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AN INTEGRATED PROCESS UTILIZING METHANE OXIDATIVE CONVERSION HEAT FOR ETHYLENE AND METHANOL PRODUCTION

TECHNICAL FIELD

[0001] The present disclosure relates to methods of producing olefins and methanol, more specifically methods of producing ethylene and methanol by integrating hydrocarbon pyrolysis with ethylene and methanol production.

BACKGROUND

[0002] Hydrocarbons, and specifically olefins such as ethylene, can be typically used to produce a wide range of products, for example, break-resistant containers and packaging materials. Currently, for industrial scale applications, ethylene is produced by heating natural gas condensates and petroleum distillates, which include ethane and higher hydrocarbons, and the produced ethylene is separated from a product mixture by using gas separation processes.

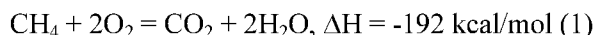
[0003] Methanol is an important chemical building block, which can be used to produce a wide range of products, such as of paints, solvents and plastics, and has found innovative applications in energy, transportation fuel and fuel cells. Methanol is commonly produced from synthesis gas. However, the formation of synthesis gas from natural gas is strongly endothermic and requires high temperatures, which translates in a high energy input.

[0004] Conversion of natural gas (e.g., methane) to useful chemicals is an area of intensive research. Currently, only methane steam reforming reaction, which produces a mixture of carbon monoxide (CO), carbon dioxide (CO₂), and hydrogen (H₂) known as synthesis gas (syngas), has been realized at commercial scale. Other methane conversion processes, such as direct oxidation of methane to methanol and oxidative coupling of methane to C₂ hydrocarbons, have not been commercialized, owing to the deep oxidation of methane to CO₂.

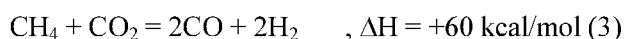
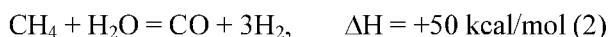
[0005] Significant research has focused on the development of a process which may lead to utilization of CO₂ for the production of useful chemicals, thus increasing an overall efficiency of oxidation reactions. Conversion of CO₂ to useful chemicals can generally be done via its reduction, which is an energy consuming process.

[0006] Given that methane oxidation reactions are exothermic and deep oxidation of methane to CO₂ also produces heat up to about 192 kcal/mol of methane, efficient utilization of deep oxidation reaction heat for conducting of endothermic reactions, particularly CO₂ reduction, could allow an overall increase in carbon and energy efficiency for oxidation reactions.

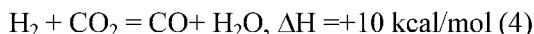
[0007] The concept of utilization of the heat of methane deep oxidation reactions has been applied for production of syngas in the autothermal methane steam reforming process, where a methane and oxygen mixture is burned in the combustion zone of an autothermal reactor to produce heat during the production of deep oxidation products according to reaction (1):



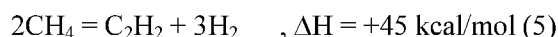
The combustion products having high temperature produced via reaction (1) enter a subsequent reaction zone (having a catalyst bed, in some configurations) where they undergo endothermic reactions (2) and (3) with methane by utilizing the heat of combustion from reaction (1):



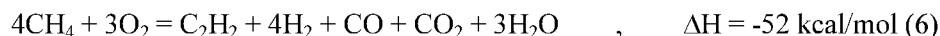
The overall reaction (4) involves the production of a mixture containing H_2 , CO and CO_2 , as well as H_2O , given the equilibrium of water gas shift reaction which takes place in the catalyst bed:



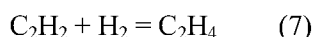
[0008] A similar concept has been used in the process of thermal pyrolysis of methane to acetylene. Generally, conversion of methane to acetylene involves (a) combustion of a portion of methane in a combustion zone to produce heat, which is then used for (b) injection of a separate portion of methane feed to the flame produced in combustion zone and conversion to acetylene according to cracking reaction (5), wherein the temperature of the flame can be more than 2500 °C:



The cracking reaction products can further undergo fast quenching to stop the reaction at the acetylene production stage, and to prevent coke formation. An overall process involving thermal gas phase water shift reaction (4) and cracking reaction (5) can be described by reaction (6):



[0009] Acetylene can be further hydrogenated to ethylene via liquid phase hydrogenation using a supported Pd ($\text{Pd}/\text{Al}_2\text{O}_3$) catalyst according to reaction (7):



which is an exothermic reaction, wherein heat removal occurs by hydrogenating in liquid phase.

[0010] Methane pyrolysis generally produces C_2H_4 , CO , H_2 , CO_2 , and H_2O , wherein a H_2/CO molar ratio is close to the ratio which can be used for methanol synthesis, thus leaving no excess H_2 .

[0011] Conversion of CO_2 needs external energy sources for the production of useful chemicals, such as methanol. Conversion of CO_2 with H_2 to methanol is a known process, but this reaction needs an external H_2 source to meet the requirement of a H_2/CO_2 molar ratio of 3.

Recycling heat is quite common in Europe. For example, Denmark gets roughly half of its electricity from recycled heat. According to a report by Lawrence Livermore National Laboratory and the Department of Energy, the U.S. wastes more than half of the produced energy. However, by using this wasted energy, the U.S. could reduce carbon dioxide emissions. In U.S., conventional coal and natural gas power plants are, on average, 33% and 41% efficient, respectively, in converting the energy in their fuel into electricity; although, the efficiency rates vary by technology, with new natural gas combined-cycle power plants being capable of greater than 50% efficiency.

[0012] Thus, there is an ongoing need for the development of processes for the conversion of methane to desired products, such as olefins (e.g., ethylene) and methanol, by integrating a variety of processes to reduce carbon dioxide emissions and to utilize the heat of exothermic reactions, thereby improving the overall efficiency of such processes.

BRIEF SUMMARY

[0013] Disclosed herein is a process for producing ethylene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product, (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2), (d) cooling at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid, and (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity.

[0014] Also disclosed herein is a process for producing ethylene and methanol comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product, (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2), (d) cooling

at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid, (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity, (f) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream, (g) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas, (h) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C₂H₂, C₂H₄, CO, and H₂, (i) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO, (j) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst, (k) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream, (l) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO, and (m) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

[0015] Further disclosed herein is a process for producing ethylene and methanol comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product, (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C₂H₂), ethylene (C₂H₄), carbon monoxide (CO), hydrogen (H₂), water (H₂O), and carbon dioxide (CO₂), (d) quenching at least a portion of the pyrolysis reaction product in a quench zone to produce a quenched pyrolysis reaction product, wherein the quenched pyrolysis reaction product comprises at least a portion of the pyrolysis reaction product, wherein the quenched pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature, (e) introducing at least a portion of the quenched pyrolysis reaction product to a heat exchanger to produce a cooled pyrolysis reaction

product and steam, wherein the cooled pyrolysis reaction product is characterized by a third temperature, and wherein the third temperature is lower than the second temperature, (f) feeding at least a portion of the steam to an electricity generator to produce electricity, (g) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream, (h) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas, (i) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C₂H₂, C₂H₄, CO, and H₂, (j) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO, (k) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst, (l) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream, (m) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO, and (n) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] For a detailed description of the preferred aspects of the disclosed methods, reference will now be made to the accompanying drawing in which:

[0017] Figure 1 displays a schematic of an ethylene and methanol production system;

[0018] Figure 2 displays another schematic of an ethylene and methanol production system; and

[0019] Figure 3 displays a graph of product concentration over time for a carbon dioxide to syngas conversion.

DETAILED DESCRIPTION

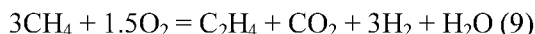
[0020] Disclosed herein are processes for producing ethylene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C₂H₂), ethylene (C₂H₄), carbon monoxide (CO), hydrogen (H₂), water (H₂O), and carbon dioxide (CO₂); (d) cooling at least a portion of the pyrolysis reaction product in a

quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid; and (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity. The process can further comprise recovering a syngas (CO and H₂) from the cooled pyrolysis reaction product, and using at least a portion of the syngas for the production of methanol (CH₃OH).

[0021] The process for producing ethylene as disclosed herein can comprise utilizing at least a portion of the heat generated by the combustion process to sustain methane pyrolysis, and also generate electricity to power water electrolysis, wherein water gets split into H₂ and oxygen (O₂), according to reaction (8):



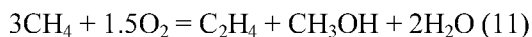
The O₂ produced by water splitting reaction (8) can be recycled to the combustion zone as the oxidant gas. The H₂ produced by water splitting reaction (8) can be further used to hydrogenate CO₂ to syngas, which can be further used for methanol production. Utilizing some of the combustion heat to produce electricity for water splitting can prevent or minimize wasting energy produced in the process. A portion of the heat can be captured during the step (d) of cooling at least a portion of the pyrolysis reaction product in a quench zone, which heat would otherwise be lost as quench waste energy. Without wishing to be limited by theory, even with utilization of quench waste energy for generation of electricity to split water according to reaction (8), an overall reaction can be written according to reaction (9):



which is an exothermic reaction. The CO₂ produced according to reaction (9) is present in the products in a H₂/CO₂ molar ratio of 3, and the CO₂ could be further converted to methanol through direct exothermic hydrogenation reaction (10):



By accounting for reaction (10), reaction (9) can be written as an overall methane conversion reaction (11):



which is also an exothermic reaction. Reaction (11) provides a pathway of methane conversion to desired chemicals, such as C₂H₄ and CH₃OH, which can be achieved in an energy efficient manner and without CO₂ emissions by utilizing the quench waste energy to generate electricity for splitting water.

[0022] Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, and the like, used in the specification and claims are to be understood as modified in all instances by the term “about.” Various numerical ranges are disclosed herein. Because these ranges are continuous, they include every value between the minimum and maximum values. The endpoints of all ranges reciting the same characteristic or component are independently

combinable and inclusive of the recited endpoint. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations. The endpoints of all ranges directed to the same component or property are inclusive of the endpoint and independently combinable. The term “from more than 0 to an amount” means that the named component is present in some amount more than 0, and up to and including the higher named amount.

[0023] The terms “a,” “an,” and “the” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. As used herein the singular forms “a,” “an,” and “the” include plural referents.

[0024] As used herein, “combinations thereof” is inclusive of one or more of the recited elements, optionally together with a like element not recited, e.g., inclusive of a combination of one or more of the named components, optionally with one or more other components not specifically named that have essentially the same function. As used herein, the term “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0025] Reference throughout the specification to “an aspect,” “another aspect,” “other aspects,” “some aspects,” and so forth, means that a particular element (e.g., feature, structure, property, and/or characteristic) described in connection with the aspect is included in at least an aspect described herein, and may or may not be present in other aspects. In addition, it is to be understood that the described element(s) can be combined in any suitable manner in the various aspects.

[0026] As used herein, the terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, include any measurable decrease or complete inhibition to achieve a desired result.

[0027] As used herein, the term “effective,” means adequate to accomplish a desired, expected, or intended result.

[0028] As used herein, the terms “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”) or “containing” (and any form of containing, such as “contain” and “contains”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0029] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art.

[0030] Compounds are described herein using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valency filled by a bond as indicated, or a hydrogen atom. A dash (“-”) that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, -CHO is attached through the carbon of the carbonyl group.

[0031] Referring to Figure 1, an ethylene and methanol production system 101 is disclosed. The ethylene and methanol production system 101 generally comprises a pyrolysis unit 10 comprising a combustion zone 11,

a cracking zone 12 (e.g., first reaction zone), and a quench zone 13; an electricity generating unit 15; a first separation unit 16; an electrolysis unit 20; a CO₂ hydrogenation to syngas unit 30; a liquid phase hydrogenation unit 40 (e.g., second reaction zone); a second separation unit 50; and a methanol production reactor 60 (e.g., third reaction zone).

[0032] Referring to Figure 2, an ethylene and methanol production system 102 is disclosed. The ethylene and methanol production system 102 generally comprises a pyrolysis unit 10 comprising a combustion zone 11, a cracking zone 12 (e.g., first reaction zone), and a quench zone 13; a heat exchanger 14; an electricity generating unit 15; a first separation unit 16; an electrolysis unit 20; a CO₂ hydrogenation to syngas unit 30; a liquid phase hydrogenation unit 40 (e.g., second reaction zone); a second separation unit 50; and a methanol production reactor 60 (e.g., third reaction zone). As will be appreciated by one of skill in the art, and with the help of this disclosure, ethylene and methanol production system components shown in Figures 1 and 2 can be in fluid communication with each other (as represented by the connecting lines indicating a direction of fluid flow) through any suitable conduits (e.g., pipes, streams, etc.). Common reference numerals refer to common components present in one or both of the Figures, and the description of a particular component is generally applicable across respective Figures wherein the component is present, except as otherwise indicated herein.

[0033] The pyrolysis unit 10 can comprise the combustion zone 11 and the cracking zone 12 (e.g., first reaction zone). Impurities and contaminants can be removed from a fuel gas stream and/or a hydrocarbon stream prior to introducing to the combustion zone 11 and/or the cracking zone 12, respectively. In some aspects, the fuel gas stream and the hydrocarbon stream can be the same (e.g., can comprise the same hydrocarbons, for example can be portions of the same gas stream feedstock). In other aspects, the fuel gas stream and the hydrocarbon stream can be different (e.g., can comprise different hydrocarbons, for example originating from different upstream sources).

[0034] The fuel gas stream and/or the hydrocarbon stream can comprise methane, ethane, propane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, heavy hydrocarbons, petcoke, naphtha, heavy oil, heavy oil residue, and the like, or combinations thereof. Generally, natural gas is a naturally occurring hydrocarbon gas mixture comprising mostly methane, but commonly including varying amounts of other higher alkanes, and sometimes a small percentage of carbon dioxide, nitrogen, hydrogen sulfide, helium, etc. Heavy oil residues generally comprise polyalkylbenzenes such as polyethylbenzenes (PEBs), as well as multi-ring compounds. Petcoke generally refers to a carbonaceous solid produced in oil refinery coker units or other cracking processes. Heavy hydrocarbons generally comprise hydrocarbons which are solid or extremely viscous at standard processing conditions, and can include materials such as, but not limited to, asphaltenes, tars, paraffin waxes, coke, refining residues, and other similar residual hydrocarbon materials. Heavy hydrocarbons can include any material that comprises a majority of hydrocarbon materials with a molecular weight range of about 700 to 2,000,000 Daltons. Heavy oil generally refers to heavy crude, oils sands bitumen,

bottom of the barrel and residue left over from refinery processes (e.g., visbreaker bottoms), and any other lower quality material that contains a substantial quantity of high boiling hydrocarbon fractions (e.g., that boil at or above 343 °C, or alternatively at or above about 524 °C). Nonlimiting examples of heavy oil feedstocks include, but are not limited to, Lloydminster heavy oil, Cold Lake bitumen, Athabasca bitumen, atmospheric tower bottoms, vacuum tower bottoms, residuum (or “resid”), resid pitch, vacuum residue, and nonvolatile liquid fractions that remain after subjecting crude oil, bitumen from tar sands, liquefied coal, oil shale, or coal tar feedstocks to distillation, hot separation, and the like; and that contain higher boiling fractions and/or asphaltenes. Naptha generally comprises flammable liquid hydrocarbon mixtures.

[0035] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise a step of introducing the fuel gas stream (e.g., comprising methane) and an oxidant gas to the combustion zone 11 to produce a combustion product. The combustion zone 11 can comprise a burner, such as an in-line burner; a furnace; or combinations thereof; wherein the fuel gas stream is burned (e.g., combusted) with the oxidant gas to produce the combustion product. The oxidant gas can comprise oxygen, purified oxygen, air, oxygen-enriched air, and the like, or combinations thereof. In some aspects, the oxidant gas is oxygen-enriched, such as oxygen-enriched air, to minimize NO_x production in the combustion zone. As will be appreciated by one of skill in the art, and with the help of this disclosure, NO_x products can be acidic and as such would necessitate downstream removal. Water or steam can be further introduced to the combustion zone to lower and thereby control the combustion product temperature. The combustion product generally comprises combustion products, such as carbon monoxide (CO), CO₂, water (H₂O), as well as some unconverted hydrocarbons (e.g., hydrocarbons that were present in the fuel gas stream and did not combust). Depending on the configuration of the pyrolysis unit 10, the combustion product may not be isolatable, and it might be introduced as produced to the cracking zone 12.

[0036] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise introducing a first reactant mixture to the cracking zone 12 (e.g., first reaction zone), wherein the first reactant mixture comprises the hydrocarbon stream (e.g., comprising methane) and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; and allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product. The pyrolysis reaction product can comprise unconverted hydrocarbons (e.g., methane), acetylene (C₂H₂), C₂H₄, CO, H₂, water, and CO₂.

[0037] In an aspect, the cracking zone 12 (e.g., first reaction zone) zone excludes a catalyst. As will be appreciated by one of skill in the art, and with the help of this disclosure, while there are catalytic processes for hydrocarbon pyrolysis (e.g., methane pyrolysis), the current disclosure does not utilize a catalyst for hydrocarbon pyrolysis; the hydrocarbon pyrolysis as disclosed herein is thermal.

[0038] In some aspects, the pyrolysis unit 10 can comprise a reactor that contains both the combustion zone 11 and the cracking zone 12. In other aspects, the pyrolysis unit 10 can comprise a furnace that contains the combustion zone 11; and a reactor that contains the cracking zone 12 and is configured to receive the combustion product from the furnace comprising the combustion zone 11. A diluent such as an inert gas (e.g., nitrogen, argon, helium, etc.) and/or steam can be further introduced to the cracking zone 12.

[0039] The hydrocarbon stream can be further pre-heated in pre-heaters (e.g., electrical heaters, heat exchangers, etc.) before being heated to the first temperature (e.g., temperature effective for the pyrolysis reaction) by direct heat exchange through contact with the combustion product. A temperature of the combustion product can be a temperature effective to reach a pyrolysis reaction temperature (e.g., first temperature, cracking zone temperature) of equal to or greater than about 1,000 °C, alternatively equal to or greater than about 1,500 °C, alternatively equal to or greater than about 2,000 °C, alternatively equal to or greater than about 2,250 °C, alternatively equal to or greater than about 2,500 °C, alternatively from about 1,000 °C to about 2,500 °C, alternatively from about 1,500 °C to about 2,500 °C, or alternatively from about 2,000 °C to about 2,500 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, higher temperatures in the cracking zone 12 favor alkyne (e.g., acetylene) formation, while lower temperatures in the cracking zone 12 favor olefin or alkene (e.g., ethylene) formation.

[0040] In an aspect, the cracking zone 12 can be characterized by a residence time effective to allow for the conversion of at least a portion of the first reactant mixture to acetylene and ethylene. The cracking zone 12 can be characterized by a residence time of from about 0.1 milliseconds (ms) to 100 ms, alternatively from about 0.5 ms to about 80 ms, or alternatively from about 1 ms to about 50 ms.

[0041] Suppression or reduction of reactions leading to products other than the desired products (e.g., alkynes, acetylene, olefins, ethylene) may be required to achieve the desired products. This may be accomplished by adjusting the reaction temperature, pressure, and/or quenching after a desired residence time. In some aspects, the hydrocarbon stream that is introduced to the cracking zone 12 can be characterized by a pressure of from about 1 bar to about 20 bar (e.g., from about 100 kPa to about 2,000 kPa), to achieve the desired products.

[0042] The pyrolysis unit 10 can be designed to accommodate one or more gas feed streams (e.g., fuel gas stream, hydrocarbon stream), which may employ natural gas combined with other gas components including, but not limited to hydrogen, carbon monoxide, carbon dioxide, ethane, and ethylene. The pyrolysis unit 10 can be designed to accommodate one or more oxidant gas streams, such as an oxygen stream and an oxygen-containing stream, for example an air stream, which employ unequal oxidant concentrations for purposes of temperature or composition control. As will be appreciated by one of skill in the art, and with the help of this disclosure, the pyrolysis unit 10 may comprise a single device or multiple devices. Each device of the pyrolysis unit 10 may comprise one or more sections. Products from the combustion zone 11 are

communicated to the cracking zone 12 via the combustion product stream. Depending on the type and configuration of the pyrolysis unit 10 used, the combustion product stream may not be isolatable (for example, in configurations where the combustion zone 11 and the cracking zone 12 are contained within a common vessel or reactor).

[0043] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise cooling at least a portion of the pyrolysis reaction product in the quench zone 13 by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid.

[0044] In some aspects, the second temperature can be from about 600 °C to about 1,000 °C, alternatively from about 700 °C to about 950 °C, or alternatively from about 800 °C to about 900 °C. The quenching fluid can be characterized by a temperature (e.g., an inlet temperature) of from about 40 °C to about 80 °C, alternatively from about 45 °C to about 75 °C, or alternatively from about 50 °C to about 70 °C. The heated quenching fluid can be characterized by a temperature (e.g., an outlet temperature) of from about 600 °C to about 800 °C, alternatively from about 625 °C to about 775 °C, or alternatively from about 650 °C to about 750 °C.

[0045] In some aspects, to stop pyrolysis reactions occurring in the cracking zone 12, prevent undesired reverse reactions, or prevent further reactions that form carbon and hydrocarbon compounds other than the desired products, rapid cooling or “quenching” of pyrolysis reaction products can be employed. In an aspect, the pyrolysis unit 10 can further comprise a quench zone 13, wherein the pyrolysis reaction products are quenched prior to exiting the pyrolysis unit 10 via the cooled pyrolysis reaction product. The quench zone 13 can employ any suitable quenching methods, for example spraying a quenching fluid such as steam, water, hydrocarbons, oil, liquid product, and the like, or combinations thereof into a reactor quench zone or chamber; conveying the product stream through or into water, natural gas feed, or liquid products; heat exchange; preheating other streams such as fuel gas stream and/or hydrocarbon stream; generating steam; expanding in a kinetic energy quench, such as a Joule Thompson expander, choke nozzle, turbo expander, etc.; or combinations thereof. As will be appreciated by one of skill in the art, and with the help of this disclosure, the quench zone 13 may be incorporated within a pyrolysis reactor, may comprise a separate vessel or device from the pyrolysis reactor, or both. Pyrolysis units for the production of acetylene and ethylene from hydrocarbons are described in more detail in U.S. Patent Nos. 5,824,834; 5,789,644; and 8,445,739; and U.S. Patent Application No. 2010/0167134 A1; each of which is incorporated by reference herein in its entirety.

[0046] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise cooling at least a portion of the pyrolysis reaction product to produce a cooled pyrolysis reaction product and

thermal energy, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature. In some aspects, the thermal energy can be recovered from the quench zone 13, e.g., the cooling of the pyrolysis reaction product to produce a cooled pyrolysis reaction product occurs substantially in the quench zone 13. In other aspects, a first portion of the thermal energy can be recovered from the quench zone 13, and a second portion of the thermal energy can be recovered in a unit subsequent to the quench zone 13, for example in the heat exchanger 14 positioned downstream of the quench zone 13.

[0047] In an aspect, thermal energy can be produced by at least a portion of the pyrolysis reaction product exchanging heat with a quenching fluid, a heat exchange fluid, or both a quenching fluid and a heat exchange fluid. In an aspect, thermal energy can be recovered from the quench zone 13 by (i) indirect heat exchange; (ii) direct heat exchange; or (iii) both direct heat exchange and indirect heat exchange. As will be appreciated by one of skill in the art, and with the help of this disclosure, during indirect heat exchange, the streams (e.g., pyrolysis reaction product, and quenching fluid and/or heat exchange fluid) that exchange heat do not contact each other, as they are separated by a wall (usually a metal wall), and the streams exchange heat across the wall. Further, as will be appreciated by one of skill in the art, and with the help of this disclosure, during direct heat exchange, the streams (e.g., pyrolysis reaction product, and quenching fluid and/or heat exchange fluid) that exchange heat contact each other, and can be further separated from each other, subsequent to exchanging heat with each other.

[0048] In some aspects, thermal energy (e.g., a first portion of the thermal energy) can be recovered from the quench zone 13 by indirect heat exchange, wherein the quenching fluid (e.g., a heat exchange fluid) can be contained inside heat exchange elements within the quench zone 13, such as pipes running through the quench zone 13. The quenching zone 13 can comprise a heat exchanger. In such aspects, the quenching fluid can be water, and the heated quenching fluid can be recovered as steam from the heat exchange elements. While the current disclosure is discussed in detail in the context of a quenching fluid and/or a heat exchange fluid comprising water, it should be understood that any suitable quenching fluid and/or heat exchange fluid can be used, such as hydrocarbons, oils, mineral oils, molten salts, etc. The quenching fluid and the heat exchange fluid can be the same or different. In configurations where the quenching fluid exchanges heat indirectly with the pyrolysis reaction product, the quenching fluid can be a heat exchange fluid.

[0049] In some aspects, thermal energy (e.g., a first portion of the thermal energy) can be recovered from the quench zone 13 by direct heat exchange, wherein the quenching fluid can be contacted directly with the pyrolysis reaction product within the quench zone 13. Depending on the composition and/or flow rate of each of the pyrolysis reaction product and the quenching fluid, the heated quenching fluid and the cooled pyrolysis reaction product can be recovered from the quenching zone 13 as separate (distinct) streams, or as a common stream, wherein the common stream can be further separated into the heated quenching fluid and the cooled

pyrolysis reaction product. In such aspects, the quenching fluid can be water, and the heated quenching fluid can be recovered as steam from the quenching zone 13 and/or from the common stream comprising both the heated quenching fluid and the cooled pyrolysis reaction product.

[0050] In aspects wherein a first portion of the thermal energy is recovered from the quench zone 13 and a second portion of the thermal energy is recovered from a unit subsequent to the quench zone 13, a process for producing ethylene and methanol as disclosed herein can comprise (i) quenching at least a portion of the pyrolysis reaction product in the quench zone 13 to produce a quenched pyrolysis reaction product and the first portion of the thermal energy, wherein the quenched pyrolysis reaction product comprises at least a portion of the pyrolysis reaction product, and wherein the quenched pyrolysis reaction product is characterized by the second temperature, wherein the second temperature is lower than the first temperature; and (ii) introducing at least a portion of the quenched pyrolysis reaction product to the heat exchanger 14 to produce a cooled pyrolysis reaction product and the second portion of the thermal energy, wherein the cooled pyrolysis reaction product is characterized by a third temperature, and wherein the third temperature is lower than the second temperature. For purposes of the disclosure herein, the cooled pyrolysis product characterized by the second temperature can also be referred to as “quenched pyrolysis reaction product.” The quenched pyrolysis reaction product can be further cooled to produce a cooled pyrolysis reaction product characterized by the third temperature, and the second portion of the thermal energy. The first portion of the thermal energy and/or the second portion of the thermal energy can be recovered as steam. The quenched pyrolysis reaction product can exchange heat with a quenching fluid and/or a heat exchange fluid comprising water to produce the cooled pyrolysis reaction product characterized by the third temperature and a heated quenching fluid and/or a heated heat exchange fluid, respectively (e.g., steam). In some aspects, the third temperature can be from about 100 °C to about 900 °C, alternatively from about 110 °C to about 700 °C, or alternatively from about 120 °C to about 500 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, in some configurations, the acetylene in the cooled pyrolysis reaction product is meant to be hydrogenated in liquid phase to ethylene, which hydrogenation process generally occurs below about 250 °C, and as such a gas mixture that will be sent to the liquid phase hydrogenation process requires a temperature below about 250 °C (e.g., cooled pyrolysis reaction product characterized by the third temperature).

[0051] In some aspects, the heated quenching fluid can comprise steam. As will be appreciated by one of skill in the art, and with the help of this disclosure, usually a water quench is applied for quenching of hot gases having high temperatures (e.g., greater than about 2,000 °C), wherein the water quench can produce high temperature steam.

[0052] In other aspects, the heated quenching fluid can be introduced to a heat exchanger to produce steam, wherein the heated quenching fluid can exchange heat with a heat exchange fluid such as water to produce steam.

[0053] In an aspect, the heated quenching fluid and/or the cooled pyrolysis reaction product characterized by the second temperature can be introduced to a heat exchanger to produce steam, wherein the heated quenching fluid and/or the cooled pyrolysis reaction product characterized by the second temperature, respectively can exchange heat with a heat exchange fluid such as water to produce steam. In some aspects, the heated quenching fluid and the cooled pyrolysis reaction product characterized by the second temperature can be separate streams introduced to the heat exchanger. In other aspects, the heated quenching fluid and the cooled pyrolysis reaction product characterized by the second temperature can be part of the same common stream introduced to the heat exchanger, wherein the cooled pyrolysis reaction product can be recovered from the common stream downstream of the heat exchanger, as the cooled pyrolysis reaction product characterized by the third temperature.

[0054] The cooled pyrolysis reaction product (regardless of its temperature) can comprise unconverted hydrocarbons (e.g., methane), acetylene, ethylene, CO, H₂, water, and CO₂. As will be appreciated by one of skill in the art, and with the help of this disclosure, in configurations where quenching of the pyrolysis reaction product occurs via indirect heat exchange (e.g., the pyrolysis reaction product does not come in direct contact with a quenching fluid such as steam, water, oil, hydrocarbons, or liquid product, etc.), the composition of the cooled pyrolysis reaction product is substantially the same as the composition of the pyrolysis reaction product, although some components could have changed phase, for example from a gas phase to a vapor phase or a liquid phase. Further, as will be appreciated by one of skill in the art, and with the help of this disclosure, in configurations where quenching of the pyrolysis reaction product occurs via direct heat exchange (e.g., the pyrolysis reaction product comes in direct contact/is sprayed with a quenching fluid such as steam, water, oil, hydrocarbons, or liquid product, etc.), the composition of the cooled pyrolysis reaction product will also account for the added quenching fluid. For example, when the quenching fluid used for direct heat exchange is water or steam, the cooled pyrolysis reaction product will have a higher water content as compared to a water content of the pyrolysis reaction product.

[0055] In some aspects, the cooled pyrolysis reaction product can be further compressed (e.g., via a compressor), for example to a pressure in the range of from about 150 psig to about 300 psig, alternatively about 175 psig to about 275 psig, or alternatively about 200 psig to about 250 psig, followed by optionally feeding the compressed cooled pyrolysis reaction product to a water removal unit. Generally, compressing a gas that contains water to increase its pressure will lead to the water condensing at the increased pressure at an increased temperature as compared to a temperature where water of an otherwise similar gas condenses at pressure lower than the increased pressure. The compressed cooled pyrolysis reaction product can be further introduced to a water removal unit (e.g., a water quench vessel and/or a cooling tower), where the compressed cooled pyrolysis reaction product can be further cooled to promote water condensation and removal. In some aspects, water can be recovered from the cooled pyrolysis reaction product as steam.

[0056] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise converting at least a portion of the thermal energy into electrical energy, for example by feeding at least a portion of the heated quenching fluid and/or at least a portion of the heated heat exchange fluid to the electricity generator 15 to produce electricity. Generally, an electricity generator is a device that converts a type of energy other than electrical energy, such as thermal energy, mechanical energy, etc., into electrical energy (e.g., electricity). The electricity generator can comprise a turbine, a thermoelectric generator, a thermionic convertor, and the like, or combinations thereof.

[0057] A fluid, such as steam, can be fed to a turbine, wherein the moving part of the turbine rotates (spins), while a shaft connected to the spinning part can be connected to a turbogenerator that can convert the mechanical spinning energy into electricity. In some aspects, the heated quenching fluid and/or the heated heat exchange fluid can comprise steam, and the turbine can comprise a steam turbine, wherein at least a portion of the steam is fed to the steam turbine to produce electricity.

[0058] Generally, a thermoelectric generator (TEG), also known as a Seebeck generator, is a solid state device that converts heat or thermal energy (temperature differences) directly into electrical energy through a thermoelectric effect known as the Seebeck effect.

[0059] A thermionic converter has two electrodes, wherein one electrode is raised to a sufficiently high temperature to become a thermionic electron emitter, or “hot plate,” and wherein the other electrode, referred to as a “collector” because it receives the emitted electrons, is operated at a significantly lower temperature than the temperature of the thermionic electron emitter. The movement of electrons between the two electrodes generates electricity. The space between the electrodes can be vacuum, or it can be filled with a low pressure vapor or gas. Thermionic converters are solid state devices with no moving parts.

[0060] In some aspects, the step of cooling the pyrolysis product in the quench zone to produce thermal energy and the step of converting at least a portion of the thermal energy into electrical energy occur about concurrently, for example by co-generating steam and electricity.

[0061] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise using at least a portion of the electricity for water electrolysis (e.g., splitting water) in the electrolysis unit 20 to produce a hydrogen stream and an oxygen stream. In an aspect, at least a portion of the oxygen stream can be recycled to the combustion zone 11.

[0062] In some aspects, water electrolysis can be conducted under conventional conditions, for example wherein liquid water can be split into hydrogen and oxygen. Water electrolysis cells or units typically employ stainless steel or nickel-based electrodes which operate in a potassium hydroxide solution at a concentration range of 6-9 molar and a temperature range of 60-80 °C.

[0063] In other aspects, high temperature steam can be subjected to electrolysis to produce hydrogen and oxygen. As will be appreciated by one of skill in the art, and with the help of this disclosure, while the steam

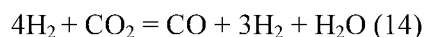
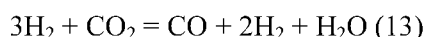
generated in the quench zone 13 and/or the heat exchanger 14 can be used for electricity generation in the electricity generator 15, a portion of the steam generated in the quench zone 13 and/or the heat exchanger 14 could be used for electrolysis.

[0064] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise separating at least a portion of the cooled pyrolysis reaction product in the first separation unit 16 into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons (e.g., methane), C₂H₂, C₂H₄, CO, and H₂.

[0065] In some aspects, least a portion of CO₂ can be removed from the cooled pyrolysis reaction product by using a CO₂ separator to produce a CO₂ stream. The CO₂ separator can comprise CO₂ removal by amine (e.g., monoethanolamine) absorption (e.g., amine scrubbing), pressure swing adsorption, temperature swing adsorption, gas separation membranes (e.g., porous inorganic membranes, palladium membranes, polymeric membranes, zeolites, etc.), and the like, or combinations thereof. In an aspect, the CO₂ separator can comprise CO₂ removal by amine absorption.

[0066] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst in the CO₂ hydrogenation to syngas unit 30 to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO. The first syngas stream can be characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1, alternatively from about 1.1:1 to about 1.95:1, or alternatively from about 1.2:1 to about 1.9:1.

[0067] CO₂ can be converted to syngas by using a hydrogenating agent, e.g., hydrogen or any suitable compound that can provide hydrogen for hydrogenation reaction. Hydrogenation of CO₂ to syngas composition can be described by reactions (12)-(14):



wherein reaction (12) is an equilibrium controlled reaction which depends on the H₂/CO₂ ratio, as it can be seen from reactions (13) and (14). A catalyst for CO₂ hydrogenation to syngas can comprise mixed oxides of redox types, for example chromium (Cr), iron (Fe), manganese (Mn), or copper (Cu) based oxides. In some aspects, the hydrogenation of carbon dioxide to syngas can be conducted in the presence of a CATOFIN catalyst, which is a chromium (Cr) based catalyst commercially available from Clariant, wherein the resulting syngas composition is suitable for methanol and/or olefins synthesis. As will be appreciated by one of skill in the art, and with the help of this disclosure, the composition of syngas produced by CO₂ hydrogenation is dependent upon the H₂/CO₂ ratio and on a CO₂ hydrogenation temperature. In some aspects, the CO₂ hydrogenation

temperature can be from about 500 °C to about 700 °C, alternatively from about 600 °C to about 650 °C, or alternatively about 630 °C.

[0068] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise introducing at least a portion of the acetylene stream and a polar aprotic solvent to the liquid phase hydrogenation unit 40 (e.g., second reaction zone), wherein the liquid phase hydrogenation unit 40 comprises an acetylene hydrogenation catalyst; and allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons (e.g., methane), C₂H₄, CO, and H₂, and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream. At least a portion of the H₂ in the acetylene stream hydrogenates at least a portion of the acetylene of the acetylene stream to produce ethylene.

[0069] Nonlimiting examples of polar aprotic solvents suitable for use in the present disclosure include N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and the like, or combinations thereof.

[0070] The liquid phase hydrogenation unit 40 can be any suitable liquid phase hydrogenation reactor, such as a fixed bed catalytic reactor (typically operated adiabatically); and/or a tubular reactor (typically operated isothermally). Generally, the liquid phase hydrogenation unit 40 comprises an acetylene hydrogenation catalyst, such as a palladium (Pd) based catalyst, which can be supported on alumina, zeolites, etc. The hydrogenation catalyst can further comprise other metals, such as platinum, silver, nickel, etc. In an aspect, the acetylene hydrogenation catalyst can comprise Pd/Al₂O₃. Liquid phase hydrogenation of acetylene processes are described in more detail in U.S. Patent No. 4,128,595, which is incorporated by reference herein in its entirety.

[0071] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise separating at least a portion of the second reaction zone effluent in the second separation unit 50 into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO. The second syngas stream can be characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1, alternatively from about 1.1:1 to about 1.95:1, or alternatively from about 1.2:1 to about 1.9:1. In some aspects, the second separation unit 50 can employ distillation and/or cryogenic distillation to produce the ethylene stream and the second syngas stream. Other components present in the effluent from the first and/or second reaction zones may be recovered via one or more additional streams produced in the first separation unit and/or the second separation unit, respectively.

[0072] In an aspect, a process for producing ethylene and methanol as disclosed herein can comprise introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to the methanol production reactor 60 (e.g., third reaction zone) comprising a methanol production catalyst to

produce a methanol stream. The methanol production reactor 60 can comprise any reactor suitable for a methanol synthesis reaction from CO and H₂, such as for example an isothermal reactor, an adiabatic reactor, a slurry reactor, a cooled multi tubular reactor, and the like, or combinations thereof.

[0073] In some aspects, at least a portion of the first syngas stream and/or at least a portion of the second syngas stream could be mixed with methane steam reforming syngas (e.g., syngas produced by steam reforming of methane), and subsequently fed to methanol synthesis (e.g., methanol production reactor 60; third reaction zone). A feed stream (e.g., the first syngas stream and/or the second syngas stream) to the methanol production reactor 60 can be characterized by a H₂/CO molar ratio of about 2:1, alternatively about 2.1:1, alternatively from about 1.5:1 to about 2.5:1, alternatively from about 1.8:1 to about 2.3:1, or alternatively from about 2.0:1 to about 2.1:1. The H₂/CO molar ratio of the feed stream to the methanol production reactor 60 can be adjusted as necessary to meet the requirements of the methanol production reactor 60, for example by mixing with methane steam reforming syngas.

[0074] In an aspect, at least a portion of the CO and at least a portion of the H₂ of a feed stream to the methanol production reactor 60 (e.g., at least a portion of the first gas stream and/or at least a portion of the second gas stream) can undergo a methanol synthesis reaction. Generally, CO and H₂ can be converted into methanol (CH₃OH) according to reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$. Methanol synthesis from CO and H₂ is a catalytic process, and is most often conducted in the presence of copper based catalysts. The methanol production reactor 60 can comprise a methanol production catalyst, such as any suitable commercial catalyst used for methanol synthesis. Nonlimiting examples of methanol production catalysts suitable for use in the methanol production reactor 60 in the current disclosure include Cu, Cu/ZnO, Cu/ThO₂, Cu/Zn/Al₂O₃, Cu/ZnO/Al₂O₃, Cu/Zr, and the like, or combinations thereof.

[0075] In an aspect, a process for producing ethylene and methanol can comprise the steps of (a) introducing a fuel gas stream (e.g., comprising methane) and an oxidant gas to a combustion zone to produce a combustion product and combustion heat; (b) reacting a first reactant mixture in a cracking zone, wherein the first reactant mixture comprises a hydrocarbon stream (e.g., comprising methane) and at least a portion of the combustion product, wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction to produce a pyrolysis reaction product, wherein the first temperature is equal to or greater than about 2,000 °C, and wherein the pyrolysis reaction product comprises unconverted hydrocarbons (e.g., methane), acetylene (C₂H₂), ethylene (C₂H₄), carbon monoxide (CO), hydrogen (H₂), water (H₂O), and carbon dioxide (CO₂); (c) cooling at least a portion of the pyrolysis reaction product to produce a cooled pyrolysis reaction product and thermal energy, wherein the cooled pyrolysis reaction product is characterized by a second temperature of from about 800 °C to about 900 °C; (d) converting at least a portion of the thermal energy into electrical energy in a steam turbine; (e) splitting water in an electrolysis unit into a hydrogen stream and an oxygen stream by using at least a portion of the electrical energy; (f) recycling at least

a portion of the oxygen stream to step (a) as the oxidant gas; (g) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons (e.g., methane), C₂H₂, C₂H₄, CO, and H₂; (h) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO in a H₂/CO molar ratio of from about 1.8:1 to about 2:1; (i) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a liquid phase hydrogenation unit, wherein the liquid phase hydrogenation unit comprises a Pd based acetylene hydrogenation catalyst; (j) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons (e.g. methane), C₂H₄, CO, and H₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream; (k) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO in a H₂/CO molar ratio of from about 1.8:1 to about 2:1; and (l) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a methanol production reactor comprising a Cu based methanol production catalyst to produce a methanol stream.

[0076] In an aspect, a process for producing ethylene and methanol as disclosed herein can advantageously display improvements in one or more process characteristics when compared to an otherwise similar process that does not integrate hydrocarbon pyrolysis with other processes for producing desired products. The process for producing ethylene and methanol as disclosed herein can advantageously use waste energy from the quench zone for generation of electricity, which electricity can be advantageously used for water electrolysis to produce hydrogen and oxygen. The hydrogen produced by electrolysis can be used to hydrogenate carbon dioxide from combustion and pyrolysis to syngas, thereby increasing the overall efficiency of the process, while minimizing CO₂ emissions.

[0077] A synthesis gas (e.g., H₂ and CO) to methanol conversion process as disclosed herein can increase further the overall efficiency of the process by producing methanol from the H₂ and CO obtained from hydrocarbon pyrolysis, as well as CO₂ hydrogenation. Methanol can be advantageously used as a liquid fuel, and can be easily transported, as compared to transporting gases. Additional advantages of the process for producing ethylene and methanol as disclosed herein can be apparent to one of skill in the art viewing this disclosure.

EXAMPLES

[0078] The subject matter having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is

understood that the examples are given by way of illustration and are not intended to limit the specification of the claims to follow in any manner.

EXAMPLE 1

[0079] The hydrogenation of CO₂ was investigated in a metal reactor at a temperature of 630 °C, and the data are displayed in Figure 3. The flow rates were 3490.2 cc/min for hydrogen, and 873.7 cc/min for CO₂. The reactor used had a diameter of 1.5 inches and a length of 1.5 meters. The catalyst used was a CATOFIN catalyst, at a loading of 123.7 ml. In different experiments, various amounts of catalyst were used, for the purpose of scaling up the process (e.g., the higher the catalyst loading, the higher the scale).

[0080] The composition of the gas effluent recovered from the reactor was similar to the composition of syngas produced via a methane steam reforming process. The produced syngas could be mixed with methane steam reforming syngas and subsequently fed for methanol synthesis.

[0081] For the purpose of any U.S. national stage filing from this application, all publications and patents mentioned in this disclosure are incorporated herein by reference in their entireties, for the purpose of describing and disclosing the constructs and methodologies described in those publications, which might be used in connection with the methods of this disclosure. Any publications and patents discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention.

[0082] In any application before the United States Patent and Trademark Office, the Abstract of this application is provided for the purpose of satisfying the requirements of 37 C.F.R. § 1.72 and the purpose stated in 37 C.F.R. § 1.72(b) “to enable the United States Patent and Trademark Office and the public generally to determine quickly from a cursory inspection the nature and gist of the technical disclosure.” Therefore, the Abstract of this application is not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Moreover, any headings that can be employed herein are also not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Any use of the past tense to describe an example otherwise indicated as constructive or prophetic is not intended to reflect that the constructive or prophetic example has actually been carried out.

[0083] The present disclosure is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort can be had to various other aspects, embodiments, modifications, and equivalents thereof which, after reading the description herein, can be suggest to one of ordinary skill in the art without departing from the spirit of the present invention or the scope of the appended claims.

ADDITIONAL DISCLOSURE

[0084] A first aspect, which is a process for producing ethylene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) cooling at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid; and (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity.

[0085] A second aspect, which is the process of the first aspect, wherein the quenching fluid comprises water, hydrocarbons, oil, or combinations thereof.

[0086] A third aspect, which is the process of any one of the first and the second aspects, wherein the electricity generator comprises a turbine, a thermoelectric generator, a thermionic convertor, or combinations thereof.

[0087] A fourth aspect, which is the process of the third aspect, wherein the heated quenching fluid comprises steam, and wherein the turbine comprises a steam turbine.

[0088] A fifth aspect, which is the process of any one of the first through the fourth aspects, wherein the quench zone comprises a heat exchanger.

[0089] A sixth aspect, which is the process of any one of the first through the fifth aspects, wherein steps (d) and (e) occur about concurrently.

[0090] A seventh aspect, which is the process of the sixth aspect further comprising co-generating steam and electricity.

[0091] An eighth aspect, which is the process of any one of the first through the seventh aspects, wherein step (e) further comprises (i) introducing the heated quenching fluid to a heat exchanger to produce steam; and (ii) feeding at least a portion of the steam to a steam turbine to produce electricity.

[0092] A ninth aspect, which is the process of any one of the first through the eighth aspects, wherein step (e) further comprises (i) introducing the cooled pyrolysis reaction product characterized by the second

temperature, the heated quenching fluid, or both to a heat exchanger to produce steam; and (ii) feeding at least a portion of the steam to a steam turbine to produce electricity.

[0093] A tenth aspect, which is the process of the ninth aspect, wherein a temperature of the cooled pyrolysis reaction product is decreased from the second temperature to a third temperature, and wherein the third temperature is from about 100 °C to about 900 °C.

[0094] An eleventh aspect, which is the process of any one of the first through the tenth aspects further comprising using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream.

[0095] A twelfth aspect, which is the process of the eleventh aspect, wherein at least a portion of the oxygen stream is recycled to the step (a) as the oxidant gas.

[0096] A thirteenth aspect, which is the process of any one of the first through the twelfth aspects further comprising (i) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C₂H₂, C₂H₄, CO, and H₂; and (ii) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO.

[0097] A fourteenth aspect, which is the process of the thirteenth aspect, wherein the CO₂ hydrogenation catalyst comprises one or more oxides of a metal selected from the group consisting of chromium (Cr), iron (Fe), manganese (Mn), and copper (Cu).

[0098] A fifteenth aspect, which is the process of any one of the first through the fourteenth aspects, wherein the first CO₂ stream is separated from the cooled pyrolysis reaction product by amine absorption.

[0099] A sixteenth aspect, which is the process of any one of the first through the fifteenth aspects further comprising (1) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst; (2) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂, and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream; and (3) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO.

[00100] A seventeenth aspect, which is the process of the sixteenth aspect, wherein the polar aprotic solvent comprises N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), or combinations thereof.

[00101] An eighteenth aspect, which is the process of any one of the first through the seventeenth aspects, wherein the acetylene hydrogenation catalyst comprises palladium (Pd).

[00102] A nineteenth aspect, which is the process of any one of the first through the eighteenth aspects, wherein the first syngas stream and/or the second syngas stream are characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1.

[00103] A twentieth aspect, which is the process of any one of the first through the nineteenth aspects further comprising introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

[00104] A twenty-first aspect, which is the process of the twentieth aspect, wherein the methanol production catalyst comprises Cu, Cu/ZnO, Cu/ThO₂, Cu/Zn/Al₂O₃, Cu/ZnO/Al₂O₃, Cu/Zr, or combinations thereof.

[00105] A twenty-second aspect, which is the process of any one of the first through the twenty-first aspects, wherein the first temperature is equal to or greater than about 2,000 °C.

[00106] A twenty-third aspect, which is the process of any one of the first through the twenty-second aspects, wherein the second temperature is from about 600 °C to about 1,000 °C.

[00107] A twenty-fourth aspect, which is the process of any one of the first through the twenty-third aspects, wherein the quenching fluid is characterized by an inlet temperature of from about 40 °C to about 80 °C.

[00108] A twenty-fifth aspect, which is the process of any one of the first through the twenty-fourth aspects, wherein the heated quenching fluid is characterized by a temperature of from about 600 °C to about 800 °C.

[00109] A twenty-sixth aspect, which is the process of any one of the first through the twenty-fifth aspects, wherein the fuel gas stream and the hydrocarbon stream are the same or different.

[00110] A twenty-seventh aspect, which is the process of any one of the first through the twenty-sixth aspects, wherein the fuel gas stream and/or the hydrocarbon stream comprise methane, ethane, propane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, heavy hydrocarbons, petcoke, naphtha, heavy oil, heavy oil residue, or combinations thereof.

[00111] A twenty-eighth aspect, which is the process of any one of the first through the twenty-seventh aspects, wherein the oxidant gas comprises oxygen, purified oxygen, air, oxygen-enriched air, or combinations thereof.

[00112] A twenty-ninth aspect, which is a process for producing ethylene and methanol comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b)

introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) cooling at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid; (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity; (f) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream; (g) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas; (h) separating at least a portion of the cooled pyrolysis reaction product into a CO_2 stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C_2H_2 , C_2H_4 , CO, and H_2 ; (i) contacting at least a portion of the hydrogen stream and at least a portion of the CO_2 stream with a CO_2 hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H_2 and CO; (j) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst; (k) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C_2H_4 , CO, and H_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the acetylene stream; (l) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H_2 and CO; and (m) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

[00113] A thirtieth aspect, which is a process for producing ethylene and methanol comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2),

ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) quenching at least a portion of the pyrolysis reaction product in a quench zone to produce a quenched pyrolysis reaction product, wherein the quenched pyrolysis reaction product comprises at least a portion of the pyrolysis reaction product, wherein the quenched pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature; (e) introducing at least a portion of the quenched pyrolysis reaction product to a heat exchanger to produce a cooled pyrolysis reaction product and steam, wherein the cooled pyrolysis reaction product is characterized by a third temperature, and wherein the third temperature is lower than the second temperature; (f) feeding at least a portion of the steam to an electricity generator to produce electricity; (g) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream; (h) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas; (i) separating at least a portion of the cooled pyrolysis reaction product into a CO_2 stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C_2H_2 , C_2H_4 , CO, and H_2 ; (j) contacting at least a portion of the hydrogen stream and at least a portion of the CO_2 stream with a CO_2 hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H_2 and CO; (k) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst; (l) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C_2H_4 , CO, and H_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the acetylene stream; (m) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H_2 and CO; and (n) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

[00114] A thirty-first aspect, which is a process for producing ethylene and methanol comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product and combustion heat; (b) reacting a first reactant mixture in a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction to produce a pyrolysis reaction product, and wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (c) cooling at least a portion of the pyrolysis reaction product to produce a cooled pyrolysis reaction product and thermal energy, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature; (d)

converting at least a portion of the thermal energy into electrical energy; (e) splitting water into a hydrogen stream and an oxygen stream by using at least a portion of the electrical energy; (f) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas; (g) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C₂H₂, C₂H₄, CO, and H₂; (h) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO; (i) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst; (j) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream; (k) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO; and (l) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

[00115] A thirty-second aspect, which is the process of the thirty-first aspect, wherein the thermal energy is produced by at least a portion of the pyrolysis reaction product exchanging heat with a quenching fluid to produce the cooled pyrolysis reaction product and a heated quenching fluid.

[00116] A thirty-third aspect, which is the process of the thirty-second aspect, wherein the heated quenching fluid comprises steam.

[00117] A thirty-fourth aspect, which is the process of any one of the thirty-first through the thirty-third aspects, wherein step (d) further comprises introducing at least a portion of the heated quenching fluid to a turbine to generate electricity.

[00118] A thirty-fifth aspect, which is the process of any one of the thirty-first through the thirty-fourth aspects, wherein the thermal energy is produced by at least a portion of the pyrolysis reaction product exchanging heat with a heat exchange fluid.

[00119] A thirty-sixth aspect, which is the process of the thirty-fifth aspect, wherein the heat exchange fluid comprises water, and wherein exchanging heat with a heat exchange fluid comprises converting at least a portion of the water to steam.

[00120] A thirty-seventh aspect, which is the process of the thirty-sixth aspect, wherein step (d) further comprises introducing at least a portion of the steam to a steam turbine to generate electricity.

[00121] A thirty-eighth aspect, which is the process of any one of the thirty-first through the thirty-seventh aspect, wherein the thermal energy is produced by at least a portion of the pyrolysis reaction product exchanging heat with a quenching fluid, a heat exchange fluid, or both.

[00122] While embodiments of the disclosure have been shown and described, modifications thereof can be made without departing from the spirit and teachings of the invention. The embodiments and examples described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

[00123] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the detailed description of the present invention. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference.

CLAIMS

What is claimed is:

1. A process for producing ethylene comprising:
 - (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product;
 - (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction;
 - (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2);
 - (d) cooling at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid; and
 - (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity.
2. The process of claim 1, wherein the quenching fluid comprises water, hydrocarbons, oil, or combinations thereof.
3. The process of any one of claims 1-2, wherein the electricity generator comprises a turbine, a thermoelectric generator, a thermionic convertor, or combinations thereof.
4. The process of claim 3, wherein the heated quenching fluid comprises steam, and wherein the turbine comprises a steam turbine.
5. The process of any one of claims 1-4, wherein the quench zone comprises a heat exchanger.
6. The process of any one of claims 1-5, wherein steps (d) and (e) occur about concurrently.
7. The process of claim 6 further comprising co-generating steam and electricity.
8. The process of any one of claims 1-7, wherein step (e) further comprises (i) introducing the heated quenching fluid to a heat exchanger to produce steam; and (ii) feeding at least a portion of the steam to a steam turbine to produce electricity.
9. The process of any one of claims 1-8, wherein step (e) further comprises (i) introducing the cooled pyrolysis reaction product characterized by the second temperature, the heated quenching fluid, or both to a

heat exchanger to produce steam; and (ii) feeding at least a portion of the steam to a steam turbine to produce electricity.

10. The process of claim 9, wherein a temperature of the cooled pyrolysis reaction product is decreased from the second temperature to a third temperature, and wherein the third temperature is from about 100 °C to about 900 °C.

11. The process of any one of claims 1-10 further comprising using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream.

12. The process of claim 11, wherein at least a portion of the oxygen stream is recycled to the step (a) as the oxidant gas.

13. The process of any one of claims 1-12 further comprising (i) separating at least a portion of the cooled pyrolysis reaction product into a CO₂ stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C₂H₂, C₂H₄, CO, and H₂; and (ii) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO.

14. The process of any one of claims 1-13 further comprising (1) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst; (2) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂, and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream; and (3) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO.

15. The process of any one of claims 1-14, wherein the first syngas stream and/or the second syngas stream are characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1.

16. The process of any one of claims 1-15 further comprising introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

17. The process of any one of claims 1-16, wherein the first temperature is equal to or greater than about 2,000 °C; and wherein the second temperature is from about 600 °C to about 1,000 °C.

18. The process of any one claims 1-17, wherein the quenching fluid is characterized by an inlet temperature of from about 40 °C to about 80 °C; and wherein the heated quenching fluid is characterized by a temperature of from about 600 °C to about 800 °C.

19. A process for producing ethylene and methanol comprising:
- (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product;
 - (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction;
 - (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2);
 - (d) cooling at least a portion of the pyrolysis reaction product in a quench zone by heat exchange with a quenching fluid to produce a cooled pyrolysis reaction product and a heated quenching fluid, wherein the cooled pyrolysis reaction product is characterized by a second temperature, wherein the second temperature is lower than the first temperature, and wherein a temperature of the heated quenching fluid is greater than a temperature of the quenching fluid;
 - (e) feeding at least a portion of the heated quenching fluid to an electricity generator to produce electricity;
 - (f) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream;
 - (g) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas;
 - (h) separating at least a portion of the cooled pyrolysis reaction product into a CO_2 stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C_2H_2 , C_2H_4 , CO, and H_2 ;
 - (i) contacting at least a portion of the hydrogen stream and at least a portion of the CO_2 stream with a CO_2 hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H_2 and CO;
 - (j) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst;
 - (k) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C_2H_4 , CO, and H_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the acetylene stream;

- (l) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H_2 and CO; and
 - (m) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.
20. A process for producing ethylene and methanol comprising:
- (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product;
 - (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction;
 - (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2);
 - (d) quenching at least a portion of the pyrolysis reaction product in a quench zone to produce a quenched pyrolysis reaction product, wherein the quenched pyrolysis reaction product comprises at least a portion of the pyrolysis reaction product, wherein the quenched pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature;
 - (e) introducing at least a portion of the quenched pyrolysis reaction product to a heat exchanger to produce a cooled pyrolysis reaction product and steam, wherein the cooled pyrolysis reaction product is characterized by a third temperature, and wherein the third temperature is lower than the second temperature;
 - (f) feeding at least a portion of the steam to an electricity generator to produce electricity;
 - (g) using at least a portion of the electricity for water electrolysis to produce a hydrogen stream and an oxygen stream;
 - (h) recycling at least a portion of the oxygen stream to step (a) as the oxidant gas;
 - (i) separating at least a portion of the cooled pyrolysis reaction product into a CO_2 stream and an acetylene stream, wherein the acetylene stream comprises unconverted hydrocarbons, C_2H_2 , C_2H_4 , CO, and H_2 ;

- (j) contacting at least a portion of the hydrogen stream and at least a portion of the CO₂ stream with a CO₂ hydrogenation catalyst to produce a first syngas stream, wherein the first syngas stream comprises H₂ and CO;
- (k) introducing at least a portion of the acetylene stream and a polar aprotic solvent to a second reaction zone, wherein the second reaction zone comprises an acetylene hydrogenation catalyst;
- (l) allowing at least a portion of the acetylene in the acetylene stream to undergo hydrogenation to ethylene to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, C₂H₄, CO, and H₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the acetylene stream;
- (m) separating at least a portion of the second reaction zone effluent into an ethylene stream and a second syngas stream, wherein the second syngas stream comprises H₂ and CO; and
- (n) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream to a third reaction zone comprising a methanol production catalyst to produce a methanol stream.

1/3

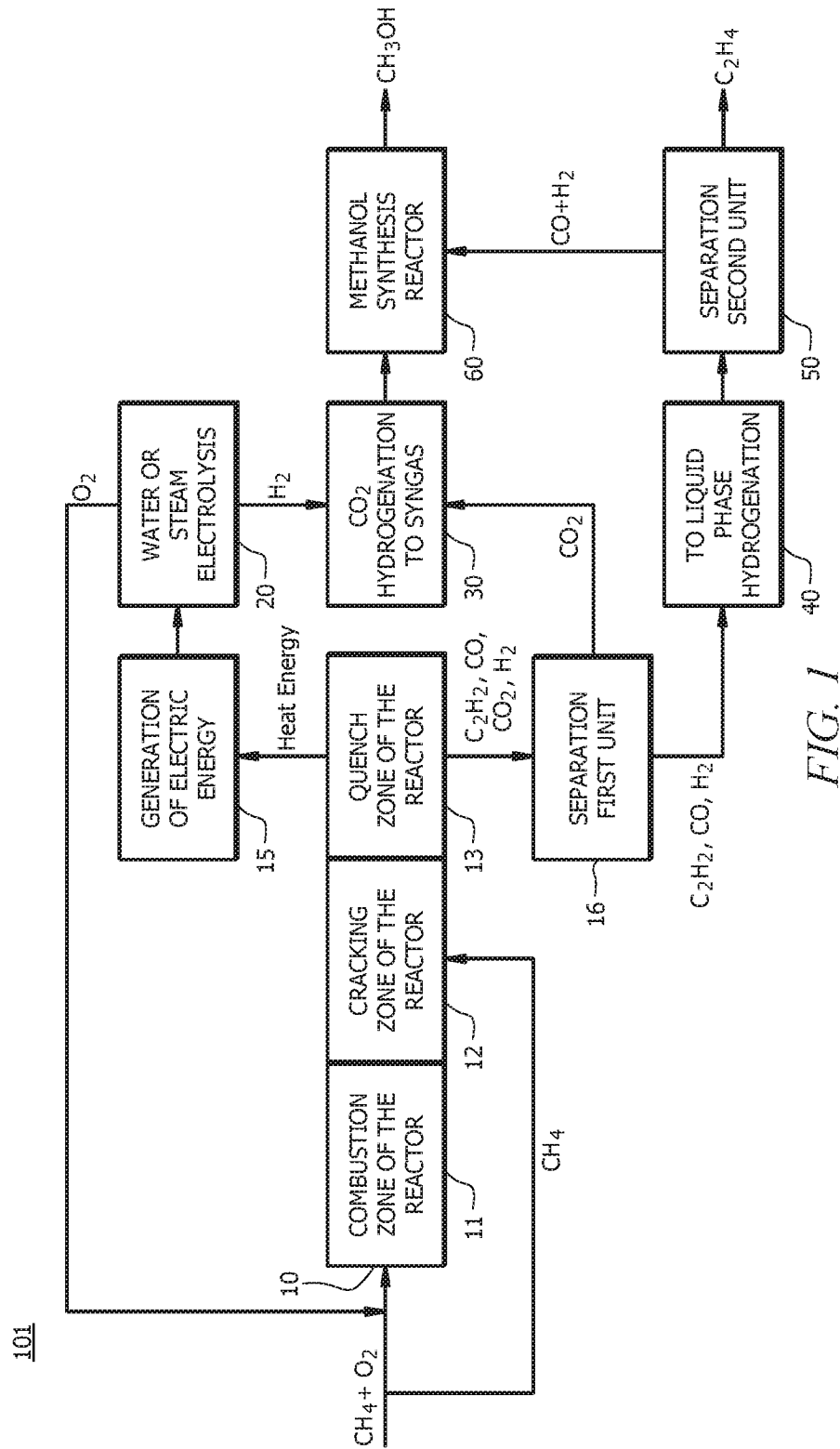
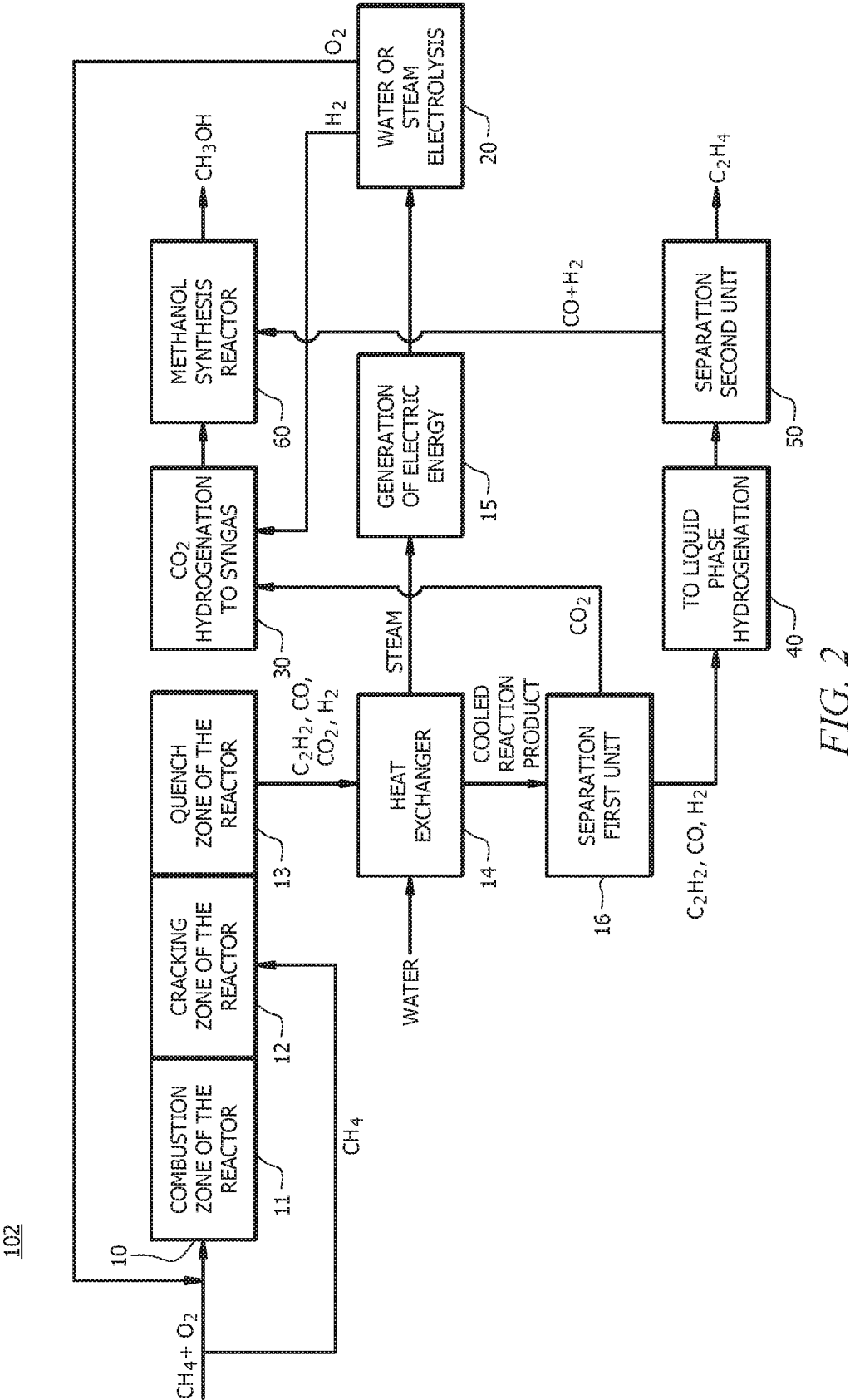


FIG. 1



3/3

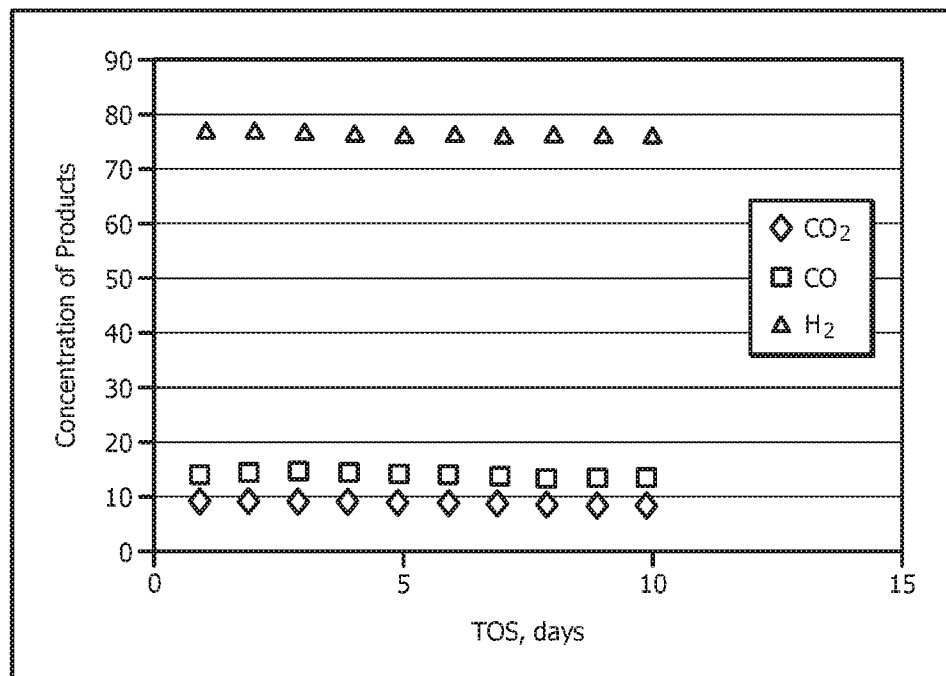


FIG. 3

A. CLASSIFICATION OF SUBJECT MATTER**C07C 2/82(2006.01)i, C07C 2/78(2006.01)i, C07C 11/04(2006.01)i, C07C 29/154(2006.01)i, C07C 31/04(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 2/82; C07C 11/02; C07C 1/12; C07C 5/08; F01K 25/08; C10J 3/72; C07C 41/09; F01K 9/00; C07C 5/09; C07C 2/78; C07C 11/04; C07C 29/154; C07C 31/04

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: producing, ethylene, fuel gas, hydrocarbon, acetylene, hydrogenation, pyrolysis

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8080697 B2 (LIN, YUNGYI et al.) 20 December 2011 See abstract; column 1, lines 53-56; column 4, line 66-column 5, line 6; column 6, lines 42-52; column 8, lines 58-61; claims 1-16; and figures 1-10.	1-4
A		19-20
Y	US 2012-0031096 A1 (ULAS ACIKGOZ, SAADET et al.) 09 February 2012 See paragraphs [0007]-[0010]; and claims 1-20.	1-4
A	US 2016-0152528 A1 (BESTRONG INTERNATIONAL LIMITED) 02 June 2016 See abstract; claims 1-15; and figures 1-4.	1-4, 19-20
A	US 9139492 B2 (SCHODEL, NICOLE et al.) 22 September 2015 See abstract; and claims 1-12.	1-4, 19-20
A	US 2016-0289143 A1 (SILURIA TECHNOLOGIES, INC.) 06 October 2016 See abstract; claims 1-24; and figures 1-20.	1-4, 19-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 April 2018 (30.04.2018)

Date of mailing of the international search report

30 April 2018 (30.04.2018)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

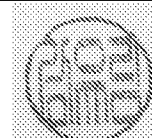


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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/012067

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.: 10,12
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:
Claims 10 and 12 do not comply with PCT Article 6 because they are referring to unsearchable claims 9 and 11 respectively.
3. ☒ Claims Nos.: 5-9,11,13-18
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:

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 an additional fees, this Authority did not invite payment of any 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.:

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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/012067

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