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(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.**
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventor; and

(71) Applicant (for BZ only): **WEST, David** [US/US]; Sabic Technology Center, 1600 Industrial Blvd., Sugar Land, TX 77478 (US).

(72) Inventors: **MAMEDOV, Aghaddin, Khanlar**; Sabic Technology Center, 1600 Industrial Blvd., Sugar Land, TX 77478 (US). **SARSANI, Sagar**; Sabic Technology Center, 1600 Industrial Blvd., Sugar Land, TX 77478 (US). **LIANG, Wugeng**; Sabic Technology Center, 1600 Industrial Blvd., Sugar Land, TX 77478 (US).

(74) Agent: **QUICKER, Katrina, M.** et al.; Baker & Hostetler LLP, 1170 Peachtree Street NE, Suite 2400, Atlanta, GA 30309-7676 (US).

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(54) Title: INTEGRATED PROCESS COMBINING METHANE OXIDATIVE COUPLING AND DRY METHANE REFORMING

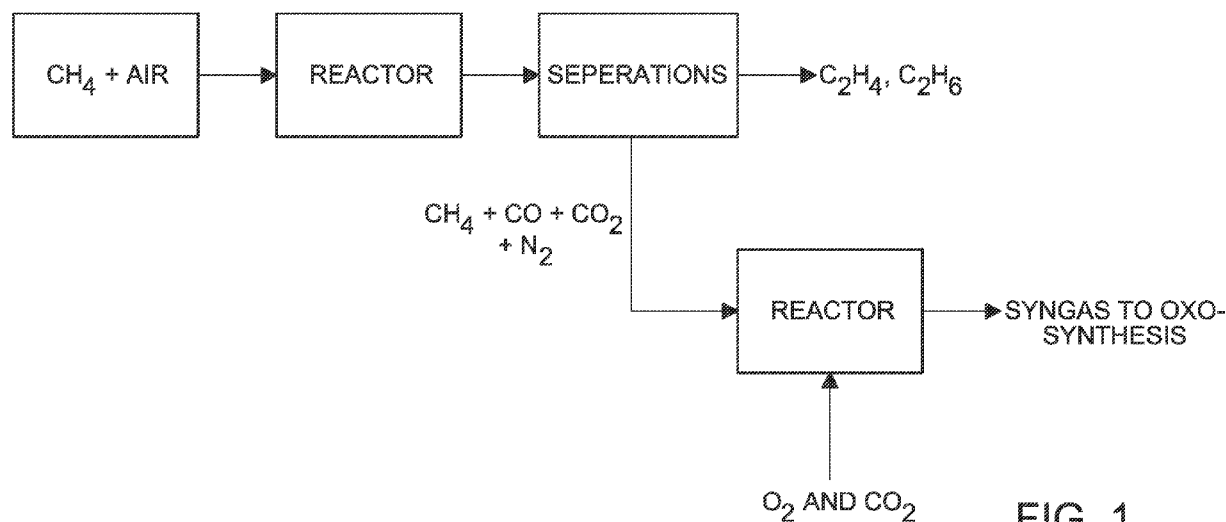


FIG. 1

(57) Abstract: The disclosure concerns processes for conversion of methane to C2 hydrocarbons comprising: (i) contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂; (ii) separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO and CO₂; and (iii) contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.



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INTEGRATED PROCESS COMBINING METHANE OXIDATIVE COUPLING AND DRY METHANE REFORMING

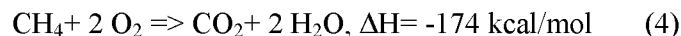
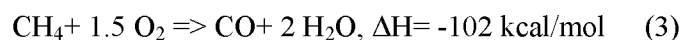
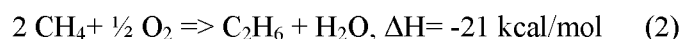
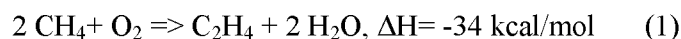
TECHNICAL FIELD

[0001] The disclosure concerns a process for conversion of methane to C2 hydrocarbons and a syngas mixture.

BACKGROUND

[0002] Olefins such as ethylene are useful in the production of a wide range of industrial products. Ethylene is typically 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] Ethylene can also be produced by oxidative coupling of methane (OCM). Oxidative coupling of methane to C2 hydrocarbons is accompanied with the deep oxidation reactions the stoichiometric reactions of which can be described by the following equations:



[0004] Formation of side products, such as CO and CO₂, leads to the decrease of selectivity and effectivity of the C2 production process and well as significant production of potential greenhouse emission gases. There is a need in the art for processes that provide improved selectivity to C2 hydrocarbons and reduced byproducts.

SUMMARY

[0005] The disclosure concerns processes for conversion of methane to C2 hydrocarbons comprising: (i) contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂; (ii) separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO and CO₂; and (iii) contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.

[0006] The disclosure also concerns integrated systems comprising: (i) a first reactor suitable for contacting methane with oxygen in the presence of a first catalyst in a first reactor to

produce a first reaction product comprising C2 hydrocarbons and CO₂; (ii) a separations column suitable for separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO and CO₂; and (iii) a second reactor suitable for contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The summary, as well as the following detailed description, is further understood when read in conjunction with the appended drawing. For the purpose of illustrating the disclosure, there are shown in the drawing exemplary and preferred aspects of the disclosure; however, the disclosure is not limited to the specific methods, compositions, and devices disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

[0008] **FIG. 1** shows a conceptual scheme of methane conversion to C2 hydrocarbons integrated with the production of oxo-synthesis gas composition.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0009] This disclosure describes an integrated process of methane conversion to C2 hydrocarbons and syngas. The method comprises a two-step process of methane oxidative conversion where first step is oxidative methane conversion to C2 hydrocarbons while the second step is the oxidative dry reforming of the unconverted methane with CO₂ to produce syngas. The produced syngas composition may be used in olefins and oxo-synthesis processes. Importantly, the instant processes improve selectivity of the methane coupling reactions. An exemplary scheme for the process is shown in FIG. 1.

Methane Conversion to C2 Hydrocarbons (the first reaction)

[0010] In a first reactor, methane is converted to C2 hydrocarbons in the presence of a catalyst and an oxygen source. In some preferred reactions, methane is converted to C2 hydrocarbons wherein the reactants introduced into the reactor are substantially free of hydrogen gas. In certain reactions, the molar ratio of methane to oxygen is from about 10:1 to about 1.25:1, preferably about 5:1 to about 1.5. The conversion of methane to C2 hydrocarbons occurs substantially free of combustion.

[0011] Separation of the products from the first reactor involves first separation of CO₂ and then separation of C2 hydrocarbons. Separation of CO₂ can be conducted by any known methods for example by amine adsorption. Separation of C2 hydrocarbons may comprise cold

box separation or Pressure Swing Adsorption (PSA). After separation of C2 hydrocarbons, CO₂ mixed with unreacted CH₄ and CO mixture with addition of the necessary amount of oxygen to make oxidative dry reforming reaction to happen may be fed to a second reactor for oxidative methane dry reforming.

[0012] Methane and an oxygen source may be premixed or fed separately to a reactor in order to convert methane to C2 hydrocarbons in the presence of a catalyst. The oxygen source may be (a) air, (b) oxygen, (c) a mixture of oxygen and an inert gas (such as nitrogen) or (d) oxygen enriched air. For example, the reaction of the first step can be carried out with mixture (i) CH₄ and air or (ii) CH₄ and O₂ or (iii) CH₄ and O₂ and N₂.

[0013] The catalysts for methane oxidative conversion to C2 hydrocarbons may be a mixture of basic oxides such as a mixture of alkali and alkali earth metals, a mixture of alkali and alkali earth metal oxides, modified with redox elements or the same modified with the alkaline chlorine instead of alkaline hydroxides. The alkali earth metals and their combinations, such as MgO, CaO, and MgO-CaO have been tested as a catalyst for methane oxidative coupling to C2 hydrocarbons. The catalyst can be also the mixture of rare earth oxides. Such as mixture may comprise La₂O₃ and Ce₂O₃ or mixture of Sm₂O₃ and La₂O₃ or mixture of Sm₂O₃ and MgO or mixture of more oxides, such as Sm₂O₃-La₂O₃-Ce₂O₃.

[0014] The process of methane oxidative coupling and methane dry reforming can be carried out at temperatures very close to each other, such as at 750-800 degrees Celsius (°C) or at a temperature of about 720-750°C for both reactors or at different temperatures. For example, the reaction temperature in the first step can be 850°C and the temperature in the second step can be 720°C.

[0015] The conversion of methane to C2 hydrocarbons may be performed in conventional reactors known to those skilled in the art. The reaction product may then be transferred to a separations unit to produce a stream rich in C2 hydrocarbons (ethane and ethylene) and a stream rich in unreacted methane, CO and CO₂. The latter stream being fed to the reactor designed for the oxidative methane dry forming reaction.

[0016] The first reactor may comprise an isothermal reactor, a fluidized sand bath reactor, an autothermal reactor, an adiabatic reactor, a tubular reactor, a cooled tubular reactor, a continuous flow reactor, a reactor lined with an inert refractory material, a glass lined reactor, a ceramic lined reactor, and the like, or combinations thereof. Inert refractory material can comprise silica, alumina, silicon carbide, boron nitride, titanium oxide, mullite, mixtures of oxides, and the like, or combinations thereof.

[0017] An isothermal reactor can comprise a tubular reactor, a cooled tubular reactor, a continuous flow reactor, and the like, or combinations thereof. An isothermal reactor can comprise a reactor vessel located inside a fluidized sand bath reactor, wherein the fluidized sand bath provides isothermal conditions (i.e., substantially constant temperature) for the reactor. In such aspects, the fluidized sand bath reactor can be a continuous flow reactor comprising an outer jacket comprising a fluidized sand bath. The fluidized sand bath can exchange heat with the reactor, thereby providing isothermal conditions for the reactor. Generally, a fluidized bath employs fluidization of a mass of finely divided inert particles (e.g., sand particles, metal oxide particles, aluminum oxide particles, metal oxides microspheres, quartz sand microspheres, aluminum oxide microspheres, silicon carbide microspheres) by means of an upward stream of gas, such as for example air, nitrogen, and the like.

[0018] A reactor can be a multi-stage reactor, wherein the multi-stage reactor can comprise multiple stages of reaction (e.g., OCM reactions). In an aspect, the multi-stage reactor can comprise from about 2 to about 10 reactors in series, alternatively from about 3 to about 8 reactors in series, or alternatively from about 4 to about 6 reactors in series. A multi-stage reactor can comprise any suitable number and arrangement of reactors (e.g., stages, reaction stages) in series and/or in parallel to achieve a desired methane conversion and selectivity to desired products. Selectivity to desired products obtained from a multi-stage reactor as disclosed herein may be higher than a selectivity to desired products obtained from a single stage reactor.

[0019] A multi-stage reactor can comprise one initial stage reactor, at least one intermediate stage reactor, and one finishing stage reactor. As will be appreciated by one of skill in the art, and with the help of this disclosure, the initial stage reactor, the intermediate stage reactor and the finishing stage reactor can each individually comprise any suitable number and arrangement of reactors (e.g., stages, reaction stages) in series and/or in parallel to achieve a desired methane conversion and selectivity to desired products.

[0020] An initial stage reactant mixture can be introduced to an initial stage reactor, wherein the initial stage reactant mixture can comprise methane and an oxygen source. An intermediate stage reactant mixture can be introduced to an intermediate stage reactor, wherein the intermediate stage reactant mixture can comprise an oxygen source. In an aspect, a finishing stage reactant mixture can be introduced to a finishing stage reactor, wherein the finishing stage reactant mixture can comprise oxygen. In an aspect, the initial stage reactor and the at least one intermediate stage reactor can operate at partial oxygen conversion, wherein the oxygen conversion can be from equal to or greater than about 50% to equal to or less than about 99%, alternatively from equal to or greater than about 55% to equal to or less than about 95%, or

alternatively from equal to or greater than about 60% to equal to or less than about 90%. Near-complete oxygen conversion can be achieved in the finishing stage reactor, e.g., oxygen conversion in the finishing stage reactor can be equal to or greater than about 99%, alternatively equal to or greater than about 99.5%, or alternatively equal to or greater than about 99.9%.

Separation of C2 Hydrocarbons from Unreacted Methane

[0021] C2 hydrocarbon separation may be performed by any technique known in the art. In some aspects, a cold box separation process may be used to separate the C2 hydrocarbons from the more volatile methane, CO and CO₂. The use of such an apparatus is known to those skilled in the art. In other aspects, Pressure Swing Adsorption (PSA) may be used for the separation of C2 hydrocarbons from the aforementioned volatiles. This technique is well known to those skilled in the art.

[0022] Separation of CO₂ can be conducted by any known methods, for example by amine adsorption. Such techniques are well known by those skilled in the art.

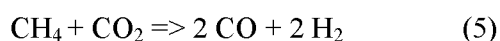
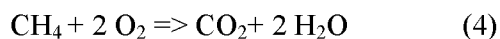
Oxidative Methane Dry Reforming (the second reaction)

[0023] The stream comprising CO₂ mixed with unreacted CH₄ and CO from the first reactor is mixed the necessary amount of oxygen (to allow dry reforming) is fed to the second reactor for oxidative methane dry reforming. A small concentration of CO, existing in reaction products, undergoes to the deep oxidation and is converted to a syngas mixture.

[0024] The feed composition for the second reactor can be varied by using the gas composition produced from the first reactor (effluent of the first reactor after C2 separation). CO₂ from the external CO₂ resources may be utilized in the reaction. In a highly efficient reaction process for the coupling of methane to produce C2 hydrocarbons, additional CO₂ may be utilized for the oxidative methane dry reforming reaction.

[0025] The reaction of the oxidative methane dry reforming reaction may be carried out in the presence of oxygen and carbon dioxide. An inert gas, such as nitrogen, may be utilized in the mixture. For example a mixture of (i) CH₄, CO₂ and O₂ or (ii) CH₄, O₂, CO₂ and N₂ may be utilized.

[0026] The deep oxidation products comprise a mixture of CO and CO₂ which in separate reactions with the unreacted methane and oxygen is converted to a syngas composition by an oxidative methane dry reforming reaction.



[0027] An oxidative methane dry reforming reaction is carried out in the presence of Ni containing catalysts. These catalysts can be supported on Al_2O_3 nickel-based catalysts or a mixture of NiO with the other oxides such as the mixture of NiO with La_2O_3 . The mixed-oxide catalysts may be prepared by mixing nitrates of the elements of the catalyst with the drying and calcination or by mixing of oxides or by co-precipitation of the elements of the catalysts.

[0028] The process of methane oxidative coupling and methane dry reforming can be carried out at temperatures very close to each other, such as at 750-800°C or at temperature about 720-750°C for both reactors or at different temperatures. For example, the reaction temperature in the first step can be 850°C and the temperature in the second step can be 720°C.

[0029] In some processes, oxidative methane dry reforming can be isothermal fixed bed reactor. Operation of such reactors is known to those skilled in the art.

[0030] Synthesis gas can be separated from the product mixture to yield recovered synthesis gas, for example by cryogenic distillation. As will be appreciated by one of skill in the art, and with the help of this disclosure, the recovery of synthesis gas is done as a simultaneous recovery of both H_2 and CO.

Illustrative Conversions

[0031] According to the instant disclosure for the first step of methane oxidative coupling, conversion of methane in the first reactor is typically about 30% to about 40% with a selectivity of about 55 to about 70% to C2 hydrocarbons, such as a conversion of 35% and a selectivity of 65% for a Na-Mn type catalyst. In one example using the catalyst Na-Mn/ SiO_2 , 33% conversion with a C2 selectivity of 60% to C2 hydrocarbons was observed. For the second reaction, conversion of methane is typically 65-85%, and most typically 80%. In one example, using the catalyst Ni/ La_2O_3 conversion of methane in the second reactor was about 74.7%.

[0032] In accordance with the disclosure, catalysts with different selectivity to C2 hydrocarbons could be applied for the present disclosure. In the case of high selective catalysts, the portion of CO_2 produced from the first reaction will be less than the amount of CO_2 needed for the second reaction. In such instances, additional CO_2 can be added from external CO_2 resources to satisfy the CO_2 needs of the second reaction.

Syngas Use In Oxo-Synthesis

[0033] Recovered synthesis gas can be converted to alkanes by using a Fisher-Tropsch process, and the alkanes can be further converted by dehydrogenation into olefins. Specifically, syngas produced in the methane dry reforming reaction may be utilized in an oxo-synthesis

reaction. An oxo synthesis process may be used for the production of aldehydes from alkenes and syngas in the presence of a catalyst. For example, propanal may be produced from the reaction of ethene and syngas. Alkenes of other lengths (C2-C14, for example) may be reacted to produce aldehydes (C3-C15 for example). In some reactions, a cobalt catalyst may be utilized. Such methods are well known to those skilled in the art.

Definitions

[0034] The methods and systems described herein are not limited to specific synthetic methods, specific components, or to particular compositions. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

[0035] Various combinations of elements of this disclosure are encompassed by this disclosure, e.g., combinations of elements from dependent claims that depend upon the same independent claim.

[0036] Moreover, it is to be understood that unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; and the number or type of aspects described in the specification.

[0037] It is to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term “comprising” can include the embodiments “consisting of” and “consisting essentially of.” Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined herein.

[0038] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural equivalents unless the context clearly dictates otherwise.

[0039] Ranges can be expressed herein as from one particular value to another particular value. When such a range is expressed, another aspect includes from the one

particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent ‘about,’ it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0040] As used herein, the terms “about” and “at or about” mean that the amount or value in question can be the value designated some other value approximately or about the same. It is generally understood, as used herein, that it is the nominal value indicated $\pm 5\%$ variation unless otherwise indicated or inferred. The term is intended to convey that similar values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is “about” or “approximate” whether or not expressly stated to be such. It is understood that where “about” is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0041] The term “substantially” generally means that less than 1% of the referenced compound exists or less than 1% of the referenced reaction occurs.

[0042] Disclosed are the components to be used to prepare the compositions of the disclosure as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and

F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the disclosure. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the methods of the disclosure.

[0043] °C is degrees Celsius.

[0044] “C2 hydrocarbons” are one or both of ethane and ethylene.

[0045] “Syngas” is a gas mixture comprising primarily of hydrogen, carbon monoxide, and very often some carbon dioxide.

[0046] “C5-C11 hydrocarbons” are a mixture of linear and branched hydrocarbons having 5-11 carbon atoms. These hydrocarbons may be saturated or unsaturated.

[0047] An “oxidative methane dry forming reaction” concerns reaction of methane in the presence of oxygen and CO₂ to produce syngas.

Aspects

[0048] The present disclosure comprises at least the following aspects. One main aspect of the disclosure is carbon efficiency of the process where CO₂ is converted high value product which is syngas. Syngas can be converted to methanol, olefins, oxo-synthesis products which can increase efficiency of the total process significantly.

[0049] Aspect 1. A process for conversion of methane to C2 hydrocarbons comprising:

- contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;
- separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂; and
- contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.

[0050] Aspect 2. The process of Aspect 1, wherein conversion of methane in the first reactor is at least 30% with a C2 selectivity of at least 55%.

[0051] Aspect 3. The process of Aspect 1 or Aspect 2, wherein the contacting methane with oxygen occurs at a temperature of from about 700 °C to about 850 °C.

[0052] Aspect 4. The process of Aspect 1 or Aspect 2, wherein the contacting methane with oxygen occurs at a temperature of from 700 °C to 850 °C.

[0053] Aspect 5. The process of Aspect 1 or Aspect 2, wherein the contacting methane with oxygen occurs at a temperature of from about 720 °C to about 820 °C.

[0054] Aspect 6. The process of Aspect 1 or Aspect 2, wherein the contacting methane with oxygen occurs at a temperature of from 6720 °C to 6820 °C.

[0055] Aspect 7. The process of any one of Aspects 1-4, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[0056] Aspect 8. The process of any one of Aspects 1-7, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 650 °C to about 750 °C.

[0057] Aspect 9. The process of any one of Aspects 1-7, wherein the contacting of the second stream with oxygen occurs at a temperature of from 650 °C to 750 °C.

[0058] Aspect 10. The process of any one of Aspects 1-9, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 660 °C to about 725 °C.

[0059] Aspect 11. The process of any one of Aspects 1-9, wherein the contacting of the second stream with oxygen occurs at a temperature of from 660 °C to 725 °C.

[0060] Aspect 12. The process of any one of Aspects 1-11, wherein the second catalyst comprises a nickel containing catalyst.

[0061] Aspect 13. The process of Aspect 12, wherein the nickel containing catalyst is supported on an Al₂O₃ support.

[0062] Aspect 14. The process of Aspect 12, wherein the nickel containing catalyst is supported on a La₂O₃ support.

[0063] Aspect 15. The process of any one of Aspects 1-14 wherein the second catalyst comprises NiO.

[0064] Aspect 16. The process of any one of Aspects 1-15, wherein the second reaction product is reacted to produce methanol.

[0065] Aspect 17. The process of Aspect 16, wherein the methanol is further reacted to produce C5-C11 hydrocarbons.

[0066] Aspect 18. The process of any one of Aspects 1-17, wherein the contacting methane with oxygen occurs in the presence of N₂.

[0067] Aspect 19. The process of any one of Aspects 1-18, wherein the second stream additionally comprises N₂.

[0068] Aspect 20. The process of any one of Aspects 1-19, wherein the C₂ hydrocarbons comprise ethylene and ethane.

[0069] Aspect 21. An integrated system comprising:

-- a first reactor suitable for contacting methane with oxygen in the presence of a first catalyst disposed within a first reactor to produce a first reaction product comprising C₂ hydrocarbons and CO₂;

-- a separations column suitable for separating the first reaction product to produce a first stream comprising C₂ hydrocarbons and a second stream comprising methane, CO, and CO₂; and

-- a second reactor suitable for contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst disposed within a second reactor to produce a second reaction product comprising H₂ and CO.

[0070] Aspect 22. The integrated system of Aspect 21, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[0071] Aspect 23. The integrated system of Aspect 21 or Aspect 22, wherein the second catalyst comprises supported NiO.

[0072] Aspect 24. The integrated system of any of Aspects 21-23, additionally comprising a reactor suitable for reacting the second reaction product to produce methanol.

[0073] Aspect 25. The integrated system of any of Aspects 21-24, additionally comprising a reactor suitable for reacting the methanol to produce C₅-C₁₁ hydrocarbons.

[0074] Aspect 26. A process for conversion of methane to C₂ hydrocarbons consisting essentially of:

-- contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C₂ hydrocarbons and CO₂;

-- separating the first reaction product to produce a first stream comprising C₂ hydrocarbons and a second stream comprising methane, CO, and CO₂; and

-- contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.

[0075] Aspect 27. The process of Aspect 26, wherein conversion of methane in the first reactor is at least 30% with a C₂ selectivity of at least 55%.

[0076] Aspect 28. The process of Aspect 26 or Aspect 27, wherein the contacting methane with oxygen occurs at a temperature of from about 700 °C to about 850 °C.

[0077] Aspect 29. The process of Aspect 26 or Aspect 27, wherein the contacting methane with oxygen occurs at a temperature of from 700 °C to 850 °C.

[0078] Aspect 30. The process of Aspect 26 or Aspect 27, wherein the contacting methane with oxygen occurs at a temperature of from about 720 °C to about 820 °C.

[0079] Aspect 31. The process of Aspect 26 or Aspect 27, wherein the contacting methane with oxygen occurs at a temperature of from 6720 °C to 6820 °C.

[0080] Aspect 32. The process of any one of Aspects 26-31, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[0081] Aspect 33. The process of any one of Aspects 26-32, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 650 °C to about 750 °C.

[0082] Aspect 34. The process of any one of Aspects 26-33, wherein the contacting of the second stream with oxygen occurs at a temperature of from 650 °C to 750 °C.

[0083] Aspect 35. The process of any one of Aspects 26-34, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 660 °C to about 725 °C.

[0084] Aspect 36. The process of any one of Aspects 26-34, wherein the contacting of the second stream with oxygen occurs at a temperature of from 660 °C to 725 °C.

[0085] Aspect 37. The process of any one of Aspects 26-36, wherein the second catalyst comprises a nickel containing catalyst.

[0086] Aspect 38. The process of Aspect 37, wherein the nickel containing catalyst is supported on an Al₂O₃ support.

[0087] Aspect 39. The process of Aspect 37, wherein the nickel containing catalyst is supported on a La₂O₃ support.

[0088] Aspect 40. The process of any one of Aspects 26-39 wherein the second catalyst comprises NiO.

[0089] Aspect 41. The process of any one of Aspects 26-40, wherein the second reaction product is reacted to produce methanol.

[0090] Aspect 42. The process of Aspect 41, wherein the methanol is further reacted to produce C5-C11 hydrocarbons.

[0091] Aspect 43. The process of any one of Aspects 26-42, wherein the contacting methane with oxygen occurs in the presence of N₂.

[0092] Aspect 44. The process of any one of Aspects 26-43, wherein the second stream additionally comprises N₂.

[0093] Aspect 45. The process of any one of Aspects 26-44, wherein the C2 hydrocarbons comprise ethylene and ethane.

[0094] Aspect 46. An integrated system consisting essentially of:

-- a first reactor suitable for contacting methane with oxygen in the presence of a first catalyst disposed within a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;

-- a separations column suitable for separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂; and

-- a second reactor suitable for contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst disposed within a second reactor to produce a second reaction product comprising H₂ and CO.

[0095] Aspect 47. The integrated system of Aspect 46, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[0096] Aspect 48. The integrated system of Aspect 46 or Aspect 47, wherein the second catalyst comprises supported NiO.

[0097] Aspect 49. The integrated system of any of Aspects 46-48, additionally comprising a reactor suitable for reacting the second reaction product to produce methanol.

[0098] Aspect 50. The integrated system of any of Aspects 46-49, additionally comprising a reactor suitable for reacting the methanol to produce C5-C11 hydrocarbons.

[0099] Aspect 51. A process for conversion of methane to C2 hydrocarbons consisting of:

-- contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;

-- separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂; and

-- contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.

[00100] Aspect 52. The process of Aspect 51, wherein conversion of methane in the first reactor is at least 30% with a C2 selectivity of at least 55%.

[00101] Aspect 53. The process of Aspect 51 or Aspect 52, wherein the contacting methane with oxygen occurs at a temperature of from about 700 °C to about 850 °C.

[00102] Aspect 54. The process of Aspect 51 or Aspect 52, wherein the contacting methane with oxygen occurs at a temperature of from 700 °C to 850 °C.

[00103] Aspect 55. The process of Aspect 51 or Aspect 52, wherein the contacting methane with oxygen occurs at a temperature of from about 720 °C to about 820 °C.

[00104] Aspect 56. The process of Aspect 51 or Aspect 52, wherein the contacting methane with oxygen occurs at a temperature of from 6720 °C to 6820 °C.

[00105] Aspect 57. The process of any one of Aspects 51-54, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[00106] Aspect 58. The process of any one of Aspects 51-57, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 650 °C to about 750 °C.

[00107] Aspect 59. The process of any one of Aspects 51-57, wherein the contacting of the second stream with oxygen occurs at a temperature of from 650 °C to 750 °C.

[00108] Aspect 60. The process of any one of Aspects 51-59, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 660 °C to about 725 °C.

[00109] Aspect 61. The process of any one of Aspects 51-59, wherein the contacting of the second stream with oxygen occurs at a temperature of from 660 °C to 725 °C.

[00110] Aspect 62. The process of any one of Aspects 51-61, wherein the second catalyst comprises a nickel containing catalyst.

[00111] Aspect 63. The process of Aspect 62, wherein the nickel containing catalyst is supported on an Al₂O₃ support.

[00112] Aspect 64. The process of Aspect 62, wherein the nickel containing catalyst is supported on a La₂O₃ support.

[00113] Aspect 65. The process of any one of Aspects 51-64 wherein the second catalyst comprises NiO.

[00114] Aspect 66. The process of any one of Aspects 51-65, wherein the second reaction product is reacted to produce methanol.

[00115] Aspect 67. The process of Aspect 66, wherein the methanol is further reacted to produce C5-C11 hydrocarbons.

[00116] Aspect 68. The process of any one of Aspects 51-67, wherein the contacting methane with oxygen occurs in the presence of N₂.

[00117] Aspect 69. The process of any one of Aspects 51-68, wherein the second stream additionally comprises N₂.

[00118] Aspect 70. The process of any one of Aspects 51-69, wherein the C2 hydrocarbons comprise ethylene and ethane.

[00119] Aspect 71. An integrated system consisting of:

-- a first reactor suitable for contacting methane with oxygen in the presence of a first catalyst disposed within a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;

-- a separations column suitable for separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂; and

-- a second reactor suitable for contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst disposed within a second reactor to produce a second reaction product comprising H₂ and CO.

[00120] Aspect 72. The integrated system of Aspect 71, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.

[00121] Aspect 73. The integrated system of Aspect 71 or Aspect 72, wherein the second catalyst comprises supported NiO.

[00122] Aspect 74. The integrated system of any of Aspects 71-73, additionally comprising a reactor suitable for reacting the second reaction product to produce methanol.

[00123] Aspect 75. The integrated system of any of Aspects 71-74, additionally comprising a reactor suitable for reacting the methanol to produce C5-C11 hydrocarbons.

Examples

[00124] The following non-limited examples illustrate certain aspects of the disclosure.

Example 1

[00125] Example 1 describes oxidative conversion of methane to C2 hydrocarbons at different temperatures. The reaction mixture comprises CH₄ and air with a CH₄/O₂ molar ratio of 2. Gas hourly space velocity (GHSV) for the reaction was 7200 hour⁻¹ (h⁻¹). The catalyst was 7%Na-10%Mn/SiO₂ with a catalyst loading of 3 milliliter (ml). The catalyst percentages are weight percent versus based on the total weight of the catalyst.

T °C	700	750	800	820
CH ₄ conversion (%)	8.5	22.0	30.3	33.5
C2 selectivity	50.0	52.2	58.0	60.4

Example 2

[00126] The Example 2 describes the experiment of the second step of methane oxidative dry reforming. The catalyst was 3%Ni/La₂O₃, with a catalyst loading of 3 ml. The catalyst percentages are weight percent versus based on the total weight of the catalyst. The molar ratio of CH₄/CO₂ was 1.6 and the molar ratio of CH₄/O₂ was 2.6. GHSV was 1440h⁻¹.

T °C	660	680	720
CH ₄ conversion (mol %)	67.7	70.5	74.7
CO ₂ conversion (mol %)	65.5	82.9	86.1
O ₂ conversion (mol %)	96.0	96.1	96.5
H ₂ /Co ratio	1.79	1.84	1.52

Example 3

[00127] Example 3 describes preparation of the catalyst for the methane oxidative coupling reaction. The necessary amount of silica-gel was impregnated with the necessary amount of Mn(NO₃)₂ and Na₂CO₃ to get catalyst composition 7%Na-10%Mn/SiO₂. The catalyst percentages are weight percent versus based on the total weight of the catalyst. After impregnation, the solid material dried 12 hours at 120°C and then calcined 4 hours at 850°C. The ready catalyst crushed for particle size 20-50 mesh.

Example 4

[00128] Example 4 describes preparation of the catalyst for the methane oxidative dry reforming. The necessary amount of salts Ni(NO₃)₃, La(NO₃)₂ dissolved in 500 ml water and to the mixture of the solutions was gradually added NH₄OH solution for co-precipitation of the ingredients of the catalyst. The precipitate washed with 500 ml water three times and dried at 120°C within 12 hours. After drying, the catalyst calcined at 600°C within 8 hours. The ready catalyst crushed for particle size 20-50 mesh.

CLAIMS

What is claimed:

1. A process for conversion of methane to C2 hydrocarbons comprising:
 - contacting methane with oxygen in the presence of a first catalyst in a first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;
 - separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂; and
 - contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst in a second reactor to produce a second reaction product comprising H₂ and CO.
2. The process of claim 1, wherein conversion of methane in the first reactor is at least 30% with a C2 selectivity of at least 55%.
3. The process of claim 1 or claim 2, wherein the contacting methane with oxygen occurs at a temperature of from about 700 °C to about 850 °C.
4. The process of claim 1 or claim 2, wherein the contacting methane with oxygen occurs at a temperature of from about 720 °C to about 820 °C.
5. The process of any one of claims 1-4, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.
6. The process of any one of claims 1-5, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 650 °C to about 750 °C.
7. The process of any one of claims 1-5, wherein the contacting of the second stream with oxygen occurs at a temperature of from about 660 °C to about 725 °C.
8. The process of any one of claims 1-7, wherein the second catalyst comprises a nickel containing catalyst.
9. The process of claim 8, wherein the nickel containing catalyst is supported on an Al₂O₃ or La₂O₃ support.

10. The process of any one of claims 1-9 wherein the second catalyst comprises supported NiO.
11. The process of any one of claims 1-10, wherein the second reaction product is reacted to produce methanol.
12. The process of claim 11, wherein the methanol is further reacted to produce C5-C11 hydrocarbons.
13. The process of any one of claims 1-12, wherein the contacting methane with oxygen occurs in the presence of N₂.
14. The process of any one of claims 1-13, wherein the C2 hydrocarbons comprise ethylene and ethane.
15. An integrated system comprising:
 - a first reactor suitable for contacting methane with oxygen in the presence of a first catalyst disposed within the first reactor to produce a first reaction product comprising C2 hydrocarbons and CO₂;
 - a separations column suitable for separating the first reaction product to produce a first stream comprising C2 hydrocarbons and a second stream comprising methane, CO, and CO₂;
 - and
 - a second reactor suitable for contacting the second stream with oxygen and additional CO₂ in the presence of a second catalyst disposed within the second reactor to produce a second reaction product comprising H₂ and CO.
16. The integrated system of claim 15, wherein the first catalyst comprises one or more of MgO, CaO, MgO-CaO, La₂O₃ and Ce₂O₃, Sm₂O₃, Sm₂O₃-La₂O₃-Ce₂O₃ and mixtures thereof.
17. The integrated system of claim 15 or claim 16, wherein the second catalyst comprises NiO.

18. The integrated system of any of claims 15-17, additionally comprising a reactor suitable for reacting the second reaction product to produce methanol.
19. The integrated system of any of claims 15-18, additionally comprising a reactor suitable for reacting the methanol to produce C5-C11 hydrocarbons.
20. The integrated system of any one of claims 15-19, wherein the C2 hydrocarbons comprise ethylene and ethane.

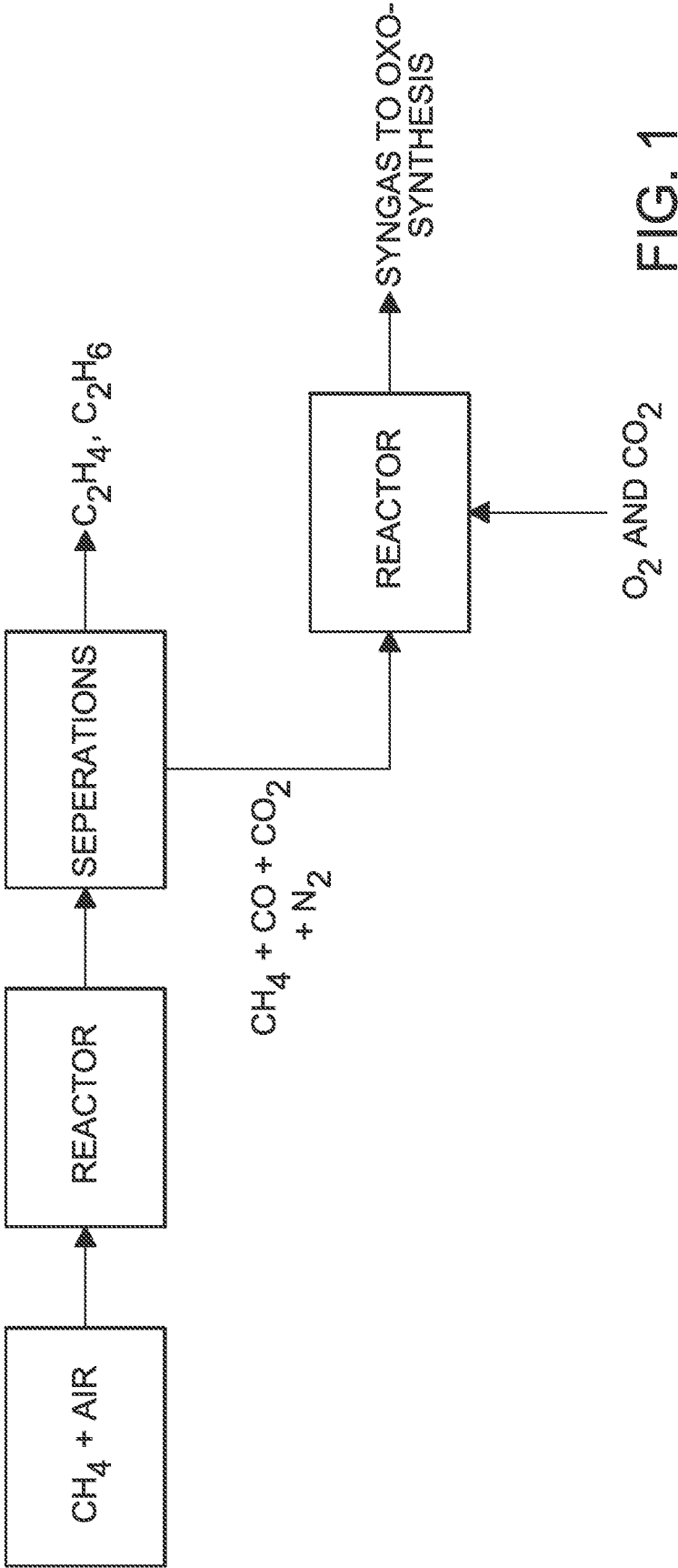


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/039875

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C07C2/84	C07C11/04
	C07C31/04	
ADD.	C01B3/38	B01J19/00
		C07C29/151
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 C01B B01J		
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)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAMID REZA GODINI ET AL: "Techno-economic analysis of integrating the methane oxidative coupling and methane reforming processes", FUEL PROCESSING TECHNOLOGY., vol. 106, 1 February 2013 (2013-02-01), pages 684-694, XP055401332, NL ISSN: 0378-3820, DOI: 10.1016/j.fuproc.2012.10.002	1-4,8,9, 13-17,20
Y	Chapter 2.3, page 688 figures 5 (b),6,7 table 10 ----- -/--	5-7, 10-12, 18,19
☒ 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		Date of mailing of the international search report
5 September 2017		25/09/2017
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 Österle, Carmen

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/039875

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GALADIMA AHMAD ET AL: "From synthesis gas production to methanol synthesis and potential upgrade to gasoline range hydrocarbons: A review", JOURNAL OF NATURAL GAS SCIENCE AND ENGINEERING, vol. 25, 2015, pages 303-316, XP029175930, ISSN: 1875-5100, DOI: 10.1016/J.JNGSE.2015.05.012 Chapters 2.2 and 3; page 306 - page 307 -----	11,12, 18,19
Y	DEBOY J M ET AL: "THE OXIDATIVE COUPLING OF METHANE OVER ALKALI, ALKALINE EARTH, AND RARE EARTH OXIDES", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, AMERICAN CHEMICAL SOCIETY, US, vol. 27, no. 9, 1 September 1988 (1988-09-01), pages 1577-1582, XP000009818, ISSN: 0888-5885, DOI: 10.1021/IE00081A004 table I -----	5
Y	LEILEI XU ET AL: "Carbon dioxide reforming of methane over ordered mesoporous NiO-MgO-Al₂O₃ composite oxides", APPLIED CATALYSIS. B, ENVIRONMENTAL, vol. 108-109, 17 May 2015 (2015-05-17), pages 177-190, XP055022691, ISSN: 0926-3373, DOI: 10.1016/j.apcatb.2011.08.028 points 2.1 and 2.2; page 178 -----	6,7,10