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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 January 2014 (16.01.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/011041 A1

(51) **International Patent Classification**:
A62D 3/37 (2007.01) *A62D 101/26* (2007.01)
B01D 53/00 (2006.01) *A62D 1/06* (2006.01)
A62D 101/06 (2007.01)

(21) **International Application Number**:
PCT/NL2013/050521

(22) **International Filing Date**:
10 July 2013 (10.07.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
12175976.5 11 July 2012 (11.07.2012) EP

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

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

Published:

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

WO 2014/011041 A1

(54) **Title**: NITROSAMINE AND/OR NITRAMINES REDUCTION IN A LIQUID MEDIUM

(57) **Abstract**: The invention is directed to a method for reducing the content of compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines, in a liquid medium. More in particular, the invention is directed to a method for depleting a gas stream of a gaseous acid compound. The method of the invention for reducing the content of compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines in a liquid medium comprises contacting the liquid medium with a gas comprising hydrogen gas in a membrane contactor in the presence of a hydrogenation catalyst.

Title: Nitrosamine and/or nitramines reduction in a liquid medium

The invention is directed to a method for reducing the content of compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines in a liquid medium. More in particular, the invention is directed to a method for depleting a gas stream of a gaseous acid compound. The invention is further directed to the use of hydrogen gas for the reduction of nitrosamines and/or nitramines.

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 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 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 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 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, SO_2).

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 either have not been demonstrated at the scale necessary for power plant application, or they would not be cost effective.

In addition, there is a need for the removal of compounds comprising an N-N or N=N bond, such as nitrosamines, hydrazines, nitramines, azo- and azoxy-compounds from waste streams, such as from sites and laboratories in which these compounds are used, produced and/or manipulated, because many of these compounds are known or suspected carcinogens and are often toxic (see US-A-4 535 154).

Presently, there is on-going research into the capture and storage of carbon dioxide, resulting in various methods available for the removal of carbon dioxide from exhaust gas streams. The classical method used in carbon dioxide capture is reactive absorption followed by thermal regeneration of the absorbent liquid (Figueroa *et al.*, *Int. J. Greenhouse Gas Control* 2008, *2*(1), 9-20). Amines used to capture carbon dioxide from gaseous streams react to form water soluble compounds, which degrade on heating to release the carbon dioxide. Monoethanol amine is a regularly used base for the capture of carbon dioxide, with effort being put into developing other possibilities.

The use of amines in carbon dioxide gas capture, however, can potentially result in the formation of nitrosamines due to the presence of NO_x within the flue gas streams (Fostås *et al.*, *Energy Procedia* 2011, *4*, 1566-1573). The subsequent release of nitrosamines into the atmosphere constitutes a potential health risk, because nitrosamines have carcinogenic properties. These nitrosamines are highly soluble in water, which makes their extraction very difficult and which additionally increases the risk due to the potential of

polluting drinking water. Accordingly, current research efforts focus on investigation of the different mechanisms for the destruction of these nitrosamines to avoid release of these components into the environment. Moreover, in a recycle system of absorbent liquid comprising amines, the formation of nitrosamines can consume the amount of available amines for carbon dioxide capture, thereby reducing the carbon dioxide capture efficiency with time.

One of the most widely applied ways used to degrade nitrosamines is by using ultraviolet irradiation (photolytic degradation). The nitrogen-oxygen double bond present in nitrosamines is susceptible to ultraviolet radiation and, as such, when passing the liquid through an ultraviolet illuminated chamber these bonds are broken. However, there are reports indicating that the effect of ultraviolet irradiation on nitrosamines is pH dependent with better performance under acidic conditions. Aside from the pH effect, the effect of ultraviolet radiation on a solution is also dependent on turbidity. Thus, a clear solution stream is necessary for enhanced nitrosamine degradation. In addition, ultraviolet radiation is not effective in many solvent applications, due to absorption by other components.

Some other methods used in the destruction of nitrosamines are catalytic hydrogenation (in which hydrogen gas is mixed with the liquid containing nitrosamines), photocatalytic oxidation and chemical oxidation. It is known from US-A-2 979 505 that hydrogen gas can be used to reduce nitrosamines in the presence of metallic catalysts like iron, nickel and palladium. The hydrogen gas is used to disrupt the nitrogen-oxygen double bond with the formation of the corresponding amine. Photocatalytic oxidation involves the use of titanium dioxide to oxidise the nitrosamine with the formation of amines and potentially ammonia. In chemical oxidation, the nitrosamine is treated with high oxygen containing compounds and as such is also oxidised to yield the less harmful amines.

GB-A-797 483 describes a process for producing a hydrazine which comprises reacting a nitrosamine with hydrogen at a pressure above atmospheric pressure and in the presence of a specific particulate catalytic material. The reactants were charged into a pressure vessel and agitated. Although a solvent is not necessary, in that case at least one reactant is in the liquid phase.

EP-A-2 243 542 describes an adsorption process using a membrane. Reducing the content of compounds comprising an N-N or N=N bond in a liquid medium is not disclosed.

EP-A-2 311 545 describes a method for absorption of acid gases using an absorbent liquid comprising an amine. Reducing the content of compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines in a liquid medium is not disclosed.

US-A-4 535 154 describes reduction of compounds comprising an N-N or N=N bond comprising contacting the compound with a hydroxide solution and a nickel-aluminium alloy.

There remains a need in the art to improve the carbon dioxide capture techniques, in particular in respect of nitrosamines control.

An objective of the invention is therefore to provide a process for reducing the content of compounds comprising an N-N or N=N bond, in particular nitrosamines in a liquid medium.

Another objective of the invention is to provide a process for reducing the content of nitrosamines in an absorbent liquid, in particular an absorbent liquid used for capturing carbon dioxide from an exhaust gas.

A further objective of the invention is to efficiently capture carbon dioxide from exhaust gases while minimising the amount of release nitrosamines to the environment.

Yet a further objective of the invention is to improve the quality of off gases that are released during post combustion carbon dioxide capture.

Yet another object of the invention is to improve the long term efficiency of a continuous carbon dioxide capture using an absorption liquid recycle.

The inventors found that one or more of these objectives can, at least in part, be met by performing reductive destruction of nitrosamines in an absorbent liquid with hydrogen gas using a membrane contactor.

Accordingly, in a first aspect the invention is directed to a method for reducing the content of compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines in a liquid medium, comprising contacting the liquid medium with a gas comprising hydrogen gas in a membrane contactor in the presence of a hydrogenation catalyst.

The invention integrates advantageous properties of a membrane contactor (such as a high surface to volume ratio) with the catalytic reduction of nitrosamines (hydrogenation). It was found that this combination is desirable for applications, such as post combustion carbon dioxide capture. In accordance with the invention, where the liquid medium is contacted with hydrogen gas in a membrane contactor, the hydrogen gas phase can advantageously be kept separate from the liquid phase. This allows for minimising explosive risks, as well as minimising risks of hydrogen emission. In addition, the invention reduces absorption liquid degradation as a result of nitrosamine formation. Amines that are converted into nitrosamines upon reaction with NO_x are converted back into the corresponding amines which can again be used for capturing carbon dioxide.

The terms “lean” and “rich” as used herein are not meant as precise indicators of the amount of gaseous acid compounds in the gas or in the solution, but only indicate the relative amount of the gaseous acid compounds therein. For example, a rich solution contains more gaseous acid compound than a lean solution.

The term “nitrosamine” (also known as nitroso amines) as used herein is meant to refer to all compounds having structural formula

RN(—R')—N=O, wherein R and R' may be the same or different residues. Some non-limitative examples of nitrosamines include *N*-nitrosonornicotine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone, *N*-nitrosodimethylamine, *N*-nitrosodiethylamine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol, *N*-nitrosoanabasine, *N*-nitrosoanatabine, *N*-nitrosarcosin, *N*-nitroso(2-hydroxyethyl)glycine, nitrosopyrrolidine, nitrosomorpholine, nitrosopiperidine, and nitrosoproline. Nitrosamines can be formed when amines are in contact with NO_x species (such as NO, NO_2, N_2O_3, N_2O_4 and HNO_2). Typically, nitrosamines form when secondary amines react with oxides of nitrogen. However, also primary amines form nitrosamines, but they are unstable and quickly decompose. Tertiary amines typically do not form nitrosamines.

The term "nitramine" (also known as nitro amines) as used herein is meant to refer to all compounds having structural formula RN(—R')—NO_2, wherein R and R' may be the same or different residues. Some non-limitative examples of nitramines include benzyl nitramine, dimethylnitramine, diethylnitramine, methylnitramine, and N-nitromorpholine. Also nitramines can be formed when amines are in contact with NO_x species.

The term "compounds comprising an N-N or N=N bond" as used herein is meant to refer to all compounds comprising at least two nitrogen atoms bonded together within a molecule by a single or double covalent bond. This includes nitrosamines, hydrazines, nitramines, azo- and azoxy compounds. An N-N bond refers to a single covalent bond between nitrogen atoms and an N=N bond to a double covalent bond between nitrogen atoms.

Compounds comprising an N-N or N=N bond include compounds having the general formula R_1-(R_2-)NR_3,
wherein R_1 and R_2 are independently selected from hydrogen or any substituted or unsubstituted individual organic groups, (including ring compounds), such as methyl, ethyl, propyl, phenyl. R_1 and R_2 can also be bonded together to form a ring with the nitrogen, forming, for example,

pyrrolidines, piperidines and morpholines. Preferably R_1 and R_2 are independently selected from hydrogen, alkyl compounds of 1 to 6 carbon atoms, aromatic groups and groups of 1 to 6 carbon atoms containing in addition nitrogen or oxygen atoms. R_3 can be NH_2 (hydrazines), NHR, RNR, NH, NR (azo compounds), N(O)H, N(O)R (azoxy compounds), NO (nitrosamines), or NO_2 (nitramines), preferably NH, NH_2, NO, NO_2 or N(O)H, wherein R is an organic group. Herein an N-N or N=N bond is between the nitrogen atom and a nitrogen atom comprised in R_3.

The liquid medium in the method of the invention is preferably an aqueous medium. For example, the liquid medium can be an aqueous waste stream from a process wherein compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines are used or produced or a waste stream that is suspected or known to be contaminated with such compounds. Suitably, the liquid medium can be an aqueous absorbent liquid, an aqueous condensate, or an aqueous wash liquid or the like.

In a preferred embodiment, the liquid medium is an aqueous absorbent liquid for absorption carbon dioxide capture from a gas stream. Such absorbent liquids are known in the art and can be used in regenerative absorption/stripping systems, having an absorption stage and a stripping stage. In the absorption stage, the gas stream to be treated containing carbon dioxide to be removed, is brought into contact with the absorbent liquid in an absorber under conditions of pressure and temperature such that the absorbent solution absorbs virtually all the carbon dioxide. Typically, the purified gas emerges at the top of the absorber and at the bottom of the absorber, the absorbent liquid enriched with carbon dioxide (*viz.* the "rich absorbent liquid") is drawn off and directed to a stripper, where the rich absorbent liquid is regenerated. The produced carbon dioxide gas is collected and regenerated absorbent liquid (*viz.* "lean absorbent liquid") is recycled back to the absorber.

The absorbent liquid preferably comprises an amine. The amine content in the absorbent liquid can be in the range of 1-10 M, such as in the range of 2-8 M, or in the range of 4-6 M. Alkanolamines, such as aqueous monoethanolamine (MEA), have been successfully applied as absorbent liquids in absorption and stripping processes for the capture of acid gases (such as carbon dioxide and hydrogen sulphide) from flue gas, natural gas, synthesis gas and other gases. Also other amines have been proposed for this purpose, such as tertiary amines.

Amino acids have been considered as alternatives to amines for carbon dioxide capture. They are believed to be more resistant to degradation by oxygen, and are considered less volatile due to the negative charge on the carboxylate group under typical carbon dioxide capture pH conditions. However, the tendency of amino acids to convert into nitrosamines and/or nitramines may be similar to, or even greater than that of amines. The electron-donating nature of the carboxylate group may enhance nitrosation of the α-terminal amine group. In the context of the present invention amino acids are considered to be specific amines, namely amines further comprising a carboxylic acid group and a side chain.

Preferably, the content of compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines, in a liquid medium is initially 0.01 g/l or more, such as 0.1 g/l or more, typically 1 g/l or more, or even 5 g/l or more. The content of compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines in a liquid medium is initially typically less than 50% w/w.

The gas comprising hydrogen gas can suitably have a hydrogen content in the range of 20-100 vol.%, such as 40-100 vol.%, 60-100 vol.% or 80-100 vol.%. Preferably, the gas comprising hydrogen gas consists of hydrogen gas.

In accordance with the invention, the liquid medium is contacted with the gas comprising hydrogen gas in a membrane contactor. A membrane

contactor is a device that allows a gaseous phase and a liquid phase to come into direct contact with each other, for the purpose of mass transfer between the phases, without dispersing one phase into the other. The membrane essentially acts as a support and/or separation between the gas and liquid phases that allows them to interface at the pore. Typically, the membrane contactor comprises a hydrophobic membrane which does not allow liquid water to pass through the pore into the gas side of the membrane. It is, however, also possible to use a hydrophilic membrane that has been equipped with a hydrophobic layer or coating. The membranes preferably have porosity greater than 70 %, more preferably greater than 80 %. Furthermore, the average pore size of the pores in the membrane as measured by the bubble point method is preferably 0.01 μm or more, more preferably 0.05 μm or more, even more preferably between 0.06 and 0.3 μm, such as between 0.07 and 0.1 μm. The water contact angle of the membrane is preferably 100° or more, such as 115° or more, 150° or more. Wetting pressure (liquid-entry pressure) of the membrane is preferably at least 1 bar, more preferably at least 1.5 bar.

Suitable membranes for use in the membrane contactor include commercially available membranes made of materials such as polytetrafluorethylene, polyvinylidene fluoride, polypropylene, polyethylene, and the like. The porous membranes can be laminated with other materials (*e.g.* non woven materials of polypropylene, polyethylene terephthalate *etc.*), which protect the membranes against abrasion, and/or give mechanical support. So-called asymmetric microfiltration membranes made of materials such as polyethersulphone, polysulphone, polyacrylonitrile, polyamides, *etc.* can also be used. In this context it is preferably to make the surface of these membranes completely or partially additionally hydrophobic, for example by means of a coating or other surface modification. The membrane can be any type of membrane, such as a planar membrane, a tubular membrane, or a hollow fibre membrane. Preferably, hollow fibre membranes are employed. The membrane may optionally be applied in spirally wound configuration.

In an embodiment, the membrane contactor comprises a metallic and/or a ceramic membrane, for example porous steel and porous Al_2O_3 membranes. Such membranes are advantageous in view of their temperature stability and chemical resistance. The internal surface of a metallic and/or ceramic membrane is preferably rendered completely or partially hydrophobic by coating, such as with fluorinated alkyl trichlorosilane.

Particularly preferred membranes are porous ceramic membranes, polymeric membranes, and dense membrane that allow hydrogen permeation through the membrane.

The hydrogen pressure at the gas side of the membrane contactor can be up to 10 bara, such as in the range of 1-10 bara, or in the range of 2-8 bara. At the liquid side of the membrane contactor, the liquid pressure may equally be up to 10 bara, such as in the range of 1-10 bara, or in the range of 2-8 bara. It is preferred that the hydrogen pressure and the liquid pressure are both above atmospheric pressure. In addition, it is preferred that the pressure at the liquid side of the membrane contactor is higher, preferably by at least 1 bar, than the pressure at the gas side of the membrane contactor.

The temperature at which the membrane contactor is operated may vary on the application type and can, for instance, range from 30 °C to 150 °C. For carbon dioxide capture applications, the operation temperature of the membrane contactor typically depends on the type of absorbent liquid. For example, when the method of the invention is used for reducing the nitrosamine content in a rich absorbent liquid, the operation temperature can be in the range of 30-70 °C, such as in the range of 40-60 °C, or about 50 °C. When the method of the invention is used for reducing the nitrosamine content in a lean absorbent liquid, the operation temperature can be in the range of 100-140 °C, such as in the range of 110-130 °C, or about 120 °C.

The hydrogenation catalyst preferably comprises one or more selected from the group consisting of iron, nickel, platinum and palladium.

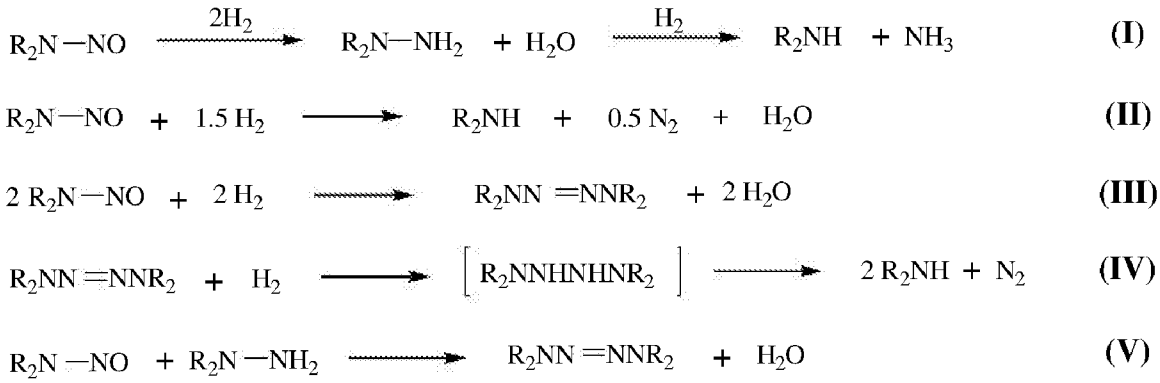
More preferably, the hydrogenation catalyst comprises palladium, and most preferably, the hydrogenation catalyst is palladium.

Optionally, the hydrogenation catalyst may be supported by a support material. Such materials are commonly known in the art. Some examples include active carbon, alumina, calcium carbonate, and barium sulphate.

Suitably, the hydrogenation catalyst can be coated on at least one membrane in the membrane contactor, *e.g.* in the form of a hydrogenation catalyst layer. Such a layer may, for instance, have a thickness up to 30 nm, such as in the range of 1-25 nm. The application of such a coating to a membrane can be performed using conventional techniques, including deposition by immersion in a dissolved catalyst solution, followed by drying and calcination. If the hydrogenation catalyst is present as a coating, then it is preferred that the coating is permeable for gas and/or liquid. Hence, it is preferred that a layer of hydrogenation catalyst is porous. Further, it is preferred that such a layer of hydrogenation catalyst is present at the liquid side of the membrane in the membrane contactor. In other words, it is preferred that the layer of hydrogenation catalyst is in contact with the liquid medium. Furthermore, in a preferred embodiment, the layer of hydrogenation catalyst is permeable at least for hydrogen gas.

A schematic illustration of an exemplary embodiment of the process of the invention (which should not be interpreted as limitative to the scope of the invention) for the reduction of compounds comprising an N-N or N=N bond, in particular a nitrosamine or nitramine is shown in figure 1. This figure shows a cross-section of a hollow fibre, which has liquid medium in the lumen and a gas comprising hydrogen gas on the shell side exerting a hydrogen pressure on the shell side of the hollow fibre (indicated with the solid arrows). The lumen of the hollow fibre is coated with a palladium coating indicated with the dashed arrow.

During operation of the method of the invention the content of compounds comprising an N-N or N=N bond, in particular nitrosamines and/or nitramines in the liquid medium is reduced as a result of the compounds, in particular nitrosamines and/or nitramines being reductively destructed by hydrogen. Typically, this process yields the corresponding amines. Various reactions have been proposed for this reduction of nitrosamines as depicted in schemes (I)-(V) below.



The destructive hydrogenation of nitramines and other compounds comprising an N-N or N=N bond, has been suggested to occur via a similar route (see for instance, US-A-4 535 154).

In an embodiment of the invention, the content of amines in the liquid medium is increased during performance of the method. This can advantageous, in particular when the compounds comprising an N-N or N=N bond, in particular nitrosamines, in the liquid medium are the result of a conversion of amines. In such a situation, the method of the invention allows for the original amines to be regenerated.

In a special embodiment of the invention, the liquid medium is an aqueous absorbent liquid for absorption of a gaseous acid compound (such as carbon dioxide) from a gas stream.

Accordingly, in an aspect the invention is directed to a method for depleting a gas stream of a gaseous acid compound, comprising the steps of:

i) contacting the gas stream with an absorbent liquid lean in said gaseous acid compound, said absorbent liquid comprising an amine, thereby obtaining absorbent liquid rich in said gaseous acid compound and a gas stream depleted of said gaseous acid compound; and

ii) subjecting said rich absorbent liquid to a regeneration step, thereby regenerating lean absorbent liquid under separation of gaseous acid compound,

wherein said method further comprises a step wherein the content of nitrosamines and/or nitramines in the absorbent liquid is reduced in accordance with a method of the invention.

This special embodiment of the invention preferably is a continuous process, wherein at least part of the regenerated lean absorbent liquid is recycled to step i) for contacting with the gas stream. Accordingly, it is preferred that a continuous flow of the gas stream is contacted with lean absorbent liquid in an absorption stage (comprising one or more absorbers) and that rich absorbent liquid is continuously regenerated in a regeneration stage (comprising one or more strippers), after which regenerated lean absorbent liquid is recycled to the absorption stage. Advantageously, degradation of amines in the absorbent liquid by reaction with NO_x is overall reduced (or even prevented).

The step of reducing the content of nitrosamines and/or nitramines in the absorbent liquid can be performed at different locations in the process. For instance, the content of nitrosamines and/or nitramines in the absorbent liquid rich in the gaseous acid compound can be reduced. This is actually preferred, since it allows operating the membrane contactor at a relatively low temperature, thereby reducing energy costs and widening the scope of possible membrane materials. Typically, the absorbent liquid will be rich in gaseous acid compound downstream an absorption stage and upstream a regeneration stage. However, it is also possible to reduce the content of nitrosamines and/or nitramines in the absorbent liquid lean in the gaseous acid compound.

Typically, the absorbent liquid will be lean in gaseous acid compound downstream a regeneration stage and upstream an absorption stage. Naturally, also combinations are possible.

In addition, it is possible to apply the method of the invention to a wash liquid (preferably an aqueous wash liquid), for instance, to remove nitrosamines and/or nitramines from the purified gas stream. Accordingly, in another aspect the invention is directed to a method for depleting a gas stream of a gaseous acid compound, comprising the steps of:

i) contacting the gas stream with an absorbent liquid lean in said gaseous acid compound, said absorbent liquid comprising an amine, thereby obtaining absorbent liquid rich in said gaseous acid compound and a gas stream depleted of said gaseous acid compound; and

ii) subjecting said rich absorbent liquid to a regeneration step, thereby regenerating lean absorbent liquid under separation of gaseous acid compound,

wherein said method further comprises a step wherein said gas stream depleted of said gaseous acid compound is washed with an wash liquid and a step wherein the content of nitrosamines and/or nitramines in the wash liquid is reduced in accordance with the method of the invention.

In the above methods, the gaseous acid compound can suitably comprise one or more selected from the group consisting of CO_2, SO_2, SO_2 NO_2 HF, H_2S, and HCl. Preferably, the gaseous acid compound at least comprises carbon dioxide.

The gas stream can be a flue gas or an exhaust gas. In an embodiment the gas stream is an exhaust gas from a fuel combustion step. One or more gaseous acid compounds are comprised in the exhaust gas. The gas stream can comprise an amount of gaseous acid compounds (such as carbon dioxide) of 18 vol.% or less, such as 15 vol.% or less, 10 vol.% or less, 8 vol.% or less, or even 5 vol.% or less. The amount of gaseous acid compounds may suitably be in the range of 0.5-18 vol.%, such as in the range of

10-15 vol.%, in the range of 5-10 vol.%, or in the range of 0.5-5 vol.%. The gas stream can typically comprise further components such as water, nitrogen and/or oxygen.

Figure 2 shows an illustration of an example of the process for the reduction of nitrosamine and/or nitramine for a post combustion carbon dioxide capture process. As mentioned before, the hydrogenation can be applied at a number of locations within the process, such as the water wash section of the absorber column to remove nitrosamines within the off gas. It can also be applied in the aqueous stream exiting or entering the absorber to reduce the nitrosamines and/or nitramines within the solvent stream. In figure 2, the unit is applied on the solvent stream exiting the absorber. The aqueous stream is passed through a membrane contactor, where it is contacted with the gas comprising hydrogen gas in the presence of a hydrogenation catalyst. For example, the aqueous stream can pass through the lumen of hollow fibre membranes, which are coated with layer of a hydrogenation catalyst, while on the other side of the membrane fibres a hydrogen gas pressure is applied. As such, the hydrogen is in contact with the palladium layer which is in contact with the solvent. Due to the presence of the catalyst, the nitrosamine and/or nitramine within the aqueous solvent is reduced in the membrane contactor yielding the amine.

In yet a further aspect, the invention relates to use of hydrogen gas for the reduction of nitrosamines and/or nitramines in an exhaust gas, preferably an exhaust gas from a fuel combustion step.

In a further aspect, the liquid medium comprises an aqueous waste stream comprising compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines. Reduction of the concentration of these compounds in waste streams is desired as many of these compounds are known or suspected carcinogens and are often toxic. The waste stream is typically a continuous waste stream from a continuous process.

The invention will now be further illustrated by means of the following examples.

Examples

A solution containing 1 g/l of nitrosodiethanolamine (NDELA) and 300 g/l of monoethanolamine (MEA) was placed in a flask covered with foil and pumped around a palladium coated ceramic membrane contactor module unit for 6 hours. A gas pressure was applied on the other side of the membrane contactor module and contact between the gas and liquid was ensured. Figure 3 shows a photo of the experimental setup used for the experiments.

Initially, the experiments were carried out with nitrogen gas as a comparative experiment and samples were withdrawn at regular intervals and analysed with High Performance Liquid Chromatography (HPLC).

Following these experiments, the nitrogen gas was replaced with hydrogen gas to observe an effect the level of the NDELA in the liquid.

Figure 4 shows the experiments carried out in the presence of hydrogen compared to the experiments carried out in the presence of nitrogen (○ = nitrogen gas; ■ = hydrogen gas). As clearly shown in figure 4, in the presence of hydrogen there is a significant reduction in the concentration of nitrosamines (NDELA) in the aqueous stream. On the other hand, when the liquid is exposed to nitrogen gas, there is no evident reduction in the concentration of the NDELA with time. The samples were also analysed with Liquid Chromatography – Mass Spectrometry (LC-MS) to determine if there are side products (hydrazines) formed and the analysis showed that the reaction product is the reduced amine, *i.e.* diethanolamine.

Claims

1. Method for reducing the content of compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines, in a liquid medium, comprising contacting the liquid medium with a gas comprising hydrogen gas in a membrane contactor in the presence of a hydrogenation catalyst.

2. Method according to claim 1, wherein the liquid medium is an aqueous medium.

3. Method according to claim 2, wherein said aqueous medium is an aqueous absorbent liquid or an aqueous wash liquid.

4. Method according to any on of claims 1-3, wherein said membrane contactor comprises a hollow fibre membrane.

5. Method according to any one of claims 1-4, wherein said membrane contactor comprises a metallic and/or a ceramic membrane.

6. Method according to any one of claims 1-5, wherein said hydrogenation catalyst is a metallic catalyst.

7. Method according to claim 6, wherein said metallic catalyst comprises one or more selected from the group consisting of iron, nickel, platinum and palladium.

8. Method according to claim 7, wherein said hydrogenation catalyst comprises palladium.

9. Method according to claim 8, wherein said hydrogenation catalyst is palladium.

10. Method according to any one of claims 1-9, wherein said hydrogenation catalyst is supported on a support.

11. Method according to claim 10, wherein said support comprises one or more selected from the group consisting of active carbon, alumina, calcium carbonate, and barium sulphate.

12. Method according to any one of claims 1-11, wherein said membrane contactor comprises at least one membrane coated with said hydrogenation catalyst.

13. Method according to any one of claims 1-12, wherein the content of amines in said liquid medium is increased.

14. Method according to any one of claims 1-13, wherein said liquid medium is an aqueous absorbent liquid for absorption of carbon dioxide from a gas stream.

15. Method for depleting a gas stream of a gaseous acid compound, comprising the steps of:

i) contacting the gas stream with an absorbent liquid lean in said gaseous acid compound, said absorbent liquid comprising an amine, thereby obtaining absorbent liquid rich in said gaseous acid compound and a gas stream depleted of said gaseous acid compound; and

ii) subjecting said rich absorbent liquid to a regeneration step, thereby regenerating lean absorbent liquid under separation of gaseous acid compound,

wherein said method further comprises a step wherein the content of nitrosamines and/or nitramines in the absorbent liquid is reduced in accordance with the method of any one of claims 1-14.

16. Method according to claim 15, wherein said step of reducing the content of nitrosamines and/or nitramines in the absorbent liquid is performed on absorbent liquid rich in said gaseous acid compound.

17. Method according to claim 15 or 16, wherein said step of reducing the content of nitrosamines and/or nitramines in the absorbent liquid is performed on absorbent liquid lean in said gaseous acid compound.

18. Method for depleting a gas stream of a gaseous acid compound, comprising the steps of:

i) contacting the gas stream with an absorbent liquid lean in said gaseous acid compound, said absorbent liquid comprising an amine, thereby obtaining absorbent liquid rich in said gaseous acid compound and a gas stream depleted of said gaseous acid compound; and

ii) subjecting said rich absorbent liquid to a regeneration step, thereby regenerating lean absorbent liquid under separation of gaseous acid compound,

wherein said method further comprises a step wherein said gas stream depleted of said gaseous acid compound is washed with an wash liquid and a step wherein the content of nitrosamines and/or nitramines in the wash liquid is reduced in accordance with the method of any one of claims 1-14.

19. Method according to any one of claims 15-18, wherein said gaseous acid compound comprises one or more selected from the group consisting of CO_2, SO_2, HF, H_2S, and HCl.

20 Method according to any one of claims 15-18, wherein said gaseous acid compound comprises CO_2.

21. Method according to any one of claims 1-20, wherein said liquid medium comprises an aqueous waste stream comprising compounds comprising an N-N or N=N bond, preferably nitrosamines and/or nitramines.

Figure 1

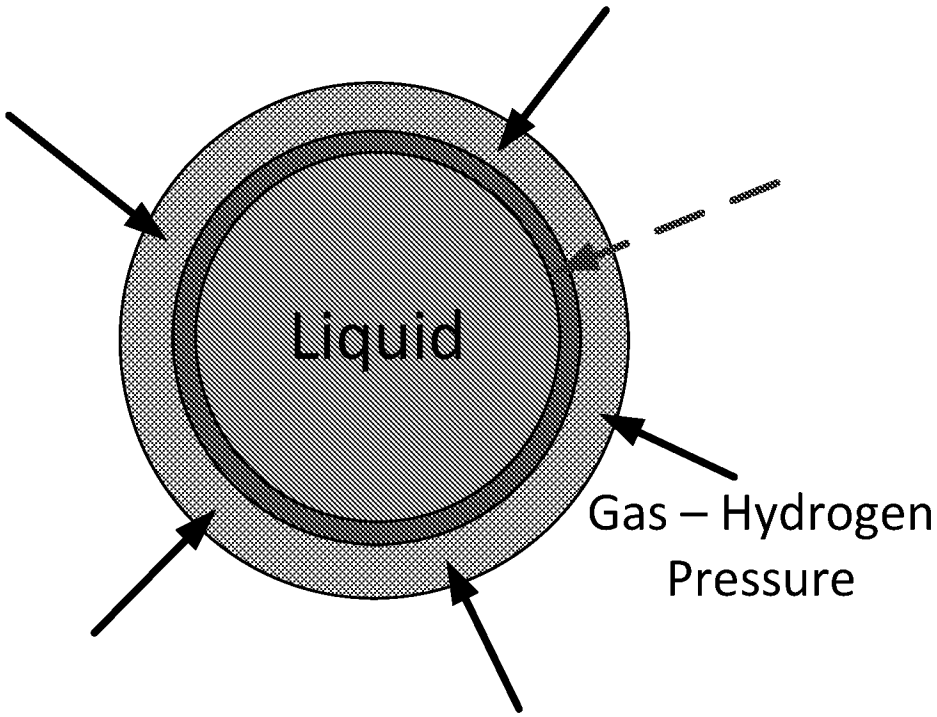


Figure 2

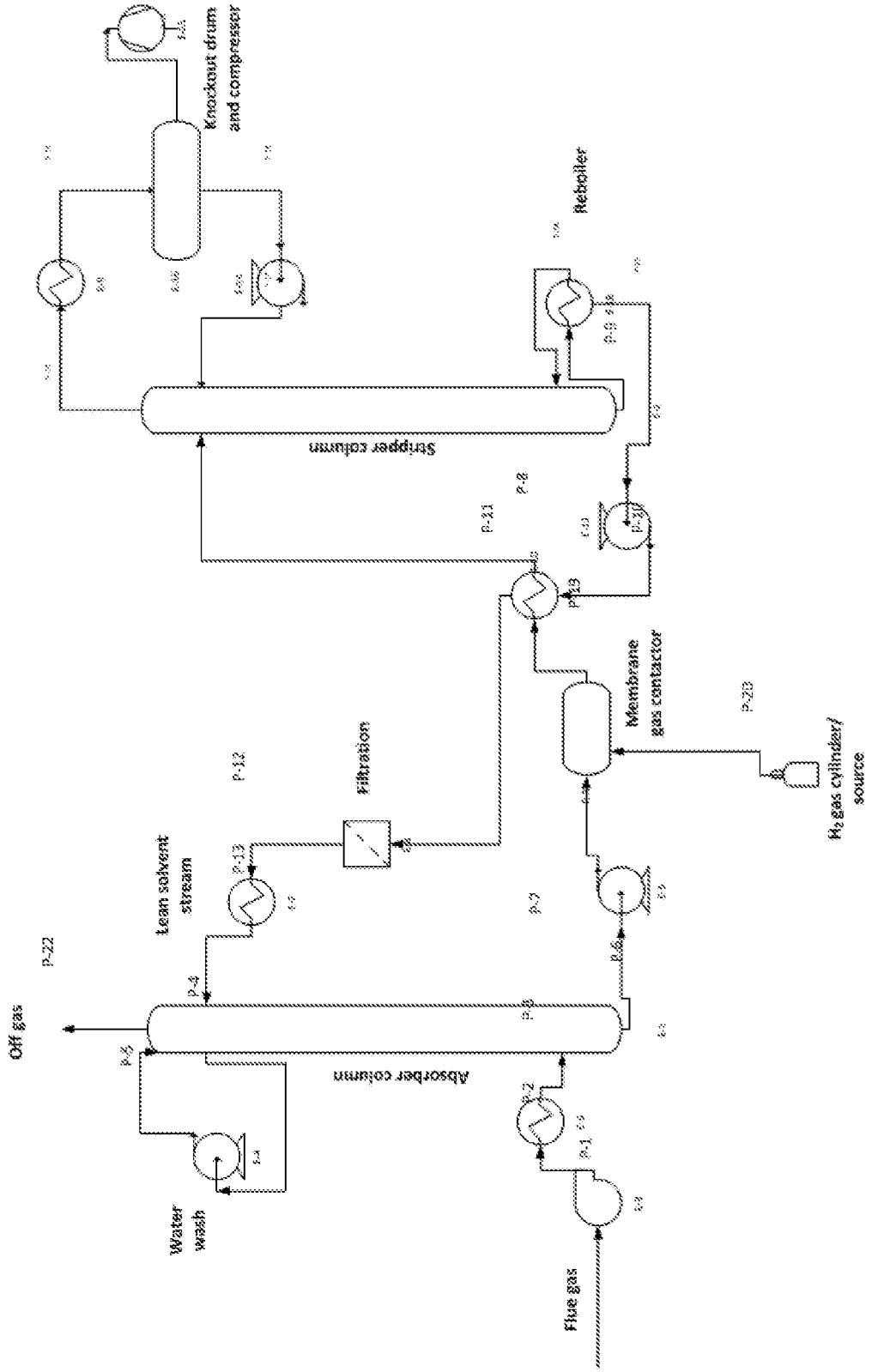

Knockout drum and compressor
Reboiler
Stripper column
Membrane gas contactor
Filtration
Lean solvent stream
Absorber column
Off gas
Water wash
Flue gas
H2 gas cylinder/ source

Figure 3

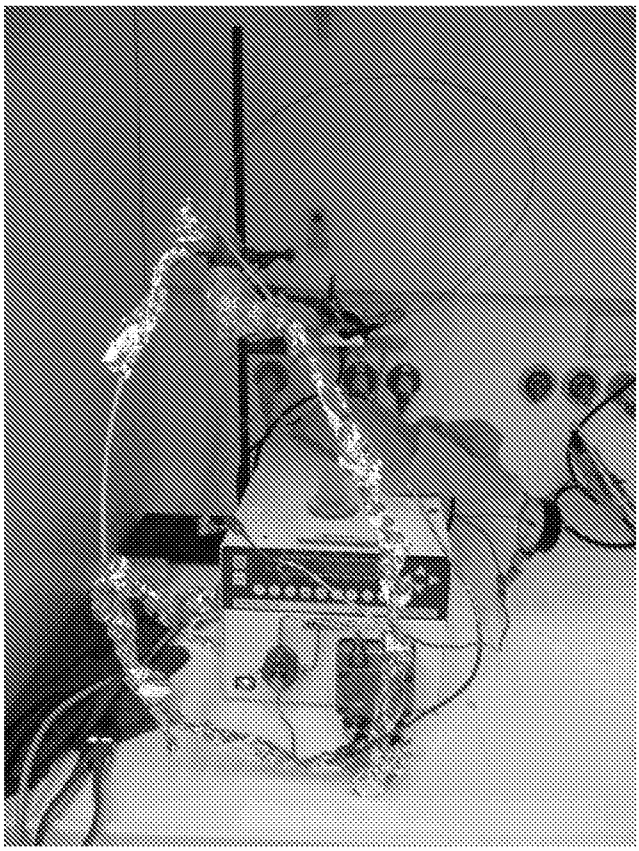
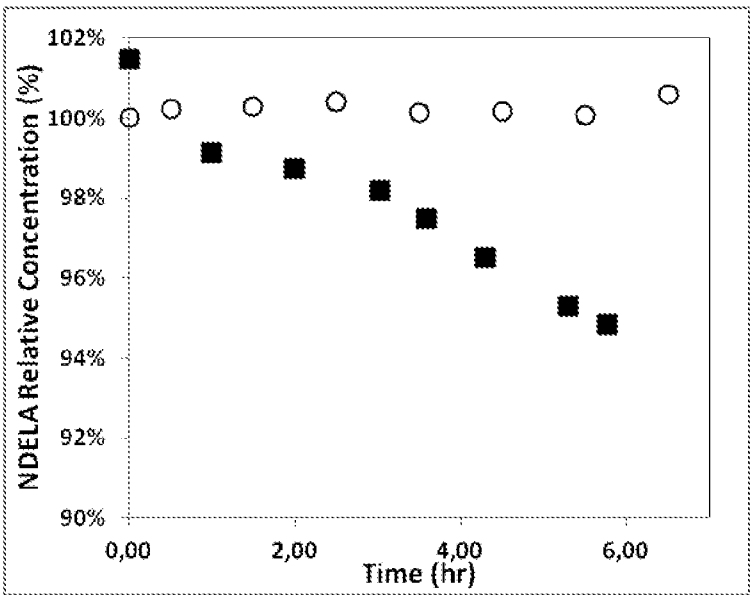


Figure 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2013/050521

A. CLASSIFICATION OF SUBJECT MATTER
INV. A62D3/37 B01D53/00
ADD. A62D101/06 A62D101/26 A62D1/06

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)
A62D C02F B01D B09C

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 979 505 A (TUEMMLER WILLIAM B ET AL) 11 April 1961 (1961-04-11) cited in the application claims	1-21
A	EP 2 243 542 A1 (TNO [NL]) 27 October 2010 (2010-10-27) cited in the application paragraphs [0042] - [0051]	15-21
A	GB 797 483 A (HERCULES POWDER CO LTD) 2 July 1958 (1958-07-02) cited in the application claims	1
A	US 4 535 154 A (KEEFER LARRY K [US] ET AL) 13 August 1985 (1985-08-13) cited in the application	1

-/--

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

[X] See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2013	14/10/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2013/050521

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 311 545 A1 (TNO [NL]) 20 April 2011 (2011-04-20) cited in the application claims -----	18-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2013/050521

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