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(54) Title: METHOD AND APPARATUS FOR PURIFICATION OF NATURAL GAS

(57) Abstract: The invention is directed to a method for absorbing CO₂ and H₂S from a methane comprising gas stream by contacting said stream with a liquid solution that comprises a physical solvent, a non-chelating amine, a metal, a chelating ligand and a stabilizer.



Title: Method and apparatus for purification of natural gas

The invention is in the field of natural gas purification. In particular the invention is directed to a method for absorption of CO₂ and H₂S from natural gas.

Natural gas is formed over a period of thousands of years by a natural process of pressurizing and heating underground layers of plants. Natural gas can be extracted from so called gas fields and can be used for a variety of purposes. Typically, it is used as a fossil energy source in for example vehicles or electricity generators. Prior to its use in such applications, it needs to be purified from contaminants such as CO₂, H₂S, COS, CS₂ and nitrogen-containing gases such as HCN and NH₃ to improve performance and avoid deposition of the contaminant on machine parts.

The composition and pressure of methane comprising natural gas is amongst others dependent on the gas field it originates from. Pressures are typically 80-200 bar and although methane is the major component, partial pressures of CO₂ up to 50 bar and H₂S up to 30 bar can be found. Hence, effective CO₂ and H₂S removal from natural gas is of key importance prior to its use.

The CO₂ and H₂S can be removed by a variety of processes, of which most concern multiple-step processes.

For instance, methane comprising gas streams contaminated with CO₂ and H₂S can be washed under high pressure by liquids comprising physical solvents. Due to a difference in solubility between methane and CO₂ and H₂S, the contaminants (*i.e.* CO₂ and H₂S) are selectively absorbed. The physical solvents can be regenerated by reducing the pressure to liberate the CO₂ and H₂S. However, H₂S can not be emitted into air and has to be treated separately in for instance a Claus process. In such a process, H₂S is converted into elementary sulfur. A major drawback of this method is the high investment and maintenance costs of Claus plants. A second

drawback is the limited absorption capacity of the physical solvent, especially under lower partial pressure of the contaminants, that consequently leads to a remaining CO₂ and H₂S in the purified gas stream.

Higher absorption efficiencies may be achieved by chemical
5 absorption whereby a non-chelating amine comprising liquid solution absorbs CO₂ and H₂S by a chemical reaction. However, also in these types of processes, H₂S has to be treated separately. Moreover, the required high amounts of water and loss of amine due to evaporation increases the environmental impacts.

10 In some multiple-step processes, as for instance taught by WO-A-2010/112500, the natural gas stream is purified by subsequent absorption steps. For instance, first H₂S is converted to elementary sulfur by a redox reaction with Fe³⁺EDTA and subsequently in a second step, CO₂ is physically or chemically absorbed.

15 In conclusion, most of the current purification technologies rely on multiple steps to remove both CO₂ and H₂S from methane comprising natural gas streams.

US-A-4400368 and US-A-4091073 both describe removing H₂S and CO₂ from methane comprising gas streams in a single procedure by
20 contacting the gas with a liquid solution comprising a metal, a chelating ligand, a stabilizer as well as an absorbent for CO₂. The absorbents are physical absorbents for CO₂ and therefore less effective at absorbing CO₂ at low (partial) pressures. It is desirable that the absorption of CO₂ is more effective at these low (partial) pressures.

25 It is an object of the present invention to provide a more effective and efficient purification process for natural gas that will require lower investment and lower maintenance costs. This is achieved by combining the absorption of CO₂ and H₂S as well as the conversion of H₂S in one single process with one liquid solution that comprises a non-chelating amine, a
30 metal and a chelating ligand and a physical solvent. Thus the present

invention is directed to a method for absorbing CO₂ and H₂S from a methane comprising gas stream by contacting said stream with a liquid solution that comprises a physical solvent, a non-chelating amine, a metal, a chelating ligand and a stabilizer. The liquid solution may be referred to as a lean liquid solution prior to absorption and as an enriched liquid solution
5 after absorption of CO₂ and H₂S.

The present invention is based on three absorption principles: physical absorption of CO₂ by a physical solvent, chemical absorption of CO₂ by a non-chelating amine and absorption of H₂S by converting this into elementary sulfur. These three absorption principles occur in one process
10 and in one liquid solution.

Figure 1 is a diagram showing the relation between CO₂ partial pressure and the concentration of CO₂ absorbed in a solvent.

Figure 2 is a schematic representation of an apparatus in
15 accordance with the present invention.

Figure 3 is a schematic representation of another embodiment of an apparatus in accordance with the present invention.

Figure 4 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

20 Figure 5 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

Figure 6 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

25 Figure 7 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

Figure 8 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

Figure 9 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

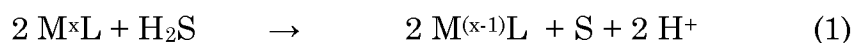
Figure 10 is a schematic representation of yet another embodiment of an apparatus in accordance with the present invention.

Although the invention aims at the purification of natural gas, it will be appreciated that the invention is also applicable for any other methane comprising gas stream at elevated pressures. For example, the gas stream may have an elevated pressure of 30 to 200 bar, preferably 50 to 120 bar, more preferably 60 to 100 bar.

In the present invention, H₂S is absorbed in the liquid solution by a redox reaction with a metal (M^x). A chelating ligand (L) is present to solubilize the metal.

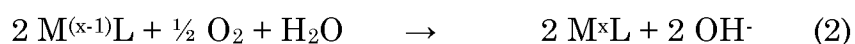
With a chelating ligand is meant a ligand that comprises three or more, typically 4 to 8, functional groups that may simultaneously bind to the metal of the present invention. With a non-chelating amine is meant an amine that comprises two or less functional groups that may simultaneously bind to the metal of the present invention. Typical functional groups in this respect are amines, carboxylic acids, hydroxides, sulfides, phosphines and the like.

The metal and chelating ligand form a metal chelate complex (M^xL) that reacts with the H₂S in the gas stream, typically according to the following reaction scheme:



in which the metal chelate complex is reduced to form M^(x-1)L and elementary sulfur S, which precipitates. Depending on the metal used, the oxidation state of M^x can be decreased by more than one as well, *e.g.* to form M^(x-2)L, *etc.* The elementary sulfur is accordingly separated from the gas stream and can be separated from the liquid solution by a liquid-solid separator. Thus no separate step is needed to convert H₂S.

For an economically feasible process, the metal chelate is preferably regenerated. The regeneration limits the required amount of metal. In the regeneration step, M^xL is regained by a reaction of $M^{(x-1)}L$ with an oxygen containing gas, preferably air, according to the following reaction scheme:



In the present invention, CO_2 is absorbed in a liquid solution via two complementary absorption principles: physical and chemical absorption.

Physical absorption is based on the absorption of CO_2 in a physical solvent and is governed by Henry's law that describes a linear relation between the partial pressure of the gas and the amount of gas that is absorbed in the physical solvent. As a consequence, at high partial pressure, much gas is absorbed in the physical solvent. However, as the partial pressure decreases during the absorption step as a consequence of it being absorbed in the physical solvent, the amount of CO_2 that is absorbed from the gas stream at the end stage of the absorption step will be lower. Therefore, at the end of the process, some CO_2 typically remains in the gas stream. Although further removal of CO_2 may be possible, this is typically not desirable, because such removal would cost large amounts of physical solvent, which may be both economically and ecologically undesirable.

Chemical absorption is based on the reaction between the chemical solvent and CO_2 . Typically, the chemical solvent is a non-chelating amine. Chemical absorption is not governed by Henry's law nor is there a linear relation between partial pressure and absorbed gas concentration. Instead, it is characterized by a very high absorption at low partial pressure and by a saturation of the chemical solvent at high pressure.

As a consequence of the above-described phenomena, below a certain partial CO_2 pressure P , chemical absorption is more effective for

absorbing CO₂ and above this pressure P , physical absorption is more effective (see figure 1).

The present invention exploits both principles to increase the overall effectiveness of CO₂ absorption by combining a physical solvent and
 5 a non-chelating amine in a single liquid solution. Hence, the majority of CO₂ is absorbed by physical absorption, without saturating the non-chelating amine, while at the end stage of the absorption process when partial CO₂ pressure is low, the remaining CO₂ is absorbed by the non-chelating amine.

The chemical absorption of CO₂ by the chemical solvent is
 10 preferably effected by a non-chelating amine that is present in the liquid solution.

In the case non-hindered primary and secondary amines are used, the reaction of the CO₂ in the gas stream with the non-chelating amine in the liquid solution typically proceeds according to the following reaction
 15 scheme:



in which half of the non-chelating amine reacts with CO₂ to form carbamate
 20 anion. The carbamate ion formed can undergo hydrolysis to form hydrogen carbonate and amine according to:



25 In the case of tertiary amines or hindered primary or secondary amines are used, the reaction typically proceeds according to:



in which the CO₂ is hydrolyzed towards carbonic acid. Carbonic acid is neutralized with the non-chelating amine, leading to protonated amine and bicarbonate.

The reaction products remain dissolved in the liquid solution and
5 a CO₂-rich solution is obtained.

It is known from the prior art (see *e.g.* GB-A-999,799, incorporated herein by reference), that for a method wherein H₂S is absorbed from a gas stream by a reaction with metal chelates, there is an optimum pH for any given chelating agent. This optimum pH lies typically
10 between 2.5 and 9. At low pH, the metal chelate shows no reactivity. At high pH, the bond between the metal and the chelate ligand is weakened, resulting in the precipitation of ferric oxide and thus loss of metal from the process.

It is also known from the prior art, that for a method wherein CO₂
15 is absorbed from a gas stream by a reaction with amine, there is an optimum pH, which is typically in the range of 9-11.

Furthermore, it is known in the art that dissolving a high amount of CO₂ in a solvent, the pH decreases. It will therefore be appreciated that in the present invention, the physical solvent stabilizes the pH and avoids a
20 large decrease when large amounts of CO₂ are absorbed.

Using the present invention, it is possible, by careful selection of the parameters that govern the absorption process, *i.e.* selection of the physical solvent, selection of the non-chelating amine and its concentration, the metal chelate, pH of the liquid solution and the temperature to combine
25 both H₂S and CO₂ absorption and the subsequent conversion of H₂S to elementary sulfur.

The metal can be any metal or mixture thereof capable of oxidizing H₂S.

The metal can be added to the process in a reactive form, *i.e.*
30 being capable of oxidizing H₂S, or in an preliminary unreactive form.

Moreover, it can be added as a complex with the chelating agents or as a salt with another counter ion. Furthermore, it can be added as a charged or as an uncharged compound. In a particular embodiment, the metal first has to be activated before it can oxidize H_2S .

5 In a preferred embodiment of the present invention, the metal is a cation selected from the group consisting of Fe, V, Cu, Zn, Mn, Mg and combinations thereof. Depending on the metal chosen, different oxidation states can be used, *e.g.* Fe^{2+}/Fe^{3+} or V^{4+}/V^{5+} .

 According to the present invention, a chelating ligand is defined
10 as an organic compound containing more than one functional groups that are capable of forming a bond with the metal in such a way that more than one coordination bonds are formed between the said organic compound and the metal.

 In a preferred embodiment, the chelating ligand contains one or
15 more amine groups and one or more oxygen-containing groups such as alcohols and carboxylic acids.

 The chelating ligand can be added as purely organic compound or as a salt thereof. Moreover, it can be added as a complex formed with the metal.

20 In a preferred embodiment, the chelating ligand is selected from the group consisting of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), (hydroxyethyl)ethylenediamine triacetic acid (HEDTA), pentetic acid (DTPA), triethanolamine (TEA), 1,2-cyclohexylenedinitrilotetraacetic acid (CyDTA), N-methyliminodiacetic acid
25 (MIDA), 1,3-propanediaminetetraacetic acid (PDTA), 1,4-butanediaminetetraacetate (BDTA), etidronic acid (HEDP), and combinations thereof.

 Degradation of the chelating ligand can occur due to reaction with oxygen during the regeneration. Hence, to avoid degradation of the
30 chelating ligand by oxidation in the regeneration, in a preferred

embodiment a stabilizer is present. Preferably the stabilizer is a radical scavenger. Such a radical scavenger is typically capable of reacting with and de-activating radicals. In a more preferred embodiment the stabilizer is selected from the group consisting of thiodiglycolic acid, 3,3-thiodipropionic acid, sodium thiocyanate, sodium dithionite, ammonium thiosulfate, sodium thiosulfate, N,N-diethylhydroxylamine, thiourea, thiosemicarbazide, bisulphite, sodium benzoate, para-toluenesulfonic acid, potassium iodide, potassium bromide, potassium chloride, 2-propanol, 1-butanol, ethylene glycol, sodium formate, sucrose, sorbitol, nitrites, amino acids, aliphatic aldehydes, aryl sulfonic acids and combinations thereof.

It has been found that amines can be lost from the process by evaporation. Therefore, amines with low or no vapor pressures are preferred, *e.g.* vapor pressures lower than 900 Pa at 25°C, preferably lower than 150 Pa at 25°C. Furthermore, amines can be lost by oxidation during the regeneration of the metal. Loss of amines should be avoided. Therefore, in a preferred embodiment of the present invention, the non-chelating amine is added as a salt thereof.

The non-chelating amine salt is preferably a salt with potassium or sodium, potassium being preferred.

The non-chelating amine is preferably an amino acid. Herein amino acid is defined as an organic compound which comprises at least one amine group and at least one acid group selected from carboxylic acid, phosphoric acid and sulfonic acid. The acid groups can be bound to one and the same atom of the organic substance (as is the case with the natural occurring amino acids) or to different atoms.

More preferably, the amino acid is selected from a group consisting of taurine, glycine, alanine, asparagine, glutamine, lysine, histidine and derivatives of these such as N-methylglycine, N-methylalanine and combinations thereof.

Alternatively, the non-chelating amine is an amine other than an amino acid. Such a non-chelating amine may be a monoamine or polyamine and is preferably selected from the group consisting of the monoamines monoethanolamine (MEA) and 2 piperidine ethanol (PE), and the
5 polyamines piperazine and aminoethylpiperazine (AEP), and combinations thereof.

In a preferred embodiment the non-chelating amine is regenerated by heating the liquid solution containing CO₂. Such a heating step is preferably conducted after regenerating the metal by oxidation.
10 Optionally, the pressure of the liquid solution may be reduced before this heating.

In the present invention, the physical solvent can be any solvent capable of absorbing CO₂.

In a preferred embodiment, the physical solvent is selected from
15 the group consisting of H₂O, MeOH, polyethylene glycol, propylene carbonate, dimethyl carbonate (DMC), N-methyl-2-pyrrolidone, N-formyl morpholine, methyl cyanoacetate, polypropyleneglycol dimethylether (PPGDME), polydimethylsiloxane (PDMS), perfluoropolyether (PFPE), and mixtures thereof.

20 In a preferred embodiment of the present invention, the lean liquid solution (*i.e.* the liquid solution prior to the absorption of CO₂ and H₂S) has a pH of 7-13, preferably a pH of 8-12, more preferably a pH of 9-11.

In a preferred embodiment of the present invention, the absorption temperature, *i.e.* the temperature whereby the absorption is
25 taking place, is between 20 and 60 °C.

In a preferred embodiment of the present invention, the content of the non-chelating amine in the lean liquid solution may be less than 30 wt%, preferably less than 20 wt%, most preferably less than 10 wt%, based on the total weight of the liquid solution. After absorption, one or more
30 further steps may be conducted to regenerate the liquid solution.

Accordingly, the method of the invention may comprise the further step of removing gas from the liquid solution, such as CO₂ and/or methane. Such release may be achieved by decreasing the pressure above the liquid solution. This step can be suitably conducted in one or more flash
5 vessels.

The method may further comprise the step of sulfur removal from the liquid solution, *e.g.* using a plate settler.

The method of the invention may further comprise a metal regeneration step by introducing an oxygen containing gas such as air in the
10 solution, as already described above.

Further, a stripper may be used to remove CO₂ from the non-chelating amine and/or further remove CO₂ from the physical solvent.

The present invention allows for a simplified natural gas purifying apparatus, *viz.* only one absorption column is required for the
15 absorption of both CO₂ and H₂S from the gas stream.

Such an apparatus (see figure 2) comprises an absorption column. The absorption column comprises a first inlet (1), preferably located at the bottom part of the absorption column, through which the gas stream may be introduced and it comprises a second inlet (2), preferably located at the top
20 part of the absorption column, through which the liquid solution may be introduced. It furthermore contains a volume (3) where said gas stream contacts the lean liquid solution. The absorption column furthermore comprises a first outlet (4), preferably located at the top part of the absorption column, through which the purified (or upgraded) gas stream, *i.e.*
25 a gas stream containing less CO₂ and H₂S compared to the gas stream that was introduced into the absorption column, may leave and it comprises a second outlet (5), preferably located at the bottom part of the absorption column through which the enriched liquid solution may leave.

The apparatus may further comprise one or more flash vessels (in order to deal with the elevated pressure of the gas to be used), which are typically connected in series with the absorption vessel.

The apparatus may further comprise a gas injection vessel such
5 as a flotation vessel, a flocculation vessel or a bubble column (for regeneration of the metal), a liquid-solid separator such as a plate settler (for sulfur removal) and a stripper (for CO₂ removal). Typically, the absorption column is connected to the one or more flash vessels, the last flash vessel is connected to the gas injection vessel, the gas injection vessel
10 is connected to the liquid-solid separator and the liquid-solid separator is connected to the stripper. In this configuration, the gas injection vessel is preferably a flocculation vessel to enhance sulfur removal. Depending on the extent of sulfur precipitation, the liquid-solid separator may also change places with the gas injection vessel (such that the liquid-solid separator will
15 be connected to the absorption column and the gas injection vessel will be connected to the stripper).

Below, a number of embodiments of the apparatus is described in order to illustrate in more detail how the different parts of the apparatus may be connected.

20 In a preferred embodiment of the apparatus (see figure 3) said second outlet (5), is connected to a first flash vessel, wherein the pressure of the enriched liquid solution may be reduced. The flash vessel comprises an inlet (6), through which the enriched liquid solution may be introduced. It furthermore comprises a first outlet (7), preferably located at the bottom,
25 through which the enriched liquid solution at a reduced pressure may leave and a second outlet, preferably located at the top, through which vapor and gases such as methane and CO₂ may leave.

In a more preferred embodiment of the apparatus (see figure 4), said first outlet (7), is further connected to a liquid-solid separator (*e.g.* a
30 plate settler), where the sulfur is removed from the liquid solution. The

liquid-solid separator comprises a first inlet (8) through which the liquid solution rich in CO₂ and sulfur may be introduced. It furthermore comprises a first outlet (9) through which the sulfur may leave and it comprises a second outlet (10) through which the liquid solution rich in CO₂ may leave.

5 In a more preferred embodiment of the apparatus (see figure 5), said second outlet (10) is further connected to a gas injection vessel which acts as a regenerator of the reduced metal complex M^(x-1)L. A gas injection vessel is a vessel that is suitable for injecting a gas such as oxygen into the vessel, *e.g.* a flotation vessel or bubble column. Said gas injection vessel
10 comprises a first inlet (11), preferably located at the top part of the gas injection vessel, through which the liquid solution rich in reduced metal may be introduced. It furthermore comprises a second inlet (12), preferably located at the bottom part, through which oxygen, preferably oxygen in air may be introduced. It furthermore comprises a volume of oxidation (15)
15 wherein said oxygen may contact said liquid solution rich in reduced metal. Moreover, said gas injection vessel comprises a first outlet (13), preferably located at the top part through which unreacted oxygen, preferably unreacted oxygen in air may leave and a second outlet (14), preferably located at the bottom through which said liquid solution rich in CO₂ and the
20 oxidized metal (*i.e.* regenerated metal) may leave. In a variant of this embodiment, the liquid-solid separator and the gas injection vessel have changed places, such that the gas injection vessel is placed between and connected to the (last) flash vessel and the liquid-solid separator (see figure 9).

25 In a more preferred embodiment (see figure 6), said second outlet (14) of the gas injection vessel is connected to a stripper by a first inlet (16) of said stripper, preferably located at the top part, through which the liquid solution rich in CO₂, an oxidized metal, a non-chelating amine, a chelating ligand and a stabilizer may be introduced. The stripper furthermore
30 comprises a volume (17) wherein said liquid solution rich in CO₂ is heated.

As a consequence the CO₂ leaves the liquid solution. Moreover said stripper comprises a first outlet (18), preferably located at the top part through which CO₂ may leave and a second outlet (19), preferably located at the bottom through which said liquid solution stripped of CO₂ may leave. In a
5 variant of this embodiment, the liquid-solid separator and the gas injection vessel have changed places (such that the gas injection vessel is placed between and connected to the (last) flash vessel and the liquid-solid separator) and the stripper will be connected to the liquid-solid separator (see figure 9).

10 In a most preferred embodiment (see figure 7) said second outlet (19) of the stripper is connected to said second inlet (2) of said absorption column in such a way that the apparatus allows for a continuous absorption and regeneration process.

In an optional embodiment of the apparatus (see figure 8), there is
15 a second flash vessel, connected in series to the first flash vessel to further reduce the pressure of the enriched solution. The second flash vessel comprises an inlet (20), through which the enriched liquid solution may be introduced. It furthermore comprises a first outlet (21), preferably located at the bottom, through which the enriched liquid solution at a reduced
20 pressure may leave and a second outlet (22), preferably located at the top, through which vapor and gases such as methane and CO₂ may leave. In such an embodiment, said first outlet (21) is then connected to the liquid-solid separator via its inlet (8).

In yet another optional embodiment (see figure 9), the metal may
25 be regenerated before the sulfur is separated from the enriched liquid solution. In such an embodiment, the outlet (7) of the first flash vessel, or optionally the outlet (21) of the second flash vessel, is connected to the gas injection vessel via its inlet (11). The second outlet of the gas injection vessel is then connected to the liquid-solid separator via its inlet (8) and the second

outlet (10) of the liquid-solid separator is then connected to the stripper via its inlet (16).

For reason of a difference in the reaction kinetics of the reaction of the metal chelate with the H_2S compared to the absorption of the CO_2 , in a preferred embodiment the apparatus comprises an absorption column that is divided into two sections or two columns. Typically, the first section or column comprises the first inlet (1; for gas to enter) and second outlet (5; for liquid to leave), while the second section or column comprises the second inlet (2; for liquid to enter) and first outlet (4; for gas to leave). The two sections or columns are connected via an outlet (23) (typically located at the top of the first section or column) and an inlet (24) (typically located at the bottom of the second column or section) through which the methane comprising gas stripped from H_2S may pass. After treatment of the gas in the first section or column, all H_2S may already have been removed and converted to sulfur (due to the fast kinetics), such that the second section or column is effectively only used to remove CO_2 . Accordingly, only part of the liquid solution has to be subjected to the solid-liquid separator and metal regeneration. The apparatus in this embodiment may thus comprise a first section or column which comprises a volume (3a) where the H_2S may be absorbed and part of the CO_2 may be absorbed and a second section or column which comprises a volume (3b) where the remaining part of the CO_2 may be absorbed.

More specifically, the absorption column may comprise a third outlet (25) located at the bottom part of the second section or column and a third inlet (26) located at the top part of the first section or column. The third outlet (25) is connected to the third inlet (26) and to an inlet (27) of an additional flash vessel, which flash vessel is connected through its outlet (28) to the inlet (16) of the stripper. Thus, part of the liquid solution rich in CO_2 may go to the second section or column via the third inlet (26) and another part of the liquid solution rich in CO_2 may go to the additional flash

vessel via its inlet (27). The additional flash vessel may furthermore comprise a second outlet (29) through which vapor and gases such as methane and CO₂ may leave.

For the purpose of clarity and a concise description, features are
5 described herein as part of the same or separate embodiments. However, it
will be appreciated that the scope of the invention may include
embodiments having combinations of all or some of the features described.

Claims

1. A method for absorbing CO₂ and H₂S from a methane comprising gas stream by contacting said stream with a liquid solution that comprises a physical solvent, a non-chelating amine, a metal, a chelating ligand and a stabilizer.
- 5 2. A method according to claim 1 wherein said gas stream comprises natural gas and wherein said gas stream has a pressure of 30-200 bar, preferably 50 to 120 bar, more preferably 60 to 100 bar.
3. A method according to any of the previous claims, further comprising a metal regeneration step, wherein said metal is oxidized,
10 preferably using oxygen, more preferably oxygen from air.
4. A method according to any of the previous claims, further comprising a non-chelating amine regeneration step by heating the solution.
5. A method according to any of the previous claims, further comprising a step wherein the CO₂ is liberated from the physical solvent by
15 decreasing the pressure above said liquid solution, which step is preferably conducted prior to the non-chelating amine regeneration step.
6. A method according to any of the previous claims, wherein the physical solvent is selected from the group consisting of H₂O, MeOH, polyethylene glycol, propylene carbonate, dimethyl carbonate (DMC), N-methyl-2-pyrrolidone, N-formyl morpholine, methyl cyanoacetate,
20 polypropyleneglycol dimethylether (PPGDME), polydimethylsiloxane (PDMS), perfluoropolyether (PFPE), and mixtures thereof.
7. A method according to any of the previous claims, wherein the non-chelating amine is an amino acid or salt thereof, wherein the amino
25 acid is preferably selected from the group consisting of taurine, glycine, alanine, asparagine, glutamine, lysine, histidine, derivatives of these such as N-methylglycine, and N-methylalanine, and combinations thereof; and

wherein the non-chelating amine is preferably a sodium or potassium salt of said amino acid, more preferably a potassium salt.

8. A method according to any of the previous claims, wherein the non-chelating amine is a non-chelating amine other than an amino acid,

5 preferably selected from the group consisting of monoamines such as monoethanolamine (MEA), 2 piperidine ethanol (PE), and polyamines such as piperazine, aminoethylpiperazine (AEP), and combinations thereof.

9. A method according to any of the previous claims, wherein the metal is a cation selected from the group consisting of Fe, V, Cu, Zn, Mn, Mg
10 and combinations thereof, preferably Fe^{3+} or V^{5+} and combinations thereof.

10. A method according to any of the previous claims, wherein the chelating ligand is selected from the group consisting of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), hydroxyethyl ethylenediamine triacetic acid (HEDTA), pentetic acid (DTPA),

15 triethanolamine (TEA), 1,2-cyclohexylenedinitrilotetraacetic acid (CyDTA), N-methyliminodiacetic acid (MIDA), 1,3-propanediaminetetraacetic acid (PDTA), 1,4-butanediaminetetraacetate (BDTA), etidronic acid (HEDP), and combinations thereof.

11. A method according to any of the previous claims wherein the
20 stabilizer is selected from the group consisting of thiodiglycolic acid, 3,3-thiodipropionic acid, sodium thiocyanate, sodium dithionite, ammonium thiosulfate, sodium thiosulfate, N,N-diethylhydroxylamine, thiourea, thiosemicarbazide, bisulphite, sodium benzoate, para-toluenesulfonic acid, potassium iodide, potassium bromide, potassium chloride, 2-propanol, 1-
25 butanol, ethylene glycol, sodium formate, sucrose, sorbitol, nitrites, amino acids, aliphatic aldehydes, aryl sulfonic acids and combinations thereof.

12. A method according to any of the previous claims, wherein the liquid solution has a pH of 7-13, preferably a pH of 8-12, more preferably a pH of 9-11.

13. A method according to any of the previous claims, wherein said absorption is carried out at a temperature of between 20 and 60 °C.

14. An apparatus for purifying a gas stream comprising an absorption column comprising:

- 5 - a first inlet (1), preferably located at the bottom part, through which said gas stream may be introduced;
 - a second inlet (2), preferably located at the top part, through which a liquid solution comprising a physical solvent, a non-chelating amine, a metal, a chelating ligand and a stabilizer may be introduced;
 - 10 - a volume of contact (3) wherein said gas stream may be contacted with said liquid solution;
 - a first outlet (4), preferably located at the top part, through which said gas stream containing less CO₂ and H₂S than upon introduction may leave;
 - 15 - a second outlet (5), preferably located at the bottom part, through which said liquid solution containing more CO₂ and sulfur than upon introduction and containing a reduced metal may leave.
15. An apparatus according to claim 14, further comprising
- one or more flash vessels connected to the absorption column;
 - 20 - a liquid-solid separator and a gas injection vessel, which are connected to each other, and wherein either the liquid-solid separator or the gas injection vessel is connected to the one or more flash vessels; and
 - a stripper connected to either the liquid-solid separator or the gas injection vessel, whichever of the two is not connected to the one or more
 - 25 flash vessels.

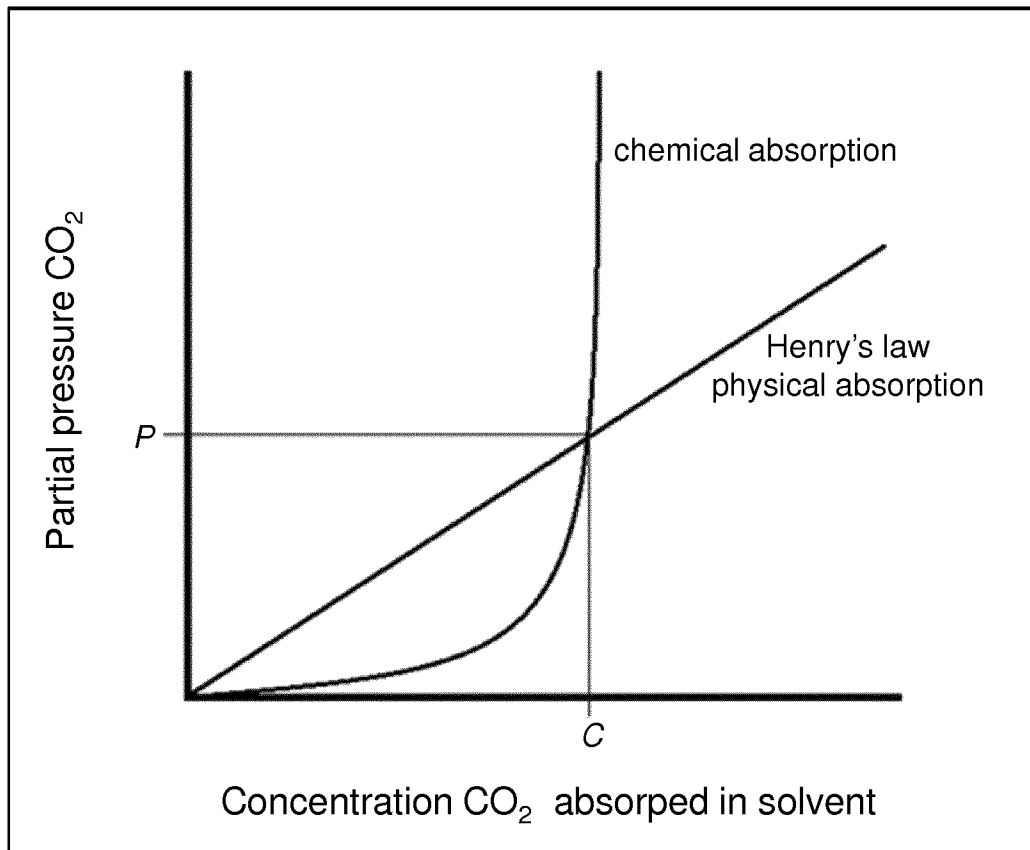


FIG. 1

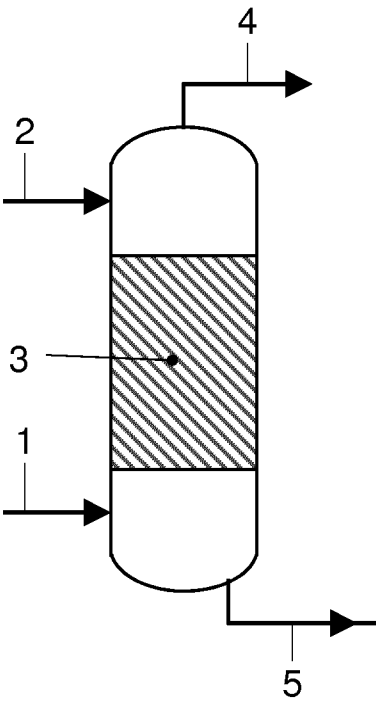


FIG. 2

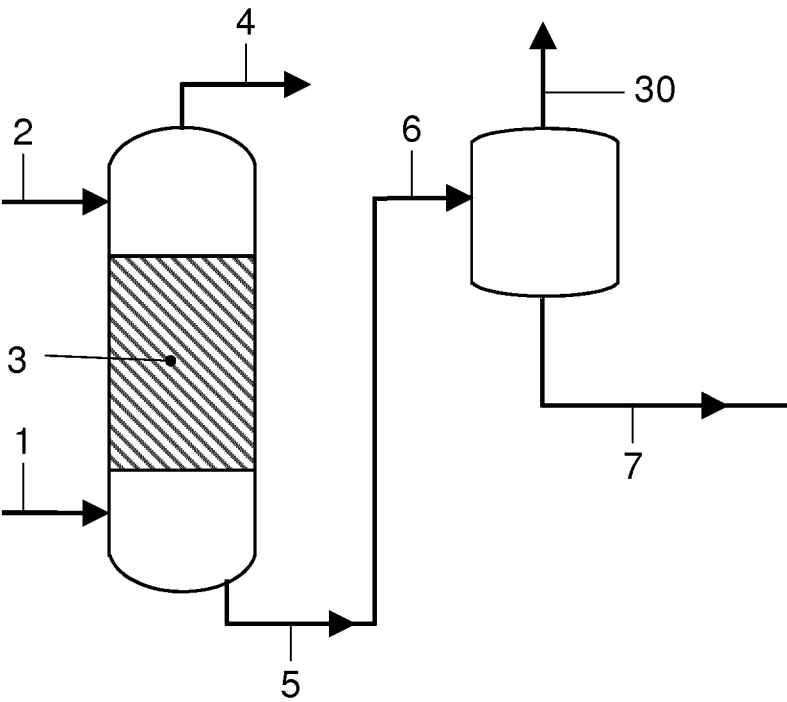


FIG. 3

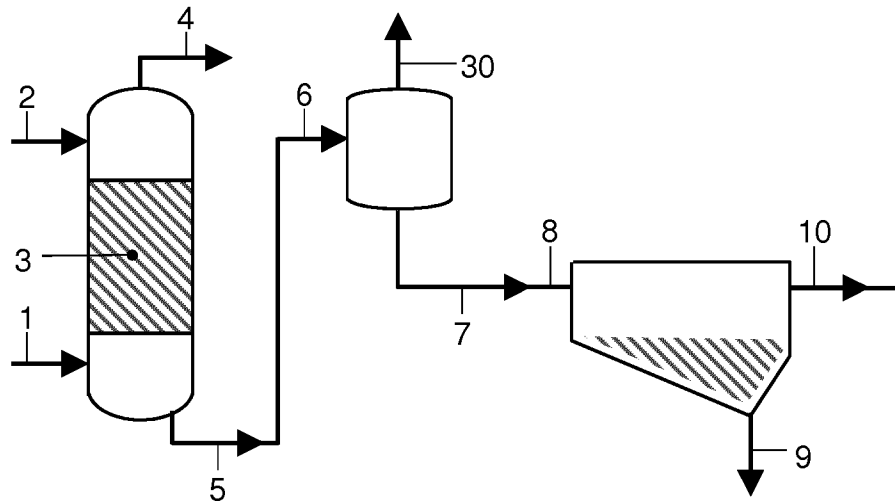


FIG. 4

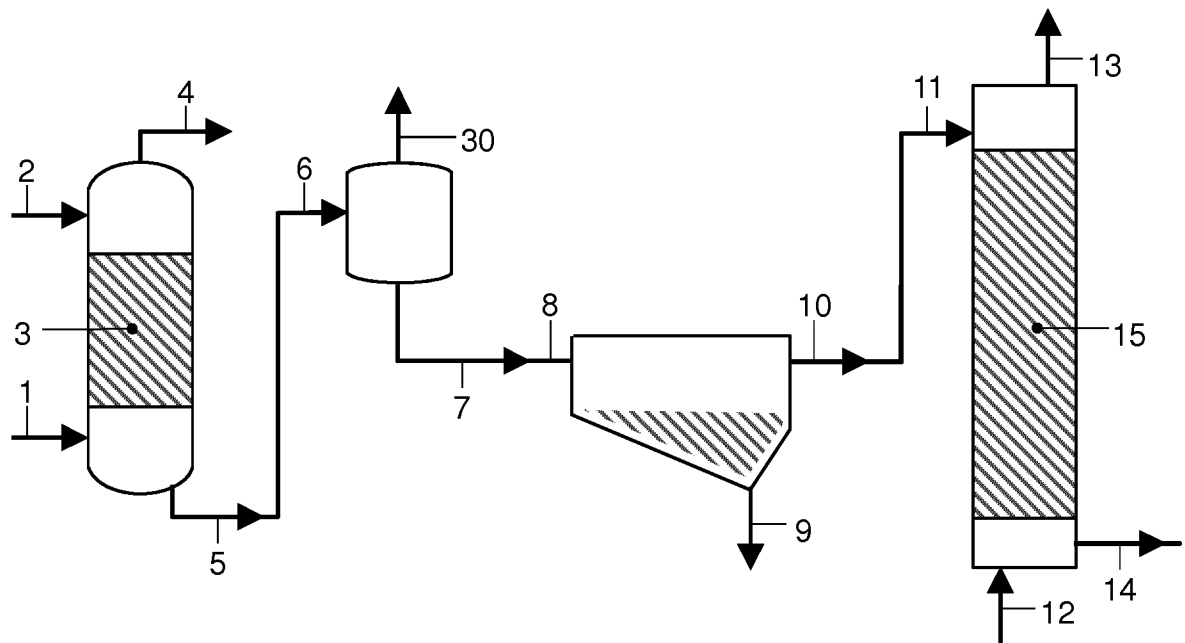


FIG. 5

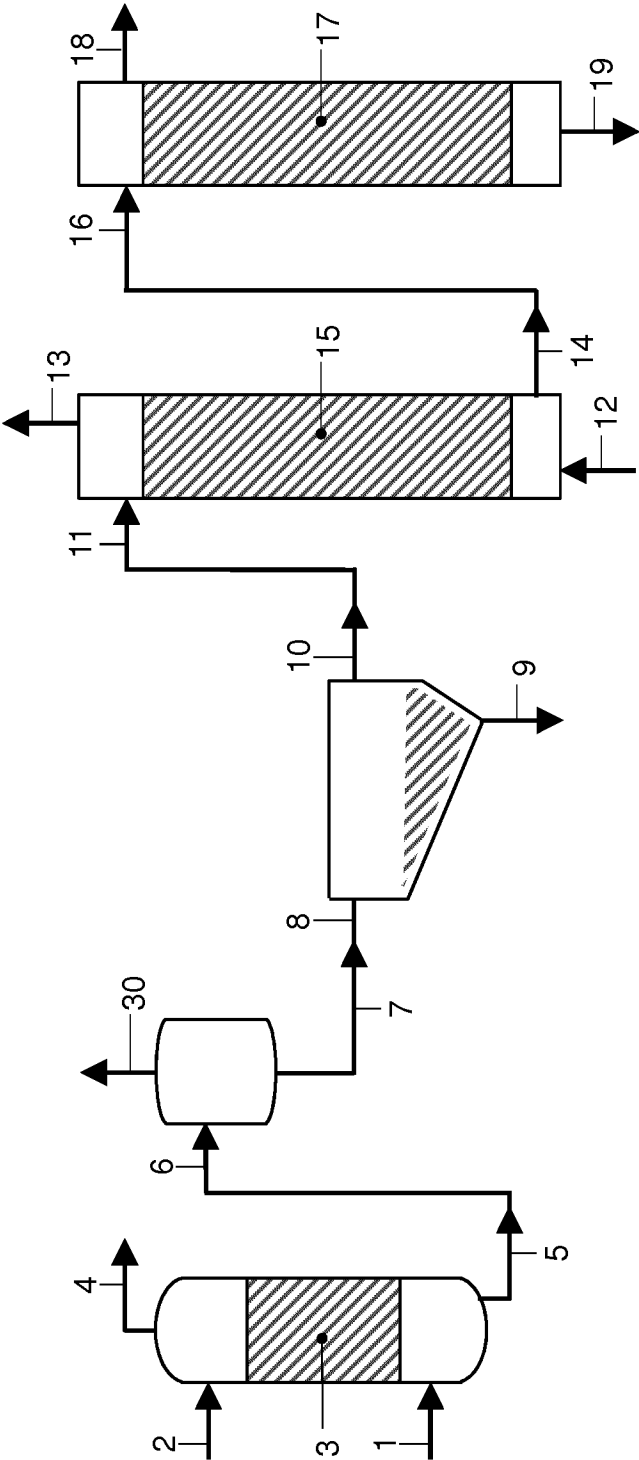


FIG. 6

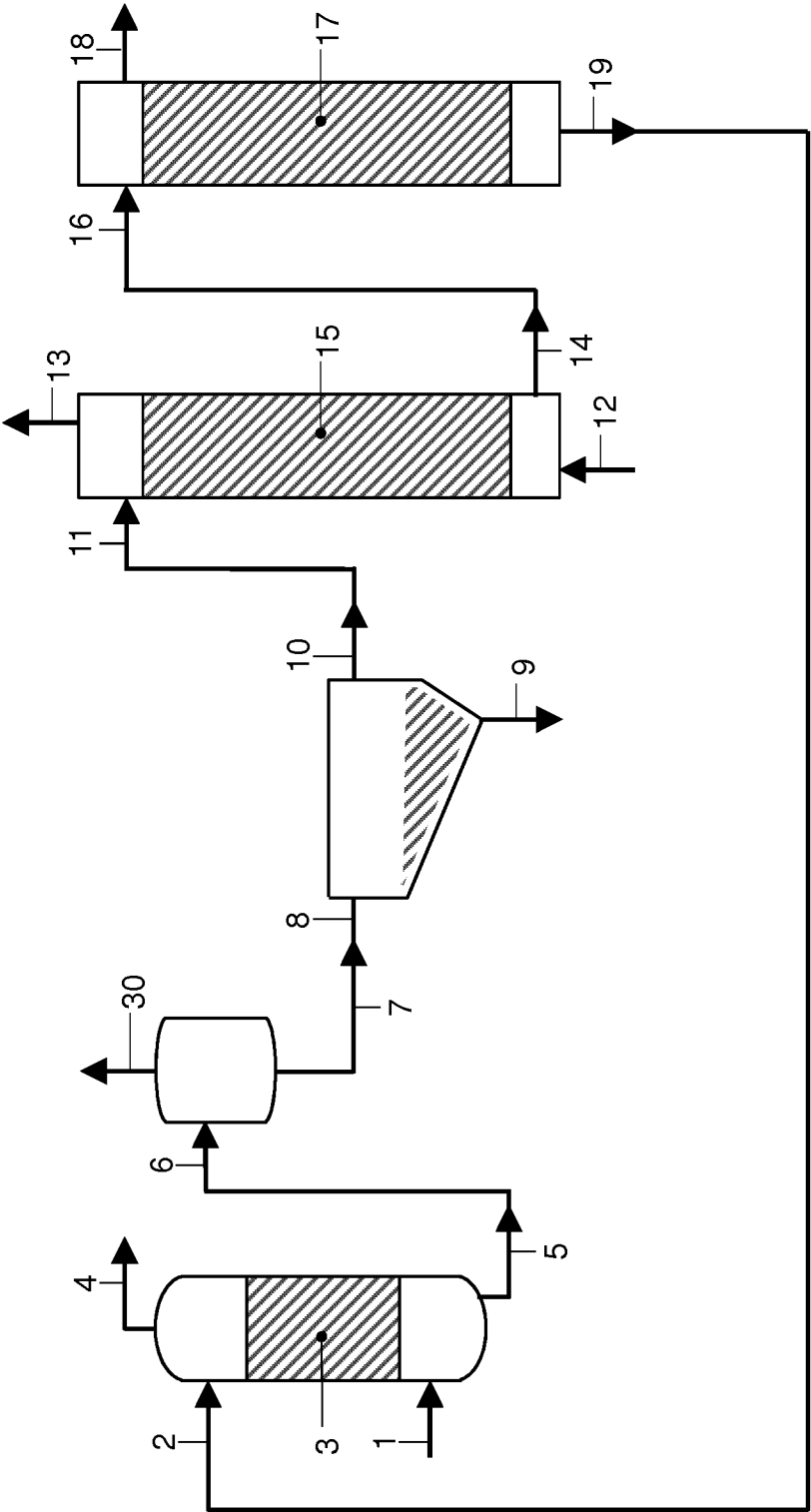


FIG. 7

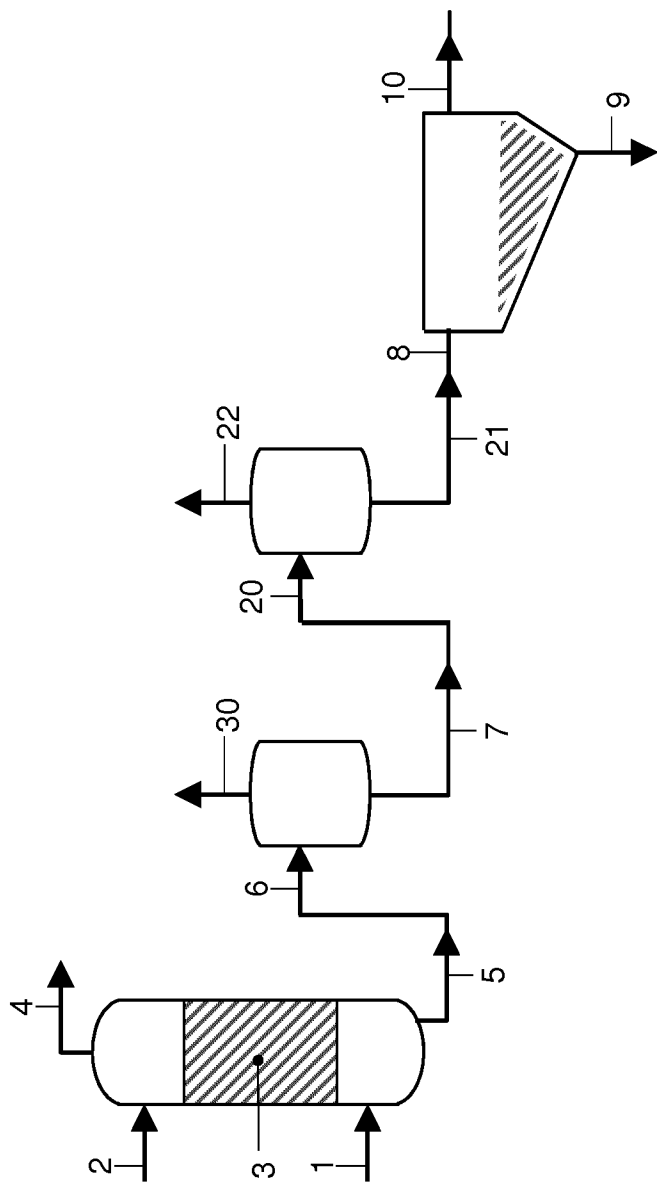


FIG. 8

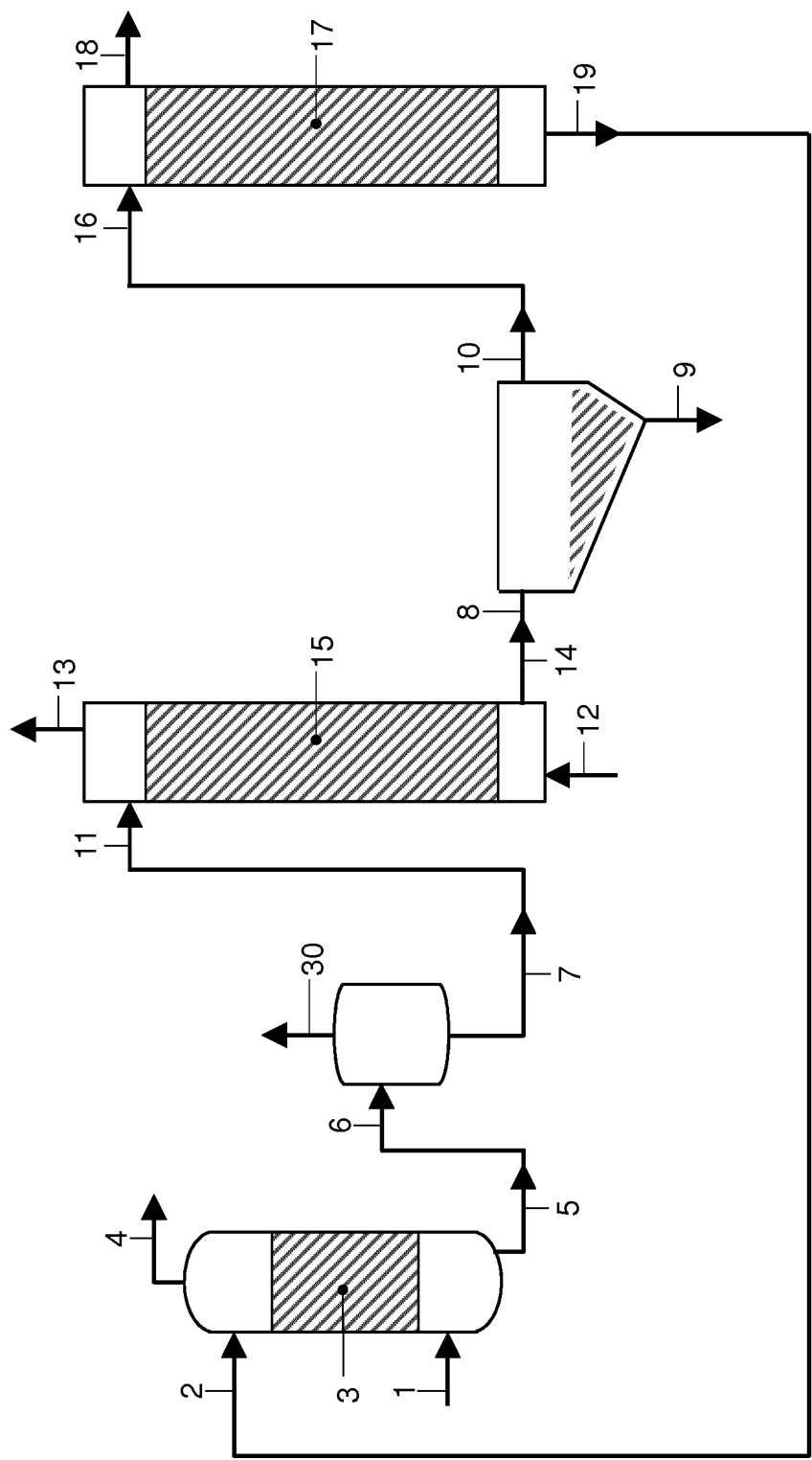


FIG. 9

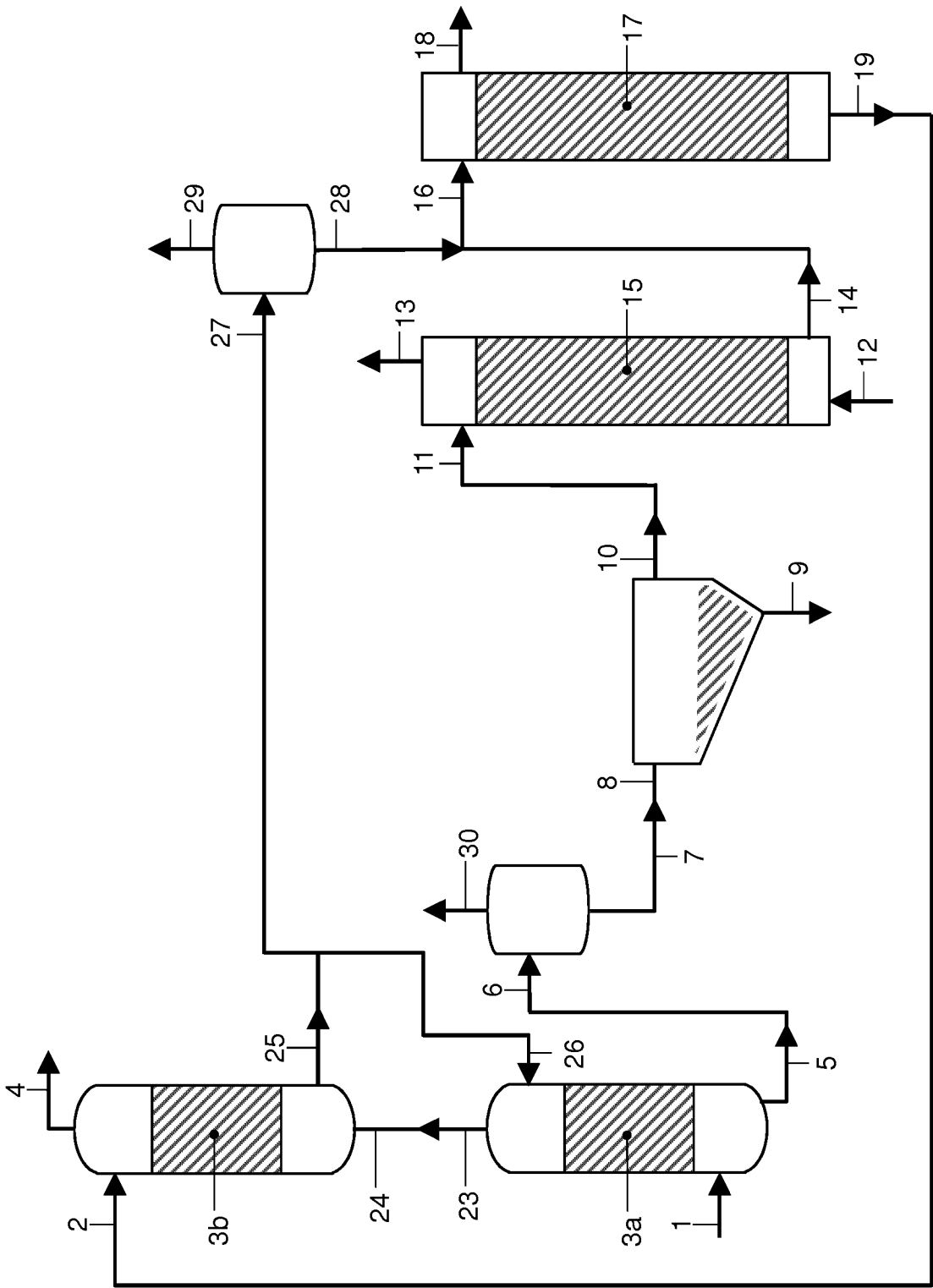


FIG. 10