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(54) Title: PROCESS FOR REMOVING SULFUR DIOXIDE FROM A GAS STREAM

(57) Abstract: The invention relates to a process for removing SO₂ from gas by contacting it with an aqueous lean absorbing medium in a primary absorption zone. The absorbing medium comprises an amine and 1 to 1.2 eq/amine mole of HSS, and has a pH of less than 6. The absorbing medium is regenerated. HSS is removed from a part of the regenerated absorbing medium. Diluted HSS lean regenerated absorbing medium is used in a second absorption zone to absorb SO₂ from off-gas leaving the first absorption zone. The diluted regenerated absorbing medium comprises an amine and 0.05 to 0.6 eq/amine mole of HSS, and has a pH between 6.5 and 8. The off-gas leaving the second absorption zone comprises a low amount of SO₂ which may be less than 5 ppmv SO₂.

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PROCESS FOR REMOVING SULFUR DIOXIDE FROM A GAS STREAM

Field of the invention

The present invention relates to a process for removing sulfur dioxide (SO_2) from a feed gas stream. The present invention especially relates to a process
5 suitable to selectively capture sulfur dioxide (SO_2) from a feed gas stream, more especially to remove SO_2 from a gas stream while not at the same time removing CO_2 from the gas stream.

Background to the invention

10 It is known that SO_2 is more soluble in water than many other components of feed gas streams. For example, measured at 1.013 bar 0°C , the solubility of SO_2 in water is 228 g/L whereas the solubility of carbon dioxide and hydrogen sulfide in water is 3.369 g/L and 7.100 g/L,
15 respectively.

The solubility of SO_2 in many other pure solvents has also been widely studied. See, for example, Fogg and Gerrard, 1991 (Solubility of Gases in Liquids, John Wiley and Sons, Chichester, U.K.) for a summary of the
20 literature solubility data of SO_2 .

Regenerable absorbents can be used to remove SO_2 from feed gas streams. Typically, a lean aqueous medium comprising the absorbent is exposed to a SO_2 containing feed gas stream, and then SO_2 is absorbed by the medium
25 producing a SO_2 lean gas stream and a spent absorbing medium. Removal (recovery) of the absorbed SO_2 from the spent absorbing medium to regenerate the aqueous medium and to provide gaseous SO_2 is typically effected by gaseous stripping using steam generated in situ.

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Amine-based absorbents can be used for SO₂ removal. See, for example, US5019361 which discloses the use of an aqueous absorbing medium containing a water-soluble half salt of a diamine. US7214358 discloses the use of an aqueous absorbing medium containing a water-soluble half salt of a diamine and an elevated level of heat stable salts (HSS). Physical solvents can also be used as SO₂ absorbents.

Commercially available steam-regenerable SO₂ capture technologies include those that rely on chemical solvents or physical solvents, such as Cansolv DSTM (amine-based absorbent-containing chemical solvent), LabsorbTM (inorganic absorbent-containing chemical solvent), ClausMasterTM (non-aqueous physical solvent), and Sea water process (chemical solvent).

Use of a combination of solvents has also been disclosed. Indian Patent Application No. 2381/DEL/2006 describes a process for the removal of SO₂ using a solvent blend comprising chemical and physical solvents. US20130039829 describes a process for the capture of sulfur dioxide from a gaseous stream utilizing a regenerable diamine absorbent comprising a diamine and a weak organic acid, such as formic acid.

In some processes SO₂ is removed from gas in an absorption zone, whereby SO₂ lean gas leaves the absorption zone and rich solvent is withdrawn and sent to regeneration zone. Regenerated solvent is recycled to the absorption zone. Depending on the solvent used and the conditions in the absorption zone, the gas leaving the absorption zone still has a higher sulfur dioxide level than desired.

One regularly used method is to further treat the gas leaving the absorption zone with a strong alkaline, for

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example caustic soda in a polisher unit downstream of the SO₂ absorption zone. A disadvantage of this procedure is the need for the extra chemical, namely the strong alkaline. Another disadvantage is that it results in a waste stream containing strong alkaline. A further disadvantage is the risk of contamination of the amine with alkali metals or alkali earth metals.

US5262139 describes a process in which two absorption zones are used. In a primary absorption zone sulfur dioxide comprising gas is treated with a diamine of which a first amine group is in salt form associated with sulfite anions, and a second amine group is in free base form. The sulfur dioxide lean gas leaving the primary absorption zone is passed to a secondary absorption zone. In one process, the sulfur dioxide lean gas is contacted in the secondary absorption zone with a diamine with both amine groups in free base form. A disadvantage of this process, as mentioned in US5262139, is the volatility of the diamine with both amine groups in free base form, which increases the risk of amine emission. A solution proposed in US5262139 is to use in the secondary absorption zone a diamine of which the first amine is in salt form associated with carbonate anions, and a second amine group in free base form. A drawback of this is that it requires contacting the sulfur dioxide lean gas leaving the primary absorption zone with a gas comprising carbon dioxide in a carbonation zone before passing it to the secondary absorption zone. This has several disadvantages such as the requirement to use a further chemical in the process, the requirement of the extra process step of carbonation, the introduction of the risk of contamination with carbon dioxide of the solvent

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stream used in the primary absorption zone, and the requirement to handle extra chemicals in exit streams.

There is a need for a process with which sulfur dioxide (SO₂) can be removed from a feed gas stream, and which process has a relatively low sulfur dioxide emission in the off-gas from the absorption zone, but without the disadvantages associated with a treatment with caustic soda, and without the disadvantages of a carbonation step between a primary and a secondary absorption step.

Summary of the invention

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

(i) contacting the feed gas stream with an aqueous lean absorbing medium in a primary absorption zone to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine;

(b) in the range of between 1 to 1.2 equivalent/amine mole heat stable salts;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6; and

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from at least a part of the spent absorbing medium obtained in step (i) in a regeneration

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zone to produce a regenerated aqueous absorbing medium and sulfur dioxide; and

(iii) recycling a part of the regenerated aqueous absorbing medium obtained in step (ii) to step (i); and

5 (iv) removing heat stable salts from a second part of the regenerated aqueous absorbing medium obtained in step (ii), preferably by means of an ion exchange resin, electrodialysis, crystallization, or thermal reclamation;

10 (v) diluting at least a part of the regenerated aqueous absorbing medium having a reduced heat stable salt content as obtained in step (iv) with water;

(vi) contacting diluted absorbing medium as obtained in step (v) with at least a part of the sulfur dioxide lean treated gas stream obtained in step (i) in a
15 secondary absorption zone to absorb sulfur dioxide and to form a further treated lean gas stream and a spent or partly spent absorbing medium,

wherein the diluted absorbing medium comprises:

20 (a) the chemical solvent comprising a regenerable absorbent;

(b) in the range of between 0.05 to 0.6 equivalent/amine mole heat stable salts;

25 wherein the pH of the diluted absorbing medium is in the range of from 6.5 to 8.0, preferably in the range of from 6.7 to 7.1; and

(vii) recycling at least a portion of the spent or partly spent absorbing medium obtained in step (iv) and/or at least a portion of the spent or partly spent absorbing medium obtained in step (vi) to step (i).

30 The process of the present invention is suitable to remove sulfur dioxide (SO₂) from a feed gas stream while having a relatively low sulfur dioxide emission, and at the same time avoiding the disadvantages associated with

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a treatment with caustic soda, and avoiding the disadvantages of a carbonation step between a primary and a secondary absorption step.

5 The process of the present invention is less complex as compared to caustic treatment of absorption off-gas, and as compared to a process with a carbonation step between a primary and a secondary absorption step. It does not require an extra chemical. And it does not result in extra waste streams. It is safe. And it does
10 not have the risk of contaminating the absorbing medium used in the primary absorption zone.

The process of the present invention is highly advantageous as it results in very low sulfur dioxide emissions. The off-gas leaving the secondary absorption
15 zone comprises a very low amount of SO₂ which may even be less than 5 ppmv SO₂. Another advantage is that there is hardly any entrainment of diamine or polyamine in the off-gas leaving the secondary absorption zone.

Figures

20 Figure 1 shows a schematic diagram of a preferred embodiment of a line-up for a process according to the invention.

Figure 2 shows data of a test according to the invention. It shows an aggregated plot of pH and SO₂
25 emissions from the second absorption zone.

Detailed description of the invention

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

30 (i) contacting the feed gas stream with an aqueous lean absorbing medium in a primary absorption zone to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

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wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine;

(b) in the range of between 1 to 1.2 equivalent/amine mole heat stable salts;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6; and

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from at least a part of the spent absorbing medium obtained in step (i) in a regeneration zone to produce a regenerated aqueous absorbing medium and sulfur dioxide; and

(iii) recycling a part of the regenerated aqueous absorbing medium obtained in step (ii) to step (i); and

(iv) removing heat stable salts from a second part of the regenerated aqueous absorbing medium obtained in step (ii), preferably by means of an ion exchange resin, electrodialysis, crystallization, or thermal reclamation;

(v) diluting at least a part of the regenerated aqueous absorbing medium having a reduced heat stable salt

content as obtained in step (iv) with water;

(vi) contacting diluted absorbing medium as obtained in step (v) with at least a part of the sulfur dioxide lean treated gas stream obtained in step (i) in a secondary absorption zone to absorb sulfur dioxide and to form a further treated lean gas stream and a spent or partly spent absorbing medium,

wherein the diluted absorbing medium comprises:

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(a) the chemical solvent comprising a regenerable absorbent;

(b) in the range of between 0.05 to 0.6 equivalent/amine mole heat stable salts;

5 wherein the pH of the diluted absorbing medium is in the range of from 6.5 to 8.0, preferably in the range of from 6.7 to 7.1; and

(vii) recycling at least a portion of the spent or partly spent absorbing medium obtained in step (iv) and/or at least a portion of the spent or partly spent absorbing medium obtained in step (vi) to step (i).

The invention relates to a process for removing sulfur dioxide from a feed gas stream. The feed gas stream used in step (i) comprises SO₂ and may comprise CO₂. The process steps are preferably performed in the order in which they are presented. Preferably the absorbing medium is present in a single liquid phase during step (i). Preferably the absorbing medium is present in a single liquid phase during step (ii). Preferably the absorbing medium is present in a single liquid phase during step (vi).

Step (i)

In step (i) a feed gas stream comprising sulfur dioxide is contacted with an aqueous lean absorbing medium in a primary absorption zone. Sulfur dioxide is absorbed. A sulfur dioxide lean treated gas stream is formed. And a spent absorbing medium is formed.

The aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine;

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(b) in the range of between 1 to 1.2 equivalent/amine mole of heat stable salts.

The feed gas stream comprises sulfur dioxide. Sulfur dioxide is commonly present in effluent streams from a variety of commercial sources. Examples are stack gases from coal fired power plants, from industrial boilers, from smelting, and from metallurgical roasting operations, and tail gas streams from Claus sulfur plants, from refineries and from chemical plants.

A sulfur dioxide comprising gas, for example an effluent stream of a commercial source, may be treated before use in step (i) of the present invention.

For example, the gas may be cooled, for example by quenching, or it may be subcooled. Additionally or alternatively the gas may be de-dusted. Additionally or alternatively the gas may be de-acidified. In one embodiment the gas is (sub)cooled and de-dusted, and optionally de-acidified before use in step (i) of the present invention.

Optionally sulfur dioxide is removed from a sulfur dioxide comprising gas before use in step (i). In most cases, however, it is not necessary to remove sulfur dioxide from an effluent stream of a commercial source as the process of the present invention is suitable for treating gas streams having a high amount of sulfur dioxide.

The sulfur dioxide concentration in the feed gas stream used in step (i) may vary. Preferably the sulfur dioxide concentration in the feed gas stream used in step (i) is in the range of between 800 ppmv and 45 volume percent, more preferably in the range of between 800 ppmv and 11 volume percent.

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The feed gas stream used in step (i) may comprise CO₂. With the process of the present invention SO₂ is removed from a gas stream while, at the same time, not or hardly removing CO₂ from the gas stream. With the process of the invention a pure SO₂ stream can be obtained that can be used for sulfuric acid make, or for use in a sulfur reduction unit in a Claus application. When stripping sulfur dioxide from the spent absorbing medium in step (ii), sulfur dioxide is obtained. The obtained sulfur dioxide is pure. The obtained sulfur dioxide does not comprise or hardly comprises contaminants such as CO₂. The obtained sulfur dioxide is water saturated. The obtained sulfur dioxide preferably comprises about 99wt% SO₂, calculated on dry product stream. If desired, water may be removed from the sulfur dioxide, e.g. by means of distillation.

The pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6.

The contact of the absorbing medium with the SO₂ containing gas stream may be effected within the temperature range from the freezing point of the absorbent up to 75°C, or from 10°C to 60°C, or from 10°C to 50°C.

The pressure in the primary absorption zone may be in the range of between 1.0 and 2 bara.

Preferably the aqueous lean absorbing medium used in step (i) comprises in the range of from 10 to 35 wt% amine, more preferably 13 to 25 wt% amine.

Preferably the aqueous lean absorbing medium used in step (i) comprises in the range of between 25wt% and 85wt% water.

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The aqueous lean absorbing medium comprises a chemical solvent and heat stable salts.

The chemical solvent comprises a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine.

The amount of heat stable salts in the aqueous lean absorbing medium may be in the range of between 0.9 to 1.3 equivalent/amine mole. Preferably the amount of heat stable salts in the aqueous lean absorbing medium is in the range of between 1 to 1.2 equivalent/amine mole. In other words, per mole amine, the aqueous lean absorbing medium may comprise in the range of between 0.9 to 1.3 mole equivalent HSS, and preferably, per mole amine, the aqueous lean absorbing medium comprises in the range of between 1 to 1.2 mole equivalent HSS. The heat stable salt may be a salt of a monoprotic, diprotic or polyprotic acid.

Step (ii)

In step (ii) absorbed sulfur dioxide from at least a part of the spent absorbing medium obtained in step (i) is stripped, preferably steam stripped, in a regeneration zone. A regenerated aqueous absorbing medium is produced. Sulfur dioxide is stripped off. Preferably gaseous sulfur dioxide is obtained.

Preferably step (ii) is performed in a reboiler, more preferably in a kettle reboiler, forced circulation reboiler, fired reboiler, falling film reboiler, direct steam reboiler, or thermosyphon, more preferably in a thermosyphon.

The reboiler may be heated by hot oil, electricity or steam, preferably steam. Alternatively, direct steam addition can be utilized.

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The temperature in the regeneration zone may be in the range of between 100 and 150 °C.

The pressure in the regeneration zone may be in the range of between 1.0 and 4.8 bara, preferably between 1.0 and 3 bara.

Preferably at least 97 vol%, preferably at least 99 vol%, more preferably at least 99.9 vol% of the spent absorbing medium formed in step (i) is stripped, preferably steam stripped, in step (ii).

The regenerated aqueous absorbing medium obtained in step (ii) is withdrawn from the regeneration zone and split in at least two streams. One stream of regenerated aqueous absorbing medium is recycled to the primary absorption zone where it is used to absorb sulfur dioxide from gas entering the primary absorption zone; this is step (iii). A second stream of regenerated aqueous absorbing medium is used in a second absorption zone to remove sulfur dioxide from SO₂ lean gas stream which leaves the primary absorption zone; this is step (vi). The second stream of absorbing medium is diluted with water before and/or in the second absorption zone (this is step (v)). In other words, step (v) may be performed before and/or during step (vi).

Step (iii)

In step (iii) a part of the regenerated aqueous absorbing medium obtained in step (ii) is recycled to step (i). It is recycled to the first absorption zone where it is used to absorb sulfur dioxide from the feed gas stream. Additionally or alternatively fresh aqueous absorbing medium may be added to the primary absorption zone.

Step (iv)

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In step (iv) heat stable salts are removed from a second part of the regenerated aqueous absorbing medium obtained in step (ii).

Heat stable salts are commonly formed in sulfur dioxide absorption processes during both the absorption and regeneration steps as by-product. The presence of HSS reduces the absorption capacity of the absorbing medium for sulfur dioxide. A limited amount of HSS is acceptable. One way of controlling the amount of HSS in the absorbing medium is a treatment to remove HSS from regenerated absorbing medium. As a result, more amine groups are in free base form.

Typically, only a slip stream of the regenerated absorbing medium needs to be treated for heat stable salt removal or heat stable anion removal. In one embodiment HSS is removed from a small fraction, preferably less than 10 percent, preferably less than 5 percent, more preferably less than 2 percent of the total amount of regenerated absorbent. The often is sufficient to achieve a substantial increase in absorption capacity for sulfur dioxide.

HSS are preferably removed by means of an ion exchange resin, electrodialysis, crystallization, and/or thermal reclamation.

After removing almost all or a part of the HSS more amine groups are in free base form. Preferably in the range of from 40% to 97%, more preferably of from 50% to 97%, even more preferably from 75% to 97% of the amine groups in the regenerated aqueous absorbing medium, which has a reduced heat stable salt content, as obtained in step (iv) is in free base form.

Step (v)

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In step (v) at least a part of the regenerated aqueous absorbing medium having a reduced heat stable salt content as obtained in step (iv) is diluted with water.

5 Step (vi)

In step (vi) diluted absorbing medium as obtained in step (v) is contacted with at least a part of the sulfur dioxide lean treated gas stream obtained in step (i) in a secondary absorption zone. Sulfur dioxide is absorbed. A
10 further treated SO₂ lean gas stream and a spent or partly spent absorbing medium are formed. The diluted absorbing medium comprises:

- (a) the chemical solvent comprising a regenerable absorbent; this is the chemical solvent as defined
15 in the description of step (i);
- (b) in the range of between 0.05 to 0.6 equivalent/amine mole of heat stable salts.

The pH of the diluted absorbing medium is in the range of from 6.5 to 8.0, preferably in the range of from
20 6.7 to 7.1. Water may be added and removed during step (vi).

The primary and secondary absorption zones may be in the same absorber vessel or in separate absorber vessels.

As mentioned above, the sulfur dioxide concentration
25 in the feed gas stream used in step (i) preferably is in the range of between 800 ppmv and 45 volume percent, more preferably in the range of between 800 ppmv and 11 volume percent. Step (vi) is especially advantageous when the sulfur dioxide lean treated gas stream obtained in
30 step (i) has a sulfur dioxide concentration in the range of between 35 and 250 ppmv, preferably 50 to 250 ppmv.

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The off-gas leaving the secondary absorption zone comprises a very low amount of SO₂ which may even be less than 5 ppmv SO₂.

5 The contact of the absorbing medium with the SO₂ containing gas stream may be effected within the temperature range from the freezing point of the absorbent up to 75°C, or from 10°C to 60°C, or from 10°C to 50°C.

10 The pressure in the secondary absorption zone may be in the range of between 1.0 and 2 bara.

As mentioned above, preferably the aqueous lean absorbing medium used in step (i) comprises in the range of from 10 to 35 wt% amine, more preferably 13 to 25 wt% amine. Preferably the diluted absorbing medium used in
15 step (vi) comprises in the range of from 0.5 to 9.5 wt% amine.

As mentioned above, preferably the aqueous lean absorbing medium used in step (i) comprises in the range of between 25wt% and 85wt% water. Preferably the diluted
20 absorbing medium used in step (vi) comprises in the range of between 40wt% and 99wt% water.

The off-gas leaving the secondary absorption zone comprises a very low amount of SO₂ which may even be less than 5 ppmv SO₂. Another advantage of a process according
25 to the present invention is that there is hardly any entrainment of diamine or polyamine in the off-gas leaving the secondary absorption zone.

During step (v) a further treated SO₂ lean gas stream and a spent or partly spent absorbing medium are formed.
30 The SO₂ lean gas stream leaving the primary absorption zone comprises a relatively small amount of SO₂. And large part of the amines of the absorbing medium is in free base form. The spent absorbing medium formed during

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step (vi) in the second absorption zone thus may be only partly spent. Partly spent absorbing medium can be passed from the second to the first absorption zone, where it can absorb more sulfur dioxide.

5 Step (vii)

In step (vii) at least a portion of the spent or partly spent absorbing medium obtained in step (iv) and/or at least a portion of the spent or partly spent absorbing medium obtained in step (vi) is recycled to
10 step (i).

The level of HSS in the absorbing medium used in step (i) may be controlled by addition of HSS lean absorbing medium as obtained in step (iv) and/or in step (vi).

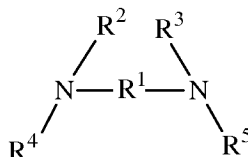
15 Additionally or alternatively at least a portion of spent or partly spent absorbing medium obtained in step (vi) is regenerated in the regeneration zone.

Absorbing medium

Preferably the regenerable absorbent is a diamine or
20 polyamine which in half salt form has a pK_a value for the free nitrogen atom of 3.0 to 5.5, preferably 3.5 to 4.7, at a temperature of 20 °C in an aqueous medium.

More preferably the regenerable absorbent is a diamine or polyamine with a pK_a value of the first amine
25 group, of from about 7.0 to 9.0, preferably 7.5 to 8.5, and a pK_a value of the second amine group is from about 3.0 to 5.5, preferably 3.5 to 4.7, at a temperature of 20 °C in an aqueous medium.

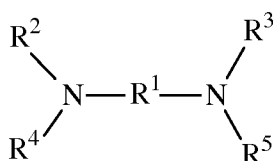
Preferably the regenerable absorbent is a diamine
30 represented by the formula:



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wherein R¹ is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, R², R³, R⁴, and R⁵ may be the same or different and can be hydrogen, alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any
 5 of R², R³, R⁴, and R⁵ may form cyclic structures.

More preferably the regenerable absorbent is a tertiary amine represented by the formula:



10

wherein R¹ is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, and R², R³, R⁴, and R⁵ can be alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R², R³, R⁴, and R⁵ may form cyclic
 15 structures.

Even more preferably the regenerable absorbent is piperazine, hydroxyethyl piperazine, bis-hydroxyethyl piperazine, hydroxyethylethylenediamine (HEED), bis-hydroxyethylethylenediamine (bis-HEED),
 20 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-[2-aminoethyl]pyridine, 2-aminomethylpyridine, 3-amino 5-methylpyrazole, 3-aminopyrazole, 3-methylpyrazole, N,N,N',N'-tetraethyldiethylenetriamine, N,N,N',N'-tetramethyldiethylenetriamine, 2-piperazinone
 25 1,4-bis[2-hydroxyethyl], or a combination thereof.

Most preferably the regenerable absorbent is piperazine, hydroxyethyl piperazine, bis-hydroxyethyl
 30 piperazine, hydroxyethylethylenediamine (HEED), bis-

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hydroxyethylethylenediamine (bis-HEED), or a combination thereof.

Acid

Preferably the lean absorbing medium used in step (i) of the process of the present invention additionally comprises an organic acid and/or an inorganic acid, preferably an inorganic acid, more preferably one or more acids chosen from the group of nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3), even more preferably sulfuric acid (H_2SO_4) and/or sulfurous acid (H_2SO_3).

Physical solvent

Preferably the lean absorbing medium used in step (i) of the process of the present invention additionally comprises a physical solvent. The physical solvent preferably has a vapour pressure less than 0.1 mmHg at 20°C with a boiling point equal to or higher than 240°C, the physical solvent more preferably is a polyol, a polycarbonate, an N-formyl morpholine, or a combination thereof.

More preferably the physical solvent is polyethyleneglycol dimethylether (PEGDME), tetraethyleneglycol dimethylether (TetraEGDME), tetraethylene glycol (TetraEG), triethyleneglycol monomethylether (TriEGMME), or a combination thereof, preferably polyethyleneglycol dimethylether (PEGDME).

Even more preferably the physical solvent is polyethyleneglycol dimethylether (PEGDME), and wherein the regenerable absorbent is 4-[hydroxyethyl]piperazine (Hep), or 1,4-bis[hydroxyethyl]piperazine (DiHep), or 3-aminopyrazole, or

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a mixture of 4-[hydroxyethyl]piperazine (Hep) and 1,4-bis[hydroxyethyl]piperazine (DiHep).

Sulfur dioxide recovery

In some embodiments, the processes as described herein further comprise a step of recovering the gaseous sulfur dioxide.

With the process of the invention a pure SO₂ stream can be obtained that can be used for sulfuric acid make, or for use in a sulfur reduction unit in a Claus application. The pure SO₂ stream is not or hardly contaminated with CO₂ or mercaptans which would contaminate sulfuric acid, or which would contaminate a Claus unit.

SO₂ removal

In general, a suitable indicator for an appropriate choice of absorbent for use in the capture of a given gaseous acid gas contaminant (such as SO₂) in a feed gas is the difference in the pK_a values between the acid gas in water and the absorbent.

The pK_a of an acid is defined as the negative logarithm to the base 10 of the equilibrium constant K_a for the ionization of the acid HA (e.g., H₂SO₃), where H is hydrogen and A is a radical capable of being an anion:

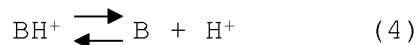


$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] \quad (2)$$

$$\text{pK}_a = -\log_{10} K_a \quad (3)$$

For a basic absorbent B, the pK_a is for the ionization reaction of the conjugate protonated acid of B, the species BH⁺:

- 20 -



5 The reaction involved in the absorption of the acid gas contaminant HA by the basic absorbent B can be shown as follows:



10 Reaction (5) is reversible:



15 When SO₂ is dissolved in water, following reaction (1), bisulphite ions (HSO₃⁻) and protons are formed. The proton may be ionically associated with the absorbent (for example, when an amine-based absorbent is used, the proton may be ionically associated with the sorbing nitrogen of the absorbent). The absorbed SO₂/desorbed SO₂ equilibrium is illustrated in the above reaction (6).
20 Absorbed SO₂ can be "stripped" from the spent absorbing medium as gaseous SO₂, for example and without limitation, by the application of steam. In this stripping process, desorbed SO₂ is released from the spent absorbing medium. "Stripping" is used herein to broadly encompass removal of absorbed SO₂ from the spent absorbing medium, and should be understood as also, more specifically, encompassing releasing desorbed SO₂ from the spent absorbing medium.

30 Heat Stable Salts (HSS)

HSS may accumulate in the medium due to, for example, sulfite/bisulfite oxidation or disproportionation, or due to the absorption of acid mist from the feed gas. These

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salts are too stable to decompose under normal steam conditions for stripping SO₂ from spent absorbing medium. Examples of such heat stable salts are those salts that are formed from strong acids such as sulfuric acid,
5 nitric acid, or hydrochloric acid. If allowed to accumulate, these heat stable salts would eventually completely neutralize the SO₂ absorption capacity of the absorbent. Therefore, management of HSS in the solution may be an important part of the SO₂ removal process to
10 maintain performance over time.

The amount of HSS formed may be affected by the absorbent used and/or the concentration of the absorbent. The amount of HSS for an absorbing medium may be controlled by using conventional means, such as an ion
15 exchange resin, eletrodialysis unit or crystallization. Amine purification units (APU) that are currently used industrially utilize weak anionic resins capable of some selectivity between sulfate (a strong conjugated base) and weaker conjugated bases in the absorbing medium. The
20 performance of such weak base resins varies depending on the concentration of sulfate in solution. These resins do not always perform well if there is a low concentration of HSS.

Ways to control the level of HSS for an organic
25 acid/physical solvent mixture may also include ion exchange with cyclo[8]pyrrole as the functional groups or by crystallization of alkaline sulfate salts (e.g. Na₂SO₄), where the cation can be sodium or potassium, most often sodium. Another way of controlling the level
30 of HSS in the organic acid/physical solvent mixture is precipitation of Ettringite (Ca₆Al₂(SO₄)₂(OH)₁₂•26H₂O).

In the alternative, HSS could also be removed by ion pairing. Without being limited by theory, it is believed

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that a low HSS amount in the absorbing medium, in accordance with some embodiments of the invention, may reduce the efficiency of the exchange of HSS with a standard anionic weak base resin. In some embodiments, it may therefore be desirable to remove HSS by ion pairing, which may permit a higher rate of removal of HSS even when the amount of salts in solution is low. Ion pairing may be achieved, for example, by using a dual function resin having different ionic functional groups (such as a combination of phenol and quaternary amine functional groups) or by liquid-liquid extraction.

Without being limited to theory, it is believed that a strong base quaternary amine functional group insensitive to suppressed salt concentrations will attract opposite charged anions regardless of their type. During regeneration, the phenolic functional group which is the active exchange site in the above described dual function resin, becomes negatively charged at a pH greater than 10.5, and repels the like charged anions.

Summary

The present invention relates to a process for removing sulfur dioxide from a feed gas stream, which process comprises:

(i) contacting the feed gas stream with an aqueous lean absorbing medium in a primary absorption zone to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine;

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(b) in the range of between 1 to 1.2 equivalent/amine mole heat stable salts;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6; and

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from at least a part of the spent absorbing medium obtained in step (i) in a regeneration zone to produce a regenerated aqueous absorbing medium and sulfur dioxide; and

(iii) recycling a part of the regenerated aqueous absorbing medium obtained in step (ii) to step (i); and

(iv) removing heat stable salts from a second part of the regenerated aqueous absorbing medium obtained in step (ii), preferably by means of an ion exchange resin, electrodialysis, crystallization, or thermal reclamation;

(v) diluting at least a part of the regenerated aqueous absorbing medium having a reduced heat stable salt content as obtained in step (iv) with water;

(vi) contacting diluted absorbing medium as obtained in step (v) with at least a part of the sulfur dioxide lean treated gas stream obtained in step (i) in a secondary absorption zone to absorb sulfur dioxide and to form a further treated lean gas stream and a spent or partly spent absorbing medium,

wherein the diluted absorbing medium comprises:

(a) the chemical solvent comprising a regenerable absorbent;

(b) in the range of between 0.05 to 0.6 equivalent/amine mole heat stable salts;

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wherein the pH of the diluted absorbing medium is in the range of from 6.5 to 8.0, preferably in the range of from 6.7 to 7.1; and

(vii) recycling at least a portion of the spent or partly spent absorbing medium obtained in step (iv) and/or at least a portion of the spent or partly spent absorbing medium obtained in step (vi) to step (i).

The feed gas stream used in step (i) comprises SO₂ and may comprise CO₂.

Preferably the absorbing medium is present in a single liquid phase during steps (i) (ii) and (vi).

Additionally or alternatively, the sulfur dioxide concentration in the feed gas stream is in the range of between 800 ppmv and 45 volume percent, preferably in the range of between 800 ppmv and 11 volume percent.

Additionally or alternatively, the sulfur dioxide lean treated gas stream obtained in step (i) has a sulfur dioxide concentration in the range of between 35 and 250 ppmv, preferably 50 to 250 ppmv.

Additionally or alternatively, the aqueous lean absorbing medium used in step (i) comprises in the range of from 10 to 35 wt% amine, preferably 13 to 25 wt% amine, and the diluted absorbing medium used in step (vi) comprises in the range of from 0.5 to 9.5 wt% amine.

Additionally or alternatively, step (ii) is performed in a reboiler, preferably in a kettle reboiler, forced circulation reboiler, fired reboiler, falling film reboiler, direct steam reboiler, or thermosyphon, more preferably in a thermosyphon.

Additionally or alternatively, at least 97 vol%, preferably at least 99 vol%, more preferably at least 99.9 vol% of the spent absorbing medium formed in step (i) is stripped, preferably steam stripped, in step (ii).

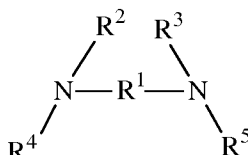
- 25 -

Additionally or alternatively, the regenerable absorbent is a diamine or polyamine which in half salt form has a pK_a value for the free nitrogen atom of 3.0 to 5.5, preferably 3.5 to 4.7, at a temperature of 20 °C in an aqueous medium.

Additionally or alternatively, the regenerable absorbent is a diamine or polyamine with a pK_a value of the first amine group, of from about 7.0 to 9.0, preferably 7.5 to 8.5, and a pK_a value of the second amine group is from about 3.0 to 5.5, preferably 3.5 to 4.7, at a temperature of 20 °C in an aqueous medium.

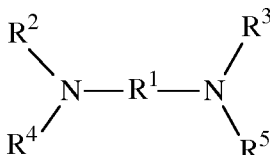
Additionally or alternatively, in the range of from 40% to 97%, preferably of from 50% to 97%, more preferably from 75% to 97% of the amine groups in the regenerated aqueous absorbing medium as obtained in step (iv) is in free base form.

Additionally or alternatively, the regenerable absorbent is a diamine represented by the formula:



wherein R^1 is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, R^2 , R^3 , R^4 , and R^5 may be the same or different and can be hydrogen, alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R^2 , R^3 , R^4 , and R^5 may form cyclic structures.

Additionally or alternatively, the regenerable absorbent is a tertiary amine represented by the formula:



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wherein R¹ is an alkylene of two or three carbon atoms as a straight chain or as a branched chain, and R², R³, R⁴, and R⁵ can be alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R², R³, R⁴, and R⁵ may form cyclic structures.

Additionally or alternatively, the regenerable absorbent is piperazine, hydroxyethyl piperazine, bis-hydroxyethyl piperazine, hydroxyethylethylenediamine (HEED), bis-hydroxyethylethylenediamine (bis-HEED), 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-[2-aminoethyl]pyridine, 2-aminomethylpyridine, 3-amino 5-methylpyrazole, 3-aminopyrazole, 3-methylpyrazole, N,N,N',N'-tetraethyldiethylenetriamine, N,N,N',N'-tetramethyldiethylenetriamine, 2-piperazinone 1,4-bis[2-hydroxyethyl], or a combination thereof.

Additionally or alternatively, the lean absorbing medium additionally comprises an organic acid and/or an inorganic acid, preferably an inorganic acid, more preferably one or more acids chosen from the group of nitric acid (HNO₃), hydrochloric acid (HCl), sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃), even more preferably sulfuric acid (H₂SO₄) and/or sulfurous acid (H₂SO₃).

Additionally or alternatively, the lean absorbing medium additionally comprises a physical solvent, the physical solvent preferably having a vapour pressure less than 0.1 mmHg at 20°C with a boiling point equal to or higher than 240°C, the physical solvent more preferably being a polyol, a polycarbonate, an N-formyl morpholine, or a combination thereof.

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Additionally or alternatively, the physical solvent is polyethyleneglycol dimethylether (PEGDME), tetraethyleneglycol dimethylether (TetraEGDME), tetraethylene glycol (TetraEG), triethyleneglycol monomethylether (TriEGMME), or a combination thereof, preferably polyethyleneglycol dimethylether (PEGDME).

Additionally or alternatively, the physical solvent is polyethyleneglycol dimethylether (PEGDME), and wherein the regenerable absorbent is 4-[hydroxyethyl]piperazine (Hep), or 1,4-bis[hydroxyethyl]piperazine (DiHep), or 3-aminopyrazole, or a mixture of 4-[hydroxyethyl]piperazine (Hep) and 1,4-bis[hydroxyethyl]piperazine (DiHep).

Figure 1

The present invention will be further elucidated with reference to a drawing. Figure 1 shows a schematic diagram of a preferred embodiment of a line-up for a process according to the invention.

A sulfur dioxide comprising feed gas stream (1) is treated in an absorption zone (2). The sulfur dioxide concentration in the feed gas stream (i) preferably is in the range of between 800 ppmv and 45 volume percent, preferably in the range of between 800 ppmv and 11 volume percent. The feed gas stream (1) is contacted with an aqueous lean absorbing medium in absorption zone (2).

SO₂ rich absorbing medium (3) is regenerated in a regeneration zone (4). Use may be made of an optional reboiler (5).

An SO₂ comprising stream is heated and sent to a reflux accumulator (6). An SO₂ product stream (7) is obtained at the top of the reflux accumulator (6). This

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product stream (7) preferably comprises about 99wt% SO₂, calculated on dry product stream.

Optionally heat exchange takes place between SO₂ rich absorbing medium (3) and regenerated aqueous absorbing medium (8). Optionally the regenerated aqueous absorbing medium (8) is heated additionally or alternatively by other means.

A part of the regenerated aqueous absorbing medium (8) is directly recycled to the absorption zone (2) via line (9). A second part of the regenerated aqueous absorbing medium (8) is sent to an amine purification unit (APU) (11) via line (10).

Heat stable salts (HSS) are removed from the regenerated aqueous absorbing medium in APU (11). HSS lean absorbing medium may be sent to the absorption zone (2) via line (12).

HSS lean absorbing medium obtained in the APU (11) is diluted with water. This may be performed at any suitable point before or during its use in secondary absorption zone (15), preferably before its use in secondary absorption zone (15). HSS lean absorbing medium may, for example, be diluted in optional tank (13) to which water may be added (not shown).

Optionally HSS lean absorbing medium is sent to an equalization zone or buffer zone.

Optional tank (13) may serve as equalization zone and may additionally or alternatively be the place at which the HSS lean absorbing medium obtained in the APU (11) is diluted with water.

Diluted HSS lean absorbing medium is contacted with sulfur dioxide lean treated gas (14) in a secondary absorption zone (15). Preferably, sulfur dioxide lean treated gas (14) contains in the range of between 35 and

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250 ppmv SO₂, more preferably in the range of between 50 and 250 ppmv.

Spent or partly spent absorbing medium may be sent to the primary absorption zone (2) via line (17).

5 Alternatively it may be sent to regeneration zone (4); not shown.

Further treated gas (16) leaves from the top of the secondary absorption zone (15). The further treated gas (16) may contain less than 5 ppmv SO₂.

10 EXAMPLES

The invention will now be illustrated by the following examples.

A test was performed using a pilot unit. The pilot unit was equipped with a primary and a secondary
15 absorption zone and a regeneration zone. The process performed using the pilot unit was a process according to the invention.

The pilot unit was also equipped with several gas and liquid sampling points. The sampling points were used to
20 take accurate measurements of the SO₂ concentration in the gas, and to take measurements of the HSS concentration in the liquid samples.

Diluted regenerated aqueous absorbing medium was used in the second regeneration zone. At least a part of the
25 diluted absorbing medium was circulated over this zone. The circulation rate in this loop varied from 1.2 to 6 L/min. This equates to a wetting range of the sulfur dioxide lean treated gas stream obtained in step (i) of 2.3 to 11.5 m³/m² per hour.

30 All tests which were conducted at the same temperature and wetting rate. The SO₂ concentration in the sulfur dioxide lean treated gas stream leaving the first absorption zone (which was treated in the secondary

- 30 -

absorption zone) was varied between 35 ppmv to 250 ppmv, calculated on dry basis.

The test conditions are summarized in Table 1.

5 Table 1: Range of test conditions

Condition	Range	Unit
Feed SO ₂ concentration	35 - 250	ppmv (dry)
Scrubbing pH	6 - 7	
Buffer pH	8.5 - 9.4	
Buffer concentration	13 - 25	wt%
Temperature	40 - 57	°C

Figure 2 shows an aggregated plot of pH and SO₂ emissions from the second absorption zone as determined in the tests.

10 Correlation data were determined; the correlation between 2 variables as defined by:

$$Correl(X,Y) = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

15 where $\bar{x}$ and $\bar{y}$ are averages.

The grouped linear correlation factor is -0.8. This indicates that the pH of the absorbing medium has a strong effect on SO₂ concentration leaving the second absorption zone.

20 The observed trend shows a negative variance between pH and outlet SO₂ concentration indicating that emissions decrease with increasing pH. The observed relationship between pH and emissions may be explained by the chemistry of absorption.

25

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A higher pH signifies a free hydronium leaner environment. Under these conditions SO₂ solubility is promoted. The solubility enhancement of the pH appears to wear off as the pH increases above approximately 6.9-7.

5 Beyond this point, further improvement in chemical enhancement no longer has effect, and SO₂ gas side diffusivity (i.e. increasing gas side resistance) in conjunction with mass transfer mechanics become the predominately limiting factors.

10 These tests demonstrate that fugitive emissions from the second absorption zone can be controlled to concentrations below 5 ppmv on a dry basis.

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C L A I M S

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

(i) contacting the feed gas stream with an aqueous lean absorbing medium in a primary absorption zone to absorb sulfur dioxide and to form a sulfur dioxide lean treated gas stream and a spent absorbing medium;

wherein the aqueous lean absorbing medium comprises:

(a) a chemical solvent comprising a regenerable absorbent which is an amine preferably a mono amine, a diamine, a polyamine, or a mixture thereof, most preferably a diamine;

(b) in the range of between 1 to 1.2 equivalent/amine mole heat stable salts;

wherein the pH of the lean absorbing medium is 6 or less, preferably 5.6 or less, more preferably in the range of from 4.5 to 5.6, even more preferably in the range of from 5.2 to 5.6; and

(ii) stripping, preferably steam stripping, absorbed sulfur dioxide from at least a part of the spent absorbing medium obtained in step (i) in a regeneration zone to produce a regenerated aqueous absorbing medium and sulfur dioxide; and

(iii) recycling a part of the regenerated aqueous absorbing medium obtained in step (ii) to step (i); and
(iv) removing heat stable salts from a second part of the regenerated aqueous absorbing medium obtained in step (ii), preferably by means of an ion exchange resin, electrodialysis, crystallization, or thermal reclamation;

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(v) diluting at least a part of the regenerated aqueous absorbing medium having a reduced heat stable salt content as obtained in step (iv) with water;

(vi) contacting diluted absorbing medium as obtained

5 in step (v) with at least a part of the sulfur dioxide lean treated gas stream obtained in step (i) in a secondary absorption zone to absorb sulfur dioxide and to form a further treated lean gas stream and a spent or partly spent absorbing medium,

10 wherein the diluted absorbing medium comprises:

(a) the chemical solvent comprising a regenerable absorbent;

(b) in the range of between 0.05 to 0.6 equivalent/amine mole heat stable salts;

15 wherein the pH of the diluted absorbing medium is in the range of from 6.5 to 8.0, preferably in the range of from 6.7 to 7.1; and

(vii) recycling at least a portion of the spent or partly spent absorbing medium obtained in step (iv)

20 and/or at least a portion of the spent or partly spent absorbing medium obtained in step (vi) to step (i).

2. The process according to claim 1, wherein the sulfur dioxide concentration in the feed gas stream is in the

25 range of between 800 ppmv and 45 volume percent, preferably in the range of between 800 ppmv and 11 volume percent.

3. The process according to claim 1 or 2, wherein the

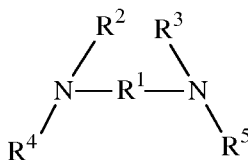
30 aqueous lean absorbing medium used in step (i) comprises in the range of from 10 to 35 wt% amine, preferably 13 to 25 wt% amine, and the diluted absorbing medium used in

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step (vi) comprises in the range of from 0.5 to 9.5 wt% amine.

4. The process according to any one of the above claims,
5 wherein the regenerable absorbent is a diamine or
polyamine with a pKa value of the first amine group, of
from about 7.0 to 9.0, preferably 7.5 to 8.5, and a pKa
value of the second amine group is from about 3.0 to 5.5,
preferably 3.5 to 4.7, at a temperature of 20 °C in an
10 aqueous medium.

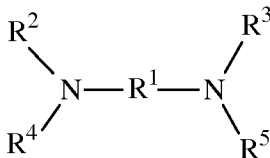
5. The process according to any one of the above claims,
wherein the regenerable absorbent is a diamine
represented by the formula:



15 wherein R¹ is an alkylene of two or three carbon atoms as
a straight chain or as a branched chain, R², R³, R⁴, and
R⁵ may be the same or different and can be hydrogen,
alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any
20 of R², R³, R⁴, and R⁵ may form cyclic structures.

6. The process according to any one of the above claims,
wherein the regenerable absorbent is a tertiary amine
represented by the formula:

25



wherein R¹ is an alkylene of two or three carbon atoms as
a straight chain or as a branched chain, and R², R³, R⁴,

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and R⁵ can be alkyl, hydroxyalkyl, aralkyl, aryl, or alkaryl, and any of R², R³, R⁴, and R⁵ may form cyclic structures.

5 7. The process according to any one of the above claims, wherein the regenerable absorbent is piperazine, hydroxyethyl piperazine, bis-hydroxyethyl piperazine, hydroxyethylethylenediamine (HEED), bis-hydroxyethylethylenediamine (bis-HEED),
10 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-[2-aminoethyl]pyridine, 2-aminomethylpyridine, 3-amino 5-methylpyrazole, 3-aminopyrazole, 3-methylpyrazole, N,N,N',N'-tetraethyldiethylenetriamine,
15 N,N,N',N'-tetramethyldiethylenetriamine, 2-piperazinone 1,4-bis[2-hydroxyethyl], or a combination thereof.

20 8. The process according to any one of the above claims, wherein the lean absorbing medium additionally comprises an organic acid and/or an inorganic acid, preferably an inorganic acid, more preferably one or more acids chosen from the group of nitric acid (HNO₃), hydrochloric acid (HCl), sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃),
25 even more preferably sulfuric acid (H₂SO₄) and/or sulfurous acid (H₂SO₃).

30 9. The method according to any one of the above claims, wherein the lean absorbing medium additionally comprises a physical solvent, the physical solvent preferably having a vapour pressure less than 0.1 mmHg at 20°C with a boiling point equal to or higher than 240°C, the physical solvent more preferably being a polyol, a

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polycarbonate, an N-formyl morpholine, or a combination thereof.

10. The process according to claim 9, wherein the
5 physical solvent is polyethyleneglycol dimethylether
(PEGDME), and
wherein the regenerable absorbent is
4-[hydroxyethyl]piperazine (Hep), or
1,4-bis[hydroxyethyl]piperazine (DiHep), or
10 3-aminopyrazole, or
a mixture of 4-[hydroxyethyl]piperazine (Hep) and
1,4-bis[hydroxyethyl]piperazine (DiHep).

Fig.1

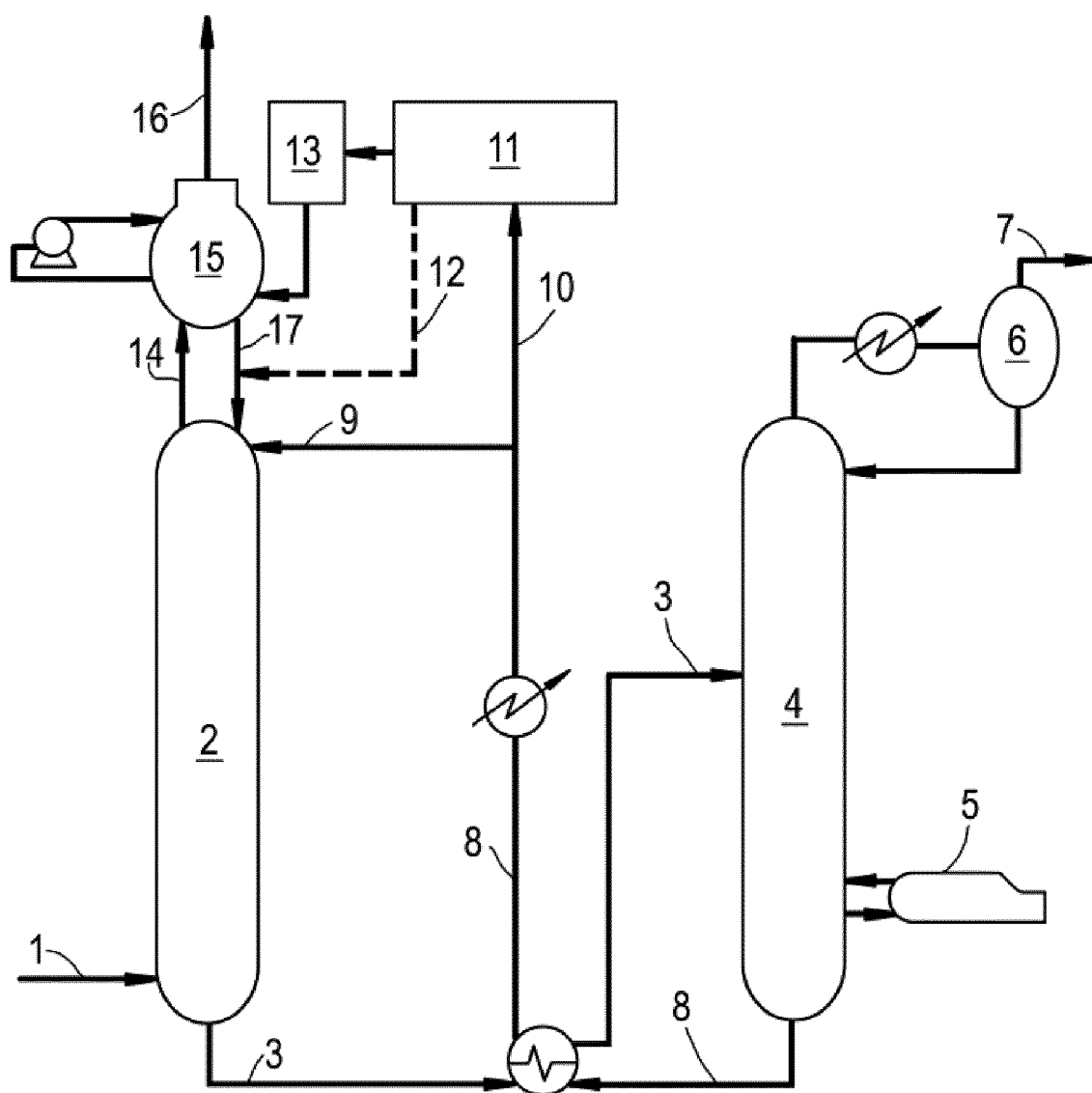
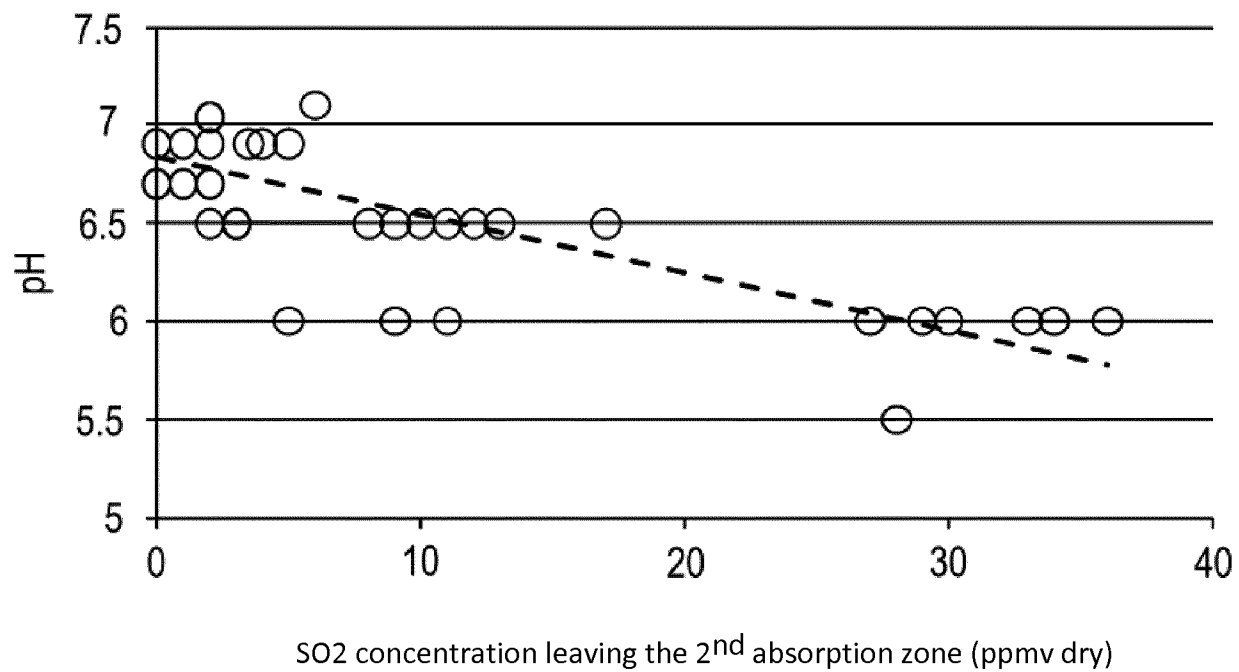


Fig.2

pH versus outlet SO₂ concentration exiting the second absorption zone

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/077542

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/50 B01D53/14
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

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Y	abstract; figure 2 paragraphs [0098] - [0109] -----	8-10
Y	WO 2015/066807 A1 (CANSOLV TECHNOLOGIES INC [CA]) 14 May 2015 (2015-05-14)	8-10
A	page 13, line 17 - page 14, line 30 -----	1-7
A	US 2006/286017 A1 (HAKKA LEO E [CA]) 21 December 2006 (2006-12-21) paragraphs [0058], [0060], [0070], [0071], [0077]; figure 1 -----	1-10
A	WO 2013/128001 A1 (BASF SE [DE]; RES TRIANGLE INST [US]) 6 September 2013 (2013-09-06) abstract; figure 12 ----- -/-	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

4 December 2017

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/077542

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 970 344 A (KELLER ALFRED E [US]) 13 November 1990 (1990-11-13) abstract -----	1

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Information on patent family members

International application No

PCT/EP2017/077542

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