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(54) **ELECTROCHEMICAL PROCESS FOR CO₂ REDUCTION TO FUEL AND SIMULTANEOUS OXYGEN GENERATION**

(57) Disclosed is an electrochemical process to simultaneously produce a syngas suitable for the Fischer-Tropsch (F-T) process and oxygen. In an example embodiment, the process includes feeding steam and CO₂ to an intermediate temperature (e.g., <700 °C) electrochemical reactor (108) to produce separate CO-rich and

O₂-rich streams. An additional electrochemical reactor (106) can be used to produce H₂. The H₂ is combined with CO from the first reactor to produce a syngas mixture ideal for a downstream F-T process. Alternatively, the electrochemical reactor can produce methane directly or a methanol stream for conversion to a hydrocarbon fuel.

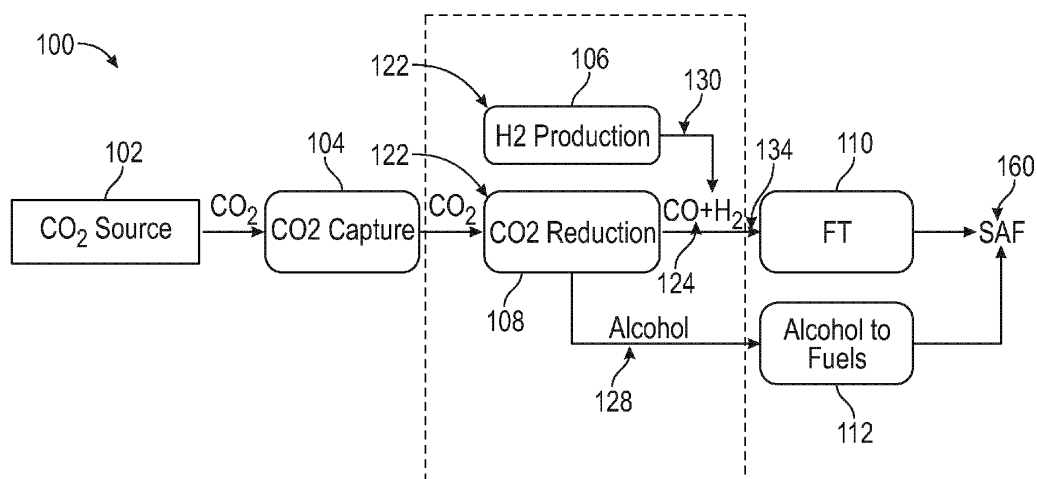


FIG. 1

Description

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Application No. 63/500,409 filed May 5, 2023.

BACKGROUND

[0002] Sustainable aviation fuel (SAF) is a green substitute for fossil fuel-based jet fuel. Syngas ($\text{CO} + \text{H}_2$) or alcohols (e.g., methanol or ethanol) are desirable intermediates for conversion into hydrocarbons through commercial processes such as Fischer-Tropsch. In general, jet fuel from corn-based alcohol has high greenhouse gas emissions equivalent to fossil-fuel derived jet fuel. Currently, there is no established, sustainable process to produce SAF from green syngas or alcohols with minimal greenhouse impact.

BRIEF DESCRIPTION

[0003] Disclosed is an electrochemical process to simultaneously produce a syngas suitable for the Fischer-Tropsch (F-T) process, and to also produce oxygen. In one embodiment, the process includes feeding steam and CO_2 to an intermediate temperature (e.g., $<700^\circ\text{C}$) electrochemical reactor to produce separate CO-rich and O_2 -rich streams. An additional electrochemical reactor can be used to produce H_2 . The H_2 is combined with CO from the first reactor to produce a syngas mixture ideal for a downstream F-T process. In one embodiment, the system operates by conducting protons to an H_2 electrode side of a reactor to react with CO_2 .

[0004] Embodiments can be used to simultaneously produce CH_4 and O_2 from CO_2 and steam in a single, integrated reactor. The electrochemical reactors can use renewable electricity and CO_2 captured from a power plant exhaust, industrial manufacturing point sources, commercial buildings, or directly from the air. The power plant can comprise, for example, a turbine.

[0005] The present disclosure provides for an electrochemical system including a first electrochemical reactor configured to accept a feed comprising steam and CO_2 and to produce a CO-rich stream, a methane or methanol-rich stream and a first O_2 -rich stream; a second electrochemical reactor configured to produce a second O_2 -rich stream and a H_2 stream; and a Fischer-Tropsch process configured to accept a feed comprising the CO-rich stream from the first electrochemical reactor mixed with the H_2 stream from the second electrochemical reactor and to produce a liquid hydrocarbon fuel stream.

[0006] Also disclosed is a method for operating electrochemical reactors. The method includes: feeding a stream comprising steam and CO_2 to a first electrochemical reactor to produce a CO-rich stream, a methane or methanol stream and a first O_2 -rich stream; operating a second electrochemical reactor to produce a second O_2 -

rich stream and a H_2 stream; and feeding the CO-rich stream from the first electrochemical reactor mixed with the H_2 stream from the second electrochemical reactor to a Fischer-Tropsch reactor to produce a liquid hydrocarbon fuel stream.

[0007] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the liquid hydrocarbon fuel stream comprises sustainable aviation fuel.

[0008] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the CO_2 in the feed comprises CO_2 captured from power plant exhaust.

[0009] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the CO_2 in the feed comprises CO_2 captured directly from air.

[0010] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the first electrochemical reactor is an intermediate temperature electrochemical reactor configured to operate at $<700^\circ\text{C}$.

[0011] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the CO_2 that is fed to the first electrochemical reactor first passes through a CO_2 capture assembly.

[0012] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the CO-rich stream and the first O_2 -rich stream produced are separated from each another.

[0013] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the methanol or methanol-rich stream is configured to be utilized in a conversion process to produce fuel.

[0014] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the second electrochemical reactor is a solid oxide fuel electrolyzer.

[0015] In addition to one or more of the features described above, or as an alternative to any of the foregoing embodiments, the first electrochemical reactor includes a catalyst, the catalyst comprising at least one of Cr, Mn, Fe, Co, Ni, Ru or alloys thereof.

[0016] The above described and other features are exemplified by the following figures and detailed description.

[0017] Any combination or permutation of embodiments is envisioned. Additional features, functions and applications of the disclosed assemblies, systems and methods of the present disclosure will be apparent from the description which follows, particularly when read in conjunction with the appended figures. All references listed in this disclosure are hereby incorporated by reference in their entireties.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The following descriptions should not be considered limiting in any way. With reference to the accompanying drawings, like elements are numbered alike.

[0019] Features and aspects of embodiments are described below with reference to the accompanying drawings, in which elements are not necessarily depicted to scale.

[0020] Example embodiments of the present disclosure are further described with reference to the appended figures. It is to be noted that the various features, steps, and combinations of features/steps described below and illustrated in the figures can be arranged and organized differently to result in embodiments which are still within the scope of the present disclosure. To assist those of ordinary skill in the art in making and using the disclosed assemblies, systems and methods, reference is made to the appended figures, wherein:

FIG. 1 is a high-level block diagram showing a process to convert CO₂ to produce a sustainable aviation fuel (SAF) from CO₂;

FIG. 2 shows a more detailed depiction of the hydrogen production block of FIG. 1; and

FIG. 3 shows a more detailed depiction of the CO₂ reduction block of FIG. 1.

DETAILED DESCRIPTION

[0021] A detailed description of one or more embodiments of the disclosed apparatus and method are presented herein by way of exemplification and not limitation with reference to the Figures.

[0022] The example embodiments disclosed herein are illustrative of electrochemical systems, and assemblies of the present disclosure and methods/techniques thereof. It should be understood, however, that the disclosed embodiments are merely examples of the present disclosure, which may be embodied in various forms. Therefore, details disclosed herein with reference to example electrochemical systems and associated processes/techniques of fabrication/assembly and use are not to be interpreted as limiting, but merely as the basis for teaching one skilled in the art how to make and use the systems/assemblies and/or alternative systems/assemblies of the present disclosure.

[0023] In general and as shown in FIGS. 1-3, the present disclosure provides for an electrochemical system 100 to simultaneously produce: (i) a syngas mixture 134 (e.g., CO-rich stream 124 plus H₂ stream 130) suitable for the Fischer-Tropsch (F-T) process 110, and to also produce oxygen streams 126, 132, as discussed further below. As more fully explained below, the system operates by conducting protons to an H₂ electrode side of a reactor to react with CO₂.

[0024] FIG. 1 shows an example of an electrochemical system 100 according to one embodiment to create sustainable aviation fuel (SAF) 160 (e.g., liquid hydrocarbon fuel 160) from CO₂. In general, the system 100 receives CO₂ from a CO₂ source 102. The CO₂ source 102 can be a power plant 102, for example, but that is not required and any suitable source 102 can be utilized. For instance, the CO₂ source 102 can be air in one embodiment.

[0025] The CO₂ from source 102 can be provided to a CO₂ capture assembly 104. For example, the CO₂ capture assembly 104 can be an adsorbent CO₂ capture assembly 104. In other embodiments, the CO₂ capture assembly 104 can be a liquid solvent absorption assembly. Such an assembly 104 may include, for example, amines. The CO₂ capture assembly 104 can be a solid absorption assembly that includes solid adsorbents in one embodiment.

[0026] In example embodiments and as shown in FIGS. 1 and 3, the system 100 can include feeding steam and/or water 122 and also CO₂ from the source 102 or the CO₂ capture system 104 (or both) to a first electrochemical reactor 108 (e.g., an intermediate temperature (<700 °C) electrochemical reactor 108) to produce a CO-rich stream 124 and to also produce a first O₂-rich stream 126, with the CO-rich stream 124 and the first O₂-rich stream 126 being separate from another (FIG. 3).

[0027] As shown in FIG. 3, it is noted that first electrochemical reactor 108 can also be used to simultaneously produce a CH₄ or methanol stream 128 and the O₂ stream 126 from the CO₂ feed 102, 104 and the steam/water feed 122, in a single, integrated reactor 108.

[0028] An additional and second electrochemical reactor 106 (FIGS. 1 and 2) can be used to produce a H₂ stream 130 and also to produce a second O₂-rich stream 132. The H₂ stream 130 from the second reactor 106 can be combined with the CO-rich stream 124 from the first reactor 108 to produce a syngas mixture 134 that can be ideal for a downstream Fischer-Tropsch (F-T) process 110 or the like to subsequently produce the fuel 160. Additionally, the CH₄ or methanol stream 128 can be utilized in a conversion process 112 to produce fuel 160.

[0029] The respective outputs 124, 130 from reactors 106, 108 can be mixed together as noted above, and such mixture 134 can be a syngas mixture 134 that can be provided to a Fischer-Tropsch synthesis process 110 where it is converted into an SAF 160.

[0030] Another output 128 from reactor 108 (e.g., methanol or CH₄+H₂O 108) can be converted to a fuel 160 by a conversion process 112. Such a conversion process 112 can be, for example, a so called methanol to jet process 112, or an alcohol to jet process 112. It shall be understood that while the process above is related to methanol, in cases where output is methane, it can be converted as well but the process in block 112 may be different.

[0031] The overall system 100 includes, in particular, a CO₂ reduction reactor 108 and a hydrogen production reactor 106.

[0032] An example of the hydrogen production reactor 106 is shown in FIG. 2. The example shown in FIG. 2 is a solid oxide fuel electrolyzer (SOEC) 106. The illustrated electrolyzer 106 splits water 122 (optionally in the form of steam 122) into substantially pure H₂ stream 130 and O₂ stream 132. Example components of a SOEC are illustrated in FIG. 2 as are example reactions. The anode of the electrolyzer 106 can include Ni+BYZ in one embodiment.

[0033] An example of the CO₂ reduction reactor 108 is shown in FIG. 3. The example reactor 108 shown in FIG. 3 is configured to provide for the co-electrolysis of steam/water 122 and CO₂ 102, 104. Example components of the reactor 108 are illustrated in FIG. 3 as are example reactions. The H₂ output 130 from the electrolyzer 106 is combined with the CO output 124 provided by the CO₂ reduction reactor 108 to form the syngas mixture 134 as discussed above. The anode of the reactor 108 can include Ni+M+ BYZ in one embodiment.

[0034] With reactor 108, it is noted that depending on the electrocatalyst at the H₂ electrode of reactor 108, the CO₂ 102/104 can be converted to various chemicals such as CO (124), and/or methanol/methane (128). The water 122 is electrolyzed to O₂ (126) and protons, with protons conducted to the H₂ electrode side of reactor 108 to react with CO₂ (102/104).

[0035] With reactor 108 and using a proton-conducting electrolyte, the proton-conducting electrolyte transfers protons from the steam 122 electrode to the hydrogen electrode of reactor 108, and enables lower temperature operation (e.g., <700 °C) than traditional oxygen-conducting electrolytes. This can be beneficial to some of the potential reactions at the hydrogen electrode side for CO₂ conversion to different fuels. In regards to electrochemical catalysts for CO₂ conversion for reactor 108, the catalysts should have excellent structural stability under highly reducing environments and should resist coke formation. Low-cost transition metal catalysts, Cr, Mn, Fe, Co, & Ni, or precious metals such as Ru (and alloys of any of the above) can be preferentially considered. To enable high metal dispersion for high performance, atomic layer deposition (ALD) can be used to provide precise control of the fabrication of catalysts. The electrochemical catalyst can be preferred over the conventional approach of using a separate catalyst to perform reaction to produce CO, methanol or CH₄, for example, via a Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) in a separate, thermochemical reactor.

[0036] Stated another way and referring back to FIG. 1, the CO 124 from the CO₂ reduction reactor 108 is combined with the H₂ 130 from the hydrogen production reactor 106 to form syngas 134 that is provided to the Fischer-Tropsch synthesis process 110 and converted to SAF 160.

[0037] The methane or methanol 128 from the CO₂ reduction reactor 108 can be provided to the conversion process 112 to produce fuel 160 as well.

[0038] It will be realized that while the precursors to

the SAF 160 are being produced (e.g., syngas 134 and methane or methanol 128), it is also noted that O₂ 126 and/or 132 is also being produced by system 100. Thus, the system 100 shown herein can be used to produce CH₄ stream 128 and O₂ stream 126 from CO₂ 102, 104 and H₂O/steam 122, which may be useful in space life support and propulsion applications or the like.

[0039] It is noted that the electrochemical reactors 106, 108 can use renewable electricity, and CO₂ 102, 104 captured and/or sourced from a variety of sources (e.g., from power plant exhaust, industrial manufacturing point sources, heating furnaces exhausts in commercial and high-rise residential buildings, or directly from the air, etc.). The example power plant can comprise, for example, a turbine.

[0040] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

[0041] The term "about" is intended to include the degree of error associated with measurement of the particular quantity based upon the equipment available at the time of filing the application.

[0042] The ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of "up to 25 wt.%, or, more specifically, 5 wt.% to 20 wt.%" is inclusive of the endpoints and all intermediate values of the ranges of "5 wt.% to 25 wt.%" etc.). "Combinations" is inclusive of blends, mixtures, alloys, reaction products, and the like. The terms "first," "second," and the like, do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. "Or" means "and/or" unless clearly stated otherwise. Reference throughout the specification to "some embodiments", "an embodiment", and so forth, means that a particular element described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. A "combination thereof is open and includes any combination comprising at least one of the listed components or properties optionally together with a like or equivalent component or property not listed.

[0043] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the present disclosure. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or

components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, element components, and/or groups thereof.

[0044] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this application belongs. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0045] While the present disclosure has been described with reference to an exemplary embodiment or embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the present disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the present disclosure without departing from the essential scope thereof. Therefore, it is intended that the present disclosure not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this present disclosure, but that the present disclosure will include all embodiments falling within the scope of the claims.

[0046] Although the assemblies, systems and methods of the present disclosure have been described with reference to example embodiments thereof, the present disclosure is not limited to such example embodiments and/or implementations. Rather, the assemblies, systems and methods of the present disclosure are susceptible to many implementations and applications, as will be readily apparent to persons skilled in the art from the disclosure hereof. The present disclosure expressly encompasses such modifications, enhancements and/or variations of the disclosed embodiments. Since many changes could be made in the above construction and many widely different embodiments of this disclosure could be made without departing from the scope thereof, it is intended that all matter contained in the drawings and specification shall be interpreted as illustrative and not in a limiting sense. Additional modifications, changes, and substitutions are intended in the foregoing disclosure. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the disclosure.

Claims

1. An electrochemical system (100) comprising:

a first electrochemical reactor (108) configured to accept a feed comprising steam and CO₂ and to produce a CO-rich stream, a methane or methanol-rich stream and a first O₂-rich stream;

a second electrochemical reactor (106) configured to produce a second O₂-rich stream and a H₂ stream; and
a Fischer-Tropsch process configured to accept a feed comprising the CO-rich stream from the first electrochemical reactor (108) mixed with the H₂ stream from the second electrochemical reactor (106) and to produce a liquid hydrocarbon fuel stream.

2. The system of claim 1, wherein the liquid hydrocarbon fuel stream comprises sustainable aviation fuel.

3. The system of claim 1 or 2, wherein the CO₂ in the feed comprises CO₂ captured from power plant exhaust; and/or wherein the CO₂ in the feed comprises CO₂ captured directly from air.

4. The system of any preceding claim, wherein the first electrochemical reactor (108) is an intermediate temperature electrochemical reactor configured to operate at <700 °C.

5. The system of any preceding claim, wherein the CO₂ that is fed to the first electrochemical reactor (108) first passes through a CO₂ capture assembly; and/or wherein the CO-rich stream and the first O₂-rich stream produced are separated from each another.

6. The system of any preceding claim, wherein the methanol or methanol-rich stream is configured to be utilized in a conversion process to produce fuel.

7. The system of any preceding claim, wherein the second electrochemical reactor (106) is a solid oxide fuel electrolyzer.

8. The system of any preceding claim, wherein the first electrochemical reactor (108) includes a catalyst, the catalyst comprising at least one of Cr, Mn, Fe, Co, Ni, Ru or alloys thereof.

9. A method for operating electrochemical reactors comprising:

feeding a stream comprising steam and CO₂ to a first electrochemical reactor (108) to produce a CO-rich stream, a methane or methanol stream and a first O₂-rich stream;
operating a second electrochemical reactor (106) to produce a second O₂-rich stream and a H₂ stream; and
feeding the CO-rich stream from the first electrochemical reactor (108) mixed with the H₂ stream from the second electrochemical reactor (106) to a Fischer-Tropsch reactor to produce a liquid hydrocarbon fuel stream.

10. The method of claim 9, wherein the liquid hydrocarbon fuel stream comprises sustainable aviation fuel.
11. The method of claim 9 or 10, wherein the CO₂ in the feed comprises CO₂ captured from power plant exhaust; and/or wherein the CO₂ in the feed comprises CO₂ captured directly from air. 5
12. The method of any of claims 9-11, wherein the first electrochemical reactor (108) is an intermediate temperature electrochemical reactor configured to operate at <700 °C. 10
13. The method of any of claims 9-12, wherein the CO₂ that is fed to the first electrochemical reactor (108) first passes through a CO₂ capture assembly; and/or wherein the CO-rich stream and the first O₂-rich stream produced are separated from each other; and/or wherein the methanol or methanol stream is configured to be utilized in a conversion process to produce fuel. 20 25
14. The method of any of claims 9-13, wherein the second electrochemical reactor (106) is a solid oxide fuel electrolyzer.
15. The method of any of claims 9-14, wherein the first electrochemical reactor (108) includes a catalyst, the catalyst comprising at least one of Cr, Mn, Fe, Co, Ni, Ru or alloys thereof. 30 35 40 45 50 55

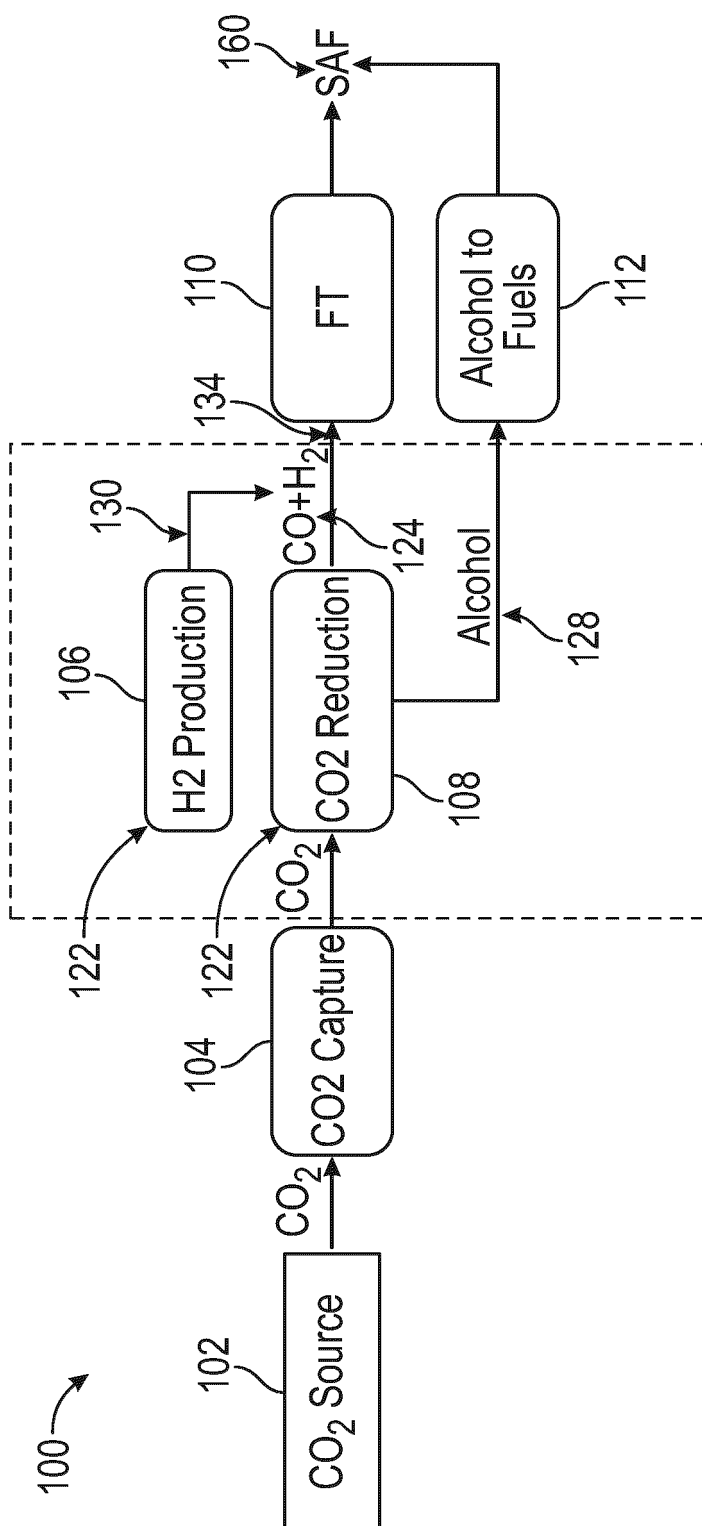


FIG. 1

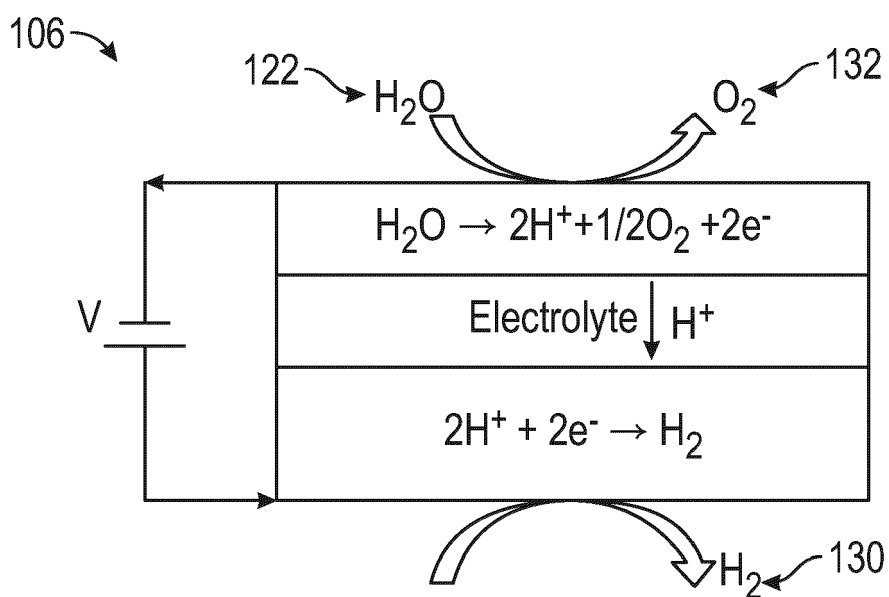


FIG. 2

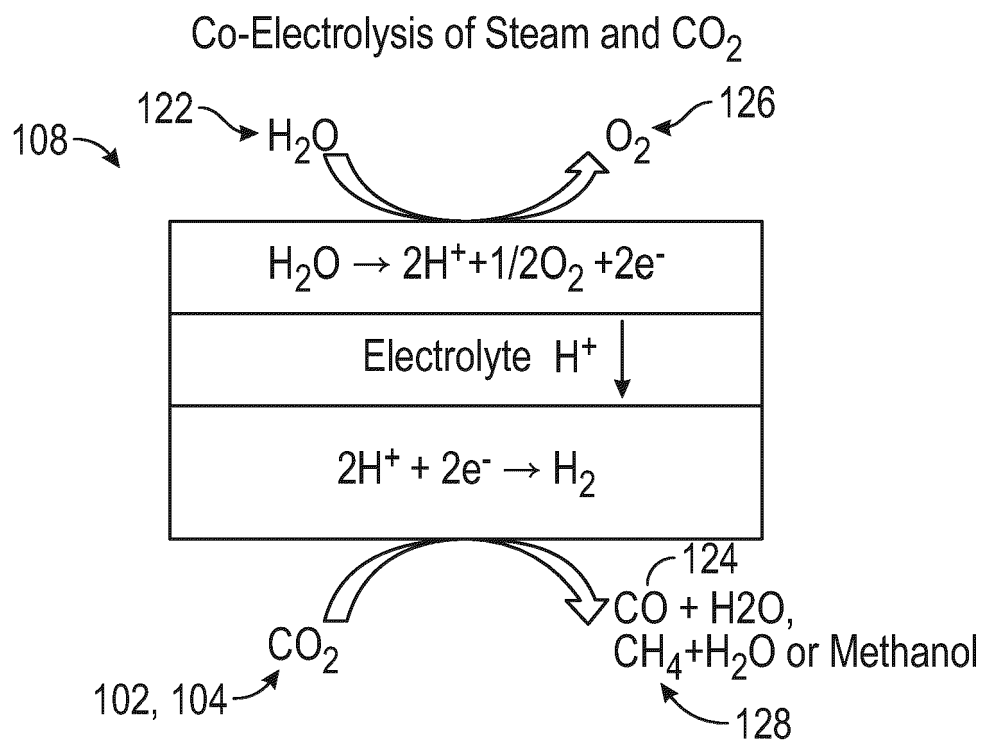


FIG. 3



EUROPEAN SEARCH REPORT

Application Number

EP 24 16 9065

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The present search report has been drawn up for all claims			

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EPO FORM 1503 03.82 (P04C01)

Place of search	Date of completion of the search	Examiner
The Hague	9 September 2024	Bernet, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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