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Perry et al.(10) **Pub. No.: US 2010/0154639 A1**(43) **Pub. Date: Jun. 24, 2010**(54) **LIQUID CARBON DIOXIDE ABSORBENT
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C09K 3/00 (2006.01)(52) **U.S. Cl.** **95/236; 252/182.3**(57) **ABSTRACT**

A carbon dioxide absorbent comprising (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that either reversibly react with CO₂ or have a high-affinity for CO₂ is provided and (ii) a hydroxy-containing solvent. The absorbent may be utilized in methods to reduce carbon dioxide in an exhaust gas, and finds particular utility in power plants.

LIQUID CARBON DIOXIDE ABSORBENT AND METHODS OF USING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation in part of U.S. patent application Ser. No. 12/343,905, filed Dec. 24, 2008. The present application is also related to co-pending United States patent application having attorney docket number 237591-1 and filed on even date herewith. Both of these applications are hereby incorporated herein by reference to the extent they are consistent with the definitions utilized herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH & DEVELOPMENT

[0002] This invention was made with Government support under grant number DE-NT0005310 awarded by the Department of Energy-NETL. The Government has certain rights in the invention.

BACKGROUND

[0003] Pulverized coal (PC) power plants currently produce over half the electricity used in the United States. In 2007, these plants emitted over 1900 million metric tons of carbon dioxide (CO₂), and as such, accounted for 83% of the total CO₂ emissions from electric power generating plants and 33% of the total US CO₂ emissions. Eliminating, or even reducing, these emissions will be essential in any plan to reduce greenhouse gas emissions.

[0004] Separating CO₂ from gas streams has been commercialized for decades in food production, natural gas sweetening, and other processes. Aqueous monoethanolamine (MEA) based solvent capture is currently considered to be the best commercially available technology to separate CO₂ from exhaust gases, and is the benchmark against which future developments in this area will be evaluated. Unfortunately, such amine-based systems were not designed for processing the large volumes of flue gas produced by a PC plant. Scaling the MEA-based CO₂ capture system to the size required for PC plants would result in an 83% increase in the overall cost of electricity for the PC plant. Applying this technology to all existing PC plants in the US would cost \$125 billion per year, making MEA-based CO₂ capture an unlikely choice for large-scale commercialization.

[0005] There are many properties that desirably would be exhibited, or enhanced, in any CO₂ capture technology contemplated to be a feasible alternative to the currently utilized MEA-based systems. For example, any such technology would desirably exhibit a high net CO₂ capacity, and could provide lower capital and operating costs (less material volume required to heat and cool, therefore less energy required). A lower heat of reaction would mean that less energy would be required to release the CO₂ from the material. Desirably, the technology would not require a pre-capture gas compression so that a high net CO₂ capacity could be achieved at low CO₂ partial pressures, lowering the energy required for capture. Technologies utilizing materials with lower viscosities would provide improved mass transfer, reducing the size of equipment needed, as well as a reduction in the cost of energy to run it. Low volatility and high thermal, chemical and hydrolytic stability of the material(s) employed could reduce the amount of material needing to be replenished and emission of degradation products. Of course, any such technology

would also desirably have low material costs so that material make-up costs for the system would be minimized. Operability of CO₂ release at high pressures could reduce the energy required for CO₂ compression prior to sequestration. Finally, such technologies would also desirably exhibit reduced corrosivity to help reduce capital and maintenance costs, and further would not require significant cooling to achieve the desired net CO₂ loading, reducing operating costs.

[0006] Unfortunately, many of the above delineated desired properties interact and/or depend on one another, so that they cannot be varied independently and trade-offs are required. For example, in order to have low volatility, the materials used in any such technology typically must have a fairly large molecular weight, but to have low viscosity, the materials must have a low molecular weight. To have a high CO₂ capacity at low pressures, the overall heat of reaction needs to be high, but to have low regeneration energy, the overall heat of reaction needs to be low.

[0007] Desirably, a CO₂ capture technology would be provided that optimizes as many of the above desired properties as possible, yet without causing substantial detriment to other desired properties. At a minimum, in order to be commercially viable, such technology would desirably be low cost, and utilize material(s) having low volatility, high thermal stability and a high net capacity for CO₂.

BRIEF DESCRIPTION

[0008] In a first aspect, there is provided a carbon dioxide absorbent comprising (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

[0009] Also, a second aspect provides a method for reducing the amount of carbon dioxide in a process stream comprising contacting the stream with a carbon dioxide absorbent comprising (i) a liquid, nonaqueous, silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

[0010] In a third aspect, a power plant is provided, comprising a carbon dioxide removal unit further comprising a carbon dioxide absorbent comprising: (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

[0011] A method of generating electricity with reduced carbon dioxide emissions is also provided. The method comprises combusting a fuel (pulverized coal, liquid hydrocarbon, natural gas and the like) and directing the flue gas comprising carbon dioxide to an electricity generating equipment, e.g. steam or gas turbine and then to a carbon dioxide removal unit comprising a carbon dioxide absorbent comprising: (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

DETAILED DESCRIPTION

[0012] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. The terms "first", "second", and the like, as used herein do not denote any order, quantity, or importance, but

rather are used to distinguish one element from another. Also, the terms “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item, and the terms “front”, “back”, “bottom”, and/or “top”, unless otherwise noted, are merely used for convenience of description, and are not limited to any one position or spatial orientation. If ranges are disclosed, the endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “up to about 25 wt. %,” or, more specifically, about 5 wt. % to about 20 wt. %,” is inclusive of the endpoints and all intermediate values of the ranges of “about 5 wt. % to about 25 wt. %,” etc.). The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity).

[0013] The subject matter disclosed herein relates generally to carbon dioxide absorbents, power plants incorporating them, and methods of using the absorbents to absorb carbon dioxide from process streams, e.g., as may be produced by methods of generating electricity. Conventional carbon dioxide absorbents lack one or more of the properties considered important, if not critical, in the commercial feasibility of their use in many technologies. MEA-based aqueous absorbents, for example, were not designed for use with large volumes of exhaust gas. As a result, use of these absorbents in such processes is extremely energy intensive and costly—too costly for implementation into power plants for post combustion CO₂ capture.

[0014] There are currently provided carbon dioxide absorbents comprising liquid, nonaqueous silicon-based materials and a hydroxy-containing solvent. Silicon-based materials are defined as molecules having between one and twenty repeat units, and thus, may include small molecules comprising silicon, i.e., molecules comprising from one to five silicon atoms, or oligomeric materials comprising between about 5 and 20 silicon atoms.

[0015] In one embodiment, the present absorbent comprises a CO₂-philic, silicon-containing oligomer, e.g., comprising less than about 20 repeating, monomeric units, and desirably from about 5 to about 10 repeating monomeric units. As used herein, the term “CO₂-philic silicon containing oligomer” means an oligomer that has an affinity for CO₂, as may be evidenced by solubility in liquid or supercritical CO₂, or an ability to physically absorb CO₂. Liquid oligomers such as poly(siloxanes), poly(ethylene glycols), poly(propylene glycols) and perfluorinated polyethers, e.g., poly(fluoroethylene glycol), are non-limiting examples of CO₂-philic short chain oligomers suitable for use in the present absorbent. These, as well as other exemplary oligomers are shown below and may be derivatized on chain or at the end of the oligomer or may be co- or ter-oligomers:

[0016] Of these, silicones are particularly well-suited for use in the present absorbents. Also correctly referred to as polymerized siloxanes or polysiloxanes, silicones are mixed inorganic-organic polymers or oligomers with the chemical formula [R₂SiO]_n, wherein R comprises a linear, branched or aromatic organic group of any number of carbons, e.g., methyl ethyl, phenyl, etc. These materials thus comprise an inorganic silicon-oxygen backbone (. . . Si—O—Si—O—Si—O . . .) with organic side groups attached to the silicon atoms, which are four-coordinate. These silicones may be

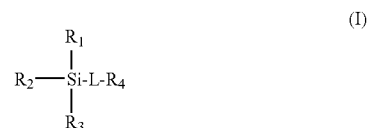
linear with R and OR' end-capping groups or cyclic containing only repeating units. An example of the latter is octamethylcyclotetrasiloxane.

[0017] Silicones have low volatility even at short chain lengths and liquid at room temperature. They are typically low cost, and stable at high temperatures, e.g., up to about 150° C. Silicones are also readily functionalized, and so, could be functionalized with groups that increase their affinity for CO₂.

[0018] Length of the silicone oligomer chain can be easily controlled during synthesis that allows control of such physical properties as viscosity and boiling point. In addition, siloxane bonds are thermally stable and hydrolytically stable in the absence of strong acids or bases. Many silicones precursors are commercially available, and so advantageously, large scale production capabilities would not have to be developed. Many of these may be utilized in the present invention. One example of a silicone suitable for functionalization in the present invention, and available from a variety of sources, comprises polyhydridomethylsiloxane.

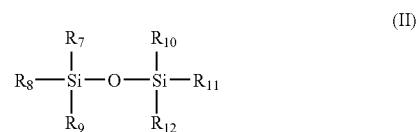
[0019] In another embodiment, the present absorbent comprises a CO₂-philic, silicon-based small molecule, e.g., comprising from about one to about five silicon atoms. As used herein, the term “CO₂-philic silicon-based small molecule” means a material that reversibly reacts with or has an affinity for CO₂.

[0020] The silicon-based small molecules may comprise one silicon atom as shown in Formula (I) wherein L=linking group of C₁-C₁₈ and may be aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof:

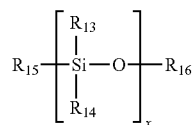


where R₁, R₂, R₃ may be the same or different and may be C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof and R₄=NR₅R₆ where at least one of R₅ or R₆ is H. The other may be C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof.

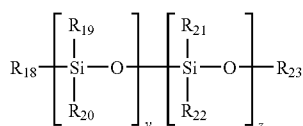
[0021] Or, the silicon-based materials may be as shown in Formulas II-VI, and, when x≤5, y+z≤5 and/or r≤5 silicon based materials represented by formulas II-VI would generally be considered silicon based small molecules. Or, when x≥5, y+z≥5 and/or r≥5, silicon based materials represented by formulas II-VI would generally be considered silicon-containing oligomers. As depicted in structures II-VI, the core of the silicon-based small molecule may be linear, cyclic or branched or combinations.



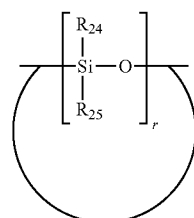
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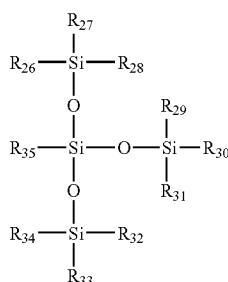
(III)



(IV)



(V)



(VI)

[0022] For Formula II, R₇-R₁₂ may be the same or different. At least one of R₇-R₁₂ will desirably be L-R₄ while the remainder are desirably C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof.

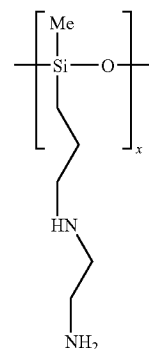
[0023] For formula III, R₁₃-R₁₆ may be the same or different. At least one of R₁₃-R₁₆ will desirably be L-R₄ while the remainder are desirably C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof, with the proviso that R₁₆ is SiRR'R'', wherein R, R' and R'' may be the same or different and may be C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof and may be L-R₄.

[0024] For formulas IV, V, and VI, R₁₈-R₂₃ and R₂₄-R₂₅ and R₂₆-R₃₅ may be the same or different and at least one of R₁₈-R₂₃=L-R₄ and at least one of R₂₄-R₂₅=L-R₄ different and at least one of R₂₆-R₃₅=L-R₄ and the rest may be C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures with the proviso that R₂₃ is SiRR'R'', wherein R, R' and R'' may be the same or different and may be C₁-C₁₈ aliphatic, aromatic, heteroaliphatic, heteroaromatic or mixtures thereof and may be L-R₄.

[0025] The silicon-based material may desirably be functionalized with groups that enhance its net capacity for CO₂. Functional groups that are expected to be CO₂-philic, and react with CO₂ in a silicon-based material they functionalize, include any of those including nitrogen, such as, for example aliphatic amines, imines, amidines, amides, heterocyclic amino compounds such as pyridine, aromatic amines such as aniline, and the like, as well as combinations of any of these.

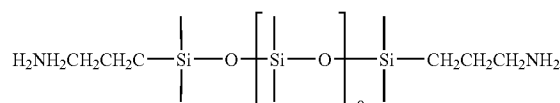
The particular functional group utilized will depend upon the silicon-based material chosen, and for those embodiments wherein the silicon-based material comprises a siloxane, amine functionality may be suitable, since many aminosiloxanes are readily commercially available, and are readily further functionalized if desired or required in order to increase CO₂ reactivity. Examples of amine functional groups that exhibit CO₂-reactivity include aminomethyl, aminoethyl, aminopropyl, aminoethyl-aminopropyl, aminoethyl-aminoisobutyl, aminoethylaminomethyl, 2-aminopyridyl, piperazine-propyl and imidazolyl propyl.

[0026] Functional groups may be located in a side chain and also be the end-capping groups. Aminoethyl-aminopropyl siloxane oligomers with functional groups in the side chain, for example the molecule shown below at Figure VII has a maximum theoretical CO₂ capacity of about 20 wt %, compared to 10 wt % for 30 wt % aqueous MEA.



(VII)

[0027] One other example of an aminosiloxane with end-capped functional groups suitable for use in the present absorbent is aminopropyl terminated polydimethyldisiloxane, shown below in Figure VIII:



(VIII)

One such aminosiloxane is used for hair conditioning and commercially available from Gelest with a number average molecular weight of from about 850 to about 900, and a calculated CO₂ absorption capacity of from about 4.4 to about 5.2%. It is expected that the addition of further amine functionality will result in an increase in this absorption capacity.

[0028] Those of ordinary skill in the art of polymer chemistry are well versed in methods of adding functional groups to the backbone of an oligomer useful in the present absorbent. Numerous methods of attachment of functional groups are known such as hydrosilylation and displacement as shown in Michael A. Brook's book *Silicon in Organic, Organometallic, and Polymer Chemistry* (Wiley VCH Press, 2000).

[0029] The absorbent also comprises one or more hydroxy-containing solvents. As used herein, the phrase "hydroxy-containing solvent" means a solvent that has one or more hydroxy groups. The hydroxy-containing solvent also desir-

ably has a low vapor pressure, e.g., of from about 0.001 to about 30 mm Hg at 100° C., so that minimal loss of the hydroxy-containing solvent occurs via evaporation. Suitable hydroxy-containing solvents are those that do not substantially chemically react with CO₂, but rather, serve as a medium for CO₂ transfer to the functionalized silicon-based material. As a result, the hydroxy-containing solvents are expected to be capable of increasing the reaction rate, e.g., by increasing the mass transfer rate, of CO₂ and the silicon-based material, and also to reduce, or substantially prevent, excessive viscosity build-up when the silicon-based material reacts with CO₂. Advantageously, many suitable hydroxyl-containing solvents may be recycled, along with the silicon-based material, if desired.

[0030] Examples of suitable hydroxy-containing solvents include, but are not limited to, those comprising one or more hydroxyl groups, such as, glycols and hydroxylated silicones. Suitable glycols may include, for example, trimethylolpropane, glycerol, ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol, to name a few. Suitable hydroxylated silicones include, for example, 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane, or the hydrosilylation reaction product of 1,1,3,3-tetramethyldisiloxane and trimethylolpropane allylether. Hydroxy compounds may also be in the form of phenols such as eugenol, isoeugenol, 2-allyl-6-methylphenol and the like.

[0031] In certain embodiments, the absorbent may comprise an amount of water, e.g., so that all water need not be removed from the process stream in order to utilize the absorbent and methods. Indeed, in some embodiments, water is desirably present and in such embodiments, can assist in the solubilization of reaction products.

[0032] Optionally, the absorbent may also include other components, such as, e.g., oxidation inhibitors to increase the oxidative stability and anti-foaming agents. The use of oxidation inhibitors, also called antioxidants, can be especially advantageous in those embodiments of the invention wherein the functional groups comprise amine groups.

[0033] The carbon dioxide absorbents provided herein are expected to provide substantial improvement when utilized to remove CO₂ from process gases, as compared to those currently commercially available and/or utilized for this purpose. As such, a method of reducing the carbon dioxide in a process stream is provided and comprises contacting the process stream with the carbon dioxide absorbents described herein. The process stream so treated may be any wherein the level of CO₂ therein is desirably reduced, and in many processes, CO₂ is desirably reduced at least in the exhaust streams produced thereby. The process stream is typically gaseous but may contain solid or liquid particulates, and may be at a wide range of temperatures and pressures depending on the application.

[0034] The carbon dioxide absorbents have low volatility, high thermal stability and are either commercially available with, or can be provided with, a high net capacity for CO₂, and as such, are appropriate for large scale implementation. And so, there is also provided a power plant utilizing the present absorbents, and method of utilizing the absorbents in a method for generating electricity with reduced carbon dioxide emissions.

Examples 1-12

[0035] Reaction of silicon-based materials with CO₂ in the presence of a hydroxy-containing co-solvent.

[0036] To illustrate the ability of the hydroxy-containing co-solvent triethylene glycol to enhance the CO₂ absorption of various silicon-based materials as well as provide a liquid medium, the following Examples 1-12 were conducted. The silicon-based materials were exposed to 1 atmosphere of CO₂ in the presence of, or not in the presence of, the hydroxyl-containing co-solvent triethylene glycol (at 50 wt %, with the exception of example 4 at 75 wt %) at 40° C. for 2 hours (h) with mechanical stirring.

Comparative Example 1

[0037] Into a pre-tared, 25 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, gas inlet and a gas outlet and heated with a temperature controlled oil bath, was charged 2.0707 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane. Dry CO₂ gas was introduced at a rate of 50 mL/min into the flask via a glass tube positioned 10 mm above the stirring liquid surface. CO₂ exposure continued for 2 h at 40° C. after which time the exterior of the flask was cleaned and the flask weighed. The total weight gain of 0.3588 g corresponded to 71% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was also a solid.

Example 2

[0038] 2.0194 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0174 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.4089 g. This corresponded to 114% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Comparative Example 3

[0039] 2.0653 g of aminoethylaminopropyl methylsiloxane oligomer were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.2110 g. This corresponded to 37% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 4

[0040] 2.0168 g of aminoethylaminopropyl methylsiloxane oligomer and 4.0292 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.4803 g. This corresponded to 87% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Comparative Example 5

[0041] 2.0295 g of 1,3-Bis(3-aminoethylaminopropyl)tetramethyldisiloxane were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.3389 g. This corre-

sponded to 64% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 6

[0042] 2.0240 g of 1,3-Bis(3-aminoethylaminopropyl)tetramethyldisiloxane and 2.0237 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.4777 g. This corresponded to 90% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Comparative Example 7

[0043] 1.1090 g of 1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.0621. This corresponded to 30% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 8

[0044] 1.0722 g of 1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane and 1.1028 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.3099 g. This corresponded to 154% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Comparative Example 9

[0045] 1.0498 g of Tetrakis(3-aminopropyldimethylsiloxy)silane were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total

weight gain was 0.1445 g. This corresponded to 87% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 10

[0046] 1.0662 g of Tetrakis(3-aminopropyldimethylsiloxy)silane and 0.11175 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.1956 g. This corresponded to 116% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Comparative Example 11

[0047] 1.2135 g of 1,3-Bis(3,9-dimethyl-5,8,11-trioxa-2-azatetradecan-13-amine) were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.0742 g. This corresponded to 44% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 12

[0048] 1.0323 g of 1,3-Bis(3,9-dimethyl-5,8,11-trioxa-2-azatetradecan-13-amine) and 1.0368 g of triethylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 1. The total weight gain was 0.0587 g. This corresponded to 41% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

[0049] The results of Examples 1-12 are summarized in Table 1, below.

TABLE 1

Example	Amine	Co-solvent present	% of Theoretical wt gain	Physical state of product
1	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	No	71	S
comparative				
2	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	Yes	114	L
3	Aminoethylaminopropyl methylsiloxane	No	37	S
comparative	oligomer			
4	Aminoethylaminopropyl methylsiloxane	Yes	87	L
comparative	oligomer			
5	1,3-Bis(3-aminoethylaminopropyl)tetramethyldisiloxane	No	64	S
6	1,3-Bis(3-aminoethylaminopropyl)tetramethyldisiloxane	Yes	90	L
7	1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane	No	30	S
comparative				
8	1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane	Yes	154	L
9	Tetrakis(3-aminopropyldimethylsiloxy)silane	No	87	S
comparative				
10	Tetrakis(3-aminopropyldimethylsiloxy)silane	Yes	116	L
11	1,3-Bis(3,9-dimethyl-5,8,11-trioxa-2-azatetradecan-13-amine)	No	44	S
comparative				

TABLE 1-continued

Example	Amine	Co-solvent present	% of Theoretical wt gain	Physical state of product
12	1,3-Bis(3,9-dimethyl-5,8,11-trioxa-2-azatetradecan-13-amine)	Yes	41	L

Examples 13-20

[0050] Reaction of a silicon-based material with CO₂ in the presence of various hydroxy-containing co-solvents.

[0051] To illustrate the ability of the hydroxy-containing co-solvents triethyleneglycol dimethyl ether and triethyleneglycol to enhance the CO₂ absorption of the silicon-based material, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, as well as provide a liquid medium, the following Examples 13-20 were conducted. In each, the silicon-based material 1,3-bis(3-aminopropyl)tetramethyldisiloxane was exposed to 1 atmosphere of CO₂ in the presence of or not in the presence of a hydroxyl-containing co-solvent (concentration?) at 40° C. for 2 hours (h) with mechanical stirring.

Comparative Example 13

[0052] Into a pre-tared, 25 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, gas inlet and a gas outlet and heated with a temperature controlled oil bath, was charged 2.0707 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane. Dry CO₂ gas was introduced at a rate of 50 mL/min into the flask via a glass tube positioned 10 mm above the stirring liquid surface. CO₂ exposure continued for 2 h at 40° C. after which time the exterior of the flask was cleaned and the flask weighed. The total weight gain of 0.3588 g corresponded to 71% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was also a solid.

Example 14

[0053] 2.0261 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.1198 g of triethyleneglycol dimethyl ether were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.2984 g. This corresponded to 83% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 15

[0054] 2.0366 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 4.0306 g of triethyleneglycol dimethyl ether were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.3566 g. This corresponded to 99% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 16

[0055] 2.0194 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0174 g of triethyleneglycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was

0.4089 g. This corresponded to 114% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Example 17

[0056] 2.0230 g of triethyleneglycol was charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.0004 g. This corresponded to <1% total weight gain. The reaction product was a liquid.

Example 18

[0057] 2.0387 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 1.0454 g of triethyleneglycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.4071 g. This corresponded to 113% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid.

Example 19

[0058] 2.0178 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 4.0734 g of triethyleneglycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.4203 g. This corresponded to 118% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

Example 20

[0059] 2.0186 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane, 1.0419 g of triethyleneglycol and 0.2245 g water were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 13. The total weight gain was 0.3545 g. This corresponded to 99% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a liquid.

[0060] The results of Examples 13-20 are summarized in Table 2, below.

TABLE 2

Example	Co-solvent	Wt ratios (Amine:solvent:water)	CO ₂ uptake (% theoretical)	Physical state
13 (control)	None	100:0:0	71	S
14	Triethyleneglycol dimethyl ether	50:50:0	83	S

TABLE 2-continued

Example	Co-solvent	Wt ratios (Amine:sol- vent:water)	CO ₂ uptake (% theoretical)	Physical state
15	Triethyleneglycol dimethyl ether	33:67:0	99	S
16	Triethyleneglycol	50:50:0	114	L
17	Triethyleneglycol	0:100:0	—	L
18	Triethyleneglycol	67:33:0	113	~S
19	Triethyleneglycol	33:67:0	118	L
20	Triethyleneglycol	62:31:07	99	L

[0061] Table 2 shows that without a co-solvent, 1,3-bis(3-aminopropyl)tetramethyldisiloxane readily forms a solid material (Example 13). When triethyleneglycol dimethyl ether is added as a co-solvent (Examples 14, 15), solid reaction products are still formed. When triethyleneglycol is added at a 1:1 weight ratio (Example 16) a homogeneous reaction product is formed that remains liquid throughout the capture process. Varying the ratio of co-solvent to capture solvent results in varying degrees of liquidity and viscosity. (Examples 17-20)

[0062] Table 2 further shows that the co-solvent alone does not physically absorb a significant amount of CO₂ (Example 17). However, the mixed system allows for enhanced capture of CO₂ via a synergistic action of the chemical capture process and physisorption. Water may optionally be present to aid in solubilizing the reaction products (Example 20).

Examples 21-33

[0063] Reaction of a silicon-based material with CO₂ in the presence of various hydroxy-containing co-solvents.

[0064] To illustrate the ability of various other hydroxy-containing co-solvents (at 50 weight % concentration) to enhance the CO₂ absorption of the silicon-based material, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, as well as provide a liquid medium, the following Examples 21-33 were conducted. In each, the silicon-based material 1,3-bis(3-aminopropyl)tetramethyldisiloxane was exposed to 1 atmosphere of CO₂ in the presence of or not in the presence of a hydroxyl-containing co-solvent at 40° C. for 2 hours (h) with mechanical stirring.

Comparative Example 21

[0065] Into a pre-tared, 25 mL, three-neck, round-bottom flask equipped with a mechanical stirrer, gas inlet and a gas outlet and heated with a temperature controlled oil bath, were charged 2.0349 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0472 g of SF1488 (a silicone polyether available from Momentive Performance Materials). Dry CO₂ gas was introduced at a rate of 50 mL/min into the flask via a glass tube positioned 10 mm above the stirring liquid surface. CO₂ exposure continued for 2 h at 40° C. after which time the exterior of the flask was cleaned and the flask weighed. The total weight gain of 0.2739 g corresponded to 76% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a waxy yellow solid.

Example 22

[0066] 2.0311 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0506 g of a diol terminated disiloxane pre-

pared via the hydrosilylation of trimethylolpropane mono allyl ether with tetramethyl disiloxane were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3491 g. This corresponded to 97% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a viscous liquid.

Example 23

[0067] 2.0337 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0653 g of tetrathylene glycol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.4182 g. This corresponded to 116% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a moderately viscous liquid.

Example 24

[0068] 2.0745 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0507 g of poly(propylene glycol) with a molecular weight of 725 were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3400 g. This corresponded to 92.5% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid that formed very quickly on introduction of the gas.

Example 25

[0069] 1.9957 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0630 g of a 3:1 blend of tetrathylene glycol and the diol terminated disiloxane from example B above, were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3937 g. This corresponded to 111% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a moderately viscous liquid.

Example 26

[0070] 2.0385 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 1.9718 g of trimethylolpropane mono allyl ether were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3876 g. This corresponded to 107% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a moderately viscous liquid.

Example 27

[0071] 2.0683 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0709 g of eugenol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3449 g. This corresponded to 94% of the theoretical amount of weight that should have been gained if all the amine groups had

reacted with a stoichiometric amount of CO₂. The reaction product was a viscous yellow liquid.

Example 28

[0072] 2.0291 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 1.9965 g of trimethylolpropane ethoxylate (4/15 EO/OH, Mn 170) were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3640 g. This corresponded to 101% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a very viscous yellow liquid.

Example 29

[0073] 2.0157 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0675 g of pentaerythritol ethoxylate (3/4 EO/OH, Mn 270) were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3855 g. This corresponded to 108% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a very viscous liquid.

Example 30

[0074] 1.9999 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0129 g of a 2:1 blend of tetraethylene glycol

flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3464 g. This corresponded to 96% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a viscous yellow liquid.

Example 32

[0076] 2.0379 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0447 g of sulfolane were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3227 g. This corresponded to 89% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a solid that formed very quickly on introduction of the gas.

Example 33

[0077] 2.0118 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0010 g of 2-allyl-6-methylphenol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.2711 g. This corresponded to 76% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a light yellow liquid.

[0078] The results of Examples 21-33 are summarized in Table 3, below.

TABLE 3

Example	Co-Solvent (50 wt %)	% of Theoretical wt gain	Physical state of product
21	SF1488 Momentive Silicone polyether	76	S
Comparative			
22	a hydrosilylation reaction product of 1,1,3,3-tetramethyldisiloxane and trimethylolpropane allyl ether	97	L
23	Tetraethylene glycol	116	L
24	Poly(propylene glycol) MW = 725	93	S
25	Mixture of tetraethylene glycol/1,3-bis(3-hydroxypropyl)tetramethyldisiloxane 3:1	111	L
26	Trimethylolpropane allyl ether	107	L
27	Eugenol	94	L
28	Trimethylolpropane ethoxylate Mn = 170	101	L
29	Pentaerythritol ethoxylate Mn = 270	108	L
30	2:1 Tetraethylene glycol/eugenol	107	L
31	Isoeugenol	96	L
32	Sulfolane	89	S
comparative			
33	2-allyl-6-methylphenol	76	L

and eugenol were charged into a flask and allowed to react with CO₂ according to the procedure described in Example 21. The total weight gain was 0.3773 g. This corresponded to 107% of the theoretical amount of weight that should have been gained if all the amine groups had reacted with a stoichiometric amount of CO₂. The reaction product was a viscous yellow liquid.

Example 31

[0075] 2.0391 g of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane and 2.0640 g of isoeugenol were charged into a

Examples 34-50

High throughput Screening Experiments

[0079] The high throughput screening experiments were carried out using a 27 well parallel reactor (React Vap III) from Pierce and a Symyx Core Module for automated weighing in 8 mL glass vials. The experiments were run using technical grade CO₂ at 1 atm and the flow was set at 1.2 mL/h (10000 cm²/min) by using a MKS gas flow controller. Each formulation was tested in triplicate. The co-solvents were purchased from Aldrich or Fisher Scientific and used without further purification.

[0080] Each vial was loaded with a stirrer bar and pre-weighed using the Symyx Core module. The vials were then loaded with the corresponding compound (200-300 μ L) and the appropriate co solvent (200-300 μ L). The resulting mixture was stirred for 15-20 min and treated with CO₂ gas (1 atm) for 60-120 min at the desired temperature (40 and 55° C.). After the CO₂ treatment, the reactor block was cooled down to room temperature and all the vials were transferred to a Symyx Core Module® for automated weighing. The physical state of each vial was visually inspected and recorded. The CO₂ adsorption performance was reported as an average of the % weight gain after each CO₂ treatment. The results of these experiments are shown in Table 4.

TABLE 4

Ex.	Silicon-based Material	Co-Solvent	Wt ratios*	%**	% wt gain	Physical state***
34	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	triethylene glycol	10:90	175	3.1	L
35	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	triethylene glycol	30:70	155	8.2	L
36	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	triethylene glycol	50:50	133	11.8	L
37	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	N methyl pyrrolidone	50:50	118	10.4	L
38	1,3-Bis(3-aminopropyl)tetramethyldisiloxane	Tetraglyme	50:50	123	10.9	S
Comp		dimethyl ether				
39	Aminoethylaminopropyl methylsiloxane oligomers	triethylene glycol	10:90	165	4.6	L
40	Aminoethylaminopropyl methylsiloxane oligomers	triethylene glycol	30:70	122	10.2	L
41	Aminoethylaminopropyl methylsiloxane oligomers	triethylene glycol	50:50	44	6.2	L
42	Aminoethylaminopropyl methylsiloxane oligomers	N methyl pyrrolidone	50:50	56	7.8	S
Comp						
43	Aminoethylaminopropyl methylsiloxane oligomers	Tetraglyme	50:50	41	5.7	S
Comp		dimethyl ether				
44	1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane	N methyl pyrrolidone	50:50	84	7.9	S
Comp						
45	1,3,5,7-tetrakis(3-aminopropyl)tetramethylcyclotetrasiloxane	Tetraglyme	50:50	53	5.0	S
Comp		dimethyl ether				
46	1,3-Bis(aminoethylaminomethyl)tetramethyldisiloxane	triethylene glycol	10:90	158	5.0	L
47	1,3-Bis(aminoethylaminomethyl)tetramethyldisiloxane	triethylene glycol	30:70	117	11.1	L
48	1,3-Bis(aminoethylaminomethyl)tetramethyldisiloxane	triethylene glycol	50:50	74	11.7	L
49	1,3-Bis(aminoethylaminomethyl)tetramethyldisiloxane	N methyl pyrrolidone	50:50	59	9.3	S
Comp						
50	1,3-Bis(aminoethylaminomethyl)tetramethyldisiloxane	Tetraglyme	50:50	64	10.1	S
Comp		dimethyl ether				

*Amine:solvent

**of theoretical

***After absorption

[0081] Generally speaking, Table 4 shows that capped-hydroxy compounds yielded solid reaction products while uncapped co-solvents yielded soluble solutions. Amide solvent, NMP, was only marginally successful as a solvent.

[0082] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

1. A carbon dioxide absorbent comprising: (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent

2. The absorbent of claim 1, wherein the functionalized silicon-based material comprises silanes, or compounds containing one or more siloxy units, or combinations of these.

3. The absorbent of claim 1, wherein the silicon-based material is functionalized with one or more nitrogen-containing groups.

4. The absorbent of claim 3, wherein the functional group (s) comprise(s) one or more aliphatic amines, imines,

amidines, amides, heterocyclic amino compounds such as pyridine, aromatic amines such as aniline, and combinations of these.

5. The absorbent of claim 4, wherein the functional group (s) comprise(s) one or more amines.

6. The absorbent of claim 5, wherein the functional group (s) comprise(s) one or more di-, tri- and polyamines or combinations of these.

7. The absorbent of claim 6, wherein the functional group (s) comprise(s) one or more aminomethyl, aminoethyl, ami-

nopropyl, aminoethylaminopropyl, piperazinopropyl, aminomethylaminoethyl, 2-aminopropylpyridyl, groups or combinations of these.

8. The absorbent of claim 7, wherein the functional group (s) comprise(s) one or more amino hydroxy groups.

9. The absorbent of claim 1, wherein the said solvent has a vapor pressure below 150 mm Hg at 100° C.

10. The absorbent of claim 9, wherein the said solvent comprises two or more hydroxyl groups.

11. The absorbent of claim 10, wherein the said solvent comprises a glycol, a hydroxylated silicone, a phenol or combinations of these.

12. The absorbent of claim 11, wherein the solvent comprises trimethylolpropane, glycerol, triethylene glycol, tetraethylene glycol, 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane, a hydrosilylation reaction product of 1,1,3,3-tetramethyldisiloxane and trimethylolpropane allyl ether, eugenol, isoeugenol, 2-allyl-6-methylphenol or combinations of these.

13. The absorbent of claim 1, further comprising water.

14. The absorbent of claim 1, further comprising antioxidants, stabilizers, accelerators, antifoaming agents or blends thereof.

15. A method for reducing the amount of carbon dioxide in a process stream comprising contacting the stream with a carbon dioxide absorbent comprising (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

16. The method of claim 15, wherein the process stream comprises an exhaust stream.

17. The method of claim 15, wherein the hydroxy-containing solvent comprises trimethylolpropane, glycerol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene, 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane, a hydrosilylation reaction product of 1,1,3,3-tetramethyldisiloxane and trimethylolpropane allylether, or combinations of these.

18. The method of claim 15, wherein the carbon dioxide solvent further comprises water.

19. The method of claim 15, wherein the functionalized silicon-based material comprises one or more aminosilicones.

20. The method of claim 15, wherein the functional group (s) comprise(s) one or more amines.

21. The method of claim 20, wherein the functional group (s) comprise(s) one or more di-, tri- and polyamines or combinations of these.

22. A power plant comprising a carbon dioxide removal unit further comprising a carbon dioxide absorbent comprising (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

23. A method of generating electricity with reduced carbon dioxide emissions comprising combusting a fuel to produce an exhaust gas comprising carbon dioxide and directing the exhaust gas to a carbon dioxide removal unit comprising a carbon dioxide absorbent comprising (i) a liquid, nonaqueous silicon-based material, functionalized with one or more groups that reversibly react with CO₂ and/or have a high-affinity for CO₂; and (ii) a hydroxy-containing solvent.

24. The method of claim 23, wherein the hydroxy-containing solvent comprises trimethylolpropane, glycerol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene, 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane, a hydrosilylation reaction product of 1,1,3,3-tetramethyldisiloxane and trimethylolpropane allylether, or combinations of these.

25. The method of claim 23, wherein the absorbent further comprises water.

26. The method of claim 23, wherein the functionalized silicon-based material comprises one or more silicones.

27. The method of claim 26, wherein the functional group (s) comprise(s) one or more amines.

* * * * *