent, and contacting the acidic gas with the final amine solvent. Amine pre-solvents can include DMAEE. Amine pre-solvents can also include additional amines, for example, a second amine. The second amine or additional amines can include AEE. The degradation product can be MAEE, particularly in the case where the first amine is DMAEE.

[0076] In certain embodiments, a method is provided for increasing the carbon dioxide absorption rate and maintaining the carbon dioxide capacity of an aqueous amine solvent which includes providing an aqueous amine solvent comprising one or more

amines, contacting the aqueous amine solvent with an acidic gas at a temperature of 120°C or higher, wherein at least one of the one or more amines forms a degradation product that is in equilibrium with the at least one of the one or more amines.

[0077] In still other embodiments, a method can include contacting a gaseous stream with an aqueous amine solvent, wherein the aqueous amine solvent comprises one or more amines and a degradation product of at least one of the one or more amines, wherein the degradation product is in equilibrium with at least one of the one or more amines at temperatures of 120°C or higher, and wherein the gaseous stream comprises an acidic gas, and allowing the acidic gas to transfer from the gaseous stream to the solvent. The method can further include forming a purified gaseous stream and a rich solvent stream. The method can further include routing the rich solvent stream through a stripper. The method can also include recycling a solvent stream exiting the stripper. Strippers can include, by way of example but not limitation, a simple stripper, a matrix stripper, a multistage flash stripper, an exchange stripper, a multipressure stripper, a flashing feed stripper, and/or a multistage stripper. Gaseous streams can be, by way of example but not limitation, flue gas, natural gas, hydrogen gas, and/or synthesis gas or any combination thereof.

[0078] In yet other embodiments, a method includes contacting a gaseous stream with an aqueous amine solvent in an absorber, wherein the aqueous amine solvent comprises one or more amines wherein a degradation product of at least one of the one or more amines is in equilibrium with at least one of the one or more amines at temperatures of 120°C or higher, and wherein the gaseous stream comprises an acidic gas, allowing the acidic gas to transfer from the gaseous stream to the solvent, forming a purified gaseous stream and a rich solvent stream, and routing the rich solvent stream through a stripper.

EXAMPLES

Solution preparation

[0079] All amines studied in this work were reagent grade chemicals from commercial sources. Aqueous DGA/DMAEE solutions were prepared by mixing DGA and DMAEE in distilled de-ionized water. CO₂ loaded solutions were prepared by gravimetrically sparging CO₂ (99.5%, Matheson Tri Gas, Basking Ridge, NJ) in unloaded amine solutions in a gas-washing bottle. The concentration of CO₂ was checked by total

inorganic carbon (TIC) analysis, described in detail previously (S.A. Freeman, J. Davis, G.T. Rochelle, Degradation of Aqueous Piperazine in Carbon Dioxide Capture, *Int. J. Greenh. Gas Control*. 4 (2010) 756–761). Acid loaded solutions were prepared by adding 10 N sulfuric acid to unloaded aqueous amine.

[0080] Due to the lack of a commercial source for large quantities of MAEE, 2-(methylamino)ethanol (MAE), which is a secondary amine with similar structure and pK_a to MAEE, was used as a proxy for MAEE for evaluation.

Thermal degradation

[0081] Thermal degradation of DGA/DMAEE under various conditions was measured in 3/8-inch 316 stainless steel Swagelok[®] cylinders with a volume of 4.5 ml and diameter of 0.95 cm. A number of cylinders were filled with 4 mL target amine solution. The cylinders were then sealed with two Swagelok[®] end caps, and placed in forced convection ovens maintained at the target temperature. Individual cylinders were removed from the ovens at each sampling time. The parent amines and degradation products in the solutions were analyzed using cation chromatography. The details of the experimental apparatus and procedure were described in detail previously (S.A. Freeman, J. Davis, G.T. Rochelle, Degradation of Aqueous Piperazine in Carbon Dioxide Capture, *Int. J. Greenh. Gas Control*. 4 (2010) 756–761).

Analytical Tools - Cation Chromatography

[0082] A Dionex ICS-2100 cation ion chromatograph (Dionex Corporation) was used to quantify parent amines and identify degradation products. A 4 × 50 mm CG17 guard column connected with a 4 × 250 mm CS17 analytical column was used for separation. The eluent contained varying concentrations of methanesulfonic acid (MSA) in analytical grade water. Ion suppression was used to improve the signal/noise ratio. Standard curves of parent amines and degradation products were prepared to quantify the amount of amine present. Due to the lack of a commercial source for methylaminoethoxyethanol (MAEE) and 2-[2-(methylamino)ethoxy]ethanol, a quaternary amine (QUAT), the standard curves for DGA and DMAEE were used to quantify MAEE and QUAT, respectively. Samples were diluted by a factor of 10,000 (mass) in analytical grade water. Degradation products were identified by matching their retention-time with standard samples. The details of the analytical methods were described in detail previously

(S.A. Freeman, J. Davis, G.T. Rochelle, Degradation of Aqueous Piperazine in Carbon Dioxide Capture, *Int. J. Greenh. Gas Control*. 4 (2010) 756–761).

Viscosity measurement

[0083] Viscosity of DGA/DMAEE/MAEE with variable concentration and CO₂ loading was measured using a Physica MCR 300 cone-and-plate rheometer (Anton Paar GmbH, Graz, Austria). The method was described in detail previously (S.A. Freeman, R.E. Dugas, D.H. Van Wagener, T. Nguyen, G.T. Rochelle, Carbon Dioxide Capture with Concentrated, Aqueous Piperazine, *Int. J. Greenh. Gas Control*. 4 (2010) 119–124).

CO₂ solubility and absorption rate

[0084] CO₂ equilibrium partial pressure ($P_{\text{CO}_2^*}$) and absorption rate in DGA/DMAEE/MAEE with variable concentration and CO₂ loading were measured at 40 °C using a wetted wall column (WWC), which counter-currently contacted an aqueous amine solution with a saturated N₂/CO₂ stream on the surface of a stainless steel rod with a known surface area to simulate CO₂ absorption in an absorber.

[0085] The equilibrium partial pressure ($P_{\text{CO}_2^*}$) of 1.75 m DGA/3.5 m DMAEE/1.75 m MAEE was also measured at 20, 40, and 60 °C using a WWC and at high temperature (100–160 °C) using a sealed autoclave. $P_{\text{CO}_2^*}$ measured by autoclave was calculated by subtracting the partial pressure of N₂ and water from the measured total pressure. The pressure of water was assumed to follow Raoult's Law and the pressure of the amine was neglected. The experimental method and calculation of CO₂ partial pressure were described in detail previously (Q. Xu, G.T. Rochelle, Total Pressure and CO₂ Solubility at High Temperature in Aqueous Amines, *Energy Proc.* 4 (2011) 117–124).

[0086] While the disclosed subject matter is described herein in terms of certain exemplary embodiments, those skilled in the art will recognize that various modifications and improvements may be made to the disclosed subject matter without departing from the scope thereof. Moreover, although individual features of one embodiment of the disclosed subject matter may be discussed herein or shown in the drawings of the one embodiment and not in other embodiments, it should be apparent that individual features of one embodiment may be combined with one or more features of another embodiment or features from a plurality of embodiments.

CLAIMS

What is claimed is:

1. An aqueous amine solvent comprising a blend of a primary alkanolamine and a tertiary alkanolamine.
2. The aqueous amine solvent of claim 1 wherein the primary alkanolamine comprises $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$ and the tertiary alkanolamine comprises $(\text{C}_1\text{-C}_2 \text{ alkyl})_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, wherein m and n are each independently 1, 2 or 3.
3. The aqueous amine solvent of claim 2 wherein m and n are both 2 or are both 3.
4. The aqueous amine solvent of claim 3 wherein the primary alkanolamine comprises 2-(2-aminoethoxy)ethanol (AEE) and the tertiary alkanolamine comprises dimethylaminoethoxyethanol (DMAEE).
5. The aqueous amine solvent of claim 4 further comprising methylaminoethoxyethanol (MAEE).
6. The aqueous amine solvent of claim 1 wherein the primary and tertiary alkanolamines are each independently present in about 20 to about 40 % of the total alkanolamine content and the secondary amine is present in about 20 to 60 % of the total alkanolamine content.
7. The aqueous amine solvent of claim 6 wherein the primary alkanolamine comprises AEE, the tertiary alkanolamine comprises DMAEE and the secondary alkanolamines comprises MAEE.
8. The aqueous amine solvent of claim 6 wherein the primary and tertiary alkanolamines are each independently present in about 30 to about 40 % of the total alkanolamine content and the secondary amine is present in about 30 to 40 % of the total alkanolamine content.
9. The aqueous amine solvent of claim 1 wherein the total alkanolamines are present in the aqueous solvent in from a lower limit of 3 to an upper limit of 20 molar amounts.
10. The aqueous amine solvent of claim 9 wherein the primary alkanolamine comprises AEE, the tertiary alkanolamine comprises DMAEE and the secondary alkanolamines comprises MAEE.
11. The aqueous amine solvent of claim 5 wherein AEE and DMAEE are each present in amounts from about 1200 to about 1400 mmol/kg of aqueous solvent and MAEE is

present in an amount from about 800 to about 900 mmol/kg of aqueous solvent.

12. The aqueous amine solvent of claim 5 wherein AEE, MAEE and DMAEE are in thermal equilibrium.

13. The aqueous amine solvent of claim 12 wherein the K_{eq} is from 0.4 to 1.0.

14. The aqueous amine solvent of claim 1 wherein the primary alkanolamine comprises monoethanolamine and the tertiary alkanolamine comprises dimethylethanolamine, diethylethanolamine, methyldiethanolamine, ethyldimethanolamine or triethanolamine.

15. A method of amine scrubbing of an acidic gas comprising contacting the acidic gas with the aqueous amine solvent of claim 1.

16. The method of claim 15 comprising contacting a gaseous stream with the aqueous amine solvent; and wherein the gaseous stream comprises the acidic gas; and allowing the acidic gas to transfer from the gaseous stream to the solvent.

17. The method of claim 15, further comprising forming a purified gaseous stream and a rich solvent stream.

18. The method of claim 17, further comprising routing the rich solvent stream through a stripper.

19. The method of claim 16 comprising contacting the gaseous stream with the aqueous amine solvent in an absorber; forming a purified gaseous stream and a rich solvent stream; and routing the rich solvent stream through a stripper.

20. The method of claim 18 or claim 19, wherein the stripper is selected from the group consisting of a simple stripper, a matrix stripper, a multistage flash stripper, an exchange stripper, a multipressure stripper, a flashing feed stripper, and a multistage stripper.

21. The method of any of claims 18-20, further comprising recycling a solvent stream exiting the stripper.

22. The method of any of claims 15-21, wherein the gaseous stream is selected from the group consisting of flue gas, a natural gas, a hydrogen gas, and a synthesis gas.

23. The method of any of claims 15-22, wherein the acidic gas is carbon dioxide.

24. The method of claim 15 comprising obtaining an aqueous amine solvent comprising a blend of a primary alkanolamine and a tertiary alkanolamine; exposing the aqueous amine solvent to a temperature of 120°C or higher for a time sufficient to allow the primary alkanolamine and the tertiary alkanolamine to interact to provide an amount of a secondary

alkanolamine.

25. The method of claim 24 wherein the primary alkanolamine, the secondary alkanolamine and the tertiary alkanolamine are in thermal equilibrium.

26. The method of claim 15 wherein the carbon dioxide absorption rate using the aqueous amine solvent comprising the blend of a primary alkanolamine and a tertiary alkanolamine is increased compared to the carbon dioxide absorption rate of an aqueous amine solvent comprising either the primary alkanolamine or the tertiary alkanolamine alone.

27. The method of claim 15 wherein the carbon dioxide capacity using the aqueous amine solvent comprising the blend of a primary alkanolamine and a tertiary alkanolamine is increased compared to the carbon dioxide capacity of an aqueous amine solvent comprising either the primary alkanolamine or the tertiary alkanolamine alone.

28. The method of claim 15 wherein the primary alkanolamine comprises $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$ and the tertiary alkanolamine comprises $(\text{C}_1\text{-C}_2 \text{ alkyl})_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, wherein m and n are each independently 1, 2 or 3.

29. The method of claim 28 wherein m and n are both 2 or are both 3.

30. The method of claim 29 wherein the primary alkanolamine comprises AEE and the tertiary alkanolamine comprises DMAEE.

31. The method of claim 23 wherein the aqueous amine solvent further comprises methylaminoethoxyethanol (MAEE).

32. The method of claim 15 wherein the primary and tertiary alkanolamines are each independently present in about 20 to about 40 % of the total alkanolamine content and the secondary amine is present in about 20 to 60 % of the total alkanolamine content.

33. The method of claim 32 wherein the primary alkanolamine comprises AEE, the tertiary alkanolamine comprises DMAEE and the secondary alkanolamines comprises MAEE.

34. The method of claim 32 wherein the primary and tertiary alkanolamines are each independently present in about 30 to about 40 % of the total alkanolamine content and the secondary amine is present in about 30 to 40 % of the total alkanolamine content.

35. The method of claim 15 wherein the total alkanolamines are present in the aqueous solvent in from a lower limit of 3 to an upper limit of 20 molar amounts.

36. The method of claim 35 wherein the primary alkanolamine comprises AEE, the tertiary alkanolamine comprises DMAEE and the secondary alkanolamines comprises MAEE.

37. The method of claim 33 wherein AEE and DMAEE are each present in amounts from about 1200 to about 1400 mmol/kg of aqueous solvent and MAEE is present in an amount from about 800 to about 900 mmol/kg of aqueous solvent.

38. The method of claim 37 wherein AEE, MAEE and DMAEE are in thermal equilibrium.

39. The method of claim 38 wherein the K_{eq} is from 0.4 to 1.0.

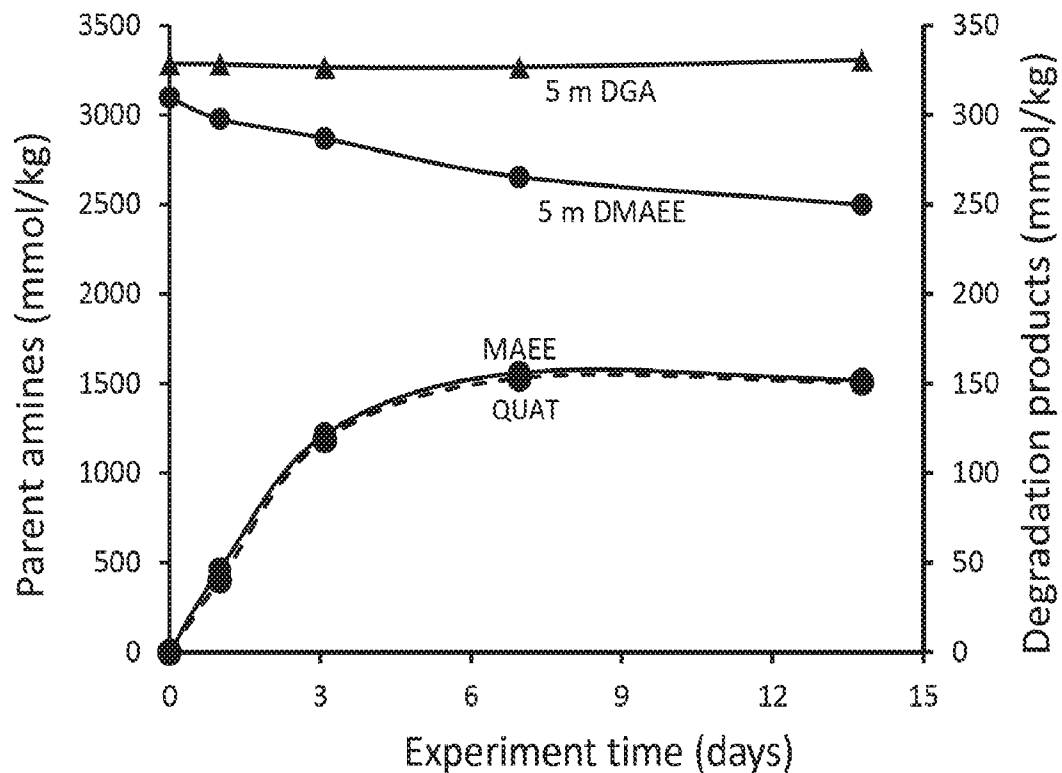


Fig. 1

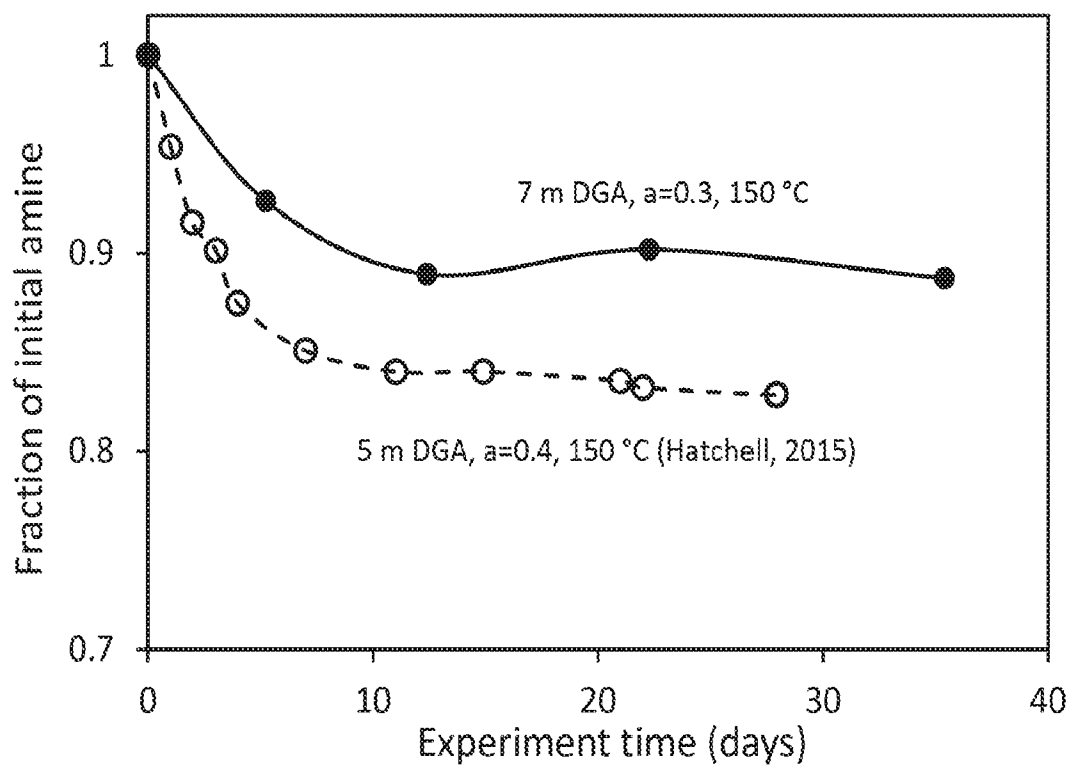


Fig. 2

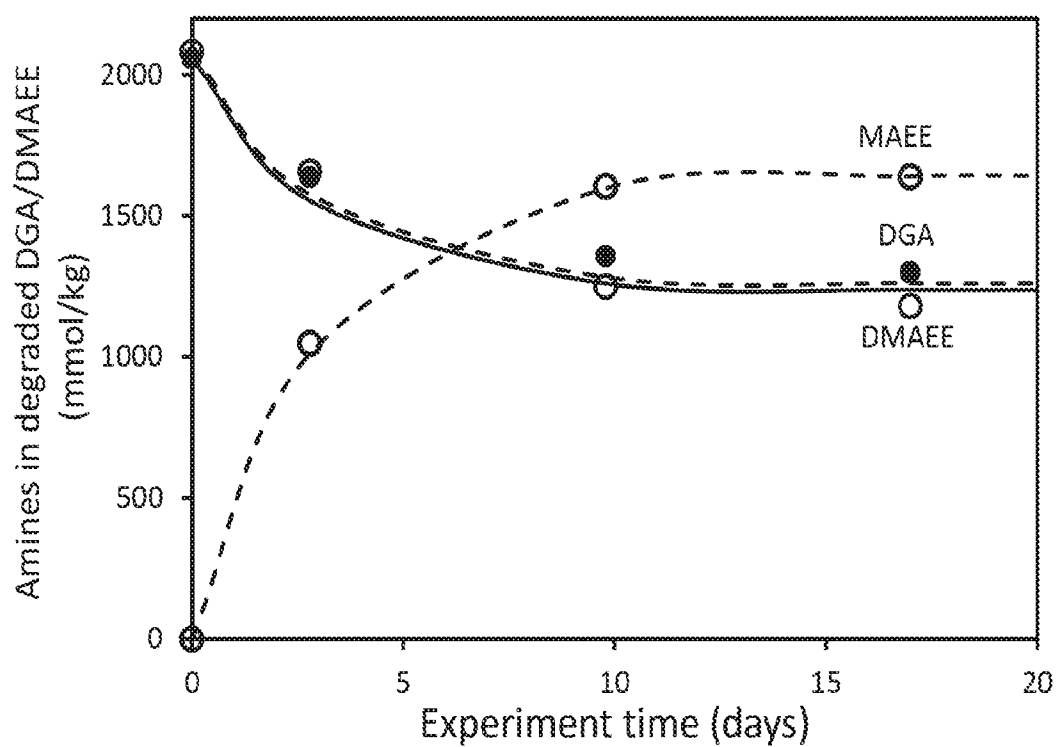


Fig. 3

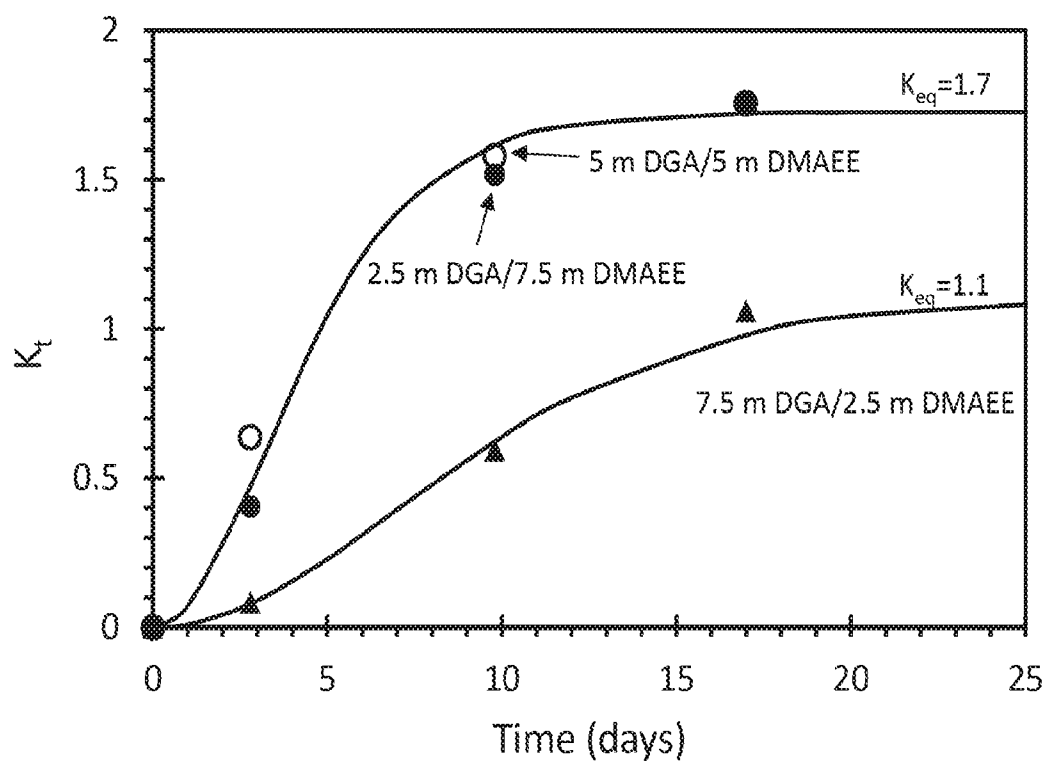


Fig. 4

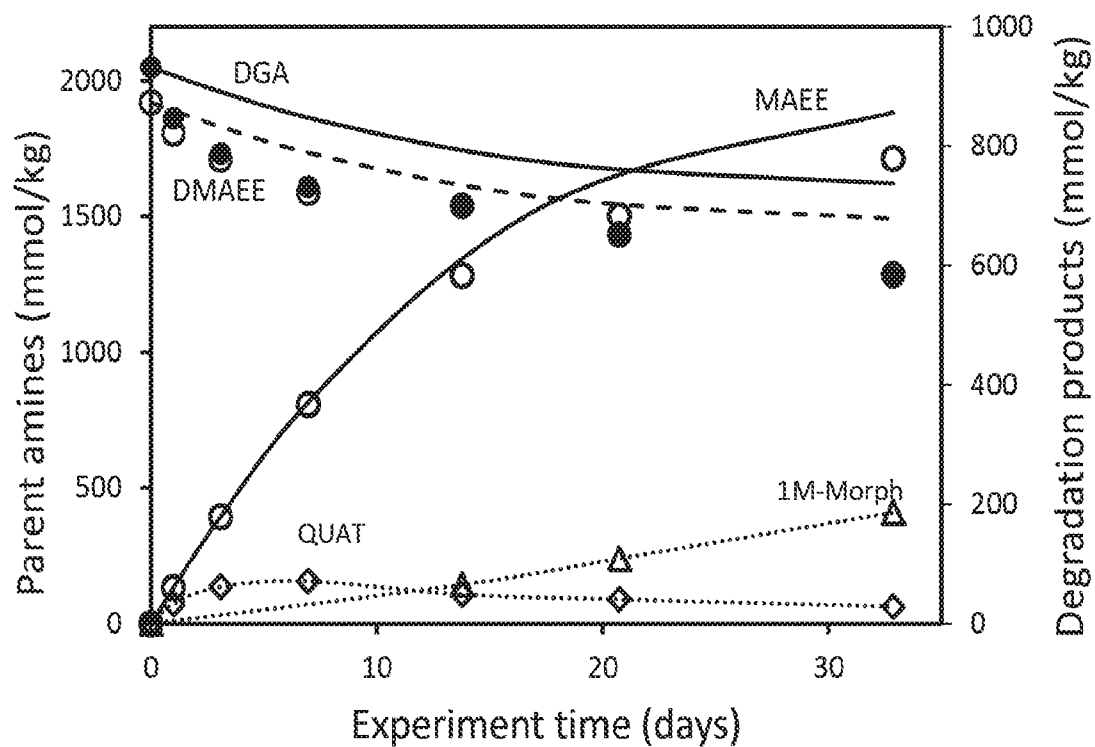


Fig. 5

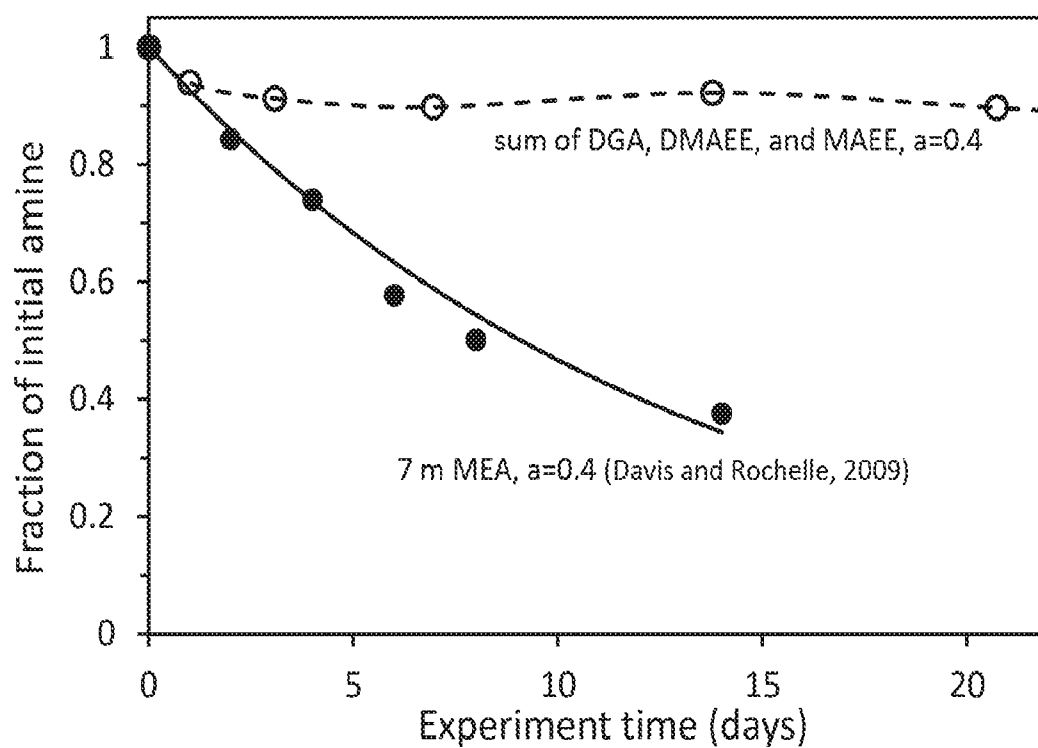


Fig. 6

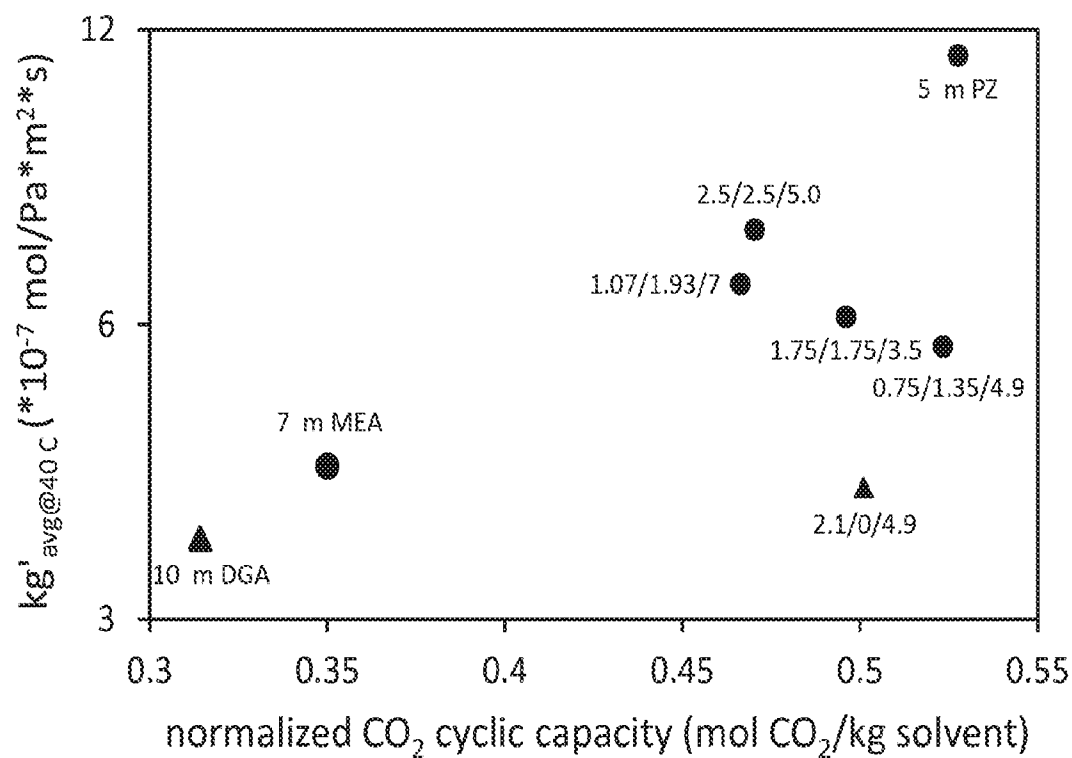


Fig. 7

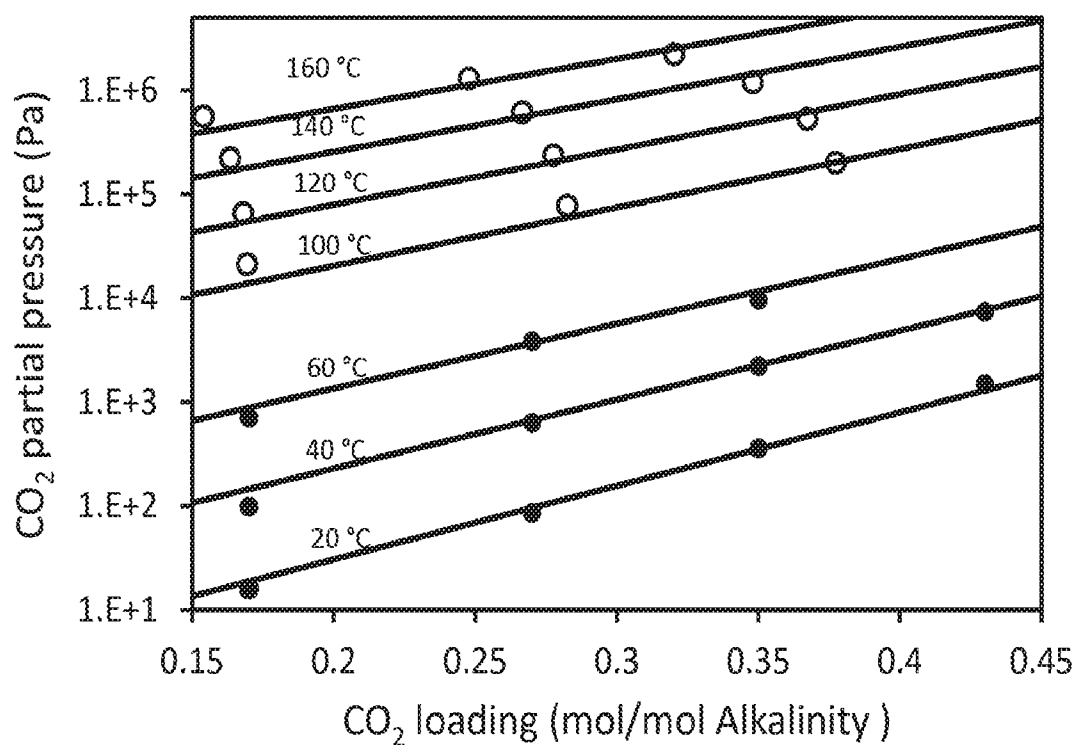


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/23288

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - C11D 7/32; G03F 7/42; B01F 17/18 (2017.01)
 CPC - G03F 7/425; H01L21/3105; C11D7/32

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)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2015/0139877 A1 (Weiss et al.) 21 May 2015 (21.05.2015) para [0023]-[0027]; [0030]; [0033]; [0035]; [0044]; [0056]; [0062]-[0063]; [0066]-[0067]; [0069]; [0073]	1-2, 6, 8-9, 14-20, 28, 32, 34-35 ----- 3-5, 7, 10-13, 29-30, 33, 36-39
X	Dawodu et al. "Degradation of alkanolamine blends by carbon dioxide" Can. J. Chem. Eng. 1996; 74(6):960-966 (doi: 10.1002/cjce.5450740620) abstract; pg 961, col 2, para 2; pg 961, col 2, para 3 - pg 962, col 1, para 1	1, 15, 24-25
X	US 6,165,432 A (Rooney) 26 December 2000 (26.12.2000) col 2, ln 12-16, 21-27, 38-42; col 3, ln 63-67; col 4, ln 6-11	1, 15, 26-27
Y	US 2007/0286783 A1 (Carrette et al.) 13 December 2007 (13.12.2007) para [0039]; [0042]; [0051]	3-5, 7, 10-13, 29-30, 33, 36-39
A	WO 2015/145182 A1 (The Queen's University Of Belfast) 01 October 2015 (01.10.2015) pg 1, ln 29-30; pg 1, ln 32 - pg 2, ln 1; pg 2, ln 5-7	27
A	US 2010/0203619 A1 (Fradette et al.) 12 August 2010 (12.08.2010) whole document	1-20, 24-30, 32-39
A	US 4,471,138 A (Stogryn) 11 September 1984 (11.09.1984) whole document	1-20, 24-30, 32-39
A	US 3,891,742 A (Yeakey et al.) 24 June 1975 (24.06.1975) whole document	1-20, 24-30, 32-39
A	US 2006/0156923 A1 (Meckl et al.) 20 July 2006 (20.07.2006) whole document	1-20, 24-30, 32-39

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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"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

12 May 2017

Date of mailing of the international search report

15 JUN 2017

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Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/23288

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 21-23, 31
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.