(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 June 2017 (29.06.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/108932 A1

(51) International Patent Classification:
B01D 53/14 (2006.01) *B01D 53/62* (2006.01)

(21) International Application Number:
PCT/EP2016/082150

(22) International Filing Date:
21 December 2016 (21.12.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15201675.4 21 December 2015 (21.12.2015) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2017/108932 A1

(54) Title: EFFICIENT CO2 RECOVERY PROCESS AND ABSORBENT THEREFOR

(57) Abstract: The present invention relates to process for removing carbon dioxide from a feed gas stream. A CO2 comprising feed gas stream is contacted with a lean absorbent composition. The lean absorbent composition comprises (a) 10 0.5-60 wt% of a hydroxide of an alkali metal, (b) 25-99.5 wt% of a polyhydric alcohol, (c) optionally 0.1-10 wt% diethylene glycol and (d) optionally 0.1-15 wt% H2O. Absorbed CO2 and H2O are removed from the spent absorbent composition with a gas or vapor stream at a temperature in 15 the range of between 50 - 120 °C. CO2 and H2O recovered from step (ii) may be subjected to condensation. Preferably at least a part of the regenerated absorbent composition is recycled from step (ii) to step (i). The invention further relates to the absorbent composition. 20

EFFICIENT CO2 RECOVERY PROCESS AND ABSORBENT THEREFOR

Field of the invention

The invention relates to a process for removing carbon dioxide from a feed gas stream. The invention especially relates to a process which is very efficient in removing CO_2, and in which the absorbent composition used can be regenerated.

Background to the invention

CO_2 absorbents are used, among others, to capture CO2 from gas streams. The captured CO2 can be used for enhanced oil recovery by injecting it into an oil reservoir to achieve a higher oil recovery from the reservoir. Other commercial uses of CO2 are carbonation of beverages, the use as mild acidification chemical, and the use as cooling agent, e.g. "dry ice".

CO_2 may, for example, be removed from off gas produced during the combustion of fossil fuels. Additionally, natural gas generally comprises carbon dioxide which may cause corrosion problems when the natural gas is transported and processed.

CO_2 may be removed by means of adsorption on solid substrates, chemical absorption, gas permeation, physical absorption, and combinations thereof. Examples of physical absorbents are polycarbonate, polyethylene glycol dimethyl ether, and n-butane. Examples of chemical absorbents are monoethanol amine (MEA), diethanol amine (DEA), methyl diethanol amine (MDEA) and diisopropanol amine (DIPA). The

CO_2 absorbents preferably are regenerable. A disadvantage of amines is that they show thermal degradation. Another disadvantage is that some amines require accelerators.

CO_2 recovery using a combination of NaOH and Ca(OH)2 is discussed in F.S. Zeman and K.S. Lackner, "Capturing carbon dioxide directly from the atmosphere", World Resour. Rev. 16, pages 157-172, 2004. In this process, CO2 is first absorbed by an alkaline NaOH solution to produce dissolved sodium carbonate: $2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$. In a next step the sodium carbonate is reacted with calcium hydroxide to produce calcium carbonate:

$$Na_2CO_{3(aq)} + Ca(OH)_{2(s)} \rightarrow 2NaOH_{(aq)} + CaCO_{3(s)}$$

Subsequently, the calcium carbonate precipitate is filtered from the solution and thermally decomposed to produce gaseous CO_2:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Then the lime (CaO) is hydrated to $Ca(OH)_2$. The thermal decomposition of calcite may be performed in a lime kiln fired with oxygen in order to avoid an additional gas separation step. A disadvantage of this procedure is the heat required for the thermal decomposition of the calcium precipitate.

CO_2 recovery using potassium carbonate (K_2CO_3) is discussed in N.P. Devries, "CO2 absorption into concentrated carbonated solutions with promoters at elevated temperatures", thesis, University of Illinois, 2014. A disadvantage of this procedure is the low reaction rate, which requires the use of promoters such as piperazine, aminomethyl propanol, and diethanolamine.

The regeneration of $KHCO_3$ to K_2CO_3 can be performed by thermal treatment. Full decarboxylation of K_2CO_3 to KOH for K_2CO_3 dissolved in water or dry K_2CO_3, however, is not possible at temperatures below 1000 K. For commercially viable processes the chemical capacity thus is limited by the reaction:

$$K_2CO_3 + H_2O + CO_2 <-> 2KHCO_3$$

Another disadvantage thus is the limited chemical capacity of the system.

US4406867 describes a process in which impurities such as hydrogen sulfide, carbon dioxide, carbonyl sulfide, sulfur dioxide and mercaptans are removed from gas streams. Water vapor may be simultaneously removed from the gas. A solution is used which has at least one of (a) hydroxides, carbonates and bicarbonates of sodium, potassium and lithium, and (b) liquid aliphatic polyhydric alcohol having a carbon to oxygen ratio of 1 to 5 and at least two oxygen thereof being separated by not more than the two sequential carbon atoms. After purifying the gas, the reaction products stream is heated to achieve thermal regeneration of the solution. As an example is mentioned that the reaction product of CO_2 and glycol solvent will decompose at 180 to 200 °C. Also mentioned is the decomposition of K_2CO_3 to release CO_2 at 180 to 200 °C.

A disadvantage of the process described in US4406867 is that regeneration is achieved by means of decomposition of reaction components. This requires that the regeneration is performed at a temperature between 125 and 200 °C. Furthermore, as the absorption of impurities from the gas is performed at a temperature between 15 and 100 °C in a

process according to US4406867. This thus requires cooling of the recycled solvent.

Hence, there is a need for an improved process for removing carbon dioxide from a feed gas stream.

Summary of the invention

The invention relates to a process for removing carbon dioxide from a feed gas stream, which process comprises the steps:

(i) contacting the feed gas stream, at a temperature in the range of from 50 - 200 °C, preferably 60 - 120 °C, more preferably 60 - 80 °C, and a pressure in the range of from 1 to 100 bara, with a lean absorbent composition to absorb carbon dioxide and to form a carbon dioxide lean treated gas stream and a spent absorbent composition,

wherein the lean absorbent composition comprises:

(a) in the range of from 0.5 to 60 wt% of a hydroxide of an alkali metal, preferably NaOH, KOH, LiOH, RbOH or CsOH, more preferably NaOH or KOH, most preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of a polyhydric alcohol, preferably a diol, more preferably an alkylene glycol, most preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition;

(ii) removing absorbed CO2 and H2O from the spent absorbent composition, at a temperature in the range of between 50 - 120 °C, preferably 60 - 100 °C, more preferably 75 - 100 °C, and a pressure in the range of from 2 - 300 mbara, preferably 20 - 200 mbara, more preferably 50 - 150 mbara, with a gas or vapor stream to produce a regenerated

absorbent composition and a stream comprising CO2 and H2O; and

(iii) optionally subjecting at least a part of the stream comprising CO2 and H2O from step (ii) to condensation; and

(iv) optionally recycling at least a part of the regenerated absorbent composition from step (ii) to step (i).

With the process of the present invention there is no need to use amines. This is advantageous because amines show thermal degradation, and some amines require accelerators. The present invention does not require an accelerator. The absorbent composition does not show, or hardly shows, thermal degradation during the process of the present invention.

Another advantage is that the composition is regenerable using simple and energy efficient methods.

There is thus no need for a heating step such as thermal decomposition of calcium precipitate as is necessary for a method using a combination of NaOH and $Ca(OH)_2$ as discussed in F.S. Zeman and K.S. Lackner, "Capturing carbon dioxide directly from the atmosphere", World Resour. Rev. 16, pages 157-172, 2004.

There is also no need for thermal treatment to regenerate $KHCO_3$ to K_2CO_3 as is necessary for a method using potassium carbonate as described in N.P. Devries, "CO2 absorption into concentrated carbonated solutions with promoters at elevated temperatures", thesis, University of Illinois, 2014.

A further advantage is that the chemical capacity of KOH for CO_2 capture is twice as large as the chemical capacity of potassium carbonate (K_2CO_3).

There is also no need for thermal decomposition of reaction products such as a reaction product of CO_2 and glycol solvent which decomposes at 180 to 200 °C, and/or decomposition of K_2CO_3 to release CO_2 at 180 to 200 °C as described in US4406867.

There is also no need to cool a recycle solvent stream as is required for a process as described in US4406867.

Another advantage is that deep CO2 removal from the feed gas stream is obtained. Additionally, a stream comprising CO_2 and water is obtained during regeneration. CO_2 and water can be easily separated by means of condensation. The obtained CO_2 stream during the regeneration in a process according to the present invention is clean; it contains no or hardly any sulfur containing components such as H_2S. The obtained CO_2 stream can thus be used for many applications. It can, for example, be used for enhanced oil recovery. Moreover, it can, for example, be used as dry ice or in beverages, as it is non-toxic.

Detailed description of the invention

The invention relates to a process for removing carbon dioxide from a feed gas stream, which process comprises the steps:

(i) contacting the feed gas stream, at a temperature in the range of from 50 - 200 °C, preferably 60 - 120 °C, more preferably 60 - 80 °C, and a pressure in the range of from 1 to 100 bara, with a lean absorbent composition to absorb

carbon dioxide and to form a carbon dioxide lean treated gas stream and a spent absorbent composition,
wherein the lean absorbent composition comprises:

(a) in the range of from 0.5 to 60 wt% of a hydroxide of an alkali metal, preferably NaOH, KOH, LiOH, RbOH or CsOH, more preferably NaOH or KOH, most preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of a polyhydric alcohol, preferably a diol, more preferably an alkylene glycol, most preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition;

(ii) removing absorbed CO2 and H2O from the spent absorbent composition, at a temperature in the range of between 50 – 120 °C, preferably 60 – 100 °C, more preferably 75 – 100 °C, and a pressure in the range of from 2 – 300 mbara, preferably 20 – 200 mbara, more preferably 50 – 150 mbara, with a gas or vapor stream to produce a regenerated absorbent composition and a stream comprising CO2 and H2O; and

(iii) optionally subjecting at least a part of the stream comprising CO2 and H2O from step (ii) to condensation; and

(iv) optionally recycling at least a part of the regenerated absorbent composition from step (ii) to step (i).

The steps are performed in the order in which they are listed.

The feed gas stream from which CO_2 is removed may be any carbon dioxide comprising gas. It may comprise hydrocarbons, especially methane. It may comprise nitrogen. It may be air. It may, for example, be or comprise natural gas. It may, for

example, be off-gas produced during combustion. Off-gas produced during combustion may, for example, be off-gas produced during the combustion of fossil fuels; this may also be referred to as post-combustion gas.

The feed gas stream may comprise 100 ppm up to 50 wt% carbon dioxide, preferably 1 to 30 wt% carbon dioxide. When entering the process, the gas may have any suitable pressure; it may be at atmospheric pressure, at 2 bara, up to 100 bara. When entering the process, the gas may have any suitable temperature. As step (i) may be performed at relatively high temperatures, it will in most cases not be necessary to cool the feed gas stream. This is especially advantageous in case the feed gas is off-gas produced during combustion, more especially in case the feed gas is off-gas produced during the combustion of fossil fuels.

The lean absorbent composition used in step (i) comprises:
(a) in the range of from 0.5 to 60 wt% of a hydroxide of an alkali metal, preferably NaOH, KOH, LiOH, RbOH or CsOH, more preferably NaOH or KOH, most preferably KOH; and
(b) in the range of from 25 to 99.5 wt% of a polyhydric alcohol, preferably a diol, more preferably an alkylene glycol, most preferably mono-ethylene glycol; and
(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and
(d) optionally in the range of from 0.1 to 15 wt% H2O,
calculated on the total weight of the lean absorbent composition.

The lean absorbent composition used in step (i) may comprise other components than the components listed. The amounts of all components in the lean absorbent composition are calculated on the total weight of the lean absorbent composition. The amounts of all components in the lean

absorbent composition used in step (i) add up to a total of 100 wt%.

In step (i) a feed gas stream is contacted with a lean absorbent composition to absorb carbon dioxide and to form a carbon dioxide lean treated gas stream and a spent absorbent composition. Step (i) preferably is performed in an absorption zone, more preferably in an absorber. The absorber may have any suitable shape and size. It may, for example, be a (steel) column. In a preferred embodiment, the feed gas stream and the lean absorbent composition are fed counter-currently to the absorber.

Preferably a CO2 comprising feed gas stream is supplied at the bottom of the absorber. A lean absorbent composition preferably is supplied at the top of the absorber or formed at the top or upper side of the absorber. Spent absorbent composition is removed from the absorber, preferably from the bottom of the absorber.

The lean absorbent composition comprises a hydroxide of an alkali metal, a polyhydric alcohol, and optionally water, and optionally diethylene glycol. In a preferred embodiment the lean absorbent composition comprises:

(a) in the range of from 0.5 to 60 wt% NaOH or KOH, preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of an alkylene glycol, preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition.

The temperature in the absorber is in the range of from 50 - 200 °C, preferably 60 - 120 °C, more preferably 60 -

80 °C. The pressure in the absorber may, for example, be in the range of from 1 to 100 bara. An exothermal reaction takes place in the absorber.

In case, for example, the lean absorbent composition comprises KOH, the following reactions take place in the absorber when a CO2 comprising gas is contacted with the lean absorbent composition.

$$2\ KOH + CO2 \rightarrow K2CO3 + H2O$$

$$K2CO3 + CO2 + H2O \rightarrow 2\ KHCO3$$

These reactions take place in the polyhydric alcohol, preferably alkylene glycol, more preferably mono-ethylene glycol (MEG). The polyhydric alcohol may serve as a solvent for one or more of the other components in the absorbent composition.

Spent absorbent composition is removed from the absorber, preferably from the bottom of the absorber. Spent absorbent composition comprises polyhydric alcohol and alkali (bi)carbonate(s).

In case, for example, the lean absorbent composition comprises KOH and MEG, the spent absorbent composition comprises KHCO3 and MEG.

In step (ii) absorbed CO2 and H2O are removed from the spent absorbent composition with a gas or vapor stream to produce a regenerated absorbent composition and a stream comprising CO2 and H2O. Step (ii) preferably is performed in a regenerator. The regenerator may have any suitable shape and size. It may, for example, be a (steel) column. Preferably step (i) is performed in an absorber and step (ii) is performed in a regenerator.

A spent absorbent composition is supplied to the regenerator, preferably at the bottom of the regenerator.

Preferably steam is injected into the regenerator, more preferably steam is injected at the bottom of the regenerator. Most preferably steam is injected at the bottom of the regenerator using a live steam injector. CO2 and H2O are removed from the regenerator, preferably from the top of the regenerator. Polyhydric alcohol comprising alkali metal, which may contain a solution of an alkali metal salt of polyhydric alcohol, is removed from the regenerator, preferably from the bottom of the regenerator.

In case, for example, the lean absorbent composition comprises KOH and a large amount of MEG, a composition comprising KMEG and MEG is removed from the regenerator.

Preferably CO2 and H2O are removed in step (ii) by withdrawing a gas or vapor stream using a gas or vapor withdrawing device, preferably using a pump and/or an eductor. The removal of CO2 and H2O may also be referred to as "stripping". The removal of H2O may also be referred to as "boiling off water".

In case, for example, the lean absorbent composition comprises KOH, the spent absorbent composition comprises KHCO3, polyhydric alcohol, preferably alkylene glycol, more preferably mono-ethylene glycol (MEG), and optionally H2O and optionally diethylene glycol.

In case, for example, the lean absorbent composition comprises KOH and a large amount of MEG, the following reaction takes place in the regenerator to which spent absorbent composition is fed:

$$KHCO3 + MEG \rightarrow KMEG + CO2 + H2O$$

In this case this reaction takes place in mono-ethylene glycol (MEG).

H2O is continuously removed from the regenerator. Nevertheless, some water may react with KMEG:

KMEG + H2O -> KOH + MEG

This is acceptable.

Preferably CO2 is removed at a relatively high speed from the regenerator in order to reduce or to avoid the following reaction:

KMEG + CO2 -> adduct

A high enough speed of CO2 removal may be achieved by means of a gas or vapor withdrawing device, preferably a pump and/or an eductor.

In case some formation of an adduct of KMEG and CO2 takes place, a slip stream of the regenerated absorption medium may be taken away, and fresh lean absorption medium may be added to the system.

In case some K2CO3 is present in the regenerated absorption medium, a slip stream of the regenerated absorption medium may be taken away, and fresh lean absorption medium may be added to the system. Additionally or alternatively, the slip stream may be treated with CO2:

$$K_2CO_3 + H_2O + CO_2 <-> 2KHCO_3$$

After treatment with CO2 the slip stream may be recycled.

The temperature in the regenerator is in the range of between 50 - 120 °C, preferably 60 - 100 °C, more preferably 75 - 100 °C. The pressure in the regenerator may, for example, be in the range of from 2 - 300 mbara, preferably 20 - 200 mbara, more preferably 50 - 150 mbara. An endothermal reaction takes place in the regenerator.

At such low temperatures CO2 can be removed selectively from the regenerator. Water will be removed simultaneously during regeneration, but CO2 can be easily removed from H2O by means of condensation. Salts comprising sulfur do not decompose at these low temperatures. The CO2 product stream

will thus not be contaminated with sulfur compounds and can be used in beverages, in enhanced oil recovery, etc. This is a major advantage as compared to the process described in US4406867.

As mentioned above, polyhydric alcohol comprising alkali metal is removed from the regenerator, preferably from the bottom of the regenerator. The withdrawn polyhydric alcohol comprising alkali metal is hygroscopic.

In case, for example, the lean absorbent composition comprises KOH and a large amount of MEG, a composition comprising KMEG and MEG is removed from the regenerator.

Preferably at least a part of the regenerated absorbent composition is recycled from step (ii) to step (i). This is step (iv). When step (iv) is performed, preferably water is added to at least a part of the regenerated absorbent composition from step (ii).

Polyhydric alcohol comprising alkali metal is removed from the regenerator. Upon the addition of water, the composition comprises a hydroxide of an alkali metal.

In case, for example, the lean absorbent composition comprises KOH and a large amount of MEG, the composition removed from the regenerator comprises KMEG and MEG.

When water is added to a composition comprising KMEG and MEG, the following reaction takes place:

$$KMEG + H2O \rightarrow KOH + MEG$$

In one embodiment at least enough water is added to produce the maximum amount of KOH:

$$KMEG + x\ H2O \rightarrow KOH + MEG + x-1\ H2O$$

wherein $x \geq 1$.

The KOH will react in the absorber with CO2 and H2O to form KHCO3. During regeneration of the composition water is removed, and a hygroscopic composition is obtained. By adding

water KOH will be formed again, which can be used again in the absorber. As KOH reacts in two steps in the absorber to form $KHCO_3$ it has a double capacity towards CO_2 as compared to K_2CO_3.

Preferably at least a part of the stream comprising CO_2 and H_2O from step (ii) is subjected to condensation. This is step (iii).

When step (iii) is performed, preferably the condensed water from step (iii) is added to at least a part of the regenerated absorbent composition from step (ii).

As mentioned above, when step (iv) is performed, preferably water is added to at least a part of the regenerated absorbent composition from step (ii). This water preferably is water obtained from condensation of the stream comprising CO_2 and H_2O from step (iii).

In one embodiment, water, preferably the condensed water from step (iii), is added to at least a part of the regenerated absorbent composition from step (ii) before it is recycled to step (i).

In a preferred embodiment, step (i) is performed in an absorption zone and the feed gas stream and the lean absorbent composition are fed to this zone counter-currently. The absorption zone may be an absorber which may have any suitable shape and size. It may, for example, be a (steel) column. A hygroscopic composition comprising polyhydric alcohol comprising alkali metal, for example comprising KMEG or comprising KMEG and MEG, is supplied to the absorption zone. Preferably the hygroscopic composition comprising polyhydric alcohol comprising alkali metal is or comprises at least a part of the hygroscopic regenerated absorbent composition from step (ii). Water, preferably water obtained from condensation of the stream comprising CO_2 and H_2O from

step (iii), is fed to the absorption zone downstream of the entry of the hygroscopic composition comprising polyhydric alcohol comprising alkali metal. I.e. downstream with respect to the flow of the hygroscopic composition comprising polyhydric alcohol comprising alkali metal, which preferably is regenerated absorbent composition.

In a more preferred embodiment, a CO2 comprising feed gas stream is supplied at the bottom of an absorber. A hygroscopic composition comprising polyhydric alcohol comprising alkali metal, for example comprising KMEG or comprising KMEG and MEG, is supplied at the top of the absorber. More preferably at least a part of the hygroscopic regenerated absorbent composition from step (ii) is supplied at the top of the absorber. Water, preferably the condensed water from step (iii), is fed below the entry area of the hygroscopic composition. In this case lean absorbent composition is formed in the absorber. For example, a composition comprising KOH and MEG may be formed. The formed lean absorbent composition is lean with regard to CO2 and may comprise some H2O from the gas stream. Spent absorbent composition is removed from the absorber, preferably from the bottom of the absorber. The water is added above the area from which spent absorbent composition is removed from the absorber. Preferably the water is added in the upper half of the absorber and below the entry area of the hygroscopic composition.

The effect of the two above described preferred embodiments is that the feed gas stream flowing counter-currently is first contacted with the lean absorbent composition formed in the absorption zone, which comprises:

(a) in the range of from 0.5 to 60 wt% of a hydroxide of an alkali metal, preferably NaOH, KOH, LiOH, RbOH or CsOH, more preferably NaOH or KOH, most preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of a polyhydric alcohol, preferably a diol, more preferably an alkylene glycol, most preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition;

and CO_2 is removed from the gas stream. Then the gas stream is contacted with the hygroscopic composition comprising polyhydric alcohol comprising alkali metal, which preferably is or comprises at least a part of the hygroscopic regenerated absorbent composition from step (ii), and H_2O is removed from the gas stream.

When considering the flow of the hygroscopic composition comprising polyhydric alcohol comprising alkali metal, the effect of the two above described preferred embodiments is as follows. The hygroscopic composition comprising polyhydric alcohol comprising alkali metal is first contacted with a CO2 lean gas stream which may still comprise some H2O. If present, most or all of the H2O is scavenged by the hygroscopic composition comprising polyhydric alcohol comprising alkali metal. Thereafter the composition is still hygroscopic. Then water is fed to the hygroscopic composition comprising polyhydric alcohol comprising alkali metal, and a CO2 lean absorbent composition as described above is formed. Thereafter the lean absorbent composition is contacted with the feed gas stream, which comprises CO2, and CO2 is absorbed.

Spent absorbent composition is removed from the absorption zone.

Lean absorption medium or a hygroscopic composition comprising polyhydric alcohol comprising alkali metal may suitably be added to the absorption zone at a temperature in the range of between 50 – 200 °C. Lean absorption medium may suitably be formed in the absorption zone at a temperature in the range of between 50 – 200 °C.

Hence, when recycling regenerated absorbent composition from step (ii) to the absorber, there is no need to cool the composition before it enters the absorber. There is no need to cool when the regenerated absorbent composition from step (ii) is mixed with water before entering the absorption zone. There is also no need to cool when it is mixed with water in the absorption zone.

The present invention, in which the CO2 absorption may take place at relatively high temperatures and the regeneration is taking place at relatively low temperatures thus requires less cooling and heating as compared to the process described in US4406867.

Examples

The invention will now be illustrated by the following examples.

Experiments were performed. Especially experiments were performed on step (ii) of the process of the invention in which absorbed CO2 and H2O are removed from spent absorbent composition with a gas or vapor stream.

Example 1

An absorbent composition comprising water, mono-ethylene glycol, inorganic potassium salt, and KHCO3 was subjected to regeneration in a vacuum distillation column consisting of more than 10 theoretical trays. A vacuum of 130 mbar absolute

pressure was applied resulting in a range of bottom temperatures depending on distillate rates. The amount of CO2 that was released (compared to total amount present) was determined by titration of the bottom product samples and plotted as function of temperature at the bottom of the column in Figure 1.

Example 1 shows that even at temperatures as low as 90 °C, more than 50% of the carbon dioxide can be released.

Example 2

An absorbent composition comprising water, mono-ethylene glycol and a salt was subjected to regeneration via stripping with an inert gas. Experiments were performed with different types of salt in the composition, see Table 1. The amount of CO2 released was analyzed with titration of the residue samples. The amount of released CO2 is presented as a percentage compared to the total amount of CO2 that was introduced in the form of salt.

Ex.	Salt (5 wt%)	CO2 release (% CO2)	Temp. (°C)	H2O (wt%)
2a	KHCO3	73	120	2
2b	KHCO3	70	120	0
2c	KHS	0 (no other gases were released)	120	0
2e	CaCO3	0	120	5
2f	K2CO3 (20 wt%)	0	120	0

These examples show that up to 120 °C CO2 can be removed selectively. Water will be removed simultaneously during

regeneration. CO2 can be easily removed from H2O by means of condensation.

Salts such as CaCO3 and K2CO3 do not decompose at these low temperatures. Large amounts of such salts in the regenerator can be avoided. For example, K2CO3 can be reacted with CO2 and H2O in the absorber to form KHCO3. If necessary, a slip stream can be removed. Such a slip stream can be treated with CO2 and then recycled.

Salts comprising sulfur do not decompose at these low temperatures. That is highly advantageous. The CO2 product stream will not be contaminated with sulfur compounds and can be used in beverages, in enhanced oil recovery, etc.

This is a major advantage as compared to the process described in US4406867.

C L A I M S

1. A process for removing carbon dioxide from a feed gas stream, which process comprises the steps:

(i) contacting the feed gas stream, at a temperature in the range of from 50 - 200 °C, preferably 60 - 120 °C, more preferably 60 - 80 °C, and a pressure in the range of from 1 to 100 bara, with a lean absorbent composition to absorb carbon dioxide and to form a carbon dioxide lean treated gas stream and a spent absorbent composition,

wherein the lean absorbent composition comprises:

(a) in the range of from 0.5 to 60 wt% of a hydroxide of an alkali metal, preferably NaOH, KOH, LiOH, RbOH or CsOH, more preferably NaOH or KOH, most preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of a polyhydric alcohol, preferably a diol, more preferably an alkylene glycol, most preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition;

(ii) removing absorbed CO2 and H2O from the spent absorbent composition, at a temperature in the range of between 50 - 120 °C, preferably 60 - 100 °C, more preferably 75 - 100 °C, and a pressure in the range of from 2 - 300 mbara, preferably 20 - 200 mbara, more preferably 50 - 150 mbara, with a gas or vapor stream to produce a regenerated absorbent composition and a stream comprising CO2 and H2O; and

(iii) optionally subjecting at least a part of the stream comprising CO2 and H2O from step (ii) to condensation; and

(iv) optionally recycling at least a part of the regenerated absorbent composition from step (ii) to step (i).

2. The process according to claim 1 wherein step (i) is performed in an absorption zone and the feed gas stream and the lean absorbent composition are fed to this zone counter-currently.

3. The process according to claim 2, wherein:
- a hygroscopic composition comprising polyhydric alcohol comprising alkali metal, preferably regenerated absorbent composition from step (ii), is fed to the absorption zone, and
- water, preferably water obtained from condensation of the stream comprising CO2 and H2O from step (iii), is fed to the absorption zone downstream of the entry of the hygroscopic composition comprising polyhydric alcohol comprising alkali metal,
to form the lean absorbent composition used in step (i).

4. The process according to claim 1 or 2, wherein step (iv) is performed, and wherein water is added to at least a part of the regenerated absorbent composition from step (ii) before it is recycled to step (i).

5. The process according to claim 4, wherein step (iii) is performed, and wherein the condensed water from step (iii) is added to at least a part of the regenerated absorbent composition from step (ii).

6. The process according to any one of the above claims in which step (i) is performed in an absorber and step (ii) is

performed in a regenerator, and steam is injected into the regenerator, preferably steam is injected at the bottom of the regenerator, more preferably steam is injected at the bottom of the regenerator using a live steam injector.

7. The process according to any one of the above claims in which in step (ii) CO2 and H2O are removed by withdrawing a gas or vapor stream using a gas or vapor withdrawing device, preferably using a pump and/or an eductor.

8. The process according to any one of the above claims in which in step (i) the lean absorbent composition comprises:

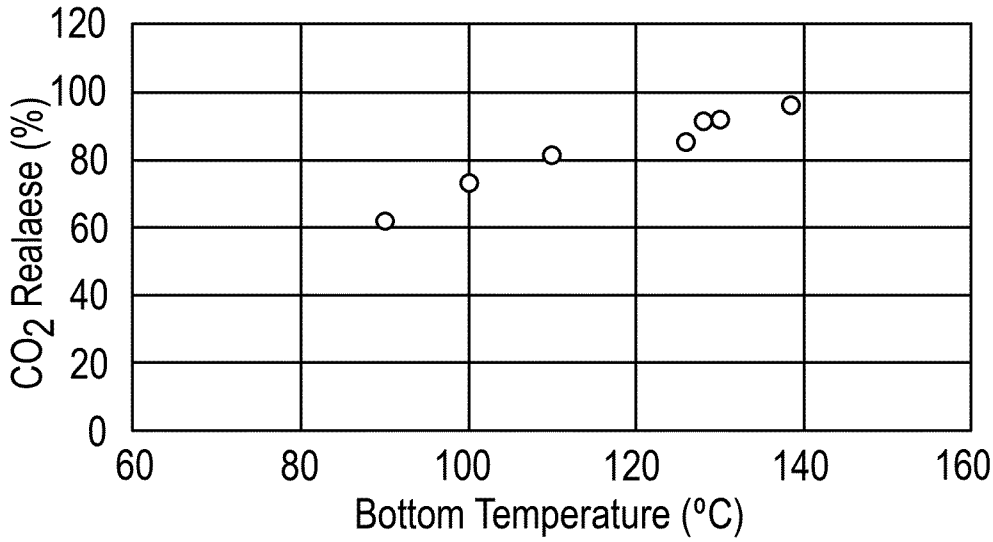
(a) in the range of from 0.5 to 60 wt% NaOH or KOH, preferably KOH; and

(b) in the range of from 25 to 99.5 wt% of an alkylene glycol, most preferably mono-ethylene glycol; and

(c) optionally in the range of from 0.1 to 10 wt% diethylene glycol; and

(d) optionally in the range of from 0.1 to 15 wt% H2O, calculated on the total weight of the lean absorbent composition.

Fig.1


120
100
80
60
40
20
0
CO_2 Realaese (%)
60
80
100
120
140
160
Bottom Temperature (°C)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082150

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14 B01D53/62
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 406 867 A (MARCINKOWSKY ARTHUR E [US] ET AL) 27 September 1983 (1983-09-27) cited in the application column 2, line 63 - column 3, line 15 column 3, lines 47-61 column 5, lines 32-55 column 6, lines 26-50 column 10, line 1 - column 11, line 40; figures 2, 4; tables II, V	1-8
A	Weiss, S. et al: "Absorption" In: Weiss, S. et al: "Verfahrenstechnische Berechnungsmethoden", 1986, VCH Verlagsgesellschaft mbH, D-6940 Weinheim, XP002768102, vol. 2, pages 194-200, the whole document	1-8

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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	Date of mailing of the international search report
13 March 2017	29/03/2017

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MAHMOUDKHANI M ET AL: "Low energy packed tower and caustic recovery for direct capture of CO2 from air", ENERGY PROCEDIA, ELSEVIER, NL, vol. 1, no. 1, 1 February 2009 (2009-02-01), pages 1535-1542, XP026472048, ISSN: 1876-6102, DOI: 10.1016/J.EGYPRO.2009.01.201 [retrieved on 2009-02-01] abstract -----	1-8
A	US 2012/171095 A1 (O'BRIEN MICHAEL JOSEPH [US] ET AL) 5 July 2012 (2012-07-05) claims 1,10-13 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/082150

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4406867 A	27-09-1983	NONE	
US 2012171095 A1	05-07-2012	NONE	