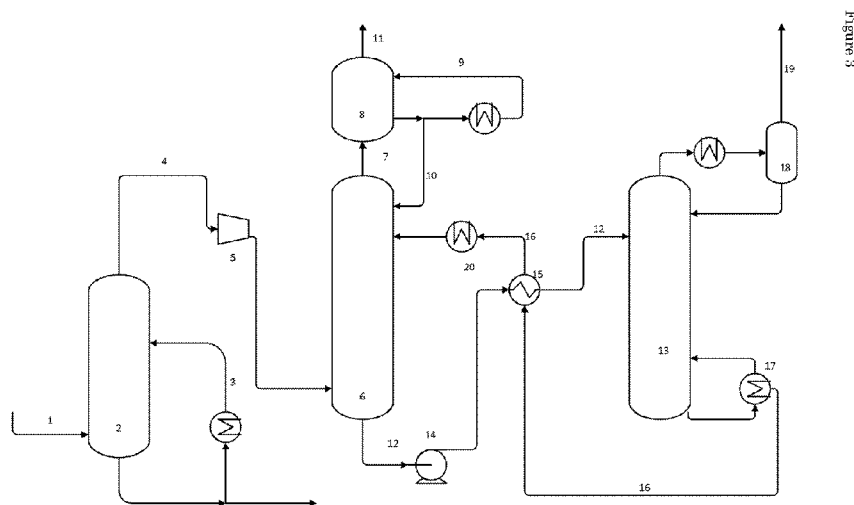




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(54) Title: AMINE REDUCTION IN AEROSOLS



(57) Abstract: The invention is directed to a method for lowering the amine content in an aerosol. More in particular, the invention relates to a post-combustion carbon dioxide capture process, wherein the content of an amine in an aerosol is lowered. The method of the invention for lowering the content of one or more amines in an aerosol comprising said one or more amines solubilised in aqueous aerosol droplets, comprises heating the aerosol and washing the aerosol with aqueous acid solution having a water activity which is lower than the water activity of the aqueous aerosol droplets.



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Title: Amine reduction in aerosols

The invention is directed to a method for lowering the amine content in an aerosol. More in particular, the invention relates to a post-combustion carbon dioxide capture process, wherein the content of an amine in an aerosol is lowered.

5 The continued usage of fossil fuels for energy production is commonly associated with the globally observed climate change. The combustion of such fuels produces carbon dioxide, a so-called greenhouse gas which is typically released into the atmosphere. Nowadays it is a common viewpoint that carbon dioxide released into the atmosphere plays a major role
10 in global climate change. Hence, the reduction of carbon dioxide emissions from fossil fuel combustion and other sources has been drawing interest as a primary means of mitigating climate change and global warming. Carbon dioxide capture involves the separation of carbon dioxide from an effluent stream. Advantageously, the carbon dioxide can thereafter be compressed to a
15 liquid or dense phase or supercritical state for transportation. It may then be injected into geological reservoirs (*e.g.* oil and gas fields, or deep saline aquifers), where the geological structure and processes are expected to store the carbon dioxide.

A major part of carbon dioxide emissions stems from the electricity
20 sector, primarily from coal-fired power plants. A wide variety of industrial facilities also emit carbon dioxide as a by- or co-product of the industrial processes inherent to their industry, such as ethanol fermentation, oil and gas refining, chemical (including ethylene and ethylene oxide) production, hydrogen production, as well as other manufacturing industries such as pulp
25 and paper, iron and steel, ammonia and fertiliser, and cement manufacturing. Carbon dioxide in exhaust (gas) streams is present to various extents, at various temperatures and pressures, and with various other constituents (including NO_x, SO₂).

There are commercially available carbon dioxide capture technologies that are currently being used in various industrial applications and being tested for power plant capture in pilot and demonstration projects. However, these technologies are still not widely used, primarily because they
5 either have not been demonstrated at the scale necessary for power plant application, or they would not be cost effective.

Presently, there is on-going research to the capture and storage of gaseous acid compounds (such as carbon dioxide), resulting in various methods available for the removal of gaseous acid compounds from exhaust gas
10 streams.

A classical method for chemical absorption of carbon dioxide from exhaust gases (post-combustion carbon dioxide capture) involves reactive absorption followed by regeneration of the absorbent liquid in a desorber. Absorption processes typically utilise the reversible chemical reaction of
15 carbon dioxide with an aqueous alkaline solvent, usually an amine. In the desorber, the absorbed carbon dioxide is stripped from the solution and a stream of carbon dioxide is sent for compression while the regenerated solvent is sent back to the absorber. Accordingly, the term "solvent" as used in this application in the context of such reactive absorption/desorption processes is
20 meant to refer to a liquid absorbent capable of chemically absorbing a gaseous acid compound, such as carbon dioxide. Such liquid absorbent can suitably be an aqueous amine solution.

A number of solvent systems have been proposed and studied for carbon dioxide capture by chemical absorption. Amines used to capture carbon
25 dioxide from gaseous streams react to form water soluble compounds, which for instance upon heating release the carbon dioxide. Monoethanolamine (MEA) has been the most widely studied system. Other amines that have been studied include secondary amines such as piperazine (PZ) and tertiary amines such as *N*-methyldiethanolamine (MDEA). Sterically hindered amines such as
30 2-amino-2-methyl-1-propanol (AMP) have also been investigated. The

performance of hindered amines was found to be better suited to absorption at higher carbon dioxide partial pressure atmospheres. Mixed amine blends are designed to take advantage of the desirable properties in a primary/secondary and a tertiary and/or sterically hindered amine. It is desired that these have
5 the high capacity and low heat of absorption characteristic of tertiary and/or sterically hindered amines and the fast rate of reaction characteristic of non-hindered primary and secondary amines. This will lead to reduced circulation rates of the solvent. Particular interest has been focused on MEA/MDEA, MEA/AMP, and AMP/PZ blends with pilot plant studies having
10 been conducted. Investigations on blends of diglycolamine (DGA) and MDEA have also been conducted. Other systems that have been proposed include using ammonia-based solutions and solutions of amino acids as absorbent for carbon dioxide capture.

A drawback of the conventional absorption processes for carbon
15 dioxide capture is that the vent gas of the absorber can comprise aerosol droplets that may contain components that are harmful to the environment. In particular, the aerosol droplets may comprise amine components from the absorbent liquid, such as MEA, MDEA, AMP, DGA, and the like. Emission of these components is undesirable and, accordingly, there is a need for removal
20 of such components from the vent gas. In particular, it was found that the contribution of aerosol based emissions can be substantially higher than vapour based emissions of one or more amines after a water wash section.

Aerosols can be formed by spontaneous condensation or desublimation mechanisms in supersaturated gases, for instance by chemical
25 reactions in the gas phase followed by desublimation of the generated components, or by crossing the dew point line by simultaneous mass and heat transfer processes.

However, the removal of environmentally harmful components that may be present in the vent gas aerosol is not easy. Efforts towards the
30 reduction of such emissions are conventionally based on the removal of the

aerosol from the gas stream, such as through applying filters, wet electrostatic scrubbers, internal column configurations, *etc.* For example, Schaber (*Chemical Engineering Science* 1995, 50(8), 1347-1360) describes a scientific study on how to avoid or suppress aerosol formation by applying favourable
5 operating conditions or by applying specific scrubbing liquids. US-B-7 025 808 describes a process for reducing aerosol-related discharge from a separation column, wherein the separation column internals are configured in a specific manner. US-B-7 867 322 describes a method of cleaning a process gas containing sulphur dioxide by applying acid wash. WO-A-2009/091437 teaches
10 a method for carbon dioxide capture wherein a wet electrostatic precipitator is applied for removing aerosols and fine particulate matter from the flue gas.

US-A-2011/0 308 389 teaches a process comprising CO₂ absorption and washing the CO₂ lean flue gas with an acidic aqueous solution to remove or substantially reduce the amount of amine(s) and alkaline degradation
15 products thereof in the gas. The acid wash section is preferably operated adiabatic or close to adiabatic, with the aim to produce a small bleed with relatively high concentration of amine-acid compounds. The content of one or more amines and/or alkaline degradation products thereof in an aerosol is not considered. No heating of any aerosol is disclosed. The mentioned reduction of
20 MEA from 80-100 ppm to 0.7 ppm with a water wash and a further reduction by adding sulphuric acid relates to gaseous MEA, not to an aerosol.

JP-A-10-033 938 discloses a process comprising CO₂ absorption with an amine absorptive liquid. The gas stream is first water washed and then led to a sulphuric acid spraying apparatus and led to a demister where mist
25 containing amine sulphate salt is captured. Neither heating, nor an aerosol is disclosed. US-A-2011/0 146 489 describes a process wherein ammonia is removed from a gas stream by contacting it with an acidic absorption liquid comprising CO₂. The acidic absorption liquid is cooled before the gas stream is contacted with it. Aerosols are not mentioned in this document.

FR-A-2 958 180 describes a process comprising acid washing of a gas stream. In the acid washing solution recycle loop, the washing solution is cooled.

Brownian diffusion candle type demisters can be used for removing
5 liquid droplets from a gas stream. An example is described in EP-B-0 418 058. A disadvantage of candle type demisters is that a low velocity is required (low flow of the aerosol stream), relative to the diffusion velocities associated with Brownian movement. In addition, the pressure drop is high and/or the demisters need a large flow area, escalating equipment costs and operating
10 costs.

Still there remains a need for alternative methods for reducing the aerosol-based emissions that are simpler and cheaper, and to effectively remove harmful components solubilised in aerosol, also when an aerosol has already been formed.

15 A first objective of the invention is to provide a method for lowering the content of one or more amines in an aerosol.

A further objective of the invention is to reduce and/or neutralise the amine components that may be present in an aerosol.

Yet a further objective of the invention is to reduce the average
20 droplet diameter of aerosol droplets.

Yet a further objective of the invention is to provide an absorption/desorption-based carbon capture process having a minimum of environmentally harmful emission, in particular emission in the form of aerosols.

25 Yet a further objective of the invention is to lower the content of one or more amines in an aerosol comprising aerosol droplets with a diameter $\leq 10 \mu\text{m}$ and comprising one or more amines.

The inventors found that one or more of these objectives can, at least in part, be met by heating the aerosol and washing the aerosol with aqueous

acid solution, such as by subjecting the aerosol and resulting vapour to an acid wash.

Accordingly, in a first aspect the invention is directed to a method for lowering the content of one or more amines in an aerosol comprising said
5 one or more amines solubilised in aqueous aerosol droplets, said method comprising heating the aerosol and washing the aerosol with aqueous acid solution, preferably aqueous acid solution having a water activity which is lower than the water activity of the aqueous aerosol droplets.

The inventors found that the invention can lead to a surprisingly
10 lower amine content in the resulting aerosol. For the case of carbon dioxide capture, this advantageously allows a reduction of the amine content in the vent gas, in particular in aerosol that is comprised in the vent gas. Without wishing to be bound by any theory, the inventors believe that the increase in temperature leads to evaporation of water from the aqueous aerosol droplets
15 when in contact with the aqueous acid solution, preferably because the water activity in the aerosol droplets is higher than in the aqueous acid solution. As a result of the water evaporation, the average aerosol droplet diameter decreases. In turn, this facilitates transfer of the one or more amines from the aerosol dispersed phase to the vapour phase by increasing the rate of mass
20 transfer.

Thus, rate of mass transfer of amine from the aerosol droplets to the vapour phase is believed to be enhanced due to the increase in contact surface area per unit volume of aerosol droplets. The evaporated amine in the vapour phase is further absorbed by the acid wash liquid phase where it is maintained
25 at low levels by the neutralisation reaction between the amine and the acid. Hence, the absorption of the amine from the vapour phase to the acid wash liquid phase is enhanced by the chemical reaction between the acid and the amine. Due to the decrease in the amine concentration in the vapour phase, the driving force between the amine present in the aerosol droplet phase and
30 the amine present in the vapour phase is higher, thereby further promoting

transfer of the amine from the aerosol dispersed phase to the vapour phase and further absorption in the acid wash liquid phase where the amine will be neutralised by the acid. As a result, the driving force for removing the amine from the aerosol in the method of the invention is very high.

5 Without wishing to be bound by way of theory, the inventors believe that water evaporation from the aqueous aerosol droplets may further facilitate transfer of the one or more amines (and/or alkaline degradation products thereof) from the aerosol dispersed phase to the vapour phase in part by the increased curvature of the droplets surface (Kelvin effect) and/or the
10 increased mole fraction of the amines component in the aerosol droplets liquid phase (Raoult's law).

 The term "amine" as used in this application is meant to refer to any compound formally derived from ammonia by replacing one, two or three
hydrogen atoms by (substituted) hydrocarbyl groups. The term "amine" is
15 meant to include primary amines having the general structure RNH_2 , secondary amines having the general structure R_2NH , as well as tertiary amines having the general structure R_3N (tertiary amines).

 The term "aerosol" as used in this application is meant to refer to a suspension of a solid or liquid or a mixture of both in a gas, and is meant to
20 encompass any associated vapours. In particular, in the context of the present invention the aerosol dispersed phase preferably comprises a liquid. The aerosol dispersed phase droplets are then referred to as the "aerosol droplets". Typically, the aerosol droplet diameter ranges from 0.001 to over 100 μm . The continuous phase preferably comprises the vent gas of an absorber.

25 The term "water activity" as used in this application is meant to refer to its commonly accepted meaning of the ratio of the equilibrium vapour pressure of water above a substance to the vapour pressure of pure water, both taken at the same temperature. Accordingly, the water activity of the liquid acid is the ratio of the equilibrium vapour pressure of water above the liquid
30 acid to the vapour pressure of pure water, both taken at the same

temperature. Similarly, the water activity of the aerosol droplets is the ratio of the equilibrium vapour pressure of water above the aerosol droplets to the vapour pressure of pure water, both taken at the same temperature. The water activity of the aerosol droplets can, for instance, be determined by using
5 electrodynamic balance (see for instance Liang *et al.*, *Aerosol Sci. Technol.* 1997, 26(3), 255-268).

As commonly known in the art, Nm³ (normal cubic meter) refers to the volume of that gas measured under the standard conditions of 0 °C and 1 bar.

10 In accordance with the invention, the one or more amines are solubilised in aqueous aerosol droplets. Typically, the one or more amines that are solubilised in aqueous aerosol droplets are in equilibrium with one or more amines that are present in the vapour phase. Preferably, the one or more amines comprise an alkanolamine. In an embodiment, the one or more amines
15 comprise one or more selected from the group consisting of monoethanolamine, diethanolamine, piperazine, *N*-methyldiethanolamine, diethylamine, triethylamine, diethylenetriamine, and 2-amino-2-methyl-1-propanol, preferably said one or more amines comprise one or more selected from monoethanolamine, *N*-methyldiethanolamine and
20 2-amino-2-methyl-1-propanol, more preferably said one or more amines comprise monoethanolamine. It is also possible that a mixture of two or more of the above amines is comprised in the aerosol droplets. The content of amine degradation products can be lowered, including degradation products such as aldehydes, organic acids, amides, nitrogen oxides and ammonia.

25 Typically, the amount of the one or more amines in the aerosol can initially (*i.e.* prior to heating and acid washing) be in the order of 0.1-4 mol/l, such as in the range of 0.2-1.5 mol/l, or in the range of 0.7-1 mol/l.

In a preferred embodiment, the aerosol is comprised in a vent gas stream of an absorber (*i.e.* the gas stream leaving the absorber and depleted in
30 absorbed species). Preferably, the vent gas stream, comprising the one or more

amines, is scrubbed in a water wash. In such a water wash step a stream of aqueous washing liquid (preferably water) is typically supplied to a water wash vessel where the gas stream is washed, preferably by counter current flow to water in a packing. The aqueous washing liquid preferably has a
5 temperature which is lower than the temperature of the gas stream comprising the one or more amines. The aqueous washing liquid can typically have a temperature in the range of 20-50 °C, preferably in the range of 30-35 °C. The aqueous washing liquid can be introduced into the water wash vessel and distributed over the packing by means of aqueous washing liquid distributors.
10 Aqueous washing liquid may be collected and recycled to the water washing vessel, such as via an aqueous washing liquid supply tank. In an embodiment the gas stream is cooled during the aqueous washing. This may be advantageous so as to condense and remove water from the passing gas stream. In order to cool the gas stream, the aqueous washing liquid may
15 optionally be actively cooled. Contaminants initially contained in the gas stream and that are washed from the gas by the aqueous washing liquid may suitably be removed via a bleed line. In a preferred embodiment, the aerosol is comprised in a gas stream leaving a water wash step.

The method of the invention comprises heating the aerosol.

20 Preferably, before said heating the aerosol has an initial (for example from the water wash) temperature in the range of 20-50 °C, more preferably in the range of 30-45 °C.

Suitably, heating of the aerosol results in the temperature of the aerosol being increased by a temperature difference in the range of 5-75 °C,
25 preferably in the range of 10-40 °C, more preferably in the range of 15-25 °C. Such a temperature increase results in evaporation of water and ensures an increase in the contact area between the aerosol dispersed phase and the vapour phase so as to facilitate transfer of amine from the aerosol dispersed phase into the vapour phase.

Heating the aerosol can comprise active heating, such as continuous active heating of the aerosol. Active heating can comprise transferring heat from an external heat source to the process streams such as the aerosol and/or aqueous acid solution.

5 Heating the aerosol can comprise heating both the aqueous aerosol droplets and the aerosol vapour phase.

The method can comprise heating the aerosol to a temperature (T_w) and washing the aerosol when heated to this temperature T_w (washing temperature T_w) with aqueous acid solution. Preferably, washing the aerosol
10 with aqueous acid solution comprises contacting the aerosol with aqueous acid solution, more preferably at washing temperature T_w , such as contacting the aerosol with aqueous acid solution with aerosol, aqueous acid solution, or both, at washing temperature T_w .

Preferably, washing temperature T_w is 50 °C or more, more
15 preferably 55 °C or more, more preferably 60 °C or more, even more preferably 65 °C or more. Preferably, T_w is less than 120°C, such as less than 100 °C.

Heating the aerosol can comprise indirect heating. Indirect heating can comprise contacting the aerosol with a relatively warmer surface, such as heated by heat exchange with a relatively warm process stream and/or Joule
20 heating.

Heating the aerosol can be achieved in different manners, such as by indirect gas-gas or gas-liquid heating, or by direct gas-liquid heating. Accordingly, in an embodiment, which is preferred, the heating comprises indirect gas-gas or gas-liquid heating wherein the aerosol is indirectly heated
25 by a heat transfer surface using a gas or liquid prior to being subjected to said washing with aqueous acid solution. In case of indirect heating, the heat transfer surface can have a temperature equal to T_w or higher, such as at least $T_w + 10$ °C or at least $T_w + 20$ °C.

In indirect gas-gas heating, the (relatively) cold aerosol can be contacted with a (relatively) hot heating surface, which in itself is heated by another hot gas stream, so as to heat the aerosol.

Hence, in an embodiment, heating of the aerosol comprises gas-gas heating wherein the aerosol is heated using a heated surface transferring heat from another gas prior to being subjected to the washing with aqueous acid solution. This can, for instance, be performed by means of a rotary regenerative gas-gas heater, also known as a Ljungstrom-type reheater. Such equipment comprises a circular rotating bed (called rotor) packed with specially formed sheets of heat transfer surface. The rotor contains two sections, one for the hot gas and one for the cold gas. The heat is transferred from the hot gas to the cold gas via the packed sheets in the rotor. An example of such a rotary regenerative gas-gas heater is shown in figure 1. Vent gas stemming from an absorption process can, for example, be heated up using hot air on the hot side of the gas-gas heater. The heat can be obtained from any available hot streams in surrounding processes. As an example, the hot exhaust gas prior to an absorber could be used as a heating medium. By this, two operations can favourably be integrated: cooling the hot exhaust gas and heating up the vent gas before being subjected to acid wash.

Indirect gas-liquid heating is also possible. The (relatively) cold aerosol is then contacted with a (relatively) hot heating surface, which in itself is heated by a hot liquid, such as by passing a hot liquid through pipes placed within the gas path. In this way, heat is transferred from the hot liquid through the pipe wall material to the aerosol containing stream. Accordingly, the aerosol may be reduced in size and the amine contained within the aerosols released to the vapour phase to enable scrubbing with aqueous acid solution. An example of such an indirect gas-liquid heater is shown in figure 2. This method of indirect heating with pipes is equally applicable for steam heating in place of the liquid.

In case of a process comprising a water wash step and indirect heating using a heat transfer surface (such as indirect gas-gas or gas-liquid heating), the aerosol is preferably indirectly heated by a heat transfer surface after the water wash step and prior to being subjected to said washing with aqueous acid solution. Preferably, the aerosol is heated to a temperature T_w , preferably the aerosol has temperature T_w at the start of washing the aerosol with aqueous acid solution.

An example of direct gas-liquid heating can be pre-heating of the aqueous acid solution. Upon contact of the aqueous acid solution with the aerosol, the aerosol will automatically be heated. Heat is then transferred to the aerosol by contacting in the acid washing.

In case of direct gas-liquid heating, the aqueous acid solution is preferably pre-heated to 50 °C or more, more preferably 60 °C or more, such as 70 °C or more. The aqueous acid solution is typically pre-heated to less than 120°C, such as less than 100 °C. The aqueous acid solution is preferably continuously pre-heated to T_w .

The aqueous acid solution used for washing the aerosol can comprise one or more acids selected from the group consisting of sulphuric acid, nitric acid, phosphoric acid, and hydrochloric acid. Preferably, the aqueous acid solution comprises sulphuric acid.

Preferably, the aqueous acid solution has a pH value in the range of 1-6, preferably in the range of 2-4. If the pH value of the aqueous acid solution is higher than 6, then there is a risk that not all amine will be neutralised. As a result some amine will remain in the vent gas which will lead to undesirable emissions. A low pH (such as less than 1) is also not desirable, because it complicates neutralisation of the bleed stream.

Suitably, the aqueous acid solution can be an aqueous acid solution, such as an aqueous solution of sulphuric acid, preferably having a concentration in the range of 0.0005-50 mM, more preferably in the range of 0.05-5 mM.

Preferably, the aqueous acid solution is recycled at least in part. Preferably, recycling aqueous acid solution comprises regenerating the aqueous acid solution at least partly. Regenerating aqueous acid solution can comprise adding water and/or acid as desired to maintain pH. Regenerating
5 aqueous acid solution may comprise reclaiming the one or more amines at least partly. Regenerating aqueous acid solution may comprise evaporating part of the aqueous acid solution.

Preferably, the method comprises evaporating the aqueous aerosol droplets in part, in particular evaporating the water component of the aqueous
10 aerosol droplets in part, preferably at least partly during the acid washing step.

During heating of the aerosol, the average aerosol droplet diameter decreases due to evaporation from the droplet, typically of water and amine. Hence, in an embodiment the average aerosol droplet diameter before carrying
15 out the method of the invention is larger than the aerosol droplet diameter after having carried out the method of the invention. More preferably, the average aerosol droplet diameter before heating is larger than the aerosol droplet diameter after heating. The initial (*i.e.* prior to heating) aerosol droplet diameter may be in the range of 5 μm to 20 μm , preferably in the range of 7-15
20 μm , such as about 10 μm . Note that the aerosol droplet diameter distribution can be very broad and the aerosol may comprise aerosol droplets having a diameter in the range of 10 nm to 25 μm . After heating, the average aerosol droplet diameter may be in the range of 1-10 μm , such as in the range of 2-5 μm . Measurement methods for determining absolute and average aerosol
25 droplet diameters are well known in the art. These diameters can for instance be determined using an electrical low pressure impactor (ELPI) or an aerodynamic particle sizer (APS).

Typically, the aerosol vapour phase comprises ammonia. Preferably, the method of the invention comprises allowing absorption and/or dissolving of ammonia from the aerosol vapour phase in the aqueous acid solution.

In case the aerosol vapour phase comprises ammonia the process
5 allows for the simultaneous reduction of the amine content of aerosol droplets and ammonia content of the aerosol vapour phase of the aerosol. This advantageously allows for one piece of equipment to remove both.

Preferably, washing the aerosol with aqueous acid solution comprises packed bed washing, such as carried out in a structured packed bed.
10 Structured packing is preferred to reduce pressure drop. The packing material is preferably corrosion resistant, for example as commercially available from Sulzer and Intalox.

In an attractive embodiment, the present invention is comprised in an absorption process wherein one or more of the amines are used as
15 absorbent. More particularly, the invention can be applied in an absorption/desorption-based process for the capture of gaseous acid compounds (such as carbon dioxide) from an exhaust gas. Such processes are well-known in the art. An example of conventional post-combustion carbon dioxide capture technology using an absorption/desorption process is schematically depicted in
20 the simplified flow diagram of figure 3. In the example of figure 3, flue gas 1 (e.g. from a power plant) enters direct contact cooler 2, where it is cooled with circulating water 3. Subsequently, gas 4 is transported with gas blower 5 to absorber 6. The gas flows through the packed bed absorbed 6 counter currently with an amine absorbent (typically an aqueous amine solution, such as an
25 aqueous monoethanolamine solution), in which the amine absorbent reacts chemically with carbon dioxide (packed bed columns are preferred over plate columns because of their higher contact area). Carbon dioxide lean gas 7 enters water wash scrubber 8 in which water and amine vapour and droplets 10 are recovered and recycled back into absorber 6 to decrease the solvent loss.
30 Treated gas 11 is typically vented to the atmosphere.

Rich absorbent 12 containing chemically bound carbon dioxide is fed to the top of stripper 13 with pump 14 via lean/rich cross heat exchanger 15 in which rich absorbent 12 is heated and the carbon dioxide lean absorbent 16 is cooled. The amine absorbent is regenerated in the stripper 13. Heat is supplied to reboiler 17 using low-pressure steam to maintain regeneration conditions. Steam is recovered in condenser 18 and fed back to stripper 13, after which produced carbon dioxide gas 19 leaves condenser 18. Finally, lean solvent 16 is pumped back to absorber 6 via the lean/rich heat exchanger 15 and cooler 20 to bring its temperature down to the absorber level.

As mentioned, amine based absorbents (such as monoethanolamine MEA) are commonly used in these processes. The vent gas stream leaving the absorber column is typically introduced to a water wash section in order to decrease the solvent loss and to maintain the water balance (water scrubber 8 in figure 3). Still, after the water wash section the gas stream leaving the aqueous liquid wash section (gas stream 11 in figure 3) can contain significant amount of amine, mostly in the form of aerosols. The process of the invention can suitably be implemented in such a conventional absorption/desorption based processes for the capture of gaseous acid compounds from an exhaust gas so as to reduce the amount of one or more amines in the gas stream in the form of aerosol leaving the water wash section.

An example of such a implementation is schematically depicted in the simplified flow diagram of figure 4. Gas stream 11 comprises an aerosol comprising amines and is not vented to the atmosphere, but heated at heater 21 (for example a indirect gas-gas or gas-liquid heater). Heated stream 22 comprising the aerosol is washed with aqueous acid solution at acid wash scrubber 23). Washed stream 24 with a lower content of one or more amines in the aerosol is typically vented to the atmosphere. Aqueous acid solution 25 is regenerated at 26.

Therefore, in a special aspect, the invention is directed to a post-combustion process for capturing one or more gaseous acid compounds

comprising a method according to the invention. Typically, the one or more gaseous acid compounds can comprise one or more from the group consisting of carbon dioxide, sulphur dioxide, sulphur trioxide, nitrogen dioxide, hydrogen fluoride, hydrogen sulphide, and hydrochloric acid. Such post-combustion
5 capture process may capture gaseous acid compounds from an exhaust gas that originates, *e.g.* from coal-fired power plant. The process preferably comprises the steps of

- i) contacting an exhaust gas stream with an absorbent lean in said one or more gaseous acid compounds, thereby obtaining a gas stream depleted of
10 said one or more gaseous acid compounds and an absorbent rich in said one or more gaseous acid compounds;
 - ii) regenerating the rich absorbent by desorbing gaseous acid compounds from said rich absorbent to produce lean absorbent; and
 - iii) recycling lean absorbent to contacting step i),
- 15 wherein said gas stream depleted of said one or more gaseous acid compounds comprises an aerosol with one or more amines solubilised in aqueous aerosol droplets and wherein the content of said one or more amines is lowered by a method comprising heating the aerosol and washing the aerosol with aqueous acid solution having a water activity which is lower than the water activity of
20 the aqueous aerosol droplets.

Preferably, the gas stream depleted of one or more gaseous acid compounds is first subjected to a washing step using an aqueous washing liquid before being heated and washed with aqueous acid solution.

In an embodiment, at least part of the one or more amines is
25 comprised in the liquid absorbent. In other words, the liquid absorbent can comprise one or more of said amines.

In an aspect, the invention relates to a method for lowering the content of one or more amines in an aerosol that comprises said one or more amines solubilised in aqueous aerosol droplets and a vapour phase, said
30 method comprising contacting the aerosol with aqueous acid washing solution

and promoting transfer of said one or more amines from said aqueous aerosol droplets to said vapour phase.

Typically, aerosol vapour phase is in contact with aqueous aerosol droplets (liquid phase) and aqueous acid washing solution and the aqueous aerosol droplets are dispersed in the aerosol vapour phase (aerosol gas phase). Preferably, said promoting transfer of said one or more amines comprises increasing the amine vapour pressure of said one or more amines in said aqueous aerosol droplets. Preferably, said increasing the amine vapour pressure comprises increasing the temperature of said aqueous aerosol droplets, such as to T_w as described. Preferably, said increasing the temperature of said aqueous aerosol droplets comprises heating the aerosol, as described.

Preferably, increasing the amine vapour pressure of said one or more amines in said aqueous aerosol droplets comprises evaporating water from said aqueous aerosol droplets. Therefore, preferably the water vapour pressure of the aqueous aerosol droplets is higher than the water vapour pressure in the aerosol vapour phase. Preferably, the water vapour pressure of the aqueous aerosol droplets is higher than the water vapour pressure of the aqueous aerosol droplets, during the contacting the aerosol with aqueous acid washing solution.

The invention will now be further elucidated by means of the following examples which are not intended to limit the invention in any manner.

Examples

Example 1

An estimate was made on the amount of monoethanolamine emission that can be removed using the invention. The reaction of monoethanolamine with the acid can be considered to be instantaneous with

an extremely high enhancement factor, thus the transfer of aerosol vapour phase (gas phase) monoethanolamine to the liquid acid (solution) is a fast process. The rate limiting step is therefore the evaporation of free monoethanolamine in the dispersed (liquid) phase (aerosol droplet) to the

5 vapour phase (aerosol). A rough estimate for the evaporation of monoethanolamine, also from the aerosol droplet phase, can be made using the Hertz-Langmuir equation for rate of evaporation as given below

$$\frac{dM}{dt} = (p_v - p_p) \sqrt{\frac{m}{2 \cdot \pi \cdot R \cdot T}},$$

wherein dM / dt is the mass loss rate of component per unit area in
 10 kg/s/m², p_v is the vapour pressure of the component at the specific temperature in N/m², p_p is the partial pressure of the component in N/m², m is the molecular mass in g/mol, R is the universal gas constant in J/mol/K, and T is the absolute temperature in K.

The Hertz-Langmuir equation is an estimate and applicable for pure
 15 liquids. Nevertheless, it can be used to compare the rate of evaporation at two different temperatures. The values used for the calculation are mentioned in table 1.

Table 1 Assumptions for calculation

	Value (43 °C)	Value (60 °C)	Unit
p_v vapour pressure of MEA	213.3	680	N/m ²
T absolute temperature	316.15	333.15	K
m molecular mass	61		g/mol
R universal gas constant	8.314		J/mol/K
Pressure	101000		N/m ²

20

Table 2 lists assumed aerosol droplet properties. The average aerosol droplet diameter is assumed to be 10 µm, but the actual aerosol droplet

diameter can range from 10 nm to 25 μm , while the number of aerosol droplets in 1 Nm^3 gas is assumed to be 10^{10} , but can vary from 10^6 to 10^{18} depending on factors such as flue gas condition, capture plant operation, *etc.*

5 Table 2 Assumptions for aerosol droplet properties

	Value	Unit
Average aerosol droplet diameter	10	μm
Number of aerosol droplets	10^{10}	Basis: 1 Nm^3 of gas

The partial pressure of MEA in the acid wash phase is negligible as all the MEA present in the acid wash phase is neutralised by the acid. Thus, by increasing the temperature from 43 °C to 60 °C, the evaporation rate of
 10 MEA from the aerosol droplet phase can be increased by a factor of 4.8, as calculated with the equation above.

Moreover, the increase in temperature would also lead to loss in water which would reduce the size of aerosols.

The following method can be used to estimate the decrease in
 15 droplet diameter as a result of water evaporation. The evaporation rate of a droplet N_c (g/s) can be given by;

$$N_c = \frac{h_c \cdot A \cdot (\Delta T)}{\lambda}$$

Where; h_c is the convective heat transfer coefficient ($\text{W}/\text{m}^2 \cdot \text{K}$), A is the surface area of the droplet (m^2), ΔT is the temperature difference between
 20 the droplet (K) and the surrounding gas and λ latent heat of vaporisation of water (kJ/kg). Table 3 presents the assumptions used for the calculation of droplet evaporation. The convective heat transfer co-efficient and the latent heat of vaporisation are readily available from literature. ΔT is in this case
 60 °C - 43 °C = 17 °C.

Table 3 Assumptions for aerosol droplet evaporation

	Value	Unit
h_c	105	W/m ² ·K
A	3.14×10^{-10}	m ²
ΔT	17	K
λ	2417	kJ/kg

Based on these assumptions, a droplet evaporation rate of 2.3×10^{-10} g/s is obtained. Assuming that the droplets are being evaporated for a time
5 period of 2 s, this would lead to a total weight loss of 4.6×10^{-10} g. The resulting diameter of the droplet would be 4.8 μ m. Thus, the surface area per unit volume of the droplet increases by a factor of 2.1 which enhances the mass transfer of components from the aerosol droplet phase to the vapour phase.

Thus, the increase in temperature leading to higher evaporation
10 rate and smaller droplets, results in a 10 fold (4.8×2.1) increase in removal rate of amine from the aerosol droplet phase. Typically, a packed column would be used for reducing the MEA in aerosol dispersed phase with a counter-current acid wash circulation. The increase in the evaporation rate of MEA from the droplet phase to the vapour phase would significantly reduce the
15 height of such a packed column.

Therefore, based on the calculation results it can be concluded that the introduction of the acid wash section after a water-wash section in a carbon dioxide capture plant improves the reduction of the monoethanolamine in the form of aerosols significantly.

20

Comparative example 1

A comparative experiment was performed using the setup as stated in US-A-2011/0 308 389. The setup consisted of a typical absorption-desorption process using monoethanolamine as the solvent as shown in figure 5. The

setup consisted of a CO₂ capture absorber, water wash section and an acid wash section.

It was possible to obtain MEA aerosols in the experimental setup and the corresponding emissions from the water wash could be measured using a FTIR (Fourier Transform Infrared Spectrometer). In a typical experiment wherein the acid wash was operated isothermally, the MEA emission levels after the water washing step and prior to the acid wash, as measured by the FTIR were in the order of 1200 mg/Nm³ with an inlet gas temperature of 38 °C. The acid wash was operated at pH 3 of the acid washing liquid and sufficient flow rate for efficient gas-liquid contact. At these conditions, the FTIR measured MEA emission levels in the order of 900 mg/Nm³ after the acid washing step where in the gas outlet temperature was 37 °C, indicating a removal efficiency of only 25 %. This in contrast to the MEA removal efficiency of greater than 90 % (before Acid wash ~10 mg/Nm³ and after acid wash < 1 mg/Nm³) in the absence of aerosols at the same operating conditions of the acid wash.

This indicates that the conventional acid wash of this comparative example is not capable of removing aerosol based MEA emissions and there is strong need for developing solutions for reducing the amine emissions by aerosols.

Example 3

An acid wash column for use in the process of the invention was designed (figure 6A) and constructed (photograph in figure 6B).

Claims

1. Method for lowering the content of one or more amines in an aerosol that comprises said one or more amines solubilised in aqueous aerosol droplets, said method comprising heating the aerosol and washing the aerosol with aqueous acid solution having a water activity which is lower than the
5 water activity of the aqueous aerosol droplets.
2. Method according to claim 1, wherein said one or more amines comprise an alkanolamine.
- 10 3. Method according to claim 1 or 2, wherein said one or more amines comprise one or more selected from the group consisting of monoethanolamine, diethanolamine, piperazine, *N*-methyldiethanolamine, diethylamine, triethylamine, diethylenetriamine, and 2-amino-2-methyl-1-propanol.
- 15 4. Method according to any one of claims 1-3, wherein said one or more amines comprise one or more selected from monoethanolamine, *N*-methyldiethanolamine and 2-amino-2-methyl-1-propanol.
5. Method according to any one of claims 1-4, wherein said one or more
20 amines comprise monoethanolamine.
6. Method according to any one of claims 1-5, wherein said aerosol is comprised in a vent gas stream of an absorber.
- 25 7. Method according to claim 6, wherein said vent gas stream is scrubbed in a water wash.
8. Method according to claim 6 or 7, wherein during said aqueous washing the gas stream comprising the one or more amines is cooled.

9. Method according to any one of claims 6-8, wherein said vent gas stream is the vent gas stream of an absorption process wherein one or more of said amines are used as absorbent.

5

10. Method according to claim 9, wherein said absorption process is an absorption process wherein gaseous acid compounds are absorbed from a feed gas.

10 11. Method according to claim 10, wherein said gaseous acid compounds comprise carbon dioxide.

12. Method according to any one of claims 1-11, wherein said aerosol before heating has a temperature in the range of 20-50 °C.

15

13. Method according to any one of claims 1-12, wherein said aerosol before heating has a temperature in the range of 30-45 °C.

14. Method according to any one of claims 1-13, wherein said aerosol is
20 heated by a temperature increase in the range of 5-50 °C.

15. Method according to any one of claims 1-14, wherein said aerosol is heated by a temperature increase in the range of 10-40 °C.

25 16. Method according to any one of claims 1-14, wherein said aerosol is heated by a temperature increase in the range of 10-25 °C.

17. Method according to any one of claims 1-16, wherein said heating comprises indirect gas-gas or gas-liquid heating wherein the aerosol is

indirectly heated by a heat transfer surface using a gas or liquid prior to being subjected to said washing with aqueous acid solution.

18. Method according to claim 17, wherein said indirect heating is
5 performed by means of a rotary regenerative gas-gas heater or tubular gas-liquid heater.

19. Method according to any one of claims 1-18, wherein said heating
10 comprises direct gas-liquid heating wherein the aqueous acid solution is pre-heated so as to heat the aerosol.

20. Method according to any one of claims 1-19, wherein said aqueous
acid solution comprises one or more selected from the group consisting of
sulphuric acid, nitric acid, phosphoric acid, and hydrochloric acid.
15

21. Method according to any one of claims 1-20, wherein said aqueous
acid solution has a pH in the range of 1-6.

22. Method according to any one of claims 1-21, wherein said aqueous
20 acid solution has a pH in the range of 2-4.

23. Method according to any one of claims 1-22, wherein the average
aerosol droplet diameter before said method is larger than after said method.

24. Method according to any one of claims 1-23, wherein before heating
25 the aerosol, the average aerosol droplet diameter ranges from 5 μm to 25 μm .

25. Post-combustion process for capturing one or more gaseous acid
compounds comprising a method according to any one of claims 1-24.
30

Figure 1

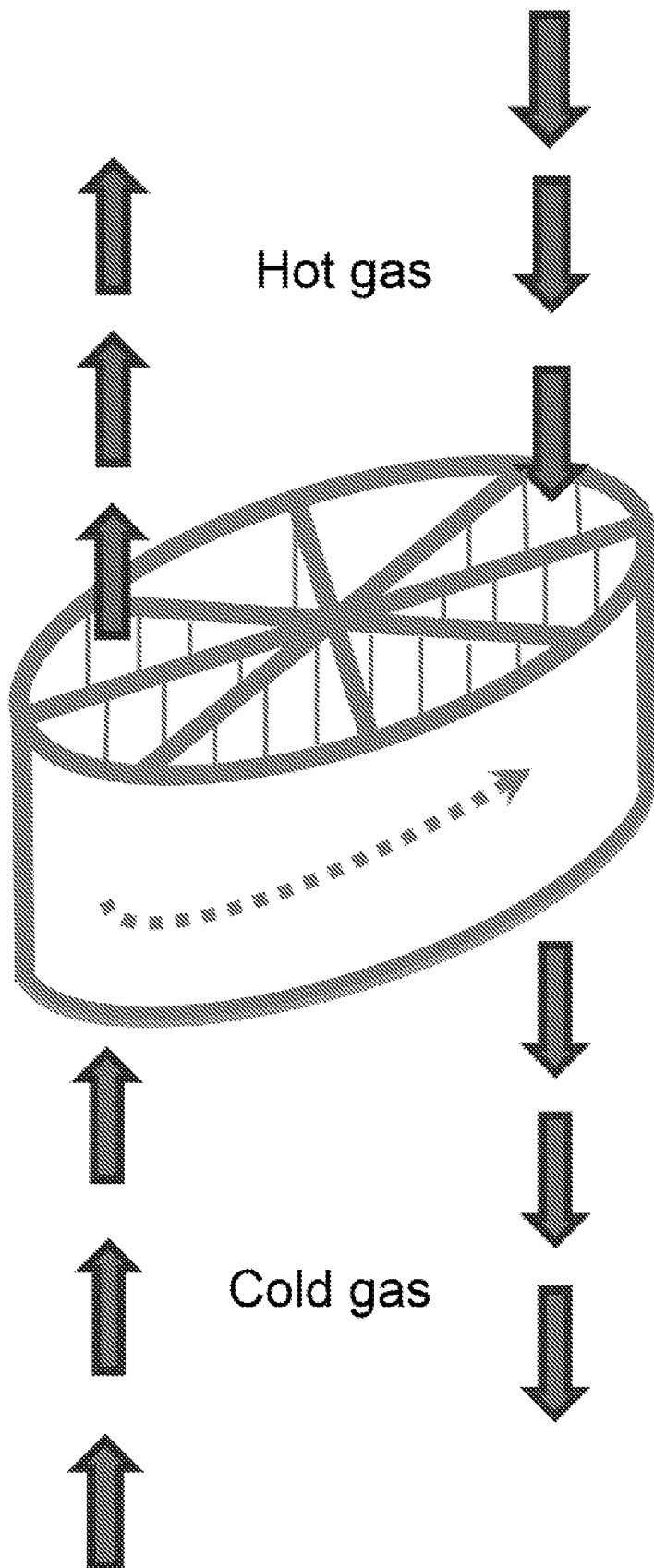


Figure 2

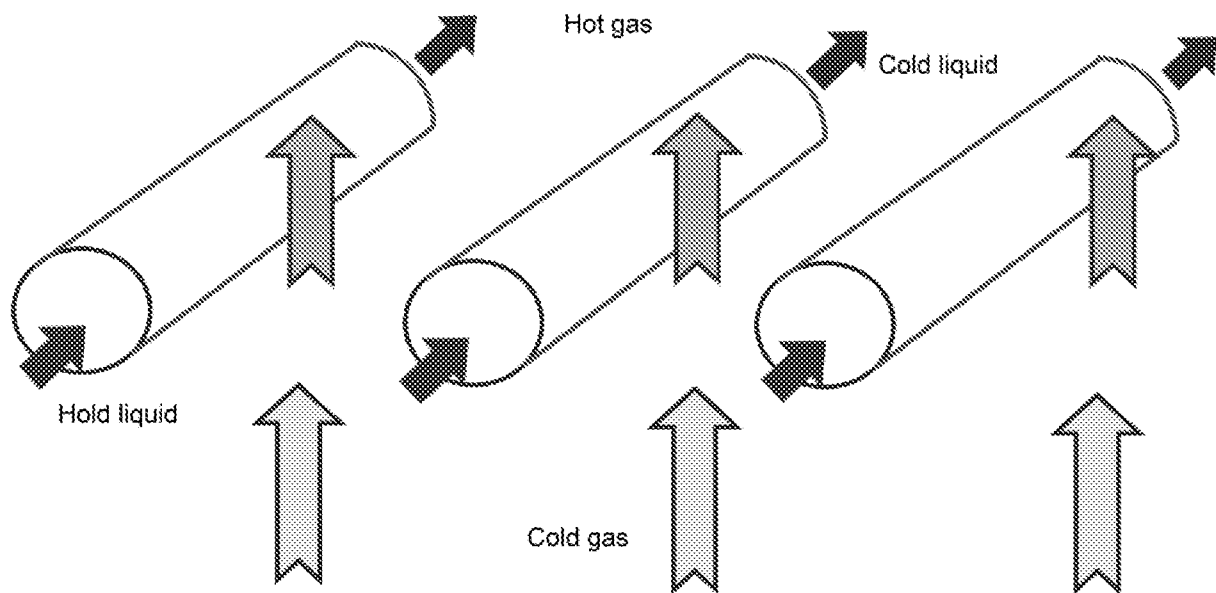


Figure 3

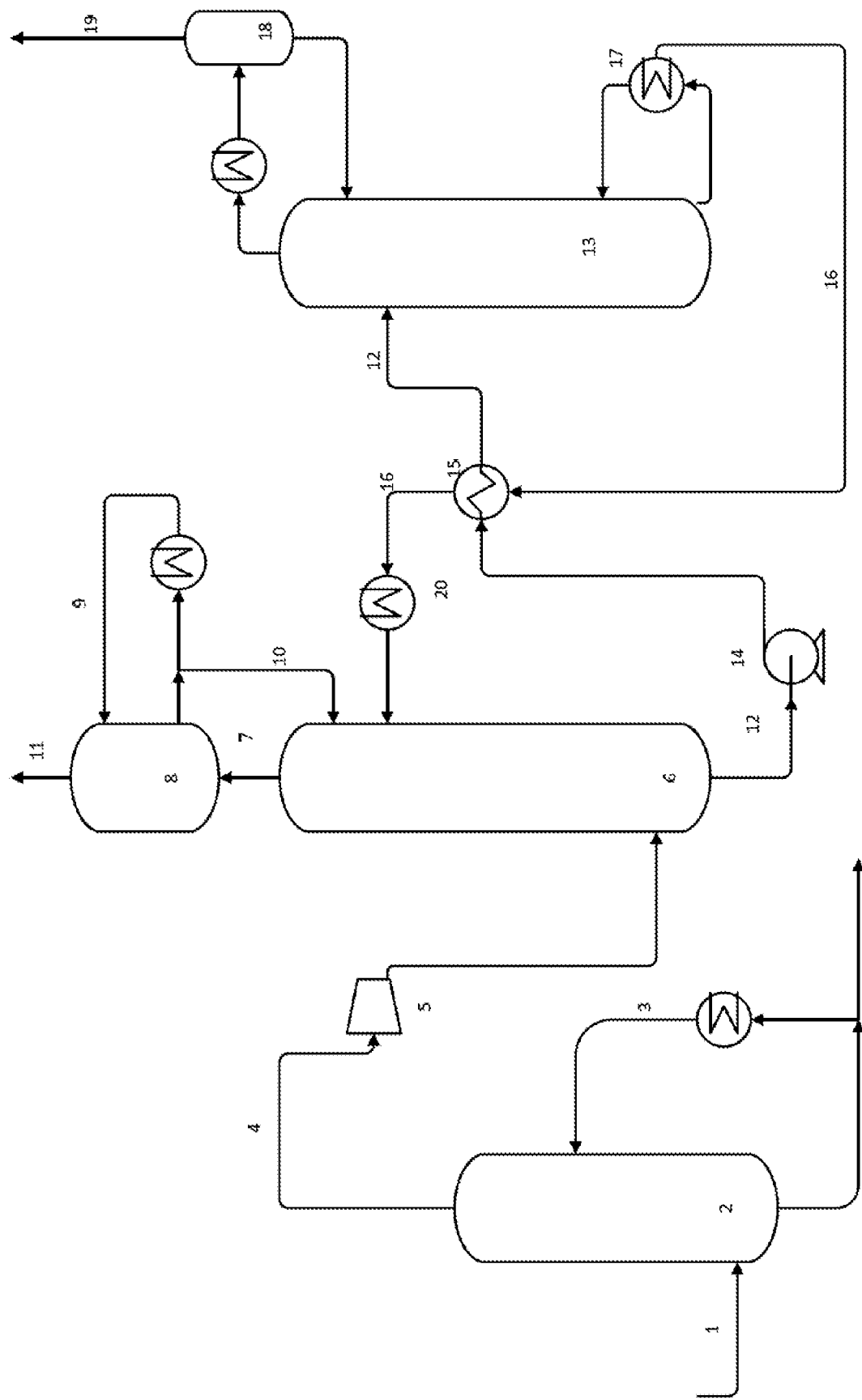


Figure 4

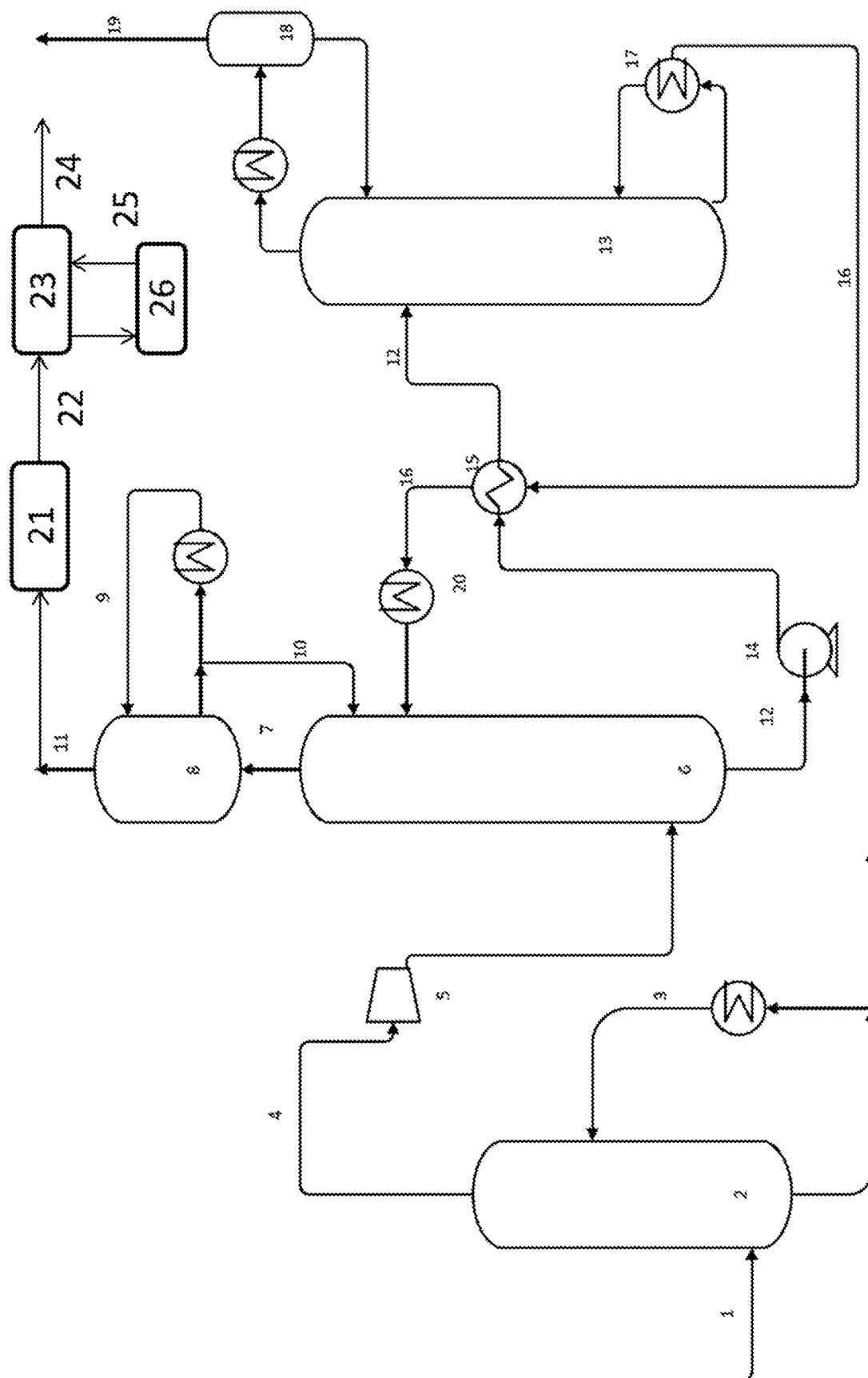


Figure 5

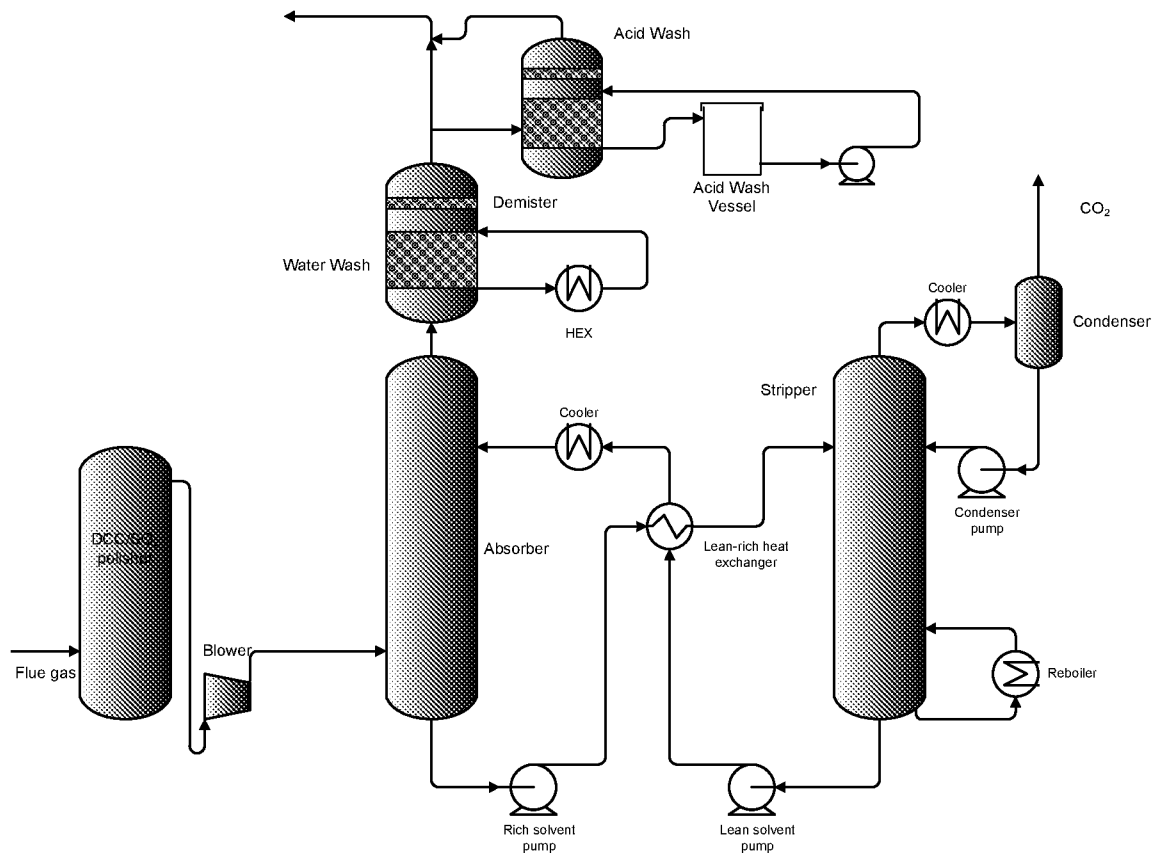


Figure 6A

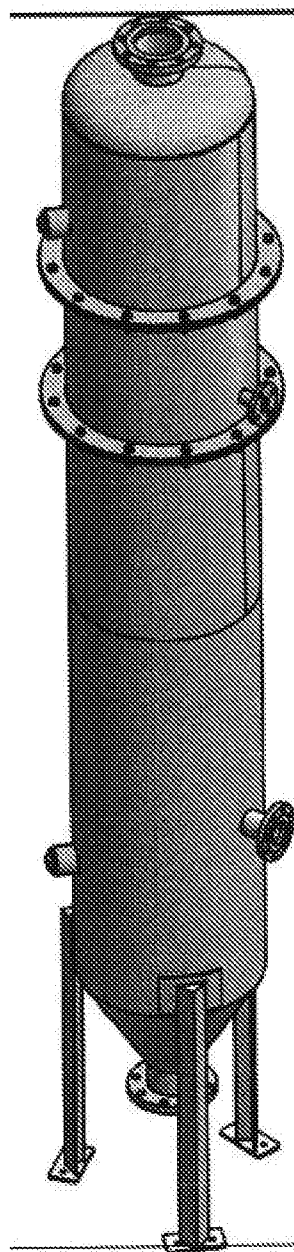
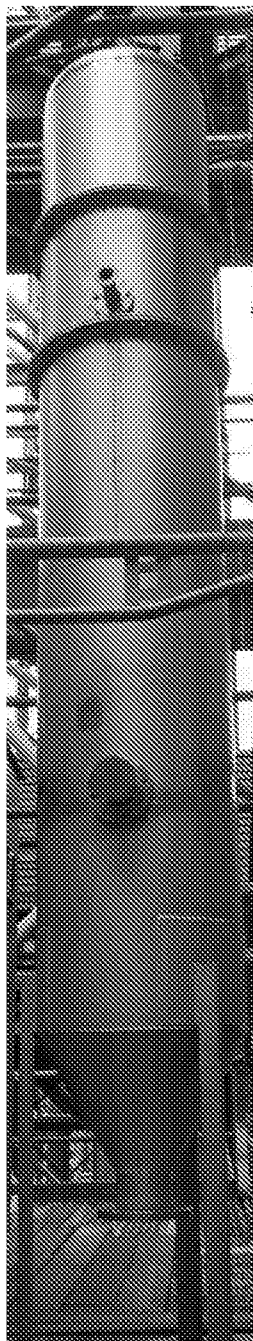


Figure 6B



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2013/050565

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14 B01D53/18 B01D47/12
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	JP 10 033938 A (MITSUBISHI HEAVY IND LTD) 10 February 1998 (1998-02-10) figure 1 -----	1-16, 19-25
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A	US 2011/146489 A1 (DUBE SANJAY KUMAR [US] ET AL) 23 June 2011 (2011-06-23) paragraphs [0027], [0028]; figure 1 ----- -/--	1



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 2013

Date of mailing of the international search report

07/10/2013

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INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2013/050565

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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Information on patent family members

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