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62/521,831 19 June 2017 (19.06.2017) US(71) Applicant: SABIC GLOBAL TECHNOLOGIES, B.V.
[NL/NL]; Plasticslaan 1, 4612px Bergen Op Zoom (NL).

(72) Inventors: CHINTA, Sivadinarayana; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). AL-GHAMDI, Miasser; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). PANT, Atul; 86

The Emphyrean, Chikkatirupathi 563160 (IN). EDREES, Rami; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). AL-AMAR, Marwan; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). AL-HAGBANI, Saud; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). RABIE, Arwa; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). KOLAH, Aspi; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). BINKHAMIS, Sulaiman; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). AL-TURKISTANI, Sultan; SABIC Corporate Research and Development Center – CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900 (SA). NARAYANASWAMY, Ravichander; Flat No. 12FF, Kempton Park, Opposite Ryan International School, Kundalahalli, Bengaluru 560037 (IN). RAJAB, Karam;

(54) Title: AN IMPROVED PROCESS FOR SYNGAS PRODUCTION FOR PETROCHEMICAL APPLICATIONS

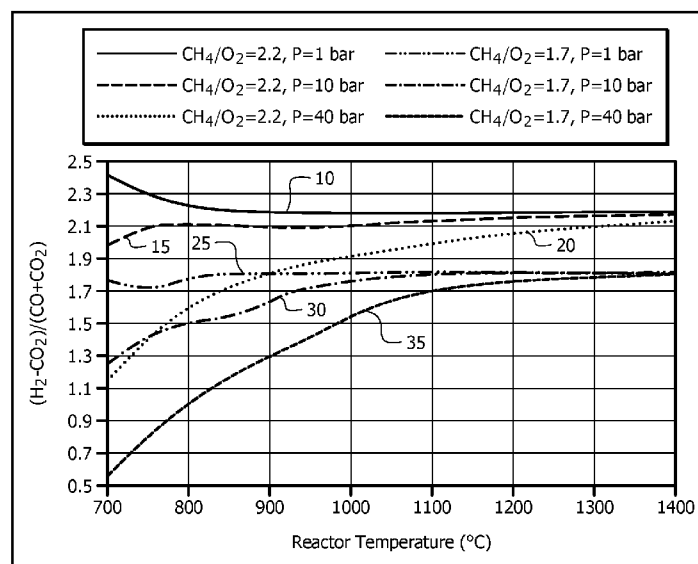


FIG. 1

(57) Abstract: A process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 s; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons.



SABIC Corporate Research and Development Center –
CRD at KAUST, P.O. Box 4545-4700, Thuwal 23955-6900
(SA).

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AN IMPROVED PROCESS FOR SYNGAS PRODUCTION FOR PETROCHEMICAL APPLICATIONS

TECHNICAL FIELD

[0001] The present disclosure relates to methods of producing syngas, more specifically methods of producing syngas by catalytic partial oxidation of hydrocarbons, such as methane.

BACKGROUND

[0002] Synthesis gas (syngas) is a mixture comprising carbon monoxide (CO) and hydrogen (H₂), as well as small amounts of carbon dioxide (CO₂), water (H₂O), and unreacted methane (CH₄). Syngas is generally used as an intermediate in the production of methanol and ammonia, as well as an intermediate in creating synthetic petroleum to use as a lubricant or fuel.

[0003] Syngas is produced conventionally by steam reforming of natural gas, although other hydrocarbon sources can be used for syngas production, such as refinery off-gases, naphtha feedstocks, heavy hydrocarbons, coal, biomass, etc.

[0004] The steam reforming is an endothermic process and requires a lot of energy input to drive the reaction forward. Further, the use of excess steam results in formation of excess hydrogen which is stoichiometrically more than what is required by a variety of processes that use syngas; such as methanol synthesis, or certain Fischer-Tropsch (FT) processes for the production of liquid hydrocarbons via a gas to liquid (GTL) process that does not employ CO₂ as a reactant.

[0005] Steam reforming can be paired with autothermal reforming (ATR) to reduce hydrogen present in syngas. In an ATR process, a portion of the natural gas is burned as fuel to drive the conversion of natural gas to syngas with resulting in relatively low hydrogen and high CO₂ concentrations. ATR could reduce the hydrogen content of the syngas, but the hydrogen content of the resulting syngas would still be more than what is required by a variety of processes that use syngas, such as methanol synthesis or certain FT processes. Further, the conventional O₂ to C ratio used in autothermal reformers can lead to production of high amounts of CO₂, significantly affecting the composition of the syngas.

[0006] Syngas can also be produced (non-commercially) by catalytic partial oxidation (CPO) of natural gas. CPO process employ partial oxidation of hydrocarbon feeds to syngas comprising CO and H₂. The CPO process is exothermic, thus eliminating the need for external heat supply. However, the composition of the produced syngas is not suitable for methanol synthesis, for example;

and requires external hydrogen addition that generally involve further investments. Typically, CPO reactors are operated in an adiabatic mode with no control of exit temperatures and hence no control of exit concentrations (e.g., no control of the composition of the produced syngas).

[0007] Syngas produced via conventional processes contains stoichiometrically excess hydrogen. Typically, downstream operations that use syngas operate at elevated pressures. Higher energy is required to compress a hydrogen rich syngas stream. Conventional syngas processes cannot produce a syngas having just stoichiometric amount of hydrogen required by the downstream processes, due to excess steam required to generate syngas in conventional processes. Consequently, hydrogen gas accumulates in recycle loops of downstream operation and/or is burned as fuel as part of the purge stream; resulting in lower energy efficiency and poor carbon efficiency of the conventional process. Thus, there is an ongoing need for the development of syngas production processes that can control the composition of the produced syngas, as well as produce a syngas that could be suitable for downstream processes.

BRIEF SUMMARY

[0008] Disclosed herein is a process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 s; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons.

[0009] Further disclosed herein is a process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in an isothermal reactor to produce syngas, wherein the reactant mixture comprises methane and oxygen, wherein the isothermal reactor comprises a CPO catalyst, wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 1.2 ms, and wherein the syngas comprises hydrogen, carbon monoxide, water, carbon dioxide, and unreacted.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] For a detailed description of the preferred aspects of the disclosed methods, reference will now be made to the accompanying drawing in which:

[0011] Figure 1 displays a graph of the variation of syngas composition with the reaction temperature under various process conditions; and

[0012] Figure 2 displays a graph of heat exchange required for maintaining isothermal conditions at different temperatures under various process conditions.

DETAILED DESCRIPTION

[0013] Disclosed herein are processes for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 seconds (s), or alternatively from about 0.001 ms to about 5 ms; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons. In some aspects, the reactant mixture can further comprise a diluent, wherein the diluent contributes to the near-isothermal conditions via direct heat exchange. Indirect heat exchange can also be employed for providing the near-isothermal conditions.

[0014] 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.

[0015] 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] As used herein, the term “effective,” means adequate to accomplish a desired, expected, or intended result.

[0020] 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.

[0021] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art.

[0022] 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.

[0023] In an aspect, a process for producing syngas as disclosed herein can comprise reacting, under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas, wherein the reactant mixture comprises hydrocarbons and oxygen.

[0024] Generally, the CPO reaction is based on partial combustion of fuels, such as various hydrocarbons, and in the case of methane, CPO can be represented by equation (1):



Without wishing to be limited by theory, side reactions can take place along with the CPO reaction depicted in equation (1), and such side reactions can produce carbon dioxide (CO₂) and water (H₂O).

[0025] Further, without wishing to be limited by theory, the CPO reaction as depicted in equation (1) is an exothermic heterogeneous catalytic reaction (i.e., a mildly exothermic reaction) and it occurs in single reactor unit (as opposed to more than one reactor unit as is the case in conventional processes for syngas production, such as steam methane reforming (SMR) - autothermal reforming (ATR) combinations). While it is possible to conduct partial oxidation of hydrocarbons as a homogeneous reaction, in the absence of a catalyst, homogeneous partial oxidation of hydrocarbons process entails excessive temperatures, long residence times, as well as excessive coke formation, which strongly reduce the controllability of the partial oxidation reaction, and may not produce syngas of the desired quality in a single reactor unit.

[0026] Furthermore, without wishing to be limited by theory, the CPO reaction is fairly resistant to chemical poisoning, and as such it allows for the use of a wide variety of hydrocarbon feedstocks, including some sulfur containing hydrocarbon feedstocks; which, in some cases, can enhance catalyst life-time and productivity.

[0027] In an aspect, the hydrocarbons suitable for use in a CPO reaction as disclosed herein can include methane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, paraffins, shale gas, shale liquids, fluid catalytic cracking (FCC) off gas, refinery process gases, stack gases, and the like, or combinations thereof. The hydrocarbons can include any suitable hydrocarbons source. In an aspect, the reactant mixture can comprise CH_4 and O_2 .

[0028] The oxygen used in the reactant mixture can comprise 100% oxygen (substantially pure O_2), oxygen gas (which may be obtained via a membrane separation process), technical oxygen (which may contain some air), air, oxygen enriched air, oxygen-containing gaseous compounds (e.g., NO), oxygen-containing mixtures (e.g., O_2/CO_2 , $\text{O}_2/\text{H}_2\text{O}$, $\text{O}_2/\text{H}_2\text{O}_2/\text{H}_2\text{O}$), oxy radical generators (e.g., CH_3OH , CH_2O), hydroxyl radical generators, and the like, or combinations thereof.

[0029] In an aspect, the reactant mixture can be characterized by a methane to oxygen (CH_4/O_2) molar ratio of equal to or greater than about 1:1, alternatively equal to or greater than about 2:1, alternatively equal to or greater than about 3:1, alternatively from about 1:1 to about 3:1, alternatively from about 1.5:1 to about 2.5:1, or alternatively from about 1.6:1 to about 2.2:1. As will be appreciated by one of skill in the art, and with the help of this disclosure, the CH_4/O_2 molar ratio can be adjusted along with other reactor process parameters (e.g., temperature, pressure, flow velocity, etc.) to provide for near-isothermal conditions, as well as a syngas with a desired composition (e.g., a syngas with a desired hydrogen to carbon monoxide (H_2/CO) molar ratio). Further, as will be

appreciated by one of skill in the art, and with the help of this disclosure, the CH_4/O_2 molar ratio can also vary with the addition of a diluent to the reactant mixture (e.g., water addition to the reactant mixture, CO_2 , addition to the reactant mixture, etc.).

[0030] In some aspects, the reactant mixture can further comprise a diluent, wherein the diluent contributes to the near-isothermal conditions via direct heat exchange, as disclosed herein. The diluent can comprise water, steam, inert gases (e.g., argon), nitrogen, carbon dioxide, and the like, or combinations thereof. Generally, the diluent is inert with respect to the CPO reaction, e.g., the diluent does not participate in the CPO reaction. However, and as will be appreciated by one of skill in the art, and with the help of this disclosure, some diluents (e.g., water, steam, carbon dioxide, etc.) might undergo chemical reactions other than the CPO reaction within the reactor, and can change the composition of the resulting syngas; while other diluents (e.g., nitrogen (N_2), argon (Ar)) might not participate in reactions that change the composition of the resulting syngas. As will be appreciated by one of skill in the art, and with the help of this disclosure, the diluent can be used to vary the composition of the resulting syngas. The diluent can be present in the reactant mixture in any suitable amount.

[0031] In an aspect, a diluent comprising water and/or steam can increase a hydrogen content of the resulting syngas. For example, in aspects where the reactant mixture comprises water and/or steam diluent, the syngas can be characterized by a hydrogen to carbon monoxide molar ratio that is increased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an otherwise similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the water and/or steam diluent. Without wishing to be limited by theory, water and/or steam diluent can react with coke inside the reactor and generate additional CO and H_2 . As will be appreciated by one of skill in the art, and with the help of this disclosure, the steam that is introduced to the reactor for use as a diluent in a CPO reaction as disclosed herein is in significantly smaller amounts than the amounts of steam utilized in steam reforming processes, and as such, a process for producing syngas as disclosed herein can yield a syngas with lower amounts of hydrogen when compared to the amounts of hydrogen in a syngas produced by steam reforming.

[0032] In another aspect, a diluent comprising carbon dioxide can increase a carbon monoxide content of the resulting syngas. For example, in aspects where the reactant mixture comprises carbon dioxide diluent, the syngas can be characterized by a hydrogen to carbon monoxide molar ratio that is decreased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an

otherwise similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the carbon dioxide diluent. Without wishing to be limited by theory, carbon dioxide can react with coke inside the reactor and generate additional CO. Further, and without wishing to be limited by theory, carbon dioxide can participate in a dry reforming of methane reaction, thereby generating additional CO and H₂. Dry reforming of methane is generally accompanied by a reaction between carbon dioxide and hydrogen which results in the formation of additional CO and water.

[0033] The CPO reaction is an exothermic reaction (e.g., heterogeneous catalytic reaction; exothermic heterogeneous catalytic reaction) that is generally conducted in the presence of a CPO catalyst comprising a catalytically active metal, i.e., a metal active for catalyzing the CPO reaction. The catalytically active metal can comprise a noble metal (e.g., Pt, Rh, Ir, Pd, Ru, Ag, and the like, or combinations thereof); a non-noble metal (e.g., Ni, Co, V, Mo, P, Fe, Cu, and the like, or combinations thereof); rare earth elements (e.g., La, Ce, Nd, Eu, and the like, or combinations thereof); oxides thereof; and the like; or combinations thereof. Generally, a noble metal is a metal that resists corrosion and oxidation in a water-containing environment. As will be appreciated by one of skill in the art, and with the help of this disclosure, the components of the CPO catalyst (e.g., metals such as noble metals, non-noble metals, etc., rare earth elements, can be either phase segregated or combined within the same phase.

[0034] In an aspect, the CPO catalysts suitable for use in the present disclosure can be supported catalysts and/or unsupported catalysts. In some aspects, the supported catalysts can comprise a support, wherein the support can be catalytically active (e.g., the support can catalyze a CPO reaction). For example, the catalytically active support can comprise a metal gauze or wire mesh (e.g., Pt gauze or wire mesh); a catalytically active metal monolithic catalyst; etc. In other aspects, the supported catalysts can comprise a support, wherein the support can be catalytically inactive (e.g., the support cannot catalyze a CPO reaction), such as SiO₂; alumina; a catalytically inactive monolithic support; etc. In yet other aspects, the supported catalysts can comprise a catalytically active support and a catalytically inactive support.

[0035] In some aspects, a CPO catalyst can be wash coated onto a support, wherein the support can be catalytically active or inactive, and wherein the support can be a monolith, a foam, an irregular catalyst particle, etc.

[0036] In some aspects, the CPO catalyst can be a monolith, a foam, a powder, a particle, etc. Non-limiting examples of CPO catalyst particle shapes suitable for use in the present disclosure

include cylindrical, discoidal, spherical, tabular, ellipsoidal, equant, irregular, cubic, acicular, and the like, or combinations thereof.

[0037] In some aspects, the support comprises an inorganic oxide, alpha, beta or theta alumina (Al_2O_3), activated Al_2O_3 , silicon dioxide (SiO_2), titanium dioxide (TiO_2), magnesium oxide (MgO), zirconium oxide (ZrO_2), lanthanum (III) oxide (La_2O_3), yttrium (III) oxide (Y_2O_3), cerium (IV) oxide (CeO_2), zeolites, ZSM-5, perovskite oxides, hydrotalcite oxides, and the like, or combinations thereof.

[0038] In an aspect, a process for producing syngas as disclosed herein can comprise conducting a CPO reaction under non-adiabatic and near-isothermal conditions to produce syngas. For purposes of the disclosure herein, the term “non-adiabatic conditions” refers to process conditions wherein a reactor is subjected to external heat exchange or transfer (e.g., the reactor is heated; or the reactor is cooled), which can be direct heat exchange and/or indirect heat exchange. By contrast, the term “adiabatic conditions” refers to process conditions wherein a reactor is not subjected to external heat exchange (e.g., the reactor is not heated; or the reactor is not cooled). Generally, external heat exchange implies an external heat exchange system (e.g., a cooling system; a heating system) that requires energy input and/or output.

[0039] As would be appreciated by one of skill in the art and with the help of this disclosure, isothermal conditions generally refer to process conditions wherein the reactor has a substantially constant temperature that can be defined as a temperature that varies by less than about $+10^\circ\text{C}$, alternatively less than about $+9^\circ\text{C}$, alternatively less than about $+8^\circ\text{C}$, alternatively less than about $+7^\circ\text{C}$, alternatively less than about $+6^\circ\text{C}$, alternatively less than about $+5^\circ\text{C}$, alternatively less than about $+4^\circ\text{C}$, alternatively less than about $+3^\circ\text{C}$, alternatively less than about $+2^\circ\text{C}$, or alternatively less than about $+1^\circ\text{C}$.

[0040] For purposes of the disclosure herein, the term “near-isothermal conditions” refers to process conditions that allow for a fairly constant temperature of the reactor, which can be defined as a temperature that varies by less than about $\pm 100^\circ\text{C}$, alternatively less than about $\pm 90^\circ\text{C}$, alternatively less than about $\pm 80^\circ\text{C}$, alternatively less than about $\pm 70^\circ\text{C}$, alternatively less than about $\pm 60^\circ\text{C}$, alternatively less than about $\pm 50^\circ\text{C}$, alternatively less than about $\pm 40^\circ\text{C}$, alternatively less than about $\pm 30^\circ\text{C}$, alternatively less than about $\pm 20^\circ\text{C}$, alternatively less than about $\pm 10^\circ\text{C}$, alternatively less than about $\pm 9^\circ\text{C}$, alternatively less than about $\pm 8^\circ\text{C}$, alternatively less than about $\pm 7^\circ\text{C}$, alternatively less than about $\pm 6^\circ\text{C}$, alternatively less than about $\pm 5^\circ\text{C}$, alternatively less than about $\pm 4^\circ\text{C}$, alternatively less than about $\pm 3^\circ\text{C}$, alternatively less than about

± 2 °C, or alternatively less than about ± 1 °C. Further, for purposes of the disclosure herein, the term “near-isothermal conditions” is understood to include “isothermal” conditions. In some aspects, near-isothermal conditions allow for a temperature variation (e.g., a temperature variation within the reactor; a temperature variation within a catalyst bed) of less than about ± 50 °C, alternatively less than about ± 25 °C, or alternatively less than about ± 10 °C.

[0041] Further, for purposes of the disclosure herein, the term “near-isothermal conditions” refers to process conditions, such as a reactor temperature, effective for achieving a desired composition of the syngas (e.g., a desired hydrogen to carbon monoxide ratio; a desired M ratio, wherein the M ratio is a molar ratio defined as $(\text{H}_2\text{-CO}_2)/(\text{CO}+\text{CO}_2)$; etc.), for a given set of operating conditions (e.g., pressure, CH_4/O_2 molar ratio, etc.).

[0042] For example, for a given set of reactor operating conditions (e.g., a given pressure and CH_4/O_2 molar ratio), a near-isothermal temperature (as compared to a targeted constant temperature) refers to the temperature effective for producing a syngas that is characterized by a hydrogen to carbon monoxide molar ratio that varies by less than about 20%, alternatively less than about 15%, alternatively less than about 10%, or alternatively less than about 5%.

[0043] As another example, for a given set of reactor operating conditions (e.g., a given pressure and CH_4/O_2 molar ratio), a near-isothermal temperature (as compared to a targeted constant temperature) refers to the temperature effective for producing a syngas that is characterized by an M ratio that varies by less than about 20%, alternatively less than about 15%, alternatively less than about 10%, or alternatively less than about 5%; wherein the M ratio is a molar ratio defined as $(\text{H}_2\text{-CO}_2)/(\text{CO}+\text{CO}_2)$.

[0044] As will be appreciated by one of skill in the art, and with the help of this disclosure, at lower operating reactor temperatures (e.g., from about 300 °C to about 1,200 °C), a near-isothermal temperature range effective for producing a syngas that is characterized by a hydrogen to carbon monoxide molar ratio that varies by less than about 20% is more narrow than at higher operating temperatures (e.g., from about 800 °C to about 1,600 °C). For example, at lower operating reactor temperatures (e.g., from about 300 °C to about 1,200 °C), a near-isothermal temperature range effective for producing a syngas that is characterized by a hydrogen to carbon monoxide molar ratio x that varies by less than about 20% can be an isothermal temperature that varies within about ± 20 °C; while at higher operating temperatures a near-isothermal temperature range effective for producing a

syngas that is characterized by the same hydrogen to carbon monoxide molar ratio x that varies by less than about 20% can be an isothermal temperature that varies within about ± 100 °C.

[0045] Further, as will be appreciated by one of skill in the art, and with the help of this disclosure, at lower operating reactor temperatures (e.g., from about 300 °C to about 1,200 °C), a near-isothermal temperature range effective for producing a syngas that is characterized by an M ratio that varies by less than about 20% is more narrow than at higher operating temperatures (e.g., from about 800 °C to about 1,600 °C). For example, at lower operating reactor temperatures (e.g., from about 300 °C to about 1,200 °C), a near-isothermal temperature range effective for producing a syngas that is characterized by an M ratio y that varies by less than about 10% can be an isothermal temperature that varies within about ± 25 °C; while at higher operating temperatures a near-isothermal temperature range effective for producing a syngas that is characterized by the same M ratio y that varies by less than about 10% can be an isothermal temperature that varies within about ± 80 °C.

[0046] Near-isothermal conditions can be provided by a variety of process and catalyst variables, such as temperature (e.g., heat exchange), pressure, gas flow rates, reactor configuration, catalyst bed configuration, catalyst bed composition, reactor cross sectional area, feed gas staging, feed gas injection, feed gas composition, and the like, or combinations thereof.

[0047] In some aspects, the near-isothermal conditions can be provided by direct heat exchange and/or indirect heat exchange. In an aspect, the near-isothermal conditions can be provided by cooling the reactor. In another aspect, the near-isothermal conditions can be provided by heating the reactor.

[0048] The indirect heat exchange can comprise heating the reactor; or cooling the reactor. In an aspect, the indirect heat exchange can comprise external heat exchange, external coolant fluid cooling, reactive cooling, liquid nitrogen cooling, cryogenic cooling, electric heating, electric arc heating, microwave heating, radiant heating, natural gas combustion, solar heating, infrared heating, and the like, or combinations thereof. For example, reactive cooling can be effected by carrying out an endothermic reaction in a cooling coil/jacket associated with (e.g., located in) the reactor.

[0049] The direct heat exchange can comprise introducing a cooling agent, such as a diluent, into the reactor, to decrease a reactor temperature, while increasing a temperature of the cooling agent and/or changing the phase of the cooling agent. The cooling agent can be reactive or non-reactive. The cooling agent can be in liquid state and/or in vapor state. As will be appreciated by one of skill in the art, and with the help of this disclosure, the cooling agent can act as a flammability retardant; for

example by reducing the temperature inside the reactor, by changing the gas mixture composition, by changing flame speed, by reducing the combustion of hydrocarbons to carbon dioxide; etc.

[0050] In an aspect, a reactor suitable for use in the present disclosure can comprise a tubular reactor, a continuous flow reactor, an isothermal reactor, a fixed bed reactor, a fluidized bed reactor, a bubbling bed reactor, a circulating bed reactor, an ebullating bed reactor, a rotary kiln reactor, and the like, or combinations thereof.

[0051] In an aspect, the reactor can comprise an isothermal reactor. For purposes of the disclosure herein, the term “isothermal reactor” refers to a reactor that has the ability of maintaining a near-isothermal reaction temperature (e.g., near-isothermal conditions, near-isothermal reaction conditions, near-isothermal reactor conditions, etc.), through direct heat exchange and/or indirect heat exchange. For purposes of the disclosure herein, the term “near-isothermal reaction temperature” can be defined as a temperature that varies by less than about ± 100 °C, alternatively less than about ± 90 °C, alternatively less than about ± 80 °C, alternatively less than about ± 70 °C, alternatively less than about ± 60 °C, alternatively less than about ± 50 °C, alternatively less than about ± 40 °C, alternatively less than about ± 30 °C, alternatively less than about ± 20 °C, alternatively less than about ± 10 °C, alternatively less than about ± 9 °C, alternatively less than about ± 8 °C, alternatively less than about ± 7 °C, alternatively less than about ± 6 °C, alternatively less than about ± 5 °C, alternatively less than about ± 4 °C, alternatively less than about ± 3 °C, alternatively less than about ± 2 °C, or alternatively less than about ± 1 °C. In some aspects, the near-isothermal reaction temperature can vary by less than about ± 50 °C, alternatively less than about ± 25 °C, or alternatively less than about ± 10 °C.

[0052] The reactor can be characterized by a near-isothermal temperature of from about 300 °C to about 1,600 °C, alternatively from about 600 °C to about 1,200 °C, or alternatively from about 700 °C to about 1,100 °C.

[0053] In some aspects, the reactor can be characterized by a near-isothermal temperature of from about 300 °C to about 1,200 °C, alternatively from about 400 °C to about 1,100 °C, or alternatively from about 500 °C to about 1,000 °C; wherein the near-isothermal conditions can be provided by removal of process heat from the reactor. Generally, at lower temperatures, it is necessary to remove heat generated in the process (e.g., cool the reactor) to achieve near-isothermal conditions, e.g., near-isothermal temperature.

[0054] In other aspects, the reactor can be characterized by a near-isothermal temperature of from about 800 °C to about 1,600 °C, alternatively from about 850 °C to about 1,400 °C, or alternatively from about 900 °C to about 1,200 °C; wherein the near-isothermal conditions can be provided by supplying heat to the reactor. Generally, at higher temperatures, it is necessary to add heat to the process (e.g., heat the reactor) to achieve near-isothermal conditions, e.g., near-isothermal temperature.

[0055] In an aspect, the reactor can be characterized by a pressure of from about 0.1 barg to about 90 barg, alternatively from about 0.1 barg to about 40 barg, or alternatively from about 1 barg to about 25 barg.

[0056] In an aspect, the reactor can be characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 s, alternatively from about 0.001 ms to about 1 s, alternatively from about 0.001 ms to about 100 ms, alternatively from about 0.001 ms to about 10 ms, alternatively from about 0.001 ms to about 5 ms, or alternatively from about 0.01 ms to about 1.2 ms. Generally, the contact time of a reactor comprising a catalyst refers to the average amount of time that a compound (e.g., a molecule of that compound) spends in contact with the catalyst (e.g., within the catalyst bed), e.g., the average amount of time that it takes for a compound (e.g., a molecule of that compound) to travel through the catalyst bed. For purposes of the disclosure herein the contact time of less than about 5 ms can be referred to as “millisecond regime” (MSR); and a process or reaction as disclosed herein characterized by a contact time of less than about 5 ms can be referred to as “millisecond regime”- CPO (MSR-CPO) process or reaction, respectively.

[0057] In some aspects, the reactor can be characterized by a contact time of from about 0.001 ms to about 5 ms, or alternatively from about 0.01 ms to about 1.2 ms.

[0058] In some aspects, the near-isothermal conditions can be provided by a catalyst bed configuration. In an aspect, the reactor (e.g., isothermal reactor) can comprise a fixed catalyst bed, wherein the fixed catalyst bed comprises the CPO catalyst.

[0059] In an aspect, the catalyst bed can comprise a bed inlet, a bed outlet, a first intermediate bed zone, a second intermediate bed zone, and optionally a third intermediate bed zone; wherein the first intermediate bed zone and the second intermediate bed zone are disposed between the bed inlet and the bed outlet; wherein the second intermediate bed zone is downflow of the first intermediate bed zone; wherein the third intermediate bed zone is disposed between the first intermediate bed zone and the second intermediate bed zone; wherein the third intermediate bed zone is downflow of the first

intermediate bed zone; wherein the third intermediate bed zone is upflow of the second intermediate bed zone; wherein a reactor inner wall surface and an outer surface of the first intermediate bed zone define a first annular space; wherein a reactor inner wall surface and an outer surface of the second intermediate bed zone define a second annular space; wherein the bed inlet is characterized by a bed inlet surface area; wherein the bed outlet is characterized by a bed outlet surface area; wherein the first intermediate bed zone is characterized by a first intermediate bed cross sectional area; wherein the second intermediate bed zone is characterized by a second intermediate bed cross sectional area; wherein the third intermediate bed zone is characterized by a third intermediate bed cross sectional area; wherein the first intermediate bed cross sectional area increases along the first intermediate bed zone in the direction of the flow through the reactor; wherein the second intermediate bed cross sectional area decreases along the second intermediate bed zone in the direction of the flow through the reactor; wherein the third intermediate bed cross sectional area is substantially constant along the third intermediate bed zone; wherein the first intermediate bed cross sectional area and the second intermediate bed cross sectional area are greater than the bed inlet surface area, the bed outlet surface area, or both; and wherein the third intermediate bed cross sectional area is greater than the first intermediate bed cross sectional area, the second intermediate bed cross sectional area, or both. In such aspect, the first annular space, the second annular space, or both can comprise a radiation shield; and/or one or more structural elements that are configured to provide for a catalyst bed configuration that is characterized by a non-uniform cross section along the catalyst bed. In some aspects, the catalyst bed can comprise a structured catalyst that provides for a catalyst bed configuration that is characterized by a non-uniform cross section along the catalyst bed; and wherein the structured catalyst comprises a metallic monolithic catalyst, a non-metallic monolithic catalyst, or both. Non-limiting examples of catalyst bed shapes suitable for use in the present disclosure include a spherical shape; a prolate spheroidal shape; an oblate spheroidal shape; etc. As another example, the first intermediate bed zone and/or the second intermediate bed zone can be characterized by a truncated conical shape, or portion thereof; half of a spherical shape, or portion thereof; half of a prolate spheroidal shape, or portion thereof; half of an oblate spheroidal shape, or portion thereof; and the like; or combinations thereof. Catalyst bed configurations suitable for use in the present disclosure are described in more detail in U.S. Provisional Application 62/522,910 (Atty. Docket 17T&I0063 (4515-06800) entitled "Improved Reactor Designs for Heterogeneous Catalytic Reactions," which is incorporated by reference herein in its entirety.

[0060] In an aspect, the syngas produced under non-adiabatic and near-isothermal conditions as disclosed herein can comprise hydrogen, carbon monoxide, water, carbon dioxide, and unreacted hydrocarbons. In some aspects, the syngas can be used in a downstream process as recovered from the reactor (e.g., “as is,” without further processing). In other aspects, the syngas can be further processed prior to being used in a downstream process. For example, unreacted hydrocarbons, diluent, water, etc. can be recovered from the syngas prior to using the syngas in a downstream process. For example, water can be condensed and separated from the syngas, for example in a cooling tower.

[0061] In an aspect, a process for producing syngas as disclosed herein can further comprise (i) recovering at least a portion of the unreacted hydrocarbons from the syngas to yield recovered hydrocarbons, and (ii) recycling at least a portion of the recovered hydrocarbons to the reactor. As will be appreciated by one of skill in the art, and with the help of this disclosure, although fairly high conversions can be achieved in CPO processes (e.g., conversions of equal to or greater than about 90%), the unconverted hydrocarbons could be recovered and recycled back to the reactor.

[0062] In an aspect, the syngas can be characterized by a H_2/CO molar ratio that varies by less than about 20%, alternatively less than about 15%, alternatively less than about 10%, or alternatively less than about 5%, (as compared to a desired ratio) under near-isothermal operating conditions for a set reactor operating conditions, such as pressure and CH_4/O_2 molar ratio.

[0063] In an aspect, the syngas can be characterized by an M ratio that varies by less than about 20%, alternatively less than about 15%, alternatively less than about 10%, or alternatively less than about 5%, (as compared to a desired M ratio) under near-isothermal operating conditions for a set reactor operating conditions, such as pressure and CH_4/O_2 molar ratio.

[0064] Syngas recovered from the reactor can be used for any suitable purpose, such as methanol production, olefins production, aromatics production, liquid hydrocarbons production, liquid hydrocarbons production via a gas to liquids (GTL) process, liquid hydrocarbons production via a Fischer-Tropsch (FT) process, dimethyl ether (DME) production, oxo-synthesis of aliphatic aldehydes and/or alcohols, petrochemicals, and the like, or combinations thereof. As will be appreciated by one of skill in the art, and with the help of this disclosure, each process that uses syngas for the synthesis of a particular product, may benefit from using a syngas with a specific composition (e.g., specific M ratio; specific H_2/CO molar ratio; etc.).

[0065] In aspects where the syngas is characterized by an M ratio of from about 1.6 to about 2.2, alternatively from about 1.9 to about 2.2, or alternatively about 2.0, the syngas can be further used for methanol production. In some aspects, at least a portion of the syngas recovered from the reactor can be contacted with a methanol production catalyst in a methanol production unit to produce methanol. The methanol production unit 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 trickle bed reactor, a fluidized bed reactor, a slurry reactor, a loop reactor, a cooled multi tubular reactor, and the like, or combinations thereof.

[0066] Generally, CO and H₂ can be converted into methanol (CH₃OH) according to reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$. CO₂ and H₂ can also be converted to methanol according to reaction $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$. Methanol synthesis from CO, CO₂ and H₂ is a catalytic process, and is most often conducted in the presence of copper based catalysts. The methanol production unit can comprise a methanol production catalyst, such as any suitable commercial catalyst used for methanol synthesis. Non-limiting examples of methanol production catalysts suitable for use in the methanol production unit in the current disclosure include Cu, Cu/ZnO, Cu/ThO₂, Cu/Zn/Al₂O₃, Cu/ZnO/Al₂O₃, Cu/Zr, and the like, or combinations thereof.

[0067] In an aspect, the syngas recovered from the reactor can be characterized by a H₂/CO molar ratio of about 1:1, wherein at least a portion of the syngas can be used for dimethyl ether (DME) production.

[0068] In an aspect, the syngas recovered from the reactor can be characterized by a H₂/CO molar ratio of about 1:1, wherein at least a portion of the syngas can be used for oxo-synthesis of aliphatic aldehydes and/or alcohols. In such aspect, the alcohol can comprise 2-ethyl hexanol.

[0069] In an aspect, the syngas recovered from the reactor can be further converted to olefins. For example, the syngas can be converted to alkanes by using a Fisher-Tropsch process, and the alkanes can be further converted by dehydrogenation into olefins.

[0070] In an aspect, the syngas recovered from the reactor can be further converted to liquid hydrocarbons (e.g., alkanes) by a Fisher-Tropsch process. In such aspect, the liquid hydrocarbons can be further converted by dehydrogenation into olefins.

[0071] In an aspect, a process for producing syngas as disclosed herein can comprise reacting under non-adiabatic and near-isothermal conditions, via a MSR-CPO reaction, a reactant mixture in an isothermal reactor to produce syngas; wherein the isothermal reactor comprises a fixed CPO

catalyst bed; wherein the reactant mixture comprises methane and oxygen; wherein the reactant mixture is characterized by a methane to oxygen (CH_4/O_2) molar ratio of from about 1.6:1 to about 2.2:1; wherein the reactor is characterized by a near-isothermal temperature of from about 600 °C to about 1,200 °C; wherein the reactor is characterized by a pressure of from about 0.1 barg to about 40 barg; wherein the reactor is characterized by a short contact time of from about 0.001 ms to about 1.2 ms; wherein the syngas comprises hydrogen, carbon monoxide, water, carbon dioxide, and unconverted hydrocarbons; and wherein the syngas is characterized by an M ratio ($(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$) that varies by less than about 10% from a targeted or desired M ratio under the near-isothermal conditions for a given set of isothermal reactor operating conditions. In such aspect, the M ratio can be from about 1.7 to about 2.2, or alternatively about 2.0, wherein the syngas can be further used for methanol production.

[0072] In an aspect, a process for producing syngas as disclosed herein can comprise selecting a set of process conditions for producing syngas; wherein the syngas comprises hydrogen, carbon monoxide, water, carbon dioxide, and unconverted hydrocarbon; and wherein the syngas is characterized by an M ratio ($(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$) that varies by less than about 20% from a targeted or desired M ratio under the near-isothermal conditions for a given set of isothermal reactor operating conditions. In such aspect, selecting the set of process conditions for producing syngas can comprise: (a) constructing a first two-coordinate graph containing a vertical axis for M ratio (syngas composition) and a horizontal axis for reactor temperature; (b) generating, via mathematical simulations and/or experimental data, one or more M ratio versus reactor temperature (M-T) data curves, wherein each M-T data curve of the one or more M-T data curves corresponds to a given set of pressure (reactor pressure) and CH_4/O_2 molar ratio values; (c) representing the one or more M-T data curves upon the first two-coordinate graph; (d) identifying a desired M ratio value, based on a downstream process intending to utilize the produced syngas; and (e) for each M-T data curve, with the help of the first two-coordinate graph, determining one or more reactor temperatures corresponding to the desired M ratio value. Selecting the set of process conditions for producing syngas can further comprise (1) calculating a slope of the M-T data curve around the data point corresponding to the desired M ratio and the reactor temperature; and (2) determining an isothermal temperature for the desired M ratio, wherein operating the reactor in a near-isothermal manner (e.g., under near-isothermal conditions) can achieve the M value within about 20% of the desired or targeted M value for a given set of isothermal reactor operating conditions (e.g., pressure and CH_4/O_2

molar ratio). Selecting the set of process conditions for producing syngas can further comprise (i) constructing a second two-coordinate graph containing a vertical axis for heat transfer necessary for maintaining a particular reactor temperature (e.g., near-isothermal temperature), and a horizontal axis for reactor temperature; (ii) generating, via mathematical simulations and/or experimental data, one or more heat versus reactor temperature (Q-T) data curves, wherein each Q-T data curve of the one or more Q-T data curves corresponds to a given set of pressure (reactor pressure) and CH_4/O_2 molar ratio values; (iii) representing the one or more Q-T data curves upon the second two-coordinate graph; and (iv) for each temperature or temperature range corresponding to the desired M ratio value determined by using the first two-coordinate graph, determining the heat transfer necessary for maintaining near-isothermal conditions within the reactor. Examples of using a first two-coordinate graph (e.g., Figure 1) and a second two-coordinate graph (e.g., Figure 2) are discussed in more detail in the Examples section. Once the near-isothermal temperatures and the heat transfer values necessary to maintain the near-isothermal temperatures are known (e.g., from the first two-coordinate graph, the second two-coordinate graph), a variety of other considerations can be applied by one of skill in the art, and with the help of this disclosure, to select the set of process conditions for producing syngas, wherein an optimum operating window of process conditions can be established based on the feedstock quality and availability, the metallurgy of the reactor and associated piping and equipment, energy utilization, needs of downstream process utilizing the produced syngas, etc.

[0073] In an aspect, a process for producing syngas as disclosed herein can advantageously display improvements in one or more process characteristics when compared to an otherwise similar process that does not employ non-adiabatic and near-isothermal process conditions for producing syngas. The process for producing syngas as disclosed herein can advantageously yield syngas of different desired qualities (e.g., syngas with specific H_2/CO molar ratios, with specific M ratios, with or without CO_2 , etc.); by employing specific combinations of process and catalyst variables, such as temperature (e.g., near-isothermal temperature), pressure, CH_4/O_2 molar ratio, gas flow, reactor configuration, catalyst bed configuration, and the like, or combinations thereof. The process for producing syngas as disclosed herein can advantageously reduce operating costs by producing syngas having a stoichiometric amount of hydrogen to CO required by downstream processes.

[0074] Conventionally, syngas is produced by steam reforming, which yields a syngas characterized by an M ratio of about 3, which is significantly greater than the syngas M ratio required by some processes, such as methanol production that requires an M ratio of about 2. In an aspect, a

process for producing syngas as disclosed herein can advantageously produce a syngas with a desired composition (e.g., with specific H_2/CO molar ratios, with specific M ratios, with or without CO_2 , etc.); and hence additional hydrogen (e.g., more than the hydrogen required by a downstream process) is not produced, thereby saving hydrocarbon feedstock (e.g., natural gas). The process for producing syngas as disclosed herein is advantageously more flexible than conventional processes for the production of syngas, and it can be easily adapted to a wide range of syngas compositions required by a downstream process.

[0075] As will be appreciated by one of skill in the art, and with the help of this disclosure, since the CPO reaction is exothermic, no additional heat supply in the form of fuel combustion is needed (except for pre-heating reactants in the reaction mixture that is supplied to a syngas generation section), when compared to conventional steam reforming. As such, the process for producing syngas as disclosed herein can advantageously generate less CO_2 through fuel burning, when compared to steam reforming.

[0076] As will be appreciated by one of skill in the art, and with the help of this disclosure, the quality of syngas (e.g., the syngas composition) that is fed to a specific process can have an important impact on the process gas flows, as well as product selectivity. For example, in the case of a methanol production process, the syngas composition used for producing methanol can change a composition of the crude methanol recovered from a methanol production reactor (e.g., a loop reactor), wherein the crude methanol can be rich in methanol (as opposed to rich in water); thereby advantageously changing the process downstream of the methanol production reactor, owing to reduced recycle streams (due to having only the necessary amount of hydrogen in the syngas), as well as to a reduced amount water in the crude methanol product. Thus, the methanol production process can advantageously be more energy efficient; owing to a lower energy consumption in a methanol purification section, for example by elimination of one or more distillation columns. Since the hydrogen amount in the syngas is reduced (for example by comparison with a syngas produced by steam reforming), recycle flow loops would be of smaller size and recycle gas compressors needed would be of smaller volumetric flow rate and thus consume less electricity. The methanol production process can advantageously be more carbon efficient, by saving hydrocarbon feedstock (e.g., natural gas) employed in the production of the syngas.

[0077] In an aspect, a process for producing syngas as disclosed herein can advantageously employ near-isothermal conditions. For example, water and/or steam diluent (e.g., the steam can be

wet, dry, saturated, superheated, etc.) can be introduced to the reactor to capture or augment process heat in order to target a near-isothermal temperature, which near-isothermal temperature enables the production of a syngas with a desired composition. Conventional processes (catalytic or thermal partial oxidation processes) are generally operated close to adiabatic mode to minimize the heat loss. The addition of steam of different qualities can enable temperature control. For example, superheated steam can enhance (e.g., augment) the heating, and hence it can be useful in a case where heat has to be added for achieving and/or maintaining near-isothermal conditions. As another example, water or wet steam can allow heat removal, which can be useful in a case where heat has to be removed for achieving and/or maintaining near-isothermal conditions.

[0078] In an aspect, a process for producing syngas as disclosed herein can advantageously employ carbon dioxide diluent. In such aspect, the use of carbon dioxide diluent can advantageously lead to a decreased amount of coke, thus decreasing catalyst deactivation (e.g., maintaining the catalyst in an active state). The use of carbon dioxide diluent can advantageously allow for producing a syngas with an increased carbon monoxide amount, as required by a downstream process. Generally, by using carbon dioxide to produce syngas, carbon dioxide emissions can advantageously be reduced.

[0079] Without wishing to be limited by theory, the reactions that the carbon dioxide diluent would participate in the reactor are generally endothermic, and hence the carbon dioxide diluent can be advantageously used for reactor temperature control via direct heat transfer, while at the same time minimizing coke, and keeping the catalyst active. As will be appreciated by one of skill in the art, and with the help of this disclosure, the use of carbon dioxide endothermic reactions for reactor temperature control via direct heat transfer can be advantageously used at relatively lower reactor operating temperatures (e.g., from about 300 °C to about 1,200 °C), where it is necessary to remove process heat for maintaining near-isothermal conditions. The direct heat transfer can advantageously allow for employing lower temperature metallurgies, as well as increasing syngas production throughput within metallurgical limits by operating the reactor at lower temperatures.

[0080] In an aspect, a process for producing syngas as disclosed herein can advantageously employ short contact times, such as the millisecond regime (MSR), which increases selectivity to a syngas having a desired composition (e.g., syngas with specific H₂/CO molar ratios, with specific M ratios, with or without CO₂, etc.). MSR in a syngas reactor can advantageously minimize side reactions, such as complete combustion, that could result in a decrease in selectivity to desired syngas

components. Additional advantages of the processes for the production of syngas as disclosed herein can be apparent to one of skill in the art viewing this disclosure.

EXAMPLES

[0081] 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

[0082] Syngas composition was investigated as a function of temperature for a catalytic partial oxidation (CPO) reaction under various process conditions. The syngas composition was calculated by using a mathematical model of the CPO reactor, and the resulting data are displayed in Figure 1. The mathematical model was developed in Aspen Plus software. The reactor was represented by a Gibbs reactor which approaches equilibrium composition for a given set of process conditions. The feed composition and reactor operating parameters were varied to obtain the change in exit stream composition. The exit stream composition was used to calculate the M ratio value. The y axis in Figure 1 plots M ratio values, wherein the M ratio is a molar ratio defined as $(\text{H}_2\text{-CO}_2)/(\text{CO}+\text{CO}_2)$.

[0083] Corresponding to the data in Figure 1, the heat (Q) transfer necessary for maintaining isothermal conditions was estimated by using the heat load predicted by the model described above, and the resulting data are displayed in Figure 2. Negative Q values represent the amount of heat that has to be removed from the reactor (reacting system), for example by cooling the reactor, to maintain a particular temperature (near-isothermal temperature). Positive Q values represent the amount of heat that has to be introduced to the reactor (reacting system), for example by heating the reactor, to maintain a particular temperature (near-isothermal temperature). A value of 0 (zero) for Q signifies that no heat transfer is necessary for achieving the particular corresponding temperature (near-isothermal temperature) under the given process conditions.

[0084] The data in Figures 1 and 2 provide an example of how to select a temperature (e.g., near-isothermal temperature) for the production of a syngas with a desired composition (e.g., with a specific M ratio). As will be appreciated by one of skill in the art, and with the help of this disclosure, the concepts herein can be carried out by using mathematical or computational simulations to generate graphs of syngas composition variation with reactor temperature, under given process conditions, such as pressure and CH_4/O_2 molar ratio. For example, the graphs of

syngas composition variation with reactor temperature could plot the M ratio versus the reactor temperature, in a similar fashion to Figure 1. As another example, the graphs of syngas composition variation with reactor temperature could plot the H_2/CO molar ratio versus the reactor temperature. Similar graphs can be generated for any feedstock of interest with any oxidant of interest. An optimum operating window of process conditions could be established based on the feedstock quality and availability, the metallurgy of the reactor and associated piping and equipment, energy utilization, needs of downstream process utilizing the produced syngas, etc.; and then graphs of syngas composition variation with reactor temperature could allow for selecting specific process operating conditions that would enable maintaining near-isothermal temperatures for the production of a syngas with a specific desired composition.

[0085] For example, and by considering the data provided in Figure 1, if it would be desired to produce a syngas having an M ratio of 1.7, there are three distinct sets of operating conditions (three options) for achieving a syngas with an M ratio of 1.7: (1) a CH_4/O_2 molar ratio of 2.2, a pressure of 40 bar, and a temperature of about 830 °C; (2) a CH_4/O_2 molar ratio of 1.7, a pressure of 10 bar, and a temperature of about 930 °C; or (3) a CH_4/O_2 molar ratio of 1.7, a pressure of 40 bar, and a temperature of about 1,100 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, the shape of the curve for each individual set of process operating conditions also has to be taken into account. For example, option (1) has a steeper curve (e.g., greater slope) going through the data point corresponding to an M ratio of 1.7 and 830 °C, indicating that a variation in temperature around the value of 830 °C will cause a larger deviation from a target M ratio value (e.g., M ratio of 1.7) of the resulting syngas when operating under near-isothermal conditions around the value of 830 °C; when compared to option (3) which has a less steep curve (e.g., smaller slope) going through the data point corresponding to an M ratio of 1.7 and 1,100 °C, indicating that a variation in temperature around the value of 1,100 °C will cause a smaller deviation from a target M ratio value (e.g., M ratio of 1.7) of the resulting syngas when operating under near-isothermal conditions around the value of 1,100 °C. Further, the data provided in Figure 2 (corresponding to the data in Figure 1) can be used for considering the magnitude of the heat transfer required for maintaining the reactor at a given temperature (near-isothermal temperature) given a particular set of process parameters. For example, option (1) requires more cooling to maintain 830 °C than option (2) for maintaining 930 °C, while option (3) requires no heat transfer for maintaining 1,100 °C.

[0086] As another example, and by considering the data provided in Figure 1, if it would be desired to produce a syngas having an M ratio of 2.0, there are two distinct sets of operating conditions (two options) for achieving a syngas with an M ratio of 2.0: (1) a CH_4/O_2 molar ratio of 2.2, a pressure of 10 bar, and a temperature of about 700 °C; or (2) a CH_4/O_2 molar ratio of 2.2, a pressure of 40 bar, and a temperature of about 1,070 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, the shape of the curve for each individual set of process operating conditions also has to be taken into account. For example, option (1) has a steeper curve (e.g., greater slope) going through the data point corresponding to an M ratio of 2.0 and 700 °C, indicating that a variation in temperature around the value of 700 °C will cause a larger deviation from a target M ratio value (e.g., M ratio of 2.0) of the resulting syngas when operating under near-isothermal conditions around the value of 700 °C; when compared to option (2) which has a less steep curve (e.g., smaller slope) going through the data point corresponding to an M ratio of 2.0 and 1,070 °C, indicating that a deviation from isothermal temperature around the value of 1,070 °C will cause a smaller deviation from a target M ratio value (e.g., M ratio of 2.0) of the resulting syngas when operating under near-isothermal conditions around the value of 1,070 °C. Further, the data provided in Figure 2 (corresponding to the data in Figure 1) can be used for considering the magnitude of the heat transfer required for maintaining the reactor at a given temperature (near-isothermal temperature) given a particular set of process parameters. For example, option (1) requires more heat transfer in terms of cooling to maintain 700 °C than option (2) requires as heat transfer in terms of heating for maintaining 1,070 °C.

[0087] As yet another example, and by considering the data provided in Figure 1, if it would be desired to produce a syngas having an M ratio of 2.1, there are two distinct sets of operating conditions (two options) for achieving a syngas with an M ratio of 2.1: (1) a CH_4/O_2 molar ratio of 2.2, a pressure of 10 bar, and a temperature of from about 740 °C to about 1,000 °C; or (2) a CH_4/O_2 molar ratio of 2.2, a pressure of 40 bar, and a temperature of from about 1,275 °C to about 1,325 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, the shape of the curve for each individual set of process operating conditions also has to be taken into account. Option (1) displays a slope of about 0 (zero) over a fairly wide temperature range (about 740 °C to about 1,000 °C), corresponding to an M ratio of 2.1, indicating that a temperature variation within the range of from about 740 °C to about 1,000 °C would not alter the M ratio. Option (2) displays a slope of about 0 (zero) over a more narrow temperature range (about 1,275 °C to about 1,325 °C),

when compared to option (1), corresponding to an M ratio of 2.1, indicating that a temperature variation within the range of from about 1,275 °C to about 1,325 °C would not alter the M ratio. Further, the data provided in Figure 2 (corresponding to the data in Figure 1) can be used for considering the magnitude of the heat transfer required for maintaining the reactor at a given temperature (near-isothermal temperature) given a particular set of process parameters. For example, option (1) may require either cooling, heating, or no heat transfer, based on the near-isothermal temperature that is desired to be maintained within the range of from about 740 °C to about 1,000 °C. Option (2) would require heating for maintaining the near-isothermal temperature that is desired to be maintained within the range of from about 1,275 °C to about 1,325 °C.

[0088] 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.

[0089] 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.

[0090] 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

[0091] A first aspect, which is a process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 s; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons.

[0092] A second aspect, which is a process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 ms; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons.

[0093] A third aspect, which is the process of any one of the first and the second aspects, wherein the near-isothermal conditions are provided by direct heat exchange and/or indirect heat exchange.

[0094] A fourth aspect, which is the process of the third aspect, wherein the indirect heat exchange comprises external heat exchange, external coolant fluid cooling, reactive cooling, liquid nitrogen cooling, cryogenic cooling, electric heating, electric arc heating, microwave heating, radiant heating, natural gas combustion, solar heating, infrared heating, or combinations thereof.

[0095] A fifth aspect, which is the process of any one of the first through the fourth aspects, wherein the reactant mixture further comprises a diluent, and wherein the diluent contributes to the near-isothermal conditions via direct heat exchange.

[0096] A sixth aspect, which is the process of the fifth aspect, wherein the diluent comprises water, steam, inert gases, nitrogen, carbon dioxide, or combinations thereof.

[0097] A seventh aspect, which is the process of any one of the first through the sixth aspects, wherein the diluent contributes to the near-isothermal conditions by phase change.

[0098] An eighth aspect, which is the process of any one of the first through the seventh aspects, wherein the reactor comprises an isothermal reactor.

[0099] A ninth aspect, which is the process of the eighth aspect, wherein the isothermal reactor comprises a fixed catalyst bed, and wherein the fixed catalyst bed comprises the CPO catalyst.

[0100] A tenth aspect, which is the process of any one of the first through the ninth aspects, wherein the reactor is characterized by a near-isothermal temperature of from about 300 °C to about 1,600 °C.

[0101] An eleventh aspect, which is the process of any one of the first through the tenth aspects, wherein the reactor is characterized by a near-isothermal temperature of from about 300 °C to about 1,200 °C, and wherein the near-isothermal conditions are provided by removal of process heat from the reactor.

[0102] A twelfth aspect, which is the process of any one of the first through the tenth aspects, wherein the reactor is characterized by a near-isothermal temperature of from about 800 °C to about 1,600 °C, and wherein the near-isothermal conditions are provided by supplying heat to the reactor.

[0103] A thirteenth aspect, which is the process of any one of the first through the twelfth aspects, wherein the reactor is characterized by a pressure of from about 0.1 barg to about 90 barg.

[0104] A fourteenth aspect, which is the process of any one of the first through the thirteenth aspects, wherein the reactant mixture is characterized by a methane to oxygen (CH_4/O_2) molar ratio of from about 1:1 to about 3:1.

[0105] A fifteenth aspect, which is the process of any one of the first through the fourteenth aspects, wherein the syngas is characterized by an M ratio that varies by less than about 20% from a desired M ratio under the near-isothermal conditions for a given set of reactor operating conditions, and wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$.

[0106] A sixteenth aspect, which is the process of any one of the first through the fifteenth aspects, wherein the syngas is characterized by an M ratio of from about 1.6 to about 2.2, wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$, and wherein the syngas is further used for methanol production.

[0107] A seventeenth aspect, which is the process of any one of the first through the sixteenth aspects, wherein the reactant mixture further comprises water and/or steam diluent, and wherein the syngas is characterized by a hydrogen to carbon monoxide molar ratio that is increased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an otherwise

similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the water and/or steam diluent.

[00108] An eighteenth aspect, which is the process of any one of the first through the seventeenth aspects, wherein the reactant mixture further comprises carbon dioxide diluent, and wherein the syngas is characterized by a hydrogen to carbon monoxide molar ratio that is decreased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an otherwise similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the carbon dioxide diluent.

[00109] A nineteenth aspect, which is the process of any one of the first through the eighteenth aspects, wherein the hydrocarbons comprise methane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, paraffins, shale gas, shale liquids, fluid catalytic cracking (FCC) off gas, refinery process gases, stack gases, or combinations thereof.

[00110] A twentieth aspect, which is the process of any one of the first through the nineteenth aspects further comprising (i) recovering at least a portion of the unreacted hydrocarbons from the syngas to yield recovered hydrocarbons, and (ii) recycling at least a portion of the recovered hydrocarbons to the reactor.

[00111] A twenty-first aspect, which is the process of any one of the first through the twentieth aspects, wherein the syngas is further used for methanol production, olefins production, aromatics production, liquid hydrocarbons production, liquid hydrocarbons production via a gas to liquids (GTL) process, liquid hydrocarbons production via a Fischer-Tropsch (FT) process, dimethyl ether (DME) production, oxo-synthesis of aliphatic aldehydes and/or alcohols, petrochemicals, or combinations thereof.

[00112] A twenty-second aspect, which is a process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in an isothermal reactor to produce syngas, wherein the reactant mixture comprises methane and oxygen, wherein the isothermal reactor comprises a CPO catalyst, wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 1.2 ms, and wherein the syngas comprises hydrogen, carbon monoxide, water, carbon dioxide, and unreacted.

[00113] A twenty-third aspect, which is the process of the twenty-second aspect, wherein the isothermal reactor comprises a tubular reactor, a continuous flow reactor, an isothermal reactor, a

fixed bed reactor, a fluidized bed reactor, a bubbling bed reactor, a circulating bed reactor, an ebullating bed reactor, a rotary kiln reactor, or combinations thereof.

[00114] A twenty-fourth aspect, which is the process of any one of the twenty-second and the twenty-third aspects, wherein the isothermal reactor comprises a fixed CPO catalyst bed comprising the CPO catalyst.

[00115] A twenty-fifth aspect, which is the process of any one of the twenty-second through the twenty-fourth aspects, wherein the reactor is characterized by a near-isothermal temperature of from about 600 °C to about 1,200 °C.

[00116] A twenty-sixth aspect, which is the process of any one of the twenty-second through the twenty-fifth aspects, wherein the reactor is characterized by a pressure of from about 0.1 barg to about 40 barg.

[00117] A twenty-seventh aspect, which is the process of any one of the twenty-second through the twenty-sixth aspects, wherein the reactant mixture is characterized by a methane to oxygen (CH_4/O_2) molar ratio of from about 1.6:1 to about 2.2:1.

[00118] A twenty-eighth aspect, which is the process of any one of the twenty-second through the twenty-seventh aspects, wherein the syngas is characterized by an M ratio that varies by less than about 10% from a desired M ratio under the near-isothermal conditions for a given set of reactor operating conditions, and wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$.

[00119] 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.

[00120] 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 syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in a reactor to produce syngas; wherein the reactant mixture comprises hydrocarbons and oxygen; wherein the reactor comprises a CPO catalyst; wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 5 s; and wherein the syngas comprises hydrogen, carbon monoxide, carbon dioxide, water, and unreacted hydrocarbons.
2. The process of claim 1, wherein the reactor is characterized by a contact time of from about 0.001 ms to about 5 ms.
3. The process of any one of claims 1-2, wherein the near-isothermal conditions are provided by direct heat exchange and/or indirect heat exchange.
4. The process of claim 3, wherein the indirect heat exchange comprises external heat exchange, external coolant fluid cooling, reactive cooling, liquid nitrogen cooling, cryogenic cooling, electric heating, electric arc heating, microwave heating, radiant heating, natural gas combustion, solar heating, infrared heating, or combinations thereof.
5. The process of any one of claims 1-4, wherein the reactant mixture further comprises a diluent, and wherein the diluent contributes to the near-isothermal conditions via direct heat exchange; and wherein the diluent comprises water, steam, inert gases, nitrogen, carbon dioxide, or combinations thereof.
6. The process of any one of claims 1-5, wherein the diluent contributes to the near-isothermal conditions by phase change.
7. The process of any one of claims 1-6, wherein the reactor comprises an isothermal reactor.
8. The process of claim 7, wherein the isothermal reactor comprises a fixed catalyst bed, and wherein the fixed catalyst bed comprises the CPO catalyst.
9. The process of any one of claims 1-8, wherein the reactor is characterized by a near-isothermal temperature of from about 300 °C to about 1,600 °C.
10. The process of any one of claims 1-9, wherein the reactor is characterized by a near-isothermal temperature of from about 300 °C to about 1,200 °C, and wherein the near-isothermal conditions are provided by removal of process heat from the reactor.

11. The process of any one of claims 1-9, wherein the reactor is characterized by a near-isothermal temperature of from about 800 °C to about 1,600 °C, and wherein the near-isothermal conditions are provided by supplying heat to the reactor.
12. The process of any one of claims 1-11, wherein the reactor is characterized by a pressure of from about 0.1 barg to about 90 barg; and wherein the reactant mixture is characterized by a methane to oxygen (CH_4/O_2) molar ratio of from about 1:1 to about 3:1.
13. The process of any one of claims 1-12, wherein the syngas is characterized by an M ratio that varies by less than about 20% from a desired M ratio under the near-isothermal conditions for a given set of reactor operating conditions, and wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$.
14. The process of any one of claims 1-13, wherein the syngas is characterized by an M ratio of from about 1.6 to about 2.2, wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$, and wherein the syngas is further used for methanol production.
15. The process of any one of claims 1-14, wherein the reactant mixture further comprises water and/or steam diluent, and wherein the syngas is characterized by a hydrogen to carbon monoxide molar ratio that is increased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an otherwise similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the water and/or steam diluent.
16. The process of any one of claims 1-15, wherein the reactant mixture further comprises carbon dioxide diluent, and wherein the syngas is characterized by a hydrogen to carbon monoxide molar ratio that is decreased when compared to a hydrogen to carbon monoxide molar ratio of a syngas produced by an otherwise similar process conducted with a reactant mixture comprising hydrocarbons and oxygen without the carbon dioxide diluent.
17. A process for producing syngas comprising reacting under non-adiabatic and near-isothermal conditions, via a catalytic partial oxidation (CPO) reaction, a reactant mixture in an isothermal reactor to produce syngas, wherein the reactant mixture comprises methane and oxygen, wherein the isothermal reactor comprises a CPO catalyst, wherein the reactor is characterized by a contact time of from about 0.001 milliseconds (ms) to about 1.2 ms, and wherein the syngas comprises hydrogen, carbon monoxide, water, carbon dioxide, and unreacted.
18. The process of claim 17, wherein the isothermal reactor comprises a tubular reactor, a continuous flow reactor, an isothermal reactor, a fixed bed reactor, a fluidized bed reactor, a

bubbling bed reactor, a circulating bed reactor, an ebullating bed reactor, a rotary kiln reactor, or combinations thereof.

19. The process of any one of claims 17-18, wherein the reactor is characterized by a near-isothermal temperature of from about 600 °C to about 1,200 °C; wherein the reactor is characterized by a pressure of from about 0.1 barg to about 40 barg; and wherein the reactant mixture is characterized by a methane to oxygen (CH_4/O_2) molar ratio of from about 1.6:1 to about 2.2:1.

20. The process of any one of claims 17-19, wherein the syngas is characterized by an M ratio that varies by less than about 10% from a desired M ratio under the near-isothermal conditions for a given set of reactor operating conditions, and wherein the M ratio is a molar ratio defined as $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$.

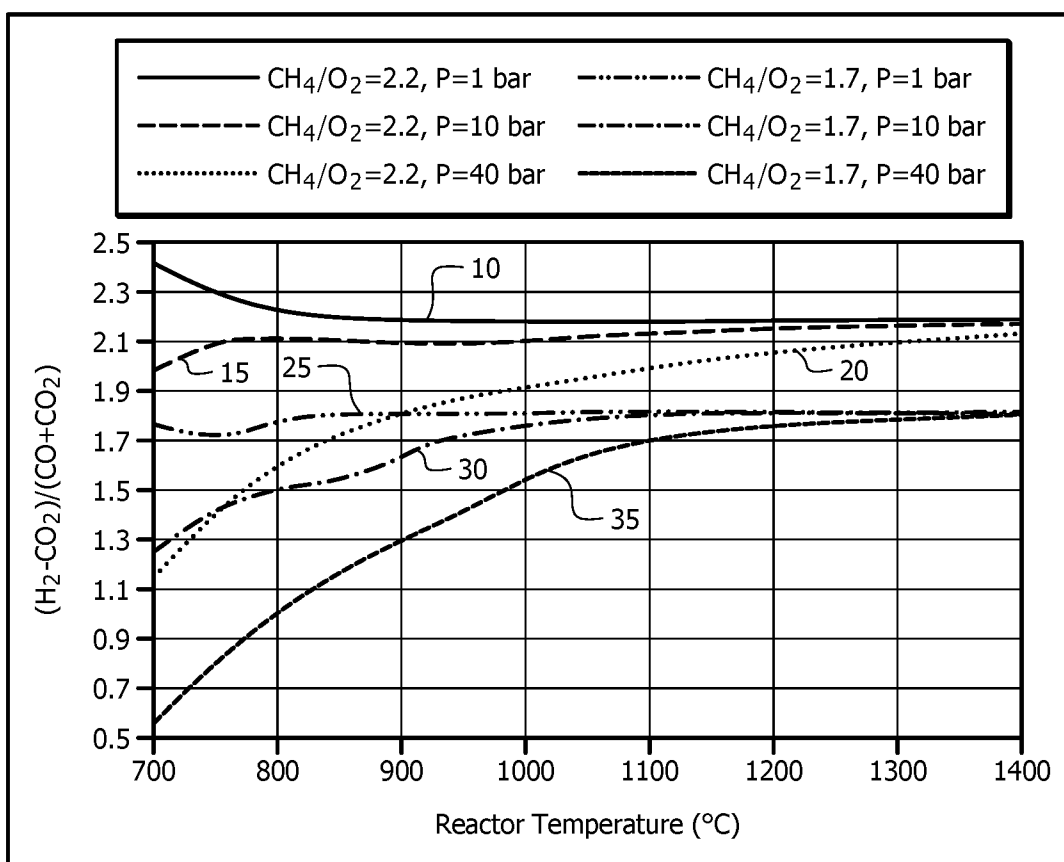


FIG. 1

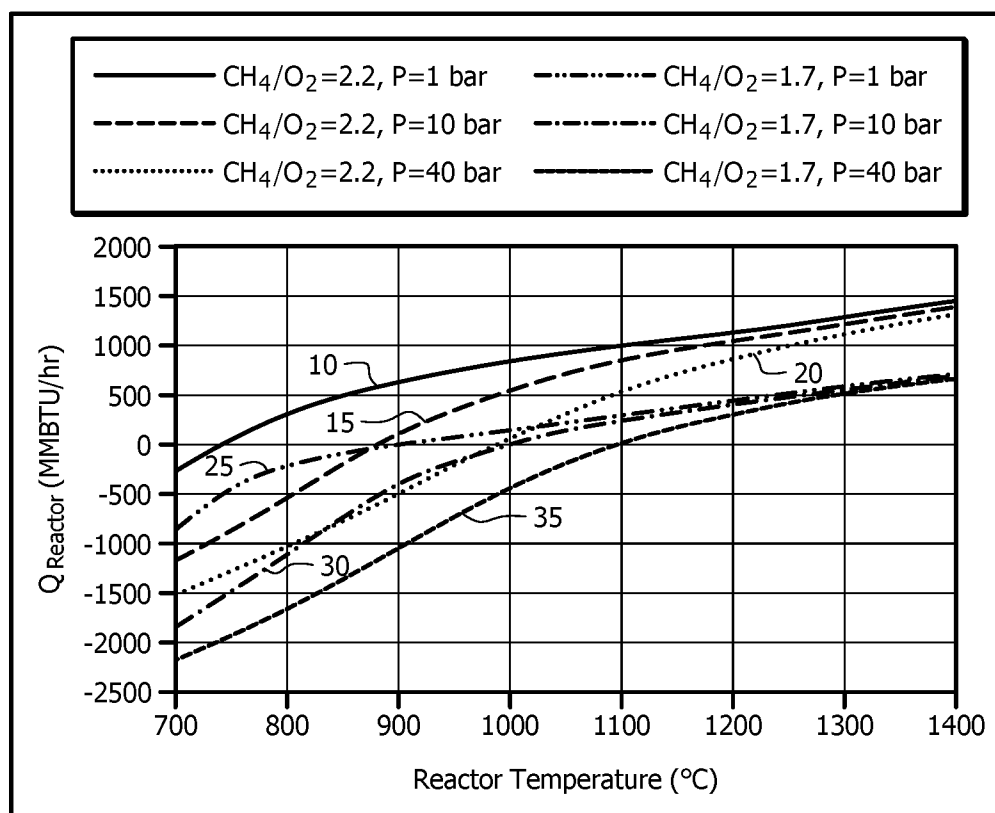


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054470

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38
ADD.

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)
C01B

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

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

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/209508 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; SANSANI VIDYA SAGAR REDDY [US]; WES) 29 December 2016 (2016-12-29) abstract claims 1-3 paragraphs [0020], [0023] - [0028], [0041]	1-20
A	L. MLECZKO, T. WURZEL: "Experimental studies of catalytic partial oxidation of methane to synthesis gas in a bubbling-bed reactor", CHEMICAL ENGINEERING JOURNAL, vol. 66, 1997, pages 193-200, XP002784530, abstract 1. Introduction 2.3 Experimental conditions	1-20



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

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"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

7 September 2018

Date of mailing of the international search report

19/09/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Alvarez Rodriguez, C

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054470

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 6 183 703 B1 (HSU MICHAEL S [US] ET AL) 6 February 2001 (2001-02-06) abstract -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/054470

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