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(54) **Title:** PROCESS FOR PURIFICATION AND CONVERSION OF CARBON DIOXIDE USING RENEWABLE ENERGY

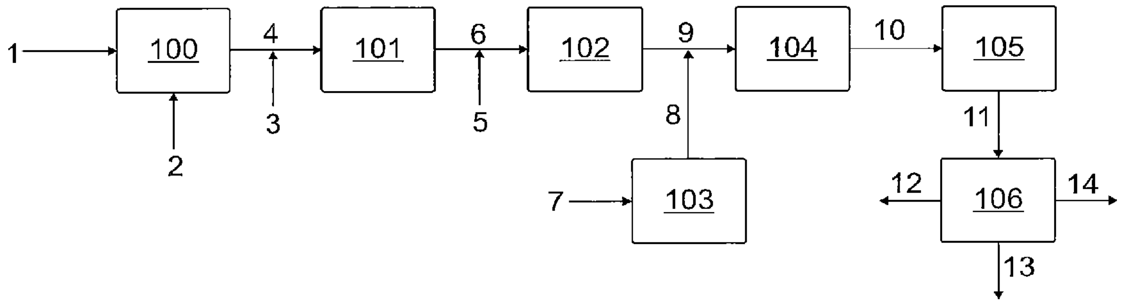

FIG. 1

(57) **Abstract:** The present invention is generally directed to processes and systems for the purification and conversion of CO2 into low-carbon or zero-carbon high quality fuels and chemicals using renewable energy. In one aspect, the present invention provides a process for producing a stream comprising at least 90 mol% CO_2. In certain cases, the CO_2 stream is processed to make low carbon fuels and chemicals. In this process at least a portion of the CO_2 is reacted with a stream comprising H2 in a Reverse Water Gas Shift (RWGS) reactor to produce a product stream that comprises CO.

[Continued on next page]

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PROCESS FOR PURIFICATION AND CONVERSION OF CARBON DIOXIDE USING RENEWABLE ENERGY

This application claims the benefit of U.S. Provisional Patent Application No. 63/258,157, filed April 13, 2021, which is incorporated by reference herein in its entirety.

Field of the Invention

The present invention is generally directed to processes and systems for the purification and conversion of CO_2 into low-carbon or zero-carbon high quality fuels and chemicals using renewable energy.

Background of the Invention

Carbon dioxide (CO_2) is produced by many industrial processes and is usually discharged into the atmosphere. However, CO_2 has been identified as a significant greenhouse gas that contributes to warming the planet, so CO_2 emissions need to be reduced from these processes (e.g., petroleum refining, power production, steel manufacture, cement manufacture, ethanol production). Efforts are underway to develop versions of these processes that emit less CO_2 and/or capture and sequester the emitted CO_2 (e.g., in geologic formations). However, capturing the CO_2 and converting it into useful fuels and chemicals can yield better economic returns compared with simply sequestering the CO_2.

The CO_2 can be converted to fuels and chemicals with the aid of electrical power. Notably, this electrical power should be derived from renewable low-carbon resources (e.g., wind or solar) so as to not attenuate or even completely defeat the benefit of using CO_2 as a feedstock in the first place. However, industrial sources of CO_2 often have certain contaminants (e.g., hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines) that prevent direct use of these feedstocks in electrochemical conversion processes. Removal of these contaminants with existing methods can have adverse economic impacts.

Summary of the Invention

Described herein are systems and methods for economical removal of contaminants from industrial CO_2 sources. The systems and methods can take advantage of the synergistic benefit of having excess high purity oxygen (O_2) available from the electrolysis of water using renewable power. The hydrogen (H_2) from electrolysis can be combined with CO (e.g., generated from CO_2 in a Reverse Water Gas Shift (RWGS) reaction) to yield fuels and chemicals, while the O_2 can be used to remove contaminants from the CO_2 feedstock. Serendipitously, using the O_2 from electrolysis can avoid introducing nitrogen (N_2) into the system (i.e., if the O_2 were derived from air) and/or avoids the cost and energy input required to enrich O_2 from air.

In one aspect, a method for preparing a carbon dioxide stream for use in the production of renewable fuels and chemicals is provided. The method comprises: providing a contaminated CO_2 stream comprising CO_2 and contaminants, which comprise of hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines, or combinations thereof; feeding the contaminated CO_2 stream to adsorbent beds to produce an outlet stream, wherein the outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb; mixing the adsorbent bed outlet stream with a stream comprising O_2 to produce a combustor feed stream; and feeding the combustor feed stream to a combustion reactor, where the contaminants are oxidized to produce a combustor product stream.

In another aspect, a method for producing a CO_2 stream comprising at least 90 mol% CO_2 is provided. The method comprises: providing a source stream comprising hydrocarbons, CO_2, and sulfur containing compounds; mixing the source stream with an H_2 stream derived from an electrolyzer to produce a low-temperature mixed source stream, wherein a mass ratio of the H_2 stream flowrate to the source stream flowrate is less than 10%; heating the low-temperature mixed source stream in a mixed stream heater that raises the temperature to produce a high-temperature mixed source stream having a temperature of at least 600°F; feeding the high-temperature mixed source stream to a hydrodesulfurization reactor to produce a hydrodesulfurization product stream that comprises CO_2 and hydrogen sulfide; feeding the hydrodesulfurization product stream to a sulfur absorbent reactor to produce an absorbent product stream that comprises CO_2 and hydrocarbons, wherein less than ten percent by weight of the hydrogen sulfide that was in the hydrodesulfurization product stream remains in the absorbent product stream; mixing the sulfur absorbent product stream with an electrolyzer O_2 stream to produce a combustion feed stream; feeding the combustion feed stream to a combustion reactor to produce a combustion reactor product stream, wherein hydrocarbons in the combustion feed stream are at least partly combusted to CO_2 carbon dioxide and H_2O; mixing the combustion reactor product stream with a supplemental H_2 stream to produce an O_2 removal reactor feed stream; and feeding the oxygen removal reactor feed stream to an O_2 removal reactor to produce a purified carbon dioxide product stream.

In another aspect, a method for producing a renewable fuel or chemical is provided. The method comprises: providing a feed stream comprising CO_2 and hydrocarbon; using renewable power to electrolyze H_2O and produce H_2 and O_2; converting the hydrocarbon in the feed stream to additional CO_2 using at least a portion of the O_2 from electrolysis; and converting the CO_2 and the H_2 into a renewable fuel or chemical.

In another aspect, a system for preparing a CO_2 stream for use in the production of renewable fuels and chemicals is provided. The system comprises: an adsorbent bed configured to convert a contaminated carbon dioxide stream into an outlet stream, wherein (i) the contaminated CO_2 stream comprises CO_2 and hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines, or combinations thereof, and (ii) the outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb; an electrolyzer configured to electrolyze H_2O to produce H_2 and O_2; and a combustion reactor configured to convert a mixture of the adsorbent bed outlet stream and the O_2 from the electrolyzer to a combustor product stream, wherein the contaminants are oxidized in the combustor product stream.

It should be appreciated that all combinations of the foregoing concepts and additional concepts discussed in greater detail below (provided such concepts are not mutually inconsistent) are contemplated as being part of the inventive subject matter disclosed herein. In particular, all combinations of subject matter within this disclosure are contemplated as being part of the inventive subject matter disclosed herein.

Still other aspects, examples, and advantages of these exemplary aspects and examples, are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and examples, and are intended to provide an overview or framework for understanding the nature and character of the claimed aspects and examples. Any example disclosed herein may be combined with any other example in any manner consistent with at least one of the objects, aims, and needs disclosed herein, and references to "an example," "some examples," "an alternate example," "various examples," "one example," "at least one example," " this and other examples" or the like are not necessarily mutually exclusive and are intended to indicate that a particular feature, structure, or characteristic described in connection with the example may be included in at least one example. The appearances of such terms herein are not necessarily all referring to the same example.

Brief Description of thc Drawings

FIG. 1 shows an example of a schematic diagram for a process to purify a CO_2 source stream comprising CO_2 that contains contaminants (e.g., inorganic sulfur and nitrogen compounds, amines, hydrocarbons, and oxygenated hydrocarbons).

Detailed Description of the Invention

The present invention describes processes and systems for the purification and conversion of CO_2 into low-carbon or zero-carbon high quality fuels and chemicals using renewable energy.

CO_2 can be converted into useful products such as fuels (e.g., diesel fuel, gasoline blend stocks, and jet fuel) and chemicals (e.g., solvents, olefins, alcohols, aromatics, and others) using renewable energy. As a result, these low-carbon products can displace fuels and chemicals produced from petroleum and natural gas, lowering the total net emissions of CO_2 into the atmosphere. As used herein, the term "low-carbon" fuels or chemicals means that the carbon intensity is at least 20% (but more preferably at least 50% or more) lower than the same fuels or chemicals produced from fossil sources calculated using carbon intensity calculators such as the Argonne National Laboratory GREET model, or other life cycle assessment tools. The term low-carbon electricity means that electricity is produced from any non-fossil source such as solar, wind, biomass, and nuclear power production plants. CO_2 can be obtained from various manufacturing plants used to produce power, cement, steel, petroleum-based fuels and chemicals, ammonia, ethanol, and commodity products such as batteries. In addition, municipal sewage treatment systems that use aerobic and anaerobic digestion of sludge produce large amounts of CO_2. CO_2 can also be captured from the atmosphere using a process called direct air capture (DAC).

Low-carbon or zero-carbon fuels and chemicals are often called e-fuels or e-chemicals because they require hydrogen produced by electrolysis of water. In an electrolyzer, electricity and heat are used to separate water into hydrogen and oxygen.

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

Electrolyzers can have an anode and a cathode separated by an electrolyte. Different electrolyzer designs function in slightly different ways. Electrolysis technologies which can be used to produce H_2 and O_2 include alkaline electrolysis, proton exchange membrane (PEM), and solid oxide electrolysis. Different electrolytes can be used including aqueous KOH and NaOH, with or without activating compounds. Activating compounds can be added to the electrolyte to improve the stability of the electrolyte. Most ionic activators for the hydrogen evolution reaction comprise an ethylenediamine-based metal chloride complex (e.g., $[M(en)_3]$Clx,M¼Co, Ni) and Na_2MoO4 or Na2WO4. Different electrocatalysts can be used on the electrodes including many different combinations of metals and oxides, such as Raney-Nickel-Aluminum, which can be enhanced by adding cobalt or molybdenum to the alloy.

Several combinations of transition metals, such as Pt_2Mo, Hf_2Fe, and TiPt, have been used as cathode materials and have shown significantly higher electrocatalytic activity.

In solid oxide electrolyzers, water at the cathode combines with electrons from the external circuit to form H_2 gas and negatively charged O_2 ions. The O_2 ions pass through the solid ceramic membrane and react at the anode to form O_2 gas and generate electrons for the external circuit. In this way, both H_2 hydrogen and O_2 gases are produced inthe electrolyzer. In some embodiments, multiple electrolyzers are operated in parallel.

The electrolyzer produces at least two product streams, an electrolyzer hydrogencomprising hydrogen, and an electrolyzer oxygen stream comprising oxygen. There are other ways to generate low carbon hydrogen streams including production of "turquoise H_2" from the pyrolysis of natural gas/methane, production of "blue H_2"using steam methane reforming (SMR) or autothermal reforming (ATR) to produce H_2 where the CO_2 emissions are captured from the flue gas stack.

Utilization of CO_2, as described herein, typically involves separating and purifying the CO_2 from a gaseous mixed stream where the CO_2 is not the major component. Typically, an alkylamine or chilled methanol is used to remove the CO_2 from the gas stream in a direct-contact process where the CO_2 is preferentially adsorbed into the contacting liquid. Alkylamines used in the process can include monoethanolamine, diethanolamine, methydiethanolamine, disopropyl-amine, aminoethoxyethanol, and other compounds and mixtures. Equipment corrosion due to the usage of alkanolamines for CO_2 absorption can be a significant problem. The corrosion rate tends reduce in the following order: monoethanolamine (MEA) > 2-amino-2-methyl-1-propanol (AMP) > diethanolamine (DEA) > methyl diethanolamine (MDEA). However, MDEA has higher CO_2 absorption capacity and requires lower energy to regenerate CO.

Compared to amines, adsorption can reduce energy and cost of the capture or separation of CO_2. To achieve this goal, adsorbents with suitable properties can be used. Metal Organic Framework (MOF) materials have can be used as a means of separating carbon dioxide from a dilute stream using chemisorption or physisorption to capture the CO_2 from the stream. Other methods to get concentrated CO_2 include chemical looping combustion where a circulating metal oxide material provides the oxygen for combustion of a carbonaceous material, in place of air, thus creating an exhaust undiluted with nitrogen and so concentrated in CO_2. Chemisorption is a subclass of adsorption where separation is driven by a chemical reaction between the sorbent and CO_2. Materials that can be used for the separation of CO_2 include but are not limited to MgO, CaO, Li_2ZrO_3, and hydrotalcites.

Membrane separation method is a continuous, steady-state, simple process for CO_2 separation. The process is relatively conservative in its energy needs. Yet, the driving force for separation can be low in low pressure applications. Furthermore, cryogenic distillation can be used to separate CO_2 from other streams and enables the production of liquid CO_2 and also its storage and transport.

CO_2 capture and compression can separate CO_2 from flue gas of oxy-fuel combustion. In some cases, cryogenic separation can be cost effective when the feed gas is available at high pressure.

CO_2 captured from industrial sources or ambient air may contain a wide array of impurities, which can adversely impact the downstream process. The nature of the impurities strongly depends on the CO_2 source and nature of the technology used to capture the CO_2. While some CO_2 sources are extremely pure, others may include sulfur impurities such as SO_2, H_2S, COS, elemental sulfur, and heavier organosulfur species. Organo-sulfur species can include mercaptanes, sulfides, disulfides and aromatic sulfur species. Sulfides and disulfides may also be aromatic. Thiophenes are polynuclear organic sulfur species, and are usually present in conjunction with heavier hydrocarbons. Hydrocarbon impurities in CO_2 are common, and include methane, ethane, more reactive olefines or alkynes, which can cause coke formation in conversion processes. Heavier hydrocarbons are commonly present in waste gas streams from petroleum refinery operations.

Other impurities in CO_2 such as N_2, NO_x, O_2 and Ar originate from air used in upstream processes. Additional impurities may include materials used for the CO_2 separation process, such as monoethanolamine (e.g., in the case of post-combustion capture) or Selexol™ (e.g., in pre-combustion capture), and their degradation products can also be carried over into the CO_2 stream.

Purification of CO_2, including the removal of sulfur containing compounds and hydrocarbons, can be necessary to avoid issues with downstream processing. The purified CO_2 produced using the methods described herein is suitable for the generation of low carbon or zero-carbon fuels and chemicals.

Hydrodesulfurization (HDS) is the method most commonly applied to remove sulfur and sulfur species from natural gas and refined products. The feed is combined with hydrogen gas, heated to 300-400°C in a heat-exchanger, or gas fired heater. The feed is then fed into a fixed-bed reactor at 10 to 130 atmospheres of absolute pressure. HDS is typically performed in the presence of a catalyst consisting of either cobalt/molybdenum or nickel/molybdenum (so called "*CoMo*" or "*NiMo*" catalyst, respectively) and may also contain related catalysts of different formulations.

This process hydrogenates the sulfur containing compounds and produces hydrogen sulfide (H_2S). The resulting stream is then either passed through a zinc oxide (ZnO) bed to absorb sulfur to form zinc sulfide (ZnS) or is cooled through heat exchangers and fed into an amine column for H_2S removal. H_2S is usually recovered from the amine gas and subsequently converted to sulfuric acid or elemental sulfur (Claus Process). At the same time, all nitrogen containing impurities in the feed stream are converted to NH_3. One of the key disadvantages of HDS is that sulfur species may not be removed completely. The reactivity of heterocyclic sulfur compounds decreases in the order of thiophene, alkylated thiophenes, benzothiophene, alkylated benzothiophenes, dibenzothiophene, and dimethyldibenzothiophene. In those cases, additional desulfurization measures are required to accomplish deep desulfurization. Also, depending on the nature of the feedstock HDS can require large amounts of valuable H_2.

Thermal oxidizers can be used to remove pollutants from industrial waste streams. The technology can remove hazardous air pollutants, volatile organic compounds (VOC), and odorous emissions from waste streams that would otherwise be discharged into the atmosphere. Thermal oxidizers may be catalytic or non-catalytic. Hydrocarbons are oxidized to form CO_2 and H_2O.

The efficacy of thermal oxidizers or combustion systems in general is affected by the fuel to oxygen ratio, temperature, residence time, and turbulence. Combustion of a hydrocarbon can be described by the exothermic reaction:

$$C_xH_yO_z + [x + y/4 - z/2\,]\,O_2 \rightarrow x\,CO_2 + y/2\,H_2O$$

The equivalence ratio is defined as the ratio of the actual fuel/oxygen ratio to the stoichiometric fuel/oxygen ratio, and can be a useful term in understanding combustion. Stoichiometric combustion occurs when all the oxygen is consumed in the reaction (i.e., and there is no molecular oxygen (O_2) in the product).

Other components in the combustor feed gas such as nitrogen or sulfur containing components can lead to the formation of SO_x and NO_x which pose serious environmental concerns and need to be removed prior to emitting the waste stream to the environment. While abatement systems are available, emissions of nitrogen oxides (NO_x) from combustion systems continue to be an environmental issue. These species can be greenhouse gases and/or acid rain precursors. The routes leading to the formation of NO_x in combustion systems mostly involve the insertion of radicals such as O, CH_x, and H, into the triple bond of molecular nitrogen in combustion air.

SO_2 can be removed by adding limestone ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) directly to the convective pass with high temperature filtration. The reaction of $CaCO_3$ may involve various reaction steps, such as:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$

$$CaSO_3 + \tfrac{1}{2}\, O_2 \rightarrow CaSO_4$$

$$CaCO_3 + \tfrac{1}{2}\, SO_2 \rightarrow CaSO_4 + \tfrac{1}{2}\, S_2$$

$CaSO_3$ decomposes at temperatures higher than 650 °C, and therefore, the overall reaction may be written as:

$$CaCO_3 + \tfrac{1}{2}\, SO_2 + \tfrac{1}{2}\, O_2 \rightarrow CaSO_4 + CO_2$$

The combustion of waste gases may also be accomplished in a catalytic oxidizer. Here, a catalyst is used to increase the rate of the combustion reaction and less fuel may be required to preheat the waste gas.

Moderate and intense low-oxygen dilution (MILD) combustion technologies can reduce the environmental concerns linked to the use of both conventional and alternative fuels. MILD combustion, also referred to as flameless or high-temperature air combustion (HiTAC), can limit the emissions of pollutants like carbon monoxide (CO), nitrogen oxides (NO_x) and soot. These processes provide elevated combustion efficiency and fuel flexibility.

Most combustion processes use air as the oxidizer. Air contains approximately 21% O_2 and 79% N_2 by volume. Using O_2-enhanced combustion can greatly improve productivity and thermal efficiency with lower exhaust gas volume and pollutant emissions. The application of thermal or catalytic oxy-combustion for the purification is typically impacted by the cost and availability of oxygen. However, in the systems and methods described herein, O_2 for thermal or catalytic oxy-combustion can be supplied by electrolysis and/or a cryogenic air separation unit (ASU). Oxygen can also be produced and supplied by the electrolysis of water.

The ASU technology uses cryogenic fractional distillation, where the components are separated by compressing the gas until it liquifies and then selectively distilled to their boiling points. As this is very costly and energy-intensive, the ASU technology is usually only applied for large scale productions.

Replacing air with pure O_2 can significantly increase the performance of a combustion system. O_2-enhanced combustion can be used in many different applications, including fluid catalytic cracking, metal processing, sulfur recovery, waste incineration, biofuels, pet-coke, and solid fuels, as well as oxy-coal combustion with CO_2 capture. The combustion process in the thermal oxidizer can be optimized for combustion performance, heat transfer, impurities, and minimization of energy penalty caused by the used by the air separation unit (ASU).

Described herein are systems and methods for the purification of streams comprising CO_2 and the use of that stream to produce low-carbon or zero-carbon fuels, in particular the removal of any combustible impurities. The CO_2 stream can be captured from industrial processes or is available from an industrial pipeline, and may also come from other CO_2 sources such as direct air capture. Provided herein is a process for producing a stream comprising at least 90 mol% CO_2 (e.g., between 90 mol% CO_2 and 95 mol% CO_2, or between 90 mol% CO_2 and 100 mol% CO_2). The process can comprise multiple steps, e.g., in sequence.

A source stream can comprise at least 50 mol% CO_2 with contaminants comprising hydrocarbons, CO_2, organic sulfur containing compounds, SO_2, H_2S, COS, N_2, amines, polar organic compounds, or combinations thereof. The source stream can be pre-heated and fed into an oxy-combustion reactor. The source stream can be mixed with an electrolyzer oxygen stream to produce a combustor reactor feed stream. The electrolyzer O_2 stream can comprise O_2 that has been produced from the electrolysis of water in an electrolyzer. The combustor feed stream can be fed to a combustor reactor where the hydrocarbons in the combustor feed stream are combusted to CO_2 and water to produce a combustion reactor product stream.

The combustor system can include a combustion chamber in which the combustible components in the CO_2 are oxidized. Depending on the composition of the original CO_2 feed, additional CO and CO_2 from hydrocarbon impurities can be generated, as well as SO_2 from organic sulfur compounds (if present). The inlet temperature in the combustor can be determined by the feedstock composition, and its ability to manage coke. The temperature may be as low as room temperature or up to about 400 °C. The heating can be accomplished using electric heaters. In some cases, the electricity used in the electric heaters is derived from a low-carbon process. If available heating may also be accomplished by integrating downstream waste-heat.

The reaction temperature depends on the heating value of the hydrocarbons in the feed stream. The heating value of the composition can depend on the type and the amounts of impurities. The energy released by the combustion of the total organics (e.g., volatile organic compounds (VOCs) we well as other hydrocarbons/organics) in the waste gas stream may not be sufficient to raise its own temperature to the desired levels. If required, auxiliary fuel may be added to raise the temperature in order to support a flame in the combustor. Auxiliary fuel may be hydrogen, methane or other hydrocarbons. In order to minimize carbon intensity of the process, natural gas can be avoided, and low-carbon intensity hydrogen can be used.

SO_2 can be removed by adding limestone ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) directly to the combustor. $CaSO_3$ can decompose at temperatures higher than 650 °C, and therefore, under typical operating conditions in the unit, the overall reaction may be written as:

$$CaCO_3 + \tfrac{1}{2}\,SO_2 + \tfrac{1}{2}\,O_2 \rightarrow CaSO_4 + CO_2$$

At high sulfur content, additional metal sorbents such as ZnO may be used. Other metal oxides that may be used are based on Fe, Cu, Mn, Mo, Co, and V.

As an alternative to limestone or dolomite addition, one can remove the organic sulfur and hydrogen sulfide upstream prior to the combustion reactor (e.g., by catalytic hydrodesulfurization) to convert the organic sulfur to hydrogen sulfide. An adsorbent bed of a material such as zinc oxide to capture the hydrogen sulfide can then be used.

The combustion reactor product stream can be free of hydrocarbons and SO_2 and comprise CO_2, CO, H_2O, and excess O_2. This stream can now be mixed with a supplemental H_2 stream to produce an O_2 removal reactor feed stream.

The O_2 removal reactor feed stream can be fed to an O_2 removal reactor to combust the excess O_2 to produce H_2O, thereby producing a product stream of purified CO_2 and H_2O. The H_2O can be removed by cooling the product stream to condense the H_2O separate the liquid H_2O from the purified CO_2. The dry, purified CO_2 product stream can have a composition of at least about 90 wt.% CO_2 (e.g., between 90 wt.% and 95 wt.% CO_2 or between 90 wt.% and 100 wt.% CO_2) in the source stream. In some cases, the CO_2 product stream has less than 50 parts per billion (ppb), or less than 20 ppb of the sulfur containing compounds. In some cases, the CO_2 product stream has less than 2,000 ppb, or less than 500 ppb hydrocarbons (e.g., which hydrocarbons were in the source stream).

Furthermore, the purified CO_2 stream can be used to produce low-carbon, or zero-carbon fuels and chemicals. The conversion process can involve conversion of CO_2, H_2O, and electricity to chemicals and fuels. The process can involve the electrolysis of water into H_2 and O_2 using renewable and/or low carbon electricity. Low carbon electricity can be electricity that is produced from wind, solar, nuclear, biomass, or other non-fossil sources. CO_2 can be collected using a CO_2 capture process, as described herein. CO_2 can be reacted with excess H_2 to produce CO and water using the reverse water-gas shift (RWGS) (often referred to as CO_2 hydrogenation) reaction where the heat of reaction is provided by a RWGS heater. The RWGS reaction can take place in a RWGS reactor in which there is a RWGS catalyst. The RWGS catalyst can be a solid solution catalyst comprising a transition metal such as nickel which is impregnated on a suitable high-surface area substrate. The RWGS product stream, comprising CO and H_2, can be converted to fuels and chemicals in a liquid fuels production (LFP) reactor that uses a catalyst to produce long chain hydrocarbons that can be used as fuels and chemicals. The final product can be a hydrocarbon mixture where the majority (e.g., 60 to 99 vol. %) of hydrocarbons in the mixture are hydrocarbons of 5 to 24 carbon atoms in length.

Turning attention to the figures, **FIG. 1** shows a schematic diagram for a process to purify a stream comprising CO_2 that can contain inorganic sulfur and nitrogen compounds, amines, hydrocarbons, and oxygenated hydrocarbons. The purified CO_2 stream of the process is stream **6.** The purified CO_2 stream is blended with H_2, heated separately or combined, and catalytically converted to syngas in reactor **104**. The syngas stream **10** is catalytically converted to fuels and chemicals.

Stream **1** is the contaminated CO_2 source stream. The pressure of this stream can typically be in the range of 25 pounds per square inch gauge (psig) to 500 psig. The temperature of stream **1** can be ambient or near ambient. Unit **100** can contain adsorbents that remove the particulates, polar inorganic sulfur, and nitrogen compounds.

The reactor **101** may be thermal (non-catalytic) if the concentration of the hydrocarbons is greater than about 3 vol. %, or catalytic if the hydrocarbon concentration is less than about 3 vol. %.

An O_2 stream **3** can be added at various flow rates, the flow rate being dependent upon the O_2 to hydrocarbon fuel ratio in the thermal reactor **101**. The O_2 can be produced by the electrolysis of H_2O using low carbon electricity. Additional hydrocarbons or methane may be added in a separate stream **4** in order to optimize the combustion in the thermal reactor **101**. Adding additional components in stream **4** may be utilized in a thermal combustion if stream **1** contains less than 3 vol. % hydrocarbons. An O_2 to fuel ratio sensor can be used to control the combustion process in thermal reactor **101** at or just below stoichiometry. The flow of the oxygen stream **3** can be controlled to keep the combustion of the hydrocarbons and oxygenated hydrocarbons at or just below stoichiometry (e.g., 0.95-1.00). In some cases, a small excess O_2 is acceptable, it can (nearly instantly) react with H_2 and not make it into the RWGS reactor. In reactor **101**, the O_2 and the hydrocarbons in stream **4** can react to primarily form CO_2 and H_2O, with a minor concentration of CO. H_2S and any other sulfur containing species can be converted to SOx. The concentration of O_2 in stream **6** can be controlled to less than about 500 ppm. Hydrated lime can be fluidized directly in reactor **101**.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$$
$$Ca(OH)_2 + SO_2 + 0.5O_2 \rightarrow CaSO_4 + H_2O$$

Lime wash can remove over 95% of SOx, as well as over 99% of HCl or HF. Transformed into calcium sulfite, calcium sulfate, calcium chloride, and calcium fluoride, the acidic gases can be captured (e.g., on bag filters) as solids. The excess hydrated lime can be re-circulated to improve lime utilization. Above 850 °C, $Ca(OH)_2$ forms CaO, which in the presence of oxygen, quickly reacts to form calcium sulphate below 1200 °C.

Additional high-purity CO_2 may be added as available (Stream **5**) and the blended stream **6** can be fed to Unit **102,** which heats the purified CO_2 stream **6** up to temperatures as high as 1,750 °F. Renewable energy can be used to heat the unit **102**.

An H_2 stream **7** can be heated in Unit **103** to a temperature as high as 1,750 °F and added to the heated stream **9,** as desired, to produce a molar H_2/CO_2 ratio that is between 1.5 and 4.0. Unit **103** can be heated using low-carbon or zero-carbon fuel gas such as tail gas from a catalytic reactor **107**. Unit **103** can also be a resistance or induction heater that can be operated with low carbon electricity.

As a result of the systems and methods described herein, stream **9** can contain less than 20 ppb of SO_2, H_2S and COS; have amine and ammonia concentrations of less than 100 ppb; have less than 500 ppm of O_2; and the hydrocarbons and oxygenated hydrocarbons in the contaminant CO_2 stream can be reduced by more than 95%.

The heated stream **9** can be feed into a catalytic reverse water gas shift (RWGS) reactor **104**. The catalytic RWGS reactor vessel can be adiabatic or nearly adiabatic and designed to minimize heat loss. In some embodiments, no heat is added to the main reactor vessel in the adiabatic mode and the temperature in the main reactor vessel can decline from the inlet to the outlet of the reactor.

The RWGS reactor **104** can be a cylindrical vessel (e.g., with a length longer than diameter). The entrance to the reactor vessel can be smaller than the overall diameter of the vessel. The reactor vessel can be a steel vessel that is lined with an inert material that is non-reactive with the heated syngas. The steel vessel can be insulated to limit heat loss. Various types of insulation include poured or castable refractory lining or insulating bricks may be used tolimit the heat losses to the environment. The reactor shell can comprise metallurgy for a cold wall vessel with a maximum external surface temperature of less than 400 °F (e.g., between 200 °F and 400 °F).

A bed of catalyst can be inside the reactor vessel **104**. The catalyst can be in the form of granules, pellets, spheres, trilobes, quadra-lobes, monoliths, or any other engineered shape (e.g., to minimize pressure drop across the reactor). The shape and particle size of the catalyst particles can be managed such that pressure drop across the reactor is less than 50 pounds per square inch (psi) (e.g., between 10 psi and 50 psi), and in some cases, less than 20 psi (e.g., between 10 psi and 20 psi). The size of the catalyst form can have a characteristic dimension of between 1 mm to 10 mm. The catalyst particle can be a porous material with an internal surface area greater than 10 m^2/g (e.g., between 10 m^2/g and 50 m^2/g), in some cases greater than 50 m^2/g (e.g., between 50 m^2/g and 100 m^2/g). The packed catalyst can be arranged as a down-flow, supported on ceramic balls. Radial flow can also be used. In some cases, the catalyst bed minimizes pressure drop (above that needed for flow distribution) at the desired high gas hourly space velocity (GHSV) design. In some embodiments, the dimensions of 4 feet inner diameter by 4 feet deep bed of catalyst gives a GHSV of approximately 26,000 h^{-1} with a pressure drop through the support balls and catalyst of 6 psi (0.21 bar). Several catalyst materials can catalyze the RWGS reaction. In some cases, the RWGS catalyst is a solid solution catalyst that primarily comprises Ni_2Mg impregnated on a high-temperature spinel. This high-performance, solid-solution, Ni-based catalyst can be highly versatile and perform the RWGS reaction efficiently. The catalyst can have high thermal stability up to 1,100°C (e.g., between 900°C and 1,100°C), does not form carbon (coking), and has good resistance to contaminants that may be present in captured CO_2 streams. This catalyst exhibits high activity at low Ni_2Mg concentrations (< 5.0 wt.%). In some cases, the use of expensive precious metals to enhance catalyst performance is not necessary.

The RWGS reactor product gas is stream **10**, which comprises CO, H_2, unreacted CO_2, H_2O, and a small amount of CH_4 (produced by a methanation reaction). The RWGS reactor product gas can be used in several ways. The product gas can be cooled, compressed, and used in downstream processes to produce fuels and chemicals. The RWGS product gas can also be cooled, compressed, and sent back to the heated chamber **102** and the RWGS reactor vessel **104**. The RWGS product gas can also be reheated in a second heated chamber and sent to a second RWGS reactor vessel where additional conversion of CO_2 to CO can occur. The second RWGS reactor product gas can also be reheated in a third heated chamber and sent to a third RWGS reactor vessel where additional conversion of CO_2 to CO can occur.

At least a portion of the RWGS reactor product stream **10** can be fed to a liquid fuel production (LFP) catalytic reactor (Unit **105**). Stream **10** can be compressed before input into Unit **105** (i.e., such that the operating pressure of the syngas stream **10** is not too low).

The catalytic reactor **105** can convert CO and H_2 (that are in stream **10**) primarily into C_1-C_{24} hydrocarbons that can be used as liquid fuels and chemicals. Stream **11** can be fed to a separation system, Unit **106**. This separation system **106** separates the products from Unit **105** into tail gas (C_1-C_5 hydrocarbons and unconverted CO and H_2) (stream **12**), liquid phase products (C_5-C_{24} hydrocarbons and oxygenated hydrocarbons) (stream **13**), and a small fraction (typically less than 5 volume%) of C_{24+} hydrocarbons (stream **14**).

The catalytic reactor **105** can use a catalyst for production of liquid fuel range hydrocarbons from syngas. In some cases, the hydrogen to carbon monoxide ratio in the stream is between 1.9 and 2.2 (v/v), but it can be varied between 1.0 and 3.0 (v/v) to modify the product distribution. The LFP reactor can be a multi-tubular fixed-bed reactor system. Each LFP reactor tube can be between 13 mm and 51 mm in diameter. The length of the reactor tube is generally greater than 6 meters in length (e.g., between 6 meters and 15 meters) and in some cases greater than 10 meters in length (e.g., between 10 meters and15 meters). Most of the length of the LFP reactor tube can be filled with LFP catalyst. The LFP catalyst may also be blended with diluent such as silica or alumina to aid in the distribution of the LFP reactor feed into and through the LFP reactor tube. The chemical reaction that takes place in the LFP reactor produces an LFP product gas that comprises most hydrocarbon productsfrom five to twenty-four carbons in length (C_5-C_{24} hydrocarbons) as well as water, although some hydrocarbons are outside this range.

In some embodiments, unit 100 may include HDS following particulate removal. H_2 may be added as stream 2 as excess H_2 available from the electrolyzer. The HDS reactor can be a pressure vessel containing hydrodesulfurization catalyst. Here, the sulfur containing compounds are converted to H_2S. The hydrodesulfurization catalyst can comprise Co and Mo or Ni and Mo, or combinations thereof. The HDS reactor product comprises carbon dioxide, hydrocarbons, excess H_2, and H_2S. The HDS reactor product stream can be fed to the sulfur adsorbent reactor. The sulfur adsorbent reactor can be filled with an H_2S adsorbent such as ZnO that reacts with the H_2S and removes it from the stream. Multiple sulfur adsorbent reactors may be present in series or in parallel or in a lead-lag configuration such that when the adsorbent is saturated with H_2S and sulfur breaks through in the stream, the reactor with the used adsorbent can be removed from service and the adsorbent replaced without reducing the overall ability of the process to remove the H_2S. In some cases, some hydrogen is present. Any hydrocarbon impurities that were in the source stream (stream 1) may still be present in their saturated form.

In some embodiments, purification of the CO_2 may include particulate removal, HDS, as well as oxycombustion. In particular, when high levels of impurities were present in stream 1. In these scenario, the temperature rise generated in unit 101 may minimize the heating requirements in unit 102.

In some embodiments, the LFP catalyst comprises cobalt as the active metal. In some cases, the LFP catalyst comprises iron as the active metal. In some embodiments, the LFP catalyst comprises combinations of iron and cobalt as the active metal. The LFP catalyst can be supported on a metal oxide support that can be chosen from a group consisting of alumina, silica, titania, activated carbon, carbon nanotubes, zeolites or other support materials. The LFP catalyst can have sufficient size, shape, pore diameter, surface area, crush strength, and effective pellet radius. The catalyst can have various shapes including lobed supports with either three, four, five, or more lobes (e.g., with two or more of the lobes being longer than the other two shorter lobes, with both the longer lobes being symmetric). The distance from the mid-point of the support or the mid-point of each lobe is called the effective pellet radius which can contribute to the desired selectivity of C_5 to C_{24} hydrocarbons.

The LFP reactor can be operated at pressures between 150 to 450 psi. The reactor is operated over a temperature range from 350 °F to 460 °F and more typically at around 410 °F (e.g., between400 °F and 420 °F). The LFP or Fischer-Tropsch (F-T) reaction is exothermic. The temperature ofthe reactor can be maintained inside the LFP reactor tubes by the reactor tube bundle being placed into a heat exchanger where boiling water is present on the outside of the LFP reactor tubes. Theboiler water temperature is at a lower temperature than the LFP reaction temperature so that heatflows from the LFP reactor tube to the lower temperature water. The shell water temperature can be maintained by controlling the pressure of the produced steam. The steam can be saturated steam. In some embodiments, the catalytic LFP reactor can be a slurry reactor, microchannel reactor, fluidized bed reactor, or other reactor type.

The CO conversion in the LFP catalytic reactor **105** can be maintained at between 40 to 60 mole% CO conversion per pass. The desired liquid hydrocarbon product can be separated from the stream by condensation or any other acceptable means **106**. The LFP tail gas comprises the unreacted CO, H_2 and $C_1 - C_5$ hydrocarbons and is shown as stream **12**.

The reactor product that contains the desired C_5-C_{24} hydrocarbons can be further processed in a separation system. The separation system can include fractionation or distillation.

The desired C_5-C_{24} products can be used for gasoline blend-stock, diesel fuel, jet fuel, or used as low-carbon chemicals that can displace chemicals derived from petroleum or natural gas. In one embodiment, a series of fractionators are used to create a high cetane diesel fuel with an adjustable flash point between 38-54 °C (100-130 °F), a stabilized naphtha (potentially a gasoline blend stock or chemical feedstock), and a light wax (C_{24}-C_{40} hydrocarbons). A basic arrangement for these columns includes:

A. Wax Stripper – This unit uses steam to recover fuel-range components from the waxy material. The overhead fuel-range components and steam are sent to the main fractionator while the wax is cooled and stored as a solid. The wax stripper is a column without a condenser or reboiler, operating at approximately 170°C (340°F) and with enough pressure, 2.75 barg (40 psig), for theoverhead vapors to enter the main fractionator column.

B. Main Fractionator – This column splits the raw fuel into naphtha and diesel range components to control the diesel flash point. This column includes a high pressure (HP) steam heated reboiler and a reflux condenser with 3-phase separation for removing water.

C. Optional naphtha stabilizer to control the Reid vapor pressure (RVP) to a spec of 8 psia. The stabilizer includes a low pressure (LP) steam reboiler and a reflux condenser.

D. Optional diesel cold-flow/kerosene vacuum column to adjust the diesel pour point for cold weather sales and/or produce a kerosene or jet fuel cut. The column includesa high temperature reboiler and a reflux condenser. In one embodiment the high temperature reboiler uses electric heating.

The primary liquid products from the LFP reactor and separation system (Unit **106**) are

C_5-C_{10} hydrocarbons and oxygenated hydrocarbons, stream **12**. Stream **13** comprises primarily hydrocarbons with between 10 and 24 carbon atoms.

In an aspect, provided herein is a method for preparing a CO_2 stream for use in the production of renewable fuels and chemicals. A contaminated CO_2 stream can comprise CO_2 and contaminants such as hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines, or combinations thereof. The contaminated CO_2 stream can be fed to adsorbent beds to produce an outlet stream, where the outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb. In some embodiments, the SO_2, H_2S and COS have a concentration that is less than 50 parts per million (ppm), 20 ppm, 10 ppm, 1 ppm, 500 ppb, 100 ppb, 50 ppb, 20 ppb, 10 ppb, or 5 ppb. In some embodiments, the amine and ammonia concentrations are less than 50 parts per million (ppm), 20 ppm, 10 ppm, 1 ppm, 500 ppb, 100 ppb, 50 ppb, 20 ppb, 10 ppb, or 5 ppb.

The systems and methods can further include mixing the adsorbent bed outlet stream with a stream comprising oxygen to produce a combustor feed stream and feeding the combustor feed stream to a combustion reactor, where the contaminants are oxidized to produce a combustor product stream.

The molar flow of O_2 in the combustor feed stream can be controlled using a sensor that senses an O_2 to fuel ratio, such that the mixing of the absorbent bed outlet stream with the stream comprising oxygen has an equivalence ratio of less than 1.00, less than 0.95, less than 0.9, or less than 0.8. The combustor product stream can have a molar amount of hydrocarbon of less than 10%, less than 8%, less than 5%, less than 3%, or less than 1% of the molar amount of hydrocarbon in the contaminated CO_2 stream.

The combustor product stream can be mixed with heated CO_2 and H_2 streams in which the ratio of H_2 and CO_2 is between 1.5 and 4.0. In some cases, the ratio of H_2 and CO_2 is greater than

1.5, greater than 2.0, greater than 2.5, greater than 3, or greater than 3.5. In some instances, the ratio of H_2 and CO_2 is less than 2.0, less than 2.5, less than 3, less than 3.5, or less than 4.0.

The H_2 and CO_2 streams can be separately (or combined) and heated to between 900 and 1,250 °F before mixing with the combustor product stream. In some cases, the streams are heated to at least 900, at least 950, at least 975, at least 1,000, at least 1025, at least 1050, at least 1075, at least 1100, at least 1125, at least 1150, at least 1175, or at least 1200 °F.

The heated streams can be further heated up to 1,750 °F before introduction into a catalytic reactor which produces a syngas stream that comprises a H_2 and CO mixture with a ratio between 1.0 and 4.0. In some instances, the streams are heated to at least 1300, at least 1400, at least 1500, at least 1600, or at least 1700 °F. The H_2 and CO mixture can have a ratio of greater than 1.0, greater than 1.5, greater than 2.0, greater than 2.5, greater than 3, or greater than 3.5. In some instances, the ratio of H_2 and CO is less than 1.5, less than 2.0, less than 2.5, less than 3, less than 3.5, or less than 4.0.

The syngas can be input to a catalytic reactor, that is heated using renewable energy to produce low-carbon fuels and chemicals. The low-carbon fuels and chemicals can have a carbon intensity value that is near zero.

The method provided herein can produce a CO_2 stream that comprises at least 90 mol% CO_2 . In some cases, the carbon dioxide stream is at least 95%, at least 97%, at least 99%, at least 99.5%, at least 99.9%, at least 99.95%, or at least 99.99% CO_2.

The method can include providing a source stream comprising hydrocarbons, CO_2, and sulfur containing compounds and mixing the source stream with a H_2 stream derived from an electrolyzer to produce a low-temperature mixed source stream, where a mass ratio of the H_2 stream flowrate to the source stream flowrate is less than 10%, less than 8%, less than 5%, less than 3%, or less than 1%. The method can further include heating the low-temperature mixed source stream in a mixed stream heater that raises the temperature to produce a high-temperature mixed source stream having a temperature of at least 600, at least 700, at least 800, at least 900, or at least 1000°F. The method can further include feeding the high-temperature mixed source stream to a hydrodesulfurization reactor to produce a hydrodesulfurization product stream that comprises CO_2 and hydrogen sulfide, and feeding the hydrodesulfurization product stream to a sulfur absorbent reactor to produce an absorbent product stream that comprises carbon dioxide and hydrocarbons, wherein less than ten percent by weight (10 wt.%) of the hydrogen sulfide that was in the hydrodesulfurization product stream remains in the absorbent product stream. In some instances, less than 8 wt.%, less than 5 wt.%, less than 3 wt.%, less than 1 wt.%, less than 0.5 wt.%, less than 0.1 wt.%, or less than 0.05 wt% of the hydrogen sulfide that was in the hydrodesulfurization product stream remains in the absorbent product stream.

The method can further include mixing the sulfur absorbent product stream with an electrolyzer O_2 stream to produce a combustion feed stream, feeding the combustion feed stream to a combustion reactor to produce a combustion reactor product stream, wherein hydrocarbons in the combustion feed stream are at least partly combusted to CO_2 and H_2O, mixing the combustion reactor product stream with a supplemental H_2 stream to produce an O_2 removal reactor feed stream; and feeding the O_2 oxygen removal reactor feed stream to an O_2 removal reactor to produce a purified CO_2 product stream.

The purified CO_2 product stream can be further processed to make low-carbon fuels. At least a portion of the purified carbon dioxide product stream is reacted with a stream comprising hydrogen in a Reverse Water Gas Shift (RWGS) reactor to produce a RWGS product. The electrolyzer H_2 stream comprises at least 90 mol%, at least 95 mol%, or at least 99 mol% H_2 that is produced from the electrolysis of H_2O in an electrolyzer.

The hydrodesulfurization reactor contains a hydrodesulfurization catalyst that comprises

Molybdenum. The sulfur absorbent reactor contains a sulfur absorbent comprising ZnO. The electrolyzer O_2 stream comprises O_2 that has been produced from the electrolysis of H_2O in an electrolyzer. The purified CO_2 product stream has a composition such that it comprises at least 90 wt.% of the CO_2 in the source stream but less than 1 wt.% of the sulfur containing compounds and less than 10 wt.% of the hydrocarbons that were in the source stream.

The following are certain embodiment of processes for the conversion of CO_2, H_2O, and renewable electricity into low or zero carbon high quality fuels and chemicals:

Embodiment 1. Water is fed into an electrolyzer powered by renewable energy. A CO_2 stream is prepared for use in the production of renewable fuels and chemicals using a system comprising an adsorbent bed configured to convert a contaminated CO_2 stream into an outlet stream. The contaminated CO_2 stream comprises CO_2 and contaminants, which may include particulates, hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, and amines. The outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb, and free of particulates. The electrolyzer is configured to electrolyze H_2O to produce H_2 and O_2. A combustion reactor is configured to convert a mixture of the adsorbent bed outlet stream and the O_2 from the electrolyzer to a combustor product stream, where the contaminants are oxidized in the combustor product stream.

A molar flow of O_2 in the combustor feed stream is controlled using a sensor that senses an O_2 to fuel ratio, such that the mixing of the absorbent bed outlet stream with the stream comprising O_2 has an equivalence ratio of about 0.98, thereby providing a combustor product stream in which a molar amount of hydrocarbon of about 4% of the molar amount of hydrocarbon in the contaminated CO_2 stream. The combustor product stream is mixed with heated CO_2 and H_2 streams in which the ratio of H_2 and CO_2 is about 2.5. The H_2 and CO_2 streams are separately heated to about 1,000 °F before mixing with the combustor product stream.

The heated streams are further heated up to about 1,750 °F before introduction into a catalytic reactor which produces a syngas stream that comprises a H_2 and CO mixture with a ratio of about 2.0. The syngas is input to a catalytic reactor, that is heated using renewable energy to produce low-carbon fuels and chemicals.

Embodiment 2. A system produces a renewable fuel or chemical. The system comprises an electrolyzer configured to use renewable power to electrolyze H_2O and produce H_2 and O_2; a conversion module configured to convert the hydrocarbon in a feed stream to additional CO_2 using at least a portion of the O_2 from the electrolyzer, where the fed stream comprising CO_2 and hydrocarbon; and a reactor configured to convert the CO_2 in the feed stream and the H_2 from the electrolyzer into a renewable fuel or chemical.

The hydrocarbon molecules have less than 8 carbon atoms. The hydrocarbon is converted into CO_2 using a thermal oxidation system with the O_2 from electrolysis. The thermal oxidation system is oxy-combustion. The concentration of hydrocarbon in the feed stream is about 6 wt.%.

The renewable fuel or chemical is a synthetic diesel fuel. The feed stream is from a CO_2 pipeline.

Embodiment 3. A system produces a renewable fuel or chemical. The system comprises an electrolyzer configured to use renewable power to electrolyze H_2O and produce H_2 and O_2; a conversion module configured to convert the hydrocarbon in a feed stream to additional CO_2 using at least a portion of the O_2 from the electrolyzer, where the fed stream comprising CO_2 and hydrocarbon; and a reactor configured to convert the CO_2 in the feed stream and the H_2 from the electrolyzer into a renewable fuel or chemical.

The hydrocarbon molecules have less than 8 carbon atoms. The hydrocarbon is converted into CO_2 using a catalytic oxidation system. The concentration of hydrocarbon in the feed stream is about 1 wt.%.

The renewable fuel or chemical is a synthetic aviation fuel (SAF). The feed stream is from the manufacturing of cement.

Embodiment 4. A system produces a renewable fuel or chemical. The system comprises an electrolyzer configured to use renewable power to electrolyze H_2O and produce H_2 and O_2; a conversion module configured to convert the hydrocarbon in a feed stream to additional CO_2 using at least a portion of the O_2 from the electrolyzer, where the fed stream comprising CO_2 and hydrocarbon; and a reactor configured to convert the CO_2 in the feed stream and the H_2 from the electrolyzer into a renewable fuel or chemical.

The hydrocarbon molecules have less than 8 carbon atoms. The hydrocarbon is converted into CO_2 using a catalytic oxidation system. The concentration of hydrocarbon in the feed stream is about 2.5 wt.%.

The renewable fuel or chemical is a mixture of C_5-C_{23} hydrocarbons. The feed stream is from petroleum refining.

The above-described embodiments can be implemented in any of numerous ways. For example, the embodiments may be implemented using hardware, software or a combination thereof. When implemented in software, the software code can be executed on any suitable processor or collection of processors, whether provided in a single computer or distributed among multiple computers. It should be appreciated that any component or collection of components that perform the functions described above can be generically considered as one or more controllers that control the above-discussed functions. The one or more controllers can be implemented in numerous ways, such as with dedicated hardware or with one or more processors programmed using microcode or software to perform the functions recited above.

In this respect, it should be appreciated that one implementation of the embodiments of the present invention comprises at least one non-transitory computer-readable storage medium (e.g., a computer memory, a portable memory, a compact disk, etc.) encoded with a computer program (i.e., a plurality of instructions), which, when executed on a processor, performs the above-discussed functions of the embodiments of the present invention. The computer-readable storage medium can be transportable such that the program stored thereon can be loaded onto any computer resource to implement the aspects of the present invention discussed herein. In addition, it should be appreciated that the reference to a computer program which, when executed, performs the above-discussed functions, is not limited to an application program running on a host computer. Rather, the term computer program is used herein in a generic sense to reference any type of computer code (e.g., software or microcode) that can be employed to program a processor to implement the above-discussed aspects of the present invention.

Various aspects of the present invention may be used alone, in combination, or in a variety of arrangements not specifically discussed in the embodiments described in the foregoing and are therefore not limited in their application to the details and arrangement of components set forth in the foregoing description or illustrated in the drawings. For example, aspects described in one embodiment may be combined in any manner with aspects described in other embodiments.

Also, embodiments of the invention may be implemented as one or more methods, of which an example has been provided. The acts performed as part of the method(s) may be ordered in any suitable way. Accordingly, embodiments may be constructed in which acts are performed in an order different than illustrated, which may include performing some acts simultaneously, even though shown as sequential acts in illustrative embodiments.

Use of ordinal terms such as “first,” “second,” “third,” etc., in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed. Such terms are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term).

The phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of "including," "comprising," "having," “containing”, “involving”, and variations thereof, is meant to encompass the items listed thereafter and additional items.

Having described several embodiments of the invention in detail, various modifications and improvements will readily occur to those skilled in the art. Such modifications and improvements are intended to be within the spirit and scope of the invention. Accordingly, the foregoing description is by way of example only, and is not intended as limiting. The invention is limited only as defined by the following claims and the equivalents thereto.

CLAIMS:

1. A method for preparing a carbon dioxide stream for use in the production of renewable fuels and chemicals, the method comprising:

   a. providing a contaminated CO_2 stream comprising CO_2 and contaminants, which contaminants comprise hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines, or combinations thereof;

   b. feeding the contaminated CO_2 stream to adsorbent beds to produce an outlet stream, wherein the outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb;

   c. mixing the adsorbent bed outlet stream with a stream comprising O_2 to produce a combustor feed stream; and

   d. feeding the combustor feed stream to a combustion reactor, where the contaminants are oxidized to produce a combustor product stream.

2. The method of Claim 1, wherein the O_2 is produced from the electrolysis of H_2O using renewable energy.

3. The method of Claim 1, wherein H_2 that is produced from the electrolysis of H_2O using renewable energy is used to purify the contaminated CO2 stream.

4. The method of Claim 1, wherein a molar flow of O_2 in the combustor feed stream is controlled using a sensor that senses an O_2 to fuel ratio, such that the mixing of the absorbent bed outlet stream with the stream comprising o O_2 has an equivalence ratio of less than 1.00, thereby providing a combustor product stream in which a molar amount of hydrocarbon of less than 5% of the molar amount of hydrocarbon in the contaminated CO_2 stream.

5. The method of Claim 1, wherein the combustor product stream is mixed with heated CO_2 and H_2 streams in which the ratio of H_2 and CO_2 is between 1.5 and 4.0.

6. The method of Claim 5, wherein the H_2 and CO_2 streams are separately heated to between 900 and 1,250 °F before mixing with the combustor product stream.

7. The method of Claim 6, wherein the heated streams are further heated up to 1,750 °F before introduction into a catalytic reactor which produces a syngas stream that comprises a H_2 and CO mixture with a ratio between 1.0 and 4.0.

8. The method of claim 7, wherein the syngas is input to a catalytic reactor, that is heated using renewable energy to produce low-carbon fuels and chemicals.

9. The method of claim 8, wherein the low-carbon fuels and chemicals have a carbon intensity value that is near zero.

10. A method for producing a CO_2 stream that comprises at least 90 mol% CO_2, the method comprising:

a. providing a source stream comprising hydrocarbons, CO_2, and sulfur containing compounds;

b. mixing the source stream with an H_2 stream derived from an electrolyzer to produce a low-temperature mixed source stream, wherein a mass ratio of the H_2 stream flowrate to the source stream flowrate is less than 10%;

c. heating the low-temperature mixed source stream in a mixed stream heater that raises the temperature to produce a high-temperature mixed source stream having a temperature of at least 600°F;

d. feeding the high-temperature mixed source stream to a hydrodesulfurization reactor to produce a hydrodesulfurization product stream that comprises CO_2 and hydrogen sulfide;

e. feeding the hydrodesulfurization product stream to a sulfur absorbent reactor to produce an absorbent product stream that comprises CO_2 and hydrocarbons, wherein less than ten percent by weight of the hydrogen sulfide that was in the hydrodesulfurization product stream remains in the absorbent product stream;

f. mixing the sulfur absorbent product stream with an electrolyzer O_2 stream to produce a combustion feed stream;

g. feeding the combustion feed stream to a combustion reactor to produce a combustion reactor product stream, wherein hydrocarbons in the combustion feed stream are at least partly combusted to CO_2 carbon dioxide and H_2O;

h. mixing the combustion reactor product stream with a supplemental H_2 stream to produce an O_2 removal reactor feed stream; and

i. feeding the oxygen removal reactor feed stream to an O_2 removal reactor to produce a purified carbon dioxide product stream.

11. The method of Claim 10, wherein the purified CO_2 product stream is further processed to make low-carbon fuels.

12. The method of Claim 10, wherein at least a portion of the purified CO_2 product stream is reacted with a stream comprising H_2 in a Reverse Water Gas Shift (RWGS) reactor to produce a RWGS product.

13. The method of Claim 10, wherein the electrolyzer H_2 stream comprises at least 90 mol% H_2 that is produced from the electrolysis of H_2O in an electrolyzer

14. The method of Claim 10, wherein the hydrodesulfurization reactor contains a hydrodesulfurization catalyst that comprises Molybdenum.

15. The method of Claim 10, wherein the sulfur absorbent reactor contains a sulfur absorbent comprising ZnO.

16. The method of Claim 10, wherein the electrolyzer O_2 stream comprises O_2 that has been produced from the electrolysis of H_2O in an electrolyzer

17. The method of Claim 10, wherein the purified product stream has a composition such that it comprises at least 90 wt.% of the CO_2 in the source stream but less than 1 wt% of the sulfur containing compounds and less than 10 wt% of the hydrocarbons that were in the source stream.

18. A method for producing a renewable fuel or chemical, the method comprising:

a. providing a feed stream comprising CO_2 and hydrocarbon;
b. using renewable power to electrolyze H_2O and produce H_2 and O_2;
c. converting the hydrocarbon in the feed stream to additional CO_2 using at least a portion of the O_2 from electrolysis; and
d. converting the CO_2 and the H_2 into a renewable fuel or chemical.

19. The method of claim 18, wherein the hydrocarbon molecules have less than 8 carbon atoms.

20. The method of claim 18, wherein the hydrocarbon is converted into CO_2 using a thermal oxidation system with the O_2 from electrolysis.

21. The method of claim 20, wherein the thermal oxidation system is oxy-combustion.

22. The method of claim 21, wherein the concentration of hydrocarbon in the feed stream is greater than about 3 wt.%.

23. The method of claim 18, wherein the hydrocarbon is converted into CO_2 using a catalytic oxidation system.

24. The method of claim 23, wherein the concentration of hydrocarbon in the feed stream is less than about 3 wt.%.

25. The method of claim 18, wherein the renewable fuel or chemical is a synthetic diesel fuel.

26. The method of claim 18, wherein the renewable fuel or chemical is a synthetic aviation fuel (SAF).

27. The method of claim 18, wherein the renewable fuel or chemical is a C_5-C_{23} hydrocarbon, alcohol, and/or olefin.

28. The method of claim 18, wherein the feed stream is from a CO_2 pipeline.

29. The method of claim 18, wherein the feed stream is from manufacturing processes.

30. The method of claim 29, wherein the manufacturing process is a process for manufacturing ethanol, cement, steel, lime, or products of petroleum refining.

31. The method of claim 18, wherein the feed stream is CO_2 captured from ambient air.

32. The method of claim 18, further comprising removing sulfur compounds and particulates from the feed stream.

33. The method of claim 18, wherein converting the hydrocarbon to additional CO_2 reduces the concentration of hydrocarbon in the feed stream to less than about 2,000 ppm.

34. The method of claim 18, wherein the hydrocarbon is converted into CO_2 at approximately atmospheric pressure.

35. The method of claim 18, wherein the hydrocarbon is converted into CO_2 at a temperature of less than about 1500 °C.

36. A system for preparing a CO_2 stream for use in the production of renewable fuels and chemicals, the system comprising:

a. an adsorbent bed configured to convert a contaminated carbon dioxide stream into an outlet stream, wherein (i) the contaminated CO_2 stream comprises CO_2 and contaminants, which contaminants comprise hydrocarbons, oxygenated hydrocarbons, SO_2, H_2S, COS, N_2, amines, or combinations thereof, and (ii) the outlet stream of the adsorbent beds has a concentration of SO_2, H_2S and COS that is less than 20 parts per billion (ppb), and amine and ammonia concentrations of less than 100 ppb;

b. an electrolyzer configured to electrolyze H_2O to produce H_2 and O_2; and

c. a combustion reactor configured to convert a mixture of the adsorbent bed outlet stream and the O_2 from the electrolyzer to a combustor product stream, wherein the contaminants are oxidized in the combustor product stream.

37. The system of Claim 36, wherein a molar flow of O_2 in the combustor feed stream is controlled using a sensor that senses an O_2 to fuel ratio, such that the mixing of the absorbent bed outlet stream with the stream comprising oxygen has an equivalence ratio of less than 1.00, thereby providing a combustor product stream in which a molar amount of hydrocarbon of less than 5% of the molar amount of hydrocarbon in the contaminated CO_2 stream.

38. The system of Claim 36, wherein the combustor product stream is mixed with heated CO_2 and H_2 streams in which the ratio of H_2 and CO_2 is between 1.5 and 4.0.

39. The system of Claim 38, wherein the H_2 and CO_2 streams are separately heated to between 900 and1,250 °F before mixing with the combustor product stream.

40. The system of Claim 39, wherein the heated streams are further heated up to 1,750 °F before introduction into a catalytic reactor which produces a syngas stream that comprises a H_2 and CO mixture with a ratio between 1.0 and 4.0.

41. The system of claim 40, wherein the syngas is input to a catalytic reactor, that is heated using renewable energy to produce low-carbon fuels and chemicals.

42. The system of claim 41, wherein the low-carbon fuels and chemicals have a carbon intensity value that is near zero.

43. A system for producing a renewable fuel or chemical, the system comprising:

a. an electrolyzer configured to use renewable power to electrolyze H_2O and produce H_2 and O_2;

b. a conversion module configured to convert the hydrocarbon in a feed stream to additional CO_2 using at least a portion of the O_2 from the electrolyzer, wherein the fed stream comprising CO_2 and hydrocarbon; and

c. a reactor configured to convert the CO_2 in the feed stream and the H_2 from the electrolyzer into a renewable fuel or chemical.

44. The system of claim 43, wherein the hydrocarbon molecules have less than 8 carbon atoms.

45. The system of claim 43, wherein the hydrocarbon is converted into CO_2 using a thermal oxidation system with the O_2 from electrolysis.

46. The system of claim 45, wherein the thermal oxidation system is oxy-combustion.

47. The system of claim 46, wherein the concentration of hydrocarbon in the feed stream is greater than about 3 wt.%.

48. The system of claim 43, wherein the hydrocarbon is converted into CO_2 using a catalytic oxidation system.

49. The system of claim 48, wherein the concentration of hydrocarbon in the feed stream is less than about 3 wt.%.

50. The system of claim 43, wherein the renewable fuel or chemical is a synthetic diesel fuel.

51. The system of claim 43, wherein the renewable fuel or chemical is a synthetic aviation fuel (SAF).

52. The system of claim 43, wherein the renewable fuel or chemical is a C_5-C_{23} hydrocarbon, alcohol, and/or olefin.

53. The system of claim 43, wherein the feed stream is from a CO_2 pipeline.

54. The system of claim 43, wherein the feed stream is from manufacturing processes.

55. The system of claim 54, wherein the manufacturing process is a process for manufacturing ethanol, cement, steel, lime, or products of petroleum refining.

56. The system of claim 43, wherein the feed stream is CO_2 captured from ambient air.

57. The system of claim 43, further comprising removing sulfur compounds and particulates from the feed stream.

58. The system of claim 43, wherein converting the hydrocarbon to additional CO_2 reduces the concentration of hydrocarbon in the feed stream to less than about 2,000 ppm.

59. The system of claim 43, wherein the hydrocarbon is converted into CO_2 at approximately atmospheric pressure.

60. The system of claim 43, wherein the hydrocarbon is converted into CO_2 at a temperature of less than about 1500 °C.

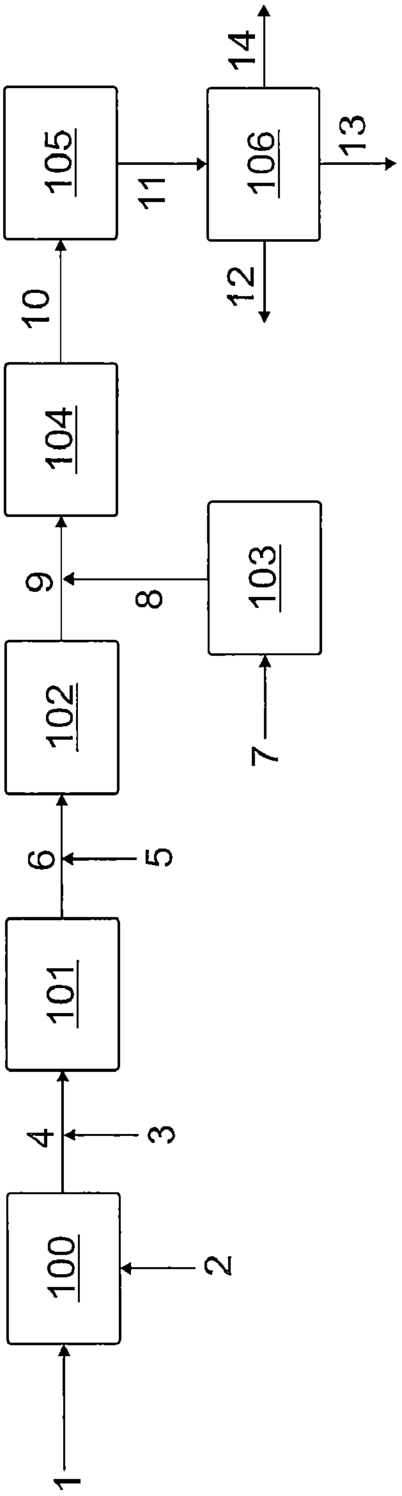

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2022/000007

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/02; B01D 53/04; C25B 1/04 (2022.01)
CPC - B01D 53/02; B01D 53/04; B01D 2256/22; C25B 1/04 (2022.05)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
see Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
see Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
see Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2006-0116325 A (CORE TECHNOLOGY) 15 November 2006 (15.11.2006) see machine translation	1-9, 36-42
Y	US 2012/0316252 A1 (HODOSHIMA et al) 13 December 2012 (13.12.2012) entire document	1-9, 36-42
Y	US 2013/0137783 A1 (KUMAR et al) 30 May 2013 (30.05.2013) entire document	1-9, 36-42
Y	US 2011/0219778 A1 (WIJMANS et al) 15 September 2011 (15.09.2011) entire document	4, 37
Y	WO 2020/208008 A1 (HALDOR TOPSØE A/S) 15 October 2020 (15.10.2020) entire document	6-9, 39-42
A	US 8,198,338 B2 (SHULENBERGER et al) 12 June 2012 (12.06.2012) entire document	1-9, 36-42

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 22 July 2022	Date of mailing of the international search report AUG 10 2022
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Taina Matos Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2022/000007

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet(s).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-9, 36-42

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-9 and 36-42 are drawn to methods for preparing a carbon dioxide stream for use in the production of renewable fuels and chemicals, and systems for preparing a CO2 stream for use in the production of renewable fuels and chemicals.

Group II, claims 10-17 are drawn to methods for producing a CO2 stream that comprises at least 90 mol% CO2.

Group III, claims 18-35 and 43-60 are drawn to methods for producing a renewable fuel or chemical, and systems for producing a renewable fuel or chemical.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, methods for preparing a carbon dioxide stream for use in the production of renewable fuels and chemicals, and systems for preparing a CO2 stream for use in the production of renewable fuels and chemicals, are not present in Groups II-III; the special technical features of Group II, methods for producing a CO 2 stream that comprises at least 90 mol% CO2, are not present in Groups I, and III; and the special technical features of Group III, methods for producing a renewable fuel or chemical, and systems for producing a renewable fuel or chemical, are not present in Groups I, and II.

Additionally, even if Groups I-III were considered to share the technical features of a. providing a contaminated CO2 stream comprising CO2 and contaminants, which contaminants comprise hydrocarbons, oxygenated hydrocarbons, SO2, H2S, CO2, N2, amines, or combinations thereof; c. mixing the adsorbent bed outlet stream with a stream comprising O2 to produce a combustor feed stream; d. feeding the combustor feed stream to a combustion reactor, where the contaminants are oxidized to produce a combustor product stream; an electrolyzer, an electrolyzer configured to electrolyze H2O to produce H2 and O2, and an electrolyzer configured to use renewable power to electrolyze H2O and produce H2 and O2; produce an absorbent product stream that comprises CO2 and hydrocarbons; and wherein hydrocarbons in the combustion feed stream are at least partly combusted to CO2 carbon dioxide, these shared technical features do not represent a contribution over the prior art as disclosed by to KR 10-2006-0116325 A to Core Technology (hereinafter, "Core") and US 8,198,338 B2 to Shulenberger, et al. (hereinafter, "Shulenberger").

Core teaches a. providing a contaminated CO2 stream comprising CO2 and contaminants (abstract, method and an apparatus for producing high purity carbon dioxide; page 3, third paragraph, h moisture, nitrogen, oxygen, methane and ethane gas, and hydrocarbon materials.), which contaminants comprise hydrocarbons, oxygenated hydrocarbons, SO2, H2S, CO2, N2, amines, or combinations thereof (page 3, third paragraph; moisture, nitrogen, oxygen, methane and ethane gas, and hydrocarbon materials); c. mixing the adsorbent bed outlet stream with a stream comprising O2 to produce a combustor feed stream (page 1, claims, part of the water is removed, and a process of separating and removing water and water by passing through an adsorption tower having an adsorbent therein to remove water and moisture from a gas containing water, water, oxygen, nitrogen, and carbon dioxide... cooling step of cooling the flow of carbon dioxide from which water and water have been removed, i.e., a combustor feed stream); d. feeding the combustor feed stream to a combustion reactor, where the contaminants are oxidized to produce a combustor product stream (a means for injecting a predetermined amount of oxygen into a flow of the low purity carbon dioxide in the gas state to easily perform oxidation reaction of the low purity carbon dioxide In the gas state; a combustion furnace(18) in which a decomposition catalyst capable of performing decomposition reaction at a low temperature is embedded to convert the methane, ethane and hydrocarbon material into water and carbon dioxide by oxidizing oxygen, and methane, ethane and hydrocarbon material contained in low purity carbon dioxide); produce an absorbent product stream that comprises CO2 and hydrocarbons (page 1, claims, part of the water is removed, and a process of separating and removing water and water by passing through an adsorption tower having an adsorbent therein to remove water and moisture from a gas containing water, water, oxygen, nitrogen, and carbon dioxide); and wherein hydrocarbons in the combustion feed stream are at least partly combusted to CO2 carbon dioxide (abstract, convert the methane, ethane and hydrocarbon material into water and carbon dioxide by oxidizing oxygen, and methane, ethane and hydrocarbon material contained in low purity carbon dioxide).

Shulenberger teaches an electrolyzer (column 5, lines, 25-26, water is electrolyzed in an electrolysis unit 4 to form hydrogen 6 and oxygen 7), an electrolyzer configured to electrolyze H2O to produce H2 and O2 (column 3, lines 1-2; column 5, lines 25-26, providing water and electricity and electrolyzing the water into hydrogen and oxygen), and an electrolyzer configured to use renewable power to electrolyze H2O and produce H2 and O2 (column 2, lines 66-67; column 3, lines 1-2, process for production of liquid fuel from carbon dioxide and water using electricity comprising: providing water and electricity and electrolyzing the water into hydrogen and oxygen,, column 4, lines 3-6, Electricity is an energy form that may be produced from alternative and renewable energy sources Such as geothermal Sources, Solar power, wind energy, hydro-power, and ocean thermal- or kinematic-power).

The inventions listed in Groups I-III therefore lack unity under Rule 13 because they do not share same or corresponding special technical features.