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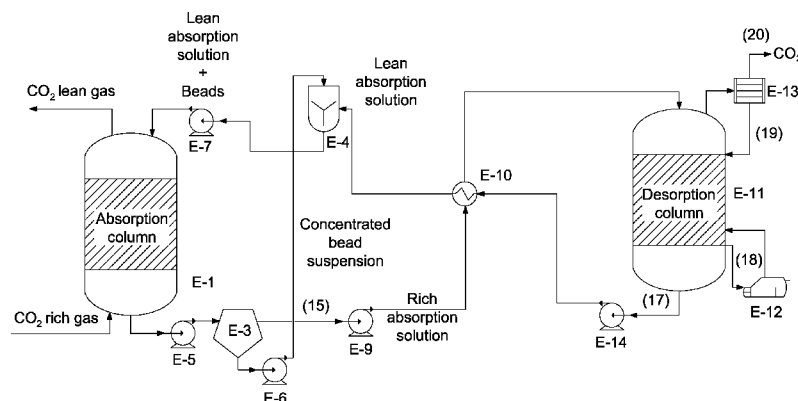


FIG. 2

(57) Abstract: Techniques for absorbing or desorbing CO₂ include sizing enzymatic particles in accordance with the reactive liquid film thickness (δ_{rf}) of the reaction medium to increase enzymatic catalysis of the CO₂ hydration or dehydration reaction. Absorption may include contacting a CO₂ containing gas with an aqueous absorption mixture and determining (δ_{rf}) of the C2O₂ hydration reaction, wherein (δ_{rf}) = (δ_i) / Ha where Ha² = (k₁.D_{co2}/(k₁))², Ha > 2 and k₁ = k₂C_{ab}, k₂ being the CO₂ hydration kinetic constant in the mixture and C_{ab} being the concentration of the absorption compound. The mixture may be under conditions that provide (δ_{rf}) that is smaller than the liquid film thickness (δ_i) through which mass transfer of the CO₂ occurs. The size ratio of the enzymatic particles and (δ_{rf}) enhances enzymatic catalysis. Various implementations including processes, systems, formulations and kits are provided.

CO₂ TREATMENTS USING ENZYMATIC PARTICLES SIZED ACCORDING TO REACTIVE LIQUID FILM THICKNESS FOR ENHANCED CATALYSIS

FIELD OF THE INVENTION

The present invention concerns the field of CO₂ absorption and desorption, particularly in gas treatment and CO₂ capture from CO₂-containing gases.

BACKGROUND OF THE INVENTION

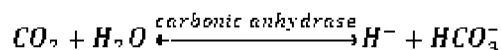
Increasingly dire warnings of the dangers of climate change by the world's scientific community combined with greater public awareness and concern over the issue has prompted increased momentum towards global regulation aimed at reducing man-made greenhouse gas (GHGs) emissions, most notably carbon dioxide. Ultimately, a significant cut in North American and global CO₂ emissions will require reductions from the electricity production sector, the single largest source of CO₂ worldwide. According to the International Energy Agency's (IEA) GHG Program, as of 2006 there were nearly 5,000 fossil fuel power plants worldwide generating nearly 11 billion tons of CO₂, representing nearly 40% of total global anthropogenic CO₂ emissions. Of these emissions from the power generation sector, 61% were from coal fired plants. Although the long-term agenda advocated by governments is replacement of fossil fuel generation by renewables, growing energy demand, combined with the enormous dependence on fossil generation in the near to medium term dictates that this fossil base remain operational. Thus, to implement an effective GHG reduction system will require that the CO₂ emissions generated by this sector be mitigated, with carbon capture and storage (CCS) providing one of the best known solutions.

The CCS process removes CO₂ from a CO₂ containing flue gas, enables production of a highly concentrated CO₂ gas stream which is compressed and transported to a sequestration site. This site may be a depleted oil field or a saline aquifer. Sequestration in oceans and mineral carbonation are two alternate ways to sequester CO₂ that are in the research phase. Captured CO₂ can also be used for enhanced oil recovery.

Some technologies for CO₂ capture are based primarily on the use of aqueous amine (e.g. alkanolamines) and carbonate solutions which are circulated through

two main distinct units: an absorption tower coupled to a desorption (or stripping) tower.

Biocatalysts have also been used for CO₂ absorption applications. For example, CO₂ transformation may be catalyzed by the enzyme carbonic anhydrase together with an aqueous solution as follows:



Under optimum conditions, the catalyzed turnover rate of this reaction may reach 1×10^6 molecules/second. Utilizing carbonic anhydrase in this way allows for the CO₂ capture process to be significantly accelerated, reducing the size of the required capture vessels and reducing associated capital costs. Additionally, by taking advantage of this accelerative mechanism, energetically favourable aqueous solvents such as tertiary and hindered amines and carbonate-bicarbonate solutions can be employed to reduce associated process energy consumption, where these solvents and solutions would normally be too slow to be used efficiently in this way.

There are some known ways of providing carbonic anhydrase in CO₂ capture reactors. One way is by immobilising the enzyme on a solid packing material in a packed tower reactor. Another way is by providing the enzyme in a soluble state in a solution within or flowing through a reactor. Both of these methods provide benefits but also some limitations. As immobilized enzymes are attached to solid surfaces they are less exposed to the gas-liquid interface than the free-floating, individual enzyme molecules. Enzyme immobilized on a solid packing material can limit the enzyme benefit since it has a limited presence in the thin reactive liquid film at the gas-liquid interface which has been said to have, for structured and/or dumped packings, a thickness of about 10 µm; enzyme on packing is several millimetres from the gas-liquid interface. Soluble enzyme brings the optimal enzyme impact, however it cannot be easily separated from the solution and if the enzyme is not robust to intense conditions such as those used in desorption operations, it will be denatured and the process will require high levels of continuous enzyme replacement.

There are several problems and challenges of the known techniques for providing biocatalysts such as carbonic anhydrase for enzymatic catalysis of reactions, such as those in CO₂ capture reactors.

SUMMARY OF THE INVENTION

The present invention responds to the above-mentioned problems and challenges by providing an enzyme delivery technique with improved enzymatic catalysis and thus increased efficiency of the process, by providing enzymatic particles that are sized according to the reactive liquid film thickness of a particular reaction medium.

There is provided a process of absorbing CO₂ from a CO₂ containing gas, including:

contacting the CO₂ containing gas with an aqueous absorption mixture including water and an absorption compound under conditions such that mass transfer of the CO₂:

first occurs through a gas film thickness (δ_g); and

then occurs through a liquid film thickness (δ_l), wherein $\delta_l = D_{CO_2} / k_L$ where k_L is the mass transfer coefficient in the liquid and D_{CO_2} is the diffusion coefficient of CO₂;

determining a reactive liquid film thickness (δ_{rf}) of CO₂ hydration reaction, wherein $\delta_{rf} = (\delta_l) / Ha$ where $Ha^2 = (k_1 \cdot D_{CO_2}) / (k_L)^2$, $Ha > 2$ and $k_1 = k_2 C_{ab}$ where k_2 is the kinetic constant for the CO₂ hydration reaction in the absorption mixture and C_{ab} is the concentration of the absorption compound in the aqueous absorption mixture; and

providing enzymatic particles in the aqueous absorption mixture, wherein the enzymatic particles are sized in accordance with the reactive liquid film thickness (δ_{rf}) to increase enzymatic catalysis of the CO₂ hydration reaction.

The process may include controlling the reactive liquid film thickness (δ_{rf}) by regulating the concentration of the absorption compound, the temperature of the process, the mass transfer coefficient (k_L) or a combination thereof.

The process may include sizing the enzymatic particles to have a diameter (d) such that $d / \delta_{rf} < 6$, $d / \delta_{rf} < 3$, $d / \delta_{rf} < 1$, $d / \delta_{rf} < 0.05$, or $d / \delta_{rf} < 0.025$.

The process may include sizing the enzymatic particles to increase a CO_2 turnover factor by at least 50% with respect to a lower turnover factor enabled by a larger enzymatic particle having a d / δ_{rf} of at least 32.7.

The process may include sizing the enzymatic particles to achieve a CO_2 turnover factor of at least 17%, 27%, or 57% of a free enzyme turnover factor obtained with soluble enzyme in the aqueous absorption mixture.

The reactive liquid film thickness (δ_{rf}) may be at most 10 μm , 5 μm , 3 μm , 2.5 μm , 2.0 μm , 1.9 μm or 1.8 μm .

The absorption compound may include an alkanolamine MDEA in a concentration, such as approximately 2M, so that the reactive liquid film thickness may be at most 3.2 μm , and the enzymatic particles may be sized to be at most 17 μm .

The enzymatic particles may include a support material and carbonic anhydrase, the support material being selected from nylon, cellulose, silica, silica gel, chitosan, polyacrylamide, polyurethane, alginate, polystyrene, polymethylmetacrylate, magnetic material, sepharose, alumina, and respective derivatives thereof, and combinations thereof

The enzymes may be immobilized with respect to the support material by an immobilization technique selected from adsorption, covalent bonding, entrapment, copolymerization, cross-linking, and encapsulation, and combinations thereof.

There is also provided a process for enzymatic catalysis of a hydration reaction of CO_2 in an aqueous absorption mixture wherein mass transfer of the CO_2 occurs through a liquid film thickness (δ_l), wherein the aqueous absorption mixture includes a liquid solution and enzymatic particles and is under conditions that provide a reactive liquid film thickness (δ_{rf}) for the hydration reaction that is smaller than the liquid film thickness (δ_l), and including enhancing the enzymatic catalysis by sizing the enzymatic particles sufficiently small with respect to the reactive liquid film thickness (δ_{rf}).

The process may include sizing the enzymatic particles to have a diameter (d) in accordance with the reactive liquid film thickness (δ_{rf}) such that $d / \delta_{rf} < 6$. The

process may include sizing the enzymatic particles such that $d / \delta_{rt} < 1$. The process may include sizing the enzymatic particles such that d is about one, two, three or four orders of magnitude smaller than δ_{rt} . The process may include sizing the enzymatic particles such that d is about two orders of magnitude smaller than δ_{rt} .

The aqueous absorption mixture may include an absorption compound and δ_{rt} may be at most 10 μm , 5 μm , 3 μm , 2.5 μm , 2.0 μm , 1.9 μm or 1.8 μm .

The absorption compound may include a primary amine, a secondary amine, a tertiary amine, a primary alkanolamine, a secondary alkanolamine, a tertiary alkanolamine, a primary amino acid, a secondary amino acid, a tertiary amino acid, or a carbonate compound, or a combination thereof. More particularly, the absorption compound may include at least one of the following: piperidine, piperazine, derivatives of piperidine or piperazine which are substituted by at least one alkanol group, monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), 2-(2-aminoethylamino)ethanol (AEE), 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS), N-methyldiethanolamine (MDEA), dimethylmonoethanolamine (DMMEA), diethylmonoethanolamine (DEMEA), triisopropanolamine (TIPA), triethanolamine, dialkylether of polyalkylene glycols, dialkylether or dimethylether of polyethylene glycol, glycine, proline, arginine, histidine, lysine, aspartic acid, glutamic acid, methionine, serine, threonine, glutamine, cysteine, asparagine, valine, leucine, isoleucine, alanine, valine, tyrosine, tryptophan, phenylalanine, and derivatives thereof, taurine, N-cyclohexyl 1,3-propanediamine, N-secondary butyl glycine, N-methyl N-secondary butyl glycine, , diethylglycine, dimethylglycine, , sarcosine, , methyl taurine, methyl- α -aminopropionic acid, N-(β -ethoxy)taurine, N-(β -aminoethyl)taurine, N-methyl alanine, 6-aminohexanoic acid and potassium or sodium salts thereof; potassium carbonate, sodium carbonate, ammonium carbonate, promoted potassium carbonate solutions and promoted sodium carbonate solutions or promoted ammonium carbonates, or combinations thereof.

The absorption compound may include an alkanolamine, which may be a tertiary alkanolamine and may more particularly be N-methyldiethanolamine (MDEA). The MDEA may be provided in a concentration, such as approximately 2M, and the

conditions of the aqueous absorption mixture may also be provided such that δ_{rt} is at most 3.2 μm and the enzymatic particles are sized to be at most 17 μm .

In addition, δ_{rt} may be based on the Hatta number (Ha) and may also be based on the liquid film thickness (δ_l). The process may include determining the reactive liquid film thickness (δ_{rt}) in accordance with the following equation:

$$(\delta_{rt}) = (\delta_l) / \text{Ha}$$

wherein Ha is defined for a first order reaction as $\text{Ha}^2 = (k_1 \cdot D_{\text{CO}_2}) / (k_L)^2$. Ha may be greater than 2.

The enzymatic particles may include a support material and carbonic anhydrase. The support material may be made of a compound other than the carbonic anhydrase. The support material may include nylon, cellulose, silica, silica gel, chitosan, polyacrylamide, polyurethane, alginate, polystyrene, polymethylmetacrylate, magnetic material, sepharose, alumina, and respective derivatives thereof or a combination thereof. The support material may have a density between about 0.6 g/ml and about 5 g/ml, or a density above about 1 g/ml.

The carbonic anhydrase may be immobilized with respect to the support material by an immobilization technique selected from adsorption, covalent bonding, entrapment, copolymerization, cross-linking, and encapsulation, and combinations thereof. The support material may include cores and an immobilization material provided on the cores, the carbonic anhydrase being immobilized by the immobilization material. Each particle may have one corresponding core. The carbonic anhydrase may also be stabilized by the immobilization technique. The carbonic anhydrase may be provided as cross-linked enzyme aggregates (CLEAs) and the support material includes a portion of the carbonic anhydrase and crosslinker. The carbonic anhydrase may be provided as cross-linked enzyme crystals (CLECs) and the support material includes a portion of the carbonic anhydrase and crosslinker.

The enzymatic particles are sized to have a diameter at or below about 17 μm , about 10 μm , about 5 μm , about 1 μm , about 0.1 μm , about 0.05 μm , or about 0.025 μm . The particles may also have a distribution of different sizes.

The process may include selecting a desired enzymatic activity level of the enzymatic particles; selecting a maximum allowable particle concentration; determining a total surface area required to reach the desired enzymatic activity level; determining a total volume of the particles to reach the maximum allowable particle concentration; and determining a maximum size of the particles to achieve the enzymatic activity level with the maximum allowable particle concentration.

The enzymatic particles may be provided in the aqueous absorption mixture at a maximum particle concentration of about 40% w/w. The maximum particle concentration may be about 30% w/w.

The particles may be sized and provided in a concentration such that the resulting suspension is pumpable.

The process may further include contacting a CO₂-containing gas with the aqueous absorption mixture in a reactor to remove at least part of the CO₂ from the CO₂-containing gas and thereby produce a CO₂-depleted gas and an ion-rich solution containing the enzymatic particles. The absorption solution and the CO₂-containing gas may flow counter-currently with respect to each other.

The process may further include removing the enzymatic particles from the ion-rich solution to produce an enzymatic particle fraction and a particle-depleted ion-rich solution. The enzymatic particles may be further sized to facilitate the removing from the ion-rich solution. The removing of the enzymatic particles may be performed by at least one of filtration mechanism, magnetic separation, centrifugation, cyclone, sedimentation, membrane separation or a combination thereof. The removing of the enzymatic particles may be performed by a removal method selected in accordance with the size, density, and presence of magnetic property, of the enzymatic particles. The removing may be performed by a clarifier, thickener, vacuum or pressure filter, batch or continuous filter, horizontal filters filter press, tubular filter, centrifugal discharge filter, rotary drum filter, scraper-discharge filter, roll-discharge filter, disc filter, sedimentation centrifuge, decanter centrifuge, filtering centrifuge, basket centrifuge, hydrocyclone, hydroclone, ultrafiltration, microfiltration device, nanofiltration device, or a combination thereof.

The process may also include performing desorption or mineral carbonation on the particle-depleted ion-rich solution to produce an ion-depleted solution. At least part of the ion-depleted solution may be recycled to form at least part of the aqueous absorption mixture. At least part of the enzymatic particle fraction may be combined with the recycled portion of the ion-depleted solution to form at least part of the aqueous absorption mixture. The ion-rich solution may include precipitates and the precipitates are removed from the ion-rich solution prior to performing the desorption or the mineral carbonation.

The process may include forming the precipitates in the ion-rich solution and providing the enzymatic particles with a characteristic facilitating separation of the enzymatic particles from the precipitates.

The process may include performing desorption or mineral carbonation on the ion-rich solution without removing the enzymatic particles to produce an ion-depleted solution. The enzymatic particles may allow catalysis of the desorption or the mineral carbonation. The enzymes may be stabilized by the enzymatic particles in a desorption reactor. The particles may be sized and provided in a concentration to be carried with the ion-rich solution through a desorption reactor to promote transformation of bicarbonate and hydrogen ions into CO₂ gas and water, thereby producing a CO₂ gas stream and the ion-depleted solution.

The process may include a further sizing the enzymatic particles with respect to a reactive liquid film thickness of a CO₂ dehydration reaction to increase enzymatic catalysis of the CO₂ dehydration reaction. The sizing consideration may take into account the absorption and desorption step in a CO₂ capture system. The ion-rich solution may include precipitates and the precipitates may be removed from the ion-rich solution prior to performing the desorption or the mineral carbonation.

Furthermore, the contacting of the aqueous absorption mixture with the CO₂-containing gas may be performed in an absorption stage including at least one reactor selected from a packed tower, a spray tower, a fluidized bed reactor and a combination thereof.

There is also provided a process for enzymatic catalysis of a dehydration reaction of CO₂ from an ion-rich aqueous mixture including bicarbonate and hydrogen ions and enzymatic particles wherein mass transfer of the CO₂ occurs through a liquid film thickness (δ_{ld}), wherein the ion-rich aqueous mixture is under conditions that

provide a reactive liquid film thickness (δ_{rfd}) for the dehydration reaction that is smaller than the liquid film thickness (δ_l), and including enhancing the enzymatic catalysis by sizing the enzymatic particles sufficiently small with respect to the reactive liquid film thickness (δ_{rf}).

It is noted that implementations and aspects of the absorption processes mentioned previously and herein-below may be used in combination with the process for enzymatic catalysis of a dehydration reaction described directly above.

There is also provided a formulation, preferably a CO₂ capture formulation, including a liquid solution including water and a reaction compound and enabling the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ to occur, wherein mass transfer of the CO₂ occurs through a liquid film thickness (δ_l) and wherein the liquid solution is conditionable to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_l); and enzymatic particles in the liquid solution having a sufficiently small size with respect to the reactive liquid film thickness (δ_{rf}) to enhance enzymatic catalysis of the reaction.

It is also noted that implementations and aspects of the absorption processes mentioned previously and herein-below related to the aqueous absorption mixture and enzymatic particles, for example, may be used in combination with the formulation described directly above.

There is also provided a system for treatment of a fluid by enzymatic catalysis of a reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ with carbonic anhydrase, including a reactor having a reaction chamber receiving the fluid and being configured to provide conditions for mass transfer of the CO₂ occurs through a liquid film thickness (δ_l) and to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_l); and enzymatic particles present in the reaction chamber and including the carbonic anhydrase, wherein the enzymatic particles have a sufficiently small size with respect to the reactive liquid film thickness (δ_{rf}) to enhance the enzymatic catalysis of the reaction.

The reactor may be configured such that the enzymatic particles flow through it with the fluid.

It is noted that implementations and aspects of the absorption and desorption processes and the formulation mentioned previously and herein-below, related to

the aqueous absorption mixture, enzymatic particles and other characteristics, may be used in combination with the system described above. The system may be for absorption or desorption and should be adapted accordingly. For example, the reaction chamber of the system may be for an absorption reactor and may have configurations and operating features as described herein for an absorption reactor. The reaction chamber of the system may be for a desorption reactor and may have configurations and operating features as described herein for a desorption reactor. Thus the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ may be considered to be a forward or backward reaction whether the system is an absorption or desorption type system. The fluid can therefore be an ion-rich liquid from which ions are converted into CO_2 gas by the backward dehydration reaction, to generate an ion-lean solution and a CO_2 gas stream, in the case of desorption. The fluid can be an absorption solution for contacting a CO_2 containing gas so that the dissolved CO_2 gas can undergo the forward hydration reaction, to generate an ion-rich solution and a treated gas stream with reduced CO_2 . It should also be noted that similar implementations are possible in relation to processes, formulations and kits as described herein.

There is also provided a kit for combination and preferable use in CO_2 capture, including a reaction compound for addition into water to form a liquid solution enabling the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ to occur, wherein mass transfer of the CO_2 occurs through a liquid film thickness (δ_l) and wherein the liquid solution is conditionable to provide a reactive liquid film thickness (δ_{rd}) for the reaction that is smaller than the liquid film thickness (δ_l); and enzymatic particles for addition to the liquid solution, the enzymatic particles having a sufficiently small size with respect to the reactive liquid film thickness (δ_{rd}) to enhance enzymatic catalysis of the reaction.

It is noted that implementations and aspects of the processes, systems and formulations mentioned previously and herein-below, may be used in combination with the kit described directly above.

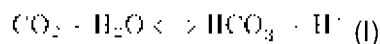
Furthermore, there is provided a process for treatment of a fluid by enzymatic catalysis of reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ with carbonic anhydrase, including providing the fluid in a reaction zone in the presence of enzymatic particles including the carbonic anhydrase, wherein mass transfer of the CO_2

occur through a liquid film thickness (δ_l); and providing conditions in the reaction zone to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_l), such that the size ratio of the enzymatic particles and the reactive liquid film thickness (δ_{rfd}) enhance the enzymatic catalysis of the reaction.

It is again noted that implementations and aspects of the processes, systems and formulations mentioned previously and herein-below, may be used in combination with the process described directly above.

The following are also provided:

- In some implementations, there is a process for capturing CO_2 from a CO_2 -containing gas including contacting the CO_2 -containing gas with an absorption mixture in a reactor, the absorption mixture including a liquid solution and particles, the particles including a support material and enzymes supported by the support material and being sized and provided in a concentration such that the particles are smaller, preferably substantially smaller, than the thickness of the reactive film and that the particles are carried with the liquid solution to promote dissolution and transformation of CO_2 into bicarbonate and hydrogen ions, thereby producing a CO_2 -depleted gas and an ion-rich mixture containing the particles.
- In some implementations, there is a process for treatment of a fluid by catalyzing reaction (I) with carbonic anhydrase in a reactive film, wherein the reaction (I) is as follows:



- In some implementations, the process including feeding the fluid into a reaction zone in the presence of enzymatic particles including the carbonic anhydrase and being sized so as to be smaller, preferably substantially smaller, than the thickness of the reactive film; allowing the reaction (I) to occur within the reaction zone, to produce a gas stream and a liquid stream; and releasing the gas stream and the liquid stream from the reaction zone.

- In some implementations, the fluid is a CO₂-containing effluent gas; the process includes feeding an absorption solution into the reactor to contact the CO₂-containing effluent gas so as to dissolve CO₂ from the CO₂-containing effluent gas into the absorption solution; the reaction (I) is a forward reaction catalyzing the hydration of dissolved CO₂ into bicarbonate ions and hydrogen ions; and the gas stream is a CO₂-depleted gas and the liquid stream is an ion-rich solution including the bicarbonate ions and hydrogen ions. The absorption solution and the CO₂-containing effluent gas may flow counter-currently with respect to each other.
- In some implementations, the fluid is an ion-rich solution including bicarbonate and hydrogen ions; and the reaction (I) is a backward reaction catalyzing the desorption of the bicarbonate ions into gaseous CO₂; the gas stream being a CO₂ stream and the liquid stream being a regenerated solution.
- In some implementations, the process includes designing, controlling or regulating the reactor parameters and operating conditions including the hydrodynamics in order to influence the thickness of the mass transfer film and reactive film so as to favour the functionality of the enzymatic particles having a given size.
- In some implementations, the particles may include a support material made of a compound other than enzyme, including nylon, cellulose, silica, silica gel, chitosan, polyacrylamide, polyurethane, alginate, polystyrene, polymethylmetacrylate, magnetic material, sepharose, their respective derivatives or a combination thereof.
- In some implementations, the absorption mixture includes water and an absorption compound. In another optional embodiment, the absorption compound includes primary, secondary and/or tertiary amines; primary, secondary and/or tertiary alkanolamines; primary, secondary and/or tertiary amino acids; and/or carbonates. In another optional embodiment, the absorption compound includes piperidine, piperazine, derivatives of piperidine or piperazine which are substituted by at least one alkanol group, monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), 2-(2-aminoethylamino)ethanol (AEE), 2-amino-2-hydroxymethyl-1,3-

propanediol (TRIS), N-methyldiethanolamine (MDEA), dimethylmonoethanolamine (DMMEA), diethylmonoethanolamine (DEMEA), triisopropanolamine (TIPA), triethanolamine, dialkylether of polyalkylene glycols, dialkylether or dimethylether of polyethylene glycol, amino acids including glycine, proline, arginine, histidine, lysine, aspartic acid, glutamic acid, methionine, serine, threonine, glutamine, cysteine, asparagine, valine, leucine, isoleucine, alanine, valine, tyrosine, tryptophan, phenylalanine, and derivatives such as taurine, N-cyclohexyl 1,3-propanediamine, N-secondary butyl glycine, N-methyl N-secondary butyl glycine, , diethylglycine, dimethylglycine, , sarcosine, , methyl taurine, methyl- α -aminopropionic acid, N-(β -ethoxy)taurine, N-(β -aminoethyl)taurine, N-methyl alanine, 6-aminohexanoic acid and potassium or sodium salts of the amino acids; potassium carbonate, sodium carbonate, ammonium carbonate, promoted potassium carbonate solutions and promoted sodium carbonate solutions or promoted ammonium carbonates; or mixtures thereof.

- In some implementations, the carbonic anhydrase is immobilized on a surface of the support material of the particles, entrapped within the support material of the particles, or a combination thereof.
- In some implementations, the carbonic anhydrase is provided as cross-linked enzyme aggregates (CLEAs) and the support material includes a portion of the carbonic anhydrase and crosslinker.
- In some implementations, the carbonic anhydrase is provided as cross-linked enzyme crystals (CLECs) and the support material includes a portion of the carbonic anhydrase and crosslinker.
- In some implementations, the process includes removing the particles from the ion-rich mixture to produce an ion-rich solution.
- In some implementations, the removing of the particles is performed by filtration mechanism, magnetic separation, centrifugation, cyclone, sedimentation, membrane separation or a combination thereof. Selection of the particle removing method may depend on particle size, particle density, the presence of a magnetic property and/or other properties. Possible removal units are clarifiers, thickeners, vacuum or pressure

filters, batch or continuous filters, horizontal filters filter press, tubular filter, centrifugal discharge filter, rotary drum filter, scraper-discharge filter, roll-discharge filter, disc filter, sedimentation centrifuge, decanter centrifuges, filtering centrifuge, basket centrifuge, ultrafiltration, microfiltration and/or nanofiltration devices.

- In some implementations, the process includes performing desorption or mineral carbonation on the ion-rich solution to produce an ion-depleted solution. It should be understood that "ion-depleted solution" means a solution from which ions have been at least partially removed and is not limited to a solution completely free of ions.
- In some implementations, the ion-rich mixture includes precipitates and the precipitates are removed from the ion-rich mixture prior to performing the desorption or the mineral carbonation.
- In some implementations, the process includes adding an amount of the particles to the ion-depleted solution before recycling the ion-depleted solution for further contacting the CO₂-containing gas.
- In some implementations, the process includes feeding the ion-rich mixture into a desorption reactor, the enzymes being stabilized by the support material and the particles being sized and provided in a concentration in the desorption reactor such that the particles are carried with the ion-rich mixture to promote transformation of the bicarbonate and hydrogen ions into CO₂ gas and water, thereby producing a CO₂ gas stream and the ion-depleted solution.
- In some implementations, the process includes performing desorption or mineral carbonation on the ion-rich solution to produce an ion-depleted solution and then removing the particles from the ion-depleted solution.
- In some implementations, the particles are sized to facilitate separation of the particles from the ion-rich mixture.
- In some implementations, the enzymatic particles are sized to have a diameter at or below about 15 µm. Optionally, the particles are sized to have a diameter at or below about 10 µm. Optionally, the particles are sized to have a diameter at or below about 5 µm. Optionally, the particles

are sized to have a diameter at or below about 1 μm . Optionally, the particles are sized to have a diameter at or below about 0.5 μm . Optionally, the particles are sized to have a diameter at or below about 0.2 μm . Optionally, the particles are sized to have a diameter at or below about 0.1 μm . In some preferred embodiments, depending on the thickness of the reactive film of given process operating parameters and conditions, the particles are sized to have a diameter of about 0.001 μm , 0.005 μm , 0.01 μm , 0.05 μm , 0.1 μm , 0.15 μm , 0.2 μm , 0.25 μm , 0.3 μm , 0.35 μm , 0.4 μm , 0.45 μm , 0.5 μm , 0.55 μm , 0.6 μm , 0.65 μm , 0.7 μm , 0.75 μm , 0.8 μm , 0.85 μm , 0.9 μm , 0.95 μm , 1 μm , 1.05 μm , 1.1 μm , 1.15 μm , 1.2 μm , 1.25 μm , 1.3 μm , 1.35 μm , 1.4 μm , 1.45 μm , 1.5 μm , 1.55 μm , 1.6 μm , 1.65 μm , 1.7 μm , 1.75 μm , 1.8 μm , 1.85 μm , 1.9 μm , 1.95 μm or 2 μm or a diameter in between any two of the aforementioned values. In some optional embodiments, the particles are sized to have a diameter about one to about four orders of magnitude below the reactive film thickness. The particles are preferably sized so as to be at least about two orders of magnitude smaller than the thickness of the reactive film.

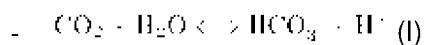
- In some implementations, the particles are sized to have a catalytic surface area including the biocatalysts having an activity density so as to provide an activity level equivalent to a corresponding activity level of soluble biocatalysts present in a concentration above about 0.05 g/L wherein the soluble biocatalysts have a minimum activity of about 260 WA units/mg. Activity may also be expressed as mg CO₂/mg E.s or mol CO₂/gE.s, which relates it to reaction rates which in some cases can be more practical.
- In some implementations, the particles are sized to have a catalytic surface area including the biocatalysts having an activity density so as to provide an activity equivalent to a corresponding activity level of soluble biocatalysts present in a concentration between about 0.01 g/L and about 5 g/L wherein the soluble biocatalysts have a minimum activity of about 260 WA units/mg.

- In some implementations, the process including forming precipitates in the ion-rich mixture and wherein the particles are provided with a characteristic facilitating separation from the precipitates.
- In some implementations, the particles have an activity density of at least about 2.67×10^{-7} WA/mm².
- In some implementations, the particles are provided in the absorption mixture at a maximum particle concentration of about 40% w/w. Optionally, the particles are provided in the absorption mixture at a maximum particle concentration of about 30% w/w.
- In some implementations, the density of the support material is between about 0.6 g/ml and about 5 g/ml. In another optional embodiment, the density of the support material is above about 1 g/ml.
- In some implementations, the process includes selecting a desired biocatalytic activity level of the particles; selecting a maximum allowable particle concentration for the packed reactor; determining a total surface area required to reach the biocatalytic activity level; determining a total volume of the particles to reach the maximum allowable particle concentration; and determining a maximum size of the particles to achieve the biocatalytic activity level with the maximum allowable particle concentration.
- In some implementations, the contacting of the absorption mixture with the CO₂-containing gas is performed in an absorption stage including at least one reactor selected from a packed tower, a spray tower, a fluidized bed reactor and a combination thereof.
- In some implementations, the invention provides a process for desorbing CO₂ gas from an ion-rich aqueous mixture including bicarbonate and hydrogen ions, including: providing enzymatic particles including carbonic anhydrase or an analogue thereof in the ion-rich aqueous mixture; feeding the ion-rich aqueous mixture into a desorption reactor; the particles being sized so as to be smaller than the thickness of a desorption reactive film and carried with the ion-rich aqueous mixture to promote transformation of the bicarbonate and hydrogen ions into CO₂ gas and water, thereby producing a CO₂ gas stream and an ion-depleted solution.

- In some implementations, there is provided a CO₂ capture formulation including water, enzymatic particles sized so as to be smaller than the thickness of a reactive film and, optionally, an absorption compound. The formulation may be in the form of a premixed composition or a kit of chemical components for combination prior to or during use.
- In some implementations, the particles are provided with enzymes and/or an analogue thereof to perform the desired catalytic reactions. It should be understood that the enzymes may be naturally occurring, modified or evolved carbonic anhydrase enzyme and the analogues thereof may be non-biological small molecules that are naturally occurring or synthesized to achieve or mimic the effect of the enzyme.
- It should be noted that each gas-liquid reactor has its own specific mass transfer film thickness, each reactor and absorption solution has its own reaction film thickness and the enzymatic particles are thus tailored to the dimensions and criteria imposed by the reactor and chemical enhancements used in the absorption or desorption system.
- In some implementations, there may be provided a process for capturing CO₂ from a CO₂-containing gas including: contacting the CO₂-containing gas with an absorption mixture in a reactor, the absorption mixture including a liquid solution and particles, the particles including a support material and enzymes or analogues thereof supported by the support material and being sized such that the particles are smaller than the thickness of the reactive film, the particles promoting dissolution and transformation of CO₂ into bicarbonate and hydrogen ions, thereby producing a CO₂-depleted gas and an ion-rich mixture.
- In some implementations, there may be provided a process for capturing CO₂ from a CO₂-containing gas including: contacting the CO₂-containing gas with an absorption mixture in a reactor, the absorption mixture including a liquid solution and particles, wherein operation of the reactor forms a reactive film having a thickness for capturing CO₂; flowing the absorption mixture through the reactor, the particles being carried with the liquid solution to promote dissolution and transformation of CO₂ into bicarbonate and hydrogen ions, thereby producing a CO₂-depleted gas

and an ion-rich mixture containing the particles; wherein the particles include a support material and enzymes or analogues thereof supported by the support material and are sized such that the particles are smaller than the thickness of the reactive film.

- In some implementations, there may be provided a process for treatment of a fluid by catalyzing reaction (I) with carbonic anhydrase in a reactive film, wherein the reaction (I) is as follows:



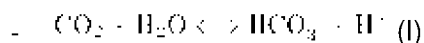
the process including: feeding the fluid into a reaction zone in the presence of enzymatic particles including the carbonic anhydrase or analogue thereof, the particles having sizes that are smaller than the thickness of the reactive film; allowing the reaction (I) to occur within the reaction zone, to produce a gas stream and a liquid stream; and releasing the gas stream and the liquid stream from the reaction zone. In one aspect, the fluid is a CO₂-containing effluent gas; the process includes feeding an absorption solution into the reactor to contact the CO₂-containing effluent gas so as to dissolve CO₂ from the CO₂-containing effluent gas into the absorption solution; the reaction (I) is a forward reaction catalyzing the hydration of dissolved CO₂ into bicarbonate ions and hydrogen ions; and the gas stream is a CO₂-depleted gas and the liquid stream is an ion-rich solution including the bicarbonate ions and hydrogen ions. In another aspect, the fluid is an ion-rich solution including bicarbonate and hydrogen ions; and the reaction (I) is a backward reaction catalyzing the desorption of the bicarbonate ions into gaseous CO₂; the gas stream being a CO₂ stream and the liquid stream being a regenerated solution.

- In some implementations, there may be provided a process for capturing CO₂ from a CO₂-containing gas including: designing, controlling or regulating parameters and operating conditions of a reactor in order to influence the thickness of the mass transfer film and reactive film so as to favour the functionality of the enzymatic particles having a given size within the mass transfer film and the reactive film. The reaction film may be at or below about 15 μm, at or below about 10 μm, at or below about 5

μm , at or below about 1 μm , at or below about 0.5 μm or at or below about 0.2 μm .

- In some implementations, there may be provided a process for desorbing CO_2 gas from an ion-rich aqueous mixture including bicarbonate and hydrogen ions, including: providing enzymatic particles including carbonic anhydrase or an analogue thereof in the ion-rich aqueous mixture; feeding the ion-rich aqueous mixture into a desorption reactor, the particles being sized so as to be smaller than the thickness of a desorption reactive film to promote transformation of the bicarbonate and hydrogen ions into CO_2 gas and water, thereby producing a CO_2 gas stream and an ion-depleted solution.
- In some implementations, the process may have a gas-liquid reactor with optional chemical absorption enhancements and/or the enzymatic particles are designed, tailored, provided, constructed and/or operated, such that the enzymatic particles can be sufficiently present in the reaction film to accelerate the reaction. The gas-liquid reactor with optional chemical absorption enhancements and/or the enzymatic particles may be designed, tailored, provided, constructed and/or operated, such that the enzymatic particles such that the enzymes can be sufficiently stabilized in particle-form and sufficiently present in the reaction film to accelerate the reaction
- In some implementations, the invention provides a process for capturing CO_2 from a CO_2 -containing gas including: contacting the CO_2 -containing gas with an absorption mixture in a gas-liquid contact reactor and forming a rate-limiting reactive film for capturing CO_2 , the absorption mixture including a liquid solution and enzymatic particles; the enzymatic particles being sized so as to be sufficiently present in the rate-limiting reactive film to promote transformation of CO_2 into bicarbonate and hydrogen ions, thereby producing a CO_2 -depleted gas and an ion-rich mixture. The process may include an absorption stage and a desorption stage, and the enzymatic particles may be present in both the absorption and desorption stages and are sized so as to be smaller than the rate-limiting reactive film of absorption and the rate-limiting reactive film desorption.

- The enzymatic particle size may be determined according any one or a combination of the methodologies described herein. The reactive film thickness may be determined according to any one or a combination of the calculation methodologies described herein.
- In some implementations, the invention provides a CO₂ capture formulation including water, enzymatic particles sized so as to be smaller than the thickness of a reactive film and, optionally, the formulation also includes an absorption compound.
- In some implementations, the invention provides a premixed composition including water, enzymatic particles sized so as to be smaller than the thickness of a reactive film and, optionally, an absorption compound.
- In some implementations, the invention provides a kit of chemical components including water, enzymatic particles sized so as to be smaller than the thickness of a reactive film and, optionally, an absorption compound.
- In some implementations, the invention provides a method of making enzymatic particles for treatment of a fluid to catalyze reaction (I) with carbonic anhydrase in a reactor using an absorption solution, wherein the reaction (I) is as follows:



the method including: determining, estimating or designing a reactive film thickness according to operating conditions of the reactor and properties of the absorption solution; and making the enzymatic particles such that a sufficient amount of the enzymatic particles have a size smaller than the reactive film thickness.

It should be noted that “enzymes” or “biocatalysts” include analogues and variants thereof. The carbonic anhydrase enzyme may be naturally occurring, modified or evolved carbonic anhydrase enzyme; analogues thereof may be non-biological small molecules that are naturally occurring or synthesized to achieve or mimic the effect of the enzyme.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments and aspects of the invention may be further appreciated and understood in light of the following figures:

Fig 1 is a process diagram of an embodiment of the present invention, wherein biocatalytic particles flow in the absorption solution.

Fig 2 is a process diagram of another embodiment of the present invention, wherein an absorption unit is coupled to a desorption unit and biocatalytic particles flow in the absorption solution.

Fig 3 is a schematic representation of the gas-liquid interface in absorption.

Fig 4 is a graph showing evolution of residual activity of enzyme particles exposed to MDEA 2M at 40°C, illustrating stability effect.

Fig 5 is a graph showing the influence of particle size on the contribution of carbonic anhydrase immobilized onto particles to the CO₂ hydration rate in a 2M MDEA solution at 25°C.

DETAILED DESCRIPTION

Processes, systems and techniques are provided for using an enzyme delivery technique for CO₂ gas treatment or capture, allowing improved enzymatic catalysis and thus increased efficiency of the process, by providing enzymatic particles that are sized according to the reactive liquid film thickness of a particular reaction medium.

The thickness of the liquid reactive film depends on certain factors including the type of gas-liquid contactor reactors, absorption solution and the gas being absorbed. Referring to Fig 3, a schematic representation of the gas liquid interface in an absorption unit is shown. In this absorption unit, the gas phase flows upward and liquid phase downward. Mass transfer between the two phases takes place in the gas film (thickness of δ_g) and the liquid film (thickness of δ_l). For CO₂ absorption, resistance to mass transfer is in the liquid phase. In some conventional absorption processes, the thickness of liquid film at the surface of the packing is several millimeters. However, the thickness of the reactive liquid film (δ_{rf}) where the mass transfer and reactions between CO₂ and the solution take place in some absorption processes is smaller than 10 μm , for example between about 0.1 μm and about 9.9 μm in many cases. The enzyme is preferably allowed to be present in this reactive liquid film δ_{rf} . Possible ways to reach this is by using

soluble enzyme or by using enzyme particles with small diameters. For comparison, enzyme immobilized to large fixed packing, which is at the surface of the packing material, is several millimeters away from the gas liquid interface and the reactive liquid film and its impact is thus relatively lower.

It should also be noted that for processes where the chemical reaction rate is fast compared to the mass transfer rate, only liquid near the gas-liquid interface will be efficiently used for the chemical conversion. Moreover, in so-called fast and instantaneously reaction regimes, the reaction that comes from the gas-phase will be completely converted near or, occasionally at, the gas-liquid interface. This means that there will be essentially no unconverted reactant present in the liquid besides from this rather small regime near the interface. An estimation of the dimensions of the mass transfer zone can be obtained by applying the film model which leads to $\delta = D/k_L$. For various gas-liquid reactors the value of k_L varies usually between $10^{-4} - 10^{-5}$ m/s and the diffusivity, D , is about 10^{-9} m.s⁻², resulting in mass transfer film thickness of 10-100 μ m. The film thickness of the reactive liquid film where the mass transfer and reactions between CO₂ and the solution take place (δ_{rf}) in other absorption processes is smaller than 10 μ m.

To take advantage of the effects associated with such reactive film thicknesses, in some implementations, the process for enzymatic catalysis of a hydration reaction of CO₂ in an aqueous absorption mixture includes enhancing enzymatic catalysis by sizing the enzymatic particles sufficiently small with respect to the reactive liquid film thickness (δ_{rf}).

The process may include contacting the CO₂ containing gas with an aqueous absorption mixture including water and an absorption compound under conditions such that mass transfer of the CO₂ first occurs through a gas film thickness (δ_g); and then occurs through a liquid film thickness (δ_l), wherein $\delta_l = D_{CO_2} / k_L$ where k_L is the mass transfer coefficient in the liquid and D_{CO_2} is the diffusion coefficient of CO₂. The process may also include determining a reactive liquid film thickness (δ_{rf}) of CO₂ hydration reaction, wherein $\delta_{rf} = (\delta_l) / Ha$ where $Ha^2 = (k_1 \cdot D_{CO_2}) / (k_L)^2$, $Ha > 2$ and $k_1 = k_2 C_{ab}$ where k_2 is the kinetic constant for the CO₂ hydration reaction in the absorption mixture and C_{ab} is the concentration of the absorption compound in the aqueous absorption mixture. The process may further include providing the enzymatic particles in the aqueous absorption mixture, wherein the

enzymatic particles are sized in accordance with the reactive liquid film thickness (δ_{rf}) to increase enzymatic catalysis of the CO₂ hydration reaction.

The process may include controlling the reactive liquid film thickness (δ_{rf}) by regulating the concentration of the absorption compound, the temperature of the process, the mass transfer coefficient (k_L) or a combination thereof.

The enzymatic particles may be sized to be smaller than the reactive film thickness, such as between about 0.001 μm and about 10 μm .

The preferred range of enzyme particle diameter will depend on several factors including the liquid concentration, gas concentration, absorption compounds in the solution, and operating conditions of the CO₂ capture reactors. The thickness of the reactive film varies with the reaction rate of the absorption compound with CO₂. The faster the absorption solution, the thinner the reactive film thickness. Solutions including primary, secondary alkanolamines and ammonia based solutions are considered to be fast absorption solutions and are expected to lead to thinner reactive films.

For example, the process may include sizing the enzymatic particles to have a diameter (d) such that $d / \delta_{rf} < 6$, $d / \delta_{rf} < 3$, $d / \delta_{rf} < 1$, $d / \delta_{rf} < 0.05$, or $d / \delta_{rf} < 0.025$. The reactive liquid film thickness (δ_{rf}) may be at most 10 μm , 5 μm , 3 μm , 2.5 μm , 2.0 μm , 1.9 μm or 1.8 μm .

Reactive film thickness varies according to the reaction rate between CO₂ and the absorption compound. For example, for MDEA the reaction rate is:

$$R = k C_{\text{MDEA}} * C_{\text{CO}_2}$$

Where R is the reaction rate, k is the reaction constant, C_{MDEA} is the MDEA concentration and C_{CO_2} is the CO₂ concentration. Increasing the absorption compound concentration leads to an increase in the reaction rate and a decrease in the thickness of the reactive film. The relationship between the solution concentration and film thickness will depend on the compound, as each has a different k coefficient. The dependence of the reaction rate on compound concentration is also different for carbonate solutions than for alkanolamine solutions and other types of solutions.

According to some embodiments of the present invention, the particles are sized in accordance with a calculated, estimated or approximated liquid mass transfer film thickness for a given absorption solution and process conditions. For example, referring to Fig 3, the liquid mass transfer film (δ_l) can be determined by the following equation:

$$\delta_l = D_{CO_2} / k_L$$

where k_L is the mass transfer coefficient in the liquid and D_{CO_2} is the diffusion coefficient of CO_2 . The coefficients k_L and D_{CO_2} may be determined in a variety of ways from existing tables in handbooks, empirical estimates or handbook data and calculations or a combination thereof. One may obtain an estimate of δ_l by using the above equation for a given absorption solution and operating conditions, and then manufacture or utilise enzymatic particles in accordance with the estimated δ_l . The process may also include continuously or periodically updated monitoring and calculations of δ_l and δ_{rt} to determine the preferred sizing and concentration of the enzyme particles, for the optimized reactivity, activity, pumpability, efficiency and overall economics of the process. The process may also include periodically or continuously controlling the process conditions and hydrodynamics to actively manage δ_l and δ_{rt} such that the enzymatic particles used in the reactor can have their intended functionality.

In addition, the ratio of the reactive film (δ_{rt}) to mass transfer film (δ_l) is roughly indicated by the so-called Hatta number (Ha), with Ha defined for a first order reaction as:

$$Ha^2 = (k_1 \cdot D_{CO_2}) / (k_L)^2$$

And for values of $Ha > 2$ it can be estimated that:

$$(\delta_{rt}) = (\delta_l) / Ha$$

Thus, Ha may be used to calculate the thickness of the reactive film for a given absorption system (absorption solution, reactor type and hydrodynamics) and then to determine the preferred enzymatic particles sizes for the given application, with Ha being preferably greater than 2.

In some embodiments of the present invention, the particles are also sized and provided in a concentration such that the resulting suspension is pumpable.

One embodiment of the process and system is shown in Fig 1 and will be described in further detail hereafter. First, the biocatalytic particles are mixed in the lean absorption solution in a mixing chamber (E-4). The lean absorption solution refers to the absorption solution characterized by a low concentration of the species to be absorbed. This solution is either fresh solution or comes from the mineral carbonation process or the CO₂ desorption process (10). The absorption solution with biocatalytic particles (11), also referred to as the absorption mixture, is then fed to the top of a packed column (E-1) with a pump (E-7). The packing material (9) may be made of conventional material like polymers, metal and ceramic. The geometry of the packing may be chosen from what is commercially available. It is also possible to choose or arrange the packing to promote certain deflections and collisions with the particles, or to avoid accumulation of the particles within the reactor. For instance, the packing preferably has limited upward facing concavities to avoid the accumulation of particles therein. Also preferably, the packing supports are much larger than the particles. Also preferably, the particles and packing are chosen so that the particles can flow through the reactor without clogging. Counter-currently, a CO₂ containing gas phase (12) is fed to the packed column (E-1) and flows on, through and/or around the packing (9) from the bottom to the top of the column. The absorption solution and biocatalytic particles flow on, through and/or around the packing material (9) from the top of the column to the bottom. As the absorption solution and biocatalytic particles progress through the absorber, the absorption solution becomes richer in the compound that is being absorbed. Biocatalytic particles, present near the gas-liquid interface, enhance CO₂ absorption by immediately catalyzing the CO₂ hydration reaction to produce bicarbonate ions and protons and thus maximizing the CO₂ concentration gradient across the interface. At the exit of the column, the rich absorption solution and biocatalytic particles (13) are pumped (E-5) to a particle separation unit (E-3). Rich absorption solution refers to the absorption solution characterized by a concentration of absorbed compound which is higher than that of the lean solution. The separation unit may include a filtration unit (such as a tangential filtration unit), a centrifuge, a cyclone, a sedimentation tank or a magnetic separator and any other units or equipments known for particle or solid separation. The separation unit also enables a certain quantity of solution to be retained with the particles so the

particles do not dry out which can denature the biocatalysts. In one optional aspect, the quantity of retained solution enables the particles to be pumped (E-6) to a storage unit or directly back to a mixing chamber (E-4) for addition into the absorption unit. In another optional aspect, the particles with retained solution may be gravity fed into the mixing chamber (E-4), which may be enabled by performing separation above the mixing unit, for example. The separation may be conducted in continuous or in batch mode, and may be managed to ensure the proper amount of solution is retained to ensure enzyme activity. It may also be preferred that the particles are provided such that they may be easily separated from any solid precipitates (e.g. bicarbonate precipitates) that may be entrained in the ion-rich solution, if need be. The absorption solution without particles (15) is then pumped (E-9) to another unit which may be a CO₂ desorption unit or a mineral carbonation unit (10). Biocatalytic particles (16) are mixed with the CO₂ lean absorption solution. This suspension is then fed once again to the absorption column (E-1).

In another embodiment, the absorption unit is coupled to a desorption unit as shown in further detail in Fig 2. In this embodiment, the absorption solution rich in CO₂ without biocatalytic particles (15) is pumped (E-9) through a heat exchanger (E-10) where it is heated and then to the desorption column (E-11). In the desorption unit, the solution is further heated in order that the CO₂ is released from the solution in a gaseous state. Because of relatively high temperature used during desorption, water also vaporizes. Part of the absorption solution (18) is directed toward a reboiler (E-12) where it is heated to a temperature enabling CO₂ desorption. Gaseous CO₂ together with water vapour are cooled down, water condenses and is fed back to the desorption unit (19). Dry gaseous CO₂ (20) is then directed toward a compression and transportation process for further processing. The liquid phase, containing less CO₂, and referred to as the lean absorption solution (17) is then pumped (E-14) to the heat exchanger (E-10) to be cooled down and fed to the mixing chamber (E-4). The temperature of the lean absorption solution (17) should be low enough not to denature the enzyme if present.

In another optional aspect of the invention, an advantage is that immobilization of the biocatalysts on or within the particles may provide increased stability to the enzyme. More regarding stability will be described below. The particles with

immobilized biocatalysts may have a longer shelf life for storage, shipping, reutilisation, and recycling within the process as the biocatalysts are stabilised on or in the support material. In some embodiments, the immobilized biocatalysts may be stable to operating conditions in process units other than the absorption unit, such as the desorption unit, and consequently particles could be used in the absorption and desorption units without the need to remove the particles prior to the desorption unit. In such a process configuration the enzymatic particles may have an impact in the absorption unit by increasing the CO₂ absorption rate but also in the desorption unit since carbonic anhydrase is also known to increase rate of bicarbonate ion transformation into CO₂ (which is one of the reactions that would take place in the desorption unit). In this configuration, the removal unit (E-3) would be required to remove deactivated particles and unit (E-4) to add fresh enzymatic particles. However, it may be advantageous to have a separation unit such as a filter between (E-11) and (E-12) to avoid flow of the enzymatic particles through the reboiler and their contact with very high temperatures (depending on the thermoresistance of the biocatalysts of the particles).

In another optional aspect of the invention, an advantage is that the particles can be easily replaced or refurbished. The mixing chamber (E-4) preferably includes an inlet for receiving recycled particles from the separation unit (E-3) and also an inlet/outlet for both removing a fraction of used particles and replacing them with new particles, thereby refurbishing the overall batch of particles in the system.

In another optional aspect of the invention, an advantage of the process and system is that the particles can be removed from the ion-rich mixture far easier than conventional free enzymes. By way of example, human carbonic anhydrase type II is an ellipsoid with dimensions of 39 Å x 42 Å x 55 Å and is difficult to separate from solution. Thus, the particles can be sized to enable both high absorption rate and easy removal for recycling. In this way, the enzymes can avoid being present in the desorption unit which can involve high temperatures and other conditions that can denature some types of enzymes and enzyme variants. In some embodiments, the biocatalytic particles are filtered (e.g. micro-filtered or nano-filtered, depending on size), centrifuged, cycloned, sedimented or separated magnetically in a separation unit. Alternatively, they can be left to circulate in the process. Optionally, other small particles such as precipitates can be separated in a preceding or subsequent separation unit.

The process/system may include a separation unit for removal of the particles. These particles are then preferably pumped back to the inlet of the absorption liquid in the packed column. The selection of the separation unit depends on the size of particles, density, cost and on their nature (e.g. magnetic or non magnetic particles). The process may also include a desorption unit in order to regenerate the ion-rich solution.

In one embodiment, the particles are used in conjunction with an absorption compound in the solution. The absorption compound may be primary, secondary and/or tertiary amines (including alkanolamines); primary, secondary and/or tertiary amino acids; and/or carbonates. The absorption compound may more particularly include amines (e.g. piperidine, piperazine and derivatives thereof which are substituted by at least one alkanol group), alkanolamines (e.g. monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), 2-(2-aminoethylamino)ethanol (AEE), 2-amino-2-hydroxymethyl-1,3-propanediol (Tris), N-methyldiethanolamine (MDEA), dimethylmonoethanolamine (DMMEA), diethylmonoethanolamine (DEMEA), triisopropanolamine (TIPA) and triethanolamine), dialkylether of polyalkylene glycols (e.g. dialkylether or dimethylether of polyethylene glycol); amino acids which may include potassium or sodium salts of amino acids, glycine, proline, arginine, histidine, lysine, aspartic acid, glutamic acid, methionine, serine, threonine, glutamine, cysteine, asparagine, valine, leucine, isoleucine, alanine, valine, tyrosine, tryptophan, phenylalanine, and derivatives such as taurine, N,cyclohexyl 1,3-propanediamine, N-secondary butyl glycine, N-methyl N-secondary butyl glycine, , diethylglycine, dimethylglycine, , sarcosine, , methyl taurine, methyl- α -aminopropionic acid, N-(β -ethoxy)taurine, N-(β -aminoethyl)taurine, N-methyl alanine, 6-aminohexanoic acid ; and which may include potassium carbonate, sodium carbonate, ammonium carbonate, ammonia based solutions, promoted potassium carbonate solutions and promoted sodium carbonate solutions or promoted ammonium carbonates; or mixtures thereof. Absorption compounds are added to the solution to aid in the CO₂ absorption and to combine with the catalytic effects of the carbonic anhydrase. Due to the structure or high concentration of some absorption compounds, the activity or longevity of the carbonic anhydrase can be threatened. For instance, free enzymes may be more vulnerable to denaturing caused by an absorption compound with high ionic strength such as carbonates. Immobilising

the carbonic anhydrase can mitigate the negative effects of such absorption compounds. By providing the carbonic anhydrase immobilised or otherwise supported by particles, the process can yield high CO₂ transfer rates in the presence of absorption compounds while mitigating the negative effects such compounds could otherwise have on free enzymes. Preferably, the absorption compound and the size of the enzymatic particles are selected to optimize the enzymatic activity and the overall economics of the process. For example, the concentration of the absorption compound and the concentration of the enzymatic particles are designed in combination with the particle size, to increase efficiency and decrease the cost of the process.

According to some embodiments of the present invention, the carbonic anhydrase is immobilized on a surface of the support material of the particles, entrapped within the support material of the particles, or a combination thereof. In some embodiments, the particles are composed of a support or encapsulation material onto or into which at least one enzyme is provided. The immobilization may be selected from adsorption, covalent bonding, entrapment, copolymerization, cross-linking, and encapsulation, and combinations thereof.

In some implementations, the enzymatic particle size is based on the reactive liquid film thickness so that the size enhances the enzymatic catalysis. In other words, the enzymatic particles are small enough to achieve improved enzymatic catalysis compared to larger particles, thus increasing the effect of the enzyme. It has been found that the effect of the enzyme on catalysis of the hydration reaction, as demonstrated by the turnover factor, has what appears to be a catalytic plateau when the particles are a certain size that is relatively larger than the reactive liquid film thickness, for example when $d / \delta_{rf} > \text{about } 30 \text{ or } 50$ (e.g. 32.7 and 48.7 in Example). However, at a certain particle size, for example when $d / \delta_{rf} < \text{about } 6$ (5.9 in Example), the reaction system increases above the plateau and achieves greater enzyme catalysis demonstrated by increased turnover factor. The enzymatic particle sizing based on the reactive liquid film thickness has been tested and shown for MDEA systems. MDEA is a tertiary alkanolamine and it should be noted that other systems including absorption compounds, which have similar or analogous effects as MDEA on absorption systems, may also utilize and benefit from the enzymatic particle sizing techniques as described herein. As mentioned further above, using different

compounds will provide different characteristics of the system, e.g. some compounds such as primary alkanolamines like TRIS provide “faster” absorption compared to MDEA; consequently, the reactive liquid film thickness can be affected by different compounds, concentrations and temperatures, and the enzymatic particle sizing can be adapted accordingly.

It should be noted that the information, methodologies and calculations described herein may be used and adapted to various absorption systems to utilize the enzymatic particle sizing techniques as described herein.

In addition, given that dehydration is the reverse reaction of hydration, the information, methodologies and calculations described herein may be used and adapted to various desorption systems, to utilize and benefit from the enzymatic particle sizing techniques as described herein. As mentioned above, the enzymatic particle sizing may be done in order to achieve increased enzymatic catalysis of both the absorption and desorption stages, for example in a combined bioreactor as shown in Fig 2 and described herein.

Furthermore, the information, methodologies and calculations described herein may be used and adapted to enzyme systems and reactions other than carbon dioxide and the corresponding hydration and dehydration reactions, to utilize and benefit from the enzymatic particle sizing techniques as described herein, insofar as the other enzymes may be immobilized with respect to particles and the reaction system involves a reactive liquid film thickness as described herein. Such other implementations may particularly be applicable in gas-liquid systems, similar to a CO₂ absorption and/or desorption system, but may also be applicable to liquid-liquid systems and other phase transfer and reaction systems with appropriate adaptation.

EXAMPLES

Example 1

Preliminary tests were performed with nylon particles of two different sizes: 50-160 µm and 2-20 µm. The tests were performed in 2M MDEA and 1.45 M K₂CO₃ under similar operation conditions in hydration cells.

This hydration cell reactor was designed and operated at set conditions to control the area of the interface between a gas phase, CO₂, and a liquid phase in an

absorption process. This device was used to evaluate impact of enzymatic particles on the CO₂ absorption rate in a given absorption solution. Tests were conducted as follows: a known volume of the unloaded absorption solution is introduced in the reactor; then a known mass of particles is added to the absorption solution (particles may or may not contain enzyme for the purpose of comparison); a CO₂ stream is flowed through the head space of the reactor and agitation is started; pH of the solution is measured as a function of time; then pH values are converted into carbon concentration in g C/L using a carbon concentration-pH correlation previously determined for the absorption solution; absorption rates are determined from a plot of C concentration as a function of time. The impact of the enzyme as a relative absorption rate is reported: ratio of absorption rate in the presence of the enzyme particles to absorption rate in the presence of particles without enzyme.

According to the results, enzyme particles resulted in a noticeable increase absorption rate only in 1.45 M K₂CO₃, which is the slower CO₂ absorption solution, for both particle sizes used. Under the tested conditions, the absorption of K₂CO₃ without enzyme would be about 10 times slower than absorption rate in 2M MDEA without enzyme. In addition, it was also observed that the impact of particles was more pronounced for smaller particles. The impact observed was also considerably less than what was obtained with a similar free enzyme concentration.

These tests show that having smaller particles, with particle sizes smaller than the reactive film, would increase the impact of the enzymatic particles.

Example 2

The particle support material may be made of nylon, silica, silica gel, chitosan, polyurethane, polystyrene, polymethylmetacrylate, cellulose, magnetic particles, alumina, and other material known to be used for biocatalysts immobilization and entrapment. The particles may also be composed of a combination of different materials. For instance, the support may have a core composed of a material having different density or other properties compared to a different surface material which is provided for immobilization or entrapment of the enzymes. For example, the core of the support may be composed of a magnetic material to enable magnetic separation and the surface material may be polymeric such as

nylon for supporting the enzyme. As noted above, in one embodiment the support material may be an aggregate of enzymes to form CLEA or CLEC. The particles may each define an integral solid volume (e.g. a bead-like shape) or may include one or more apertures traversing the main volume of the particle (e.g. a pipe or donut shape). By way of example, the particles may be ovoid, spherical, cylindrical, etc.

The particles may be sized in accordance with the requirements of given process conditions. The compounds, materials and process equipment should be chosen to allow sufficient flow and pumpability of the absorption mixture.

Example 3

An experiment was conducted in an absorption packed column. The absorption solution is an aqueous solution of methyldiethanolamine (MDEA) 4M. This absorption solution is contacted counter-currently with a gas phase with a CO₂ concentration of 130,000 ppm. Liquid flow rate was 0.65 g/min and gas flow rate was 65 g/min corresponding to L/G of 10 (g/g). Gas and absorption solution were at room temperature. Operating pressure of the absorber was set at 1.4 psig. The column has a 7.5 cm diameter and a 50 cm height. Packing material is polymeric Raschig rings 0.25 inch. Three tests were performed: the first with no catalyst, the second with carbonic anhydrase immobilized to packing support and the third using carbonic anhydrase free in solution at a concentration of 0.5 g per liter of solution.

The results obtained showed that CO₂ transfer rate or CO₂ removal rate increased from 6 to 14 mmol CO₂/min with carbonic anhydrase immobilized onto the surface of Raschig rings. In the presence of free enzyme i.e. carbonic anhydrase free flowing in the solution, the transfer rate increased to 29 mmol/min. These results demonstrate the positive impact of adding the enzyme in a packed column and that particles including enzymes can enable improvements.

Similar tests were also performed with solutions of potassium carbonate (20% w/w -1.45 M)) and sodium carbonate 0.5 M. The impact of free and immobilized enzyme follows the same trend as for MDEA 4 M.

Example 4

Tests were conducted with cross linked enzyme aggregates (CLEA) of carbonic anhydrase (using a non optimized protocol). The enzyme used is a thermoresistant variant of enzyme HCAII, designated as 5X. CLEA contains 26% (w/w) of the 5X enzyme. Particle size ranges between 4-9 μm . Absorption solution was 1.45 M K_2CO_3 . Testing temperature was 20°C. Enzyme based concentration of the CLEA was 0.5 g/L. Methodology is as described in Example 1. Tests were conducted with CLEAs and then with deactivated CLEAs as a reference to enable determination of the enzyme impact. Results indicate that the CLEAs increased the CO_2 absorption rate by a factor of 3.2.

Example 5

Tests were conducted with cross linked enzyme aggregates (CLEA) of carbonic anhydrase (using a non optimized protocol). The enzyme used is a thermoresistant variant of enzyme HCAII, designated as 5X. CLEA contains 26% (w/w) of the 5X enzyme. Particle size ranges between 4-9 μm . Absorption solution was 1M MDEA. Testing temperature was 25°C. Enzyme concentration was 0.5 g/L. CO_2 absorption tests were performed in a stirred cell, a simple device that can be used to evaluate CO_2 absorption rates under different conditions. The stirred cell contains the absorption solution (and the enzyme when required). A known pressure of pure CO_2 is applied to the solution. In these tests, initial CO_2 pressure is 1000 mbar. Then the pressure decrease is monitored and used to calculate CO_2 transfer rate in the absorption. Tests were conducted with particles with CLEAs and without CLEAs to enable determination of the enzyme impact. Results are expressed as a ratio of the CO_2 transfer rate with CLEAs to the CO_2 transfer rate in the absence of CLEAs. Results indicate that CLEAs increase CO_2 absorption rate by a factor of 1.3 to 1.7 in the MDEA.

Example 6

Tests were conducted with HCAII immobilised at the surface of magnetic silica coated iron oxide particles (using a non optimized immobilization protocol). The particle size was 5 μm . The absorption solution was 1.45 M K_2CO_3 . The testing temperature was 20°C. The enzyme concentration was 0.2 g/L. The methodology is as described in Example 1. Results indicated that enzyme on magnetic particles increased the CO_2 absorption rate by a factor of 1.6.

Example 7

This example provides calculations for the preferred minimum activity density for a given particle size, for an embodiment of the process.

Data:

Activity level to be reached in the absorption solution: 5×10^6 units/L (corresponding to 1g/L soluble carbonic anhydrase).

Material density: 1.1 g/mL for nylon particles (~ 1100 g/L).

Maximum allowable particle concentration: 300 g/L.

Particle diameter: 10 μm .

Calculations:

1. Surface area of a 10 μm particle

$$A_p = 4\pi (\text{radius})^2 = 4\pi (5)^2 = 314 \mu\text{m}^2$$

2. Volume of a 10 μm particle

$$V_p = 4/3 \pi (\text{radius})^3 = 4/3 \pi (5)^3 = 524 \mu\text{m}^3$$

3. Total volume of particles per liter to reach the maximum allowable particle concentration:

$$\text{Total volume of particles } (V_T) = \frac{\text{Maximum particle mass per liter}}{\text{particle density}}$$

$$V_T = 300 \text{ g} / (1,100 \text{ g/L}) = 0.272 \text{ L (corresponding to } 2.72 \times 10^{14} \mu\text{m}^3)$$

4. Number of particles (n_p) in 1 L of solution:

$$n_p = \frac{V_T}{V_p}$$

$$n_p = 2.72 \times 10^{14} \mu\text{m}^3 / 524 \mu\text{m}^3 = 5.21 \times 10^{11}$$

5. Total particles surface area (A_T)

$$A_T = n_p * A_p = 5.21 \times 10^{11} * 314 = 1.64 \times 10^{14} \mu\text{m}^2 (1.64 \times 10^8 \text{ mm}^2)$$

6. Minimum activity density

$$\text{Activity density} = \text{Activity level}/A_T = 5 \times 10^6 / 1.64 \times 10^8 = 0.03 \text{ Unit WA/mm}^2$$

Thus, for 10 μm particles, the minimum activity density to reach an activity level of 5×10^6 units WA/L, is 0.03 unit WA/mm².

Thus, if the activity density is higher than 0.03 unit WA/mm², a particle concentration lower than 300 g/L would be needed. Additional examples are shown in the Table below.

Table: Examples of minimum activity density for given particle size scenarios

Equivalent free enzyme concentration (g/L)	Desired enzyme activity (Units WA/L)	Particle size (μm)	Surface area of one particle (Ap) (μm ²)	Volume of one particle (Vp) (μm ³)	Desired maximum particle concentration (g/L)	Material density (g/mL)	Total volume of particles (μm ³)	Number of particles/L of solution	Total particle surface area (mm ²)	Minimum required activity density (Units WA/mm ²)
5	2.50E+07	10	314.16	524	300	1.1	2.73E+14	5.21E+11	1.64E+08	1.53E-01
5	2.50E+07	5	78.54	65	300	1.1	2.73E+14	4.17E+12	3.27E+08	7.64E-02
5	2.50E+07	1	3.1416	0.524	300	1.1	2.73E+14	5.21E+14	1.64E+09	1.53E-02
5	2.50E+07	0.1	3.14E-02	5.E-04	300	1.1	2.73E+14	5.21E+17	1.64E+10	1.53E-03
5	2.50E+07	0.01	3.14E-04	5.E-07	300	2	1.50E+14	2.86E+20	9.00E+10	2.78E-04
5	2.50E+07	0.001	3.1416E-06	5.E-10	300	3	1.00E+14	1.91E+23	6.00E+11	4.17E-05
5	2.50E+07	10	314.16	5.E+02	50	3	1.67E+13	3.18E+10	1.00E+07	2.50E+00
5	2.50E+07	5	78.54	65	50	1.6	3.13E+13	4.77E+11	3.75E+07	6.67E-01
5	2.50E+07	1	3.1416	0.524	50	1.6	3.13E+13	5.97E+13	1.88E+08	1.33E-01
5	2.50E+07	0.1	0.031416	5.E-04	50	1.6	3.13E+13	5.97E+16	1.88E+09	1.33E-02
5	2.50E+07	0.01	0.00031416	5.E-07	50	1.1	4.55E+13	8.68E+19	2.73E+10	9.17E-04
5	2.50E+07	0.001	3.1416E-06	5.E-10	50	1.6	3.13E+13	5.97E+22	1.88E+11	1.33E-04
1	5.00E+06	10	314.16	524	300	1.1	2.73E+14	5.21E+11	1.64E+08	3.06E-02
1	5.00E+06	5	78.54	65	300	1.1	2.73E+14	4.17E+12	3.27E+08	1.53E-02
1	5.00E+06	1	3.1416	0.524	300	1.1	2.73E+14	5.21E+14	1.64E+09	3.06E-03
1	5.00E+06	0.1	3.14E-02	5.E-04	300	1.1	2.73E+14	5.21E+17	1.64E+10	3.06E-04
1	5.00E+06	0.01	3.14E-04	5.E-07	300	2	1.50E+14	2.86E+20	9.00E+10	5.56E-05
1	5.00E+06	0.001	3.1416E-06	5.E-10	300	3	1.00E+14	1.91E+23	6.00E+11	8.33E-06
1	5.00E+06	10	314.16	524	50	1.6	3.13E+13	5.97E+10	1.88E+07	2.67E-01
1	5.00E+06	5	78.54	65	50	1.6	3.13E+13	4.77E+11	3.75E+07	1.33E-01
1	5.00E+06	1	3.1416	0.524	50	1.6	3.13E+13	5.97E+13	1.88E+08	2.67E-02
1	5.00E+06	0.1	0.031416	5.E-04	50	1.6	3.13E+13	5.97E+16	1.88E+09	2.67E-03
1	5.00E+06	0.01	0.00031416	5.E-07	50	1.1	4.55E+13	8.68E+19	2.73E+10	1.83E-04
1	5.00E+06	0.001	3.1416E-06	5.E-10	50	1.6	3.13E+13	5.97E+22	1.88E+11	2.67E-05
0.1	5.00E+05	10	314.16	524	300	1.1	2.73E+14	5.21E+11	1.64E+08	3.06E-03
0.1	5.00E+05	5	78.54	65	300	1.1	2.73E+14	4.17E+12	3.27E+08	1.53E-03
0.1	5.00E+05	1	3.1416	0.524	300	1.1	2.73E+14	5.21E+14	1.64E+09	3.06E-04
0.1	5.00E+05	0.1	3.14E-02	5.E-04	300	1.1	2.73E+14	5.21E+17	1.64E+10	3.06E-05
0.1	5.00E+05	0.01	3.14E-04	5.E-07	300	2	1.50E+14	2.86E+20	9.00E+10	5.56E-06

0.1	5.00E+05	0.001	3.1416E-06	5.E-10	300	3	1.00E+14	1.91E+23	6.00E+11	8.33E-07
0.1	5.00E+05	10	314.16	524	50	1.6	3.13E+13	5.97E+10	1.88E+07	2.67E-02
0.1	5.00E+05	5	78.54	65	50	1.6	3.13E+13	4.77E+11	3.75E+07	1.33E-02
0.1	5.00E+05	1	3.1416	0.524	50	1.6	3.13E+13	5.97E+13	1.88E+08	2.67E-03
0.1	5.00E+05	0.1	0.031416	5.E-04	50	1.6	3.13E+13	5.97E+16	1.88E+09	2.67E-04
0.1	5.00E+05	0.01	0.00031416	5.E-07	50	1.1	4.55E+13	8.68E+19	2.73E+10	1.83E-05
0.1	5.00E+05	0.001	3.1416E-06	5.E-10	50	1.6	3.13E+13	5.97E+22	1.88E+11	2.67E-06
0.01	5.00E+04	10	314.16	524	300	1.1	2.73E+14	5.21E+11	1.64E+08	3.06E-04
0.01	5.00E+04	5	78.54	65	300	1.1	2.73E+14	4.17E+12	3.27E+08	1.53E-04
0.01	5.00E+04	1	3.1416	10.524	300	1.1	2.73E+14	5.21E+14	1.64E+09	3.06E-05
0.01	5.00E+04	0.1	3.14E-02	5.E-04	300	1.1	2.73E+14	5.21E+17	1.64E+10	3.06E-06
0.01	5.00E+04	0.01	3.14E-04	5.E-07	300	2	1.50E+14	2.86E+20	9.00E+10	5.56E-07
0.01	5.00E+04	0.001	3.1416E-06	5.E-10	300	3	1.00E+14	1.91E+23	6.00E+11	8.33E-08
0.01	5.00E+04	10	314.16	524	50	1.6	3.13E+13	5.97E+10	1.88E+07	2.67E-03
0.01	5.00E+04	5	78.54	65	50	1.6	3.13E+13	4.77E+11	3.75E+07	1.33E-03
0.01	5.00E+04	1	3.1416	0.524	50	1.6	3.13E+13	5.97E+13	1.88E+08	2.67E-04
0.01	5.00E+04	0.1	0.031416	5.E-04	50	1.6	3.13E+13	5.97E+16	1.88E+09	2.67E-05
0.01	5.00E+04	0.01	0.00031416	5.E-07	50	1.1	4.55E+13	8.68E+19	2.73E+10	1.83E-06
0.01	5.00E+04	0.001	3.1416E-06	5.E-10	50	1.6	3.13E+13	5.97E+22	1.88E+11	2.67E-07

Example 8

This example provides calculations for the preferred maximum particle size for a given particle concentration, for an embodiment of the process.

Data:

Activity level to be reached in the absorption solution: 5×10^6 units/ (corresponding to 1 g/L soluble carbonic anhydrase).

Activity density on particles: 0.51 unit/mm².

Material density: 1.1 g/mL for nylon particles (~ 1 100 g/L).

Maximum allowable particle concentration: 300 g/L.

Calculations:

1. Total surface area required to reach the activity level:

$$\text{Total surface area } (A_T) = \frac{\text{activity level}}{\text{activity density}}$$

$$A_T = 5 \times 10^6 \text{ units/L} / (0.51 \text{ unit/mm}^2) = 9\,803\,922 \text{ mm}^2$$

2. Total volume of particles per liter to reach the maximum allowable particle concentration:

$$\text{Total volume of particles } (V_T) = \frac{\text{Maximum particle mass per liter}}{\text{particle density}}$$

$$V_T = 300 \text{ g} / (1\,100 \text{ g/L}) = 0.272 \text{ L (corresponding to } 272\,727 \text{ mm}^3)$$

So, a volume of 272 727 mm³ of particles would be present per liter of mixture.

3. Maximum radius of a particle:

For spherical particles:

- $A_p = 4\pi (\text{radius})^2$
- $V_p = 4/3 \pi (\text{radius})^3$

Thus:

$$\frac{A_p}{V_p} = \frac{3}{radius}$$

And:

$$radius = 3 \times \frac{V_p}{A_p} = 3 \times \frac{272\,727}{9\,803\,922} = 0.083\,mm\,(83\,microns)$$

Thus, the preferred maximum size of a particle would have a diameter of about 166 μm . So, if particles are of a smaller diameter, the resulting mixture or absorption solution will be pumpable.

This method can be used to evaluate the maximum particle size allowable for many conditions of activity level, activity density, particle density and maximum allowable particle concentration.

While the calculations in the above Examples are for spherical particles, corresponding calculations or estimations may be performed for other particle geometries. The Table below shows different scenarios and corresponding particle sizes.

Table: Examples of maximum particle size scenarios

Desired free enzyme activity Level (units/L)	Desired activity density (Units WA/mm ²)	Total required surface area (mm ²)	Material density (g/mL)	Maximum desired particle concentration (g/L)	Maximum volume of particles (mm ³)	Maximum particle radius (mm)	Maximum particle diameter (microns)
5.00E+06	0.51	9.80E+06	1.1	300	272,727	8.35E-02	167
1.00E+07	0.51	1.96E+07	1.1	300	272,727	4.17E-02	83
2.00E+06	0.51	3.92E+06	1.1	300	272,727	2.09E-01	417
5.00E+06	0.51	9.80E+06	1.6	300	187,500	5.74E-02	115
1.00E+07	0.51	1.96E+07	1.6	300	187,500	2.87E-02	57
2.00E+06	0.51	3.92E+06	1.6	300	187,500	1.43E-01	287
5.00E+06	1	5.00E+06	1.1	300	272,727	1.64E-01	327
5.00E+06	1	5.00E+06	1.6	300	187,500	1.13E-01	225
5.00E+06	1	5.00E+06	3	300	100,000	6.00E-02	120
5.00E+06	0.51	9.80E+06	1.1	400	363,636	1.11E-01	223

5.00E+06	0.51	9.80E+06	1.6	400	250,000	7.65E-02	153
5.00E+06	0.51	9.80E+06	3	400	133,333	4.08E-02	82
5.00E+06	0.51	9.80E+06	1.1	200	181,818	5.56E-02	111
5.00E+06	0.51	9.80E+06	1.6	200	125,000	3.83E-02	77
5.00E+06	0.51	9.80E+06	3	200	66,667	2.04E-02	41
5.00E+06	0.51	9.80E+06	1.1	100	90,909	2.78E-02	56
5.00E+06	0.51	9.80E+06	1.6	100	62,500	1.91E-02	38
5.00E+06	0.51	9.80E+06	3	100	33,333	1.02E-02	20
5.00E+06	0.51	9.80E+06	1.1	50	45,455	1.39E-02	28
5.00E+06	0.51	9.80E+06	1.6	50	31,250	9.56E-03	19
5.00E+06	0.51	9.80E+06	3	50	16,667	5.10E-03	10
5.00E+06	0.51	9.80E+06	1.1	10	9,091	2.78E-03	6
5.00E+06	0.51	9.80E+06	1.6	10	6,250	1.91E-03	4
5.00E+06	0.51	9.80E+06	3	10	3,333	1.02E-03	2
5.00E+06	0.51	9.80E+06	1.1	1	909	2.78E-04	1
5.00E+06	0.51	9.80E+06	1.6	1	625	1.91E-04	0.4
5.00E+06	0.51	9.80E+06	3	1	333	1.02E-04	0.2
5.00E+06	1	5.00E+06	1.1	1	909	5.45E-04	1.1
5.00E+06	1	5.00E+06	1.6	1	625	3.75E-04	0.8
5.00E+06	1	5.00E+06	3	1	333	2.00E-04	0.4
5.00E+06	0.51	9.80E+06	1.1	0.5	455	1.39E-04	0.3
1.00E+07	0.51	1.96E+07	1.1	0.5	455	6.95E-05	0.1
2.00E+06	0.51	3.92E+06	1.1	0.5	455	3.48E-04	0.7
5.00E+06	0.05	1.00E+08	1.1	0.5	455	1.36E-05	2.7E-02
1.00E+07	0.05	2.00E+08	1.1	0.5	455	6.82E-06	1.4E-02
2.00E+06	0.05	4.00E+07	1.1	0.5	455	3.41E-05	6.8E-02
5.00E+06	0.05	1.00E+08	1.1	10	9,091	2.73E-04	5.5E-01
1.00E+07	0.05	2.00E+08	1.1	10	9,091	1.36E-04	2.7E-01
2.00E+06	0.05	4.00E+07	1.1	10	9,091	6.82E-04	1.4E+00
5.00E+06	0.05	1.00E+08	1.6	10	6,250	1.88E-04	3.8E-01
1.00E+07	0.05	2.00E+08	3	10	3,333	5.00E-05	1.0E-01
1.00E+08	0.05	2.00E+09	1.1	10	9,091	1.36E-05	2.7E-02
5.00E+06	0.05	1.00E+08	1.6	0.5	313	9.38E-06	1.9E-02
1.00E+07	0.05	2.00E+08	3	0.5	167	2.50E-06	5.0E-03
1.00E+08	0.05	2.00E+09	1.1	0.5	455	6.82E-07	1.4E-03

This Table also illustrates another advantage of the smaller particles. The CO₂ capture process in which the particles are used requires a lower mass concentration of particles in the absorption solution compared to larger particles or large packing material.

Example 9

An experiment was conducted in an absorption packed column. The absorption solution is an aqueous solution of potassium carbonate (K₂CO₃) 1.45 M. This absorption solution is contacted counter-currently with a gas phase with a CO₂ concentration of 130,000 ppm. Liquid flow rate was 0.60 g/min and gas flow rate was 60 g/min corresponding to L/G of 10 (g/g). Gas and absorption solution were at room temperature. Operating pressure of the absorber was set at 1.4 psig. The column has a 7.5 cm diameter and a 50 cm height. Packing material is polymeric Raschig rings 0.25 inch. Two tests were performed: the first with no activator, the second with CLEAs containing 26% (w/w) of the 5X enzyme. Particle size ranged between 4-9 µm. The enzyme concentration in the absorption solution was 0.1 g/L.

The results obtained showed that CO₂ transfer rate was increased by a factor of 2.7 as the CO₂ removal rate went from 11 to 30 mmol/min with the CLEAs.

Example 10

This example provides data to demonstrate that enzyme immobilization increases enzyme stability. Data are shown for enzyme immobilized on nylon particles. To evaluate the impact of immobilization on enzyme stability, the stability of immobilized enzymes was evaluated and compared to the stability of the same enzyme in a soluble form. The particles were prepared through the following non-optimized steps:

- Surface treatment of nylon particles with glutaraldehyde
- Addition of polyethyleneimine
- Addition of glutaraldehyde
- Enzyme fixation (human carbonic anhydrase type II)

- Aldehyde group blocking with polyethyleneimine

Following immobilization, the enzyme particles and soluble enzyme were exposed to MDEA 2M at 40°C. At specific exposure times, samples were withdrawn and activity was measured. Results are expressed as residual activity, which is the ratio of the activity of the enzyme at a given exposure time t to the enzyme activity at time 0. Fig 4 illustrates the results.

Results show that free enzyme loses all activity with 10 days, whereas particles still retain 40% residual activity after 30 days and 25% residual activity after 56 days. From this result, it is clear that immobilization increases enzyme stability under these conditions.

These results show the potential of immobilization to increase the stability of carbonic anhydrase at higher temperature conditions that are found in a CO₂ capture process. In optional aspects of the present invention, the particles enable increased stability of around or above the stability increase illustrated in the examples.

Example 11

An example of the calculation of the ideal particle size for 2 and 4 M MDEA solutions is presented. For this purpose, data on kinetics, diffusion coefficients and mass transfer coefficients were available.

From scientific literature, it is known that the CO₂ reaction in a MDEA solution is a pseudo-first order reaction where the overall reaction rate is governed by the following equation:

$$R_{CO_2} = k_{ov} C_{CO_2}$$

where R_{CO_2} is the CO₂ reaction rate in mol/L.s, k_{ov} is the overall pseudo-first order kinetic constant (s⁻¹) and C_{CO_2} is the CO₂ concentration in mol/L. The kinetic constant k_{ov} is defined as:

$$k_{ov} = k_2 C_{mdea}$$

where C_{MDEA} is the MDEA concentration in mol/m³ and k_2 is the kinetic constant for the reaction of CO₂ in a MDEA solution.

From scientific literature, $k_2 = 1.34 \times 10^6 \exp(-5771/T)$ in $\text{m}^3/(\text{mol.s})$

At 25°C, k_2 is equal to $0.0052 \text{ m}^3/(\text{mol.s})$, then values for k_{ov} are the following:

For 2M MDEA, $k_{ov} = 10.4 \text{ s}^{-1}$

For 4M MDEA, $k_{ov} = 20.8 \text{ s}^{-1}$

The data used in the above calculation were obtained from literature, but in other cases they may be estimated from literature or determined experimentally.

In the present case, diffusion coefficient and mass transfer coefficient were determined from experiments conducted in a stirred cell at 25°C. Data obtained are shown below.

MDEA concentration (M)	Mass transfer coefficient k_L (m/s)	CO ₂ diffusion coefficient D_{CO_2} (m ² /s)
2	11.4×10^{-6}	10.8×10^{-10}
4	8.54×10^{-6}	6.05×10^{-10}

With these data, Hatta numbers and the thickness of the mass transfer film (δ_L) were calculated. The thickness of the reactive film is then determined as follows:

$$\delta_l = D_{\text{CO}_2} / k_L$$

$$\text{Ha}^2 = (k_1 \cdot D_{\text{CO}_2}) / (k_L)^2 \text{ for the present example, } k_1 = k_{ov}$$

And for values of $\text{Ha} > 2$ it can be estimated that:

$$(\delta_{rf}) = (\delta_l) / \text{Ha}$$

Results are shown in the Table below.

MDEA concentration (M)	Hatta number	δ_L (μm)	δ_{rf} (μm)
2	10.4	95	9.1
4	13.2	71	5.4

From these results, enzymatic particles used in MDEA solutions should be designed to be smaller than 9.1 μm for a 2M solution and smaller than 5.4 μm for a 4M solution.

Example 12

As clearly explained herein, a variety of methods for immobilizing or entrapping or otherwise providing the enzymes on the particles may be used in connection with the present invention. Some preferred immobilization techniques are described herein. For additional information regarding optional immobilization techniques, literature may be consulted. In one optional aspect, an immobilization technique such as the one described in US application No. 11/411,774, which is hereby incorporated by reference, may be used. In addition, in above Examples 1, 3 and 10, immobilization on nylon was as per the teaching of US application No. 11/411,774; in above Example 6 immobilization at the surface of magnetic silica coated iron oxide particles was as per the supplier's technique; in above Examples regarding CLEAs, the particles were prepared as per known preparation of CLEAs, used by supplier CLEA Tech.

As per the examples of US application No. 11/411,774:

“Methanolysis of the solid support with a Raschig ring geometry (GE polymer shapes) was performed at 50 degrees C during 60 minutes. The remaining steps have been performed at room temperature. The support was then washed 5 times with dechlorinated water. Hydrolysis of the support was performed with an HCl solution (3.93 N, obtained from Lab Mat) for 1 hour. The support was then washed 5 times with dechlorinated water and with NaOH (0.1M, obtained from Lab Mat) for 1 hour. The support was then washed 12 times with dechlorinated water. The support was pretreated by immersion in a carbonate buffer (Sigma, 0.2M pH 8.5) for 1 hour. The support was then treated with a glutaraldehyde (Sigma) solution (2.5% in a carbonate buffer 0.2M pH 8.5) for 1 hour. The support was then washed 5 times with dechlorinated water. The support was incubated 18 hours in a polyethylenimine (PEI, obtained from Sigma) solution (0.5% in a phosphate buffer 0.1M pH 8.0). The support was then washed 5 times with dechlorinated water. The support was then blocked with a mixture of amino acids (L-phenylalanine, D-leucine, L-arginine, glycine, D- and L-aspartic acid, obtained

from Sigma) solution (0.5% in a phosphate buffer solution 0.1M pH 8.0). The support was then washed 5 times with dechlorinated water. The support was pretreated with a carbonate buffer 0.2 M pH 8.5 for 1 hour. The support was treated with a glutaraldehyde 2.5% solution in a carbonate buffer 0.2 M pH 8.5 for 15 minutes. The support was then washed 5 times with dechlorinated water. The enzyme (carbonic anhydrase isolated from human blood and obtained from CO.sub.2 Solution) was then added to the support at a concentration of 1.0 mg/ml in a carbonate buffer for 2 hours. The support was then washed 4 times with dechlorinated water, 1 time with a NaCl (Sigma) solution (1.0 M) and 4 times with dechlorinated water. The immobilization was completed in a period of four (4) days.

This method allows for the covalent immobilization of carbonic anhydrase on a support having hydrophilic character, the enzyme being held through covalent bonds to the support. This method also provides enzyme activity and stability superior to what is currently known in the art.”

“Every step of this immobilization method was performed at room temperature. The chemicals/biologicals used are the same as those described in Example I. The enzyme carbonic anhydrase was immobilized on Raschig.TM. rings (5kg) made of Nylon 6/6. The solid support was hydrolyzed for 1 hour with a HCl solution (3.93 N). The support was then washed 6 times with dechlorinated water and 1 time with a NaOH solution (0.1 M). The support was further washed 4 times with dechlorinated water. The support was then incubated between 2 and 18 hours with a PEI solution (concentration of 0.5M in a carbonate buffer 0.2 M pH 8.3). The length of the incubation was adjusted to the physico-chemical conditions sought. The support was then left to drain and was not washed prior to its incubation with glutaraldehyde. The support was incubated 2 hours in a glutaraldehyde solution (1.0% in carbonate buffer 0.2 M pH 8.3). The support was then incubated 2 hours in a carbonic anhydrase solution (0.5 mg/ml). The support was then washed 3 times with dechlorinated water and 1 time with a NaCl solution (1.0M). The support was finally washed 3 times with dechlorinated

water. This procedure can be performed in a single day or it may be divided into two days at the step of adding the polyethylenimine to facilitate working hours. In the latter, the solid support may then be placed in contact with the polyethylenimine during the entire night. The use of a single step of glutaraldehyde addition contributes to not only reducing the production time and its cost but also the reduction of production of toxic waste."

The particles may have an enzyme immobilization system including or consisting essentially of: a support; a first spacer having a polyamine molecule; a first linker having a first aldehyde group and a second aldehyde group; and a biologically active entity; wherein said support is linked to the polyamine molecule of said spacer, wherein said spacer is linked to the first aldehyde group of said first linker and wherein said biologically active entity is linked to the second aldehyde group said first linker. There may also be a second linker having a first aldehyde group and a second aldehyde group, wherein the first aldehyde group of said second linker is linked to the polyamine molecule of said spacer and the second aldehyde group of said second linker is linked to said support. The support may be made of a compound selected from the group consisting of plastic, biopolymer, polytetrafluoroethylene (PTFE), ceramic, polyethylene, polypropylene, polystyrene, nylon, silica, carbonate, a derivative thereof and a combination thereof. The polyamine molecule of the spacer may be selected from the group consisting of a hydrocarbon, an acyclic hydrocarbon an alkene, a polyene, a polyethylene, an imine and a polyethylenimine. The polyamine molecule of said spacer may be hydrophilic. The first linker may be selected from the group consisting of glutaraldehyde, glutardialdehyde, 1,3-diformylpropane, glutaral, 1,5-pentanedial, 1,5-pentanedione and cidex. The second linker is selected from the group consisting of glutaraldehyde, glutardialdehyde, 1,3-diformylpropane, glutaral, 1,5-pentanedial, 1,5-pentanedione and cidex.

It should also be noted that other immobilization and entrapment techniques may be used in connection with the small particles and processes of the present invention, for instance, immobilizations as described in US patent No. 6,524,843, which is incorporated herein by reference.

It should also be noted that the absorption and desorption units that may be used with embodiments of the present invention can be different types depending on various parameters and operating conditions. The units may be, for example, in the form of a packed reactor, spray reactor, fluidised bed reactor, etc., may have various configurations such as vertical, horizontal, etc., and the overall system may use multiple units in parallel or in series, as the case may be.

It should also be noted that certain embodiments may be used to remove other types of gases from effluents and other gas mixtures using different types of biocatalysts such as enzymes. Different gas-liquid contact absorption processes may be used with enzymatic particles with enzymes designed to catalyze a given reaction in the thin reactive film.

It is also noted that it is well known that phenomena of mass transfer accompanied by complex (reversible) chemical reaction(s) is very difficult to describe from first principles; moreover, exact analytical solutions of the governing equations are not attainable. Simplifying models have been thus been developed that allow (partial) solving of such equations, such as the film model. The present invention bases particle sizing based on the film model, which has features to describe the CO₂ capture phenomena both quantitatively and qualitatively in a manner that is straightforward, comprehensive and allowing advantageous determination of particle sizes for a given CO₂ capture system and operation.

It should be understood that the embodiments described and illustrated above do not restrict what has actually been invented.

Example 13

In this example, particles of different sizes were used to immobilize the enzyme carbonic anhydrase. The particles were made of nylon and had the following mean particle size (in microns): 9, 17, 88 and 131. Carbonic anhydrase was also immobilized onto 50 nm alumina particles. The impact of particle size on the impact of the enzyme on CO₂ absorption into 2M MDEA at 25°C was determined using a stirred cell. The enzyme concentration was 0.2 g/l. A stirred cell is a reaction device where a given volume of absorption solution, containing the particles with enzymes,

is exposed to a predetermined CO₂ partial pressure. The solution is stirred to disperse the particles homogenously. As CO₂ is absorbed into the solution, the CO₂ partial pressure drops until it reaches equilibrium. Based on the pressure data, one can determine the rate of CO₂ reaction with the aqueous solution. By calculating the ratio of the reaction rate with enzyme to the reaction rate without any enzyme, one obtains the Turnover Factor (ToF). Results obtained are shown in Table below and in Fig 5. Experimental data were also used to calculate the reactive film thickness in presence of the enzyme, free or immobilized to particles (see Example 11 for details).

Particle size (microns)	Turnover Factor	δ_{rf} (microns)	Particle size/ δ_{rf}
0 (Soluble enzyme)	19,500	1.7	
0.05	11,191	1.9	0.025
9	5,333	2.4	2.3
17	3,300	3.2	5.9
88	2,200	3.4	32.7
131	2,200	3.4	48.7

From these data, it should be first understood that a particle size of zero corresponds to the case of using soluble carbonic anhydrase. It can also be observed that immobilizing the enzyme diminishes the CO₂ hydration rate. It can further be observed that adding enzyme free or immobilized into the solution decreases the thickness of the reactive film from 9 microns (see Example 11) to below 4 microns. It can also be observed that the impact of the enzyme increases as the particle size decreases, reaching nearly 60% of the Turnover Factor obtained with the soluble enzyme. Results also suggest that to have an impact of the particles higher than 15% of the impact of corresponding free enzyme concentration, the particle size should be smaller than about 6 times the reactive film (see 5.9 times the reactive film thickness

for 17 micron particles that increased the Turnover Factor). It is also noted that particles below the reactive film thickness show significant increase in Turnover Factor with respect to larger particles.

CLAIMS

1. A process of absorbing CO₂ from a CO₂ containing gas, comprising:

contacting the CO₂ containing gas with an aqueous absorption mixture comprising water and an absorption compound under conditions such that mass transfer of the CO₂:

first occurs through a gas film thickness (δ_g); and

then occurs through a liquid film thickness (δ_l), wherein $\delta_l = D_{CO_2} / k_L$ where k_L is the mass transfer coefficient in the liquid and D_{CO_2} is the diffusion coefficient of CO₂;

determining a reactive liquid film thickness (δ_{rf}) of CO₂ hydration reaction, wherein $\delta_{rf} = (\delta_l) / Ha$ where $Ha^2 = (k_1 \cdot D_{CO_2}) / (k_L)^2$, $Ha > 2$ and $k_1 = k_2 C_{ab}$ where k_2 is the kinetic constant for the CO₂ hydration reaction in the absorption mixture and C_{ab} is the concentration of the absorption compound in the aqueous absorption mixture; and

providing enzymatic particles in the aqueous absorption mixture, wherein the enzymatic particles are sized in accordance with the reactive liquid film thickness (δ_{rf}) to increase enzymatic catalysis of the CO₂ hydration reaction.

2. The process of claim 1, comprising controlling the reactive liquid film thickness (δ_{rf}) by regulating the concentration of the absorption compound, the temperature of the process, the mass transfer coefficient (k_L) or a combination thereof.
3. The process of claim 1 or 2, comprising sizing the enzymatic particles to have a diameter (d) such that $d / \delta_{rf} < 6$, $d / \delta_{rf} < 3$, $d / \delta_{rf} < 1$, $d / \delta_{rf} < 0.05$, or $d / \delta_{rf} < 0.025$.
4. The process of any one of claims 1 to 3, comprising sizing the enzymatic particles to increase a CO₂ turnover factor by at least 50% with respect to a lower turnover factor enabled by a larger enzymatic particle having a d / δ_{rf} of at least 32.7.

5. The process of any one of claims 1 to 4, comprising sizing the enzymatic particles to achieve a CO₂ turnover factor of at least 17%, 27%, or 57% of a free enzyme turnover factor obtained with soluble enzyme in the aqueous absorption mixture.
6. The process of any one of claims 1 to 5, wherein the reactive liquid film thickness (δ_{rf}) is at most 10 μm , 5 μm , 3 μm , 2.5 μm , 2.0 μm , 1.9 μm or 1.8 μm .
7. The process of any one of claims 1 to 6, wherein the absorption compound comprises an alkanolamine MDEA in a concentration such that the reactive liquid film thickness is at most 3.2 μm , and the enzymatic particles are sized to be at most 17 μm .
8. The process of any one of claims 1 to 7, wherein the enzymatic particles comprise a support material and carbonic anhydrase, the support material being selected from nylon, cellulose, silica, silica gel, chitosan, polyacrylamide, polyurethane, alginate, polystyrene, polymethylmetacrylate, magnetic material, sepharose, alumina, and respective derivatives thereof, and combinations thereof
9. The process of claim 8, wherein the enzymes are immobilized with respect to the support material by an immobilization technique selected from adsorption, covalent bonding, entrapment, copolymerization, cross-linking, and encapsulation, and combinations thereof.
10. A process for enzymatic catalysis of a hydration reaction of CO₂ in an aqueous absorption mixture wherein mass transfer of the CO₂ occurs through a liquid film thickness (δ_l), wherein the aqueous absorption mixture comprises a liquid solution and enzymatic particles and is under conditions that provide a reactive liquid film thickness (δ_{rf}) for the hydration reaction that is smaller than the liquid film thickness (δ_l), and comprising enhancing the enzymatic catalysis by sizing the enzymatic particles sufficiently small with respect to the reactive liquid film thickness (δ_{rf}).
11. The process of claim 10, comprising sizing the enzymatic particles to have a diameter (d) in accordance with the reactive liquid film thickness (δ_{rf}) such that $d / \delta_{rf} < 6$.

12. The process of claim 11, comprising sizing the enzymatic particles such that $d / \delta_{rt} < 1$.
13. The process of claim 12, comprising sizing the enzymatic particles such that d is about one, two, three or four orders of magnitude smaller than δ_{rt} .
14. The process of claim 13, comprising sizing the enzymatic particles such that d is about two orders of magnitude smaller than δ_{rt} .
15. The process of any one of claims 10 to 14, wherein the aqueous absorption mixture comprises an absorption compound and δ_{rt} is at most 10 μm .
16. The process of claim 15, wherein δ_{rt} is at most 5 μm .
17. The process of claim 16, wherein δ_{rt} is at most 3 μm .
18. The process of claim 17, wherein δ_{rt} is at most 2.5 μm , 2.0 μm , 1.9 μm or 1.8 μm .
19. The process of any one of claims 15 to 18, wherein the absorption compound comprises a primary amine, a secondary amine, a tertiary amine, a primary alkanolamine, a secondary alkanolamine, a tertiary alkanolamine, a primary amino acid, a secondary amino acid, a tertiary amino acid, or a carbonate compound, or a combination thereof.
20. The process of any one of claims 15 to 18, wherein the absorption compound comprises at least one of the following: piperidine, piperazine, derivatives of piperidine or piperazine which are substituted by at least one alkanol group, monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), 2-(2-aminoethylamino)ethanol (AEE), 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS), N-methyldiethanolamine (MDEA), dimethylmonoethanolamine (DMMEA), diethylmonoethanolamine (DEMEA), triisopropanolamine (TIPA), triethanolamine, dialkylether of polyalkylene glycols, dialkylether or dimethylether of polyethylene glycol, glycine, proline, arginine, histidine, lysine, aspartic acid, glutamic acid, methionine, serine, threonine, glutamine, cysteine, asparagine, valine, leucine, isoleucine, alanine, valine, tyrosine, tryptophan, phenylalanine, and derivatives thereof, taurine, N,cyclohexyl 1,3-propanediamine, N-secondary butyl glycine, N-methyl N-secondary butyl glycine, , diethylglycine, dimethylglycine, , sarcosine, ,

methyl taurine, methyl- α -aminopropionic acid, N-(β -ethoxy)taurine, N-(β -aminoethyl)taurine, N-methyl alanine, 6-aminohexanoic acid and potassium or sodium salts thereof; potassium carbonate, sodium carbonate, ammonium carbonate, promoted potassium carbonate solutions and promoted sodium carbonate solutions or promoted ammonium carbonates, or combinations thereof.

21. The process of any one of claims 15 to 18, wherein the absorption compound comprises an alkanolamine.
22. The process of claim 21, wherein the absorption compound comprises a tertiary alkanolamine.
23. The process of claim 22, wherein the absorption compound comprises N-methyldiethanolamine (MDEA).
24. The process of claim 23, wherein the MDEA has a concentration and the conditions of the aqueous absorption mixture are provided such that δ_{rt} is at most $3.2 \mu\text{m}$ and the enzymatic particles are sized to be at most $17 \mu\text{m}$.
25. The process of any one of claims 10 to 24, wherein δ_{rt} is based on the Hatta number (Ha).
26. The process of claim 25, wherein δ_{rt} is also based on the liquid film thickness (δ_l).
27. The process of claim 26, comprising determining the reactive liquid film thickness (δ_{rf}) in accordance with the following equation:

$$(\delta_{rf}) = (\delta_l) / \text{Ha}$$

wherein Ha is defined for a first order reaction as $\text{Ha}^2 = (k_1 \cdot D_{\text{CO}_2}) / (k_L)^2$.

28. The process of any one of claims 25 to 27, wherein Ha is greater than 2.
29. The process of any one of claims 10 to 28, wherein the enzymatic particles comprise a support material and carbonic anhydrase.
30. The process of claim 29, wherein the support material is made of a compound other than the carbonic anhydrase.

31. The process of claim 30, wherein the support material comprises nylon, cellulose, silica, silica gel, chitosan, polyacrylamide, polyurethane, alginate, polystyrene, polymethylmetacrylate, magnetic material, sepharose, alumina, and respective derivatives thereof or a combination thereof.
32. The process of claim 31, wherein the support material has a density between about 0.6 g/ml and about 5 g/ml.
33. The process of claim 31 or 32, wherein the support material has a density above about 1 g/ml.
34. The process of any one of claims 30 to 33, wherein the carbonic anhydrase is immobilized with respect to the support material by an immobilization technique selected from adsorption, covalent bonding, entrapment, copolymerization, cross-linking, and encapsulation, and combinations thereof.
35. The process of claim 34, wherein the support material comprises cores and an immobilization material provided on the cores, the carbonic anhydrase being immobilized by the immobilization material.
36. The process of claim 34 or 35, wherein the carbonic anhydrase is stabilized by the immobilization technique.
37. The process of claim 29, wherein the carbonic anhydrase is provided as cross-linked enzyme aggregates (CLEAs) and the support material comprises a portion of the carbonic anhydrase and crosslinker.
38. The process of claim 29, wherein the carbonic anhydrase is provided as cross-linked enzyme crystals (CLECs) and the support material comprises a portion of the carbonic anhydrase and crosslinker.
39. The process of any one of claims 10 to 38, wherein the enzymatic particles are sized to have a diameter at or below about 17 μm .
40. The process of claim 39, wherein the enzymatic particles are sized to have a diameter at or below about 10 μm .

41. The process of claim 40, wherein the enzymatic particles are sized to have a diameter at or below about 5 μm .
42. The process of claim 41, wherein the enzymatic particles are sized to have a diameter at or below about 1 μm .
43. The process of claim 42, wherein the enzymatic particles are sized to have a diameter at or below about 0.1 μm .
44. The process of claim 43, wherein the enzymatic particles are sized to have a diameter at or below about 0.05 μm .
45. The process of claim 43, wherein the enzymatic particles are sized to have a diameter at or below about 0.025 μm .
46. The process of any one of claims 10 to 45, comprising:
 - selecting a desired enzymatic activity level of the enzymatic particles;
 - selecting a maximum allowable particle concentration;
 - determining a total surface area required to reach the desired enzymatic activity level;
 - determining a total volume of the particles to reach the maximum allowable particle concentration; and
 - determining a maximum size of the particles to achieve the enzymatic activity level with the maximum allowable particle concentration.
47. The process of any one of claims 10 to 46, wherein the enzymatic particles are provided in the aqueous absorption mixture at a maximum particle concentration of about 40% w/w.
48. The process of claim 47, wherein the maximum particle concentration is about 30% w/w.
49. The process of any one of claims 10 to 48, wherein the particles are sized and provided in a concentration such that the resulting suspension is pumpable.

50. The process of any one of claims 10 to 49, comprising contacting a CO₂-containing gas with the aqueous absorption mixture in a reactor to remove at least part of the CO₂ from the CO₂-containing gas and thereby produce a CO₂-depleted gas and an ion-rich solution containing the enzymatic particles.
51. The process of claim 50, wherein the absorption solution and the CO₂-containing gas flow counter-currently with respect to each other.
52. The process of claim 50 or 51, comprising removing the enzymatic particles from the ion-rich solution to produce an enzymatic particle fraction and a particle-depleted ion-rich solution.
53. The process of claim 52, wherein the enzymatic particles are further sized to facilitate the removing from the ion-rich solution.
54. The process of claim 52 or 53, wherein the removing of the enzymatic particles is performed by at least one of filtration mechanism, magnetic separation, centrifugation, cyclone, sedimentation, membrane separation or a combination thereof.
55. The process of any one of claims 52 to 54, wherein the removing of the enzymatic particles is performed by a removal method selected in accordance with the size, density, and presence of magnetic property, of the enzymatic particles.
56. The process of any one of claims 52 to 55, wherein the removing is performed by a clarifier, thickener, vacuum or pressure filter, batch or continuous filter, horizontal filters filter press, tubular filter, centrifugal discharge filter, rotary drum filter, scraper-discharge filter, roll-discharge filter, disc filter, sedimentation centrifuge, decanter centrifuge, filtering centrifuge, basket centrifuge, hydrocyclone, hydroclone, ultrafiltration, microfiltration device, nanofiltration device, or a combination thereof.
57. The process of any one of claims 52 to 56, comprising performing desorption or mineral carbonation on the particle-depleted ion-rich solution to produce an ion-depleted solution.

58. The process of claim 57, wherein at least part of the ion-depleted solution is recycled to form at least part of the aqueous absorption mixture.
59. The process of claim 58, wherein at least part of the enzymatic particle fraction is combined with the recycled portion of the ion-depleted solution to form at least part of the aqueous absorption mixture.
60. The process of any one of claims 57 to 59, wherein the ion-rich solution comprises precipitates and the precipitates are removed from the ion-rich solution prior to performing the desorption or the mineral carbonation.
61. The process of claim 60, comprising forming the precipitates in the ion-rich solution and providing the enzymatic particles with a characteristic facilitating separation of the enzymatic particles from the precipitates.
62. The process of claim 50 or 51, comprising performing desorption or mineral carbonation on the ion-rich solution to produce an ion-depleted solution.
63. The process of claim 62, wherein the enzymatic particles allow catalysis of the desorption or the mineral carbonation.
64. The process of claim 62 or 63, wherein the enzymes are stabilized by the enzymatic particles and the particles are sized and provided in a concentration to be carried with the ion-rich solution through a desorption reactor to promote transformation of bicarbonate and hydrogen ions into CO₂ gas and water, thereby producing a CO₂ gas stream and the ion-depleted solution.
65. The process of claim 64, comprising further sizing the enzymatic particles with respect to a reactive liquid film thickness of a CO₂ dehydration reaction to increase enzymatic catalysis of the CO₂ dehydration reaction in the desorption.
66. The process of any one of claims 62 to 65, wherein the ion-rich solution comprises precipitates and the precipitates are removed from the ion-rich solution prior to performing the desorption or the mineral carbonation.
67. The process of any one of claims 50 to 66, wherein the contacting of the aqueous absorption mixture with the CO₂-containing gas is performed in an absorption

stage comprising at least one reactor selected from a packed tower, a spray tower, a fluidized bed reactor and a combination thereof.

68. A process for enzymatic catalysis of a dehydration reaction of CO_2 from an ion-rich aqueous mixture comprising bicarbonate and hydrogen ions and enzymatic particles wherein mass transfer of the CO_2 occurs through a liquid film thickness (δ_{ld}), wherein the ion-rich aqueous mixture is under conditions that provide a reactive liquid film thickness (δ_{rfd}) for the dehydration reaction that is smaller than the liquid film thickness (δ_{ld}), and comprising enhancing the enzymatic catalysis by sizing the enzymatic particles sufficiently small with respect to the reactive liquid film thickness (δ_{rf}).

69. A CO_2 capture formulation, comprising:

liquid solution comprising water and a reaction compound and enabling the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ to occur, wherein mass transfer of the CO_2 occurs through a liquid film thickness (δ_{l}) and wherein the liquid solution is conditionable to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_{l}); and

enzymatic particles in the liquid solution having a sufficiently small size with respect to the reactive liquid film thickness (δ_{rf}) to enhance enzymatic catalysis of the reaction.

70. A system for treatment of a fluid by enzymatic catalysis of a reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ with carbonic anhydrase, comprising:

a reactor having a reaction chamber receiving the fluid and being configured to provide conditions for mass transfer of the CO_2 occurs through a liquid film thickness (δ_{l}) and to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_{l}); and

enzymatic particles present in the reaction chamber and comprising the carbonic anhydrase, wherein the enzymatic particles have a sufficiently small size with respect to the reactive liquid film thickness (δ_{rf}) to enhance the enzymatic catalysis of the reaction.

71. The system of claim 70, wherein the reactor is configured such that the enzymatic particles flow therethrough with the fluid.

72. A kit for combination and use in CO₂ capture, comprising:

a reaction compound for addition into water to form a liquid solution enabling the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ to occur, wherein mass transfer of the CO₂ occurs through a liquid film thickness (δ_l) and wherein the liquid solution is conditionable to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_l); and

enzymatic particles for addition to the liquid solution, the enzymatic particles having a sufficiently small size with respect to the reactive liquid film thickness (δ_{rf}) to enhance enzymatic catalysis of the reaction.

73. A process for treatment of a fluid by enzymatic catalysis of reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ with carbonic anhydrase, comprising:

providing the fluid in a reaction zone in the presence of enzymatic particles comprising the carbonic anhydrase, wherein mass transfer of the CO₂ occur through a liquid film thickness (δ_l); and

providing conditions in the reaction zone to provide to provide a reactive liquid film thickness (δ_{rfd}) for the reaction that is smaller than the liquid film thickness (δ_l), such that the size ratio of the enzymatic particles and the reactive liquid film thickness (δ_{rfd}) enhance the enzymatic catalysis of the reaction.

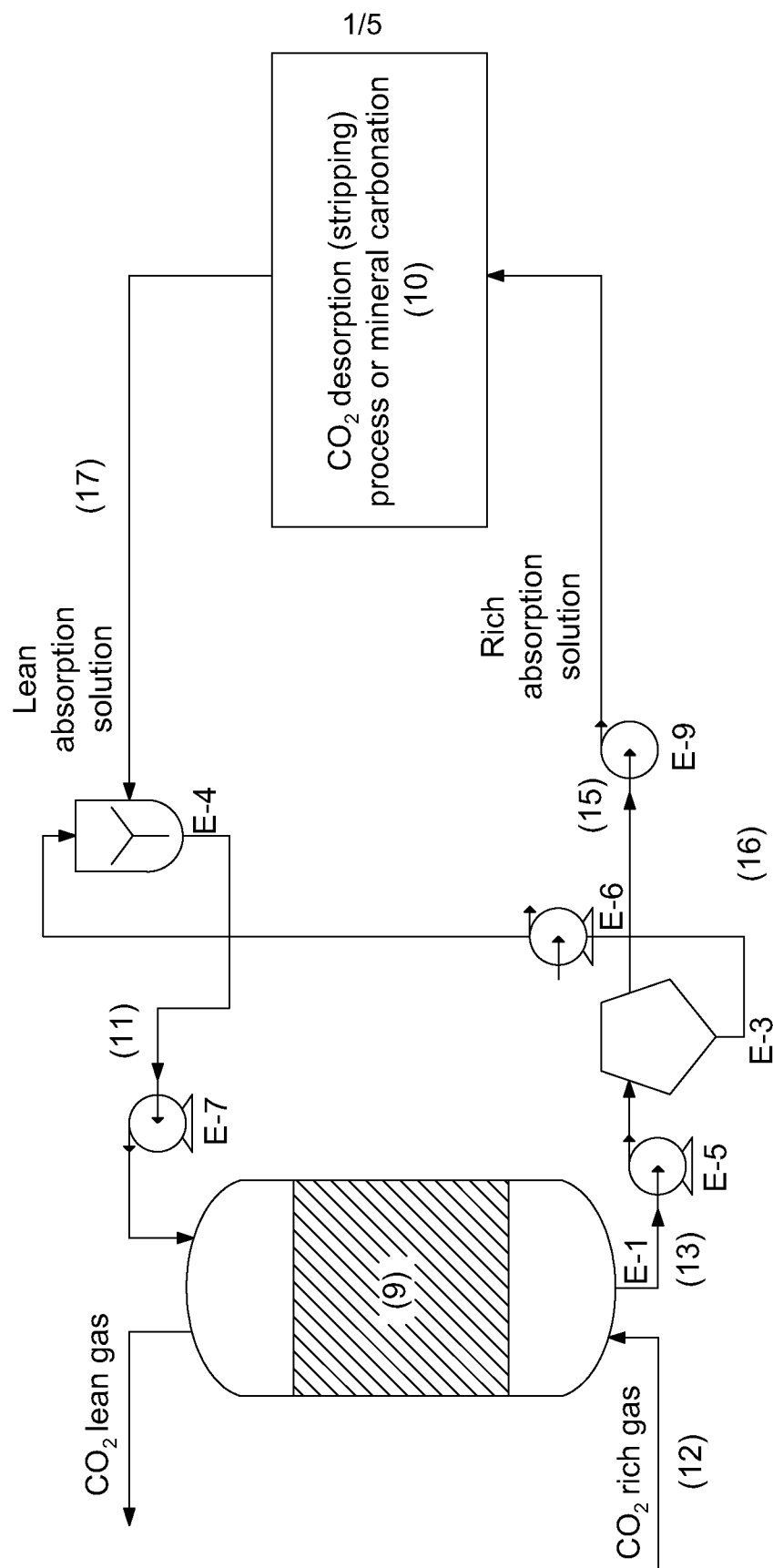


FIG. 1

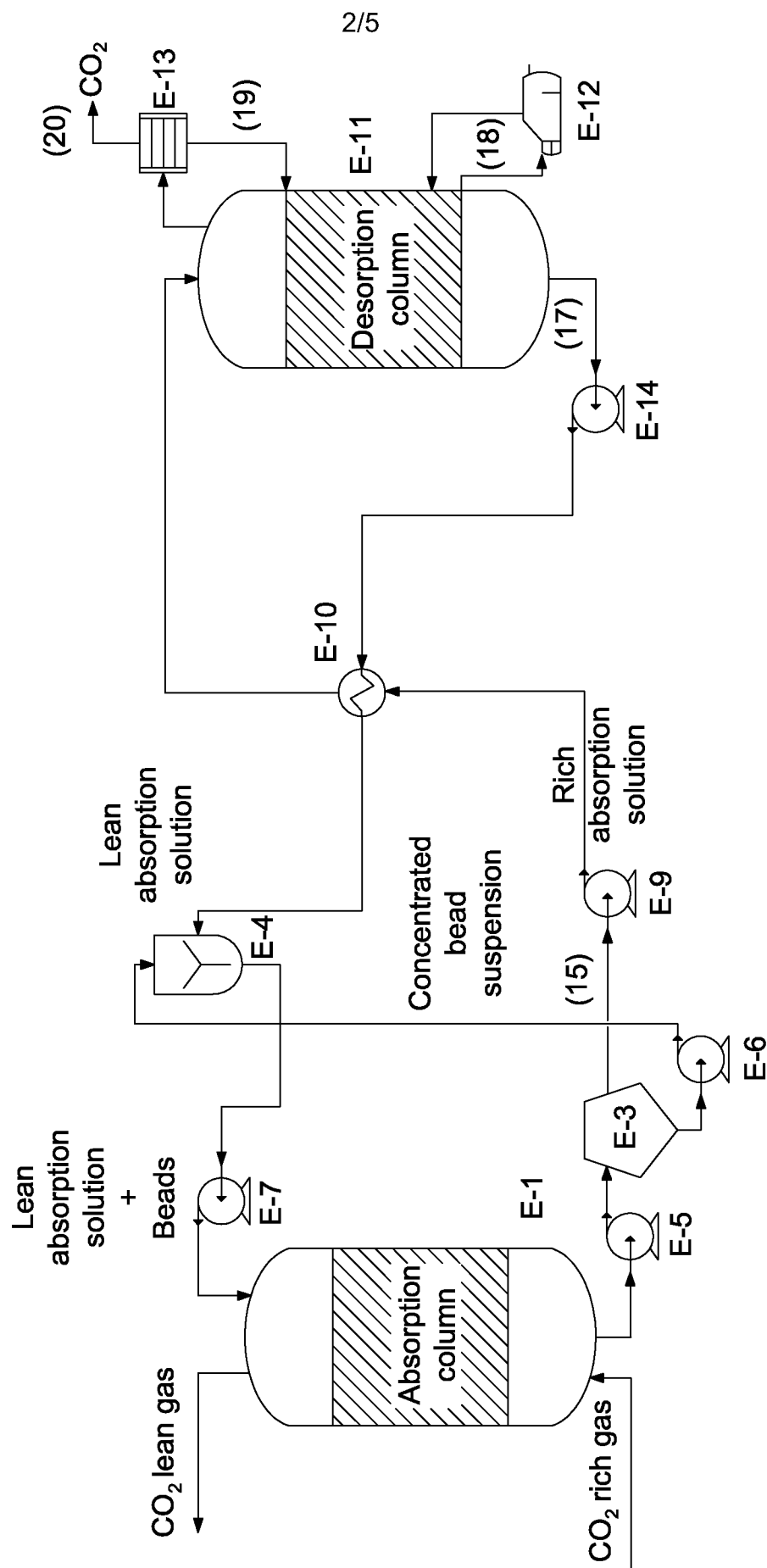


FIG. 2

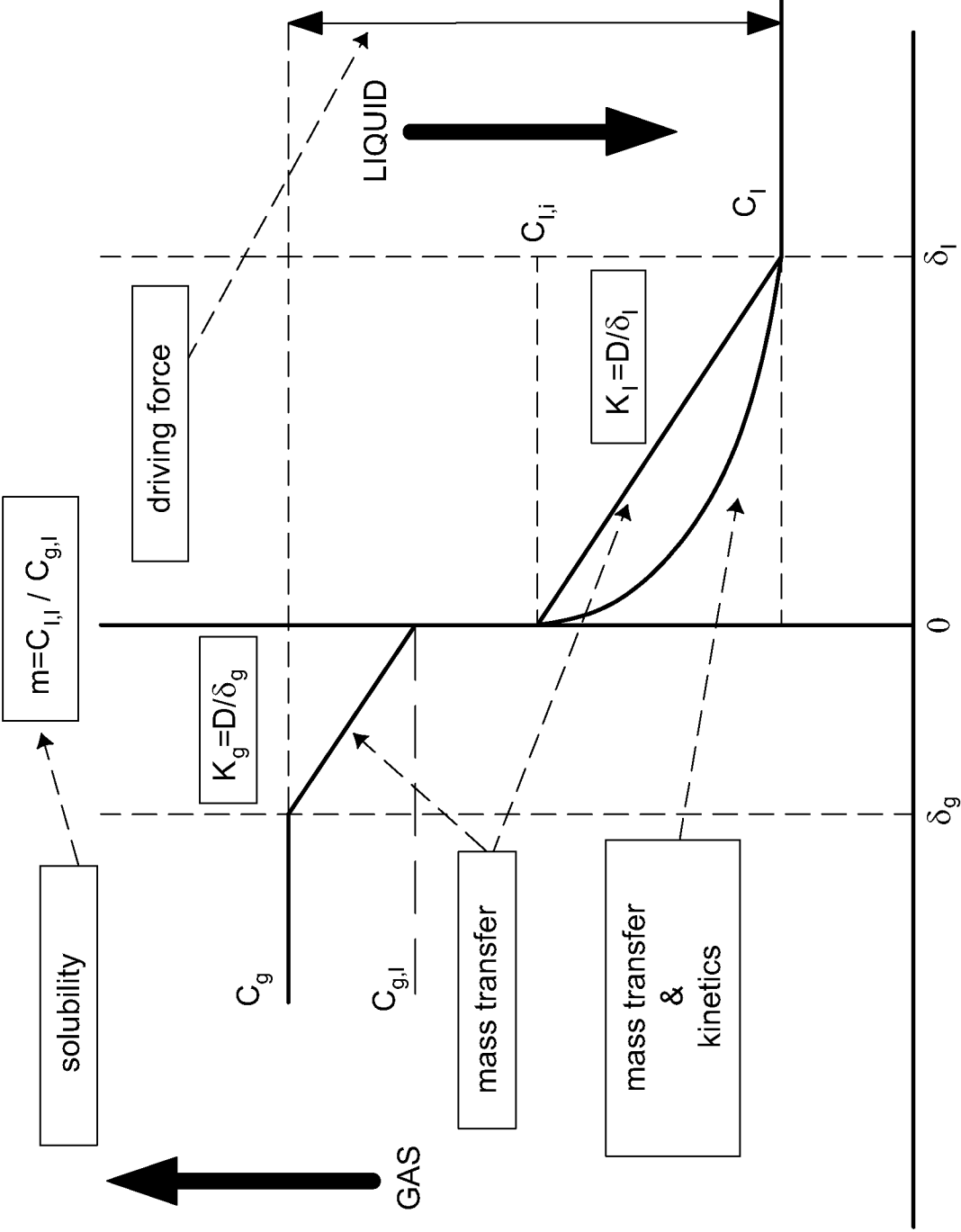


FIG. 3

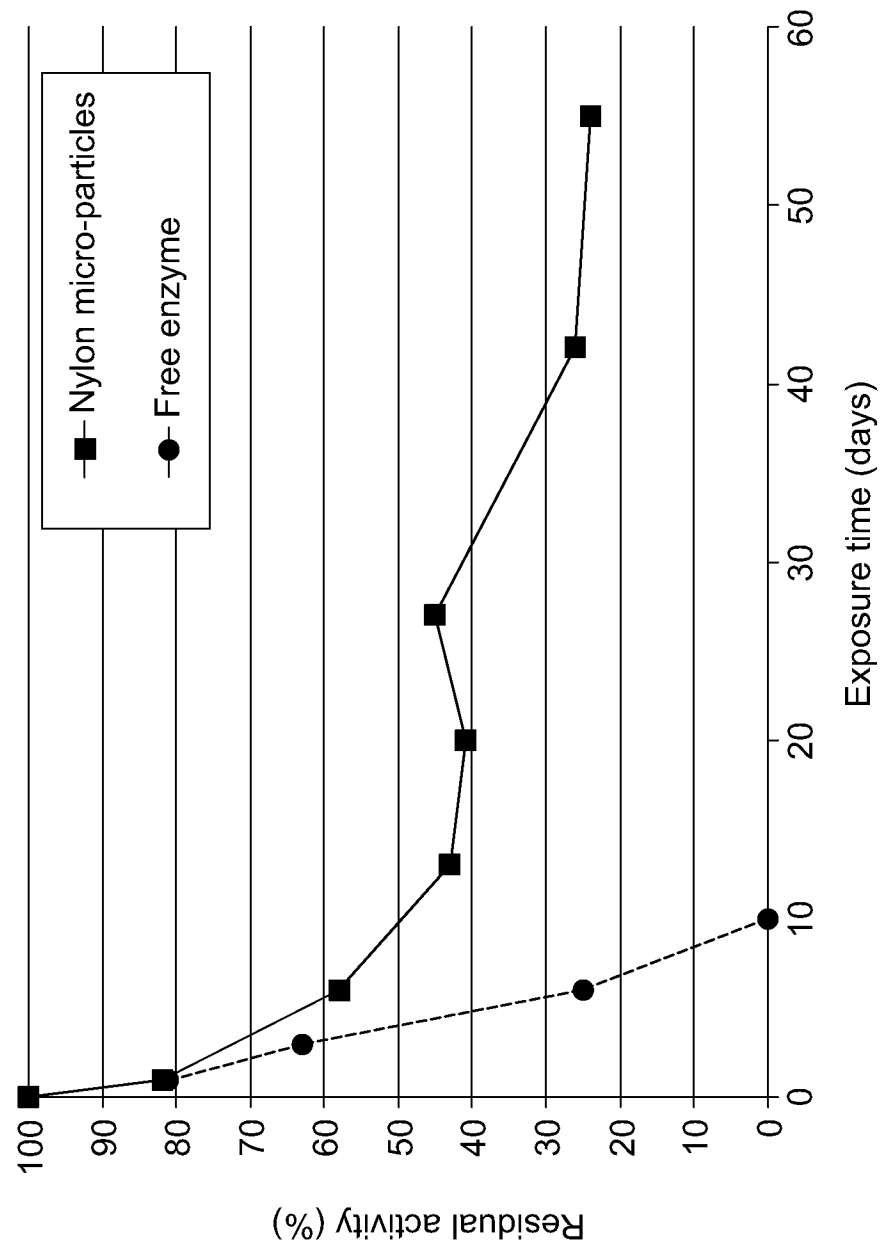


FIG. 4

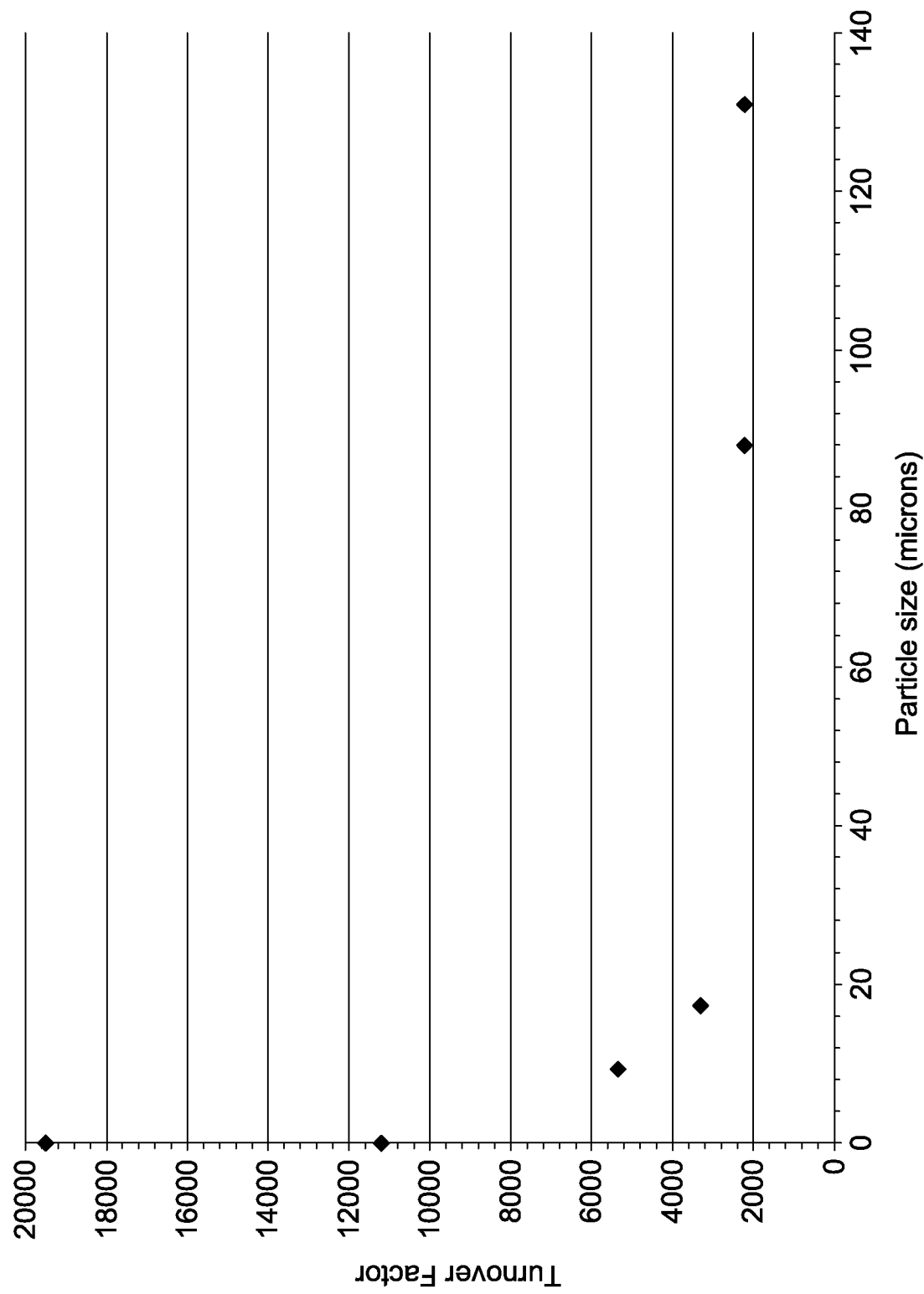


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2012/050063

A. CLASSIFICATION OF SUBJECT MATTER IPC: B01D 53/62 (2006.01) , B01D 53/14 (2006.01) , B01D 53/86 (2006.01) 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) IPC: B01D 53/62 (2006.01) , B01D 53/14 (2006.01) , B01D 53/86 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Total Patent, EPOQUE (EPODOC), Canadian Patents Database (keywords: carbon dioxide, enzyme, carbonic anhydrase, film, immobilized, particles), Internet																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X,P</td> <td>CA2738061A1, (FRADETTE, S. et al.) 10 February 2011 (10-02-2011) * the whole document *</td> <td>1-73</td> </tr> <tr> <td>X,P</td> <td>WO2011054107A1, (FRADETTE, S. et al.) 12 May 2011 (12-05-2011) * pages 11-12 *</td> <td>1, 3, 6, 10-12, 15, 19-23, 25-26, 28-30, 37-40, 46, 49-51, 62, 68-73</td> </tr> <tr> <td>A</td> <td>LACROIX, O., "CO₂ capture using immobilized carbonic anhydrase in Robinson-Mahoney basket and packed absorption column reactors, Masters thesis, Département de Génie Chimique, Faculté des Sciences et de Génie, Université Laval, Québec, Canada, 2008</td> <td>1-73</td> </tr> <tr> <td>A</td> <td>CA2291785A1, 10 December 1998 (10-12-1998) * pages 7-10 *</td> <td>1-73</td> </tr> <tr> <td>A</td> <td>BHATTACHARYA, S. et al., "CO₂ hydration by immobilized carbonic anhydrase, Biotechnol. Appl. Biochem., vol. 38, pp. 111-117, Great Britain, 2003 * pages 112, first column, last 2 lines *</td> <td>1-73</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X,P	CA2738061A1, (FRADETTE, S. et al.) 10 February 2011 (10-02-2011) * the whole document *	1-73	X,P	WO2011054107A1, (FRADETTE, S. et al.) 12 May 2011 (12-05-2011) * pages 11-12 *	1, 3, 6, 10-12, 15, 19-23, 25-26, 28-30, 37-40, 46, 49-51, 62, 68-73	A	LACROIX, O., "CO ₂ capture using immobilized carbonic anhydrase in Robinson-Mahoney basket and packed absorption column reactors, Masters thesis, Département de Génie Chimique, Faculté des Sciences et de Génie, Université Laval, Québec, Canada, 2008	1-73	A	CA2291785A1, 10 December 1998 (10-12-1998) * pages 7-10 *	1-73	A	BHATTACHARYA, S. et al., "CO ₂ hydration by immobilized carbonic anhydrase, Biotechnol. Appl. Biochem., vol. 38, pp. 111-117, Great Britain, 2003 * pages 112, first column, last 2 lines *	1-73
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex. <table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"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</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"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	"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"&" document member of the same patent family	"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							
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Date of the actual completion of the international search 19 March 2012 (19-03-2012)		Date of mailing of the international search report 30 April 2012 (30-04-2012)																		
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Pierre Cuerrier (819) 997-4379																		

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2012/050063

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
CA2738061A1	10 February 2011 (10-02-2011)	CA2738061A1 WO2011014956A1	10 February 2011 (10-02-2011) 10 February 2011 (10-02-2011)
WO2011054107A1	12 May 2011 (12-05-2011)	None	
CA2291785A1	10 December 1998 (10-12-1998)	AT238094T AU7753398A CA2291785C DE69813811D1 DE69813811T2 EP0991462A1 EP0991462B1 GB9711439D0 JP2002508702A US6524843B1 WO9855210A1	15 May 2003 (15-05-2003) 21 December 1998 (21-12-1998) 16 August 2005 (16-08-2005) 28 May 2003 (28-05-2003) 11 March 2004 (11-03-2004) 12 April 2000 (12-04-2000) 23 April 2003 (23-04-2003) 30 July 1997 (30-07-1997) 19 March 2002 (19-03-2002) 25 February 2003 (25-02-2003) 10 December 1998 (10-12-1998)