(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
14 August 2014 (14.08.2014)

WIPO | PCT

(10) **International Publication Number**
WO 2014/124011 A1

(51) **International Patent Classification**:
C01B 3/00 (2006.01)
C01B 3/02 (2006.01)
C01B 3/22 (2006.01)
C01B 3/26 (2006.01)
C01B 3/28 (2006.01)
C01B 3/32 (2006.01)
B01J 8/00 (2006.01)
B01J 8/08 (2006.01)
B01J 19/18 (2006.01)

(21) **International Application Number**:
PCT/US2014/014877

(22) **International Filing Date**:
5 February 2014 (05.02.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:

61/761,016	5 February 2013 (05.02.2013)	US
61/779,243	13 March 2013 (13.03.2013)	US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

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(54) **Title**: METHODS FOR FUEL CONVERSION

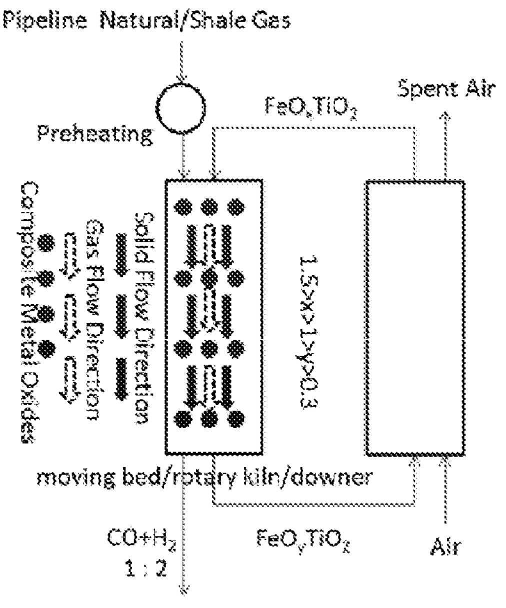

FIG. 3(a)

(57) **Abstract**: In one embodiment described herein, fuel may be converted into syngas by a method comprising feeding the fuel and composite metal oxides into a reduction reactor in a co-current flow pattern relative to one another, reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides, transporting the reduced composite metal oxides to an oxidation reactor, regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant in the oxidation reactor, and recycling the regenerated composite metal oxides to the reduction reactor for subsequent reduction reactions to produce syngas. The composite metal oxides may be solid particles comprising a primary metal oxide and a secondary metal oxide.

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SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

METHODS FOR FUEL CONVERSION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to U.S. Provisional Patent Application No. 61/761,016, filed February 5, 2013, entitled "High Quality Syngas Production Using Composite Metal Oxides" (Docket OSU 0080 MA) and to U.S. Provisional Patent Application No. 61/779,243, filed March 13, 2013, entitled "Systems and Methods for Co-Current Chemical Looping Systems" (Docket OSU 0080 M2), the teachings of both of which are incorporated by reference herein.

BACKGROUND

Field

[0002] The present disclosure relates to chemical looping systems and methods, and specifically to systems and methods for producing syngas from feedstock fuels.

Technical Background

[0003] There is a constant need for clean and efficient energy generation systems. Many of the commercial processes that generate energy carriers such as steam, hydrogen, synthesis gas (syngas), liquid fuels, and/or electricity are based on fossil fuels. Furthermore, the dependence on fossil fuels is expected to continue in the foreseeable future due to the lower costs compared to some renewable sources. Current conversion methods of carbonaceous fuels may emit large quantities of carbon dioxide to the environment and may require significant capital and operational costs. Sulfur and nitrogen compounds may also be generated in these processes due to the complex contents of coal.

[0004] A need is present for improved systems and methods for converting fuel, and system components therein, which can convert fuel effectively while reducing pollutants.

SUMMARY

[0005] In one embodiment, fuel may be converted into syngas by a method comprising feeding the fuel and composite metal oxides into a reduction reactor in a co-current flow pattern relative to one another, reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides, transporting the reduced composite metal oxides to an oxidation reactor, regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant in the oxidation reactor, and recycling the regenerated composite metal oxides to the reduction reactor for subsequent reduction reactions to produce syngas. The composite metal oxides may be solid particles comprising a primary metal oxide and a secondary metal oxide.

[0006] In another embodiment, natural gas may be used as a fuel and may be converted into syngas by a method comprising feeding the fuel and composite metal oxides into a reduction reactor in a co-current flow pattern relative to one another, reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides, transporting the reduced composite metal oxides to an oxidation reactor, regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant in the oxidation reactor, and recycling the regenerated composite metal oxides to the reduction reactor for subsequent reduction reactions to produce syngas. The composite metal oxides may be solid particles comprising a primary metal oxide and a secondary metal oxide. The composite metal oxide may comprise iron oxide and titanium oxide, or the composite metal oxide comprises iron oxide and aluminum oxide. The iron oxide may be reduced in the reduction reaction from FeO_x to FeO_y and $1.5>x>1>y>0.3$.

According to yet another embodiment, fuel may be converted by a method comprising reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides, and regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant. The composite metal oxides are solid particles may comrprise primary metal oxide and a secondary metal oxide. The composite metal oxide may comprise iron oxide and titanium oxide, or the composite metal oxide may comprise iron oxide and aluminum oxide. The reducing of the composite metal oxides and the oxidizing of the composite metal oxides may be carried out in a fixed bed with a gas switching system. Alternatively, the reducing of the composite metal oxides may occur in a reduction reactor, wherein the reduction reactor is a moving bed reactor comprising two gas outlets and the reducing of the composite metal oxides produces syngas and CO_2. Alternatively, the reducing and oxidizing of composite metal oxide may occur in a membrane based reactor, wherein the composite metal oxides are integrated to the fuel side of the membrane based reactor.

[0007] Additional features and advantages of the devices and methods for chemical conversion systems and methods and processes for manufacturing the same will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0008] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0010] FIG. 1 is a graph comparing the equilibrium carbon distribution difference with various ratios between methane and single/composite metal oxides, according to one or more embodiments shown and described herein;

[0011] FIG. 2 is a graph comparing the equilibrium syngas composition difference between pure FeO and composite metal oxides, according to one or more embodiments shown and described herein;

[0012] FIG. 3(a) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using gaseous fuel, according to one or more embodiments shown and described herein;

[0013] FIG. 3(b) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using gaseous fuel, according to one or more embodiments shown and described herein;

[0014] FIG. 4(a) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using solid fuel, according to one or more embodiments shown and described herein;

[0015] FIG. 4(b) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using solid fuel, according to one or more embodiments shown and described herein;

[0016] FIG. 5(a) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using liquid fuel, according to one or more embodiments shown and described herein;

[0017] FIG. 5(b) is a schematic flow diagram of a fuel conversion system using a co-current reactor for the reduction reaction of composite metal oxide using liquid fuel, according to one or more embodiments shown and described herein;

[0018] FIG. 6 is a schematic flow diagram of a fuel conversion system using a fixed bed reactor, according to one or more embodiments shown and described herein;

[0019] FIG. 7 is a schematic flow diagram of a fuel conversion system using a counter-current moving bed reactor with syngas produced from the middle and concentrated CO_2 stream from the top in the reduction reaction of composite metal oxide, according to one or more embodiments shown and described herein;

[0020] FIG. 8 is a schematic flow diagram of a fuel conversion system using a moving bed reactor with fuel introduced in the middle and syngas produced from the bottom and concentrated CO_2 stream from the top in the reduction (endothermic) reaction of composite metal oxide, according to one or more embodiments shown and described herein;

[0021] Fig. 9 is a schematic flow diagram of a fuel conversion system with additional hydrogen production from steam in a separate counter-current moving bed reactor, according to one or more embodiments shown and described herein;

[0022] FIG. 10 is a schematic flow diagram of a fuel conversion system using solar energy to provide the heat of reaction in the two-step conversion scheme, according to one or more embodiments shown and described herein;

[0023] FIG. 11 is a schematic flow diagram of a fuel conversion system using a OTM/ITM based membrane reactor with the composite metal oxide material at fuel side for syngas production, according to one or more embodiments shown and described herein;

[0024] FIG. 12 is a schematic diagram of the co-current moving bed experimental apparatus;

[0025] FIG. 13 is a graph illustrating CO/CO_2 and H_2/CO ratios as a function of time for co-current moving bed experimental setup using coal as the feedstock fuel, according to one or more embodiments shown and described herein;

[0026] FIG. 14 is a graph illustrating CO/CO_2 and H_2/CO ratios as a function of time for a co-current moving bed experimental setup using both coal and methane as feedstock, according to one or more embodiments shown and described herein; and

[0027] FIG. 15 is a graph illustrating co-current moving bed experimental data using methane as feedstock, according to one or more embodiments shown and described herein.

DETAILED DESCRIPTION

[0028] Described herein are systems and method for converting fuel sources, sometimes referred to as feedstock fuels, into syngas. Generally, syngas comprises carbon monoxide and hydrogen, and may comprise some other chemicals, such as, but not limited to, carbon dioxide and steam (H_2O). In one embodiment, a reduction reaction of composite metal oxides may produce syngas from a fuel and an oxidation reaction may regenerate the reduced composite metal oxides. As used herein, the reduction reaction may be referred to as a “first step” or “step one”, and the oxidation reaction may be referred to as “second step” or “step two”. The reduction reaction may take place in a reduction reactor and the oxidation reaction may take place in a separate oxidation reactor. In some embodiments, syngas may comprise at least about at least about 50 mol%, at least about 60 mol%, at least about 70 mol%, at least about 80 mol%, or even at least about 85% of the combination of carbon monoxide and hydrogen, such that the sum of the mol% of carbon monoxide and the mol% of hydrogen is at least about 50 mol%, at least about 60 mol%, at least about 70 mol%, at least about 80 mol%, or even at least about 85%. The stoichiometric ratio of carbon monoxide to hydrogen in the syngas produced may be about 1:2, such as between about 1:3 and about 1:1. However, the ratio may be controlled by the process parameters such as reaction conditions and reactants. The syngas may have little carbon dioxide and steam present, such as, for example, less than about 10 mol%, less than about 5%, or even less than about 2% of carbon dioxide and less than about 10 mol%%, less than about 5%, or even less than about 2% steam, respectively. The syngas may have little carbon formation, such as less than about 10 mol%. The syngas may be ready for use in downstream synthesis reactions to produce various hydrocarbons ($C \geq 1$) such as, but not limited to, methanol, dimethyl ether, gasoline, and diesel. The reduced composite metal oxide from the reduction reaction (after the syngas production) may be regenerated by oxidation with air, or another oxidant such as oxygen, steam, carbon dioxide, or combinations thereof, and then may be recycled back to the initial reduction reactor, such that the composite metal oxides may be recycled and may be continually used in the oxidation and reduction reactions. The cyclic reduction (endothermic) and oxidation (exothermic) reactions of composite metal oxides may form a reaction and heat integrated process loop that may perpetuate.

[0029] The fuel and composite metal oxides may flow in a co-current pattern relative to one another in the reduction reactor. For example, in one embodiment the co-current gas-solid flow may be either upward or downward. The reduction reactor may be, for example, a moving bed reactor, rotary kiln, riser, downer, or gas switching fixed bed. In one embodiment, the co-current reactor design may allow the natural gas, or other fuel, conversion to achieve completion wherein the composite metal oxides may be reduced to an oxidation state that provides a high quality of product syngas (i.e., at least about 90 mol % carbon monoxide and hydrogen). The composite metal oxides may act as a heat and oxygen transfer media to balance the energy and mass between the two steps (the oxidation and reduction reactions).

[0030] The composite metal oxides may act as oxygen carrying materials in the processes described herein. The composite metal oxides may comprise primary metal oxides and secondary metal oxides, including, but not limited to, FeO_x (primary) - Al_2O_3 (secondary) and FeO_x (primary) -TiO_2 (secondary), where $0.3<x<1$. The primary to secondary metal oxide weight ratios may be about 15:85 to about 85:15, which may promote high CO/CO_2 and H_2/H_2O ratios (i.e., at least about 6) in the product syngas and to avoid carbon formation. Primary metal oxides may comprise, for example, oxides of Fe, V, Cr, Mn, Co, Ni, Cu, Zn, W, Pb, Ce , Sn, Mo, or combinations thereof. Secondary metal oxides may comprise, for example, oxides of Ti, Al, Si, Ca, Y and Zr, or combinations thereof. The composite metal oxide may further comprise dopants/promoters, such as, but not limited to, Ca, Ce, Pt, Ru, Rh, La, Fe, Cu, oxides thereof, and combinations thereof. The dopants/promoters may assist in the oxidation and/or reduction reactions and to enhance the rate of reactions, and may serve as an inert support or binder that may enhance the mechanical properties of the composite metal oxides. Through the reduction reaction, the composite metal oxide may provide a high quality of product syngas at the outlet of the reactor. Following the reduction reaction, the reduced state composite metal oxide (any weight percentage) may comprise primary and secondary metal oxides, such as FeO_x - Al_2O_3 or FeO_x -TiO_2, at oxidation states of the +0 state, i.e., Fe, and the +2 state, i.e., FeO.

[0031] In addition to natural gas, other carbonaceous fuels in the form of gas, liquid and solid may also be used, such as feedstock fuels including, but not limited to, coal, biomass, petroleum coke, naphtha, residual oil, shale gas, C_2-C_4 light hydrocarbons, and combinations thereof. The systems and methods described herein may convert these feedstock fuels using the same type of reactors and same types of composite metal oxides as for natural gas, to carbon monoxide and hydrogen at near the stoichiometric ratio, e.g., 1:0.6 to 1:0.8 for biomass, with little carbon dioxide presence (less than about 10 mol%). In one embodiment, feedstock fuel may be co-injected with a carbon-rich or hydrogen-rich reactant to change the carbon monoxide to hydrogen ratio of the syngas. For these feedstocks, the CO/H_2 ratio of the product syngas may be adjusted to any desired ratio for downstream product synthesis, such as 1:2, by means of co-injection of these feedstock fuels with "carbon-rich" (such as CO_2 and coal) or "hydrogen-rich" (such as H_2O and CH_4) reactants. For example, with biomass as the feedstock fuel, the CO/H_2 ratio may be adjusted to 1:1 by co-injection of the biomass with methane, a hydrogen-rich reactant. Such syngas composition adjustment in the system and method described herein may require only a minimal amount of co-injecting reactants and may be significantly lower compared to the amount of the co-injecting reactants used in the conventional methods. .

[0032] In another embodiment, the CO/H_2 ratio may be adjusted to produce a high hydrogen content syngas by reaction of the reduced composite metal oxide with steam to produce hydrogen. The hydrogen may then be used to adjust the syngas CO/H_2 ratio to a higher level in H_2 contents. The steam oxidized composite metal oxide may be oxidized by air to its original oxidation state of the composite metal oxide for reuse in an oxidation reaction in an oxidation reactor.

[0033] Conventional syngas production methods from natural gas or other carbonaceous feedstocks may require cost intensive heat-exchanger type reactor, air separation unit, and/or a large amount of CO_2/H_2O reactants for controlling the feedstock conversion and product quality. The system and method described herein that carries out the selective oxidation reaction by the redox cycle of composite metal oxides may eliminate the need for the use of complicated reactors, air separation unit and excessive CO_2/H_2O reactants. The specially tailored composite metal oxides described herein coupled with the gas-solid co-current flow reactor design may directly convert the feedstock fuel to a high quality syngas yielding a high feedstock fuel conversion efficiency, flexible syngas product CO to H_2 ratio, low CO_2 and H_2O concentrations in the product gas, and little carbon deposition. The overall process may be auto-thermal with composite metal oxides transferring heat between the reactions. The operation temperature may range from about 500°C to about 1200°C for the reduction (endothermic) reaction of composite metal oxide, and from about 600°C to about 1250°C for the oxidation (exothermic) reaction of composite metal oxide. The operation pressure may range from about 1 to about 50 bars, which may depend on the pressure of feedstocks as well as the requirement of downstream syngas conversion process. The feedstocks such as air and fuel may be preheated up to 1000°C to increase the fuel to syngas conversion efficiency.

[0034] Syngas may be a chemical precursor for synthesis of liquid fuels and chemicals. It may be a mixture of predominantly carbon monoxide (CO) and hydrogen (H_2) produced from the partial oxidation of a variety of feedstocks including, but not limited to, natural gas, shale gas, coal, biomass, naphtha, residual oil, petroleum coke, etc. Depending on the feedstocks and processing methods, the syngas composition and quality may vary significantly. Table 1 compares some conventional syngas production approaches, including steam methane reforming (SMR), dry methane reforming (DMR), partial oxidation (POX), autothermal reforming (ATR)/two-step reforming, dry coal gasification, and coal slurry gasification.

Process	Feedstocks	CO: H_2 molar ratio	CO_2 level	Temperature, °C	Reactor(s)
SMR	CH_4, H_2O	1:2.8-4.8	High	800-900	externally heated tubular catalytic reactor
DMR	CH_4, CO_2 H_2O	1:1-3	high	800-900	externally heated tubular catalytic reactor
POX	CH_4, O_2	1:1.7-1.8	low	>1300	high temperature non-catalytic reactor
ATR/two step	CH_4, O_2, H_2O	1:1.8-4	high	900-1100	combination of SMR and POX
Dry coal gasification	Coal, O_2	1:1-1.2	low	1500	Entrained bed with heat recovery
Coal slurry gasification	Coal, O_2, H_2O	1:1.2-1.5	high	1400	Entrained bed

Table 1. Conventional Syngas Production Processes

[0035] The CO to H_2 ratio may directly affect the downstream application of the produced syngas. For example, a molar ratio of CO to H_2 of 1:2 may be commonly used for the synthesis of liquid fuels such as, but not limited to, gasoline, diesel, and methanol, while a ratio of about 1:1 may be used for production of acetic acid, acetic anhydride, or formaldehyde. Ratios less than 1:3 may be used in combination with a water gas shift unit for hydrogen production and ammonia synthesis.

[0036] As shown in Table 1, a conventional SMR process may produce a hydrogen rich syngas due to the excess amount of steam introduction, which may limit its application to hydrogen and ammonia synthesis. Due to the reduced steam flow and slow CO_2 reaction kinetics of DMR, carbon formation from methane decomposition may result. The reactions occurring in the SMR and DMR processes may be endothermic, favoring higher operating temperature for greater fuel conversion. Both processes may be commonly performed using costly heat exchanger type reactors, where fuel combustion externally provides the heat necessary to drive the catalytic reactions for syngas production. Considering the reactor materials, the SMR and DMR processes may operate below 900°C, thermodynamically restricting the methane conversion.

[0037] POX and dry coal gasification processes may be operated at a much higher temperature as the partial oxidation of the fuel with oxygen may be exothermic and may provide the heat for the process. The CO to H_2 ratio from these processes may depend upon the atomic carbon and hydrogen content of the fuel feedstock, which may pose limitations on downstream chemical and fuel synthesis. Their associated high process temperatures also may require capital-intensive heat recovery systems. In ATR, two-step methane reforming, and coal slurry gasification processes, steam and/or water may be introduced to promote a water gas shift reaction and boost hydrogen content. H_2O reactions with C and CH_4 may be endothermic, which lowers the operation temperature, allowing for high fuel conversion with cost-effective reactor design and construction. However, these syngas generation technologies all require air separation units (ASU) to supply concentrated oxygen and account for 40% to 50% of the overall capital and operating costs of a chemical/liquid fuel production plant.

[0038] The content of CO_2 and H_2O in the syngas may be an important aspect for the syngas quality control. In many existing processes, excess amounts of O_2 and H_2O may be usually introduced, which may result in promoting combustion and water gas shift reactions, respectively. A significant amount of CO_2 and/or H_2O may exist in the syngas stream, lowering the syngas production selectivity and efficiency.

[0039] In processes such as DMR, carbon deposition and formation may occur, when the fuel may be exposed to metallic substances such as Ni and Fe in a low CO_2 and low H_2O content environment. The metallic substance may catalyze the methane decomposition to carbon and hydrogen, where the absence of oxidizing gas, such as CO_2, H_2O and O_2, prevents the deposited carbon from being gasified. The negative effects of carbon deposition are two-fold: it may reduce the fuel conversion efficiency and selectivity, and may cause catalyst deactivation.

[0040] Thus, controlling the CO_2/H_2O ratio and concentration, and preventing carbon deposition may be two opposing challenges in many conventional syngas production processes. Many of these processes use excess CO_2/H_2O to suppress carbon formation. Such tradeoff may result in a syngas product stream with more than 15% CO_2 and/or H_2O, requiring downstream syngas purification steps and may result in a decreased fuel to syngas production efficiency. The process described herein may minimize excess CO_2 and/or H_2O use and production while preventing carbon formation and deposition, greatly improving the syngas production efficiency.

[0041] Described herein are chemical looping processes that have been developed for natural gas conversion to syngas. Oxides such as, but not limited to, Fe_2O_3, NiO, ZnO, PbO, CoO, Cr_2O_3, $BaSO_4$ have been considered as oxygen carriers to partially oxidize methane to CO and H_2. The reduced metal oxides and sulfates may be regenerated with air in a separate reactor. The chemical looping approach avoids the direct mixing between methane and air, and thus eliminates the need for an ASU and has the potential to significantly reduce syngas production costs.

[0042] However, in order to produce a low H_2O and CO_2 content syngas (less than 10 mol% respectively) from the chemical looping system, the thermodynamic phase equilibrium of single metal oxides and/or sulfates dictates that complete reduction to metallic phase or metal sulfide may be required in the fuel reactor (reduction reactor). The complete reduction may irreversibly change the oxygen carrier structure, causing its deactivation during the redox cycles. In addition, the extensive formation of the reduced metallic phase may accelerate methane decomposition resulting in carbon formation/deposition. For example, when 70% of Fe_2O_3 is reduced to Fe, carbon deposition may become a dominant process. Also, the reduction extent of metal oxides and sulfates affects the CO to H_2 ratio, which may require a careful control of the solid circulation rate and operation condition.

[0043] The composite metal oxide may be in the form of particles, pellets, or monolith, depending on the reactor design. The pellet size may range from 300 microns to 4000 microns, which may be suitable for moving bed operation. In one embodiment, the density of the composite metal oxide may be from about 1000 to about 5000 kg/m^3. The relatively large pellet size and relatively high density may also assist the separation of process fines when solid fuels are used as the feedstock fuel. The composite metal oxide materials may be chemically and physically stable during the redox cycle. The synthesis procedure includes dry/wet mixing, particle/pellet formation, and sintering. Alternative techniques include sol-gel, wet impregnation, and dry-freezing.

[0044] In addition to natural gas, the feedstock fuels may be any gas, solid, and liquid fuel, or combinations thereof. Gaseous fuels include shale gas (including dry gas and wet gas), tail gas containing light hydrocarbons from downstream syngas conversion and hydroprocessing units such as Fischer-Tropsch synthesis. The composite material may be effective in converting C1-C4 hydrocarbons as well as CO_2 and H_2O to high quality syngas from the feedstock fuels sources. In certain embodiments, the composite material may handle sulfur compound in the fuel gas without deactivation. Therefore, no fuel pretreatments, such as CO_2 removal and sulfur removal, may be needed. The methods described herein may also convert solid fuels such as coal, petroleum coke, and biomass, as well as liquid fuels, such as naphtha and residual oil. In one embodiment, when solid fuels are introduced with the metal oxide composite in a moving bed process, the solid fuel may be in pellet form with a size ranging from about 300 to about 4000 microns. Such operation may ease the solid fuel injection and enhance the solid-solid distribution inside the reactor bed.

[0045] In some embodiments, solar energy may be used as a heat source for the endothermic reactions of the fuel conversion in the reduction reaction. Such arrangement may directly convert CO_2 and H_2O into syngas and other fuel forms for solar energy storage and utilization. In another embodiment, oxygen or oxygen releasing material may be introduced in the reduction reaction to increase reaction kinetics for syngas production. In yet another embodiment, the composite metal oxide materials may release oxygen for fuel conversion.

[0046] In one embodiment, a co-current flow reactor may be used for syngas production in the first step (reduction reaction). In one embodiment, a moving packed bed reactor may be used with both fuel and the composite metal oxides fed from the top and discharged from the bottom. The co-current downward flow moving bed reactor may ensure a full conversion of fuel into syngas as well as a desired composite metal oxide conversion which, may control the syngas product composition and may avoid carbon formation. The solid flow in the reduction reactor may be controlled by a non-mechanical valve system positioned at the bottom of the reactor. The reduced composite metal oxide may be then transported to the second step, an air fluidized bed reactor that oxidizes the composite metal oxide to a higher oxidation state. Alternative reactor designs for the first step include rotary kiln, riser, and downer, which may provide similar gas solid co-current flow patterns. The overall process may be auto-thermal with composite metal oxides transferring heat between the reactors.

[0047] In one embodiment, the two-step conversion (reduction and oxidation) may be conducted in a fixed bed reactor and a gas switching system for syngas production from gaseous fuel. The fixed bed may be filled with composite metal oxide pellets, particles or a monolithic bed structure. The fuel gas may be introduced to the fixed bed, where the composite metal oxide may be reduced within a certain extent and high quality syngas may be produced. When the composite metal oxide conversion reaches a determined state, the fuel gas may be switched to a preheated air stream for the composite metal oxide regeneration. In one exemplary embodiment, the fuel and air streams may be preheated and the gas switching system may be operated at high temperatures (at least about 1000°C).

[0048] In yet another embodiment, a counter-current moving bed reactor may be used for the first step with fuel introduced from the bottom and composite metal oxide introduced from the top. A conversion profile of the composite metal oxide may be formed inside the moving bed reactor. There may be two gas outlets in the moving bed reactor, one at the top for concentrated CO_2 and H_2O production, another in the middle of the bed where the composite metal oxide conversion may be suitable for high quality syngas production. For the second step, the reduced composite metal oxide may be reoxidized with air. In this embodiment, high quality syngas may be obtained with sequestration ready CO_2 stream. The yield between syngas and CO_2 stream may be adjusted by the process heat balance and flowrates from the two gas outlets of the moving bed reactor.

[0049] In another embodiment, a moving bed reactor may be used for simultaneous high quality syngas and high purity CO_2 productions. For the first step, the composite metal oxide may be introduced from the top, and the fuel may be introduced at the middle. Two gas outlets may be positioned at the top and bottom of the moving bed reactor. The gas coming out from the top may encounter higher oxidation state composite metal oxides resulting in high purity CO_2 and H_2O production, while the gas from the bottom may be high quality syngas controlled by the reduced composite metal oxide. The reduced composite metal oxide may be reoxidized by air in another reactor for the second step. For this two-step process, high quality syngas may be obtained with sequestration ready CO_2 stream. The yield between syngas and CO_2 stream may be adjusted by the process heat balance and the fuel split ratio in the moving bed reactor.

[0050] In another embodiment, the reduced composite metal oxide from the first step may be oxidized by H_2O, CO_2 or a mixture thereof, for production of H_2, CO or syngas in an additional reactor. In one embodiment, the additional reactor may be a moving bed reactor with counter-current gas (H_2O, CO_2) — solid (reduced composite metal oxide) contacting pattern. The operation temperature may be from about 500°C to about 1100°C.

[0051] The oxidation state of the single metal oxide may significantly affect the syngas composition and possibility of carbon formation. As shown in FIG. 1 and FIG. 2, for example, when FeO may be used to partially oxidize methane to syngas, a low selectivity to CO_2 and H_2O may be obtained when the FeO to CH_4 ratio may be below 2. In such condition, however, metallic Fe may be formed and may catalytically decompose methane causing carbon deposition. Carbon deposition/formation may be avoided by reducing the extent of the metal oxide reduction by increasing the FeO to CH_4 ratio. Conversely, increasing this ratio results in an increase in CO_2 and H_2O levels to more than 30 mol%, lowering the syngas selectivity and yield. Thus, the use of a single metal oxide material pose challenges in syngas quality control.

[0052] The subject matter of the present disclosure may be integrated with various fuel and chemical synthesis processes in light of its ability to produce flexible CO to H_2 ratio. Depending on the downstream application, the CO to H_2 ratio may be adjusted to the desired value in the first step by introducing CO_2 or H_2O together with the fuel. The CO_2 and H_2O may also enhance the initial conversion of methane and carbon via reforming and gasification reactions, respectively. Thus, the need for cost and energy intensive downstream processes to adjust the syngas composition may be removed or reduced to a minimal. In some embodiments, the reduced composite metal oxide may be also used for hydrogen production by steam oxidation. The hydrogen produced may be used for hydroprocessing or product upgrading. In certain embodiments, less than 20 wt% of dopants may be added to the composite to catalyze certain reactions such as methane decomposition, carbon gasification, and tar cracking. The dopants may be selected from the group consisting of at least one of Ca, Ce, Pt, Ru, Rh, La, Fe, Cu, and oxides thereof. In yet another embodiment, the composite metal oxide material may also release oxygen for fuel conversion. Binders such as bentonite and PVC material may be also used for binding purpose in the synthesis process.

[0053] The composite metal oxide material may be chemically and physically stable during multiple redox cycles. Single metal oxide materials may not be able to sustain multiple redox cycles due to changes in mechanical and crystal structure. The composite metal oxide materials may be synthesized by dispersing active metal oxide compounds in a physically stable structure, and thus may be repeatedly used in the process with little change to its reactivity and oxygen carrying capacity.

[0054] In other embodiments, as shown in FIG. 3(a) and FIG. 3(b), a co-current flow reactor may be used for syngas production in the first step from a natural gas or shale gas feedstock fuel. The CO to H_2 ratio in the syngas may be about 1:2, which may be suitable for F-T and methanol synthesis. The tail-gas of the syngas conversion step containing C_1-C_4 hydrocarbons may be recycled to the first step reactor to maximize the fuel to product yield and efficiency. The CO:H_2 ratio may be adjusted to other ratios by introducing minimal amount of the CO_2 and H_2O in step 1. For example, when CO_2 or other carbon rich feedstocks may be introduced together with methane, the CO to H_2 ratio may be adjusted to 1:1, suitable for acetic acid, acetic anhydride, and/or formaldehyde synthesis. In one embodiment, a moving packed bed reactor may be used with both fuel and the said composite metal oxides fed from the top and discharged from the bottom. The co-current downward flow moving bed reactor may promote a full conversion of fuel into syngas as well as a desired composite metal oxide conversion which may control the syngas product composition and avoid carbon formation. For example, the composite metal oxide may be introduced as FeO_x-TiO_2 at the top, and may be converted to FeO_y-TiO_2 at the bottom of the reactor. In one embodiment, the operation range of $1.5>x>1>y>0.3$ may be used to increase the particle oxygen carrying capacity and control the syngas quality. Alternatives to the first step reactor designs include rotary kiln, riser, and downer, which may provide similar gas solid co-current flow pattern as the moving packed bed reactor. The reduced composite metal oxide may be then transported to the second step, an air fluidized bed reactor that oxidizes the composite metal oxide to a higher oxidation state. For example, the main reactions in the first and second steps may be:

$$2FeOTiO_2 + CH_4 = 2FeO_{0.5}TiO_2 + CO + 2H_2 \qquad \Delta H = 235 \text{ kJ @ } 1000°C$$

$$2FeO_{0.5}TiO_2 + 1/2O_2 = 2FeOTiO_2 \qquad \Delta H = -359 \text{ kJ @ } 1000°C$$

[0055] Still referring to FIGS. 3(a) and 3(b), the overall heat of reaction may be thus exothermic, rendering a flexible process heat balance. In one embodiment, the operation temperature may be from 500°C to 1200°C for the first step, and from 600°C to 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to 1000°C to increase the fuel to syngas efficiency. The operation pressure may range from 1 to 50 bars, depending on the pressure of feedstocks as well as the requirement of the downstream syngas conversion process.

[0056] In other embodiments, as shown in FIG. 4(a) and FIG. 4(b), a co-current flow reactor may be used for syngas production from solid fuels such as biomass and/or coal. The CO to H_2 ratio in the syngas may be about 1:0.6 to about 1:0.8, and may depend on the composition of the feedstock fuels. Co-injection of hydrogen rich feedstocks such as CH_4 and H_2O may adjust the CO to H_2 ratio to about 1:1 or about 1:2, which may be suitable for downstream chemical and fuel synthesis. In one embodiment, a moving packed bed reactor may be used with similar sized solid fuel and the said composite metal oxides fed from the top and discharged from the bottom. The co-current downward flow moving bed reactor may promote full fuel conversion into syngas as well as a desired composite metal oxide conversion which may control the syngas product composition and avoid carbon formation. For example, the composite metal oxide may be introduced at the top of the first step reactor as FeO_xTiO_2 and may be converted to FeO_yTiO_2 when it reaches the bottom. In one embodiment, the operation range of $1.5>x>1>y>0.3$ may be used to maintain a high particle oxygen carrying capacity and to control the syngas quality. The solid flow may be controlled by a non-mechanical valve system positioned at the bottom of the reactor. The reduced composite metal oxide may be then transported to the second step, an air fluidized bed reactor that oxidizes the composite metal oxide to a higher oxidation state. In one embodiment, the operating temperature may range from about 500°C to about 1200°C for the first step, and from about 600°C to about 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to at least about 1000°C to increase the fuel to syngas efficiency. The operating pressure may range from about 1 bar to about 50 bars, depending on the pressure of the feedstocks as well as the requirement of the downstream syngas conversion process. Alternatives to the first step reactor designs include rotary kiln, riser, and downer, which may provide similar gas solid co-current flow pattern as the moving packed bed reactor.

[0057] In other embodiments, as shown in FIG. 5(a) and FIG. 5(b), a co-current flow reactor may be used for syngas production from liquid fuels such as, but not limited to, naphtha. In one embodiment, a moving packed bed reactor may be used with preheated liquid fuel and the said composite metal oxides fed from the top and discharged from the bottom. The co-current downward flow moving bed reactor may promote full fuel conversion into syngas as well as a desired composite metal oxide conversion which may control the syngas product composition and avoid carbon formation. For example, the composite metal oxide may be introduced in the first step reactor as FeO_xTiO_2 at the top, and may be converted to FeO_yTiO_2 when it reaches the bottom. In one embodiment, the operation range of $1.5>x>1>y>0.3$ may be used to maintain a high particle oxygen carrying capacity and control the syngas quality. The solid flow may be controlled by a non-mechanical valve system positioned at the bottom of the reactor. The reduced composite metal oxide may then be transported to the second step, an air fluidized bed reactor that oxidizes the composite metal oxide to a higher oxidation state. In one embodiment, the operating temperature ranges from 500°C to 1200°C for the first step, and from 600°C to 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to 1000°C to increase the fuel to syngas efficiency. The operating pressure may range from 1 to 50 bars, depending on the pressure of feedstocks as well as the requirement of the downstream syngas conversion process.

[0058] In another embodiment, as shown in FIG. 6, the two step conversion may be conducted in a fixed bed reactor with a gas switching system for syngas production from gaseous fuel. The fixed bed may be filled with composite pellets, particles or a monolithic bed structure. The fuel gas may be introduced to the fixed bed, where the composite metal oxide may be reduced within a certain range and high quality syngas may be produced. When the composite metal oxide conversion reaches a certain extent of reduction, the fuel gas may be switched to preheated air for the composite metal oxide regeneration. For example, the composite metal oxide may be reduced in the first step reactor from FeO_xTiO_2 to FeO_yTiO_2 before switching the gas feed to the second step. In one embodiment, the operating range of $1>x>y>0.3$ may be used to control the syngas quality. In one embodiment, the fuel and air streams may be preheated and the gas switching system may be operated at high temperatures. In one embodiment, the operating temperature may range from about 500°C to about 1200°C for the first step, and from about 600°C to about 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to at least about 1000°C to increase the fuel to syngas efficiency. The operating pressure may range from about 1 bar to about 50 bars, depending on the pressure of the feedstocks as well as the requirement of the downstream syngas conversion process.

[0059] In another embodiment, as shown in FIG. 7, a counter-current moving bed reactor may be used for the first step with fuel introduced from the bottom and composite metal oxide introduced from the top. This gas-solid contact design may form a conversion profile of the composite metal oxide along the height of the moving bed reactor. Two gas outlets may be placed on the moving bed reactor, one at top for concentrated CO_2 and H_2O production, and the other at or near the middle where the composite metal oxide conversion may be suitable for high quality syngas production. In the second step, the reduced composite metal oxide may be reoxidized with air. For this two-step process, high quality syngas may be obtained in conjuction with a high purity/sequestration ready CO_2 stream. For example, the composite metal oxide may be introduced in the first step reactor as FeO_xTiO_2 at the top, and may be converted to FeO_yTiO_2 when it reaches the middle, and may be converted to FeO_zTiO_2 when it reaches the bottom. In one embodiment, the operation range of $1.5>x>1>y>z>0.3$ may be used to maintain a high particle oxygen carrying capacity and control the syngas quality. The yield between syngas and CO_2 stream may be adjusted by the process heat balance and flowrates from the two gas outlets of the moving bed reactor. The operating temperature may range from about 500°C to about 1200°C for the first step, and from about 600°C to about 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to at least about 1000°C to increase the fuel to syngas efficiency. The operating pressure may range from about 1 bar to about 50 bars, depending on the pressure of the feedstocks as well as the requirement of the downstream syngas conversion process.

[0060] In another embodiment, as shown in FIG. 8, a moving bed reactor may be used for full fuel conversion to high quality syngas and high purity CO_2 co-production. The composite metal oxide may be introduced from the top, and the fuel may be introduced at or near the middle of the reactor. Two gas outlets may be positioned at the top and bottom of the moving bed reactor. The gas coming out from the top may encounter higher oxidation state composite metal oxides resulting in high purity CO_2 and H_2O production, while the gas from the bottom may be high quality syngas controlled by the reduced composite metal oxide. For the second step, the reduced composite metal oxide may be reoxidized with air. For this two-step process, high quality syngas may be obtained in conjuction with a high purity/sequestration ready CO_2 stream. In one embodiment, the operation range of $1.5>x>1>y>z>0.3$ may be used to maintain a high particle oxygen carrying capacity and control the syngas quality. The yield between syngas and CO_2 stream may be adjusted by the process heat balance and the fuel split ratio in the moving bed reactor. The operating temperature may range from about 500°C to about 1200°C for the first step, and from about 600°C to about 1250°C for the second step. The fuel and oxidizing gas feedstocks for the first and second step, respectively, may be preheated up to at least about 1000°C to increase the fuel to syngas efficiency. The operating pressure may range from about 1 bar to about 50 bars, depending on the pressure of the feedstocks as well as the requirement of the downstream syngas conversion process. In certain embodiments, as shown in FIG. 9, the reduced composite metal oxide may be also used for hydrogen production by steam oxidation or syngas production using a mixture of CO_2 and H_2O. The hydrogen produced may be used for hydroprocessing or product upgrading.

[0061] In another embodiment, as shown in FIG. 10, the reduced composite metal oxide from the first step may be used for hydrogen production by steam oxidation or for syngas production using a mixture of H_2O, CO_2. In one embodiment, the additional reactor may be a moving bed reactor with countercurrent gas solid contacting pattern. The operation temperature may be from about 500°C to about 1100°C and the heat may be supplied directly from an external heat source such as a solar energy collecting system.

[0062] In yet another embodiment, as shown in FIG. 11, the composite metal oxide material may be coated on the fuel side of a membrane system, such as an OTM/ITM based membrane system for syngas production. Here, the composite material may be stabilized with an x value between 0.3 and 1 to control the syngas quality.

[0063] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

[0064] In another embodiment, the fuel conversion system may be designed in compact, modular, mobile mode and used for offshore and remote well applications.

Examples

[0065] The various embodiments of systems and methods for converting fuel will be further clarified by the following examples. The examples are illustrative in nature, and should not be understood to limit the subject matter of the present disclosure.

Example 1

[0066] A fixed bed experiment was conducted to study the methane to syngas reaction. The lower section of the reactor was filled with 23.1g FeO-TiO_2 particles, and the upper section was filled with 8.3g Fe_2O_3-TiO_2 particles. When the temperature of the reactor reached 990°C, 50mL/min CH_4 and 50mL/min N_2 was injected into the reactor by digital mass controllers. The outlet gas composition was analyzed using a CAI gas analyzer as well as a gas chromatography. The gas concentration at the outlet reached a quasi-steady state in half an hour with methane conversion >95%, CO:CO_2 ratio around 10, CO:H_2 ratio around 1:2.

Example 2

[0067] A moving bed reactor test apparatus was constructed, as shown in FIG. 12, and experiments were conducted to study the solid feedstock to syngas reaction using Powder River Basin (PRB) coal as prototype coal. The PRB coal tested has about 25% moisture and the corresponding molecular formula may be $CH_{0.8}O_{0.2}$ on a dry basis. The coal powder was mixed with particles at the mass ratio of 1:5 and then fed into the moving bed system from the top in a batch mode. The solid flowrate was controlled to be 20g/min by the screw feeder at the bottom. The temperature was controlled by the external heating to be 1030°C. At the steady state, the coal conversion is over 90%, H_2/CO ratio fluctuated between 0.5-0.7 and CO/CO_2 ratio fluctuated between 5-12, as shown in FIG. 13, respectively. The fluctuation is due to the batch feeding mode of the solid material. Furthermore, CH_4 was also co-injected to adjust the H_2/CO ratio. The co-injection of CH_4 (870ml/min, coal 2.7 g/min, particles 20g/min) could give adjusted the CO/H_2 ratio effectively around 1.1 with CO/CO_2 ratio maintained high, as shown in FIG. 14.

Example 3

[0068] A moving bed reactor test was conducted to study the solid feedstock conversion to syngas using biomass. The corresponding molecular formula was $CH_{1.4}O_{0.6}$. The biomass material was mixed with particles at a mass ratio of 1:3 and then injected into the moving bed system from the top. The solid fuel and composite particles followed a co-current contacting mode. The composite particle flowrate was controlled to 20g/min using the screw feeder at the bottom. The temperature was controlled to 1040°C using the external heaters. At steady state operation, the biomass conversion was over 95% with CO:CO_2 ratio around 10 and CO:H_2 ratio around 1:0.8. In this case, the carbon monoxide and hydrogen concentration in the high quality syngas from the syngas production reactor was higher than 91 mol%. Additionally, CH_4 was co-injected to adjust the CO:H_2 ratio. The co-injection of CH_4 (540ml/min, biomass 5g/min, particles 26g/min) gave an almost complete fuel conversion (95%) with CO:H_2 ratio about 1:1. Given longer fuel residence time, a 100% fuel conversion may be achieved.

Example 4

[0069] A moving bed reactor test was conducted to study the gas feedstock to syngas reaction using methane as a feedstock. FIG. 15 shows a graph illustrating the co-current moving bed experimental data using methane as feedstock.

CLAIMS

1. A method for converting fuel into syngas, the method comprising:

feeding the fuel and composite metal oxides into a reduction reactor in a co-current flow pattern relative to one another, wherein the composite metal oxides are solid particles comprising a primary metal oxide and a secondary metal oxide;

reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides;

transporting the reduced composite metal oxides to an oxidation reactor;

regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant in the oxidation reactor; and

recycling the regenerated composite metal oxides to the reduction reactor for subsequent reduction reactions to produce syngas.

2. The method of claim 1, wherein the fuel is a gas.

3. The method of claim 1, wherein the fuel is natural gas.

4. The method of claim 1, wherein the fuel is natural gas, coal, biomass, petroleum coke, naphtha, residual oil, shale gas, C_2-C_4 light hydrocarbons, and combinations thereof.

5. The method of claim 1, wherein the oxidizing reactant comprises air, oxygen, steam, carbon dioxide, or combinations thereof.

6. The method of claim 1, wherein the ratio of hydrogen to carbon monoxide can be controlled.

7. The method of claim 1, wherein the syngas comprises a stoichiometric ratio of carbon monoxide to hydrogen of about 1:2 and the fuel is natural gas.

8. The method of claim 1, wherein the fuel is co-injected with a carbon-rich or hydrogen-rich reactant to change the carbon monoxide to hydrogen ratio of the syngas.

9. The method of claim 1, wherein oxygen or oxygen releasing material is introduced in the reduction reaction to increase reaction kinetics for syngas production.

10. The method of claim 1, wherein the reducing of the composite metal oxides occurs at a temperature in the range of between about 500°C and about 1200°C.

11. The method of claim 1, further comprising reacting the reduced composite metal oxides with steam to produce hydrogen used to adjust the carbon monoxide to hydrogen ratio of the syngas.

12. The method of claim 1, wherein the syngas comprises at least about 85 mol% carbon monoxide and hydrogen.

13. The method of claim 1, wherein the syngas comprises less than about 10 mol% of carbon dioxide and less than about 10 mol% steam.

14. The method of claim 1, wherein the reduction reactor is a moving bed reactor, rotary kiln, riser, gas switching fixed bed reactor, downer, or combinations thereof in series.

15. The method of claim 1, wherein:

the primary metal oxides comprises oxides of Fe, V, Cr, Mn, Co, Ni, Cu, Zn, W, Pb, Ce , Sn, Mo, or combinations thereof; and

the secondary metal oxides comprises oxides of Ti, Al, Si, Ca, Y and Zr, or combinations thereof.

16. The method of claim 1, wherein the composite metal oxides further comprises a dopant/promoter comprising Ca, Ce, Pt, Ru, Rh, La, Fe, Cu, oxides thereof, or combinations thereof.

17. The method of claim 1, wherein:

the composite metal oxides comprises iron oxide and titanium oxide; or

the composite metal oxides comprises iron oxide and aluminum oxide.

18. The method of claim 17, wherein the iron oxide is reduced in the reduction reaction from FeO_x to FeO_y and $1.5>x>1>y>0.3$

19. The method of claim 1, wherein the CO to H_2 ratio may be adjusted by introducing CO_2, H_2O, or both, into the reduction reaction.

20. The method of claimed 1, wherein the process is auto-thermal, the fuel is preheated, and solar energy is introduced to the reduction reactor.

21. A method for converting fuel into syngas, the method comprising:

feeding the fuel and composite metal oxides into a reduction reactor in a co-current flow pattern relative to one another, wherein:

the composite metal oxides are solid particles comprising a primary metal oxide and a secondary metal oxide;

the fuel is natural gas; and

the composite metal oxide comprises iron oxide and titanium oxide, or the composite metal oxide comprises iron oxide and aluminum oxide; and

reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides, wherein the iron oxide is reduced in the reduction reaction from FeO_x to FeO_y and $1.5>x>1>y>0.3$;

transporting the reduced composite metal oxides to an oxidation reactor;

regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant in the oxidation reactor; and

recycling the regenerated composite metal oxides to the reduction reactor for subsequent reduction reactions to produce syngas.

22. A method for converting fuel into syngas, the method comprising:

reducing the composite metal oxides with the fuel to form syngas and reduced composite metal oxides; and

regenerating the composite metal oxides by oxidizing the reduced composite metal oxides with an oxidizing reactant, wherein:

the composite metal oxides are solid particles comprising a primary metal oxide and a secondary metal oxide; and

the composite metal oxide comprises iron oxide and titanium oxide, or the composite metal oxide comprises iron oxide and aluminum oxide.

23. The method of claim 22, wherein the reduction of the composite metal oxides and the oxidizing of the composite metal oxides is carried out in a fixed bed reactor with a gas switching system.

24. The method of claim 22, wherein the reduction of the composite metal oxides occurs in a reduction reactor, wherein the reduction reactor is a moving bed reactor comprising two gas outlets and the reduction of the composite metal oxides produces syngas and CO_2.

25. The method of claim 22, wherein the reduction and oxidation of the composite metal oxides occurs in a membrane based reactor, wherein the composite metal oxides are integrated to the fuel side of the membrane based reactor.

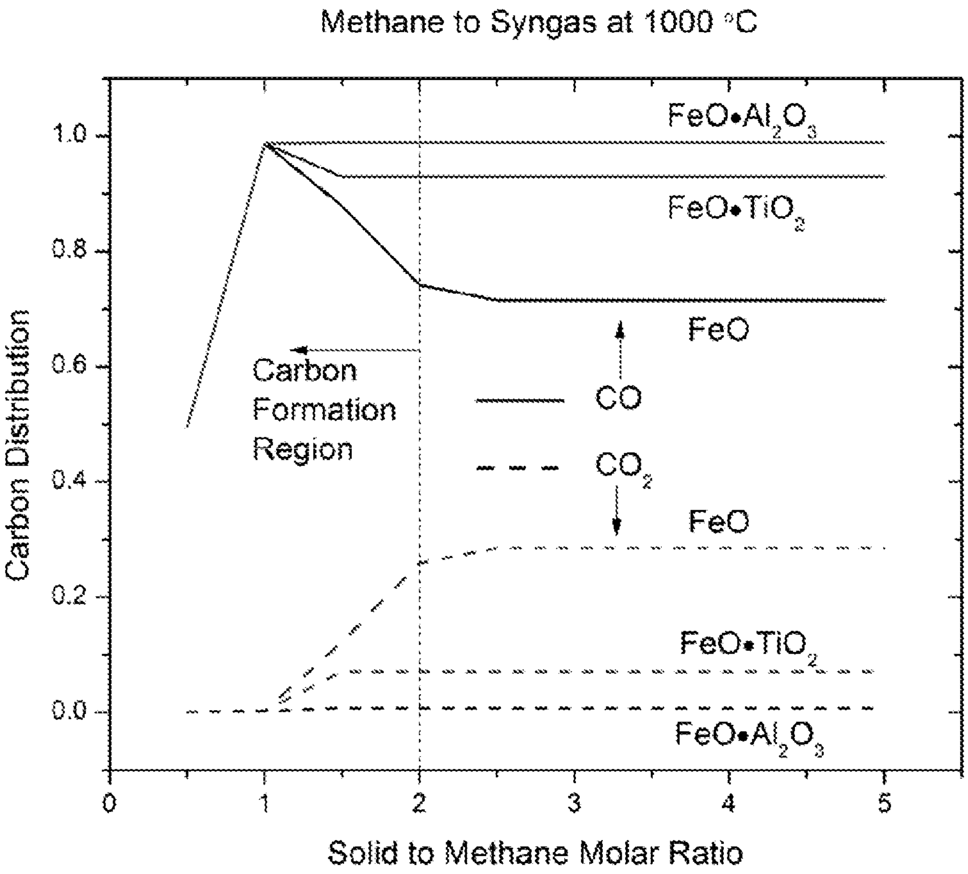

Methane to Syngas at 1000 °C
Carbon Distribution
Solid to Methane Molar Ratio
0
1
2
3
4
5
0.0
0.2
0.4
0.6
0.8
1.0
FeO•Al$_2$O$_3$
FeO•TiO$_2$
FeO
Carbon Formation Region
CO
CO$_2$
FeO
FeO•TiO$_2$
FeO•Al$_2$O$_3$

FIG. 1

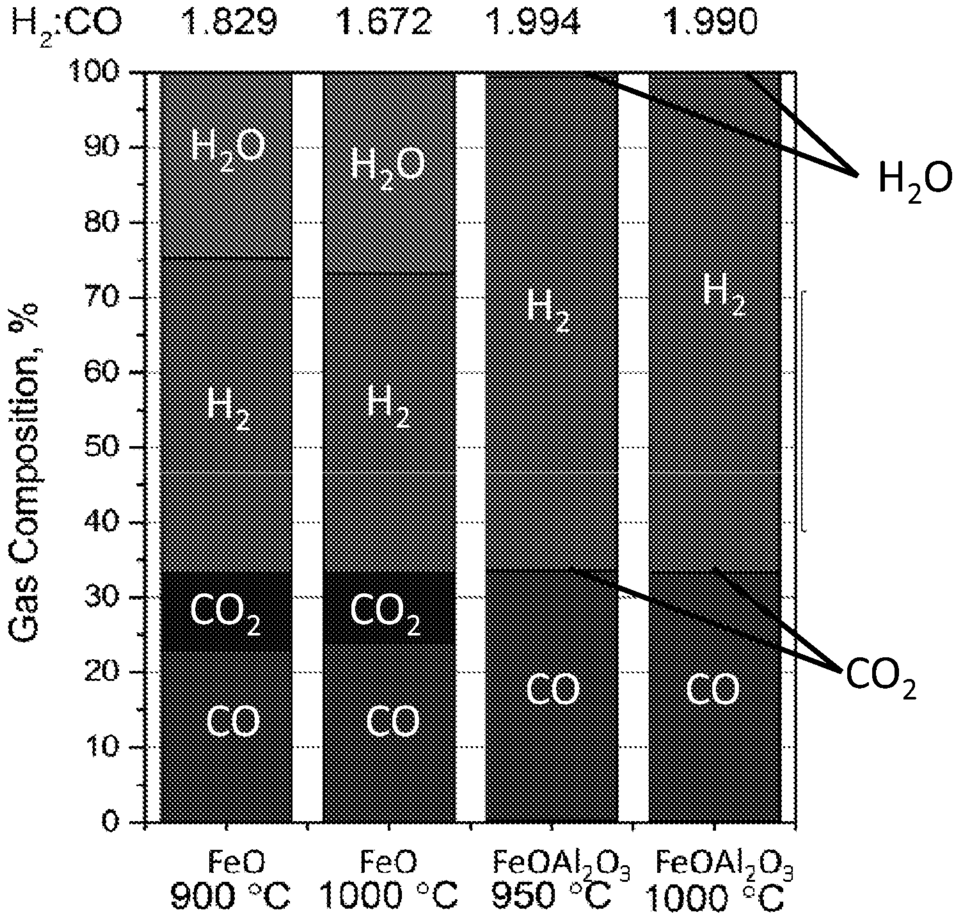

H2:CO
1.829
1.672
1.994
1.990
Gas Composition, %
100
90
80
70
60
50
40
30
20
10
0
H2O
H2
CO2
CO
H2O
H2
CO2
CO
H2
CO
H2
CO
H2O
CO2
FeO 900 °C
FeO 1000 °C
FeOAl2O3 950 °C
FeOAl2O3 1000 °C

FIG. 2

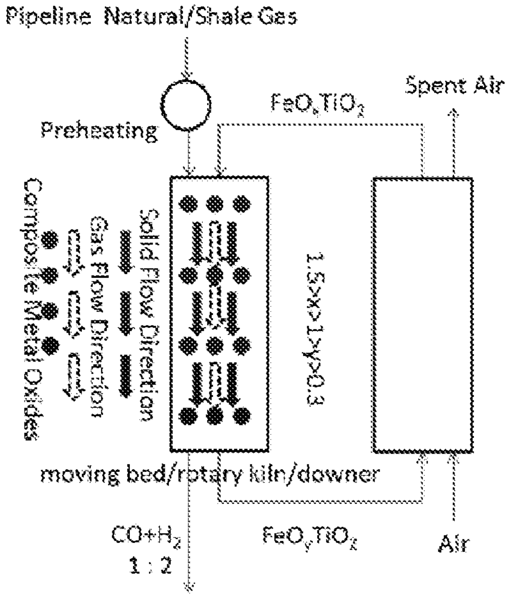

Pipeline Natural/Shale Gas
Preheating
FeO_xTiO_2
Spent Air
Composite Metal Oxides
Gas Flow Direction
Solid Flow Direction
1.5>x>1>y>0.3
moving bed/rotary kiln/downer
CO+H$_2$
1 : 2
FeO_yTiO_2
Air

FIG. 3(a)

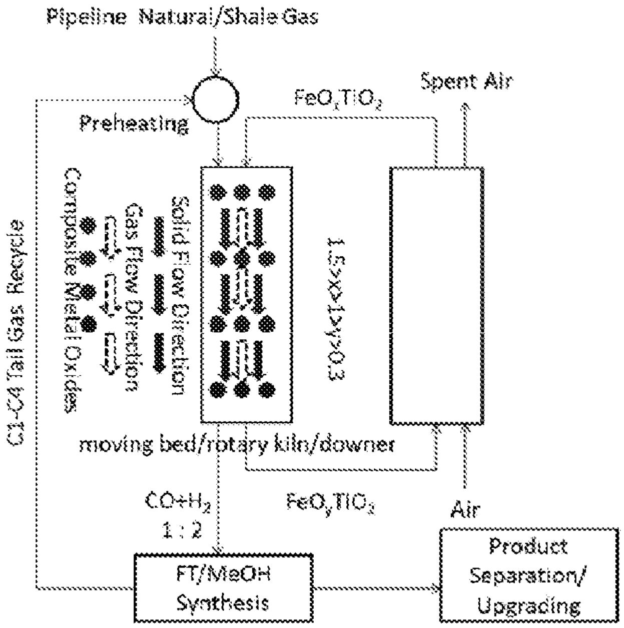

Pipeline Natural/Shale Gas
C1-C4 Tail Gas Recycle
Preheating
FeO_xTiO_2
Spent Air
Composite Metal Oxides
Gas Flow Direction
Solid Flow Direction
1.5>x>1>y>0.3
moving bed/rotary kiln/downer
CO+H$_2$
1 : 2
FeO_yTiO_2
Air
FT/MeOH Synthesis
Product Separation/ Upgrading

FIG. 3(b)

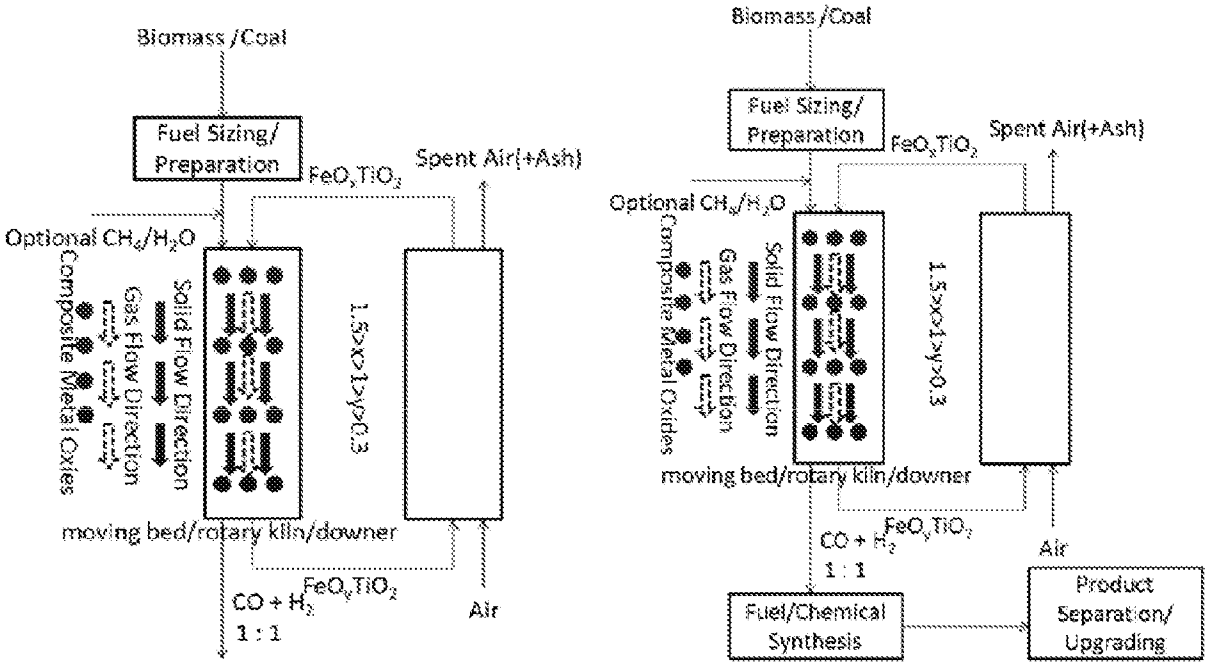


FIG. 4(a)

FIG. 4(b)

FIG. 4

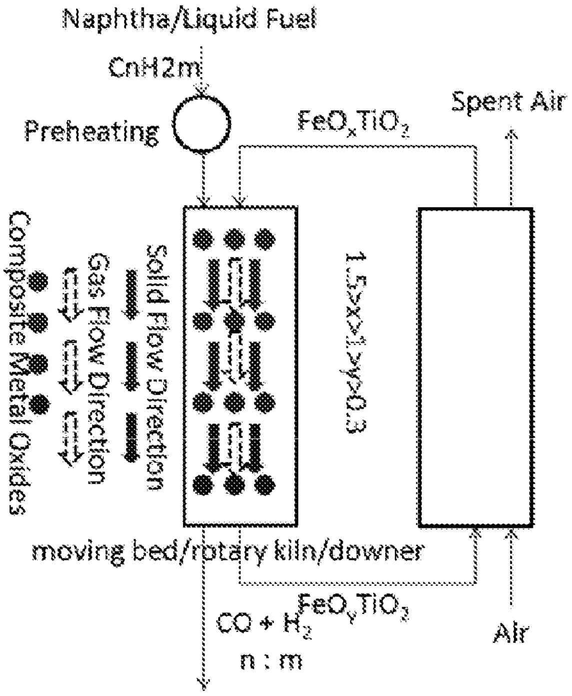

Naphtha/Liquid Fuel
CnH2m
Preheating
FeO$_x$TiO$_2$
Spent Air
Solid Flow Direction
Gas Flow Direction
Composite Metal Oxides
1.5>x>1>y>0.3
moving bed/rotary kiln/downer
CO + H$_2$
n : m
FeO$_y$TiO$_2$
Air

FIG. 5(a)

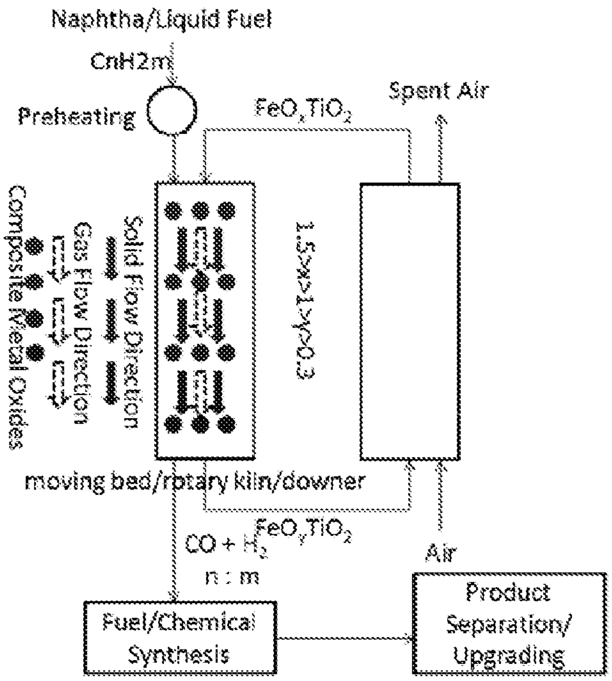
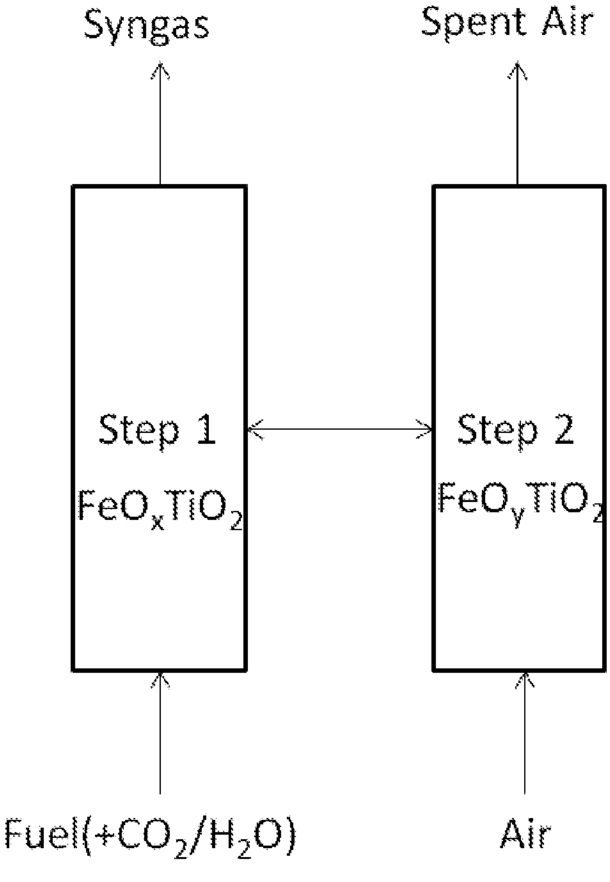

Naphtha/Liquid Fuel
CnH2m
Preheating
FeO$_x$TiO$_2$
Spent Air
Solid Flow Direction
Gas Flow Direction
Composite Metal Oxides
1.5>x>1>y>0.3
moving bed/rotary kiln/downer
FeO$_y$TiO$_2$
CO + H$_2$
n : m
Air
Fuel/Chemical Synthesis
Product Separation/ Upgrading

FIG. 5(b)


Syngas
Spent Air
Step 1
FeO_xTiO_2
Step 2
FeO_yTiO_2
Fuel(+CO_2/H_2O)
Air

$1>x>y>0.3$

FIG. 6

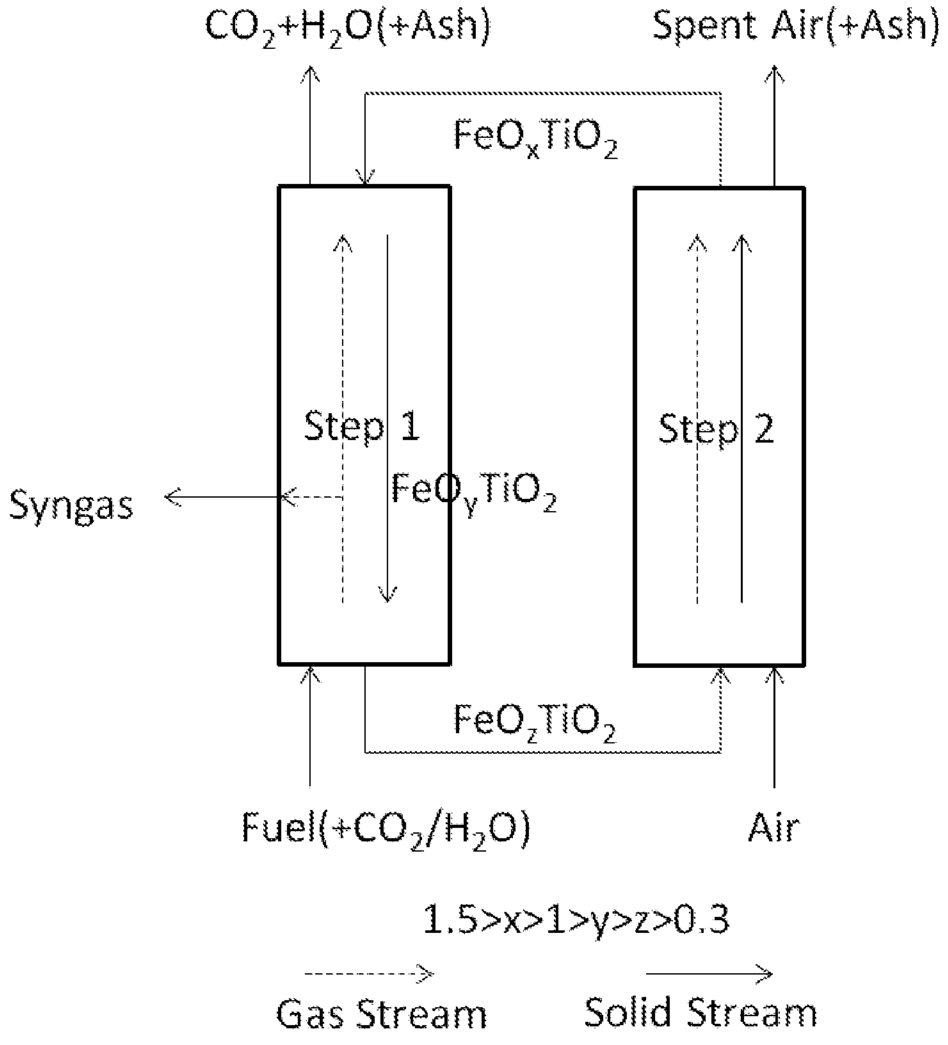

CO_2+H_2O(+Ash)
Spent Air(+Ash)
FeO_xTiO_2
Step 1
Step 2
Syngas
FeO_yTiO_2
FeO_zTiO_2
Fuel(+CO_2/H_2O)
Air
1.5>x>1>y>z>0.3
Gas Stream
Solid Stream

FIG. 7

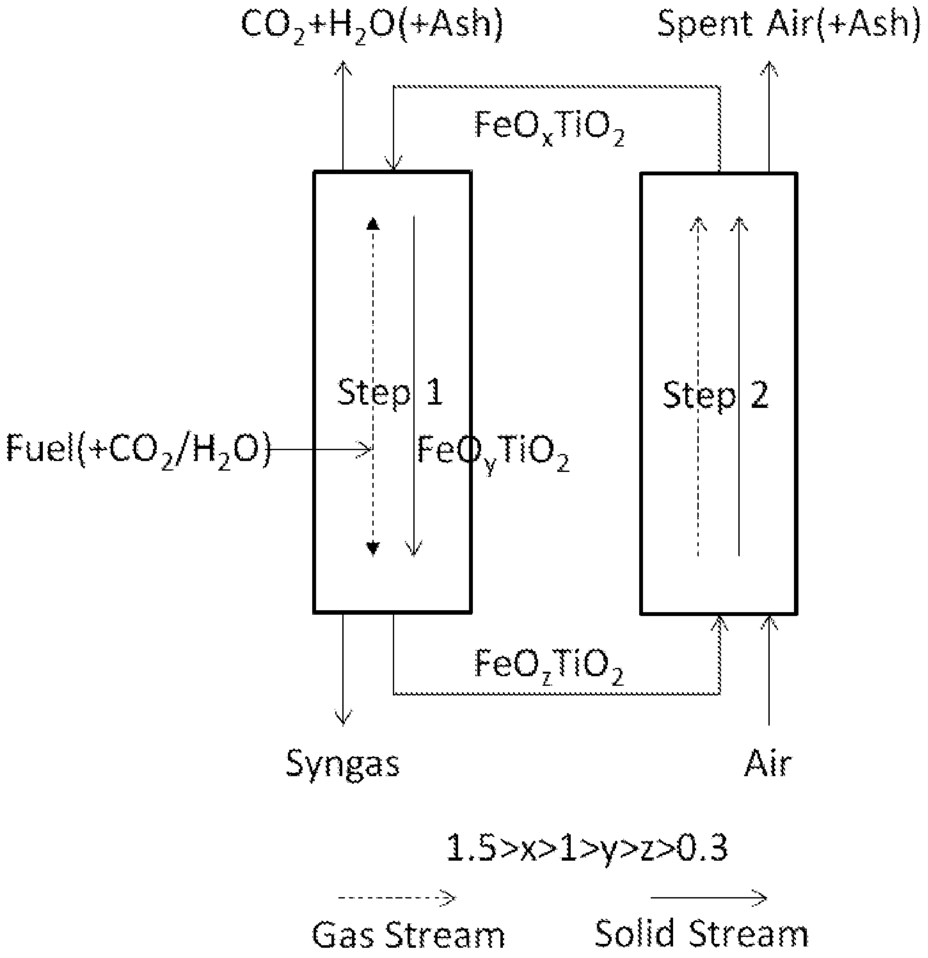

CO_2+H_2O(+Ash)
Spent Air(+Ash)
FeO_xTiO_2
Step 1
Step 2
Fuel(+CO_2/H_2O)
FeO_yTiO_2
FeO_zTiO_2
Syngas
Air
1.5>x>1>y>z>0.3
Gas Stream
Solid Stream

FIG. 8

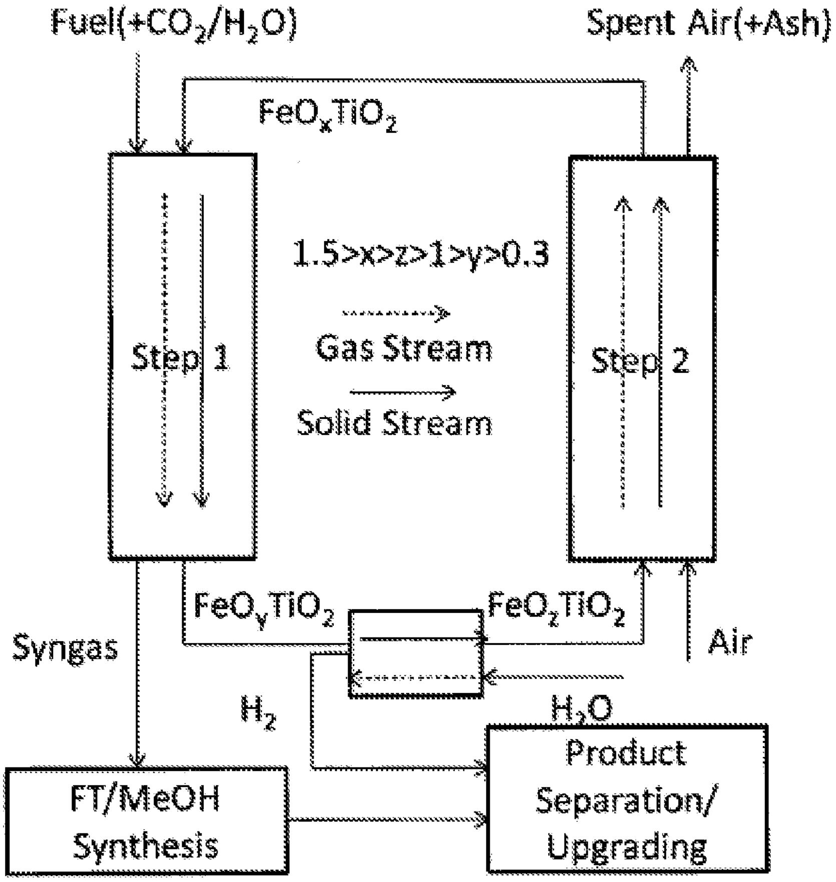

Fuel(+CO_2/H_2O)
Spent Air(+Ash)
FeO_xTiO_2
1.5>x>z>1>y>0.3
Gas Stream
Solid Stream
Step 1
Step 2
Syngas
FeO_yTiO_2
FeO_zTiO_2
Air
H_2
H_2O
FT/MeOH Synthesis
Product Separation/ Upgrading

FIG. 9

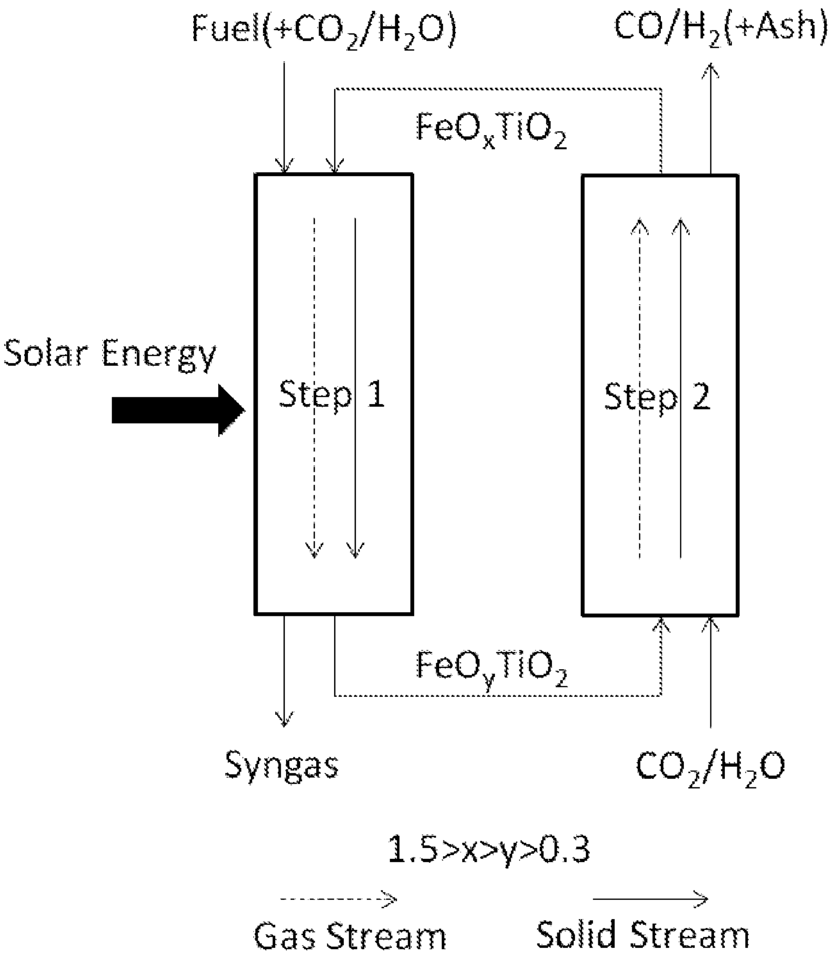

Fuel(+CO_2/H_2O)
CO/H_2(+Ash)
FeO_xTiO_2
Solar Energy
Step 1
Step 2
FeO_yTiO_2
Syngas
CO_2/H_2O
1.5>x>y>0.3
Gas Stream
Solid Stream

FIG. 10

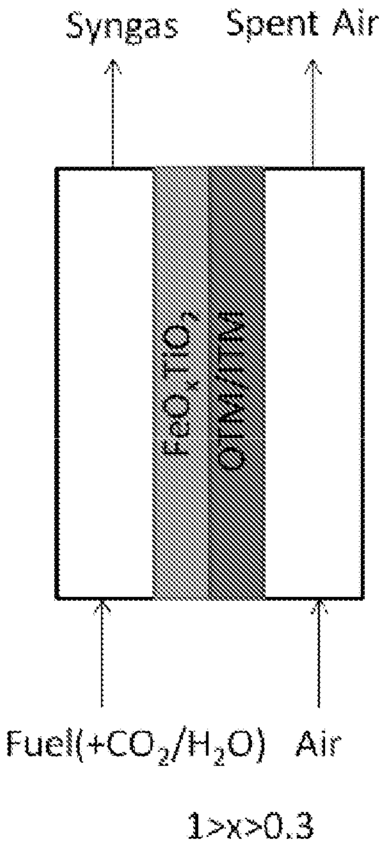


FIG. 11

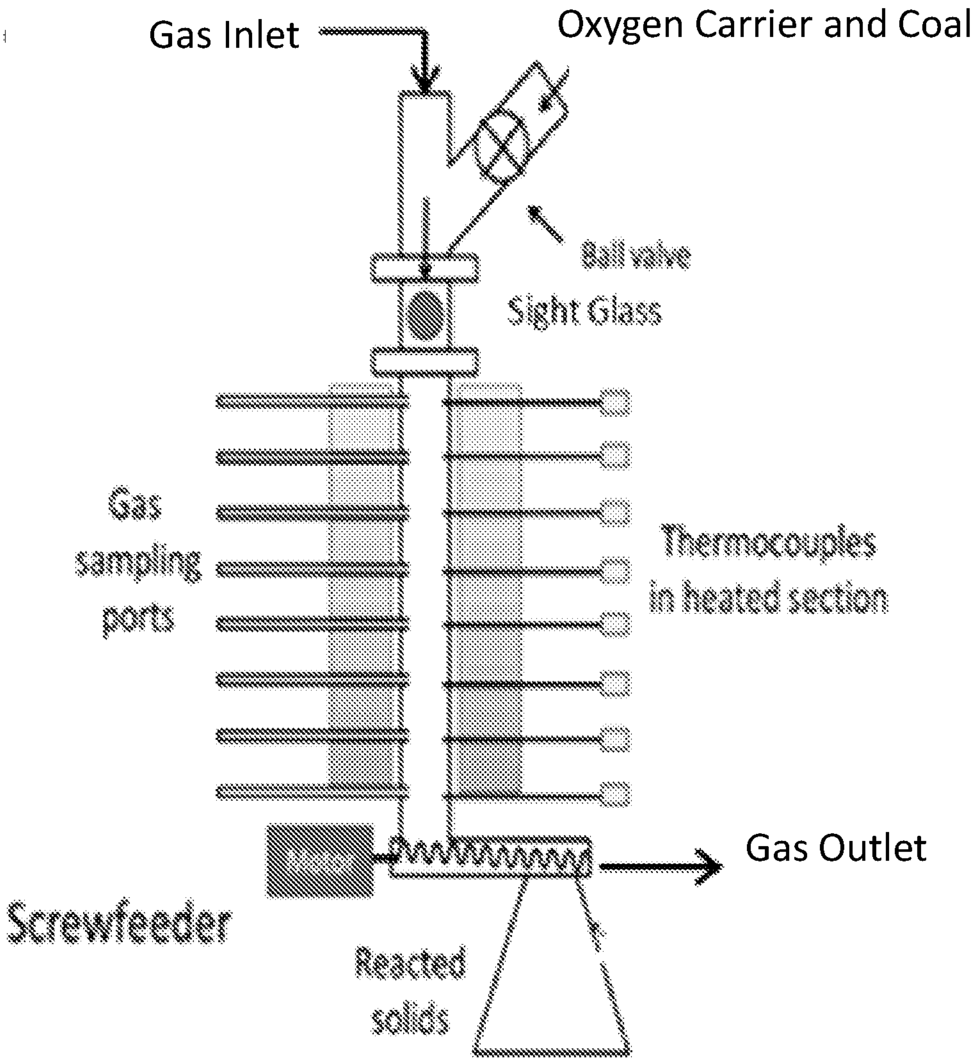

Gas Inlet
Oxygen Carrier and Coal
Ball valve
Sight Glass
Gas sampling ports
Thermocouples in heated section
Gas Outlet
Screwfeeder
Reacted solids

FIG. 12

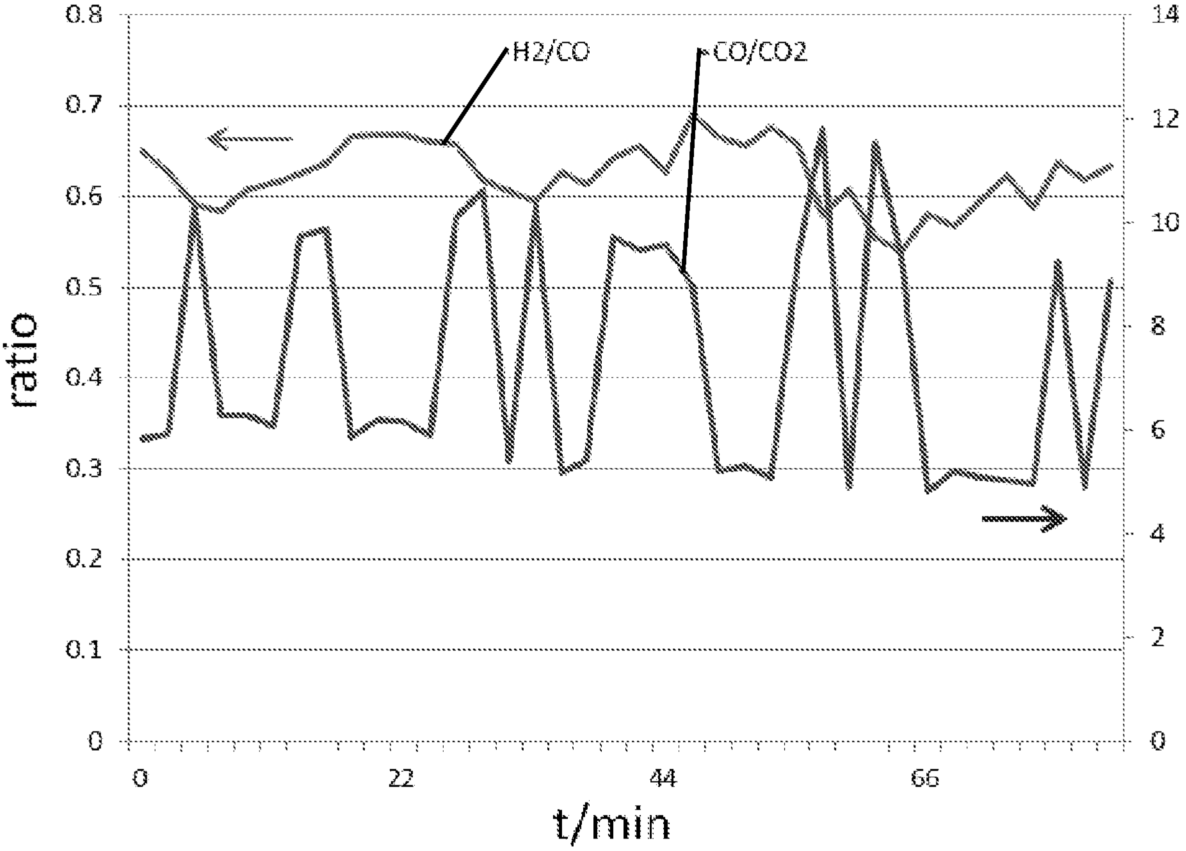

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ratio
14
12
10
8
6
4
2
0
H2/CO
CO/CO2
0
22
44
66
t/min

FIG. 13

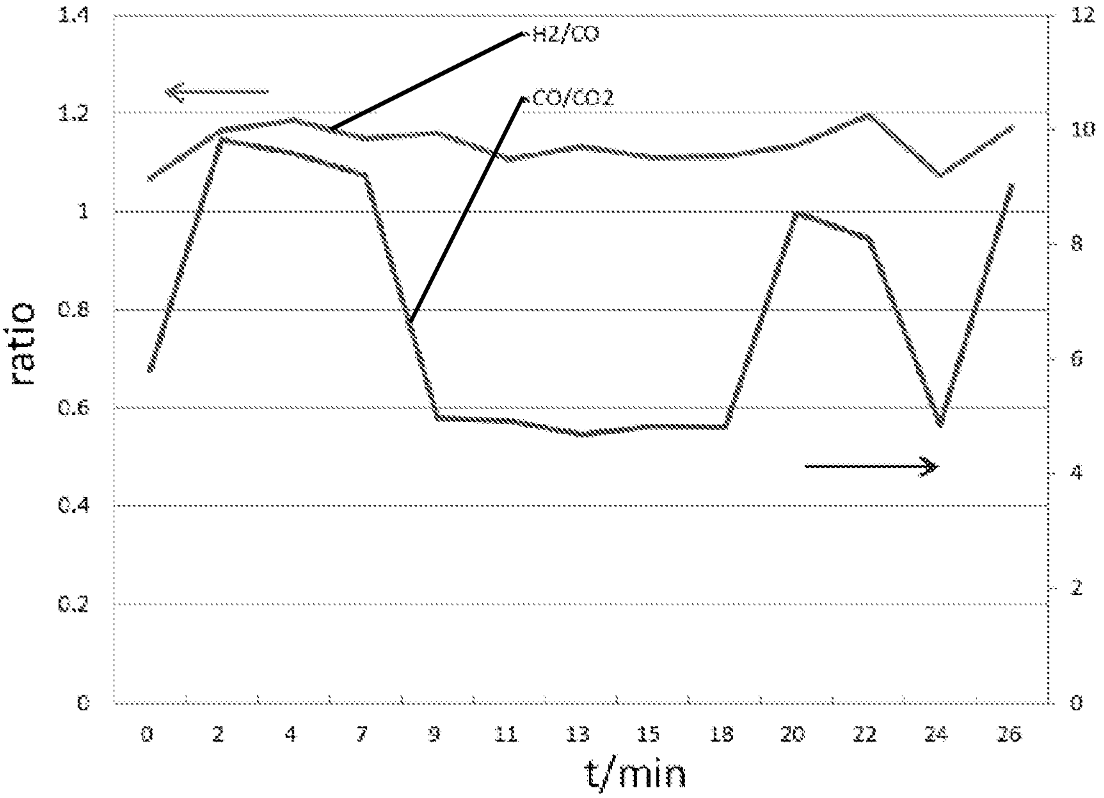

H2/CO
CO/CO2
ratio
t/min
1.4
1.2
1
0.8
0.6
0.4
0.2
0
12
10
8
6
4
2
0
0
2
4
7
9
11
13
15
18
20
22
24
26

FIG. 14

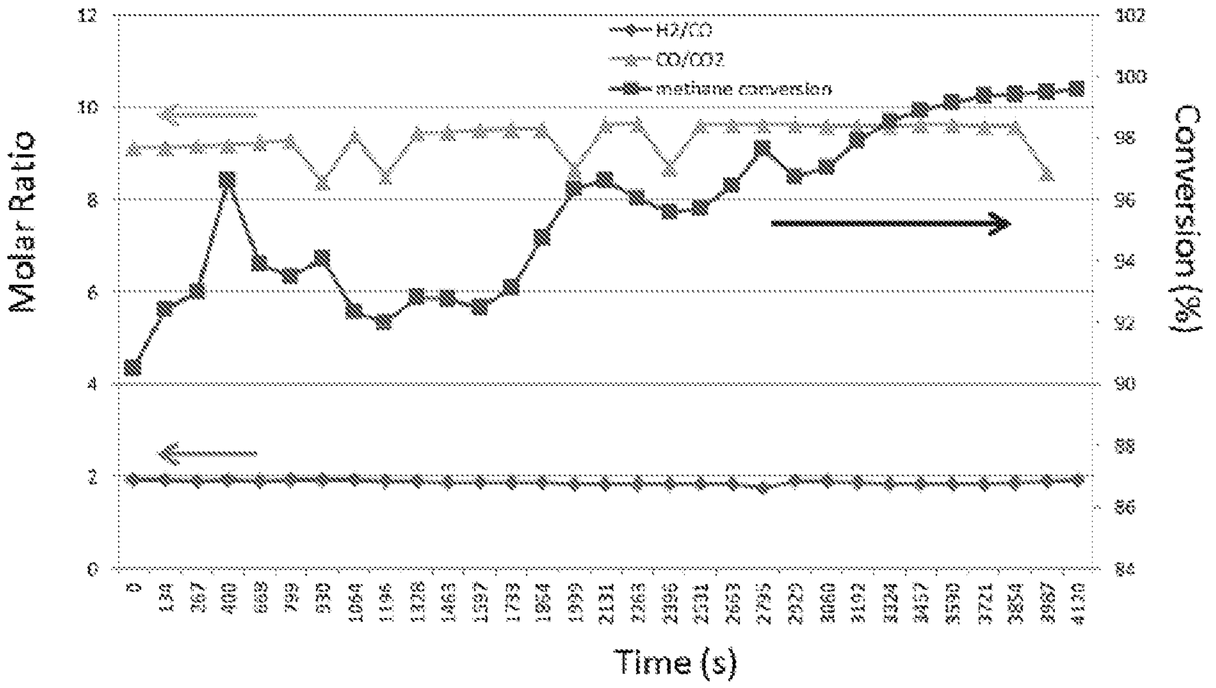

H2/CO
CO/CO2
methane conversion
Molar Ratio
Conversion (%)
Time (s)
0
2
4
6
8
10
12
86
86
88
90
92
94
96
98
100
102
0
134
267
400
668
799
930
1064
1196
1328
1463
1597
1733
1864
1999
2131
2263
2396
2531
2663
2795
2928
3060
3192
3324
3457
3590
3721
3854
3987
4130

FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US14/14877

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C01B 3/00, 3/02, 3/22, 3/26, 3/28, 3/32; B01J 8/00, 8/08, 19/18 (2014.01)
USPC - 423/651, 656, 657; 422/211, 213; 48/127.9, 198.1, 198.5, 198.7
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)
IPC(8): C01B 3/00, 3/02, 3/22, 3/26, 3/28, 3/32; B01J 8/00, 8/08, 19/18 (2014.01)
USPC: 423/651, 656, 657; 422/211, 213; 48/127.9, 198.1, 198.5, 198.7

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)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; IP.com; Google/Google Scholar; Key Words: syngas, synthesis gas, fuel, natural gas, methane, CH4, reactor*, reduc*, oxida*, catalyst, metal oxide*, composite, iron oxide, Fe2O3, FeO, Fe3O4, titania, titanium oxide, TiO2, regenerat*, recycl*, hydrogen, H2, carbon monoxide, CO, steam, H2O

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2009/0000194 A1 (FAN, LS et al.) 01 January 2009; abstract; paragraphs [0006], [0039]-[0041], [0050], [0059], [0066], [0072]; claims 1, 3, 5, 9-10, 13, 22, 36	22 ---- 1-21, 23-25
Y	WO 2012/064712 A1 (FAN, LS et al.) 18 May 2012; page 7, lines 2-4	1-21
Y	US 2011/0291051 A1 (HERSHKOWITZ, F et al.) 01 December 2011; abstract; paragraph [0018]	23
Y	US 7,244,399 B2 (MYOHANEN, K et al.) 17 July 2007; abstract; column 7, lines 5-7	24
Y	US 2007/0157517 A1 (TSAY, D et al.) 12 July 2007; abstract; figure 2A; claim 7	25
Y	US 4,272,399 A (DAVIS, GD et al.) 09 June 1981; example 5	12-13
Y	US 2004/0265224 A1 (PAPAVASSILIOU, V et al.) 30 December 2004; abstract; paragraph [0047]	20
Y	US 2010/0258429 A1 (UGOLIN, N) 14 October 2010; abstract	20
A	US 5,447,024 A (ISHIDA, M et al.) 05 September 1995; entire document	1-25
A	US 7,767,191 B2 (THOMAS, TJ et al.) 03 August 2010; entire document	1-25
A	US 2011/0303875 A1 (HOTEIT, A et al.) 15 December 2011; entire document	1-25

☐ Further documents are listed in the continuation of Box C. ☐

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

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

Date of the actual completion of the international search 30 April 2014 (30.04.2014)	Date of mailing of the international search report 14 MAY 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774