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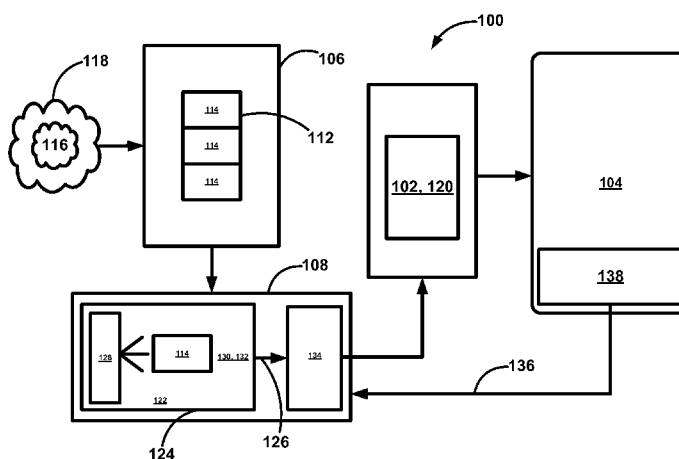


FIG. 1

(57) **Abstract:** Methods and systems for producing a biomass precursor to a biofuel using feedstock including carbon dioxide captured from ambient air are disclosed. In some embodiments, the methods include the following: capturing carbon dioxide from ambient air; transferring the carbon dioxide to a solution thereby forming a carbon-enriched solution; providing predetermined minerals; and feeding the carbon-enriched solution and the predetermined minerals to predetermined autotrophic microorganisms capable of oxidizing the predetermined minerals. In some embodiments, the systems include the following: a carbon dioxide collector including filter units for capturing carbon dioxide from ambient air; a regeneration unit for rinsing the filter units thereby transferring the carbon dioxide captured by the filter units to a solution thereby forming a carbon-enriched solution; and an interface unit including a vessel for containing the carbon-enriched solution and a conduit for supplying the carbon-enriched solution to an autotrophic bioreactor.

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METHODS AND SYSTEMS FOR GENERATING A SOURCE OF CARBON DIOXIDE FOR CONSUMPTION IN AN AUTOTROPHIC BIOREACTOR

CROSS REFERENCE TO RELATED APPLICATION(S)

- 5 [0001] This application claims the benefit of U.S. Provisional Application No. 61/408,089, filed October 29, 2010, which is incorporated by reference as if disclosed herein in its entirety.

BACKGROUND

10 [0002] The great importance of and large demand for transportation fuels in modern society has led to enormous pressures on the current supply infrastructure, which stretches from the well to the wheel. Liquid hydrocarbon fuels are unique in their ability to carry large amounts of energy virtually anywhere. Nearly all transportation fuels are made from petroleum whose future availability is uncertain. The resource size is not well understood and predictions of impending shortfalls abound, even though a case could be made that
15 there very well may be a lot of oil left in the ground. Nevertheless, the highly uneven geographic distribution of petroleum reserves has created large tensions between petroleum suppliers and consumers. Thus, the development of large sources of alternative fuels, e.g., biofuels is of paramount importance.

20 [0003] Concerns over climate change limit the options further. It is becoming increasingly evident that the accumulation of carbon dioxide in the atmosphere needs to be stopped. Unfortunately, holding carbon dioxide in the atmosphere constant is tantamount to stopping carbon dioxide emissions. A reduction of worldwide carbon dioxide emissions to 30% of current levels would slow down but not stop the rise of carbon dioxide in the atmosphere. However, a future world population sharing into a total emission budget of
25 30% would have a per capita emission allowance that is 30 times smaller than the current per capita emission rate in the United States. For all practical purposes this means that solving the climate change problem requires a transition to an energy infrastructure that is carbon neutral. This does not just apply to the electricity sector, but to the transportation sector as well.

[0004] Replacing petroleum based fuels with liquid hydrocarbon fuels derived from another source is only possible, if the carbon dioxide emissions are either eliminated or compensated for. This means that the carbon that enters into the fuel has to be directly or indirectly derived from the air. If the carbon dioxide is left in the air, the fuel production system is fundamentally unsustainable. Biofuels made from agricultural products do get their carbon feedstock from the air, and thus naturally close the carbon cycle. However, intensifying biomass production, for example by moving to algae ponds, is straining the rate at which the open air can supply carbon dioxide directly.

[0005] Autotrophic, non-photosynthetic organisms can utilize the energy stored in various metal ions that are common in minerals. Apart from energy these organisms need a source of carbon atoms to produce biomass. Autotrophs typically start with oxidized carbon, i.e., carbon dioxide or carbonate as the source of their carbon. The autotrophic organisms reduce the carbon and thus produce biomass, which can then be incorporated into useful hydrocarbon fuels to provide the energy for the transportation sector. In order to close the carbon cycle, the carbon fed to the autotrophs must come from the atmosphere. Otherwise the carbon from the spent fuel would unavoidably accumulate in the atmosphere as carbon dioxide. This carbon dioxide would stay in the atmosphere for thousands of years. Only if this carbon dioxide is actively captured, removed from the atmosphere, and reused for producing the next generation of transportation fuels, is the carbon cycle closed, and the energy system sustainable for the long term.

[0006] Chemotrophic organisms that fix carbon dioxide usually have lower specific metabolic rates and cell yields primarily owing to the thermodynamic energy requirements for carbon dioxide fixation into cellular biomass. However, in well designed systems, it is possible to greatly increase the supply of the energy (in this case in the form of Fe(II), carbon dioxide and water. In such a system one can expect much higher biomass production than in natural environments. The biomass, which collects the energy initially available in Fe(II), provides the raw material for fuel production. Thus, capturing carbon dioxide from air is an enabling technology, which lies squarely on the critical path toward a fuel production system relying on chemolithoautotrophic organisms to convert carbon dioxide into fuel precursors. Other sources of carbon dioxide, for example the exhaust from power plants could offer a start, but such sources are not sustainable because this

carbon dioxide would be regenerated at the point of fuel consumption and released to the atmosphere, where it would add to the carbon dioxide concentration. Without ready access to carbon dioxide from the air this approach to fuel production cannot take advantage of its biggest strength, i.e., that it can operate large bioreactors in a small footprint.

SUMMARY

[0007] Autotrophic, non-photosynthetic organisms can only grow if they are provided with a continuous supply of inorganic carbon that can be converted into cellular material and eventually into electrofuels. The sustainable use of these fuels without accumulation of carbon dioxide in the atmosphere requires that the carbon dioxide resulting from their consumption is recaptured from the air and recycled. A highly efficient air capture system for carbon dioxide could remove the most difficult supply bottleneck in any autotrophic bioreactor system and with chemotrophic organisms allow for a system design that is far more compact than a photosynthetic bioreactor could ever be. The disclosed subject matter includes methods and systems for feeding carbon dioxide captured from air to autotrophic bioreactors. Carbon dioxide is captured directly from the atmosphere and used to produce a carbon-enriched solution that is fed to chemotrophic organisms.

[0008] Non-photosynthetic autotrophic organisms provide a novel avenue toward bio-derived energy and liquid fuels. These organisms use inorganic building blocks, like carbon dioxide and water to form biomass. The biomass is the first step in fuel generation. The energy required to produce this biomass is typically derived from the oxidation of certain minerals containing for example sulfur, iron or hydrogen that can be oxidized in the presence of oxygen. Because they feed on minerals, these organisms are also known as lithotrophs. They consume water and carbon dioxide to produce biomass, which then can be converted into fuel. Thus, one must feed them not only the minerals that provide the energy but also the carbon dioxide that is to be converted into fuel. This carbon dioxide must ultimately come from the air, because at the point of consumption the carbon dioxide that is produced from the fuel is released to the air. It will accumulate in the air unless some action is taken to remove it again.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The drawings show embodiments of the disclosed subject matter for the purpose of illustrating the invention. However, it should be understood that the present application is not limited to the precise arrangements and instrumentalities shown in the drawings, wherein:

[0010] FIG. 1 is a schematic diagram of methods and systems according to some embodiments of the disclosed subject matter; and

[0011] FIG. 2 is a chart of a method according to some embodiments of the disclosed subject matter;

[0012] FIG. 3 is a chart of a method according to some embodiments of the disclosed subject matter.

DETAILED DESCRIPTION

[0013] Referring now to FIGS. 1-4, aspects of the disclosed subject matter include methods and systems for capturing carbon dioxide from ambient air and preparing it for consumption by autotrophic microorganisms in a bioreactor. Without limiting the disclosed subject matter to a specific autotrophic set of organisms, iron oxidizing autotrophs are discussed as one example of organisms suitable for use in some embodiments. These organisms can convert carbon dioxide, which was taken from the air and dissolved as bicarbonate, and reduce the bicarbonate to organic carbon or biomass.

The energy for this reaction is obtained from oxidizing Fe(II) with oxygen to Fe(III). Olivines, for example, are a rich source of Fe(II) that can be oxidized to Fe(III) and in turn convert bicarbonate to, among other materials, methane even with exclusively abiogenic processes.

[0014] Referring now to FIG. 1, some embodiments include a system 100 for generating a source 102 of carbon dioxide for consumption by an autotrophic bioreactor 104. System 100 includes the following interactive components: a carbon dioxide collector 106; a regeneration unit 108; and an interface unit 110.

[0015] Carbon dioxide collector 106 includes filter units 112 having anionic exchange resin 114 for capturing carbon dioxide 116 from ambient air 118. Anion exchange resin 114 is typically fabricated so as to readily absorb carbon dioxide 116 when substantially dry and release carbon dioxide when it is exposed to moisture. A dry anion exchange resin 114 absorbs carbon dioxide from the air. When wetted, resin 114 releases carbon dioxide against a backpressure of about 0.1 bar. Resin 114 then reverts back to the carbonate state, i.e., a state with 1 carbon for every two positive charges attached to the resin matrix. Exposed to open air again, resin 114 dries out, and begins another carbon dioxide absorption cycle.

10 [0016] In some embodiments, regeneration unit 108, which is used for rinsing filter units 112 thereby transferring carbon dioxide 116 captured by the filter units to a solution to form a carbon-enriched solution 120, includes a rinse chamber 122, a containment vessel 124, and a conduit 126 for releasing carbon dioxide from the containment vessel.

[0017] Rinse chamber 122 is used for rinsing anionic exchange resin 114 loaded with carbon dioxide 116 with water 128 thereby releasing the carbon dioxide into air 130 adjacent the anion exchange resin. In some embodiments, anionic exchange resin 114 is rinsed with is a carbonate solution or a bicarbonate solution.

[0018] Containment vessel 124 contains carbon dioxide 116 in air 130 adjacent anion exchange resin 114 thereby forming a carbon dioxide-enriched air 132. System 100 also includes a supply of nutrient solution 134. Conduit 126 directs carbon dioxide-enriched air 132 so that it contacts nutrient solution 134 thereby forming carbon-enriched solution 120.

[0019] Alternatively, as shown by arrow 136 in FIG. 1, a rinse solution 138, which recycled from autotrophic bioreactor 104 is use to rinse anion exchange resin 114. Solution 138 is typically substantially free of chlorides and sulfates.

[0020] Interface unit 110 includes a vessel 140 for containing carbon-enriched solution 120 or 138 and a conduit 142 for supplying the carbon-enriched solution to autotrophic bioreactor 104.

[0021] Referring now to FIG. 3, some embodiments include a method 200 of generating a source of carbon dioxide for consumption by autotrophic microorganisms in an autotrophic bioreactor. At 202, carbon dioxide is captured from ambient air by exposing the ambient air to an anionic exchange resin thereby loading the anionic exchange resin with carbon dioxide. The anionic exchange resin is fabricated so as to readily absorb carbon dioxide when substantially dry and release carbon dioxide when it is exposed to moisture. Then, at 204, the carbon dioxide is transferred to a solution thereby forming a carbon-enriched solution by rinsing the anionic exchange resin loaded with the carbon dioxide with water thereby releasing the carbon dioxide into air adjacent the anion exchange resin. In some embodiments, the resin is rinsed with either a carbonate or a bicarbonate solution instead of water. At 206, the carbon dioxide in the air adjacent the anion exchange resin is contained thereby forming a carbon dioxide-enriched air. Typically, the carbon dioxide-enriched air is about five percent carbon dioxide by weight.

[0022] The basic approach to extracting carbon dioxide from ambient air has been developed by us. We use an anionic exchange resin that readily absorbs carbon dioxide from the air when it is dry and releases the carbon dioxide again when it is exposed to moisture. Hence we refer to the process as a moisture swing absorption system. In the case envisioned here, we intend to accomplish the moisture swing by washing the dry and carbon dioxide filled resin either with water or a carbonate solution. An aqueous carbonate solution has been shown to drive the carbon dioxide off the resin, but it is sufficiently alkaline to retain the carbon dioxide as it is immediately absorbed into the solution. As a result, the solution is transformed into a bicarbonate brine. A water wash also drives the carbon dioxide off the resin, but the solubility of carbon dioxide in water is small and unless the water volume is very large, the carbon dioxide is released from the water into the surrounding gas volume. If the resin during the wash is confined to a closed space, the carbon dioxide partial pressure in the head space above the water will gradually approach a partial pressure of five to ten percent of an atmosphere.

[0023] The moisture swing has a number of practical advantages, which become of particular importance in the context of feeding autotrophic organisms the carbon dioxide they need. The moisture swing in its current implementation can only produce carbon dioxide at sub-atmospheric pressure. Hence, production of pure carbon dioxide requires

chambers strong enough to pump the air out of, and pumps and compressors to take low pressure carbon dioxide to liquid density. In feeding autotrophs it is, however, quite sufficient to produce carbon dioxide enriched air, or an aqueous solution in equilibrium with carbon dioxide enriched air. This greatly simplifies the design of the system and removes nearly all of the energy requirement that is present in a system to produce pipeline-ready carbon dioxide.

[0024] The carbon dioxide partial pressure one can reach in the current system is between 5,000 Pa and 10,000 Pa, i.e. between 5 and 10 percent of atmospheric pressure. This is more than sufficient for feeding autotrophs. As a result the moisture swing absorption system is ideally suited to this application and will result in an extremely energy efficient implementation, which we will discuss in more detail below. In short, the dominant energy consumption in the system will be in the water preparation for the moisture swing.

[0025] Then, at 208, the carbon dioxide-enriched air is placed in contact with a nutrient solution thereby forming the carbon-enriched solution. In some embodiments, the nutrient solution is prevented from contacting the anionic exchange resin. Alternatively, as shown at 210, the anionic exchange resin loaded with the carbon dioxide is rinsed with a solution recycled from the autotrophic bioreactor thereby forming the carbon-enriched solution. The rinse solution is substantially free of chlorides and sulfates. At 212, the carbon-enriched solution is fed to autotrophic microorganisms in the autotrophic bioreactor.

[0026] Referring now to FIG. 3, some embodiments include a method 300 of producing a biomass precursor to a biofuel using feedstock including carbon dioxide captured from ambient air. At 302, carbon dioxide is captured from ambient air by exposing the ambient air to an anionic exchange resin thereby loading the anionic exchange resin with carbon dioxide. Then, at 304, the carbon dioxide is transferred to a solution thereby forming a carbon-enriched solution by rinsing the anionic exchange resin loaded with the carbon dioxide with water thereby releasing the carbon dioxide into air adjacent the anion exchange resin. In some embodiments, the resin is rinsed with either a carbonate or a bicarbonate solution instead of water. At 306, the carbon dioxide in the air adjacent the anion exchange resin is contained thereby forming a carbon dioxide-enriched

air. At 308, the carbon dioxide-enriched air is placed in contact with a nutrient solution thereby forming a carbon-enriched solution. Alternatively, as shown at 310, the anionic exchange resin loaded with the carbon dioxide is rinsed with a solution recycled from an autotrophic bioreactor thereby forming the carbon-enriched solution. The rinse solution is typically substantially free of chlorides and sulfates. At 312, predetermined minerals are provided depending on a variety of factors including the type of biofuel that is desired. In some embodiments, the predetermined minerals include at least one of sulfur and iron. At 314, the carbon-enriched solution and the predetermined minerals are fed to predetermined autotrophic microorganisms capable of oxidizing the predetermined minerals. In some embodiments the autotrophic microorganisms and predetermined minerals are positioned in an autotrophic bioreactor. In some embodiments, the autotrophic microorganisms and predetermined minerals are positioned in situ at the natural location of the predetermined minerals. In some embodiments, hydrogen is produced during oxidation of the predetermined minerals by the predetermined autotrophic microorganisms and ultimately consumed by the microorganisms.

[0027] Non-photosynthetic, autotrophic processes have a fundamental advantage over photosynthetic processes, because they do not rely on dilute sunlight to operate. Therefore, the output of chemotrophic bioreactors can scale with the volume of the reactor vessel, which stands in contrast to algae bioreactors whose output scales with the surface area that is exposed to sunlight. It is possible to create large reactor vessels that are deep and thus can have a much smaller footprint than algae ponds. A large autotrophic reactor can be made more compact until it reaches the next binding constraint, which typically is access to the carbon dioxide that provides the raw material for producing fuel. Thus autotrophic reactors, even more than algae reactors, benefit from the delivery of carbon dioxide from external sources.

[0028] Biological systems take advantage of a large variety of pathways for utilizing energy that is present in the environment. Photosynthesis is the most dominant pathway, but there are also many chemical pathways available to a great variety of organisms that are known as chemotrophs. Chemotrophs are quite common. For example, it is well known that chemotrophic autotrophs form the foundation of a thriving ecological food chain around hydrothermal vents in the deep ocean. Sulfur oxidation is the largest

contributor of energy in these ecosystems, but it is known that iron oxidation and manganese oxidation also play a role. In some situations, in which sulfur is rare, organisms that oxidize iron to drive their metabolism provide the dominant source of energy. At low pH, there is *Thiobacillus ferrooxidans* and at circumneutral pH, there is, for example, *Gallionella ferruginea*. These two species are classic examples of iron oxidizers. In special cases, even rarer energy sources are utilized. For example, in Yellowstone National Park, it is hydrogen that seems to feed a large fraction of the chemotrophs that live within the hot springs. Redox systems based on rare elements could prove useful, because inorganic processes can produce these intermediates, which then are digested by bacteria or other organism. For example, it is known that olivines in contact with high temperature brines can produce hydrogen by oxidizing iron. This hydrogen can then in turn be utilized by lithotrophs.

[0029] Our goal is not to propose a particular form of an autotrophic fuel, but to enable the sustainable production of any autotrophic fuel by completely closing the carbon cycle. As this carbon dioxide could be utilized by any autotrophic bioreactor, the fuels produced could of course be generated in a way that satisfies all of the general requirements. Fuels could include diesel fuel, JP-8 aviation fuel and/or high octane automotive fuels. Energy in excess of 32 MJ/kg or heat consumption of less than 0.5 MJ/kg is clearly feasible. The system would have overall energy efficiency of at least greater than 1%, and would not include rare earth elements or organic redox shuttles.

[0030] A major advantage of chemotrophic bioreactors is that they can be very compact. Thus, the rate at which carbon dioxide can be provided rapidly becomes rate limiting. This already poses a serious problem to algae farms, which cannot become as compact as chemotrophic bioreactors because they rely on sunshine for their energy source. Since direct chemical capture of carbon dioxide from the air can achieve uptake rates three orders of magnitude higher than photosynthetic organisms have achieved, air capture can go a long way in mitigating the carbon dioxide bottleneck.

[0031] Although the disclosed subject matter has been described and illustrated with respect to embodiments thereof, it should be understood by those skilled in the art that features of the disclosed embodiments can be combined, rearranged, etc., to produce additional embodiments within the scope of the invention, and that various other changes,

omissions, and additions may be made therein and thereto, without parting from the spirit and scope of the present invention.

CLAIMS

What is claimed is:

1. A method of generating a source of carbon dioxide for consumption by autotrophic microorganisms in an autotrophic bioreactor, said method comprising:
 - 5 capturing carbon dioxide from ambient air;
 - transferring said carbon dioxide to a solution thereby forming a carbon-enriched solution; and
 - feeding said carbon-enriched solution to autotrophic microorganisms in an autotrophic bioreactor.
- 10 2. The method according to claim 1, wherein said capturing further comprises:
 - exposing said ambient air to an anionic exchange resin thereby loading said anionic exchange resin with carbon dioxide.
3. The method according to claim 2, wherein said anionic exchange resin is fabricated so as to readily absorb carbon dioxide when substantially dry and release carbon dioxide
15 when it is exposed to moisture.
4. The method according to claim 2, wherein said transferring further comprises:
 - rinsing said anionic exchange resin loaded with said carbon dioxide with water thereby releasing said carbon dioxide into air adjacent said anion exchange resin;
 - 20 containing said carbon dioxide in said air adjacent said anion exchange resin thereby forming a carbon dioxide-enriched air;
 - contacting said carbon dioxide-enriched air with a nutrient solution thereby forming said carbon-enriched solution.
5. The method according to claim 4, wherein said carbon dioxide-enriched air is about five percent carbon dioxide by weight.
- 25 6. The method according to claim 4, wherein said nutrient solution is prevented from contacting said anionic exchange resin.
7. The method according to claim 2, wherein said transferring further comprises:
 - rinsing said anionic exchange resin loaded with said carbon dioxide with a rinse

solution thereby forming said carbon-enriched solution, wherein said rinse solution is one of a carbonate solution, a bicarbonate solution, a solution recycled from said autotrophic bioreactor that is substantially free of chlorides and sulfates, and a combination thereof.

5 8. A system for generating a source of carbon dioxide for consumption by an autotrophic bioreactor, said system comprising:

a carbon dioxide collector including filter units for capturing carbon dioxide from ambient air;

10 a regeneration unit for rinsing said filter units thereby transferring said carbon dioxide captured by said filter units to a solution thereby forming a carbon-enriched solution; and

an interface unit including a vessel for containing said carbon-enriched solution and a conduit for supplying said carbon-enriched solution to an autotrophic bioreactor.

9. The system according to claim 8, wherein said filter units further comprise:

15 anionic exchange resin for capturing carbon dioxide from ambient air thereby loading said anionic exchange resin with carbon dioxide.

10. The system according to claim 9, wherein said regeneration unit further comprises:

20 a rinse chamber for rinsing said anionic exchange resin loaded with said carbon dioxide with water thereby releasing said carbon dioxide into air adjacent said anion exchange resin;

a containment vessel for containing said carbon dioxide in said air adjacent said anion exchange resin thereby forming a carbon dioxide-enriched air;

a supply of nutrient solution; and

25 a conduit for directing said carbon dioxide-enriched air so that it contacts said nutrient solution thereby forming said carbon-enriched solution.

11. The system according to claim 9, wherein said regeneration unit further comprises:

a rinse chamber for rinsing said anionic exchange resin loaded with said carbon dioxide with a rinse solution thereby forming said carbon-enriched solution, wherein said rinse solution is one of a carbonate solution, a bicarbonate solution, a solution

recycled from said autotrophic bioreactor that is substantially free of chlorides and sulfates, and a combination thereof.

12. A method of producing a biomass precursor to a biofuel using feedstock including carbon dioxide captured from ambient air, said method comprising:

- 5 capturing carbon dioxide from ambient air;
transferring said carbon dioxide to a solution thereby forming a carbon-enriched solution;
providing predetermined minerals; and
feeding said carbon-enriched solution and said predetermined minerals to
10 predetermined autotrophic microorganisms capable of oxidizing said predetermined minerals.

13. The method according to claim 12, wherein said capturing further comprises:

exposing said ambient air to an anionic exchange resin thereby loading said anionic exchange resin with carbon dioxide.

15 14. The method according to claim 13, wherein said transferring further comprises:

rinsing said anionic exchange resin loaded with said carbon dioxide with water thereby releasing said carbon dioxide into air adjacent said anion exchange resin;

containing said carbon dioxide in said air adjacent said anion exchange resin thereby forming a carbon dioxide-enriched air;

20 contacting said carbon dioxide-enriched air with a nutrient solution thereby forming said carbon-enriched solution.

15. The method according to claim 13, wherein said transferring further comprises:

rinsing said anionic exchange resin loaded with said carbon dioxide with a rinse solution thereby forming said carbon-enriched solution, wherein said rinse solution is

25 one of a carbonate solution, a bicarbonate solution, a solution recycled from said autotrophic bioreactor that is substantially free of chlorides and sulfates, and a combination thereof.

16. The method according to claim 12, wherein said predetermined minerals include at least one of sulfur and iron.

17. The method according to claim 12, wherein said predetermined autotrophic microorganisms include at least one of an iron oxidizing microorganism and a sulfur oxidizing microorganism.
18. The method according to claim 12, wherein feeding said carbon-enriched solution and
5 said predetermined minerals to predetermined autotrophic microorganisms capable of oxidizing said predetermined minerals is done in an autotrophic bioreactor.
19. The method according to claim 12, wherein said predetermined minerals are in situ.
20. The method according to claim 12, wherein hydrogen is produced during oxidation of said predetermined minerals by said predetermined autotrophic microorganisms.

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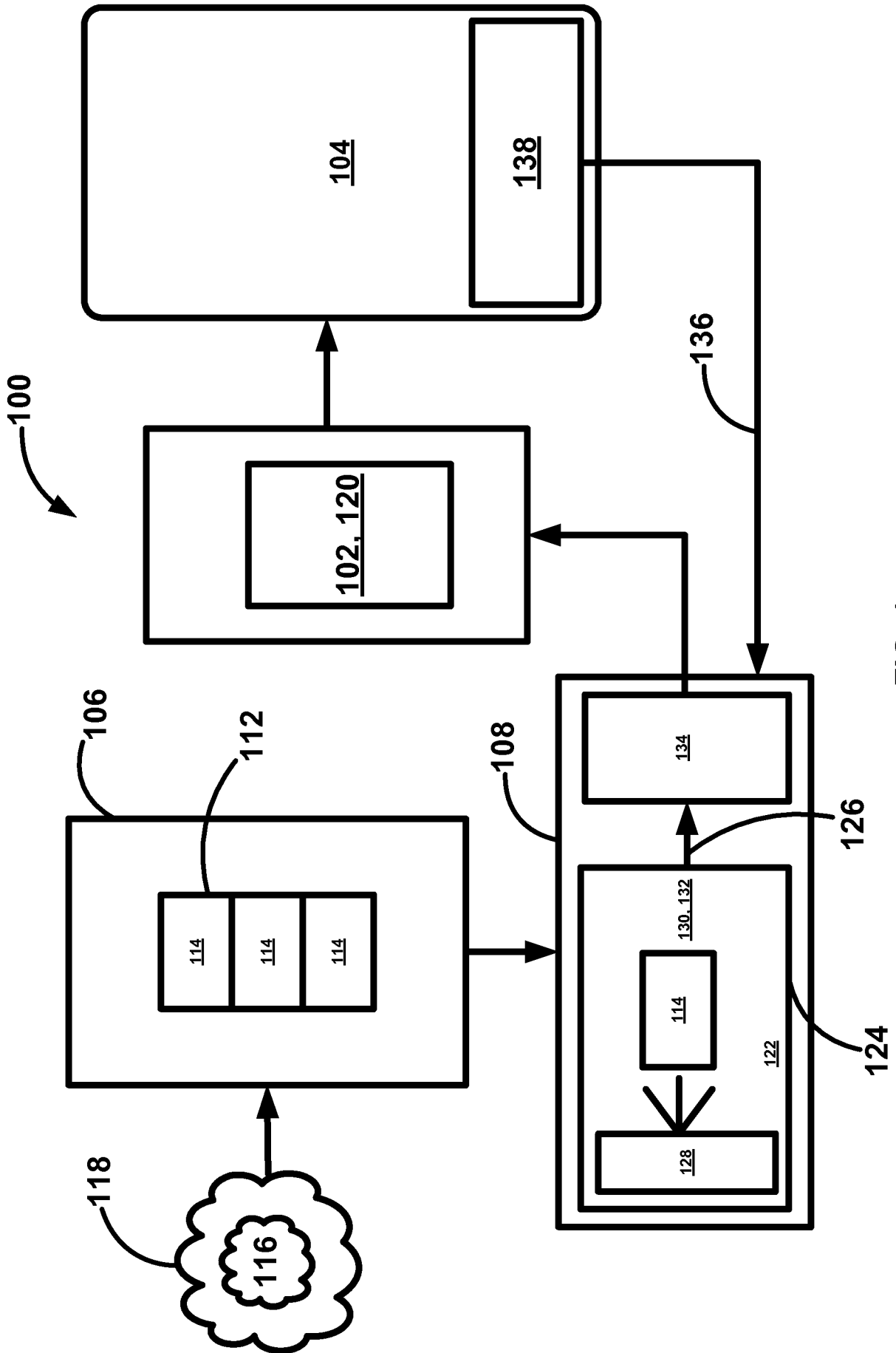


FIG. 1

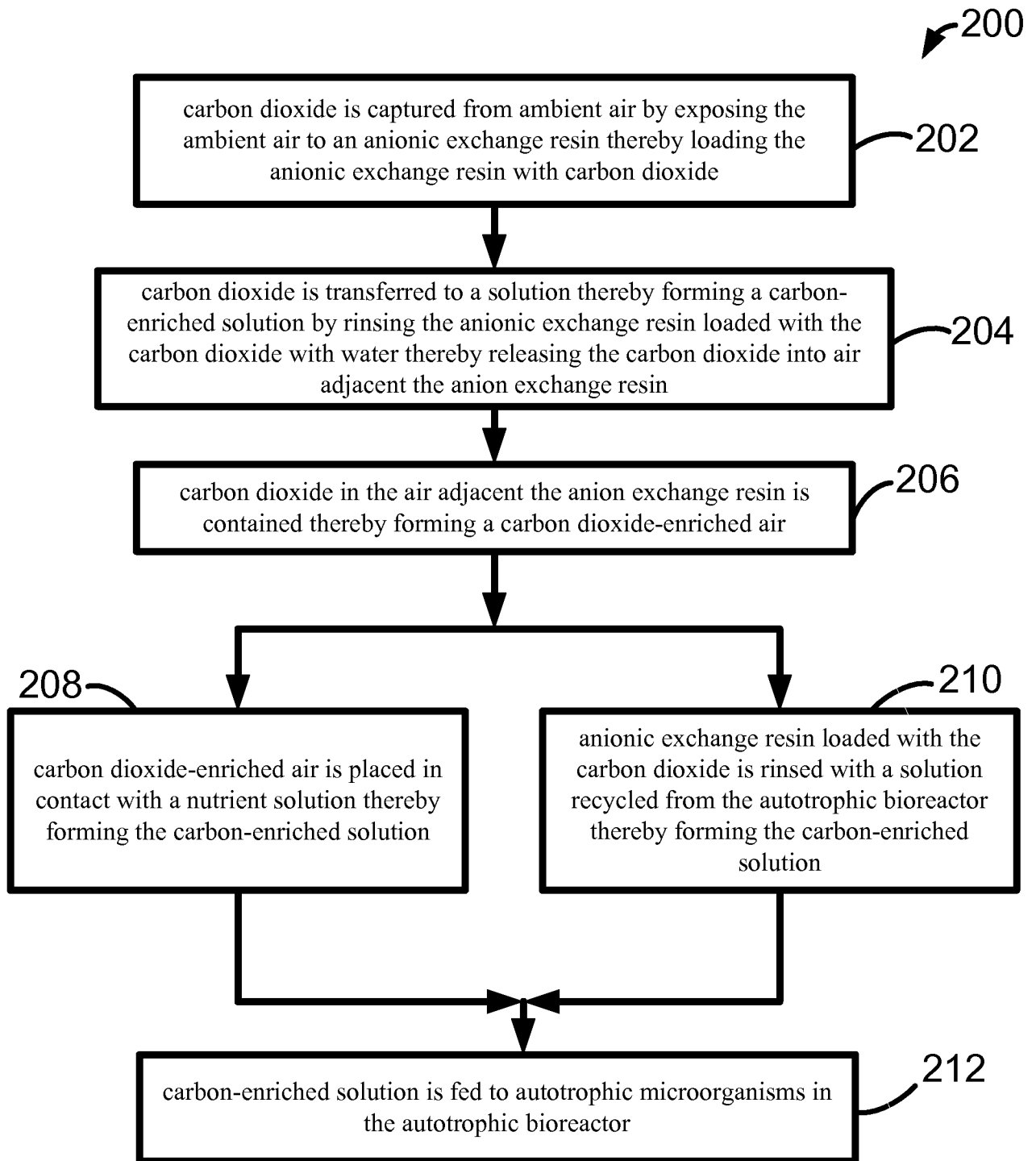


FIG. 2

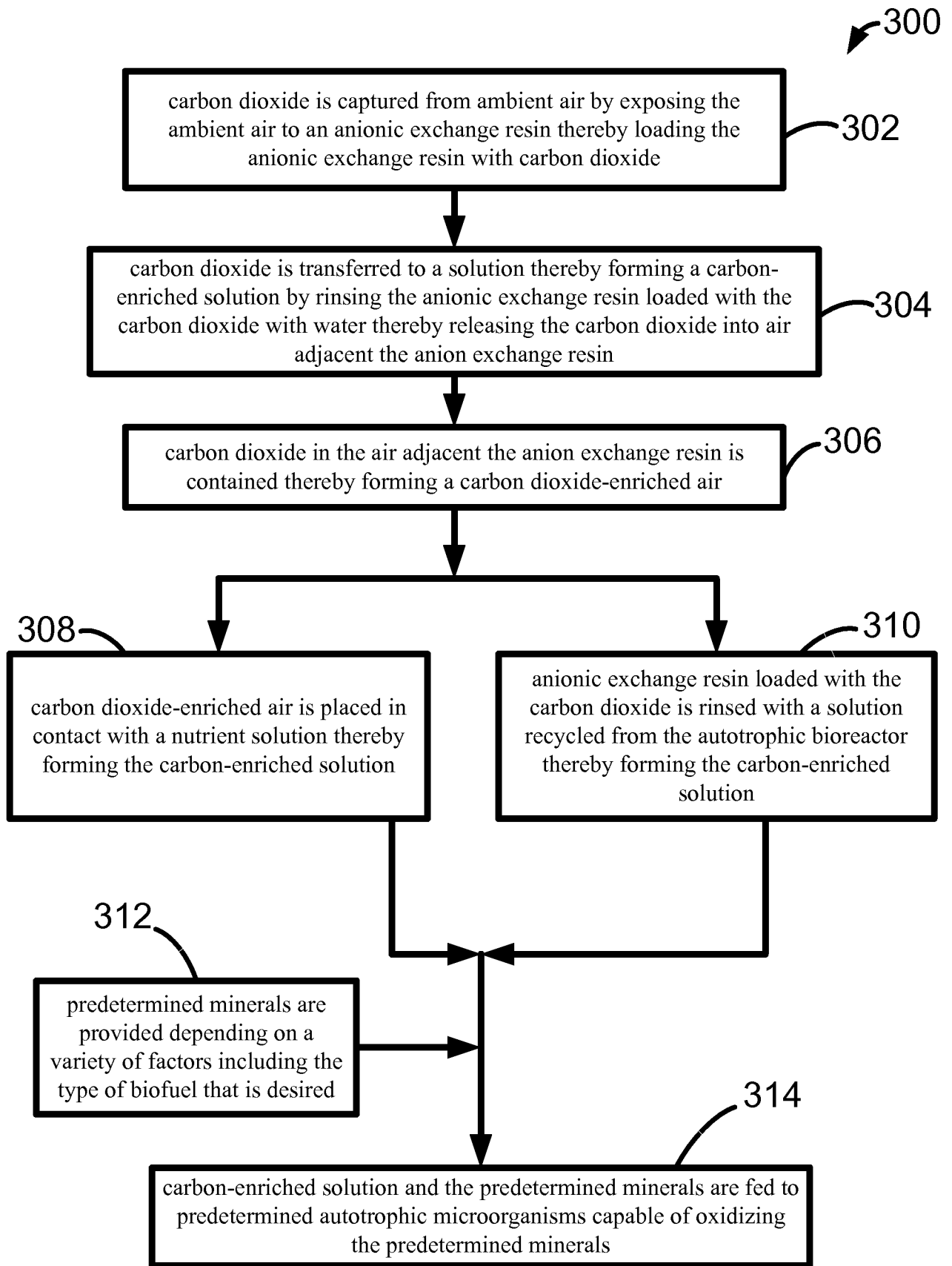


FIG. 3