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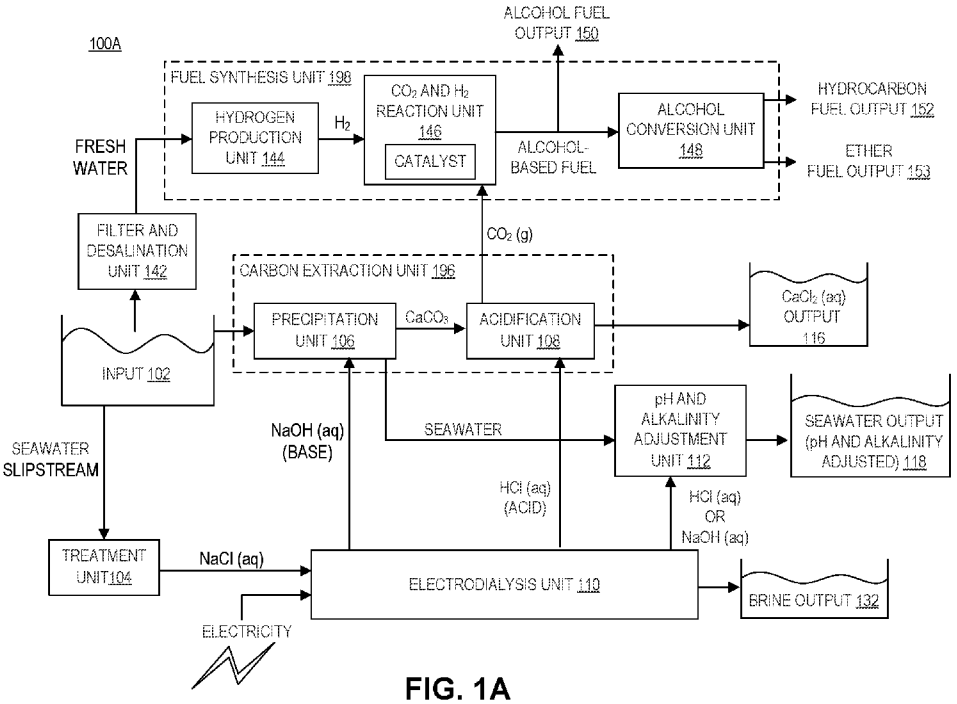

FIG. 1A

(57) Abstract: A method of synthesizing fuel from an aqueous solution includes pumping the aqueous solution, containing dissolved inorganic carbon, from a body of water into a carbon extraction unit. The method further includes extracting the dissolved inorganic carbon from the aqueous solution to create CO_2 by changing a pH of the aqueous solution in the carbon extraction unit. The CO_2 derived in the carbon extraction unit is received by a fuel synthesis unit, and the CO_2 is converted into fuel including at least one of a hydrocarbon, an ether, or an alcohol using the fuel synthesis unit.

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FUEL SYNTHESIS FROM AN AQUEOUS SOLUTION

TECHNICAL FIELD

[0001] This disclosure relates generally to fuel synthesis.

BACKGROUND INFORMATION

[0002] Pure carbon dioxide (CO_2) has many industrial uses. The separation of CO_2 from a mixed-gas source may be accomplished by a capture and regeneration process. More specifically, the process generally includes a selective capture of CO_2, by, for example, contacting a mixed-gas source with a solid or liquid adsorber/absorber followed by a generation or desorption of CO_2 from the adsorber/absorber. One technique describes the use of bipolar membrane electrodialysis for CO_2 extraction/removal from potassium carbonate and bicarbonate solutions.

[0003] For capture/regeneration systems, a volume of gas that is processed is generally inversely related to a concentration of CO_2 in the mixed-gas source, adding significant challenges to the separation of CO_2 from dilute sources such as the atmosphere. CO_2 in the atmosphere, however, establishes equilibrium with the total dissolved inorganic carbon in the oceans, which is largely in the form of bicarbonate ions (HCO_3-) at an ocean pH of 8.1-8.3. Therefore, a method for extracting CO_2 from the dissolved inorganic carbon of the oceans would effectively enable the separation of CO_2 from atmosphere without the need to process large volumes of air.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Non-limiting and non-exhaustive embodiments of the invention are described with reference to the following figures, wherein like reference numerals refer to like parts throughout the various views unless otherwise specified. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles being described.

[0005] FIG. 1A is an illustration of a system for fuel synthesis, in accordance with an embodiment of the disclosure.

[0006] FIG. 1B is an illustration of a system for fuel synthesis, in accordance with an embodiment of the disclosure.

[0007] FIG. 1C is an illustration of a system for fuel synthesis, in accordance with an embodiment of the disclosure.

[0008] FIG. 2 is an example electrodialysis unit, in accordance with an embodiment of the disclosure.

[0009] FIG. 3 is an example application of a system for fuel synthesis, in accordance with an embodiment of the disclosure.

[0010] FIG. 4 is an illustration of a method for synthesizing fuel from an aqueous solution, in accordance with an embodiment of the disclosure.

DETAILED DESCRIPTION

[0011] Embodiments of an apparatus and method for synthesizing fuel from an aqueous solution are described herein. In the following description numerous specific details are set forth to provide a thorough understanding of the embodiments. One skilled in the relevant art will recognize, however, that the techniques described herein can be practiced without one or more of the specific details, or with other methods, components, materials, etc. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring certain aspects.

[0012] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

[0013] Throughout the specification and claims, compounds/elements are referred to both by their chemical name (*e.g.,* carbon dioxide) and chemical symbol (*e.g.,* CO_2). It is appreciated that both chemical names and symbols may be used interchangeably and have the same meaning.

[0014] This disclosure provides for the removal of carbon from water sources containing dissolved inorganic carbon (*e.g.,* bicarbonate ions HCO_3^-), converting the dissolved carbon into CO_2 gas, and processing the CO_2 gas to produce alcohol, ether or hydrocarbon based fuels. The ability to produce alcohol, ether, and hydrocarbon fuel from nothing more than seawater is highly desirable in many industries. For example, a ship capable of making fuels from seawater could sail the oceans refueling airplanes on its own deck and/or refueling other ships without docking in port. Also, remote or isolated islands or coastal communities could make their own liquid fuels from seawater and electricity without the need for imported fuel delivery. Furthermore, the system and method for fuel synthesis presented here is carbon neutral (if powered with carbon-free electricity) because the

elemental constituents of the hydrocarbons/ethers/alcohols formed are extracted from the ocean. Thus, there is no net carbon emission.

[0015] FIG. 1A is an illustration of system 100A for fuel synthesis, in accordance with an embodiment of the disclosure. System 100A includes: input 102 (to input an aqueous solution containing dissolved inorganic carbon), treatment unit 104, carbon extraction unit 196 (including precipitation unit 106 and acidification unit 108), electrodialysis unit 110, pH and alkalinity adjustment unit 112, $CaCl_2$ output 116, water output 118, brine output 132, filter and desalination unit 142, and fuel synthesis unit 198. In the depicted embodiment, fuel synthesis unit 198 includes: hydrogen production unit 144, CO_2 and H_2 reaction unit 146, alcohol conversion unit 148, alcohol fuel output 150, hydrocarbon fuel output 152, and ether fuel output 153.

[0016] As shown, input 102 is coupled to a water reservoir containing dissolved inorganic carbon (*e.g.,* bicarbonate ions). The water reservoir may be an ocean, lake, river, manmade reservoir, or brine outflow from a reverse osmosis ("RO") process. Input 102 may receive the water through a system of channels, pipes, and/or pumps depending on the specific design of the facility. As shown, water received through input 102 is diverted into three separate sections of system 100A. A first (smaller) portion of the water is diverted to treatment unit 104, a second (larger) portion of the water is diverted to precipitation unit 106, and a third (smaller) portion of water is diverted to filter and desalination unit 142. In one embodiment, the inputs to filter and desalination unit 142 and treatment unit 104 may come from the output of pH and alkalinity adjustment unit 112, since the output of pH and alkalinity adjustment unit 112 has already been pre-softened via $CaCO_3$ removal in precipitation unit 106. One skilled in the art will appreciate that large aggregate may be removed from the water at any time during the intake process.

[0017] In the illustrated embodiment, the first portion of water is diverted into treatment unit 104. Treatment unit 104 outputs a relatively pure stream of aqueous NaCl. In other words, an aqueous solution (possibly including seawater) is input to treatment unit 104, and aqueous NaCl is output from treatment unit 104. Treatment unit 104 may be used to remove organic compounds and other minerals (other than NaCl) not needed in, or harmful to, subsequent processing steps. For example, removal of chemicals in the water may mitigate scale buildup in electrodialysis unit 110. Treatment unit 104 may include filtering systems such as: nanofilters, RO units, ion exchange resins, precipitation units, microfilters, screen filters, disk filters, media filters, sand filters, cloth filters, and biological filters (such as algae scrubbers), or the like. Additionally, treatment unit 104 may include chemical filters to removed dissolved minerals/ions. One skilled in the art will appreciate that any number of

screening and/or filtering methods may be used by treatment unit 104 to remove materials, chemicals, aggregate, biologicals, or the like.

[0018] Electrodialysis unit 110 is coupled to receive aqueous NaCl and electricity, and output aqueous HCl, aqueous NaOH, and brine (to brine output 132). Aqueous HCl and aqueous NaOH output from electrodialysis unit 110 may be used to drive chemical reactions in system 100A. The specific design and internal geometry of electrodialysis unit 110 is discussed in greater detail in connection with FIG. 2 (*see infra* FIG. 2). Brine output from electrodialysis unit 110 may be used in any applicable portion of system 100A. For example, brine may be cycled back into electrodialysis unit 110 as a source of aqueous NaCl, or may be simply expelled from system 100A as wastewater.

[0019] In the depicted embodiment, carbon extraction unit 196 includes precipitation unit 106 and acidification unit 108. Precipitation unit 106 has a first input coupled to receive an aqueous solution including dissolved inorganic carbon (*e.g.,* seawater) from input 102. Precipitation unit 106 also has a second input coupled to electrodialysis unit 110 to receive aqueous NaOH. In response to receiving the aqueous solution and the aqueous NaOH, precipitation unit 106 precipitates calcium salts (for example, but not limited to, $CaCO_3$) and outputs the aqueous solution. However, in other embodiments, other chemical processes may be used to basify the aqueous solution in precipitation unit 106. For example, other bases (not derived from the input aqueous solution) may be added to the aqueous solution to precipitate calcium salts.

[0020] In one embodiment, NaOH is added to incoming seawater until the pH is sufficiently high to allow precipitation of calcium salts without significant precipitation of $Mg(OH)_2$. The exact pH when precipitation of $CaCO_3$ occurs (without significant precipitation of $Mg(OH)_2$) will depend on the properties of the incoming seawater (alkalinity, temperature, composition, etc.); however, a pH of 9.3 is typical of seawater at a temperature of 25 °C. In a different embodiment, the quantity of NaOH added is sufficient to precipitate $CaCO_3$ and $Mg(OH)_2$, then the pH is lowered (*e.g.,* by adding HCl from electrodialysis unit 110 until the pH is <9.3) so that the $Mg(OH)_2$ (but not $CaCO_3$) redissolves.

[0021] In one embodiment, precipitation unit 106 may be a large vat or tank. In other embodiments precipitation unit 106 may include a series of ponds/pools. In this embodiment, precipitation of calcium salts may occur via evaporation driven concentration (for example using solar ponds) rather than, or in combination with, adding basic substances. Precipitation unit 106 may contain internal structures with a high surface area to promote nucleation of $CaCO_3$; these high surface area structures may be removed from the precipitation unit 106 to collect nucleated $CaCO_3$. Precipitation unit 106 may include an

interior with $CaCO_3$ to increase nucleation kinetics by supplying seed crystals. The bottom of precipitation unit 106 may be designed to continually collect and extract precipitate to prevent large quantities of scale buildup.

[0022] In another or the same embodiment, heat may be used to aid precipitation. For example solar ponds may be used to heat basified water. In continuously flowing systems, low temperature waste heat solution may be flowed through heat exchange tubes with basified seawater on the outside of the tubes. Alternatively, heating the bottom of precipitation unit 106 may be used to speed up precipitation.

[0023] After $CaCO_3$ is precipitated from the water, $CaCO_3$ is transferred to acidification unit 108. In the depicted embodiment, acidification unit 108 is coupled to receive $CaCO_3$ from precipitation unit 106 and coupled to receive aqueous HCl from electrodialysis unit 110. In response to receiving $CaCO_3$ and aqueous HCl, acidification unit 108 produces CO_2 gas. In the depicted embodiment, acidification unit 108 is used to evolve $CaCO_3$ into CO_2 gas and aqueous $CaCl_2$ according to the following reaction: $CaCO_3$ (s) + 2HCl (aq) $\rightarrow$ $CaCl_2$ (aq) + H_2O (l) + CO_2 (g). Reaction kinetics may be increased by agitating/heating the acidified mixture. By adding HCl to $CaCO_3$, CO_2 gas is spontaneously released due to the high equilibrium partial pressure of CO_2 gas. This may eliminate the need for membrane contactors or vacuum systems.

[0024] Once all CO_2 has been extracted from acidification unit 108, wastewater containing $CaCl_2$ is output from system 100A via $CaCl_2$ output 116. In one embodiment, the wastewater is returned to the ocean or other water source after the pH of the wastewater has been adjusted.

[0025] In the depicted embodiment, the second portion of seawater (that was used as a carbon source in precipitation unit 106) is flowed to a pH and alkalinity adjustment unit 112. The pH and alkalinity adjustment unit 112 is coupled to electrodialysis unit 110 to receive HCl and NaOH, and adjust a pH and alkalinity of the combined second portion of the aqueous solution and basic solution to a desired pH and alkalinity. In one embodiment, the pH and alkalinity of wastewater flowed into pH and alkalinity adjustment unit 112 is monitored in real time, and HCl or NaOH is flowed into pH and alkalinity adjustment unit 112 in response to the real time measurements. Adjusting the pH of wastewater flowing from system 100A ensures minimal environmental impact of running system 100A, while adjusting the alkalinity ensures sufficient reabsorption of atmospheric CO_2 once the water is returned to the ocean.

[0026] As shown, input 102 is also coupled to send water to filter and desalination unit 142. Filter and desalination unit 142 removes aggregate and minerals from the water,

thus the water leaving filter and desalination unit 142 is relatively pure fresh water. One skilled in the art will realize that a variety of commercial systems may be used to desalinate and purify water; many of these systems are already installed on commercial seafaring vessels.

[0027] Freshwater from filter and desalination unit 142 is then diverted into fuel synthesis unit 198. More specifically, in the depicted embodiment, the fresh water is sent to hydrogen production unit 144 which may separate hydrogen (H_2) from the fresh water via alkaline electrolysis, polymer electrolyte membrane electrolysis, solid oxide electrolysis, or the like. O_2 resulting from the decomposition of the fresh water may be used in other chemical processes, or may simply be expelled from system 100A.

[0028] The CO_2 evolved from carbon extraction unit 196 and the H_2 produced by hydrogen production unit 144 is received by CO_2 and H_2 reaction unit 146. In the depicted embodiment, CO_2 and H_2 reaction unit 146 reacts the CO_2 with hydrogen to produce alcohol. In one embodiment, the alcohol includes methanol. In a different or the same embodiment, reacting the CO_2 with the hydrogen includes reacting the hydrogen and the CO_2 over a catalyst (*e.g.,* Cu/ZnO, AlO_x, GaO_x, ZrO_x, Cr_xO_x, and other metal-oxide-based catalysts) to produce the methanol.

[0029] As shown, the derived alcohol can be output from the system via alcohol fuel output 150, or may be converted into hydrocarbon or ether fuel. As one skilled in the art will appreciate, alcohols, ethers, and hydrocarbons have many uses not limited to fuel. And while this disclosure refers to deriving "fuels" from CO_2, the alcohols, ethers, and hydrocarbons output from system 100A may be used for any reasonable purpose such as fuel additives, solvents, and feedstock for the conversion into other commodity chemicals and plastics, etc.

[0030] In the depicted embodiment, at least some of the alcohol generated by CO_2 and H_2 reaction unit 146 is sent to alcohol conversion unit 148, where the alcohol is converted into a hydrocarbon or ether. In one embodiment, this is achieved by dehydrating the methanol to produce dimethyl ether, which itself can be used as a fuel (output from ether fuel output 153), and optionally further dehydrating the dimethyl ether to produce the hydrocarbon. In this embodiment, the methanol may be polymerized in the presence of a zeolite (*i.e.,* aluminosilicate such as ZSM-5) catalyst to yield hydrocarbon fuels. Using this process, the polymerized methanol may yield hydrocarbons where 80% of the hydrocarbon molecules include five or more carbon atoms. In some embodiments, these hydrocarbon molecules may be separated by molecular weight and/or structure prior to being output by hydrocarbon fuel output 152.

[0031] FIG. 1B is an illustration of system 100B for fuel synthesis, in accordance with an embodiment of the disclosure. System 100B is similar in many respects to system 100A; however, carbon extraction unit 196 includes CO_2 desorption unit 107 in lieu of precipitation unit 106 and acidification unit 108. System 100B is also lacking $CaCl_2$ output 118 since acidification of calcium salts is not necessary in system 100B.

[0032] In the depicted embodiment, electrodialysis unit 110 is coupled to receive aqueous NaCl, and to output aqueous HCl and aqueous NaOH. Degasification unit 107 has a first input coupled to receive an aqueous solution including dissolved inorganic carbon, and a second input coupled to electrodialysis unit 110 to receive the aqueous HCl. In response to receiving the aqueous solution and the aqueous HCl, degasification unit 107 evolves CO_2 from the aqueous solution and outputs the aqueous solution. As shown, the aqueous solution may include seawater, and the aqueous NaCl may also be derived, at least in part, from seawater. Degasification unit 107 may include membrane contactors to remove dissolved N_2 and O_2 gas from the aqueous solution, prior to evolving the CO_2 from the aqueous solution. It is worth noting that in other embodiments, other gases may be extracted from the aqueous solution. Furthermore, any of the processes described above may be vacuum assisted.

[0033] FIG. 1C is an illustration of system 100C for fuel synthesis, in accordance with an embodiment of the disclosure. System 100C is similar in many respects to system 100B; however, fuel synthesis unit 198 includes: CO_2 and H_2O reaction unit 170 and Fisher-Tropsch unit 172, in lieu of hydrogen production unit 144, CO_2 and H_2 reaction unit 146, alcohol conversion unit 148, ether fuel output 153, and alcohol fuel output 150. System 100C also includes heating unit 143.

[0034] In the depicted embodiment, fuel synthesis unit 198 receives gaseous fresh water from filter and desalination unit 142 and heating unit 143. This may be advantageous because filter and desalination unit 142 and heating unit 143 merely need to boil water to separate minerals and unwanted aggregate from the steam that filter and desalination unit 142 outputs. The gaseous fresh water from filter and desalination unit 142, and CO_2 from carbon extraction unit 196 is then received by CO_2 and H_2O reaction unit 170. In one embodiment, CO_2 and H_2O reaction unit 170 converts the CO_2 to CO for syngas. In one embodiment (not depicted in FIG. 1C), the syngas may then be reacted in the presence of a catalyst (*e.g.*, copper and zinc oxides, supported on alumina) to produce methanol.

[0035] In the depicted embodiment, the syngas is sent to Fisher-Tropsch unit 172, which reacts the CO with hydrogen to produce the hydrocarbon. The growth of hydrocarbon chains via Fisher-Tropsch reactions involves repeat steps where hydrogen atoms are added to both carbon and oxygen atoms. The C/O-bond is split and a C/C-bond forms ($CO + 2H_2 \rightarrow$

$(CH_2)_n + H_2O$). The hydrogenated molecules formed may be separated both molecular weight and structure to yield pure fuels (*e.g.,* octane).

[0036] Systems 100A-100C may be coupled to, and run by, electronic control systems. Regulation and monitoring may be accomplished by a number of sensors throughout the system that either send signals to a controller or are queried by controller. For example, with reference to electrodialysis unit 110, monitors may include one or more pH gauges to monitor a pH within the units as well as pressure sensors to monitor a pressure among the compartments in electrodialysis unit 110 (to avoid inadvertent mechanical damage to electrodialysis unit 110). Another monitor may be a pH gauge placed within precipitation unit 106 to monitor a pH within the tank. The signals from such pH monitor or monitors allows a controller to control a flow of brine solution (from input 102) and a basified solution (from electrodialysis unit 110) to maintain a pH value of a combined solution that will result in a precipitation of $CaCO_3$.

[0037] Alternatively, systems 100A-100C may be controlled manually. For example, a worker may open and close valves to control the various water, acid, and base flows in systems 100A-100C. Additionally, a worker may remove precipitated calcium salts from precipitation unit 106. However, one skilled in the relevant art will appreciate that systems 100A-100C may be controlled by a combination of manual labor and mechanical automation, in accordance with the teachings of the present disclosure. Further, all components in systems 100A-100C are interchangeable between the various embodiments, and may be directly coupled to one another.

[0038] FIG. 2 is an example electrodialysis unit 110 (*e.g.,* electrodialysis unit 110 of FIG. 1A-1C), in accordance with an embodiment of the disclosure. Electrodialysis unit 110 may be used to convert seawater (or other NaCl-containing aqueous solutions) into NaOH and HCl. As shown, in FIGs. 1A-1C, NaOH and HCl may be used to adjust the pH of the aqueous solution to evolve CO_2 gas. In one embodiment, electrodialysis unit 110 is a bipolar membrane electrodialysis unit.

[0039] In the depicted embodiment, electrodialysis unit 110 representatively consists of several cells in series, with each cell including a basified solution compartment (compartments 210A and 210B illustrated); an acidified solution compartment (compartments 225A and 225B illustrated); and a brine solution compartment (compartments 215A and 215B). FIG. 2 also shows a bipolar membrane (BPM) between a basified solution compartment and an acidified solution compartment (BPM 220A and 220B illustrated). A suitable BPM is a Neosepta BP-1E, commercially available from Ameridia Corp. Also depicted are anion exchange membranes (AEM), such as Neosepta ACS (commercially

available from Ameridia Corp.), disposed between a brine compartment and an acidified solution compartment (AEM 230A and 230B illustrated). A cation exchange membrane (CEM) such as Neosepta CMX-S (commercially available from Ameridia Corp.), is disposed adjacent to a brine compartment (CEM 240A and CEM 240B illustrated). Finally, FIG. 2 shows end cap membranes 245A and 245B (such as Nafion® membranes) that separate the membrane stack from electrode solution compartment 250A and electrode solution compartment 250B, respectively.

[0040] Broadly speaking, under an applied voltage provided to electrodialysis unit 110, water dissociation inside the BPM (and the ion-selective membranes comprising a BPM) will result in the transport of hydrogen ions (H+) from one side of the BPM, and hydroxyl ions (OH-) from the opposite side. AEMs/CEMs, as their names suggest, allow the transport of negatively/positively charged ions through the membrane. The properties of these membranes such as electrical resistance, burst strength, and thickness are provided by the manufacturer (*e.g.,* Neosepta ACS and CMX-S are monovalent-anion and monovalent-cation permselective membranes, respectively). In one embodiment, electrodialysis unit 110 includes electrodes 260A and 260B of, for example, nickel manufactured by De Nora Tech Inc. FIG. 2 also shows electrode solution compartment 250A and electrode solution compartment 250B through which, in one embodiment, a NaOH(aq) solution is flowed. Where electrode 260A is a positively-charged electrode, sodium ions (Na+) will be encouraged to move across cap membrane 245A and where electrode 260B is negatively-charged, sodium ions will be attracted to electrode solution compartment 250B. In one embodiment, the solution compartments between adjacent membranes are filled with polyethylene mesh spacers (e.g., 762 μm thick polyethylene mesh spacers), and these compartments are sealed against leaks using axial pressure and 794 mm thick EPDM rubber gaskets.

[0041] FIG. 3 is an example application of system 300 for fuel synthesis, in accordance with an embodiment of the disclosure. As depicted, system 300 (*e.g.,* systems 100A-100C) for fuel synthesis is included on a large commercial vessel (which may include a ship, oil rig, or the like). Here, the vessel is able to create alcohol/ether/hydrocarbon fuels using an on-board power plant. In one embodiment, a nuclear reactor is used to power electrolysis equipment to generate the necessary acids and bases to create the alcohol, ether, or hydrocarbon based fuels. These fuels may be used by helicopters and other aircraft for delivering food and aid supplies, or for other reasons, such as refueling ships at sea.

[0042] FIG. 4 is an illustration of method 400 for synthesizing fuel from an aqueous solution, in accordance with an embodiment of the disclosure. The order in which some or

all of process blocks 401 - 407 appear in method 400 should not be deemed limiting. Rather, one of ordinary skill in the art having the benefit of the present disclosure will understand that some of method 400 may be executed in a variety of orders not illustrated, or even in parallel. Additionally, method 400 may include additional blocks or have fewer blocks than shown, in accordance with the teachings of the present disclosure.

[0043] Block 401 illustrates pumping the aqueous solution, containing dissolved inorganic carbon, from a body of water into a carbon extraction unit. In one embodiment, the aqueous solution includes seawater containing bicarbonate ions (HCO_3^-).

[0044] Block 403 discloses extracting the dissolved inorganic carbon from the aqueous solution to create CO_2 by changing a pH of the aqueous solution in the carbon extraction unit. In one embodiment, extracting the dissolved inorganic carbon includes increasing the pH of the aqueous solution to precipitate salts containing carbon, and applying acid to the salts to evolve CO_2 gas. This may involve adding aqueous NaOH to the aqueous solution, and adding aqueous HCl to the salts to evolve the CO_2. In an alternate embodiment, extracting the dissolved inorganic carbon includes decreasing the pH of the aqueous solution (*e.g.,* with HCl) to remove CO_2 gas from the aqueous solution.

[0045] Block 405 shows receiving the CO_2 from the carbon extraction unit with a fuel synthesis unit. In several embodiments, the fuel synthesis unit may include devices to drive chemical reactions between the CO_2 and hydrogen containing materials (*e.g.,* H_2, H_2O, or the like). To supply H_2, water may be decomposed into hydrogen and oxygen via at least one of alkaline electrolysis, polymer electrolyte membrane electrolysis, or solid oxide electrolysis. To facilitate fuel-building reactions, fuel synthesis unit may contain a number of different metal oxide catalysts, chambers, pipes, pumps, etc.

[0046] Block 407 illustrates converting the CO_2 into fuel including at least one of a hydrocarbon, ether, or an alcohol using the fuel synthesis unit. Conversion of CO_2 may yield methanol or higher order alcohols (*e.g.,* ethyl alcohol, butyl alcohol, isopropyl alcohol, or the like) and/or the creation of linear hydrocarbons/ethers such as (methane, ethane, propane, butane, pentane, hexane, octane, and oxygen-substituted ether equivalents) as well as branched and cyclical derivatives (*e.g.,* isopentane, cyclohexane, to name a few). In one embodiment, reacting the CO_2 with the hydrogen includes reacting gaseous water (hydrogen containing material) and the CO_2 to produce CO, hydrogen, and O_2; the CO and the hydrogen are reacted in the presence of a catalyst to produce methanol. In another embodiment, converting the CO_2 into the fuel includes reacting gaseous water and the CO_2 to produce CO, hydrogen, and O_2, and using the CO and the hydrogen to perform a Fisher-Tropsch reaction to produce hydrocarbons. This may involve feeding gaseous water and CO_2 into a solid

oxide electrolysis cell to produce syngas. One skilled in the art will realize that there are many different reactions to yield alcohols and hydrocarbons from CO_2. Furthermore, the reactions discussed above may yield any number of synthetic byproducts depending on the processing conditions. All of these byproducts may be sorted by chemcial structure and molecular weight to achieve commonly employed fuels (*e.g.*, *n*-octane) and fuel additives.

[0047] The above description of illustrated embodiments of the invention, including what is described in the Abstract, is not intended to be exhaustive or to limit the invention to the precise forms disclosed. While specific embodiments of, and examples for, the invention are described herein for illustrative purposes, various modifications are possible within the scope of the invention, as those skilled in the relevant art will recognize.

[0048] These modifications can be made to the invention in light of the above detailed description. The terms used in the following claims should not be construed to limit the invention to the specific embodiments disclosed in the specification. Rather, the scope of the invention is to be determined entirely by the following claims, which are to be construed in accordance with established doctrines of claim interpretation.

CLAIMS

What is claimed is:

1. A method of synthesizing fuel from an aqueous solution, comprising:

pumping the aqueous solution containing dissolved inorganic carbon from a body of water into a carbon extraction unit;

extracting the dissolved inorganic carbon from the aqueous solution to create CO_2 by changing a pH of the aqueous solution in the carbon extraction unit;

receiving the CO_2 from the carbon extraction unit with a fuel synthesis unit; and

converting the CO_2 into the fuel including at least one of a hydrocarbon, an alcohol, or an ether using the fuel synthesis unit.

2. The method of claim 1, wherein converting the CO_2 into the fuel includes reacting the CO_2 with hydrogen to produce the alcohol, and wherein the alcohol includes methanol.

3. The method of claim 2, further comprising decomposing water into the hydrogen and oxygen, using at least one of alkaline electrolysis, polymer electrolyte membrane electrolysis, or solid oxide electrolysis.

4. The method of claim 2, wherein reacting the CO_2 with the hydrogen includes decomposing water in the aqueous solution into the hydrogen and oxygen, and reacting the hydrogen and the CO_2 in the presence of a catalyst to produce the methanol.

5. The method of claim 2, further comprising at least one of dehydrating the methanol to produce dimethyl ether, or dehydrating the methanol to produce the dimethyl ether and dehydrating the dimethyl ether to produce the hydrocarbon.

6. The method of claim 2, wherein reacting the CO_2 with the hydrogen includes:

reacting gaseous water and the CO_2 to produce CO, the hydrogen, and O_2; and

reacting the CO and the hydrogen in the presence of a catalyst to produce the methanol.

7. The method of claim 1, wherein converting the CO_2 into the fuel includes:

reacting gaseous water and the CO_2 to produce CO, hydrogen, and O_2; and

using the CO and the hydrogen to perform a Fisher-Tropsch reaction to produce the hydrocarbon.

8. The method of claim 7, wherein reacting the gaseous water and the CO_2 includes feeding the gaseous water and the CO_2 into a solid oxide electrolysis cell.

9. The method of claim 1, wherein extracting the dissolved inorganic carbon includes:

increasing the pH of the aqueous solution to precipitate salts containing carbon, wherein the aqueous solution includes seawater; and

applying acid to the salts to evolve CO_2 gas.

10. The method of claim 9, wherein increasing the pH includes adding aqueous NaOH to the aqueous solution, and wherein applying the acid to the salts includes applying aqueous HCl to the salts.

11. The method of claim 1, wherein extracting the dissolved inorganic carbon includes decreasing the pH of the aqueous solution to remove CO_2 gas from the aqueous solution, wherein the aqueous solution includes seawater.

12. A system for fuel synthesis, comprising:

an electrodialysis unit coupled to receive aqueous NaCl and to output aqueous HCl and aqueous NaOH;

a precipitation unit with a first input coupled to receive an aqueous solution including dissolved inorganic carbon, and a second input coupled to the electrodialysis unit to receive the aqueous NaOH, wherein in response to receiving the aqueous solution and the aqueous NaOH, the precipitation unit precipitates calcium salts and outputs the aqueous solution;

an acidification unit coupled to receive the calcium salts from the precipitation unit and the aqueous HCl from the electrodialysis unit, wherein in response to receiving the calcium salts and the aqueous HCl, the acidification unit produces CO_2; and

a fuel synthesis unit coupled to the acidification unit to receive the CO_2, wherein in response to receiving the CO_2 and a hydrogen containing substance, the fuel synthesis unit outputs at least one of an alcohol, an ether, or a hydrocarbon.

13. The system of claim 12, wherein the fuel synthesis unit includes a catalyst to convert the CO_2 and the hydrogen containing substance into methanol.

14. The system of claim 13, wherein the fuel synthesis unit includes an alcohol conversion unit to dehydrate the methanol to produce dimethyl ether, and dehydrate the dimethyl ether to produce the hydrocarbon.

15. The system of claim 12, wherein the fuel synthesis unit converts the CO_2 to CO.

16. The system of claim 15, wherein the fuel synthesis unit includes a Fischer-Tropsch unit, and wherein the Fischer-Tropsch unit reacts the CO with hydrogen from the hydrogen containing substance to produce the hydrocarbon.

17. A system for fuel synthesis, comprising:

an electrodialysis unit coupled to receive aqueous NaCl, and to output aqueous HCl and aqueous NaOH;

a degasification unit with a first input coupled to receive an aqueous solution including dissolved inorganic carbon, and a second input coupled to the electrodialysis unit to receive the aqueous HCl, wherein in response to receiving the aqueous solution and the aqueous HCl, the degasification unit evolves CO_2 from the aqueous solution and outputs the aqueous solution; and

a fuel synthesis unit coupled to the degasification unit to receive the CO_2, wherein in response to receiving the CO_2 and a hydrogen containing substance, the fuel synthesis unit outputs at least one of an alcohol, an ether, or a hydrocarbon.

18. The system of claim 17, wherein the fuel synthesis unit includes a catalyst to convert the CO_2 and the hydrogen containing substance into methanol.

19. The system of claim 18, wherein the fuel synthesis unit includes an alcohol conversion unit to dehydrate the methanol to produce dimethyl ether, and dehydrate the dimethyl ether to produce the hydrocarbon.

20. The system of claim 17, wherein the fuel synthesis unit converts the CO_2 to CO.

21. The system of claim 20, wherein the fuel synthesis unit includes a Fischer-Tropsch unit, and wherein the Fischer-Tropsch unit reacts the CO with hydrogen from the hydrogen containing substance to produce the hydrocarbon.

22. The system of claim 17, wherein the hydrogen containing substance includes one of H_2 or gaseous water.

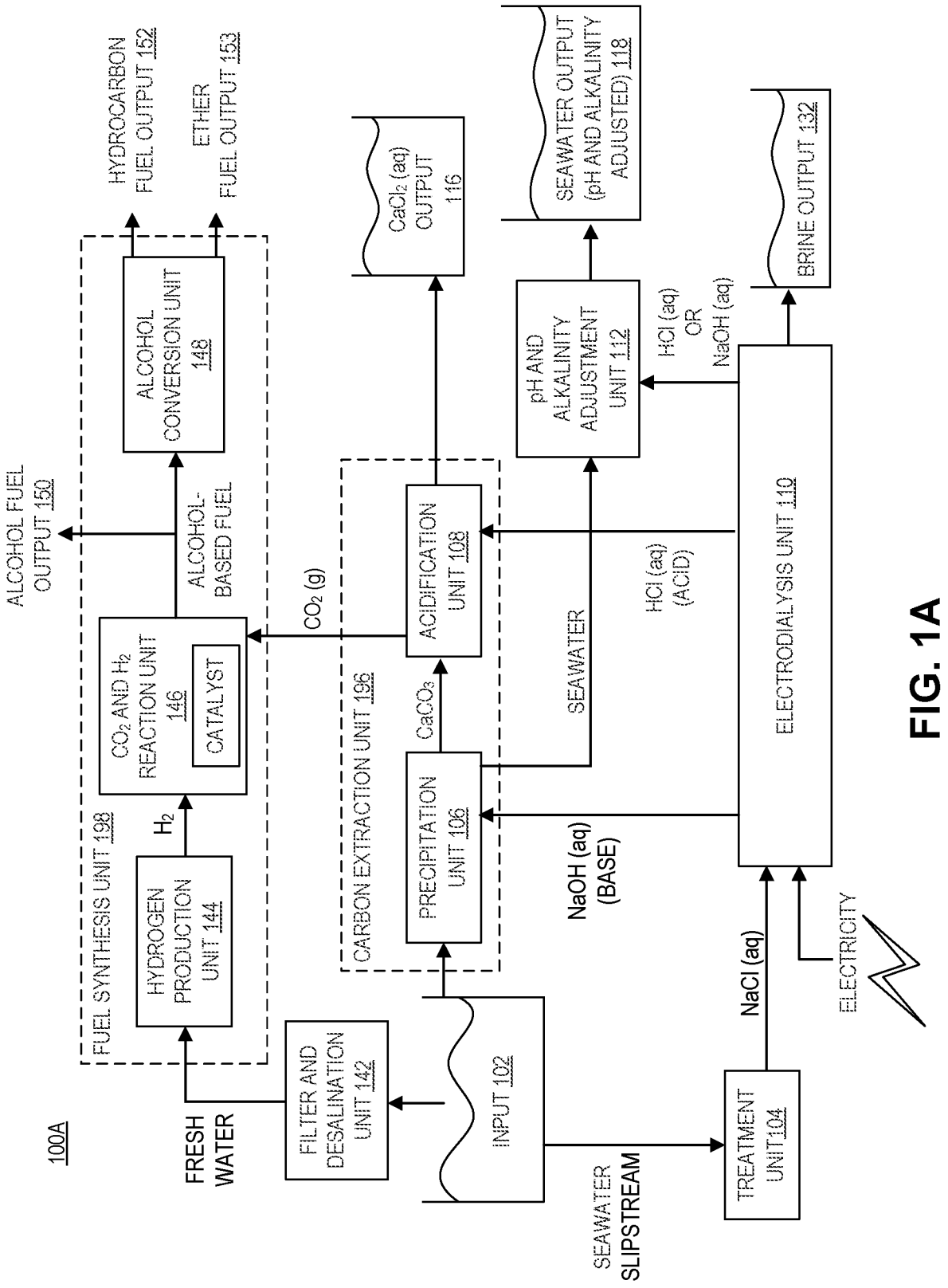
100A
FRESH WATER
SEAWATER SLIPSTREAM
FILTER AND DESALINATION UNIT 142
INPUT 102
TREATMENT UNIT104
NaCl (aq)
ELECTRICITY
ELECTRODIALYSIS UNIT 110
BRINE OUTPUT 132
SEAWATER OUTPUT (pH AND ALKALINITY ADJUSTED) 118
HCl (aq) OR NaOH (aq)
pH AND ALKALINITY ADJUSTMENT UNIT 112
HCl (aq) (ACID)
NaOH (aq) (BASE)
SEAWATER
CARBON EXTRACTION UNIT 196
PRECIPITATION UNIT 106
CaCO3
ACIDIFICATION UNIT 108
CaCl2 (aq) OUTPUT 116
CO2 (g)
FUEL SYNTHESIS UNIT 198
HYDROGEN PRODUCTION UNIT 144
H2
CO2 AND H2 REACTION UNIT 146
CATALYST
ALCOHOL-BASED FUEL
ALCOHOL CONVERSION UNIT 148
ALCOHOL FUEL OUTPUT 150
HYDROCARBON FUEL OUTPUT 152
ETHER FUEL OUTPUT 153

FIG. 1A

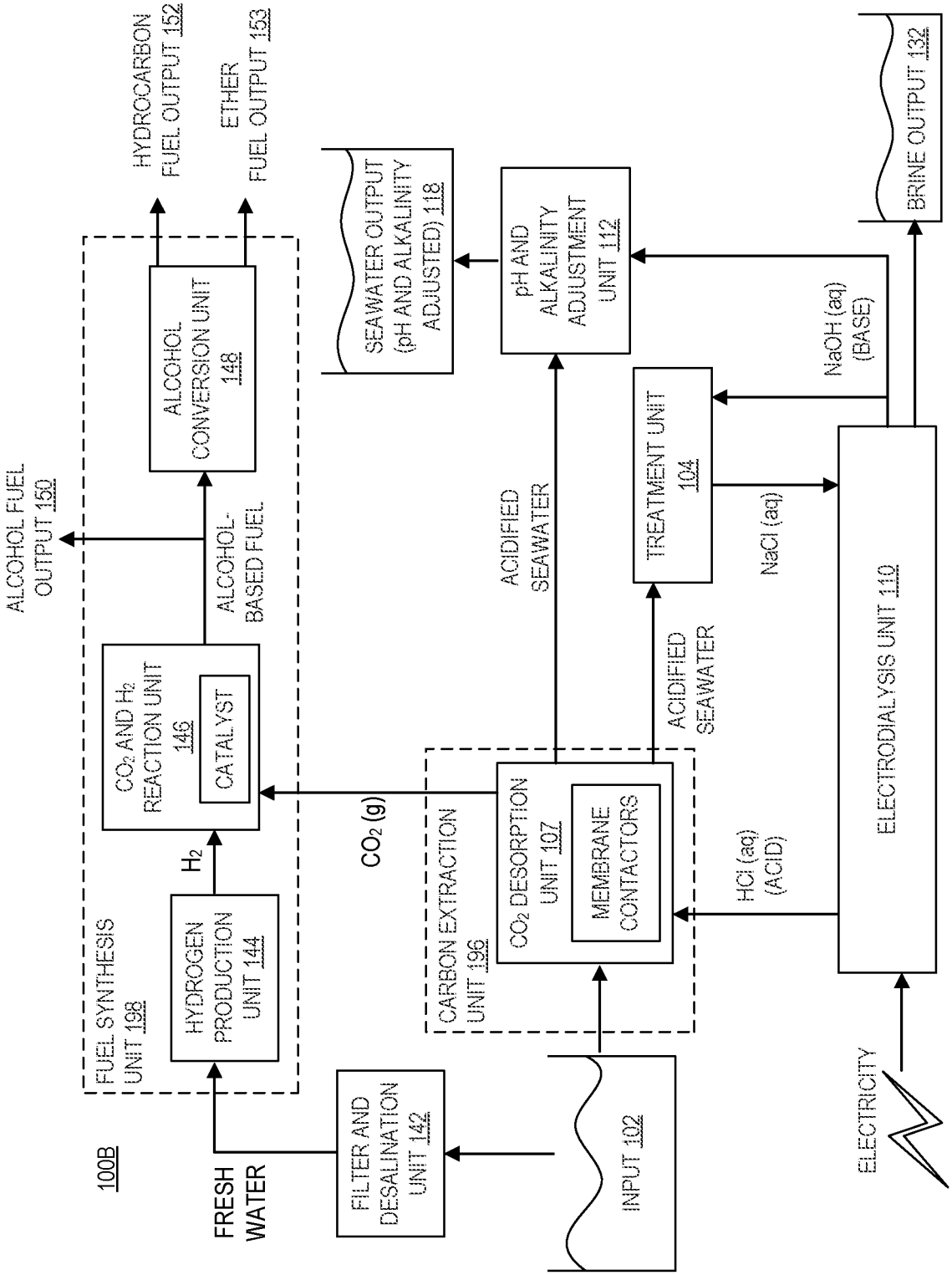
100B
FRESH WATER
FILTER AND DESALINATION UNIT 142
INPUT 102
ELECTRICITY
FUEL SYNTHESIS UNIT 198
HYDROGEN PRODUCTION UNIT 144
H_2
CO_2 AND H_2 REACTION UNIT 146
CATALYST
CO_2 (g)
ALCOHOL-BASED FUEL
ALCOHOL CONVERSION UNIT 148
ALCOHOL FUEL OUTPUT 150
HYDROCARBON FUEL OUTPUT 152
ETHER FUEL OUTPUT 153
CARBON EXTRACTION UNIT 196
CO_2 DESORPTION UNIT 107
MEMBRANE CONTACTORS
ACIDIFIED SEAWATER
ACIDIFIED SEAWATER
TREATMENT UNIT 104
HCl (aq) (ACID)
NaCl (aq)
ELECTRODIALYSIS UNIT 110
NaOH (aq) (BASE)
pH AND ALKALINITY ADJUSTMENT UNIT 112
SEAWATER OUTPUT (pH AND ALKALINITY ADJUSTED) 118
BRINE OUTPUT 132

FIG. 1B

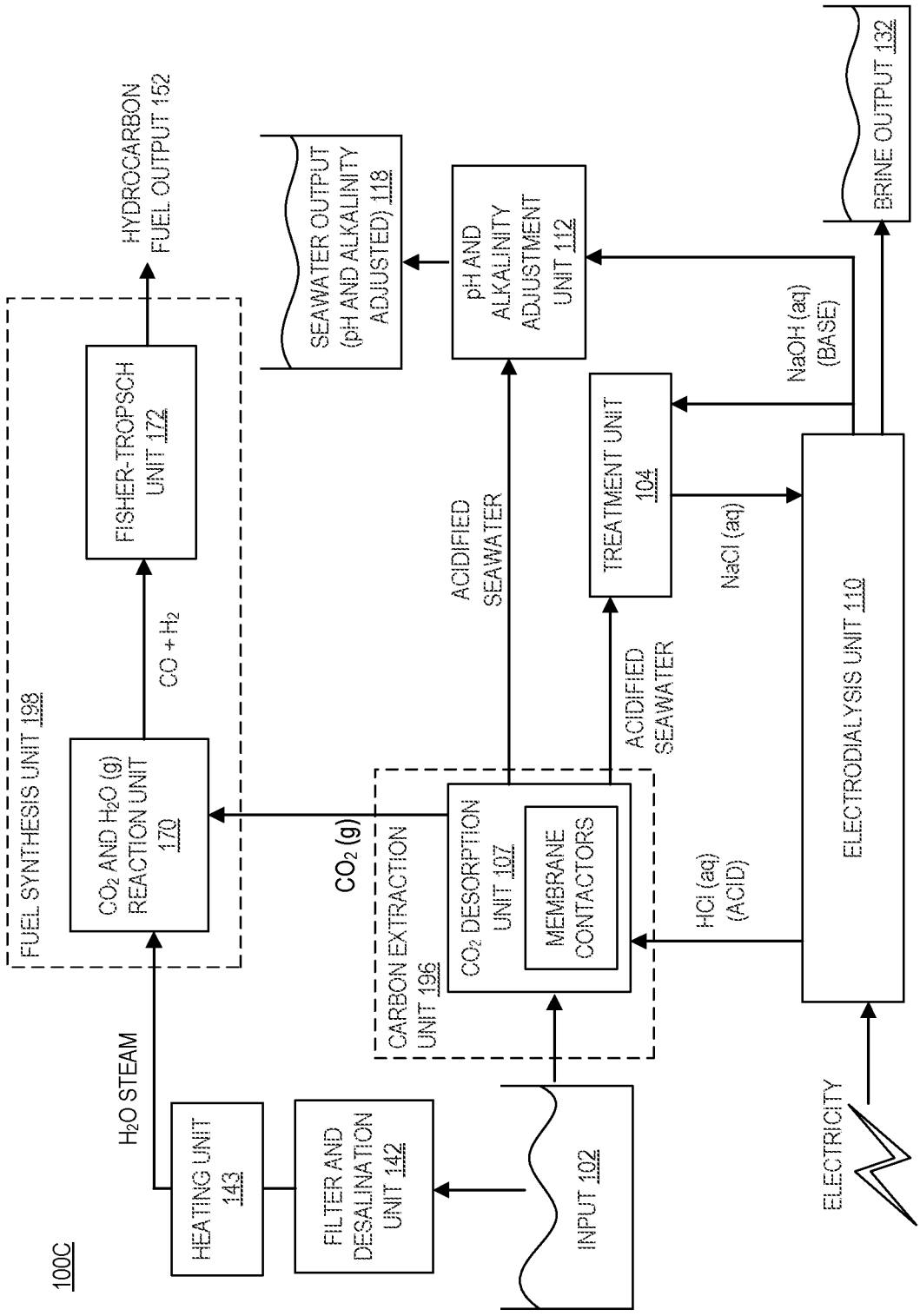
100C
INPUT 102
FILTER AND DESALINATION UNIT 142
HEATING UNIT 143
H2O STEAM
ELECTRICITY
ELECTRODIALYSIS UNIT 110
BRINE OUTPUT 132
HCl (aq) (ACID)
NaCl (aq)
NaOH (aq) (BASE)
CARBON EXTRACTION UNIT 196
CO2 DESORPTION UNIT 107
MEMBRANE CONTACTORS
CO2 (g)
ACIDIFIED SEAWATER
TREATMENT UNIT 104
ACIDIFIED SEAWATER
pH AND ALKALINITY ADJUSTMENT UNIT 112
SEAWATER OUTPUT (pH AND ALKALINITY ADJUSTED) 118
FUEL SYNTHESIS UNIT 198
CO2 AND H2O (g) REACTION UNIT 170
CO + H2
FISHER-TROPSCH UNIT 172
HYDROCARBON FUEL OUTPUT 152

FIG. 1C

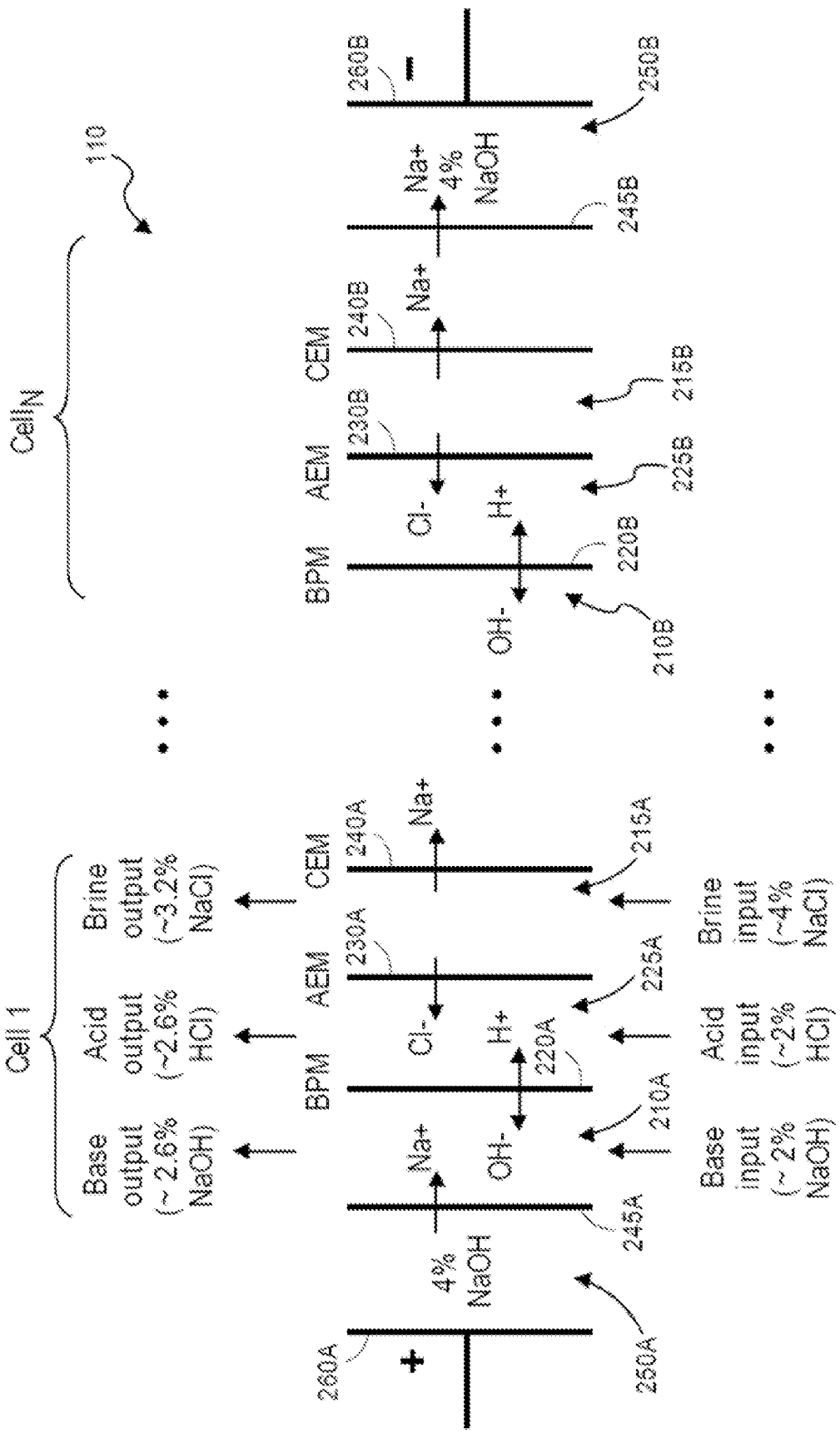
Cell 1
Base output (~ 2.6% NaOH)
Acid output (~2.6% HCl)
Brine output (~3.2% NaCl)
Base input (~ 2% NaOH)
Acid input (~2% HCl)
Brine input (~4% NaCl)
4% NaOH
Na+
OH-
Cl-
H+
BPM
AEM
CEM
260A
250A
245A
210A
220A
225A
230A
240A
215A
260B
250B
245B
210B
220B
225B
230B
240B
215B
+
−
Cell$_N$
110

FIG. 2

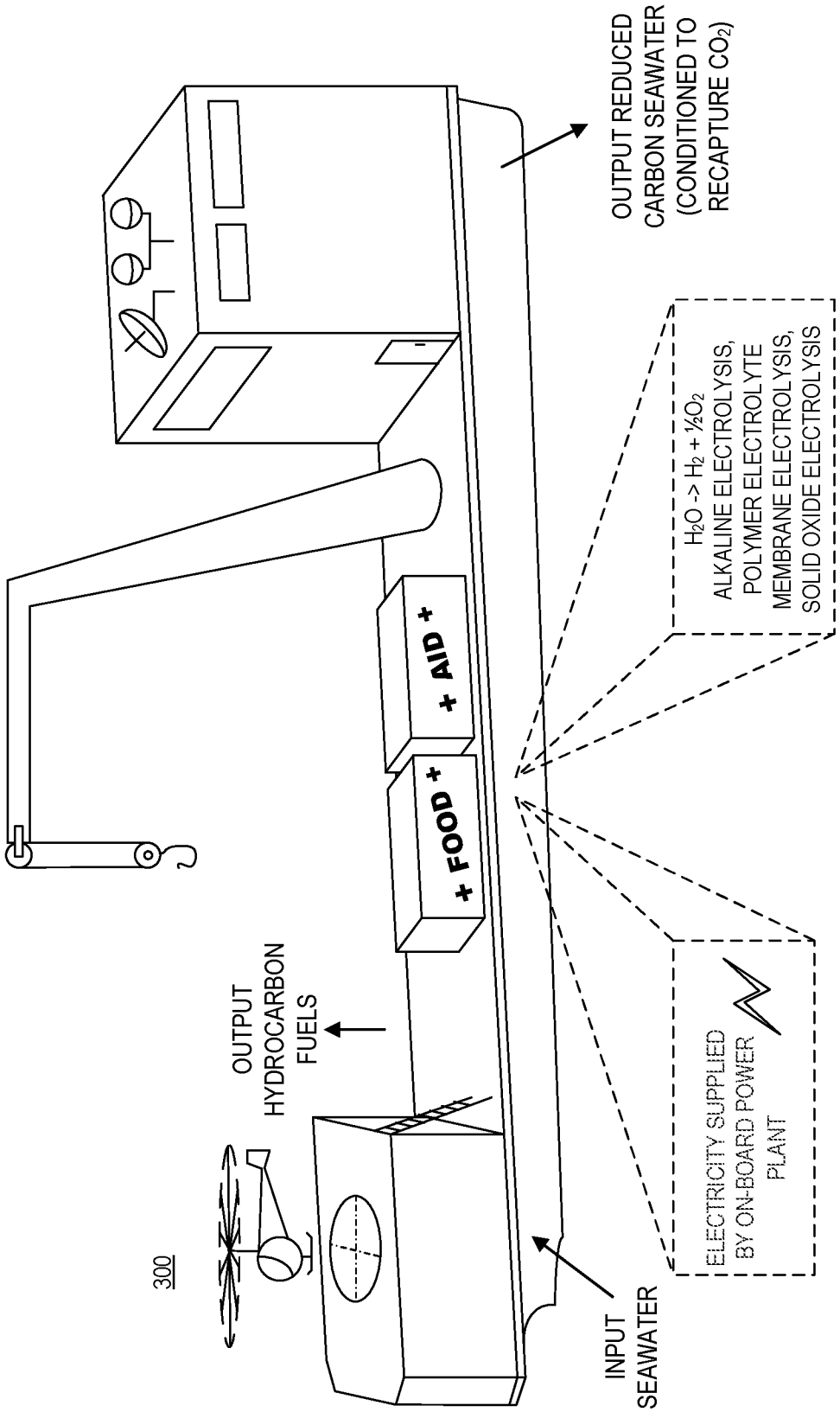
OUTPUT REDUCED CARBON SEAWATER (CONDITIONED TO RECAPTURE CO_2)
H_2O -> H_2 + ½O_2
ALKALINE ELECTROLYSIS,
POLYMER ELECTROLYTE MEMBRANE ELECTROLYSIS,
SOLID OXIDE ELECTROLYSIS
+ AID +
+ FOOD +
OUTPUT HYDROCARBON FUELS
ELECTRICITY SUPPLIED BY ON-BOARD POWER PLANT
300
INPUT SEAWATER

FIG. 3

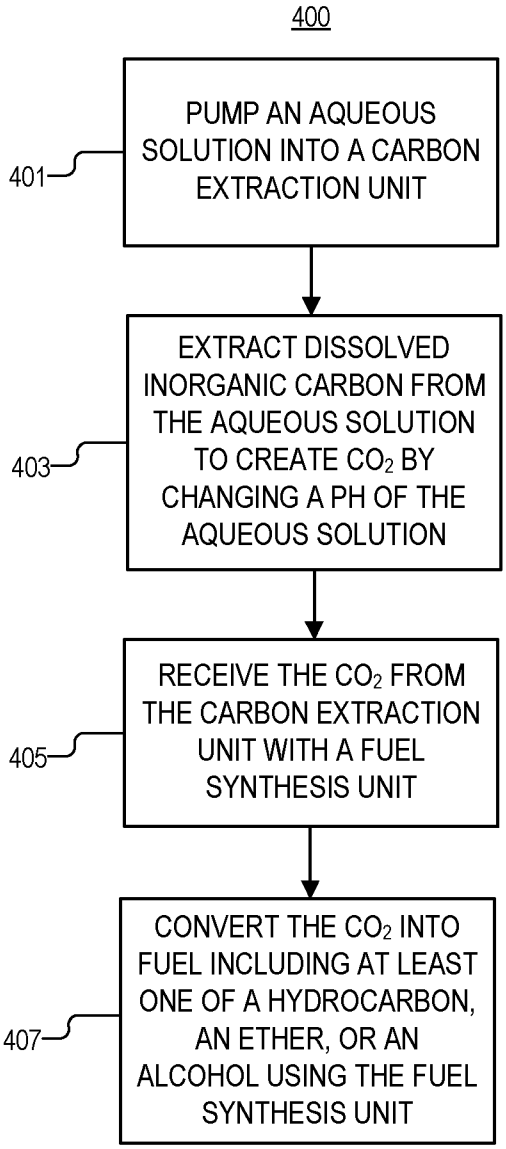
400
PUMP AN AQUEOUS SOLUTION INTO A CARBON EXTRACTION UNIT
401
EXTRACT DISSOLVED INORGANIC CARBON FROM THE AQUEOUS SOLUTION TO CREATE CO_2 BY CHANGING A PH OF THE AQUEOUS SOLUTION
403
RECEIVE THE CO_2 FROM THE CARBON EXTRACTION UNIT WITH A FUEL SYNTHESIS UNIT
405
CONVERT THE CO_2 INTO FUEL INCLUDING AT LEAST ONE OF A HYDROCARBON, AN ETHER, OR AN ALCOHOL USING THE FUEL SYNTHESIS UNIT
407

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/031519

A. CLASSIFICATION OF SUBJECT MATTER

C10L 1/16(2006.01)i, C10L 1/185(2006.01)i

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)
C10L 1/16; C25B 1/04; B01D 15/04; B01J 19/00; B01J 19/08; B01D 61/02; C10L 1/185

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: seawater, electrodialysis, precipitation, calcium salt, NaCl, HCl, NaOH, fuel synthesis, methanol, ether, hydrocarbon, extraction, carbon dioxide, pH, aqueous solution

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3627479 A (YEE, WILLIAM C.) 14 December 1971 See column 1, line 25-column 2, line 63; claims 1-3; and figure 1.	1-8,11,17-22
A		9,10,12-16
Y	US 2012-0201717 A1 (SINGH, SHWETANK et al.) 09 August 2012 See paragraphs [0038]-[0046], [0061], [0069]; claims 1, 6, 11; and figures 1-3.	1-8,11,17-22
Y	US 2011-0206566 A1 (STOOTS, CARL M. et al.) 25 August 2011 See paragraphs [0006], [0023]-[0027], [0052], [0053]; and claims 1-5.	6-8
A	US 2013-0206605 A1 (DIMASCIO, FELICE et al.) 15 August 2013 See paragraphs [0028], [0029], [0040], [0041], [0056], [0057], [0063], [0064]; claims 1, 2, 7-16; and figures 2, 3, 7, 8.	1-22
A	WO 2014-043322 A1 (SEVERN TRENT WATER PURIFICATION, INC.) 20 March 2014 See paragraphs [0032]-[0039], [0081]-[0085]; claims 1, 15; and figures 1, 4.	1-22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 August 2017 (18.08.2017)	**18 August 2017 (18.08.2017)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2017/031519

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 8198338 B2	12/06/2012
		US 8506910 B2	13/08/2013
		WO 2007-108014 A1	27/09/2007
US 2011-0206566 A1	25/08/2011	US 2008-0023338 A1	31/01/2008
		US 7951283 B2	31/05/2011
		WO 2008-016728 A2	07/02/2008
		WO 2008-016728 A3	18/12/2008
US 2013-0206605 A1	15/08/2013	EP 2569270 A1	20/03/2013
		US 2011-0281959 A1	17/11/2011
		US 2016-0215403 A1	28/07/2016
		US 9303323 B2	05/04/2016
		WO 2011-142854 A1	17/11/2011
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		AU 2013-315460 B2	01/09/2016
		CN 104640610 A	20/05/2015
		US 2014-0076817 A1	20/03/2014
		US 2016-0311701 A1	27/10/2016
		US 9403698 B2	02/08/2016