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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
07 June 2018 (07.06.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/102070 A2

(51) International Patent Classification:
C25B 3/04 (2006.01) *C12P 5/02* (2006.01)

(21) International Application Number:
PCT/US2017/059912

(22) International Filing Date:
03 November 2017 (03.11.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/416,894 03 November 2016 (03.11.2016) US

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

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

Published:
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: BIOELECTROSYNTHESIS OF ORGANIC COMPOUNDS

(57) Abstract: In some aspects, the present disclosure provides a method of bioelectric production of organic compounds such as acetate. In further aspects, the present disclosure also provides methods of producing a hydrocarbon based fuel using C02 as the carbon source.

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DESCRIPTION

BIOELECTROSYNTHESIS OF ORGANIC COMPOUNDS

[0001] This application claims the benefit of United States Provisional Patent Application No. 62/416,894, filed November 3, 2016, the entirety of which is incorporated herein by reference.

[0002] The invention was made with government support under Grant No. N00014-15-2219 awarded by the United States Office of Naval Research. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0003] The present invention relates generally to the fields of electrochemical synthesis and microbiology. More particularly, it concerns methods for producing organic compounds, such as acetate, by bioelectric synthesis.

2. Description of Related Art

[0004] World economies, in particular that of the U.S., are heavily reliant on the use of fossil-based carbon to produce many commodity chemicals and fuels. However, due to supply difficulties, the inevitable decline of these resources, increased world demand and environmental concerns, a shift away from coal and oil to alternatives such as solar and wind is occurring. However, most of these energy sources are either limited by fluctuations in price and availability or are nonrenewable as in the case of natural gas. These factors have encouraged research into the development of renewable energy technologies powered by microbes. Of particular interest are microorganisms that can capture the global greenhouse gas CO_2 and convert it to a valuable commodity, such as a fuel, industrial chemicals, food and health ingredients.

[0005] The production of liquid hydrocarbons from CO_2 instead of from petroleum would obviously avoid the release of climate altering carbon into the atmosphere and could usher in new economic development. Photosynthetic capture of CO_2 and conversion into advanced biofuels, directly or following the processing of lignocellulosic plant biomass, is possible but has not yet become economically achievable due to technical limitations. Previous work (WO 2014/043690, which is incorporated herein by reference) has shown that CO_2 can

be converted into acetate using biosynthetic pathways and that process is enhanced in the presence of voltage potential. As such, new methods of utilizing captured CO_2 and converting the greenhouse gas into useable hydrocarbon feedstocks are desirable in providing fuel, chemical and food sources.

SUMMARY OF THE INVENTION

[0006] In a first embodiment there is provided a method for bioelectric synthesis of H_2 and organic compounds comprising: (a) culturing a microbial population in a media in a cathode chamber of an electrochemical cell; (b) maintaining the microbial population in the cathode chamber in the presence of: (i) constant current of between 0.1 and 100 A per liter (or between 0.1 and 50 A or 1 and 50 A per liter) of cathode chamber volume; (ii) CO_2 gas; and (iii) a flow of media nutrients, thereby producing organic compounds; and (c) collecting the produced organic compounds. In some aspects, maintaining the microbial population may be in the presence of between 1 and 20 A per liter of cathode chamber volume. In further aspects, maintaining the microbial population may be in the presence of between 3 and 15 A per liter of cathode chamber volume.

[0007] In certain aspects, maintaining the microbial population may be in the presence of a constant current for at least 10, 20, 30, 40, 50, 60, 120 or 180 days. In some specific aspects, maintaining the microbial population is in the presence of a constant current for 60 to 180 days. In additional aspects, the constant flow of media nutrients may be filtered to maintain the cells of the microbial population in the cathode chamber.

[0008] In certain aspects, an electrochemical cell of the embodiments comprises a probe for measuring pH (*e.g.*, in the cathode chamber). In several aspects, the media in the cathode chamber comprises a pH buffer system. In further aspects, the pH buffer system is a phosphate or carbonate buffer system. In particular aspects, the method additionally comprises maintaining the media in the cathode chamber in a constant pH range, such as a pH of between 8.0 and 4.5 or between 6.0 and 4.5. In certain aspects, the constant pH range is maintained by an automated system.

[0009] In some aspects, the flow of media nutrients is constant. In other aspects, the flow of media nutrients is intermittent. In some aspects, the cathode chamber may be flushed with CO_2 or supplied with bicarbonate periodically. In more specific aspects, the cathode chamber is flushed with CO_2 or supplied with bicarbonate on average every 3 to 10 days. In a

certain aspect, the cathode chamber is supplied with a continuous in flow of CO_2 or bicarbonate. In some particular aspects, the CO_2 is obtained from waste gas or captured from the anaerobic digestion of waste. In yet further aspects, the produced organic compounds are removed periodically (e.g., hourly, daily, every two days, every three days or weekly) or continuously. In still further aspects, waste products in the media are removed periodically (e.g., hourly, daily, every two days, every three days or weekly) or continuously.

[0010] In some aspects, cathode chamber may be maintained at a temperature of between 15 and 40 °C. More specifically, the cathode chamber may be maintained at a temperature of between 20 and 30 °C.

[0011] In still further aspects, the microbial population may comprise bacteria from at least two, three or four families selected from the group consisting of Eubaceriaceae, Campylobacteraceae, Helicobacteraceae, Porphyromonadaceae, WCHB1-69, Spirochaetaceae, Deferribacteraceae, Rhodobacteraceae, Synergistaceae and Rhodocyclaceae. In some aspects, the microbial population comprises two or more different species of bacteria. In other aspects, the microbial population is essentially a pure culture of one species of bacteria. In certain aspects, the microbial population comprises Bacteria from the Helicobacteraceae, WCHB1-69, Spirochaetaceae, or Synergistaceae families. In other aspects, the microbial population may comprise bacteria from the genus *Acetobacterium, Sulfurospirillum, Wolinella, Paludibacter, Spirochaeta, Geovibrio, Desulfovibrio* or *Azovibrio*. In some specific aspects, the microbial population comprises bacteria from the genera *Acetobacterium*, *Sulfurospirillum* and/or, optionally, from the family Rhodobacteraceae. In certain particular aspects, the microbial population comprises *Acetobacterium woodii, Acetobacterium weiringae, Sporomusa ovata, Clostridium ljugdahlii*, *Clostridium carboxydivorans*, *Clostridium autoethanogenum* or a mixture thereof. In one aspect, the microbial population comprises *Acetobacterium* sp., *Sulfurospirillum* sp., and *Desulfovibrio* sp. In further aspects, the microbial population comprises the Electrobiome® mixture (see, Marshall *et al.*, 2017, incorporated herein by reference). More specifically, the microbial population may comprise at least 85% *Acetobacterium* sp. I still further aspects, the microbial population comprises *Acetobacterium woodii, Acetobacterium weiringae, Sporomusa ovata, Clostridium ljugdahlii, Clostridium autoethanogenum, Clostridium carboxydivorans* either as an essentially pure culture or as mixture of two or more of these organisms.

[0012] In additional aspects, the method does not involve the addition of compounds that inhibit methanogenic organisms. In certain aspects, the microbial population may be essentially free of methanogenic organisms. In yet further aspects, a method of the embodiments uses a growth media that does not comprise yeast extract and/or does not comprise a reducing agent. For example, the media can be essentially free of methyl reductase inhibitors, such as 2-bromoethanesulfonic acid (BESA) or 2-chloroethanesulfonic acid (CESA).

[0013] In yet still further aspects, the cathode may comprise reticulated vitreous carbon (RVC), carbon paper, carbon cloth, carbon felt, carbon wool, carbon foam, graphite, porous graphite, graphite powder, graphene, carbon nanotubes, electrospun carbon fibers, carbon coated stainless steel mesh, a conductive polymer, platinum, palladium, titanium, gold, silver, nickel, copper (*e.g.*, copper foam or copper wool), tin, iron, cobalt, tungsten, stainless steel (*e.g.*, steel foam or steal wool), and combinations thereof. In a specific aspect, the cathode comprises RVC and the RVC may be coated with carbon nanotubes. In some aspects, the cathode may be a porous material. For example, the cathode may comprise 10 to 1000 pores per inch (ppi). In a particular aspect, the cathode comprises RVC having 10 to 100 or 10 to 200 pores per inch (ppi).

[0014] In some aspects, the electrochemical cell comprises an anode composed of carbon paper, carbon cloth, carbon felt, carbon wool, carbon foam, graphite, porous graphite, graphite powder, graphene, carbon nanotubes, electrically conductive woven fabric, electrospun carbon fibers, a conductive polymer, platinum, palladium, titanium, gold, silver, nickel, copper, tin, iron, cobalt, cobalt phosphate, tungsten, stainless steel, coated titanium, a mixed metal oxide or a combination thereof. In certain aspects, the anode may be an electrically conductive woven fabric. In a specific aspect, the electrically conductive woven fabric comprises polydimethyl siloxane hollow fiber membranes and carbon fiber. In another aspect, the anode is a coated titanium anode. In several aspects, the anode may be coated with a metal oxide or with IrO_2 and/or Ta_2O_5.

[0015] In still further aspects, the organic compounds may comprise acetate, butyrate, isobutyrate, propionate, 3-hydroxypropionate, 3-hydroxybutyrate, formate or an alcohol (*e.g.*, ethanol). In certain aspects, the organic compound comprises ethanol and the culture media includes tungsten. In certain aspects, the method may further comprise contacting the microbial culture with a methyl reductase inhibitor, thereby selectively promoting acetate

production. In some aspects, the methyl reductase inhibitor is 2-bromoethanesulfonic acid (BESA) or 2-chloroethanesulfonic acid (CESA).

[0016] In additional aspects, the method may be further defined as a method for electrosynthesis of polyhydroxyalkanoate (PHA) bioplastics and further comprising (d) mixing the collected H_2 or organic compound with oxygen in a reaction chamber that comprises a second microbial population, thereby producing a PHA bioplastic. In certain specific aspects, the second microbial population may be a methanotroph or methanotrophic community. In another aspect, the second microbial population is comprised in a nitrogen- or phosphate-limited environment. In some particular aspects, the media at the cathode comprises a potassium phosphate buffer. In another specific aspect, the PHA bioplastic comprises polyhydroxybutyrate. In some aspects, the second microbial population may comprise *Ralstonia eutropha*, *Escherichia coli*, or *Cupriavidus*. In a certain particular aspect, the second microbial population is an essentially pure culture of *Ralstonia eutropha*, *Escherichia coli*, or *Cupriavidus*.

[0017] In yet still further aspects, the reaction chamber that comprises the second microbial population may be directly connected to the electrochemical cell via an anion exchange membrane. In some aspects, the method further comprises isolating the PHA bioplastic from the cells of the second chamber.

[0018] In another embodiment there is provided a method of producing a greater than C_5 hydrocarbon (e.g., C_5-C_{40} hydrocarbon) comprising providing acetate to a culture of algae, dinoflagellate algae and/or Thraustochytrids capable of producing long-chain hydrocarbons and organic products, said acetate produced in an electroacetogenic bioreactor. In certain aspects, the acetate is produced by any of the embodiments or aspects described above. Thus, in some aspects, a method comprises (a) generating acetate in a first reactor at a biocathode comprising an electroacetogenic microbial population at a cathode, CO_2, and a voltage potential at the cathode to produce acetate; (b) providing the acetate produced into a second reactor containing the algae; and (c) allowing the algae to convert the acetate into the C_5-C_{40} hydrocarbon or organic compound. In still further aspects, the method further comprises collecting and/or distilling the C_5-C_{40} hydrocarbon from the second reactor.

[0019] In yet a further embodiment there is provided a long-chain hydrocarbon mixture (e.g., a mixture of C_5-C_{40} hydrocarbons) produced by a method of the embodiments. In some

aspects, the mixture further comprises a green microalga, such as a viable green microalga cell. In further aspects, the mixture comprises trace amounts of acetate, such as at least 0.001, 0.01, 0.1 or even as much as 1%, 2%, 3%, 4% or 5% acetate. In still further aspects, the long-chain hydrocarbons in the mixture have a ^{14}C content not less than 10% of the ^{14}C content in atmospheric CO_2.

[0020] In some aspects, a second bioreactor of the embodiments comprises an organism, such as *Crypthecodinium cohnii Chlamydomonas rheinhardtii Haematococcus pluvialis, Schizochytrium spp.* or green microalga such as *Botryococcus braunii*. When supplied with an acetate source, such as an algae can produce long-chain hydrocarbons greater than C_5, such as C_5-C_{40} hydrocarbons, C_{20}-C_{40} hydrocarbon or C_{23}-C_{33} hydrocarbons. Thus, in some aspects, the long-chain hydrocarbons produced are defined as a fuel. In certain aspects, algal culture produces an amount of hydrocarbon greater than 4, 5, 6, 7 or 8 gfuel/L (*e.g.*, greater than 10 gfuel/L). In still further aspects, the rate of fuel production is about or greater than about 0.75 or 1.0 gfuel/gcdw/hr. In yet further aspects, the algal culture the second bioreactor has a reaction energy efficiency of greater than 50%, 55%, 60%, 65%, 70%, 75%, 80% or 85%. For example, in some aspects an algal culture has an average carbon yield from acetate of about or greater than about 50%, 55%, 60%, or 65% (e.g., such as about 67%).

[0021] In certain aspects, methods concern providing acetate into a second reactor. For example in some aspects, acetate can be provided by diffusion. For example, the first and second bioreactors may be separated by a membrane that allows acetate molecules to diffuse in the second reactor. Preferably such a diffusion membrane has a pore size that is sufficiently small to exclude long-chain hydrocarbons from diffusing into the first bioreactor.

[0022] In certain aspects a method of the embodiments comprises purification of organic compounds such as acetate from the culture system. For example, the purification may comprise by freeze concentration or electrodialysis. In some aspects the inorganic compounds are separated from the reactor (such as in an acetate production stream). For example, the inorganic compound can comprises struvite ($NH_4MgPO_4 \cdot 6H_2O$).

[0023] In certain aspects, a method of the embodiments further comprises collecting a long-chain hydrocarbon from a second bioreactor. In some aspects, collecting the hydrocarbon can comprise exposing the culture of the second reactor to a solvent, such as an organic solvent, to remove the hydrocarbon. In preferred aspects, a solvent extracts greater than 50%, 60%,

70%, 80%, 90% or 95% of the hydrocarbon from the media. In yet further aspects, a method comprises distilling the long chain hydrocarbons. For example, the hydrocarbons can be distilled to produce a diesel or gasoline composition. In further aspects, organic compounds produced by the methods of the embodimentscomprise omega 3 fatty acids, polyunsaturated fatty acids (PUFAs) or carotenoid compounds such as astaxanthin.

[0024] In a preferred embodiment a microbial population for use according to the methods comprises at least a first acetogen. As used herein an "acetogen" refers to a CO_2 reducing acetogen microbe that uses the Acetyl CoA Pathway. Acetogenic organisms are well recognized in the art see, *e,g.,* Impkamp and Muller, "Acetogenic Bacteria" Encyclopedia of Life Sciences, 2007, incorporated herein by reference.

[0025] As used herein the specification, "a" or "an" may mean one or more. As used herein in the claim(s), when used in conjunction with the word "comprising", the words "a" or "an" may mean one or more than one.

[0026] The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or." As used herein "another" may mean at least a second or more.

[0027] Throughout this application, the term "about" is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

[0028] Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

[0030] FIG. 1A-B: A, Three dimensional rendering of the components of the bioelectrochemical reactor. This is also designed for modular construction. B, An example of a constructed continuous flow bioelectrochemical cell.

[0031] FIG. 2: OD_{600nm} of effluent from triplicate bioelectrochemical reactors.

[0032] FIG. 3: Growth of the Electrobiome on 45 ppi RVC. Left: uninoculated RVC. Right: biomass on inoculated RVC. Both images taken during operation and H_2 gas bubbles are visible. Microbubbles were more uniform and visible in the uninoculated reactor and less visible in the inoculated reactors.

[0033] FIG. 4: Space time yield for acetate in triplicate continuous flow/culture bioelectrochemical reactors.

[0034] FIG. 5: Hydrogen production by uninoculated electrochemical reactor.

[0035] FIG. 6: Coulombic efficiency of triplicate bioelectrochemical reactors.

[0036] FIG. 7: Energy efficiency of triplicate bioelectrochemical reactors.

[0037] FIG. 8: (A) Space time yield and (B) Coulombic efficiency of secondary products produced in triplicate bioelectrochemical reactors (SD, n=3).

[0038] FIG. 9: Hydrogen production of an uninoculated abiotic reactor operated under the same conditions as biotic reactors.

[0039] FIG. 10: Power consumption of triplicate bioelectrochemical reactors (SD, n=3).

[0040] FIG. 11A-H: Further organic compound production systems of the embodiments.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0041] Microbial electrosynthesis is a promising new technology that when developed could result in a sustainable supply of chemicals and fuels from renewable electricity and CO2. However, to date the rates, yields, and efficiencies (energetic and Coulombic) have been too low for commercial consideration. Methods and systems disclosed herein provide for significantly enhanced synthesis of organic compounds such as acetate. In particular, the bioreactors and methods provided here are designed for operation with the microbial community maintained in a two chamber electrochemical cell, and include one or more of the following features: 1) maintenance under Galvanostatic (constant current) control; 2) a continuous supply of nutrients, water, and CO_2; 3) continuous removal of products and waste media; 4) on a reticulated vitreous carbon (RVC) foam cathode; and 5) with a mixed metal oxide (MMO) anode. For example, the combination of Galvanostatic control and the high surface area RVC reduces the electron limitation and the continuous flow eliminates the nutrient limitation and avoids the accumulation of toxic compounds. These conditions were set with the intention of operating the biocathode through the production of H_2. Biofilm growth occurred on unmodified RVC regardless of vigorous H_2 generation on the cathode surface. Surprisingly, productivity and efficiency were significantly improved as follows. A maximum volumetric rate or space time yield of 0.78 g/Lcatholyte/hour was achieved with 8 A/Lcatholyte (83.3 A/m^2 projected surface area of cathode) supplied to the continuous flow/culture bioelectrochemical reactors. The total Coulombic efficiency in H_2 and acetate ranged from approximately 80% to 100%, with a maximum of 35% in acetate. The overall energy efficiency ranged from approximately 35% to 40% with a maximum to acetate of ~12%. These rates and efficiencies are within the ranges for acetogenesis from H_2:CO_2 in gas-liquid contacting reactors when supplied with H_2 from an electrolyzer. Thus, the new methods and systems provided here allow for significantly more efficient synthesis of organic compounds, which can enable commercial exploitation of this new technology.

[0042] In further aspects, there are also provided methods of producing hydrocarbons from an acetotrophic organism such as a green microalga wherein the organism is feed a supply of acetate, such as acetate produced through an electroacetogenic cell. Thus, in some embodiments, there is provided a bioreactor which produces acetate and the produced acetate is supplied (*e.g.*, via diffusion) to a second reactor which comprises a microalga or other organism to process the acetate into long chain hydrocarbons. Without being bound by theory,

the organisms in such a second bioreactor can utilize modified fatty acid biosynthetic pathways, which result in the production of a long chain hydrocarbon, such as omega 3 fatty acids and astaxanthin. In some aspects, long chain hydrocarbons for production according to the instant embodiments has between 5 and 40 carbons. Methods of the embodiments may also comprise purification (e.g., distillation) of long-chain hydrocarbon (e.g., for use as commercial fuel).

I. Electroacetotogenic Cell

A. Microbial Community

[0043] An autotrophic microbial community from brewery wastewater was selected on a cathode of a bioelectrochemical system. Acetate was sustainably and reproducibly generated electrosynthetically using a cathode potential. In some embodiments, additional byproducts may also be produced by such a reactor, such as hydrogen. Carbon dioxide is a substrate in the acetate production step while being a byproduct of the hydrocarbon producing step. Using bioelectrochemical systems, sustained rates of acetogenesis based on cathode volume surpassed what has thus far been discovered for electrosynthesis of these compounds by use of a constant current and constant flow of nutrients into the system. More details of such systems can be found in International Application WO 2014/043690 and in LaBelle and May 2017, each of which is incorporated herein by reference.

[0044] Without being bound by theory, microbial communities are well known for the intricate interactions between microorganisms that frequently result in an efficient and productive process due to the natural selection of microorganisms that will operate in stable consortia. For example, when a potential of -590 mV was applied the result was a microbial community that would electrosynthesize acetate very efficiently. In some aspects, a microbial population may be one of those described in PCT Application WO 2014/043690 and Marshall *et al.* 2017 each incorporated herein by reference.

[0045] Previous studies using a biocathode indicate that at least one member of the community will interact directly with the electrode. An *Acetobacterium sp.* was the most prevalent and active Bacteria on the electrode when acetate was produced (see Marshall *et al.* 2017, incorporated herein by reference). Previous attempts to electrosynthesize acetate with *Acetobacterium woodii* failed (Nevin *et al.* 2011). The *Acetobacterium* sp. detected here was strongly associated with the electrode and often formed the dominate population within the community. Without being bound by theory, either this *Acetobacterium* sp. is quite different

from *A. woodii* or the microbial community on the electrode affords *Acetobacterium* with advantages unrecognized in the pure culture. All members of the microbial community could potentially be responsible for facilitating electrode oxidation.

[0046] In some embodiments, the other major active bacteria on the biocathode could include *Sulfurospirillum* and *Rhodobacteraceae*, consistent with the community in the original reactor generating acetate. However, it is unclear what role *Sulfurospirillum* and *Rhodobacteraceae* play despite their prevalence and continued presence in the biocathodes. In previous studies, the reactor systems were operated in both the light and the dark, with no observable effect on current or product formation. Without being bound by theory, one possibility for the role of these two bacteria could be to draw electrons directly from the electrode and produce hydrogen. In other embodiments, the biocathode could contain other bacteria including *Desulfovibrio*.

[0047] Electron micrographs indicated an increase of cells observed on the cathode over time. Increases in electrode-attached biofilm coverage is a common feature of anodes in microbial fuel cells (McLean *et al.* 2010; Ren *et al.* 2011), and cathode-associated biofilm development appears to also be possible during electrosynthesis in MESs.

B. Importance and Production of Acetate

[0048] Acetic acid is another valuable commodity chemical made from fossil fuels that is used in industrial processes to produce vinyl acetate for paints and adhesives (Cheung *et al.* 2005). Production for human consumption, *e.g.* food and cosmetics, requires a higher degree of purity, which is achieved by microbial fermentation of sugars to acetic acid (vinegar) (Drake *et al.* 2008; Parrondo *et al.* 2003). Acetate is also a key intermediate in the production of biofuels, as it has been shown to be a feedstock for a microbial community to produce ethanol in BESs using methyl viologen as an electron carrier (Steinbusch *et al.* 2010). Any biosynthetic pathway that involves reducing CO_2 to multicarbon compounds must first pass through acetyl-coA and acetate can be readily converted to acetyl-coA by microbes. Hence, electroacetate could be used as a precursor for fuel production or for the production of high purity foods and cosmetics. In addition, a synthetic biology approach could be coupled with electroacetogenesis to produce commodity chemicals including long chain hydrocarbons. A similar approach was taken by Li *et al.* with formic acid as a feedstock to make isobutanol (Li *et al.* 2012).

[0049] Electrosynthesis potentially offers a revolutionary way of producing the chemicals needed to sustain modern culture. The carbon source for the process, CO_2, is plentiful and inexpensive, the electrons may be supplied from sustainable non-carbon based sources, land mass requirements are negligible and will not compete with food crop production, and being strictly carbon neutral electrosynthesis presents an attractive way to combat climate change. Analogous to the field of microbial fuel cells where intensive research has led to a better understanding of the process and exponential gains in current generation (Logan BE 2009), here it has been demonstrated that the rates of production of multiple commodity chemicals by electrosynthesis can be further increased, thereby advancing the technology closer to becoming competitive with the fossil-carbon based industries.

[0050] Microbial electrosynthesis fixes carbon dioxide from electricity and microbial catalysts with a high Coulombic efficiency. The fixed carbon products can be used as a feedstock in lieu of sugar, surpassing the efficiency of photosynthesis.

[0051] As discussed in WO 2014/043690, which is incorporated herein by reference, the seven day yield test conducted after 121 days of electrosynthetic reactor operation, acetate production reached 17.25 mM d^{-1}; a rate that is 100× faster than any pure culture on unmodified graphite electrodes (Nevin *et al.* 2010). The use of naturally selected electrosynthetic microbiomes and the extended enrichment at −590 mV are partially responsible for the improvements in rates. All of these aforementioned attributes were evident in the reactors given that the biofilm coverage increased, dominant members of the active microbiome persisted, and the acetate production rates increased with prolonged incubation. Another explanation for the increased acetate rates was the higher CO_2 concentration available to the microbes during continuous sparging. Acetate formation is thermodynamically more favorable under increasing CO_2 concentrations (Bar-Even *et al.* 2012); thus, the constant sparging with 100% CO_2 could contribute to the higher rates observed in this long-term study. Without being bound by theory, the improvements in production rates could also be partially attributed to the higher Coulombic efficiency observed in the present study compared to the previously reported Coulombic efficiency in reactors. Long term stability of the system has also been studied and is reported previously.

[0052] Stability was confirmed by the phylogenetic analyses of the active members of the microbiomes. *Acetobacterium* remained the dominant microbiome on the graphite biocathodes. The sequence identity is closely matched to *Acetobacterium wieringae*, an

acetogenic bacterium that couples growth to CO_2 fixation via the Wood–Ljungdahl pathway (Braun *et al.* 1982; Drake *et al.* 2008). It seems likely that microorganisms from the *Acetobacterium* genus are primarily responsible for electroacetogenesis in the MESs, given their continued presence whenever acetate is produced by the biocathode (see LeBelle *et al.*, 2017).

[0053] The increase in cells observed on the cathodes corresponded with an increase in rates of acetate production driven by electrons from an electrode. The highest observed rates of electroacetogenesis in previous studies were 1 g L^{-1} d^{-1}, a rate that approaches the fastest acetogenic rates in bioreactors pressurized with H_2/CO_2 gas (Demler *et al.* 2011). The sustained rates of biocatalysis reported begin to address key issues with taking microbial electrosynthesis to an industrial scale. Also, LaBelle 2014 achieved 52 mM/day, which is 3.1 g/L/day (0.13 g/L/hr). In contrast the production rates using the methods provided herein were at least 18.8 g/L/day (0.78 g/L/hr).

C. Algae

[0054] In some embodiments, an algal culture, such as culture comprising *Botryococcus braunii* is used to convert acetate to a long chain hydrocarbon. It is also contemplated that other green microalga capable of using acetate as a feedstock and converting that carbon source into a hydrocarbon are also envision. Such microalga is capable of growing on acetate and producing liquid hydrocarbons (C21+) at up to 86% per cell dry weight (10g/L cell density, μ=0.1 h^{-1}) (Casadevall, 1985). This particular microalga will accept acetate as a feedstock (Marshall, 2012 and Marshall 2013). *Botryococcus* naturally secretes hydrocarbons outside the cell and stores hydrocarbons in the extracellular matrix where cells are connected to form colonies (Hirose, 2013). The secreted hydrocarbons are recovered through short contact with solvent. This process does not impair hydrocarbon yield of subsequent cultures, allowing continuous cultivation and milking of *B. braunii* for hydrocarbon production without major increase in cell biomass. In some embodiments, the methods may incorporate a mutant with an optimized acetate feeding rate, medium composition, and/or temperature. In some embodiments, these mutants will have a cell growth and hydrocarbon secretion rate is expected to reach up to 1.2 h^{-1}. Additionally, in some embodiments, the microalga can be grown in the dark, which can stimulate growth (Tanoi, 2011).

D. Hydrocarbons

An "alkane" or "hydrocarbon" refers to the compound H–R, wherein R is alkyl as this term is defined above. The term "alkyl" refers to a monovalent saturated aliphatic group with a carbon atom as the point of attachment, a linear or branched, cyclo, cyclic or acyclic structure, and no atoms other than carbon and hydrogen. Thus, as used herein cycloalkyl is a subset of alkyl, with the carbon atom that forms the point of attachment also being a member of one or more non-aromatic ring structures wherein the cycloalkyl group consists of no atoms other than carbon and hydrogen. As used herein, the term does not preclude the presence of one or more alkyl groups (carbon number limitation permitting) attached to the ring or ring system. The groups $-CH_3$ (Me), $-CH_2CH_3$ (Et), $-CH_2CH_2CH_3$ (*n*-Pr or propyl), $-CH(CH_3)_2$ (*i*-Pr, ^{i}Pr or isopropyl), $-CH(CH_2)_2$ (cyclopropyl), $-CH_2CH_2CH_2CH_3$ (*n*-Bu), $-CH(CH_3)CH_2CH_3$ (*sec*-butyl), $-CH_2CH(CH_3)_2$ (isobutyl), $-C(CH_3)_3$ (*tert*-butyl, *t*-butyl, *t*-Bu or ^{t}Bu), $-CH_2C(CH_3)_3$ (*neo*-pentyl), cyclobutyl, cyclopentyl, cyclohexyl, and cyclohexylmethyl are non-limiting examples of alkyl groups. Additionally, a "long chain hydrocarbon" is a subset of "hydrocarbon" wherein the aliphatic group is a linear chain. For this term, the following parenthetical subscripts further define the number of carbon atoms contained within that term as follows: "(Cn)" defines the exact number (n) of carbon atoms in the group/class. "(C≤n)" defines the maximum number (n) of carbon atoms that can be in the group/class, with the minimum number as small as possible for the group in question. For example, "alkyl$_{(C\leq 10)}$" designates those alkyl groups having from 1 to 10 carbon atoms. (Cn-n′) defines both the minimum (n) and maximum number (n′) of carbon atoms in the group. Similarly, "alkyl$_{(C2\text{-}10)}$" designates those alkyl groups having from 2 to 10 carbon atoms.

II. Examples

[0055] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1 – Materials and Methods

[0056] *Electrochemical Reactor.* The anode compartment consisted of a polypropylene spacer and a mixed metal oxide (IrO_2/Ta_2O_5) catalyzed titanium anode (MMO) (Magneto, NL). The anolyte was 80 mL of 50 mM sodium sulfate acidified with sulfuric acid to pH=2. The cathode was a 45 ppi reticulated vitreous carbon foam (KR Reynolds Company, CA), 0.6x6x8 cm. It was pretreated in 2 N nitric acid and rinsed thoroughly with MilliQ water. It was then attached to a 6x6 mesh, 0.35 in diameter 316L stainless steel mesh (6x8 cm) that was coated with a conductive carbon glue (Ted Pella Inc., CA) that was thinned with 1:1 acetone. Two applications were coated onto the mesh before the same glue was used to attach the RVC foam. Custom machined polypropylene spacers were used with customized Viton gaskets to sandwich a cation exchange membrane between the electrodes with a 316L stainless steel endplate and a poly(methyl methacrylate) cathode viewing plate held together by stainless steel nuts, bolts and washers. (FIG. 1)

[0057] The catholyte was 50 mL of a phosphate-based medium described in LaBelle 2014. It contained salts, vitamins and trace metals and minerals. 50 mM NaCl was used instead of sodium bromoethanesulfonate. No yeast extract, sulfide or cysteine was used. The medium was filter sterilized and flowed through the reactors at 250 mL/day using a peristaltic pump and Pharmed BPT tubing.

[0058] *Inoculum.* The cells (Electrobiome® Platform) used to inoculate the reactors were obtained from an electroacetogenic reactor (LaBelle 2014). They were concentrated using tangential flow filtration using a 0.2 μm polyether sulfone filter, spun at 5000 (RCF) for 10 minutes and re-suspended in fresh medium.

[0059] The reactor was operated in constant current at 8 $A/L_{catholyte}$ with current supplied from a VMP3 Potentiostat (Biologic) set in Galvanostatic mode and the voltage monitored by EC Lab software. 100% CO_2 was passed through the headspace at an initially set rate of 25 mL/min. Medium was flowed though the reactor at a rate of 250 mL/day using a peristaltic pump.

[0060] The gas flow rate was monitored with an Agilent gas flow meter when sampling headspace for gas chromatographic analysis. Fatty acids were analyzed via HPLC. pH was spot checked with a pH meter (Mettler Toledo). OD_{600nm} was measured using a Genesys UV/Vis spectrophotometer.

Example 2 – Results

[0061] *Biomass Growth.* The initial inoculum resulted in an optical density (OD_{600nm}) of 0.340 ± 0.010 (n=3) within the cathode chamber of three inoculated reactors (FIG. 2). The continuous flow of media through the reactors, and perhaps adsorption of biomass to the electrode surface, drove the OD_{600nm} down by more than an order of magnitude. However, shortly after that the OD_{600nm} began to steadily increase and eventually remained near or above 0.1 within the reactors, indicating a constant production of bacterial cells including those that remained planktonic and washed away with the effluent. Colonization of the unmodified cathode surface with yellow and off-white biomaterial became apparent within a week of inoculation and continued to grow through the end of the experiment (FIG. 3). The inoculum is dominated by *Acetobacterium* sp. (LaBelle 2014). The surface of the electrode and the interstitial space within the honeycomb structure became heavily populated as the experiment continued and colonization appeared to still be ongoing when the experiment was terminated. The biofilm formed and continued until it covered the cathode even though H_2 gas bubbles were vigorously generated. While the yellowish biomaterial increased with time with the inoculated reactors, the uninoculated control cathode never exhibited any visible changes. Microscopic examination of the material of the electrode surface and from within the interstitial space also revealed a dense biofilm full of bacterial cells with the morphology of *Acetobacterium*. Unmodified RVC has been reported to be a poor surface for bioelectrochemical systems (Flexer 2013), and it did not support the electrosynthesis of any acetate with another microbial community (Jourdin 2014). In contrast, the microbial community used under the conditions described here readily colonized unmodified RVC, and as demonstrated below, it readily generates acetate with this material serving as a cathode.

[0062] *Productivity.* The space time yield (STY) or volumetric rate of acetate production was monitored in three continuous flow/constant current bioelectrochemical reactors (FIG. 4). Within the first 4 days of operation, the STY rapidly increased to approximately >0.4 g/Lcatholyte/day. From this point forward the rate steadily increased and was accelerating at the end of the experiment (day 36) when the STY reached a maximum of 0.78 $g/L_{catholyte}$/hour, 0.74 ± 0.05 $g/L_{catholyte}$/hour in replicates (n=3). The acetate produced per electrode surface area was 8.2 $g/m^2_{projected}$/hour. Hydrogen was produced as a co-product at 0.2 $g/L_{catholyte}$/hour at the end of the experiment. No methane was detected and growth and production were sustained without the addition of methanogenic inhibitors, yeast extract, or chemical reducing agents.

[0063] After inoculation, the pH of the biotic reactors rose abruptly to 8.88 ± 0.53 due to the natural production of base at the cathode of the electrochemical cell. However, the continuous supply of CO_2 returned the pH to 6.75 ± 0.03 (medium was initially prepared at pH 7 under 100% N_2) within 24 hours. The pH decreased as the microbial production of acetic acid increased and the change in pH was more rapid at the end of the experiment. A single uninoculated reactor was maintained under the same conditions as the 3 inoculated reactors (FIG. 5). After an initial upward spike in pH during the first day, the pH stabilized at 6.67 ± 0.03 for the remainder of the experiment. After an initial upward spike in pH during the first day, the pH trended downwards, which appears to correspond increased product yield.

[0064] *Efficiency.* Following the initial start-up, the overall Coulombic efficiency (CE) or electron recovery ranged from approximately 75% to 85% with about 20% in acetate (FIG. 6). From then to the end of the experiment the overall CE ranged between 80% and 100% with most of the variability in the measurement of H_2 (the CE for the single uninoculated control reactor was 88%). The electron recovery in acetate steadily increased to 33.2% ± 2.3% (n=3) at day 36 with 35% in one reactor.

[0065] The trend in energy efficiency (FIG. 7) generally followed that of the Coulombic efficiency (FIG. 6), and both efficiencies paralleled the increase in the space time yield of acetate (FIG. 4). Following the initial increase in productivity during the first 4 days of incubation the energy efficiency fluctuated between 30% and 35% with approximately 7% invested in acetate. From then to the end of the experiment the overall energy efficiency ranged between 35 and 42% while the energetic efficiency in acetate steadily increased to 11.2% ± 0.8% (n=3) with a 12.1% maximum in one reactor at the end of the experiment. Both the CE and energy transferred to acetate appeared to still be increasing at the end of the experiment.

Example 3 – Proposed production of long-chain hydrocarbons from Green microalga using an acetate-fed system

[0066] Green microalga, *Botryococcus braunii*, can be used to convert electrosynthetic acetate into liquid hydrocarbons. This alga is capable of growing on acetate and producing liquid hydrocarbons ($C21^+$) at up to 86% per cell dry weight (10g/L cell density, μ=0.1 h-1). *Botryococcus* naturally secretes hydrocarbons outside the cell and stores hydrocarbons in the extracellular matrix where cells are connected to form colonies. The secreted hydrocarbons

can be recovered through short contact with solvent. This process does not impair hydrocarbon yield of subsequent cultures, allowing continuous cultivation and milking of *B. braunii* for hydrocarbon production without major increase in cell biomass. To further increase cell yield and hydrocarbon production, *B. braunii* mutants generated through chemical mutagenesis will be adapted and screened on the acetate-containing medium for mutants with improved phenotype. Selected mutants will be grown in bioreactors and optimized for acetate feeding rate, medium composition, and temperature. Cell growth and hydrocarbon secretion rate is expected to reach up to 1.2 h^{-1}. Cell density will be increased to 12 g/L with a hydrocarbon content of ca. 80-86% to reach or exceed the final titer of 10 gfuel/L (12 g/L biomass concentration*85% hydrocarbon content=10.2 gfuel/L). Up to 80% carbon yield (80%-86% hydrocarbon content* 95% carbon utilization efficiency=ca. 80% carbon yield) and 80% energy efficiency (20% heat loss) are anticipated. The goal is to reach 1 gfuel/gcdw/h productivity [(12 g/L biomass concentration*1.2 h-1*85% hydrocarbon content)/(12 gcdw/L)= 1.02 gfuel/gcdw/h]. An example system for hydrocarbon production is shown in FIG. 8.

Example 4 – Further Exemplary Production Systems of the Embodiments

A. Production of Hydrocarbon Fuels from CO_2 and Electricity, and Struvite from Electrobiome® Medium.

[0067] A phosphate buffered medium and carbon dioxide is continuously flowed through a bioelectrochemical cell under a constant current. The Electrobiome® or other acetogen(s) reside in the cathode compartment whereby the electrons and carbon dioxide are converted to acetate. The bacterial cells are separated from the effluent to produce a cell-free acetate stream. A stoichiometric amount of ammonium hydroxide matching the phosphate content is added to the acetate stream, the pH is raised to pH~ 8-9, and a stoichiometric amount of a magnesium salt matching the phosphate is added and struvite is precipitated out and separated as a value added product (a slow release fertilizer). The acetate stream is subjected to electrodialysis to generate concentrated acetic acid and a sodium hydroxide stream, the latter of which can be recycled into the struvite precipitation step. In other embodiments, a freeze concentration step can be performed before or after the electrodialysis step to achieve a desired strength of acetic acid. The acetic acid is fed by a pH auxostat system along with the anodic oxygen (and air) to heterotrophic or mixotrophic algae (*e.g. Chlamydomonas rheinhardtii, Chorella vulgaris, Crypthecodinium cohnii*), and after separation, the algae and bacterial biomass constantly made by the two bioreactors are subjected to hydrothermal liquefaction

(HTL) to generate a biocrude oil, which is further treated with hydrotreatment using the cathodic hydrogen to generate hydrocarbon fuels. See FIG. 11A.

B. Production of Hydrocarbon Fuels from CO_2 and Electricity.

[0068] In another embodiment, a bicarbonate buffer is used with the Electrobiome® in place of the phosphate. In this case struvite production is avoided and the sodium hydroxide produced during electrodialysis is used to scrub carbon dioxide from the bioelectrochemical cell, purifying the hydrogen and regenerating the sodium bicarbonate buffer. The scrubber could also remove carbon dioxide from the air, or from other process steps such as the heterotrophic algal production or the HTL step. See, FIG. 11B.

C. Production of Astaxathin and Hydrocarbon Fuels from CO_2 and Electricity, and Struvite from Electrobiome® Medium.

[0069] In still another embodiment the Electrobiome® is again operated with a phosphate buffer and acetate and struvite are produced as in example #1. However, in this case the acetic acid produced after electrodialysis is used to heterotrophically grow *Haematococcus pluvialis*, which is then exposed to stress by light, low nitrogen, or high concentrations of acetate from the Electrobiome® to induce the production of the highly valuable carotenoid, astaxanthin. The latter is then extracted in dimethyl ether and the residual algal biomass plus Electrobiome® biomass is subjected to HTL and hydrotreatment to produce liquid fuels. See, FIG. 11C.

D. Production of Astaxathin and Hydrocarbon Fuels from CO_2 and Electricity.

[0070] In yet another embodiment the phosphate medium is replaced with a carbonate buffer, similar as done in B above, and struvite production is avoided. Carbon dioxide is scrubbed while using sodium hydroxide produced during electrodialysis (as described in B). Acetate is used to heterotrophically grow *H. pluvialis* and produce astaxanthin and fuels as described for C above. See. FIG. 11D.

E. Production of Omega 3 Fatty Acids and Hydrocarbon Fuels from CO_2 and Electricity, and Struvite from Electrobiome® Medium.

[0071] In another embodiment the phosphate medium is once again used with the Electrobiome® so struvite is produced. In this case the acetic acid produced after

electrodialysis is used to heterotrophically grow *Crypthecodinium cohnii* to produce omega 3 fatty acids (the acetic acid may also be supplied to the omega 3 producing thraustochytrid *Schizochytrium*). Once again, the residual Electrobiome and algae biomass is used to produce liquid fuels. See, FIG. 11E.

F. Production of Omega 3 Fatty Acids and Hydrocarbon Fuels from CO_2 and Electricity.

[0072] In another embodiment the carbonate based medium is used with the Electrobiome® and struvite production is avoided. Otherwise, the steps are as described in example #5 and omega 3 fatty acids and liquid hydrocarbon fuels are produced. See, FIG. 11F.

G. Production of Hydrocarbons, Fatty Alcohols, and Esters from CO_2 and Electricity, and Struvite from Electrobiome® Medium.

[0073] In another embodiment the phosphate based medium is used with the Electrobiome® to again produce acetate to grow algae heterotrophically (similar to A). Struvite is produced. However, the algae are saponified to carboxylates, which are then converted into hydrocarbons, fatty alcohols, and esters by Kolbe electrolsysis or the Hofer-Moest reaction. In addition to these products, $NaHCO_3$ is generated. Once again, the residual Electrobiome® and algal biomass is converted to liquid fuels by HTL and hydrotreatment. See, FIG. 11G.

H. Production of Hydrocarbons, Fatty Alcohols, and Esters from CO_2 and Electricity.

[0074] In another embodiment the carbonate based medium is used with the Electrobiome® and the algae produced are saponified to carboxylates as described in G for Kolbe or Hofer-Moest conversion to hydrocarbons, fatty alcohols, and esters. Again, residual biomass is converted to liquid fuel by HTL. See, FIG. 11H.

* * *

[0075] All of the methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. More specifically, it will be apparent that certain

agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

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WHAT IS CLAIMED IS:

1. A method for bioelectric synthesis of H_2 and organic compounds comprising:

(a) culturing a microbial population in a media in a cathode chamber of an electrochemical cell; and

(b) maintaining the microbial population in the cathode chamber in the presence of:

(i) constant current of between 1.0 and 50 A per liter of cathode chamber volume;

(ii) CO_2 gas; and

(iii) a flow of media nutrients,

thereby producing organic compounds;

(c) collecting the produced organic compounds.

2. The method of claim 1, comprising maintaining the microbial population in the presence of between 1 and 20 A per liter of cathode chamber volume.

3. The method of claim 2, comprising maintaining the microbial population in the presence of between 3 and 15 A per liter of cathode chamber volume.

4. The method of claim 1, comprising maintaining the microbial population in the presence of a constant current for at least 10, 20, 30, 40, 50, 60, 120 or 180 days.

5. The method of claim 1, comprising maintaining the microbial population in the presence of a constant current for 60 to 180 days.

6. The method of claim 1, wherein the constant flow of media nutrients is filtered to maintain the cells of the microbial population in the cathode chamber.

7. The method of claim 1, wherein the electrochemical cell further comprises a probe for measuring pH.

8. The method of claim 1, wherein the media in the cathode chamber comprises a pH buffer system.

9. The method of claim 8, wherein the pH buffer system is a phosphate or carbonate buffer system.

10. The method of claim 1, further comprising maintaining the media in the cathode chamber at a pH of between 9.0 and 4.5.

11. The method of claim 10, further comprising maintaining the media in the cathode chamber at a pH of between 7.0 and 4.5.

12. The method of claim 1, wherein the flow of media nutrients is constant.

13. The method of claim 1, wherein the flow of media nutrients is intermittent.

14. The method of claim 1, wherein the CO_2 is provided by bicarbonate.

15. The method of claim 1, wherein the cathode chamber is flushed with CO_2 periodically.

16. The method of claim 15, wherein the cathode chamber is flushed with CO_2 on average every 3 to 10 days.

17. The method of claim 15, wherein the cathode chamber is supplied with a continuous in flow of CO_2.

18. The method according to claim 1, wherein the CO_2 is obtained from waste gas or captured from the anaerobic digestion of waste.

19. The method according to claim 1, wherein cathode chamber is maintained at a temperature of between 15 and 40 °C.

20. The method according to claim 19, wherein cathode chamber is maintained at a temperature of between 20 and 30 °C.

21. The method of claim 1, wherein the microbial population comprises at least about 50% acetogens.

22. The method of claim 1, wherein the microbial population comprises *Acetobacterium woodii, Acetobacterium weiringae, Sporomusa ovata, Clostridium ljugdahlii, Clostridium autoethanogenum, Clostridium carboxydivorans* or a mixture thereof.

23. The method of claim 1, wherein the microbial population comprises an essentially pure population of a single acetogen.

24. The method of claim 1, wherein the microbial population comprises an essentially pure population of *Acetobacterium woodii, Acetobacterium weiringae, Sporomusa ovata, Clostridium ljugdahlii, Clostridium autoethanogenum,* or *Clostridium carboxydivorans.*

25. The method of claim 1, wherein the microbial population comprises Bacteria from at least three families selected from the group consisting of Eubacteriaeae, Campylobacteraceae, Helicobacteraceae, Porphyromonadaceae, WCHB1-69, Spirochaetaceae, Deferribacteraceae, Rhodobacteraceae, Synergistaceae and Rhodocyclaceae.

26. The method of claim 1, wherein the microbial population comprises Bacteria from the Helicobacteraceae, WCHB1-69, Spirochaetaceae, or Synergistaceae families.

27. The method of claim 1, wherein the microbial population comprises bacteria from the genus *Acetobacterium, Sulfurospirillum, Wolinella, Paludibacter, Spirochaeta, Geovibrio, Desulfovibrio* or *Azovibrio.*

28. The method of claim 1, wherein the microbial population comprises bacteria from the genera *Acetobacterium*, *Sulfurospirillum* and, optionally, the family Rhodobacteraceae.

29. The method of claim 1, wherein the microbial population comprises *Acetobacterium woodii, Acetobacterium weiringae, Sporomusa ovata, Clostridium ljungdahlii* and/or *Clostridium autoethanogenum.*

30. The method of claim 1, wherein the microbial population comprises *Acetobacterium* sp., *Sulfurospirillum* sp., and *Desulfovibrio* sp.

31. The method of claim 1, wherein the microbial population comprises at least 85% *Acetobacterium* sp.

32. The method of claim 1, wherein the microbial population is essentially free of methanogenic organisms.

33. The method of claim 1, wherein the cathode comprises reticulated vitreous carbon (RVC), carbon paper, carbon cloth, carbon felt, carbon wool, carbon foam, graphite, porous graphite, graphite powder, graphene, carbon nanotubes, electrospun carbon fibers, carbon coated stainless steel mesh, a conductive polymer, platinum, palladium, titanium, gold, silver, nickel, copper, tin, iron, cobalt, tungsten, stainless steel, and combinations thereof.

34. The method of claim 33, wherein the cathode comprises RVC.

35. The method of claim 34, wherein the RCV is coated with carbon nanotubes.

36. The method of claim 1, wherein the cathode is a porous material.

37. The method of claim 36, wherein the cathode comprises 10 to 1000 pores per inch (ppi).

38. The method of claim 36, wherein the cathode comprises RVC having 10 to 1000 pores per inch (ppi).

39. The method of claim 38, wherein the cathode comprises RVC having 10 to 100 pores per inch (ppi).

40. The method of claim 38, wherein the cathode comprises RVC having 10 to 200 pores per inch (ppi).

41. The method of claim 1, wherein the electrochemical cell comprises an anode composed of carbon paper, carbon cloth, carbon felt, carbon wool, carbon foam, graphite, porous graphite, graphite powder, graphene, carbon nanotubes, electrically conductive woven fabric, electrospun carbon fibers, a conductive polymer, platinum, palladium, titanium, gold, silver, nickel, copper, tin, iron, cobalt, cobalt phosphate, tungsten, stainless steel, coated titanium, a mixed metal oxide or a combination thereof.

42. The method of claim 41, wherein the anode comprises a mixed metal oxide.

43. The method of claim 41, wherein the anode is a coated titanium anode.

44. The method of claim 43, wherein the anode is coated with a metal oxide.

45. The method of claim 43, wherein the anode is coated with IrO_2 and/or Ta_2O_5.

46. The method of claim 1, wherein waste productions and/or organic compounds are periodically removed from the media.

47. The method of claim 46, wherein waste productions and/or organic compounds are continuously removed from the media.

48. The method of claim 1, wherein organic compounds are purified by freeze concentration or electrodialysis.

49. The method of claim 1, wherein the organic compounds comprise acetate, butyrate, isobutyrate, propionate, 3-hydroxypropionate, 3-hydroxybutyrate, formate or an alcohol.

50. The method of claim 49, wherein the organic compounds comprise ethanol.

51. The method of claim 49, wherein the organic compounds comprise acetate.

52. The method of claim 1, further comprising separating struvite from the media.

53. The method of claim 1, wherein the cathode chamber is essentially free of methyl reductase inhibitor.

54. The method of claim 1, wherein the cathode chamber is essentially free of 2-bromoethanesulfonic acid (BESA) or 2-chloroethanesulfonic acid (CESA).

55. A system configured to provide bioelectric synthesis of organic compounds in accordance with any one of claims 1-54.

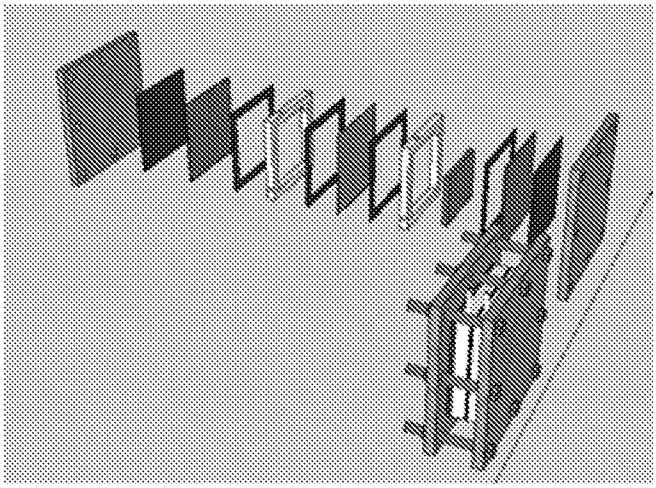

FIG. 1A

FIG. 1B

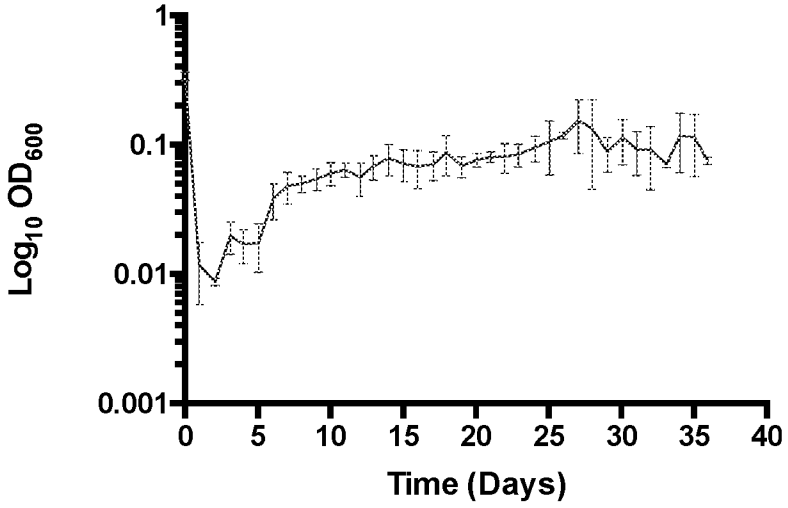

FIG. 2

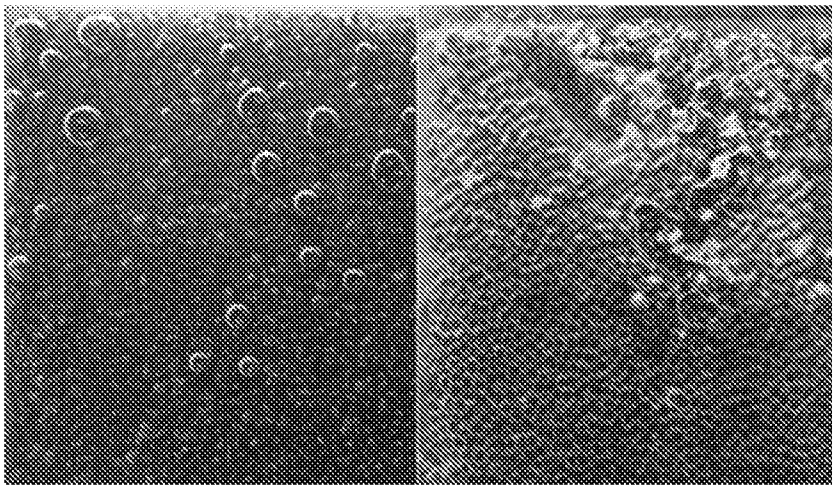

FIG. 3

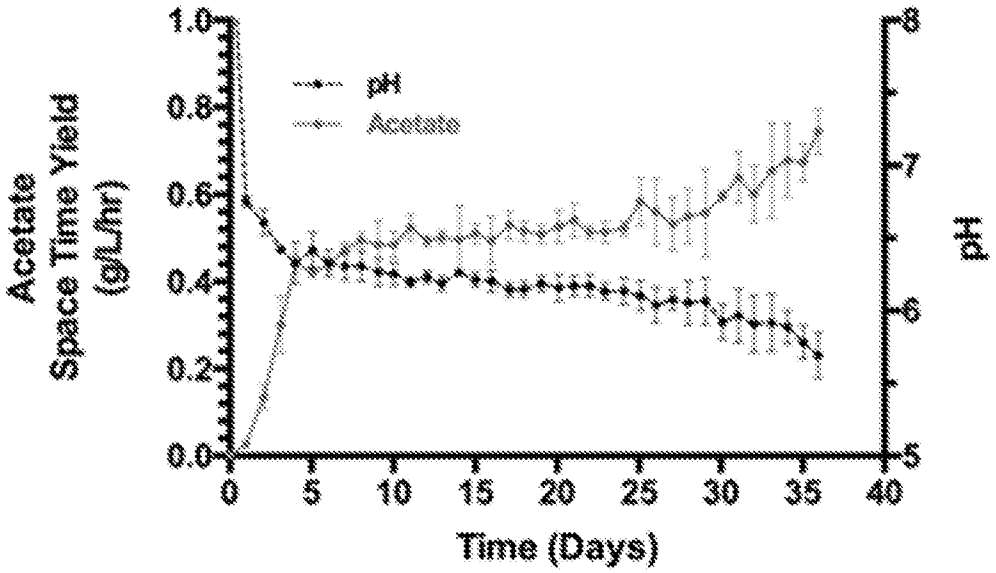
Acetate
Space Time Yield
(g/L/hr)
1.0
0.8
0.6
0.4
0.2
0.0
pH
Acetate
8
7
6
5
pH
0
5
10
15
20
25
30
35
40
Time (Days)

FIG. 4

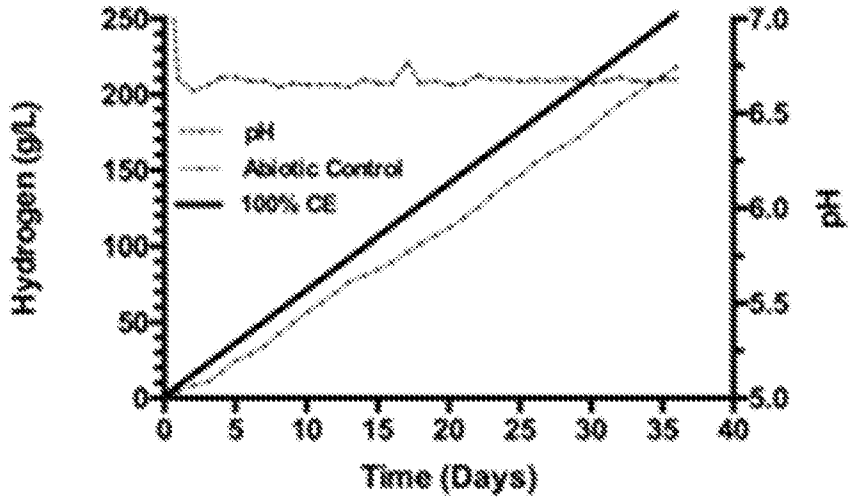
Hydrogen (g/L)
250
200
150
100
50
0
pH
Abiotic Control
100% CE
7.0
6.5
6.0
5.5
5.0
pH
0
5
10
15
20
25
30
35
40
Time (Days)

FIG. 5

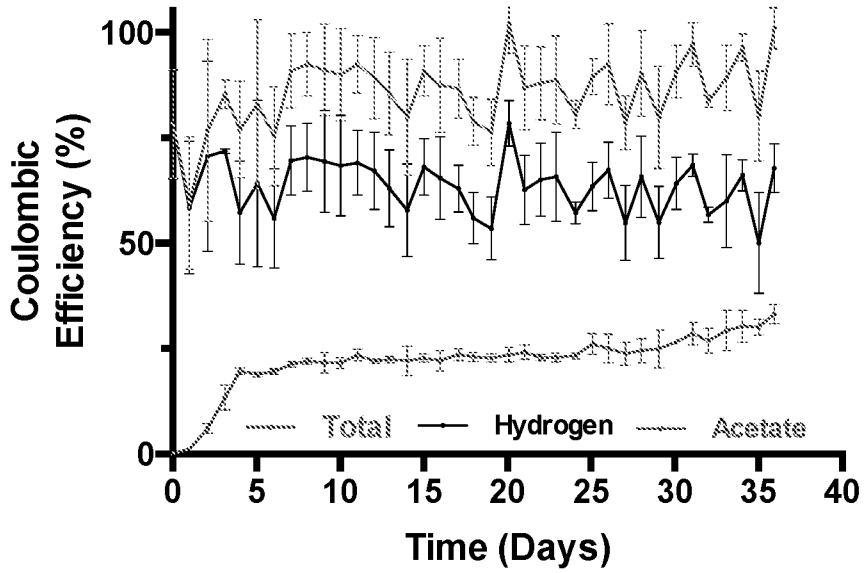
Coulombic Efficiency (%)
100
50
0
Total
Hydrogen
Acetate
0
5
10
15
20
25
30
35
40
Time (Days)

FIG. 6

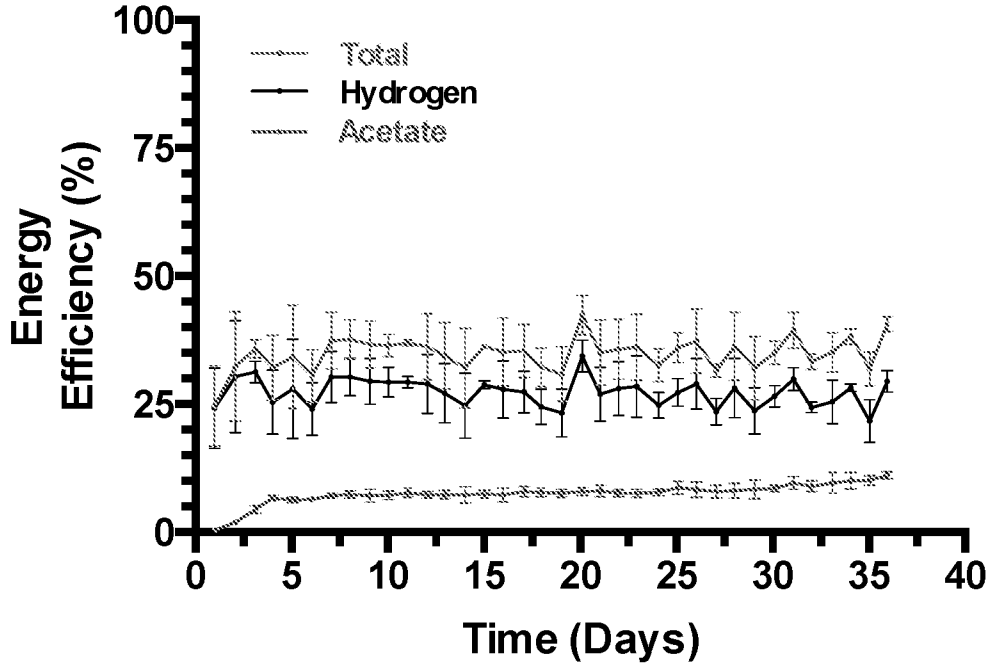
Total
Hydrogen
Acetate
Energy Efficiency (%)
100
75
50
25
0
0
5
10
15
20
25
30
35
40
Time (Days)

FIG. 7

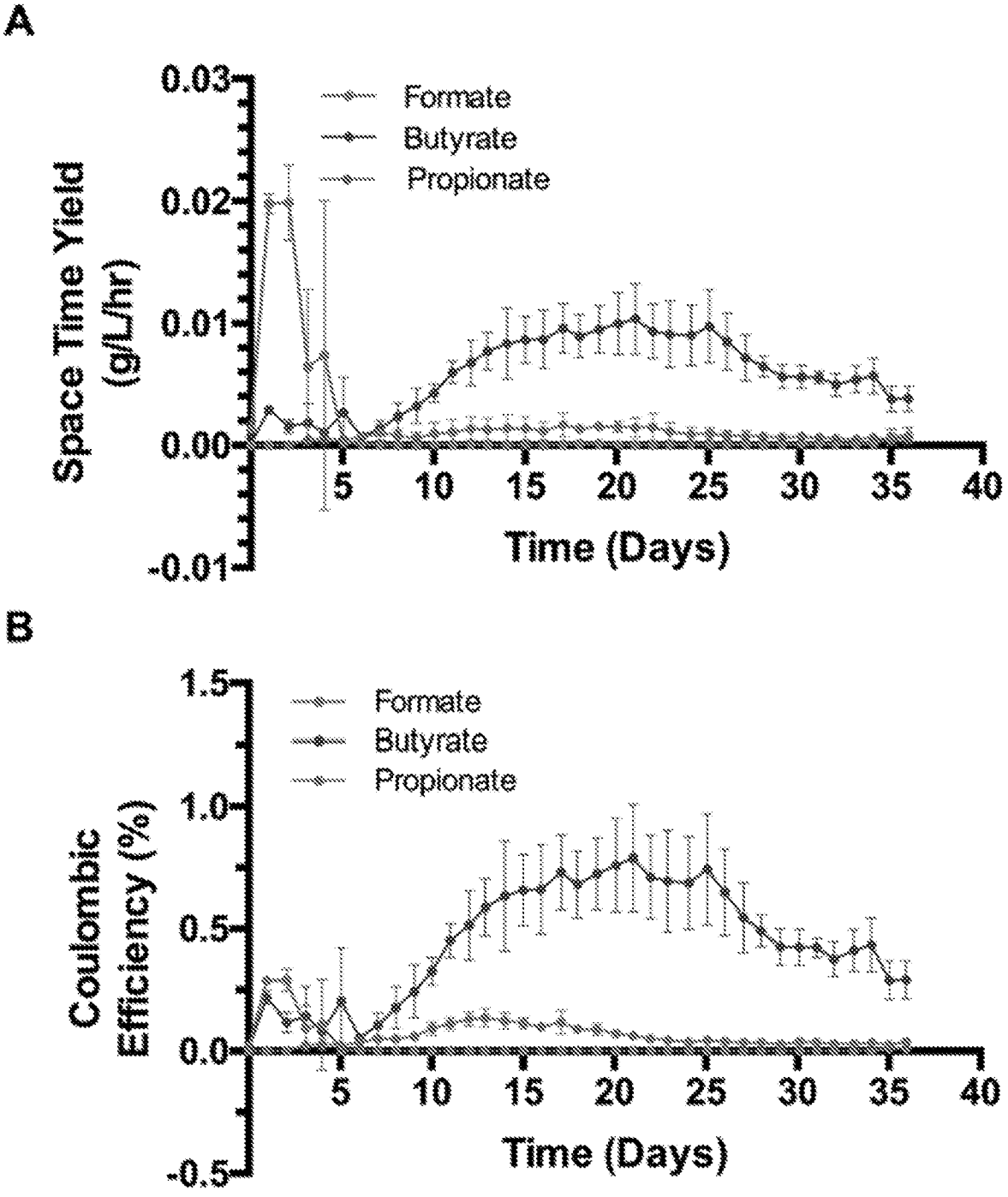
A
Space Time Yield (g/L/hr)
0.03
0.02
0.01
0.00
-0.01
Formate
Butyrate
Propionate
5
10
15
20
25
30
35
40
Time (Days)
B
Coulombic Efficiency (%)
1.5
1.0
0.5
0.0
-0.5
Formate
Butyrate
Propionate
5
10
15
20
25
30
35
40
Time (Days)

FIG. 8

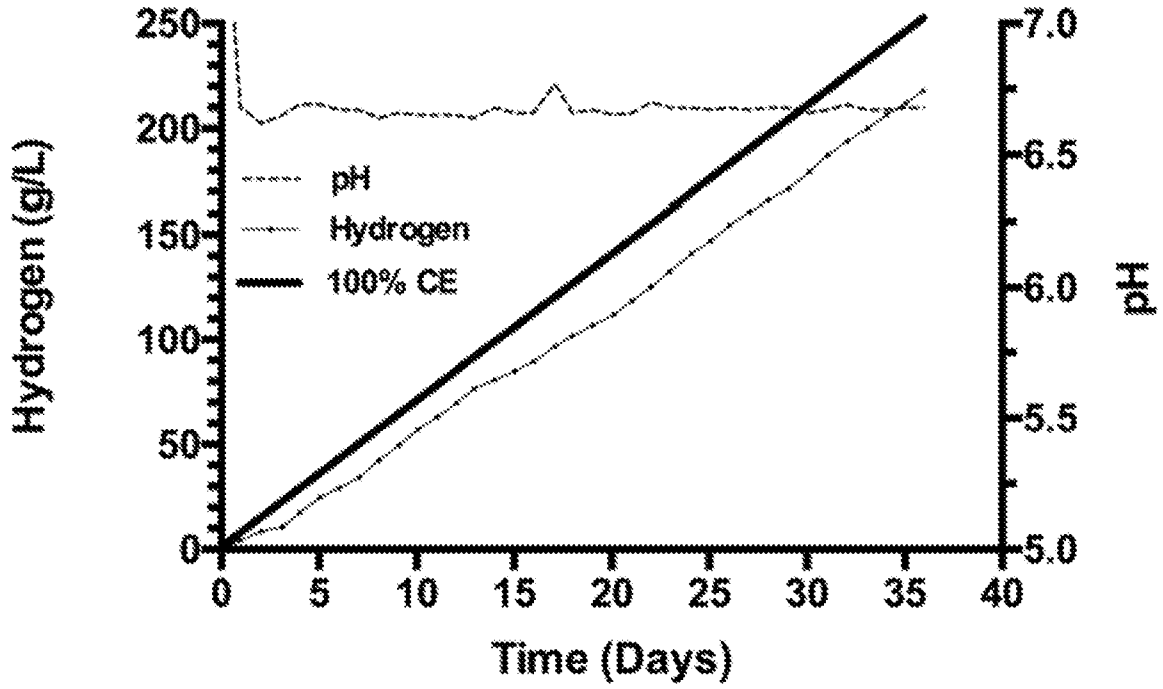
Hydrogen (g/L)
250
200
150
100
50
0
pH
Hydrogen
100% CE
7.0
6.5
6.0
5.5
5.0
pH
0
5
10
15
20
25
30
35
40
Time (Days)

FIG. 9

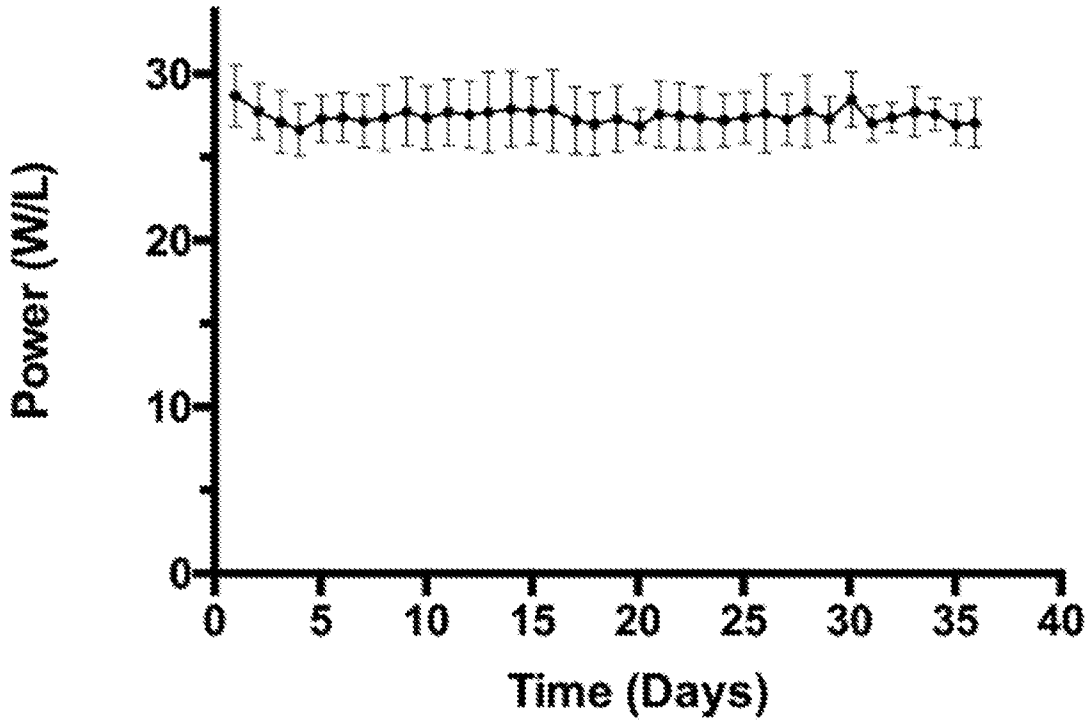

FIG. 10

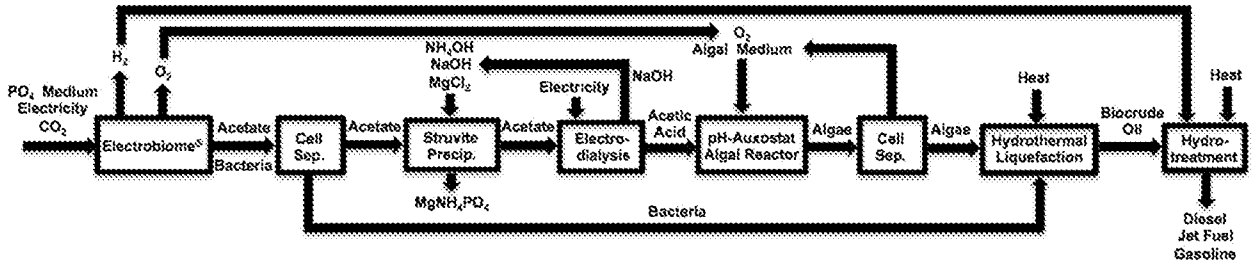

FIG. 11A

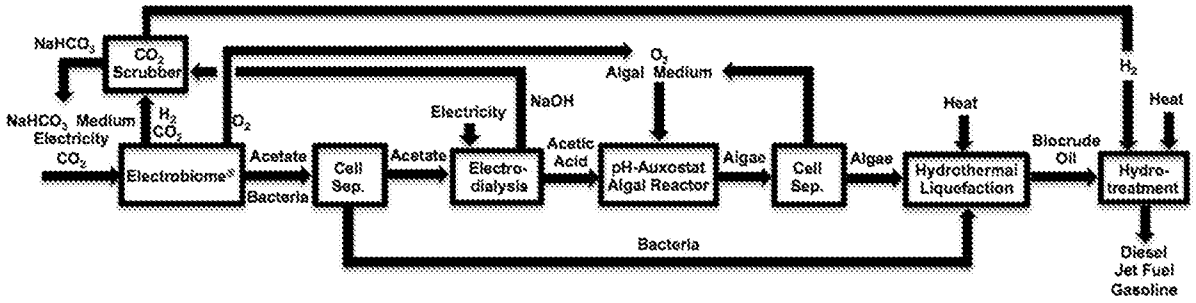

FIG. 11B

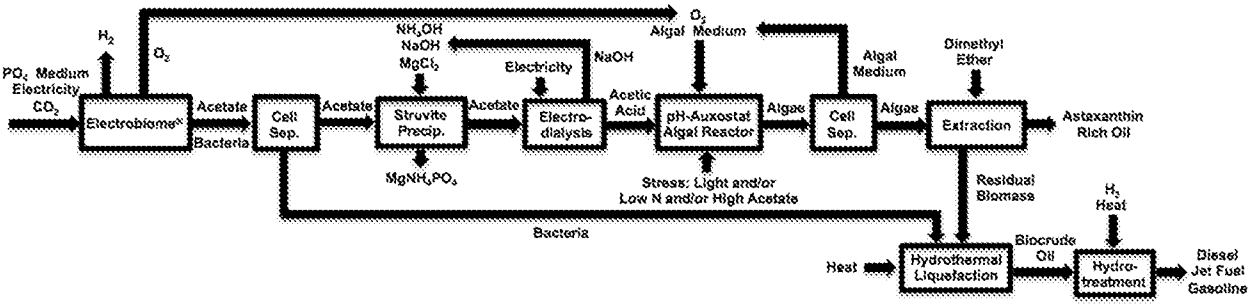

FIG. 11C

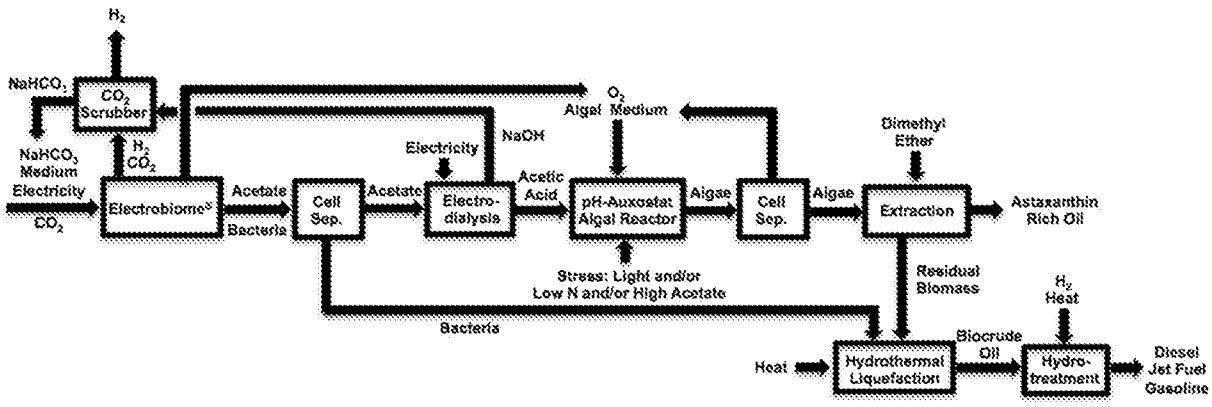

FIG. 11D

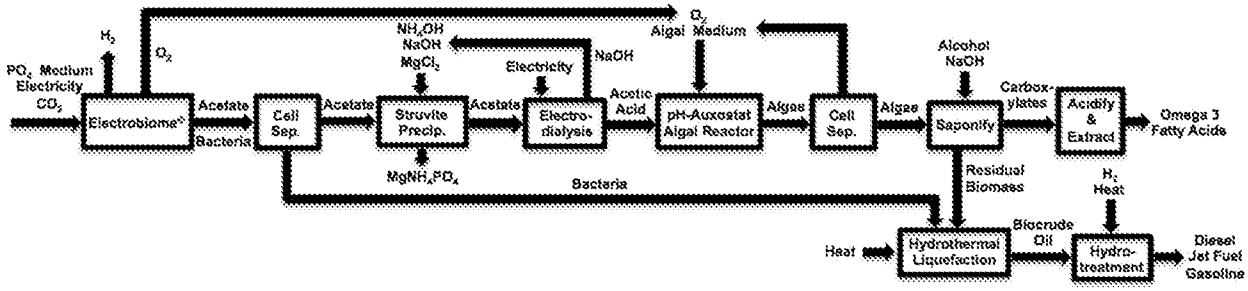

FIG. 11E

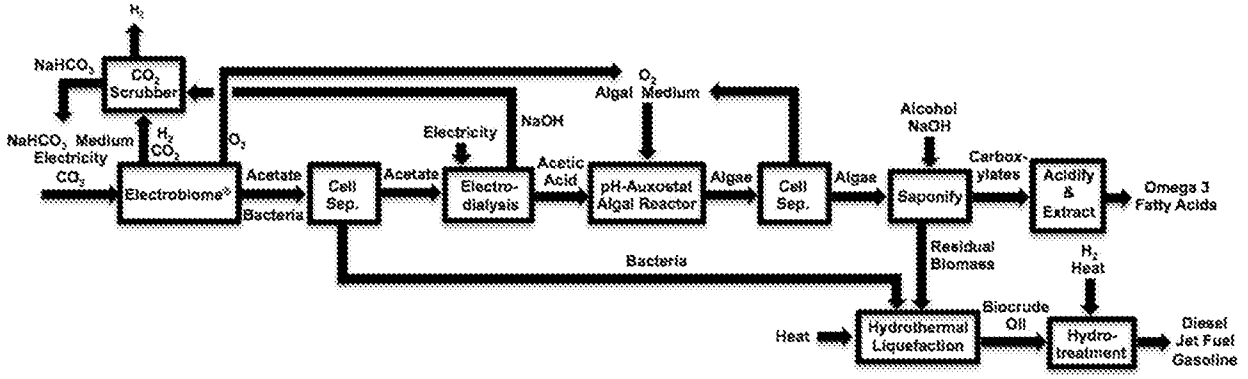

FIG. 11F

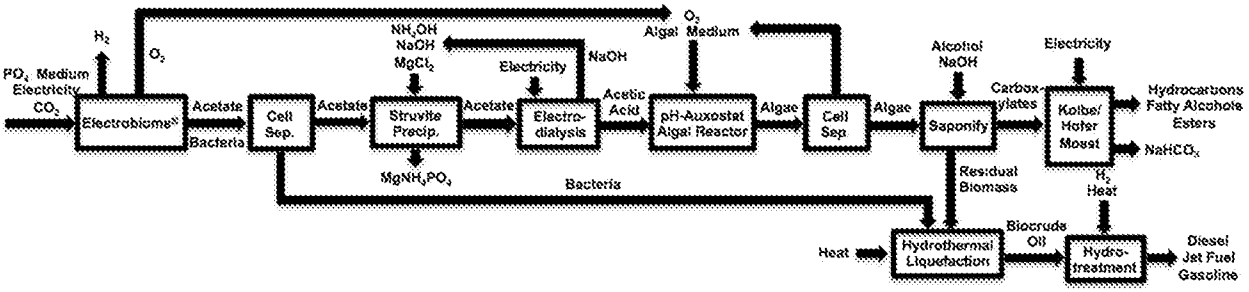

FIG. 11G

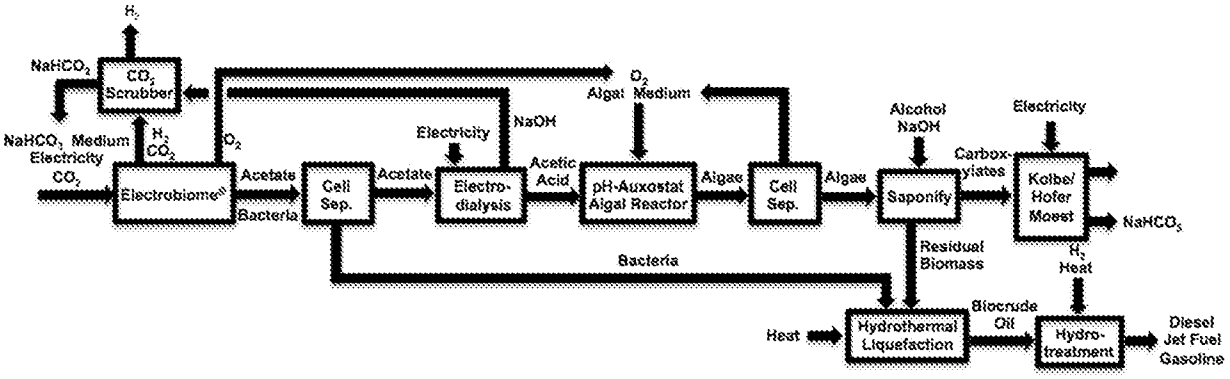
H_2
$NaHCO_3$
CO_2 Scrubber
O_2
Algal Medium
Alcohol NaOH
Electricity
$NaHCO_3$ Medium Electricity
H_2 CO_2
O_2
Electricity
NaOH
CO_2
Electrobiome
Acetate
Bacteria
Cell Sep.
Acetate
Electro-dialysis
Acetic Acid
pH-Auxostat Algal Reactor
Algae
Cell Sep.
Algae
Saponify
Carboxylates
Kolbe/ Hofer Moest
$NaHCO_3$
Residual Biomass
H_2 Heat
Bacteria
Heat
Hydrothermal Liquefaction
Biocrude Oil
Hydro-treatment
Diesel Jet Fuel Gasoline

FIG. 11H