

**INTEGRATED OPTIMIZED MEMBRANE-BASED HORIZONTAL BOXED LIQUID
SOLVENT CARBON CAPTURE SYSTEM FOR POST-COMBUSTION EMISSIONS**

FIELD OF THE INVENTION

The present invention is directed to a system for carbon capture, more specifically, a
5 system for the carbon capture from post-combustion emissions.

BACKGROUND OF THE INVENTION

Carbon capture from high pressure post-combustion exhaust streams is well established.
For low pressure exhaust streams such as internal combustion engines using natural gas and/or
diesel to power processing equipment limited economical commercial applications for carbon
10 capture are available. A few commercial applications for Carbon capture on combusted coal are
practiced though. In all of the above cases, the cost of carbon capture is still a challenge even
with increasing carbon taxes. This novel concept presented is a membrane based horizontal
boxed liquid solvent carbon capture system to reduce the cost of carbon capture on low pressure
streams by removing/minimising the need for a water wash step and reclaiming of solvent in
15 addition to reducing the size of both the carbon capture and solvent regeneration steps while
incorporating a method and apparatus that only requires thin-walled vessels for the carbon
capture step and reduces the number of vessel walls by sharing walls between processes. By
applying the novel concept, the cost of carbon capture processes will become even more
competitive with upcoming carbon taxes in Canada (2030 onward).

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Patent US9291083 teaches a membrane separation system to reduce emissions of target
emission gasses such as sulfur oxides, nitrogen oxides, and carbon oxides from combustion
exhaust from sources such as marine engines. The membrane separation system consists of an

absorption system containing semi-permeable hollow fiber membranes through which is circulated a liquid absorbent. Exhaust gases contact the exterior surface of the membranes and the target gasses selectively permeate the membrane wall and are absorbed by the liquid carrier(s) within the bore and thereby are removed from the exhaust stream. The invention disclosed in

5 Patent US9291083 does not include embodiments having solvent on the outside of the membrane walls and gases within the membranes. Patent US9291083 does not disclose combining multiple processes into a single vessel and it discloses a membrane where the material is ceramic whereas the present invention uses hydrophobic plastic for the hollow fibre membrane with absorption the key driving force to transport the CO₂ across the membrane barrier.

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US6156096A discloses a method of separating at least one gaseous component from a feed comprising a mixture of gases using a liquid membrane barrier and a sweep fluid is disclosed that includes selecting a sweep gas or a sweep liquid membrane and providing a treatment zone in a treatment chamber having a plurality of hydrophobic microporous hollow fibers, the treatment

15 chamber having opposed end walls with ports including feed and membrane inlets and a sweep outlet at one end and a sweep inlet and a feed and membrane outlets at the opposed end and a plurality of hydrophobic elongated microporous hollow fibers extending between the feed and sweep inlet ports and feed and sweep outlet ports respectively and arranged for counter-current flow of feed gas and sweep fluids therethrough.

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US20070214957A1 discloses a method for separating CO₂ from a CO₂-rich liquid, comprising a step wherein, under elevated pressure, said liquid is contacted with a membrane based on polyacetylene substituted with trimethylsilyl groups, such that the pressure difference

across the membrane is at least 1 bar and that at least a part of the CO₂ is transported from the liquid through the membrane.

US7537200B2 discloses a method and apparatus for controlling the dissolved gas content
5 of aqueous liquid containing a dissolved gas by providing a microporous hydrophobic hollow fibre membrane, to provide at equilibrium a stable interface between an aqueous liquid phase containing dissolved gas on one side of the membrane and a gaseous phase on the other side of the membrane, and controlling the aqueous phase and gaseous phase pressures, such that in operation the gaseous phase pressure is up to but not exceeding the aqueous phase pressure, and
10 flowing the gaseous and liquid phases across the membrane, to provide simultaneous mass transfer through the membrane of a first gas in the gaseous phase into the liquid phase and of a second gas dissolved in the aqueous liquid into the gaseous phase, whereby the gas content of the first gas in the aqueous phase is increased, the gas content of the second gas in the gaseous phase is decreased and the total dissolved gas pressure (TG) of the aqueous phase is altered.

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US20120055385A1 discloses a method for the separation of gases comprising the method steps of: (i) passing an exhaust gas stream containing CO₂ through a first membrane separation system to produce a pre-concentrated gas stream containing at least carbon dioxide and a reject stream; and (ii) directing the pre-concentrated gas stream to at least one purification step to
20 produce a purified CO₂ stream; wherein sulphur-containing gases (SO_x) are also substantially separated from the exhaust gas stream by the first membrane separation step into the pre-concentrated gas stream, and the purified CO₂ stream is substantially free of nitrogen gas.

US patent no. 8,313,557 B2 discloses a system to recover CO₂ from seawater and/or aqueous bicarbonate systems, comprising: a gas permeable membrane comprising multiple layers; and, a solution comprising seawater, aqueous bicarbonate, or both, wherein the solution is under a pressure greater than 100 psig; wherein the solution comprises bound CO₂ in the ionic form of bicarbonate and carbonate and wherein these ions dissociate and release CO₂; and wherein gaseous CO₂ and dissociated CO₂ diffuse from the solution through the membrane.

Patent US7938887 shares various piperazine water blends for CO₂ capture from various gaseous streams. The patent teaches a range of piperazine concentrations such as 25.6-63.0 wt% (4-20 moles PZ/kg H₂O) and a lean CO₂ loading in the range of 0.3-0.9 mol CO₂/mol solvent.

In light of the state of the art, there still exists a need for improved processes for carbon capture, especially for post combustion emissions.

An improved method and apparatus to capture carbon dioxide from a post-combustion exhaust, such as an engine, has been developed using hydrophobic plastic membranes. The novel invention takes hot exhaust through ducting to a rectangular boxed, and horizontally connected and arranged series of vertical membrane contactor vessels/cartridges containing hollow-fibre hydrophobic membranes. Firstly, the engine exhaust can be cooled with a direct counter current contact water spray using mass and heat transfer arrangement in an internal chamber. If required, solvents such as NaOH or KOH can be sprayed in the same chamber to remove contaminants such as SO_x which can be present in engine exhaust. The cooled exhaust is then directed through an internal channel to a second internal chamber that contains hollow-fibre hydrophobic

membranes. The cooled exhaust passes through the inside of the hollow-fibre membrane while liquid solvent passes on the outside of the membrane at a higher pressure than the gas on the inside of the membrane, with the gas occupying pores within the fibrous membrane. The CO₂ in the membrane pores is attracted to the solvent and absorptive forces move the CO₂ across the
5 membrane barrier into the solvent.

There is minimal contact between the solvent and the rest of the exhaust gas components thus retaining the activity of the solvent due to the short gas residence time (<1.5 sec), and minimising the degradation of the solvent, resulting in no need or smaller solvent reclaimer. The CO₂-reduced post-absorption exhaust stream can then be directed straight to atmosphere without
10 the need or minimum requirement for a water wash, which typically captures any solvent entrained in such exhaust stream, due to there being no or negligible solvent losses to the exhaust from the membrane operation. The CO₂-rich liquid solvent is heated and directed to a regeneration step that also includes a membrane to separate the vaporized CO₂ from the liquid solvent. The solvent with reduced CO₂ content is redirected back to the membrane CO₂ capture
15 step. The choice of solvent, ideally an amine and water blend, allows the regeneration to be at an elevated pressure and the vaporized CO₂ to leave also at an elevated pressure. The elevated pressure reduces the need for overall compression of CO₂ for transport purposes, further reducing the cost of the entire carbon capture process.

It is to be understood that other aspects of the present invention will become readily
20 apparent to those skilled in the art from the following detailed description, wherein various embodiments of the invention are shown and described by way of illustration. As will be realized, the invention is capable for other and different embodiments and its several details are capable of modification in various other respects, all without departing from the spirit and scope

of the present invention. Accordingly the drawings and detailed description are to be regarded as illustrative in nature and not as restrictive.

SUMMARY OF THE INVENTION

- According to one aspect of the present invention, there is provided a process to capture
- 5 carbon dioxide from post-combustion exhaust, such process comprising steps such as :
- a) a first step consisting of:
 - i. a direct contact cooling of said post-combustion exhaust; and
 - ii. condensation and removal in a first chamber;
 - b) a second step of carbon dioxide capture by a liquid solvent absorption in a second
 - 10 chamber using series of vertical membrane contactor vessels/cartridges containing hollow-fibre hydrophobic membranes; and
 - c) a third step to regenerate solvent by removing carbon dioxide from said liquid solvent, which includes, but is not limited to, a membrane to separate the vaporized CO₂ from the liquid solvent at a pressure range of 110 kPag to 600 kPag, other solvent
 - 15 regeneration;
 - d) optionally, a reclaiming of a regenerated solvent.

According to a preferred embodiment of the present invention, the second chamber comprises a membrane used for said liquid solvent absorption; wherein said membrane has a cross-sectional area and pore openings large enough to reduce pressure drop from a solvent side

20 of said membrane to an exhaust gas side of said membrane to a point where membranes perform mass transfer without requiring additional power to be generated.

Preferably, the membrane is hydrophobic.

According to a preferred embodiment of the present invention, the membrane is made into hollow fiber.

According to a preferred embodiment of the present invention, the membrane material of
5 construction is plastic or ceramic.

According to a preferred embodiment of the present invention, the membrane provides absorption-derived transport across the membrane.

According to a preferred embodiment of the present invention, a pressure on said solvent side of said membrane is greater than a pressure on said exhaust gas side of said membrane to
10 prevent physical transport of exhaust gas across the membrane.

According to a preferred embodiment of the present invention, the direct contact cooling and liquid solvent absorption steps are carried out using at least two thin-walled vessels.

According to one aspect of the present invention, the CO₂ absorbing solvent contains a mass transfer solvent which is compatible with the short mass transfer time in the membrane.

According to a preferred embodiment of the present invention, said mass transfer solvent
15 comprises of at least 15% of alkanolamine, consisting of primary and secondary amine

According to a preferred embodiment of the present invention, said primary amine is a monoethanolamine.

According to a preferred embodiment of the present invention, said alkanolamine is
20 selected from the group consisting of: N-methylmonoethanolamine, N-ethylmonoethanolamine, piperazine, Diethanolamine, diisopropanolamine and combinations thereof.

According to a preferred embodiment of the present invention, the CO₂ recovery with the combination of membrane and absorbing solvent is greater than or equal to 90%.

According to a preferred embodiment of the present invention, the CO₂ product purity is greater than or equal to 90%.

- 5 According to a preferred embodiment of the present invention, the membrane operates up to 600 kPa reducing the CO₂ product compression by at least 1 stage, preferably by 2 stages.

According to a preferred embodiment of the present invention, the membrane operates up to 600 kPag at the solvent regeneration system, thus reducing the CO₂ product compression by at least 2 stages.

- 10 According to an embodiment of the present invention, one of the absorption or regeneration step is performed using standard mass transfer equipment while the other step uses a membrane.

- According to a preferred embodiment of the present invention, a combination of at least one of a reboiler and preheater is used to generate heat to support the desorption in the membrane
15 of CO₂ from the solvent.

According to a preferred embodiment of the present invention the removal of the vaporized water in the CO₂ product stream occurs in one vessel with multiple heat transfer steps.

According to a preferred embodiment of the present invention the vessel with multiple heat transfer steps is connected directly to the membrane in claim 1 step 3 or is a separate vessel.

- 20 According to a preferred embodiment of the present invention the thin walled vessel for CO₂

absorption contains louvres to enable ambient air to cool the membranes performing CO₂ absorption.

According to a preferred embodiment of the present invention the CO₂ regeneration membrane can be placed in either the horizontal or vertical position or on any angle in between.

- 5 According to a preferred embodiment of the present invention the exhaust gas and solvent can travel on either side of the membrane, and may travel upward or downward in counter-current or co-current fashion in the CO₂ absorption step.

Preferably, no caustic addition to the direct contact cooler is required.

Preferably also, no water wash is needed in concert with the contactor membrane.

- 10 Preferably also, no reclaiming is needed to extend the life of the CO₂ liquid solvent.

BRIEF DESCRIPTION OF THE FIGURES

The detailed description will be better understood in conjunction with the accompanying drawings as follows:

- 15 **Figure 1** illustrates a general embodiment of a liquid absorbent-based carbon capture process using a membrane box contactor;

Figure 2 shows an embodiment of the horizontal integrated liquid absorbent-based carbon capture system using a membrane box contactor absorption unit;

Figure 3 shows the contact between exhaust gas and liquid solvent molecules as the membrane acts to enable capture CO₂ pressure with the liquid solvent; and

Figure 4a-c illustrate three feasible embodiments of a liquid solvent regeneration processes with a membrane, rather than an amine column with trays/packing, used to separate the vapourized CO₂ from the liquid solvent.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

5 The description which follows and the embodiments described therein are provided by way of illustration of an example or examples of particular embodiments of the principles of the present invention. In the following description of the invention, examples are provided and specific details are set forth for the purposes of explanation and not limitation in order to provide a thorough understanding of the invention. Those that are skilled in the art will readily appreciate
10 that the well-known methods, procedures and/or components will not be described as to focus on the invention in question. Accordingly, in some instances, certain structures and techniques have not been described or shown in detail in order not to obscure the invention.

Figure 1 shows a typical absorption carbon capture process where stream **5** is a feed from
15 any hydrocarbon post-combustion exhaust processed in unit **10**. The liquid adsorbent that preferentially absorbs carbon dioxide (CO₂) can be any liquid or combination of liquids blended with water if desired such as primary amines (ex. MEA, MDEA, DEA) carbonates (ex. potassium), propanediols (2-Amino-2-methylpropan-1-ol, 2-amino-2-methyl-1,3-propanediol) and/or secondary amines. Unit **10** captures carbon dioxide preferentially at low pressures (< 101
20 kPag) and temperatures (< 60°C) with stream **15** leaving as a depleted carbon dioxide vapour stream. Unit **10** can be an absorption tower with mass transfer internals, a rotating packed bed or a membrane. Stream **25** leaves unit **10** as a carbon dioxide rich liquid absorbent stream. Stream **25** is routed to unit **200** to remove the CO₂ from liquid absorbent. Unit **200** operates at elevated

temperatures ($> 50^{\circ}\text{C}$) and pressures (110-600 kPag) reducing the size of downstream CO_2 compression equipment. Stream **45** leaves unit **200** as a rich CO_2 vapour stream. Stream **55** is a regenerated liquid absorbent that is returned to unit **10** to capture more CO_2 . Stream **35** is a make-up stream for any liquid absorbent lost in the process such as in stream **45**. Unit **200** can be a
5 conventional tower for liquid absorbent regeneration to separate CO_2 from the liquid absorbent or to reduce the overall size of unit **200** a rotating packed bed or a membrane can be used.

In a preferred embodiment, process **10**, as shown in **Figure 2**, contains 2 steps only in a single vessel to capture the CO_2 : a direct contact cooler chamber **100** and a membrane-based CO_2 capture chamber **600**. Stream **5** feeds process **10** near the bottom of chamber **100** and is typically
10 at temperatures higher ($> 50^{\circ}\text{C}$) than what is desired for optimal liquid absorption (i.e., $< 40^{\circ}\text{C}$). Stream **5** comprises oxygen, nitrogen, carbon dioxide, carbon monoxide, water, unconverted methane and other trace hydrocarbon post-combustion products. Stream **515** enters chamber **100** near the top of the vessel and is composed of cooler water. Chamber **100** acts as a direct contact cooler. The water at reduced temperatures (down to 17°C ideally) is directed through a
15 distribution device **110** to counter-currently contact the up flowing vapour stream in the mass and heat transfer equipment **120**. Mass and heat transfer equipment **120** is preferably structured packing, with the best mass and heat transfer for high vapour and low liquid rates ($< 50 \text{ m}^3/\text{m}^2/\text{hr}$), which can be more easily installed in a boxed/rectangular arrangement than a round vessel. Other equivalent mass and heat transfer equipment can be trays or random packing. The
20 cooled water reduces the temperature of the vapour stream ($\sim 25^{\circ}\text{C}$) to a point where a portion of the water vapour condenses. The cooling water and the condensed water from the vapour stream are collected at the bottom of chamber **100** and leave via stream **155**. Any excess water is removed through stream **175** with the remaining water entering heat exchanger device **500**, a

water-containing vessel or pond, that cools the water for reuse. A portion of the water in device **500** is moved to pump **550** through stream **505** and becomes stream **515**, the water feed to chamber **100**.

The upward flowing vapour leaving mass and heat transfer device **120** travels up through
5 a demister **140** to a blower or fan **190** via stream **185**. The blower can be within its own chamber within the vessel or can be placed on top or around the vessel depending on spatial constraints and overall capital costs. If the blower is needed, the pressure increase can be between 10-40 kPa to push the exhaust gas through chamber **600** and to atmosphere. The lower the pressure increase, the lower the power load needed to run the blower and thus the lower the parasitic CO₂ load
10 needed to be captured in the carbon capture unit. The pressurized cooler exhaust enters the membrane chamber **600** via stream **195**. Chambers **100** and **600** share a common wall, **130**, which reduces the amount of material needed to fabricate the entire apparatus by sharing common walls. Also, there are no internal flow paths and ducting needed to convey the exhaust gas between chambers which lowers the pressure drop needed to be overcome by the blower **190**. The
15 membrane **620** is supported by an inner wall, **630**, that can also act as a support for the entire **600** vessel. The membrane can be as long horizontally as needed to obtain the necessary CO₂ absorption thus keeping the height of the vessel in process **10** below both transport and material thickness increase thresholds. In addition, the liquid/vapour contact height from the membrane enables a shorter chamber in the 4-6m range to be fabricated than a common absorption column
20 (upwards of 20 to 30m). As a benefit, vessel **10** can either be a box or round, with the walls of the vessel and chambers made of a combination of material and thickness only required to support up to 6m of structure which fits under the road transport shipping limits in Western Canada. The walls can be made of one of or a combination of stainless steel, carbon steel, plastic, or wood.

Internal supports can serve as baffles serving two purposes—reducing the amount of material and footprint needed to achieve the process requirements. Pressure drops are also reduced with the integrated design which reduces power needs to run the unit translating to less CO₂ generated.

The exhaust gas travels downward through the membrane chamber **620** and then changes
5 direction upward and leaves as depleted gas as stream **15**. The change in direction allows for liquid to fall out of the vapour stream and collect in a sump at the bottom of chamber **600**. A demister, **670** is optional if additional de-entrainment of liquid is needed before depleted exhaust gas is sent to atmosphere in stream **15**. The lean solvent, referring to CO₂ absorbing solvent low in CO₂ content, in stream **55**, enters the membrane **620** from the bottom and is distributed through
10 a manifold. In another embodiment, the exhaust gas is directed upward through the membrane chamber **620** while the CO₂ absorbing solvent in stream **55** is directed down through the membrane **620** to facilitate CO₂ absorption. In another embodiment, the exhaust gas can flow in a cross-flow pattern with the solvent flowing in the membrane **620**. The selection of flow direction for the exhaust gas and solvent is based on pressure drop and capital cost trade-offs. The lean
15 solvent collects CO₂, creating a rich solvent stream **255** that is returned to unit **20** for regeneration via pump **260** and stream **275**. The CO₂ product from unit **20** leaves via stream **45**. A bottom sump in vessel **600** collects any small volume of liquid solvent that passes through the membrane. This liquid is collected as stream **635** and pumped via pump **640** through stream **645** to be reused in the process. In this set-up a water wash set up is optional. A recycle line, stream 256 off of the
20 rich solvent stream 255 may be present to direct a portion of the stream 255 flow to the lean solvent stream 55 to create a combined stream 56. The recycle line may serve as a means to improve mass transfer and performance with increased solvent flow to capture more CO₂ from the exhaust gas.

To improve the recovery of CO₂, vessel **600** may be equipped (not shown in figures) with movable/controllable louvres/panels/or valves on the chamber walls to enable a cross flow of ambient air through the box. The louvres can be adjusted to adjust air flow and thus temperature in the chamber to improve the CO₂ recovery.

5 In one embodiment, the membrane **620** comprises an outer shell or cylinder **622** that contains the hydrophobic membrane **625** with exhaust stream **195** flowing on the inside of the hydrophobic membrane and solvent stream **55** flowing on the outside of the hydrophobic membrane **625**. In another embodiment, the exhaust stream **195** may flow on the outside of the hydrophobic membrane and the solvent stream **55** may flow on the inside of the membrane. The
10 selection of which side of the hydrophobic hollow fibre membrane the solvent and exhaust flow are based on pressure drop and capital cost trade-offs. The CO₂ in the exhaust stream is attracted by the solvent and crosses the hydrophobic membrane barrier of **625** into the liquid solvent stream **55** as shown in **Figure 3**. The CO₂ contactor membrane in unit **600** is operated with higher pressure on the solvent side to reduce the exposure of the solvent to oxygen and oxygenated
15 molecules in the exhaust, minimizing solvent degradation, which means no reclaimer requiring power is needed. The higher solvent side pressure also prevents any non-CO₂ molecules from entering and passing through the membrane. The CO₂ is attracted to the solvent and diffuses through the pores of the membrane as the solvent passes in and out of the membrane cartridge. This hydrophobic membrane in concert with the solvent and its higher pressure act as a unique
20 barrier and separation device. Only gas molecules that are attracted to the solvent are absorbed into the pores of the membrane and are carried away with the solvent as it travels in, through the pores, and out of the membrane casing. The pressure is managed at the membrane interface to limit solvent breakthrough, defined as the breakthrough pressure. The membrane is sufficiently

hydrophobic to repel the water in the solvent, reducing the tendency for the water/solvent blend from passing through the membrane. Amines have a strong attraction to water, forming hydrogen bonds, which makes amines soluble in water with the amines preferring to stay in water rather than passing across the membrane barrier alone. With minimal to no solvent breakthrough across the membrane, the common water wash, required in a typical contactor to prevent amine emissions in the exhaust to atmosphere, is reduced in size or not needed at all. The solvent contains a mass transfer solvent which is compatible with the short mass transfer time in the membrane.

Solvents with faster mass transfer is compatible with the short mass transfer time in the membrane, such as primary and secondary amines, are best suited to match short contact times with membranes to obtain over 90% recovery and can achieve over 95% CO₂ recovery. Depending on the concentration of CO₂ in the exhaust, operating conditions of the CO₂ contactor and loading on the solvent, amines water blend mass transfer coefficients (KGA) are in the 1.7-1.8 Kmol/(m² h kPa) range while amine water blends are in the 3.5-4 Kmol/(m² h kPa). The higher amine mass transfer coefficient makes it a preferred solvent when combined with a hydrophobic plastic membrane for CO₂ recovery.

Secondary alkanolamines linked to an alkyl group constitute a further class of candidate amines with good potential for gas purification. These sterically hindered amines offer high CO₂ absorption capacity and reaction rates. Moreover, they are more resistant to corrosion than MEA even at high amine concentrations and their regeneration energy requirement is lower than that of MEA and many other amine blends, so more waste heat can be used for power generation.

In a preferred embodiment, **Figures 4 a-c** show a liquid solvent regeneration process **200** with a membrane **220** used to separate the vapourized CO₂ from the liquid solvent which is

preferentially an amine/water blend. The membrane **220** replaces a typical amine column with trays/packing to separate the vapourized CO₂ from the liquid solvent. The height of the mass transfer zone in the membrane arrangement is less than what is required for a typical amine column allowing for less material needed for construction saving on fabrication, civil and construction costs. Figures 4a-c illustrate three feasible embodiments of a liquid solvent regeneration processes with a membrane, rather than an amine column with trays/packing, used to separate the vapourized CO₂ from the liquid solvent.

As shown in Figure 4a, the rich amine **275** from chamber **600** is warmed in cross heat exchange involve one or more exchangers **210a**, **210b** which can be shell and tube, spiral, plate or frame or a similar style. Stream **275** can have a filter (not shown) on the entire stream on the partial stream to remove any solids or precipitates from vessel **10**. The warmed rich amine stream **215** has experienced some vapourization with primarily CO₂ vaporized and enters the membrane **220** shell as a two-phase stream. The higher operating pressure of the membrane shell side forces the vapourized CO₂ and water (steam) through the pores and into the hollow fibre membrane and is separated from the remaining liquid solvent. The remaining liquid solvent leaves the membrane as stream **222** and enters a reboiler **235**, which can be a kettle style in a preferred embodiment, where the liquid solvent is further heated to vapourize more CO₂ and water. The vapourized CO₂ and steam leave the reboiler as stream **237** and enter the membrane vessel on the vapour side of the hollow fibre membrane, joining the first vapourized CO₂ and steam in stream **215**. The combined CO₂ vapour and steam leave the membrane as stream **239**. The remaining liquid solvent in reboiler **230** has a reduced CO₂ content and is termed lean and leaves the reboiler as stream **235** where it is cooled in the **210b** cross exchanger. It becomes stream **55**, lean liquid solvent, which is reused in the absorption process in chamber **600**. Stream **55** may also pass through a separator and

another cooler (both not shown) to condition the solvent to meet the desired absorption operating conditions of the absorption process. Absorption is improved at lower temperatures than the regeneration step.

For the regeneration step, the amine/water blend with the 15-40wt% amine, preferably
5 secondary amines, in addition to a faster mass transfer rate, also has a higher degradation temperature than typical amines, MEA (~120°C) and other amines. With a higher 130-150°C degradation temperature range, the regeneration can occur at a higher pressure, in the range of 300 to 650 kPa. All the separated CO₂ and steam leaves the membrane as stream **239** at an elevated pressure and is cooled in cross exchanger **210a**. The cooling is used to condense the
10 steam into water for reuse in the system and to purify the CO₂ to over 90 and 95% for downstream requirements. Stream **245** leaves **210a** exchanger and may enter another cooler **240** and separator **250** to further condense steam to water and separate from the CO₂ vapour further purifying the CO₂ up to and over 99wt%. Cooling media such as water enters in stream **292** and leaves warmer as stream **293**, cooling the now two-phase CO₂/water stream **245**, and leaves
15 cooler **240** as stream **246**. CO₂ leaves the separator **250** as stream **45** for further transport and/or processing. Stream **45** is close to 500 kPa and up to 650 kPa so further compression needs for transport and sequestration, or processing are reduced, dropping the overall cost of the process. The condensed and collected water in separator **250** leaves as stream **265** and can be returned to the solvent stream 55 for continued use.

20 The membrane regeneration step is effective in separating the CO₂ from the liquid solvent and may reduce the CO₂ content to below 0.4 and even to 0.2 mol CO₂/mol solvent to make a lean solvent for absorption. With less CO₂ in the solvent, more CO₂ can be absorbed in the

membrane chamber **600**, decreasing the total amount of liquid solvent that needs to be circulation which reduces the power needs for the system.

Figure 4b shows another embodiment of the solvent regeneration process step using a
5 membrane **200**. The rich amine **275** from chamber **600** is heated in a cross heat exchange involving one or more exchangers **210a**, **210b** which can be shell and tube, spiral, plate or frame or a similar style. Stream **275** can have a filter (not shown) on the entire stream on the partial stream to remove any solids or precipitates from vessel **10**. The warmed rich amine stream **215** is directed to a heater **290** which can be inline heater, shell and tube, spiral, plate of frame or a
10 similar style which works to provide some vaporization with primarily CO₂ and water (steam) vaporized in stream **295**. Stream **295** enters the membrane **220** shell as a two-phase stream. The higher operating pressure of the membrane shell side forces the vapourized CO₂ and water (steam) through the pores of the hollow fibre membrane and is separated from the remaining liquid solvent. The water(steam) in the hollow fiber tube then strips the CO₂ from the solvent at
15 the membrane **220** shell. The combined CO₂ vapour and steam leave the membrane as stream **239**. The remaining liquid solvent has a reduced CO₂ content and is termed semi lean and leaves the membrane **220** as stream **235** where it is cooled in the **210b** cross exchanger. It becomes stream **55**, semi lean liquid solvent, which is reused in the absorption process in chamber **600**. Stream **55** may also pass through a separator and another cooler (both not shown) to condition the
20 solvent to meet the desired absorption operating conditions of the absorption process. Absorption is improved at lower temperatures than the regeneration step.

For the regeneration step, the amine/water blend with the 15-40wt% amine, in addition to a faster mass transfer rate, it also has a higher degradation temperature than typical amines

(~120°C) and other amines. With a 130-150°C degradation temperature range, the regeneration can occur at a higher pressure, in the range of 300 to 650 kPA. All the separated CO₂ and steam leaves the membrane as stream **239** at an elevated pressure and is cooled in cross exchanger **210a**. The cooling is used to condense the steam into water for reuse in the system and to purify the CO₂ to over 90% and preferably over 95% for downstream requirements. Stream **245** leaves **210a** exchanger and may enter another cooler **240** and separator **250** to further condense steam to water and separate from the CO₂ vapour further purifying the CO₂ up to and over 99wt%. Cooling media such as water enters in stream **292** and leaves warmer as stream **293**, cooling the now two-phase CO₂/water stream **245**, and leaves cooler **240** as stream **246**. CO₂ leaves the separator **250** as stream **45** for further transport and/or processing. Stream **45** is close to 500 kPA and may be up to 650 kPA so further compression needs for transport and sequestration, or processing are reduced, dropping the overall cost of the process. The condensed and collected water in separator 250 leaves as stream **265** and can be returned to the solvent stream 55 for continued use.

Figure 4c shows another embodiment of the solvent regeneration process step using a membrane **200**. As in Figure 4b, the rich amine **275** from chamber **600** is warmed in cross heat exchange involve one or more exchangers **210a** which can be shell and tube, spiral, plate or frame or a similar style and exchanger **201c** which is located inside vessel **300**. Vessel **300** combines multiple heat transfer steps into one vessel saving capital cost. Stream **275** can have a filter (not shown) on the entire stream on the partial stream to remove any solids or precipitates from vessel **10**. The warmed rich amine stream **215** then enters heater **290** which can be inline heater, shell and tube, spiral, plate of frame or a similar style providing some vaporization with primarily CO₂ and water (steam) vaporized as stream **295**. Stream **295** enters the membrane **220 shell** as a two-phase stream. The higher operating pressure of the membrane shell side forces the vapourized

CO₂ and water (steam) through the pores of the hollow fibre membrane and is separated from the remaining liquid solvent. The water(steam) in the hollow fiber tube then strips the CO₂ from the solvent at the membrane **220** shell. The combined CO₂ vapour and steam leave the membrane as stream **239**. The remaining liquid solvent has a reduced CO₂ content and is termed semi lean and leaves the membrane **220** as stream **235** where it is cooled in the **210b** cross exchanger. It becomes stream **55**, semi lean liquid solvent, which is reused in the absorption process in chamber **600**. Stream **55** may also pass through a separator and another cooler (both not shown) to condition the solvent to meet the desired absorption operating conditions of the absorption process. Absorption is improved at lower temperatures than the regeneration step.

For the regeneration step, the amine/water blend with the 15-40wt% amine, in addition to a faster mass transfer rate, it also has a higher degradation temperature than typical amines (~120°C) and other amines. With a 130-150°C degradation temperature range, the regeneration can occur at a higher pressure, in the range of 300 to 650 kPA. All the separated CO₂ and steam leaves the membrane as stream **239** at an elevated pressure and enters vessel **300** for cooling to condense steam in the CO₂/steam mixture. The cooling is used to condense the steam into water for reuse in the system and to purify the CO₂ to over 90 and 95% for downstream requirements. The internal vapour stream in vessel **300** is first cooled by the internal exchanger **210c** and then further cooled by another cooling step shows as heat transfer device **310**. **310** is shown as a direct contact cooler using water in stream **305** to spray onto packing and/or trays to cool the upward flowing vapour and condense more water. The collected water is sent out of the column as stream **315** to be reused in the process. Device **310** can also be an indirect heat exchanger using tubes, or plates for heat transfer. The cooled vapour with now mostly CO₂ with purity over 99 wt% leaves vessel **300** as stream **45** for further transport and/or processing. Stream **45** is close to 500 kPA and

up to 650 kPa so further compression needs for transport and sequestration, or processing are reduced, dropping the overall cost of the process. The condensed and collected water in the bottom of vessel **300** leaves as stream **315** and can be returned to the process via stream **55** or other for continued use.

5 In a preferred embodiment, the combination of the fast mass transfer amine/water blend solvent with a membrane limits the contact and contact time between the secondary amine and exhaust gas components such as oxygen-based components, which can lead to the degradation of the solvent with extended contact, but still allows for desired CO₂ capture. As a result, various mitigating common steps can be avoided, reducing the power needs and overall cost of the
10 process. Reliability is also increased. Caustic (NaOH) treatment in the direct contact cooler which is normally included in a design for post-combustion carbon capture, or selective catalytic reduction or a similar step that reduces NO_x and SO_x in the exhaust gas, can be avoided in this preferred embodiment. Also, reclaiming of the liquid solvent, whether by common methods of thermal, ion-exchange or electro-dialysis, is not required since the generation of dissolved heat-
15 stable salts in the solvent is not an issue for post-combustion of natural gas combustion-derived exhaust gas. In addition, with controlled pressure in the membrane, leakage and entrainment of the solvent into the exhaust gas is effectively eliminated, so a water wash system, which is normally required, is not needed prior to the exhaust being released to the atmosphere.

 In another embodiment, the horizontally shown membranes **220** for CO₂ regeneration in
20 Figures 4a, b and c may also be arranged in a vertical position for footprint savings and for integration benefits with vessels **250** or **300**.

 In another preferred embodiment, where high levels of contaminants are present, treatment of NO_x and SO_x, water wash to suppress solvent emissions to the atmosphere and reclaiming of

the solvent are included in the design as a precautionary measure with the overall process still not requiring additional power to run the CO₂ capture and transmission steps.

5 The examples and corresponding diagrams used herein are for illustrative purposes only. The principles discussed herein can be implemented in other systems and apparatuses. Different configurations and terminology can be used without departing from the principles expressed herein. For instance, steps, equipment, components, and modules can be added, deleted, modified, or re-arranged without departing from these principles.

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Unless the context clearly requires otherwise, throughout the description and the claims: "comprise," "comprising," and the like are to be construed in an inclusive sense, as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to". "Herein," "above," "below," and words of similar import, when used to describe this specification shall refer to this specification as a whole and not to any particular portions of this specification. "Or" in reference to a list of two or more items, covers all of the following interpretations of the word: any of the items in the list, all of the items in the list, and any combination of the items in the list. The singular forms "a", "an", and "the" also include the meaning of any appropriate plural forms.

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Where a component is referred to above, unless otherwise indicated, reference to that component should be interpreted as including as equivalents of that component, any component which performs the function of the described component (i.e., that is functionally equivalent),

including components which are not structurally or compositionally equivalent to the disclosed structure or composition which performs the function in the illustrated exemplary implementations of the invention.

5 Specific examples of compositions, systems, methods and apparatuses have been described herein for purposes of illustration. These are only examples. Many alterations, modifications, additions, omissions and permutations are possible within the practice of this invention. This invention includes variations on described compositions, processes or uses that would be apparent to the skilled addressee, including variations obtained by: replacing features or
10 elements with equivalent features or elements; mixing and matching of features or elements from different examples; combining features or elements from examples as described herein with features or elements of other technology; omitting or combining features or elements from described examples.

15 It is therefore intended that the following appended claims and claims hereafter introduced are interpreted to include all such modifications, permutations, additions, omissions and sub-combinations as may reasonably be inferred. The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

CLAIMS

1. A process to capture carbon dioxide from post-combustion exhaust, such process comprising steps such as:
 - a) a first step consisting of:
 - 5 i. a direct contact cooling of said post-combustion exhaust; and
 - ii. condensation and removal in a first chamber;
 - b) a second step of carbon dioxide capture by a liquid solvent absorption in a second chamber;; and
 - c) a third step to regenerate solvent by removing carbon dioxide from said liquid
10 solvent;;
 - d) optionally, a reclaiming of a regenerated solvent.
2. The process of claim 1 where the second chamber comprises a membrane used for said liquid solvent absorption; wherein said membrane has a cross-sectional area and pore openings large enough to reduce pressure drop from a solvent side of said membrane to
15 an exhaust gas side of said membrane to a point where membranes perform mass transfer without requiring additional power to be generated.
3. The process of claim 2 where the membrane is hydrophobic.
4. The process of claims 2 or 3 where the membrane is made into hollow fiber.
5. The process according to any of claims 2 to 4 where the membrane material of
20 construction is plastic or ceramic.
6. The process according to any of claims 2 to 5 wherein the membrane provides absorption-derived transport across the membrane.

7. The process according to any of claims 2 to 6 wherein a pressure on said solvent side of said membrane is greater than a pressure on said exhaust gas side of said membrane to prevent physical transport of exhaust gas across the membrane.
8. The process according to any of claims 1 to 7 where the direct contact cooling and liquid solvent absorption steps are carried out using at least two thin-walled vessels.
9. The process according to any one of claims 1 to 8 where the CO₂ absorbing solvent contains a mass transfer solvent which is compatible with the short mass transfer time in the membrane.
10. The process of claim 9 where said mass transfer solvent comprises of at least 15wt% amine.
11. The process of claim 10 where said primary amine is a monoethanolamine.
12. The process of claim 11 where said alkanolamine is selected from the group consisting of: N-methylmonoethanolamine, N-ethylmonoethanolamine, piperazine, Diethanolamine, diisopropanolamine and combinations thereof.
13. The process according to any one of claims 1 to 12 where the CO₂ recovery with the combination of membrane and absorbing solvent is greater than or equal to 90%.
14. The process according to any one of claims 1 to 13 where the CO₂ product purity is greater than or equal to 90%.
15. The process according to any one of claims 2 to 14 where a membrane in step 3 of claim 1 operates up to 600 kPa reducing the CO₂ product compression by at least 1 stage, preferably by 2 stages.

16. The process according to any one of claims 2 to 15 where the membrane in step 2 of claim 1 operates up to 600 kPag, reducing the CO₂ product compression by at least 2 stages.
17. The process according to any one of claims 2 to 16 where the regeneration step 3 in claim 5 1 is performed used standard mass transfer equipment.
18. The process of claim 1 where the second chamber comprises standard mass transfer equipment used for said liquid solvent absorption and the membrane is used in step 3 for regeneration of the solvent.
19. The process of claim 18 where a combination of at least one of a reboiler and preheater is 10 used to generate heat to support the desorption in the membrane of CO₂ from the solvent.
20. The process of claim 18 where a preheater is used to generate heat to support the desorption in the membrane of CO₂ from the solvent.
21. The process of any claims 1-20 where the removal of the vaporized water in the CO₂ product stream occurs in one vessel with multiple heat transfer steps.
- 15 22. The process of claim 21 where the vessel with multiple heat transfer steps is connected directly to the membrane in claim 1 step 3 or is a separate vessel.
23. The process of any claims 1-22 where the thin walled vessel for CO₂ absorption contains louvres to enable ambient air to cool the membranes performing CO₂ absorption.
24. The process of any claims 1-23 where the CO₂ regeneration membrane can be placed in 20 either the horizontal or vertical position or on any angle in between.
25. The process of any claims 1-24 where the exhaust gas and solvent can travel on either side of the membrane, and may travel upward or downward in counter-current or co-current fashion in the CO₂ absorption step.