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(54) Title: CONTINUOUS UTILIZATION OF INDUSTRIAL FLUE GAS EFFLUENT FOR THE THERMOCHEMICAL REFORMING OF METHANE

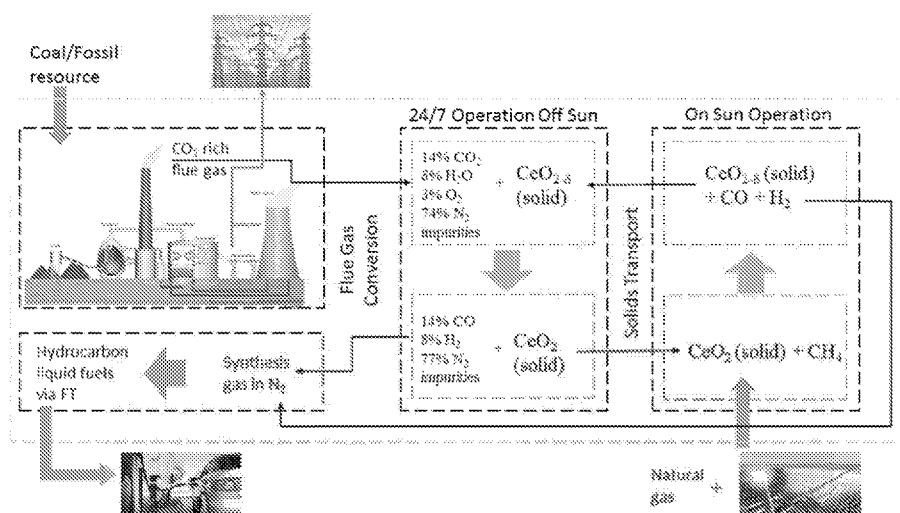


FIG. 1

(57) Abstract: Methods and systems of the present disclosure can function to capture flue gas and convert the flue gas to a synthesis gas, which can be further processed to other components such as liquid fuels. Aspects of the present disclosure provide for a process designed to capture flue gas from large scale (i.e. ~GW), fossil based power plants in a 24/7 continuous operation. In addition, the method and system can convert the flue gas to a synthesis gas (mainly carbon monoxide and hydrogen), which will be processed into high quality liquid fuels, like diesel.



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
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CONTINUOUS UTILIZATION OF INDUSTRIAL FLUE GAS EFFLUENT FOR THE THERMOCHEMICAL REFORMING OF METHANE

CLAIM OF PRIORITY TO RELATED APPLICATION

This application claims priority to co-pending U.S. provisional application entitled “Continuous utilization of industrial flue gas effluent for the thermochemical reforming of methane” having Serial No.: 62/760,487 filed on November 13, 2018, and also this application claims priority to co-pending U.S. provisional application entitled “Continuous utilization of industrial flue gas effluent for the thermochemical reforming of methane” having Serial No.: 62/797,630, filed on January 28, 2019, both of which are entirely incorporated herein by reference.

BACKGROUND

Global increases in natural gas reserves coupled with increasing liquid fuel prices have supported the emergence of methane-driven, gas-to-liquids (GTL) technologies. These processes typically utilize either CO₂ or H₂O as feedstocks, both of which are found in flue gases from fossil fuel power plants. Utilizing industrial flue gases to produce liquid fuels may be a financially achievable while also reducing harmful gases emitted.

SUMMARY

Methods and systems of the present disclosure can function to capture flue gas and convert the flue gas to a synthesis gas, which can be further processed to other components such as liquid fuels.

The present disclosure provides for a method of continuously processing flue gas, comprising: a) introducing a flue gas comprising CO₂ to a material selected from a solid metal or an oxygen deficient metal oxide; b) forming a first gas mixture comprising CO by the reduction reaction of the flue gas with the material, wherein the material is oxidized to form an oxidized solid material; c) separating the first gas mixture from the oxidized solid material; d) introducing the oxidized solid material to a reducing environment; e) forming a second gas mixture by reducing the oxidized solid material to form the material selected from the solid metal or the oxygen deficient metal oxide; f) separating the second gas mixture from the reduced material; and g) go to step a).

The present disclosure provides for a system for processing flue gas, comprising: a first reactor comprising a flue gas and a material selected from a solid metal or an oxygen-deficient metal oxide, wherein the flue gas comprises CO₂, wherein the first reactor is configured to form a first mixture comprising CO by the oxidation reaction of the flue gas with the material, wherein the material is

oxidized to form an oxidized solid; a first transport apparatus to move the oxidized solid oxide to a second reactor, wherein the first reactor and the second reactor are separate reactors; the second reactor comprises the oxidized solid oxide, wherein the second reactor is configured to reduce the oxidized solid oxide to the material and to form a second mixture comprising either CO and H₂, O₂ or O₂ mixed with inert gas; and a second transport apparatus to move the material to the first reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, with emphasis instead being placed upon clearly illustrating the principles of the disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

Figure 1 illustrates a schematic for flue gas utilization coupled with solar driven methane reforming. Flue gases are converted to synthesis gases which are the precursors to fungible liquid fuels. A distinction of this process is the decoupling of the solar utilization (far right) and flue gas utilization (middle); this enables 24/7 utilization of the flue gases and eliminates any storage requirements.

Figure 2 (top) illustrates a schematic of solar reactor utilized for the partial oxidation of methane to synthesis gas over ceria. Particles were fed with gravity, reacted with CH₄ in the hot zone, and finally collected in a hopper at the exit following their reduction. Figure 2 (bottom) illustrates the ceria mass flow rate average $\dot{m}_{\text{CeO}_2} = 0.13 \text{ g s}^{-1}$ (left axis), and CH₄ inlet/outlet, H₂, CO, and CO₂ molar flow rates (right axis) as a function of time during a representative experimental run. The subscript 0 indicates the inlet condition. Experimental conditions: $T_{\text{tube}} = 1302 \text{ }^{\circ}\text{C}$, $\delta_{\text{final}} = 0.16$, $\dot{V}_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1}$, co-current flow configuration.

Figure 3 illustrates the continuous syngas production for over 60 min with stable outlet gas composition. Experimental conditions: $T_{\text{tube}} = 1291 \text{ }^{\circ}\text{C}$, $\delta = 0.15$, $\dot{V}_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1}$, $x_{\text{CH}_4,0} = 0.1$, mean $\dot{m}_{\text{CeO}_2} = 0.15 \text{ g s}^{-1}$ ($\dot{n}_{\text{CeO}_2} = 53.7 \text{ mmol min}^{-1}$), co-current flow configuration.

Figure 4 (top) illustrates the evolution of the mean reduction extent, δ_{av} , over the first 8 cycles. Error bars correspond to 95% confidence intervals. Experimental conditions: $\dot{m}_{\text{CeO}_2} = 50$ and 120 mg s^{-1} , $\dot{V}_{\text{Ar}} = 0.5 \text{ L min}^{-1}$, $p_{\text{O}_2, \text{baseline}} < 5 \times 10^{-5} \text{ atm}$, $T_1 = 1873 \text{ K}$. Figure 4 (bottom) illustrates the agglomerate sizes obtained from corresponding primary particle size distributions obtained by laser scattering for cycles 1, 3, 5, and 7.

Figure 5 illustrates a schematic of tubular reactor developed to study heterogeneous reaction kinetics with CO₂/O₂/H₂O.

Figure 6 illustrates exemplary experimental data in which the oxidation state of a ceria sample was cycled by shifting the pO_2 via step changes in the input H_2O flow rate. (a) Reactor temperature versus time elapsed. (b) Input H_2 molar flow rate (left vertical axis) and input H_2O molar flow rate (right vertical axis) versus time elapsed. (c) H_2 molar flow rate in the reactor effluent, as measured by the mass spectrometer, versus time elapsed.

Figure 7 illustrates the theoretical $\eta_{\text{solar-to-fuel}}$ as a function of increasing reduction temperature T_{red} and different cooling temperatures T_{cool} . The dashed lines indicate perfect solid-phase heat recuperation; gas-phase heat recuperation was not considered. The conditions for each considered scenario are as follows: $T_{\text{ox}} = 625\text{ }^{\circ}\text{C}$, $n_{i,\text{CH}_4} = 0.5\text{ mol}_{\text{CH}_4}\text{ mol}_{\text{CeO}_2}^{-1}$, $n_{i,\text{CO}_2} = 3\text{ mol}_{\text{CO}_2}\text{ mol}_{\text{CeO}_2}^{-1}$, and $p_{\text{system}} = 1\text{ bar}$.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

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. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, inorganic chemistry, material science, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in atmosphere. Standard temperature and pressure are defined as 25 °C and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Discussion

Methods and systems of the present disclosure can function to capture flue gas and convert the flue gas to a synthesis gas, which can be further processed to other components such as liquid fuels. Aspects of the present disclosure provide for a process designed to capture flue gas from large scale (*i.e.* ~ GW), fossil based power plants in a 24/7 continuous operation. In addition, the methods and systems can convert the flue gas to a synthesis gas (mainly carbon monoxide and hydrogen), which will be processed into high quality liquid fuels, like diesel.

In an aspect, an integrated process where natural gas and/or solar energy (*e.g.* and/or other energy source such as an alternative energy source such as hydroelectric, wind, geothermal, and the like that can produce thermal energy) is used to reduce a material (*e.g.*, a solid metal or an oxygen deficient metal oxide) that has a reaction enthalpy (Δh_{rxn}) greater than the magnitude of formation enthalpies of H₂O ($\Delta h_{\text{f,H}_2\text{O}}$) and CO₂ ($\Delta h_{\text{f,CO}_2}$). The material can be comprised of a transition metal (*e.g.*, or an oxide, alloy

thereof, and the like), lanthanide material (e.g., or an oxide, allow thereof, and the like), for example a cerium based material (e.g., CeO₂-based material), or a combination thereof.

Now having described the present disclosure in general, additional details will be described and then specific examples are provided. The method can include continuously processing flue gas, for example in a large scale fossil fuel power plant or other industrial process that consumes fossil fuels. The method can be a continuous cycle or nearly (e.g., minor interruptions of the cycle) continuous cycle or in a cycle that is not continuous. The method can be used in a non-cyclical manner. Figure 1 in example 1 illustrates an embodiment of the cycle.

A starting point for the cycle is when a flue gas comprising CO₂ is introduced to a material, where the material can be a solid metal or an oxygen deficient metal oxide. The flue gas and the material can be mixed at a pressure of about 1 atm to 50 atm (e.g., about 1 atm to 10 atm, about 1 atm to 20 atm, about 10 atm to 20 atm, about 10 atm to 30 atm, about 30 atm to 50 atm, about 40 atm to 50 atm, about 1 atm to 5 atm about 1 atm to 2 atm, and the like), at a temperature of about ambient to about 1400° C (about 25° C to 500° C, about 25° C to 200° C, about 500° C to 1400° C, about 700° C to 1400° C, about 500° C to 1000° C, about 1000° C to 1400° C, and the like), and/or for a time period of about a minute to 24 hours (e.g. about 1 hour to 6 hours, about 1 hour to 12 hours, about 6 hours to 12 hours, about 6 hours to 18 hours, about 12 hours to 18 hours, about 18 hours to 24 hours, and the like). After a time period, a first gas mixture comprising (or consisting of or alternatively consisting essentially of (e.g., the mixture include trace amounts of other gases or particles that do not detract in a material way from the method)) CO is formed by the reduction reaction of the flue gas with the material, where the material is oxidized to form an oxidized solid material. Next, the first gas mixture and the oxidized solid material are separated. Subsequently, the oxidized solid material is introduced to a reducing environment and a second gas mixture is formed by reducing the oxidized solid material to form the material (e.g., the solid metal or the oxygen deficient metal oxide). The second gas mixture is then separated from the reduced material and the entire process is repeated.

Specifically, the method includes: a) introducing a flue gas comprising CO₂ to a material selected from a solid metal or an oxygen deficient metal oxide; b) forming a first gas mixture comprising (e.g., consisting of or consisting essentially of) CO by the reduction reaction of the flue gas with the material, where the material is oxidized to form an oxidized solid material; c) separating the first gas mixture from the oxidized solid material; d) introducing the oxidized solid material to a reducing environment; e) forming a second gas mixture by reducing the oxidized solid material to form the material selected from the solid metal or the oxygen deficient metal oxide; f) separating the second gas mixture from the reduced material; and g) repeat step a)-e) for the time frame desired.

The reduction in the method includes using a heat source at sufficiently high temperature and/or sufficiently low partial pressure of oxygen (pO_2). The heat source can be solar radiation or another source that producing a high temperature of about 500 to 1600 °C.

The low pO_2 can be achieved via vacuum pumping, rendering O_2 as or part of the second gas mixture. In another aspect, the low pO_2 can be achieved via inert gas, rendering O_2 and inert gas as or part of the second gas mixture. In yet another aspect, the low pO_2 can be achieved via a fuel source, rendering CO and H_2 as or part of the second gas mixture. In still another aspect, the low pO_2 is achieved via a fuel mixture containing methane, rendering CO and H_2 as or part of the second gas mixture. Also, a combination of each of these can be used to achieve the low pO_2 .

In an embodiment, the material can have a partial molar enthalpy (Δh_o), or enthalpy of reaction with gaseous O_2 that is greater than the magnitude of formation enthalpies of H_2O ($\Delta h_{f,H_2O}$) and CO_2 ($\Delta h_{f,CO_2}$). In general, the material can be a transition metal, a lanthanide material, or a combination thereof or an oxide thereof. In particular, the solid oxide can be $M(1)O_{2-\delta}$ and δ is MO_2 nonstoichiometry, where $0 < \delta \leq 0.5$. In an aspect, the solid oxide can be $M(1)_xM(2)_{1-x}O_{2-\delta}$ and δ is MO_2 nonstoichiometry, where x ranges from 0 to 0.5, and where $0 < \delta \leq 0.5$. In each instance above and as appropriate for the formula, M(1) can be Ce and M(2) can be Zr, Hf, or a combination thereof. In another aspect, the solid oxide can be $M(3)_xCe_{1-x}O_{2-\delta}$, where x ranges from 0 to 0.5, and δ is CeO_2 nonstoichiometry, where $0 < \delta \leq 0.5$. M(3) can be a transition metal or a combination thereof and can specifically be selected from La, Mn, Cr, Al, Sr, Co, Fe, or a combination thereof.

In an embodiment, steps b) and e) are conducted in separate reactors, where b) is conducted in a fluidized bed reactor and step e) is conducted in a solar drop-tube reactor (Scheffe, Jonathan R., Michael Welte, and Aldo Steinfeld. "Thermal reduction of ceria within an aerosol reactor for H_2O and CO_2 splitting." *Industrial & Engineering Chemistry Research* 53.6 (2014): 2175-2182, Welte, Michael, et al. "Experimental demonstration of the thermochemical reduction of ceria in a solar aerosol reactor." *Industrial & engineering chemistry research* 55.40 (2016): 10618-10625, Welte, Michael, et al. "Combined ceria reduction and methane reforming in a solar-driven particle-transport reactor." *Industrial & engineering chemistry research* 56.37 (2017): 10300-10308), each of which are incorporated for in their entirety as it pertains to bed reactors and solar drop-tube reactors.).

In an aspect, the first gas mixture and the second gas mixture are combined to form a third gas mixture. The first, second, or third gas mixture can each be further processed to form a hydrocarbon liquid fuel. The method can further include the step of processing the third mixture to form a hydrocarbon liquid fuel.

In a particular aspect, during on-sun (or other alternative energy source) operation and/or using natural gas, the thermal energy captured or generated can be used to reduce the ceria particles in a reactor (e.g., drop-tube reactor), which has been demonstrated on a 10 kW scale. Because particles are used, they may be collected, stored and later transported to a secondary reactor (e.g. fluidized bed) that is decoupled from the solar reactor and/or natural gas reactor (e.g., and/or other alternative energy source). There, particles will be reoxidized with flue gas components (CO_2 , H_2O , O_2) to selectively generate the synthesis gas. Additional synthesis gas is generated from the reaction between the natural gas and the ceria particles. After reoxidation the ceria particles are returned to the solar reactor to begin the cycle again.

The present disclosure also includes a system for processing flue gas. The system can include a first reactor including the flue gas and the material. The flue gas can include CO_2 . The first reactor can be configured to form a first mixture including CO by the oxidation reaction of the flue gas with the material. The first reactor can operate at a pressure of 1 atm to 50 atm, a temperature of ambient to 1600 °C, and/or for a time frame of up to 24 hours. The material can be oxidized to form an oxidized solid in the first reactor. The system can include a first transport apparatus to move the oxidized solid oxide to a second reactor, where the first reactor and the second reactor are separate reactors. The first transport apparatus can include an elevator hopper, transporting fluidized bed, etc. The system also includes the second reactor that includes the oxidized solid oxide, where the second reactor is configured to reduce the oxidized solid oxide to the material and to form a second mixture including either CO and H_2 , O_2 or O_2 mixed with inert gas. The system can also include a second transport apparatus (optionally the first and second transport apparatus are the same) to move the material to the first reactor. The second transport apparatus can include an elevator hopper, transporting fluidized bed, etc. The second reactor can operate at a pressure of vacuum (10^{-7} atm) to 1 atm, a temperature of 600 to 1800 °C, and/or for a time frame of up to 8 hours.

Optionally and in addition, the system can include a third reactor that is in gaseous communication (e.g., tubing, pumps, and the like) with the first reactor, the second reactor, or both. The third reactor is configured to receive the first mixture, the second mixture, or both.

In an aspect, the first reactor can be a fluidized bed reactor (Milanese, Marco, et al. "Multi-parameter optimization of double-loop fluidized bed solar reactor for thermochemical fuel production." Energy 134 (2017): 919-932, Bellan, Selvan, et al. "Heat transfer and particulate flow analysis of a 30 kW directly irradiated solar fluidized bed reactor for thermochemical cycling." Chemical Engineering Science (2018).), trickle bed reactor (Kruesi, Michael, et al. "Analysis of solar-driven gasification of biochar trickling through an interconnected porous structure." AIChE Journal 61.3 (2015): 867-879.), moving bed reactor (Henley, John P., et al. "Moving bed process for carbothermally synthesizing non-oxide ceramic

powders." U.S. Patent No. 5,607,297. 4 Mar. 1997.) or conveyor type reactor (Biswas, Akash, and Anthony H. McDaniel. High Efficiency Solar Thermochemical Reactor for Hydrogen Production. No. SAND2016-7117D. Sandia National Lab.(SNL-CA), Livermore, CA (United States), 2016.), each of which is incorporated in its entirety as it pertains to bed reactors.

In an aspect, the second reactor can be a solar drop-tube reactor (Scheffé, Jonathan R., Michael Welte, and Aldo Steinfeld. "Thermal reduction of ceria within an aerosol reactor for H₂O and CO₂ splitting." *Industrial & Engineering Chemistry Research* 53.6 (2014): 2175-2182, Welte, Michael, et al. "Experimental demonstration of the thermochemical reduction of ceria in a solar aerosol reactor." *Industrial & engineering chemistry research* 55.40 (2016): 10618-10625, Welte, Michael, et al. "Combined ceria reduction and methane reforming in a solar-driven particle-transport reactor." *Industrial & engineering chemistry research* 56.37 (2017): 10300-10308), a fluidized bed reactor (Milanese, Marco, et al. "Multi-parameter optimization of double-loop fluidized bed solar reactor for thermochemical fuel production." *Energy* 134 (2017): 919-932, Bellan, Selvan, et al. "Heat transfer and particulate flow analysis of a 30 kW directly irradiated solar fluidized bed reactor for thermochemical cycling." *Chemical Engineering Science* (2018).), trickle bed reactor (Kruesi, Michael, et al. "Analysis of solar-driven gasification of biochar trickling through an interconnected porous structure." *AIChE Journal* 61.3 (2015): 867-879.), moving bed reactor (Henley, John P., et al. "Moving bed process for carbothermally synthesizing nonoxide ceramic powders." U.S. Patent No. 5,607,297. 4 Mar. 1997.) or conveyor type reactor (Biswas, Akash, and Anthony H. McDaniel. High Efficiency Solar Thermochemical Reactor for Hydrogen Production. No. SAND2016-7117D. Sandia National Lab.(SNL-CA), Livermore, CA (United States), 2016.), each of which is incorporated in its entirety as it pertains solar drop-tube reactors.

The following clauses provide additional description of embodiments of the present disclosure.

Clause 1. A method of continuously processing flue gas, comprising (or consisting of or consisting essentially of):

- a) introducing a flue gas comprising CO₂ to a material selected from a solid metal or an oxygen deficient metal oxide;
- b) forming a first gas mixture comprising CO by the reduction reaction of the flue gas with the material, wherein the material is oxidized to form an oxidized solid material;
- c) separating the first gas mixture from the oxidized solid material;
- d) introducing the oxidized solid material to a reducing environment;
- e) forming a second gas mixture by reducing the oxidized solid material to form the material selected from the solid metal or the oxygen deficient metal oxide;
- f) separating the second gas mixture from the reduced material; and

g) go to step a).

Clause 2. The method of claim 1, wherein reduction includes using a heat source at sufficiently high temperature and sufficiently low partial pressure of oxygen (pO_2).

Clause 3. The method of claim 2, wherein the heat source is solar radiation.

Clause 4. The method of claim 2, wherein the low pO_2 is achieved via vacuum pumping, rendering the second gas mixture as comprising (or consisting of or consisting essentially of) O_2 .

Clause 5. The method of claim 2, wherein the low pO_2 is achieved via an inert gas, rendering the second gas mixture comprising (or consisting of or consisting essentially of) O_2 and the inert gas.

Clause 6. The method of claim 2, wherein the low pO_2 is achieved via a fuel source, rendering second gas mixture as comprising (or consisting of or consisting essentially of) CO and H_2 .

Clause 7. The method of claim 2, wherein the low pO_2 is achieved via a fuel mixture containing methane, rendering the second gas mixture as comprising (or consisting of or consisting essentially of) CO and H_2 .

Clause 8. The method of any of the preceding clauses, wherein the material has partial molar enthalpy (Δh_o), or enthalpy of reaction with gaseous O_2 that is greater than the magnitude of formation enthalpies of H_2O ($\Delta h_{f,H_2O}$) and CO_2 ($\Delta h_{f,CO_2}$).

Clause 9. The method of any of the preceding clauses, wherein the solid oxide is $M(1)O_{2-\delta}$ and δ is MO_2 nonstoichiometry, wherein $0 < \delta \leq 0.5$.

Clause 10. The method of claim 9, wherein $M(1)$ is Ce.

Clause 11. The method of any of the preceding clauses, wherein the solid oxide is $M(1)_xM(2)_{1-x}O_{2-\delta}$ and δ is MO_2 nonstoichiometry, wherein x ranges from 0 to 0.5, wherein $0 < \delta \leq 2$.

Clause 12. The method of claim 11, wherein $M(1)$ is Ce and $M(2)$ is Zr, Hf or a combination thereof.

Clause 13. The method of any of the preceding clauses, wherein the solid oxide is $M(3)_xCe_{1-x}O_{2-\delta}$, wherein x ranges from 0 to 0.5, and δ is CeO_2 nonstoichiometry, wherein $0 < \delta \leq 2$.

Clause 14. The method of claim 13, wherein $M(3)$ is a transition metal or a combination thereof.

Clause 15. The method of claim 13, wherein the $M(3)$ is selected from La, Mn, Cr, Al, Sr, Co, Fe, or a combination thereof.

Clause 16. The method of any of the preceding clauses, wherein the material is selected from a transition metal, lanthanide material, or a combination thereof.

Clause 17. The method of any of the preceding clauses, wherein steps b) and e) are conducted in separate reactors.

Clause 18. The method of claim 17, wherein step b) is conducted in a fluidized bed reactor.

Clause 19. The method of claim 17, wherein step e) is conducted in a solar drop-tube reactor.

Clause 20. The method of any of the preceding clauses, wherein the first gas mixture and the second gas mixture are combined to form a third gas mixture.

Clause 21. The method of any of the preceding clauses, wherein the first, second or third gas mixture is further processed to form a hydrocarbon liquid fuel.

Clause 22. The method of claim 11, further comprising: processing the third mixture to form a hydrocarbon liquid fuel.

Clause 23. A system for processing flue gas, comprising (or consisting of or consisting essentially of):

a first reactor comprising a flue gas and a material selected from a solid metal or an oxygen-deficient metal oxide, wherein the flue gas comprises CO₂, wherein the first reactor is configured to form a first mixture comprising CO by the oxidation reaction of the flue gas with the material, wherein the material is oxidized to form an oxidized solid;

a first transport apparatus to move the oxidized solid oxide to a second reactor, wherein the first reactor and the second reactor are separate reactors;

the second reactor comprises the oxidized solid oxide, wherein the second reactor is configured to reduce the oxidized solid oxide to the material and to form a second mixture comprising either CO and H₂, O₂ or O₂ mixed with inert gas; and

a second transport apparatus to move the material to the first reactor.

Clause 24. The system of claim 23, further comprising: a third reactor in gaseous communication with the first reactor, the second reactor, or both, wherein the third reactor is configured to receive the first mixture, the second mixture, or both.

Clause 25. The system of any of the preceding clauses, wherein first reactor is a fluidized bed reactor.

Clause 26. The system of any of the preceding clauses, wherein second reactor is a solar drop-tube reactor.

Clause 267. The system of any of the preceding clauses, wherein the material is described in clauses 9 to 16.

Clause 28. The system of any of the preceding clauses, wherein the system is configured to operate under the conditions provided for in clauses 2 to 8.

EXAMPLES

Now having described the embodiments of the disclosure, in general, the examples describe some additional embodiments. While embodiments of the present disclosure are described in connection with

the example and the corresponding text and figures, there is no intent to limit embodiments of the disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1

This example aims to develop technology capable of utilizing flue gas from large scale (i.e. ~ GW), fossil based power plants¹, to produce synthesis gas, a precursor to drop-in liquid fuels. We propose to do this via integration with a methane reformation driven redox cycle powered by solar energy, where the solar step and flue gas utilization step are separated in both space and time. This is vitally important for 24/7 operation and utilization of flue gas because at the industrial scales at which it is generated, storage is not a viable option.

A schematic of the process is shown in Figure 1. The on-sun, endothermic step of this process (far right side) is the partial oxidation of methane over ceria based particles in a drop-tube reactor, like we have demonstrated prior at the 10 kW scale². Because particles are used, they may be collected and transported to a secondary reactor (e.g. fluidized bed) that is decoupled from the solar reactor. There, they will be oxidized in an exothermic reaction with flue gas components (CO_2 , H_2O , O_2) to selectively generate CO/H_2 in N_2 (and heat to drive the process) and then returned to the solar reforming reactor to begin the cycle again. At the same time this process affords the economical utilization and transformation of solar energy and methane or natural gas to a valuable synthesis gas that can be further converted to a high quality, drop-in, diesel fuel and other added value chemicals that can be stored and transported.

Industrial syngas production through these means is primarily governed by two objectives: high methane conversion and appropriate product composition.⁵ Today, catalytic steam methane reforming (SMR) is the most prominent technique and is characterized by the endothermic conversion over metal (generally nickel-based) catalysts. To increase CO selectivity and enforce appropriate H_2/CO ratios for Fischer-Tropsch synthesis (FTS), researchers have also investigated the dry reformation of methane (DRM), which leverages sequestered CO_2 and CH_4 to produce syngas. Application is limited in practice however, due to a highly negative thermodynamic potential for coke formation and simultaneous presence of H_2 and CO_2 in the product stream leading, by the reverse water-gas shift reaction, to product recombination.⁶ Since SMR and DMR are endothermic, current industrial practices generally supply the required process heat through combusting a portion of the methane feedstock. In the partial oxidation of methane (POM), CH_4 is exposed to a less than stoichiometric amount of O_2 that inhibits complete combustion to H_2O and CO_2 .⁷ Although syngas ratios are sufficient for FTS, disadvantages associated with conventional POM include a significant cost for pure O_2 from air separation⁸, safety concerns with

co-feeding CH_4 and O_2 under explosive conditions⁹, and catalyst deactivation through carbon deposition and/or temperature degradation¹⁰. These concerns, however, have not deterred recent commercialization of this technology (i.e., conventional POM coupled with FTS).

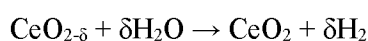
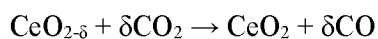
Noting the prominence of GTL technologies in industrial fuel production, development of more sustainable approaches towards syngas production has motivated several research endeavors.¹¹⁻¹³ Sunlight, once concentrated, can deliver sustainable process heat to drive high temperature thermochemical reactions. Of these reactions, H_2O and CO_2 splitting have been studied extensively for the production of syngas (a mixture of H_2 and CO).¹⁴ Depending on the H_2/CO ratio, well documented catalytic pathways like FTS can convert syngas into a variety of hydrocarbon liquid fuels (e.g., diesel and jet fuel) at a higher quality than if derived through crude oil refinement.¹⁵ Direct solar thermolysis of $\text{H}_2\text{O}/\text{CO}_2$ requires operating temperatures that exceed 2200°C , rendering the process infeasible.¹⁶ Therefore, typical solar thermal $\text{H}_2\text{O}/\text{CO}_2$ splitting schemes employ metal oxides in a reduction-oxidation (redox) cycle to bisect the desired reaction and lower overall operating temperatures. Ceria ($\text{CeO}_{2-\delta}$) has emerged as a candidate oxygen-exchange material because it maintains a stable cubic fluorite structure for relatively large changes in oxygen stoichiometry^{17, 18}, demonstrates remarkable stability through extensive thermal cycling^{19, 20}, exhibits fast rates of oxygen-ion diffusion¹⁹, and can reversibly shift between oxidation states²¹. Several experimental demonstrations of solar reactors utilizing ceria have been conducted; to date, solar-to-fuel conversion efficiencies ($\eta_{\text{solar-to-fuel}}$) have yet to eclipse 6%.²²⁻²⁴ These relatively low efficiencies are largely attributed to the temperature disparity between the reduction ($T > 1450^\circ\text{C}$) and oxidation ($T < 1000^\circ\text{C}$) regimes.²⁴ This results in substantial sensible heat losses that can only be abated with the inclusion of efficient solid-solid heat recuperation between each regime, as proposed in Sandia National Laboratory's CR5²⁵ and elevating-particle reactor concepts²⁶.

Recently, we and others have demonstrated the promise of reforming methane via solar driven ceria based redox cycles.^{2, 13, 27-29} Compared to the state of the art solar thermochemical cycles that have limited efficiencies because large temperature swings and extreme operating temperatures, this process operates at much lower temperatures ($T < 1000^\circ\text{C}$) where traditional reactor materials may be utilized. Further, because both steps are operated at the same temperature, sensible heating losses are minimized. Ultimately, solar conversion efficiencies greater than 40% are realistic; we have already demonstrated ~10%-12% efficiency as proof of concept without any reactor optimization.^{27, 2} Compared to iron oxide based materials that were most commonly used in prior studies, ceria based materials offer a plethora of advantages related to morphological stability, rapid kinetics and more favourable thermodynamics.³⁰⁻³⁴

Using ceria, this cycle proceeds in two distinct steps. The first is the endothermic and solar driven oxidation of methane over ceria to produce synthesis gas. In this step, ceria is reduced and oxygen is released from its bulk, the extent of which is characterized by its nonstoichiometry, δ .



Ceria, once reduced, is then exposed to either H_2O or CO_2 and is re-oxidized, resulting in further synthesis gas production and the cycle is then repeated. It is important to note that the oxidation with H_2O and CO_2 are both ubiquitously known to be completely selective to H_2 and CO , respectively.



Once reduced, the oxidation of ceria is well known to be thermodynamically and kinetically favourable over a large range of temperatures for the splitting of CO_2 and H_2O ^{19, 35}, and an even larger range for oxidation with percentage levels of O_2 ³⁶. Further, the splitting reactions are completely selective to CO and H_2 formation, unless selective catalysts are employed on the surface^{22, 37-39}. In general, the oxidation of ceria is typically studied under conditions with only a single reactant (i.e. CO_2 or H_2O or O_2), and there are only a few select studies that have investigated the impact of co-feeding reactants. For example, Furler et al. co-fed different ratios of CO_2 and H_2O to determine the impact on the outlet CO/H_2 compositions, but this was very specific to the reactor utilized in that study⁴⁰.

There are several unique factors that make such a cycle ideal for utilization of flue gas from fossil-based power plants. First, it is highly scalable and thus capable of matching the demands required from megawatt and gigawatt sized power plants that are emitting vast quantities of flue gases^{1, 41}. Secondly, because the process operates in two distinct steps, the solar driven step and flue gas utilization step may be separated in both space and time if particles are transported. This means that although sunlight may only be used intermittently, flue gas can be utilized continuously (24/7) which eliminates the need for CO_2 storage. Further, the oxidation step is extremely flexible in the sense that the selectivity to CO and H_2 is 100 %^{22, 24, 39}, and residual oxygen left from incomplete combustion will simply be consumed by the ceria to oxidize it further. Thus, ceria is capable of being integrated with a range of different types of flue gas emissions (natural gas, coal, etc.) and only the finer details of reaction kinetics in the presence of different gas compositions will have to be studied. The influence of impurities on the process such as NO_x , SO_2 and particulates⁴² are not well understood.

Typically, these cycles are operated in either batch mode or continuous mode. In batch mode the solid reactants are stationary and enclosed in a cavity receiver; gaseous reactants and the solar input change with time depending on whether the reduction or oxidation step is being performed^{22, 24, 39}. In

continuous mode, particles are cycled between separate reduction and oxidation reactors where the thermal input and gaseous reactants remain constant^{2, 26, 43, 44}. We have demonstrated the viability of both process in our lab^{2, 27}, but again for utilization of flue gas 24/7 the latter approach is what we propose to do here.

Stechel *et al.* have shown that the production of solar fuels via thermochemical routes offers the potential to produce 75 million barrels of oil per day (5.3 TW) given a high enough solar to fuel conversion efficiency (10% for the entire system efficiency) to produce \$3/gasoline gallon equivalent (gge)⁴¹. This is largely in line with other economic studies of similar processes^{49, 50}. This assumes a cost of CO₂ from concentrated sources of \$39 to \$80 per metric ton (\$0.039–0.080/kg) which results in a cost contribution from CO₂ of less than \$0.35–0.71/gge⁴¹. This is minimal compared to the cost contribution of CO₂ from direct air capture of about \$1.80/gge; however, in the latter case there is the potential for a net carbon neutral scenario, whereas for CO₂ from point sources, the carbon is effectively utilized twice before being emitted to the atmosphere. Kim *et al.* has investigated the environmental impact for solar derived fuels that utilize CO₂ from flue gases and determined that with the current vehicle fleet in a sample city (Victorville, California), 3.6 Mt CO₂-eq and 77% of the total regional emissions could be mitigated.⁵⁰

Recently we demonstrated the simultaneous reduction of ceria and partial oxidation of methane in a drop tube reactor, shown below in Figure 2². The reactor was driven by a 2 kW_{th} solar simulator at 2264 suns peak flux (1 sun = 1 kW m⁻²) that served as the heat source. Particles were gravity fed into the reactor using a particle feeder where they were subsequently heated and reacted with CH₄ that was traveling either co-currently or con-currently to the particle flow. Methane conversions of 89 % were achieved for particle residence times as short as 1 s and $\eta_{\text{solar-to-fuel}}$ reached 12%. The syngas produced had a H₂:CO molar ratio of 2, and its calorific value was solar-upgraded by 24% over that of the CH₄ reformed.

Extended reaction times were investigated in order to assess the stability of the system. Figure 3 shows continuous syngas production for an experimental run over 60 min with co-current flow configuration and for $T_{\text{tube}} = 1291^{\circ}\text{C}$, $\dot{V}_{\text{CH}_4/\text{Ar}} = 2 \text{ L}_\text{N} \text{ min}^{-1}$, $x_{\text{CH}_4,0} = 0.1$ and mean $\dot{m}_{\text{CeO}_2} = 0.15 \text{ g s}^{-1}$. Shortly after the particle feeder and the inlet gas flow were initiated and despite the fluctuation in $\dot{m}_{\text{CeO}_2}$, the CO and H₂ flow rates reached steady-state conditions at about 6 mmol min⁻¹ and 13.7 mmol min⁻¹, respectively, resulting in a H₂:CO ratio of 2.3. The deviation from 2 is due to trace amounts of CO₂ production ($x_{\text{CO}_2} = 0.015$) and carbon deposition ($x_{\text{C}} = 0.029$). For this run, methane conversion was 0.85 and $\eta_{\text{solar-to-fuel}} = 8.3\%$. No evidence of a reaction between ceria particles and the Al₂O₃ tube was observed. A very small amount of carbon deposition was observed but did not exceed $x_{\text{C}} = 0.029$. This was not

observed in our prior studies with batch type systems^{27, 28} and although the reason for this is not entirely clear, we hypothesize that this may be in part due to quenching of the particles to lower temperatures where methane cracking is favourable²⁷. Regardless we expect that any carbon resulting from cracking will easily be oxidized during the subsequent oxidation step to form more synthesis gas²⁷. Carbon deposition was also observed on the Al_2O_3 reaction tubes which could be detrimental if allowed to accumulate over time but this may be remedied by delivering oxygen through the reaction tube intermittently.

In this study, the effect of repeated cycling on particle attrition and reactivity was not investigated. We have investigated the effect of repetitive cycling on ceria particles that were subjected to higher temperatures in the same reaction tube where only thermal energy was used (i.e. no methane)⁵¹. There, we observed some particle agglomeration in the reaction zone and subsequent particle sintering that led to larger particle sizes and increased reaction extents over the first four cycles, as seen in Figure 4. However, as the particles were cycled further, this process became less severe and ultimately after 8 cycles further increases in particle sizes and changes in reaction extents were not observed. Assessing the impact of repetitive cycling on particle attrition and reactivity during methane oxidation and flue gas reduction will be a focus of this proposal.

We have recently developed a system specifically designed for studying the kinetics of gas-solid reactions using a variety of reactive gases, including H_2O , CO_2 and O_2 . A simple schematic of the reactor system is shown in Figure 5 below. The sample temperature is controlled via a Carbolite STF 16/180 high-temperature tube furnace capable of achieving temperatures up to 1873 K. An MKS Type 640B absolute pressure controller coupled with an Edwards E2M0.7 rotary vane pump allows for examination under p_{tot} ranging from vacuum to ambient. Gaseous H_2O (ranging from 0.18 to 9 g/hr) is metered into the reactor's work tube via a vapor delivery system consisting of a Bronkhorst Controlled Evaporator Mixer (CEM) and LIQUI-FLOW liquid flow controller (LFC) and an MKS GE50A mass flow controller (MFC). All reactor plumbing downstream of the vapor delivery system is wrapped with flexible electric heating tape and basalt fabric insulation to prevent condensation of the vapor mixture. Two additional MKS GE50A MFC's are used to deliver other desired reactant gases (e.g. CO_2/O_2). After passing through the work tube, all gases travel through a vacuum trap submerged in an ice bath before being sampled by a Stanford Research Systems QMS series residual gas analyzer.

Experiments to date have been performed with $\text{H}_2\text{O}/\text{H}_2/\text{Ar}$ mixtures to study the H_2O splitting and H_2 oxidation relaxation rates over ceria. Here, all experiments were performed with a total pressure of 1 atm. Figure 6 shows exemplary data alongside experimental conditions obtained with pure ceria for an experiment performed at 1373 K. Here, the sample (approximately 2.0 g) was initially reduced by heating

from 773 to 1373 K at a rate of 20 K min⁻¹ with $p\text{H}_2\text{O}:p\text{H}_2 = 2.25$. At 1373 K and the flow conditions described, the $p\text{O}_2$ was 4.83×10^{-13} atm and δ_r was 0.0679. Following equilibration, several reduction and oxidation reactions were initiated by varying the H_2O input between $p\text{H}_2\text{O}:p\text{H}_2$ from 1.12-6.75 at 1373 K; in doing so, a maximum δ of 0.0908 ($p\text{O}_2 = 1.21 \times 10^{-13}$) and a minimum δ of 0.0334 ($p\text{O}_2 = 4.35 \times 10^{-12}$) were measured. Following the series of isothermal reactions, the sample was completely re-oxidized by cooling to 773 K under the same flow conditions as utilized during the initial nonisothermal reduction reaction.

We have performed solar to fuel conversion efficiency calculations ($\eta_{\text{solar-to-fuel}}$) for the proposed methane driven redox cycle. The main concern is the effect of the energetic penalty associated with cooling the particles below the oxidation temperature so that they may be transported to the flue gas reactor; in a typical redox process the particles would not be cooled below the oxidation temperature in order to limit the amount of sensible heat needed to reach the reduction temperature^{27, 37}. Shown below in Figure 7 is the predicted efficiency as a function of reduction temperature, for three different cooling temperatures (i.e. temperature at which particles are cooled and then transported to the flue gas reactor). Here, the oxidation temperature is assumed to be 625 °C, and the efficiency (and other assumptions) is as we have defined in a prior publication²⁷ as the heating value of the synthesis products produced minus the heating value of methane supplied, all divided by the solar power input. As seen, the expected efficiency, even when cooling particles to ambient temperature (yellow curve), is predicted to be greater than 30% over all conditions considered. As expected, the efficiency increases if the particles are not cooled all the way to ambient temperature (and if solid-solid heat recuperation is integrated, blue dashed curve), but for the sake of being economically viable it is typically assumed that the process should be capable of achieving a 20% solar to fuel energy conversion efficiency or higher.^{41, 49, 52}

References for Example 1

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CLAIMS

We claim the following:

1. A method of continuously processing flue gas, comprising:
 - a) introducing a flue gas comprising CO_2 to a material selected from a solid metal or an oxygen deficient metal oxide;
 - b) forming a first gas mixture comprising CO by the reduction reaction of the flue gas with the material, wherein the material is oxidized to form an oxidized solid material;
 - c) separating the first gas mixture from the oxidized solid material;
 - d) introducing the oxidized solid material to a reducing environment;
 - e) forming a second gas mixture by reducing the oxidized solid material to form the material selected from the solid metal or the oxygen deficient metal oxide;
 - f) separating the second gas mixture from the reduced material; and
 - g) go to step a).
2. The method of claim 1, wherein reduction includes using a heat source at sufficiently high temperature and sufficiently low partial pressure of oxygen ($p\text{O}_2$).
3. The method of claim 2, wherein the heat source is solar radiation.
4. The method of claim 2, wherein the low $p\text{O}_2$ is achieved via vacuum pumping, rendering the second gas mixture as comprising O_2 .
5. The method of claim 2, wherein the low $p\text{O}_2$ is achieved via an inert gas, rendering the second gas mixture comprising O_2 and the inert gas.
6. The method of claim 2, wherein the low $p\text{O}_2$ is achieved via a fuel source, rendering second gas mixture as comprising CO and H_2 .
7. The method of claim 2, wherein the low $p\text{O}_2$ is achieved via a fuel mixture containing methane, rendering the second gas mixture as comprising CO and H_2 .

8. The method of claim 1, wherein the material has partial molar enthalpy (Δh_o), or enthalpy of reaction with gaseous O_2 that is greater than the magnitude of formation enthalpies of H_2O ($\Delta h_{f,H_2O}$) and CO_2 ($\Delta h_{f,CO_2}$).
9. The method of claim 1, wherein the solid oxide is $M(1)O_{2-\delta}$ and δ is MO_2 nonstoichiometry, wherein $0 < \delta \leq 0.5$.
10. The method of claim 9, wherein $M(1)$ is Ce.
11. The method of claim 1, wherein the solid oxide is $M(1)_xM(2)_{1-x}O_{2-\delta}$ and δ is MO_2 nonstoichiometry, wherein x ranges from 0 to 0.5, wherein $0 < \delta \leq 2$.
12. The method of claim 11, wherein $M(1)$ is Ce and $M(2)$ is Zr, Hf or a combination thereof.
13. The method of claim 1, wherein the solid oxide is $M(3)_xCe_{1-x}O_{2-\delta}$, wherein x ranges from 0 to 0.5, and δ is CeO_2 nonstoichiometry, wherein $0 < \delta \leq 2$.
14. The method of claim 13, wherein $M(3)$ is a transition metal or a combination thereof.
15. The method of claim 13, wherein the $M(3)$ is selected from La, Mn, Cr, Al, Sr, Co, Fe, or a combination thereof.
16. The method of claim 1, wherein the material is selected from a transition metal, lanthanide material, or a combination thereof.
17. The method of claim 1, wherein steps b) and e) are conducted in separate reactors.
18. The method of claim 17, wherein step b) is conducted in a fluidized bed reactor.
19. The method of claim 17, wherein step e) is conducted in a solar drop-tube reactor.
20. The method of claim 1, wherein the first gas mixture and the second gas mixture are combined to form a third gas mixture.

21. The method of claim 1, wherein the first, second or third gas mixture is further processed to form a hydrocarbon liquid fuel.
22. The method of claim 11, further comprising: processing the third mixture to form a hydrocarbon liquid fuel.
23. A system for processing flue gas, comprising:
a first reactor comprising a flue gas and a material selected from a solid metal or an oxygen-deficient metal oxide, wherein the flue gas comprises CO₂, wherein the first reactor is configured to form a first mixture comprising CO by the oxidation reaction of the flue gas with the material, wherein the material is oxidized to form an oxidized solid;
a first transport apparatus to move the oxidized solid oxide to a second reactor, wherein the first reactor and the second reactor are separate reactors;
the second reactor comprises the oxidized solid oxide, wherein the second reactor is configured to reduce the oxidized solid oxide to the material and to form a second mixture comprising either CO and H₂, O₂ or O₂ mixed with inert gas; and
a second transport apparatus to move the material to the first reactor.
24. The system of claim 23, further comprising: a third reactor in gaseous communication with the first reactor, the second reactor, or both, wherein the third reactor is configured to receive the first mixture, the second mixture, or both.
25. The system of claim 23, wherein first reactor is a fluidized bed reactor.
26. The method of claim 25, wherein second reactor is a solar drop-tube reactor.

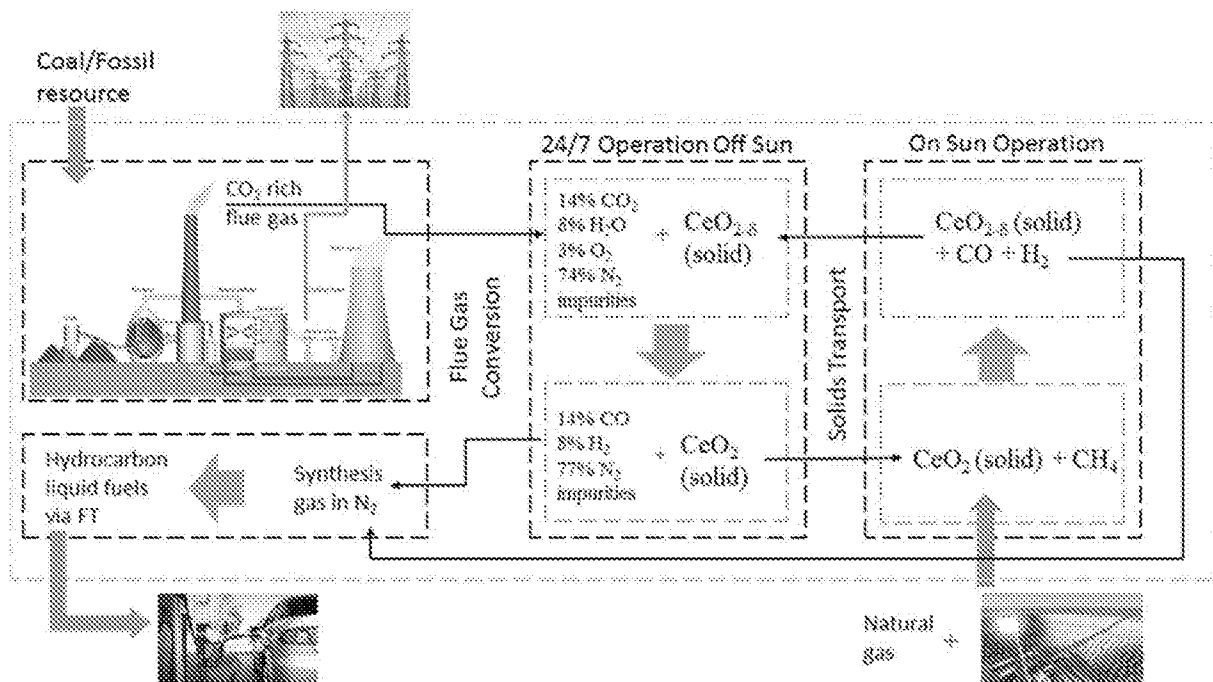


FIG. 1

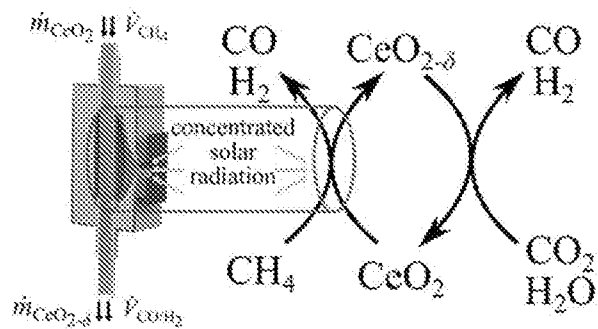
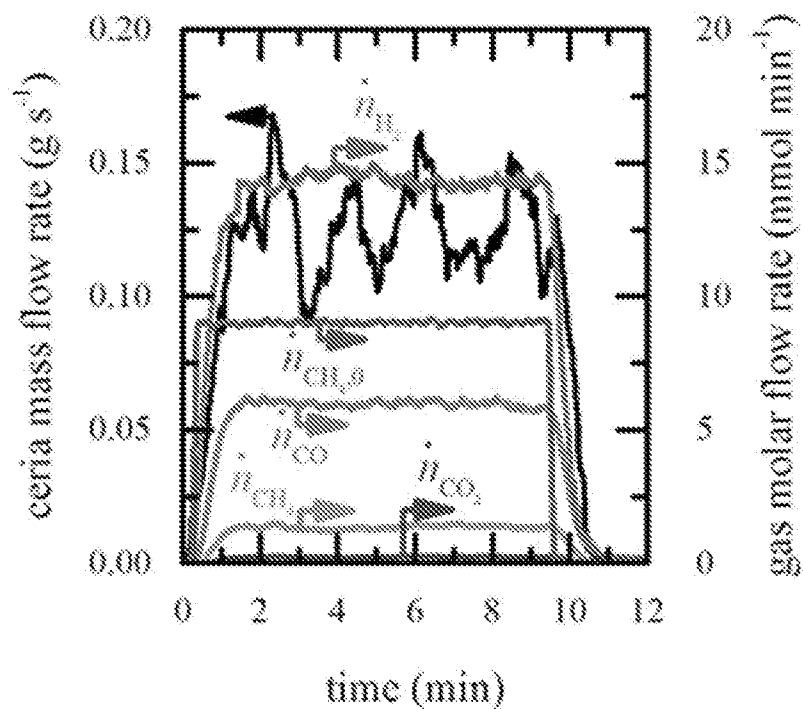
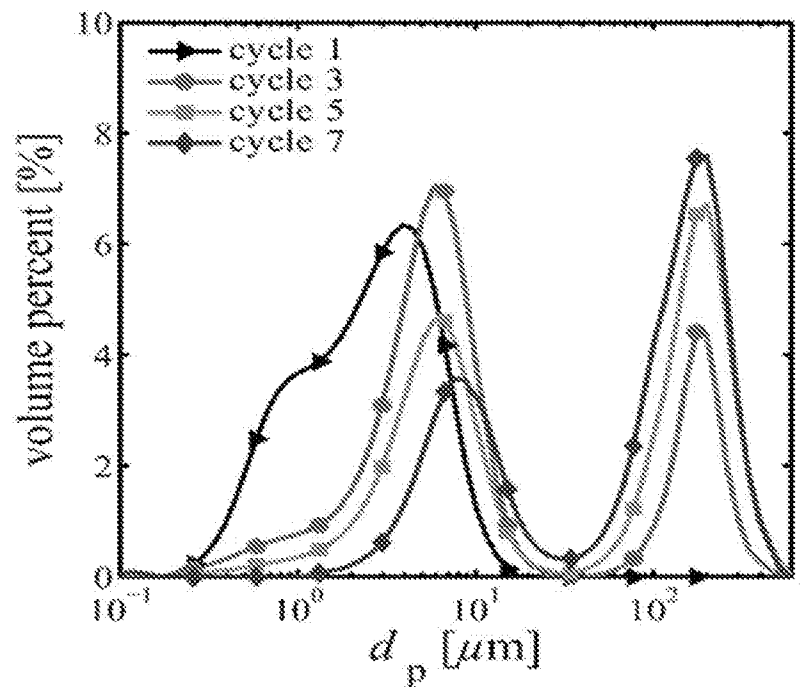
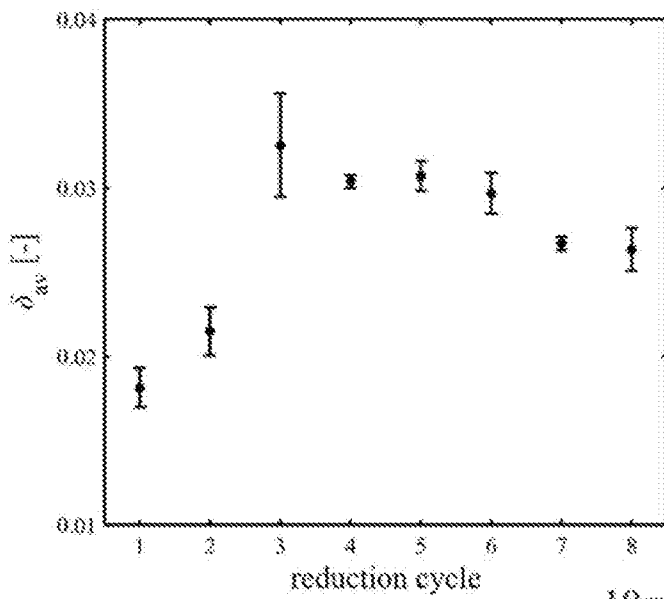
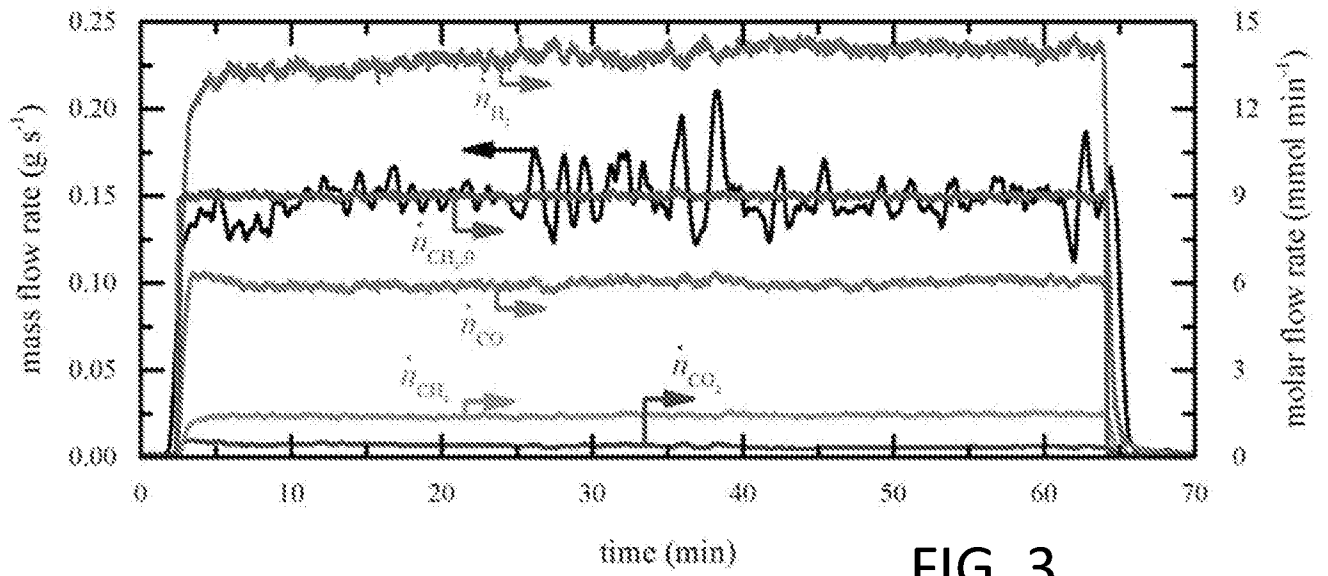


FIG. 2





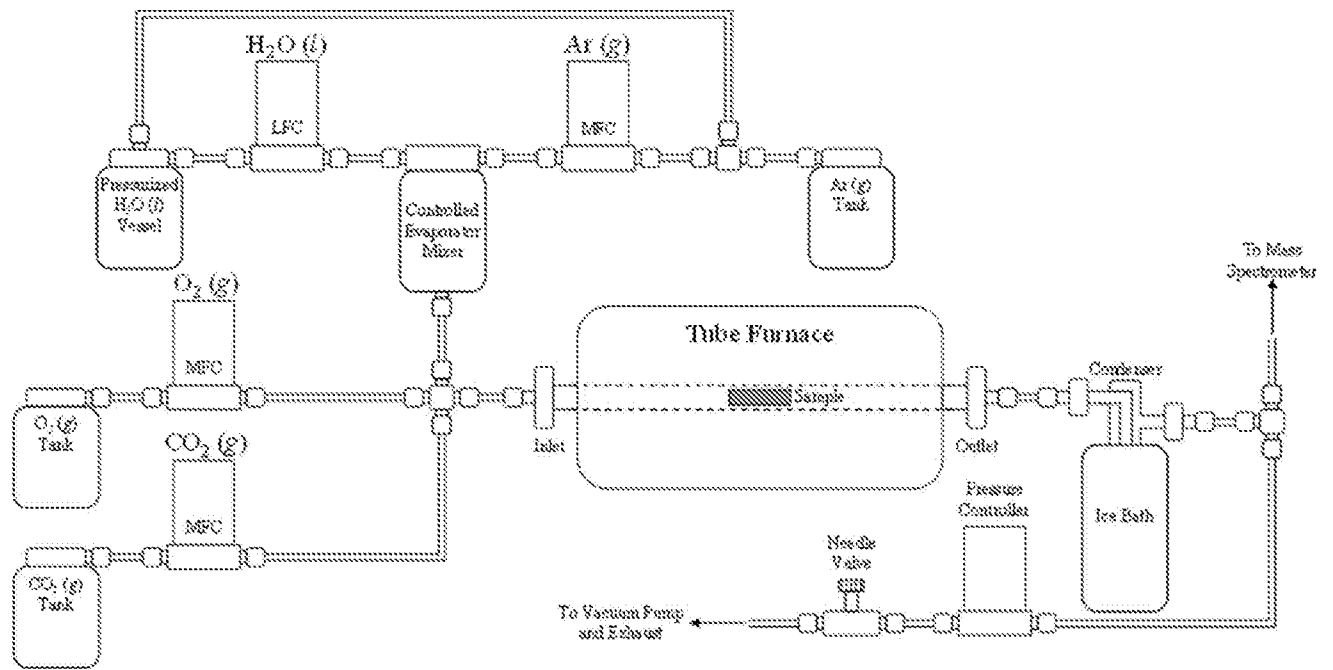


FIG. 5

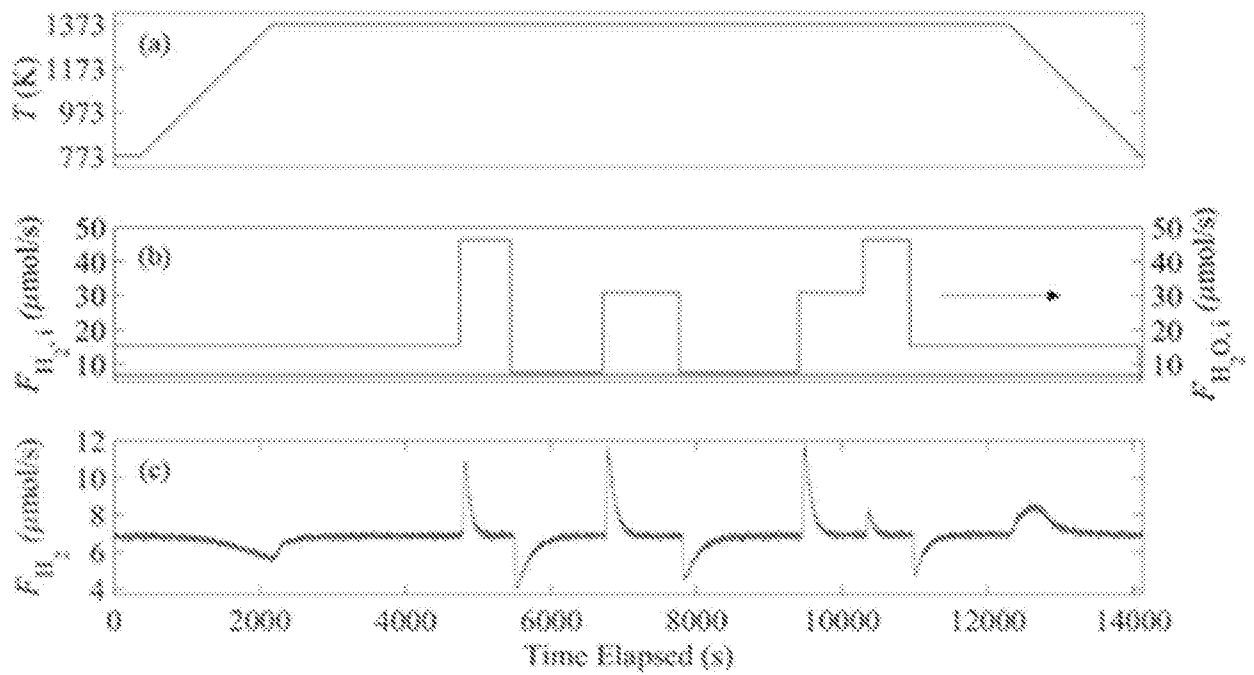


FIG. 6

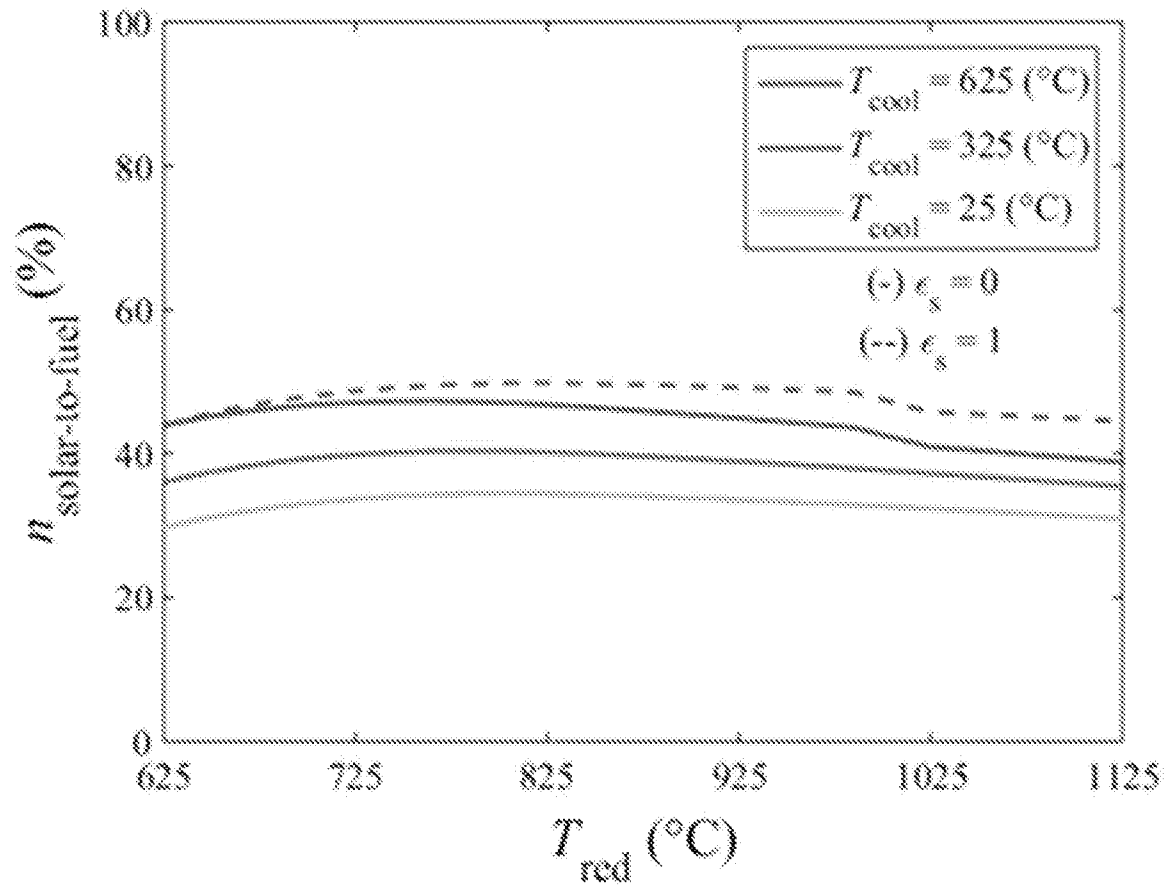


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/58743

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C07C 29/159; C10J 1/20; C10L 3/08 (2019.01)

CPC - C01B 3/34; C07C 29/1518; C10J 1/20; C10L3/08

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ----- A	US 2014/0158030 A1 (Jadhav), 12 June 2014 (12.06.2014) Abstract; Figure 1; para [0008]-[0017], para [0022], para [0021], and entire document	1-10,16-26 ----- 11-15
Y ----- A	Welte et al.; "Combined Ceria Reduction and Methane Reforming in a Solar-Driven Particle-Transport Reactor"; Ind. Eng. Chem. Res.; Vol 56 pp 10300-10308; Published online 22 August 2017 (22.08.2017); Abstract; Figure 1; and entire document	1-10,16-26 ----- 11-15
A	Welte et al.; "Experimental Demonstration of the Thermochemical Reduction of Ceria in a Solar Aerosol Reactor", Ind. Eng. Chem. Res.; Vol 55 pp 10618-10625; Published online 23 September 2016 (23.09.2016) Entire document	1-26
A	Pullar et al.; "A Review of Solar Thermochemical CO ₂ Splitting Using Ceria-Based Ceramics With Designed Morphologies and Microstructures", Frontiers in Chemistry; Vol 7, Article 601; Published 4 September 2019 (04.09.2019)	1-26
A	US 2007/0124997 A1 (Liu et al.) 7 June 2007 (07.06.2007) Abstract; Figure 1; para [0005]-[0008]	1-26
A	US 2017/0259240 A1 (Saudi Arabian Oil Co.) 14 September 2017 (14.09.2017) Abstract; Figure 2; para [0014]-[0017]	1-26

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

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"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

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Date of the actual completion of the international search

27 December 2019

Date of mailing of the international search report

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