A Solar Thermochemical Fuel Production System Integrated with Fossil Fuels

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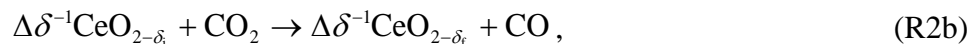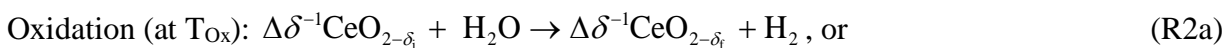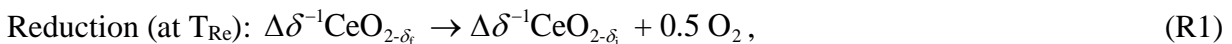
Abstract:

Thermochemical cycling (TC) is a promising means of harvesting solar energy. In a typical two-step TC, a redox-active metal oxide (e.g., cerium dioxide, or ceria) serves as a reaction intermediate that is initially reduced at a high temperature (e.g. 1500°C, by concentrating sunlight) and then yield fuels (e.g. H_2 or CO) by dissociating H_2O or CO_2. Isothermal TC recently emerged as an important special case of two-step TC due to the relatively ease of heat recovery from the fluid phase (rather than the solid phase as in traditional non-isothermal TC) and thus potentially high attainable efficiencies. Such advantages shall result in much alleviated thermal (and thus mechanical) shock in reactor design and less irreversibility in concentrated solar energy utilization. The high efficiency of isothermal TC is contingent upon effective gas-phase heat recovery, which however is immature at temperatures above 1100°C. Instead of direct heat recovery via heat exchanger, we propose a novel approach of simultaneously recovering waste heat and unreacted gas (e.g. H_2O or CO_2) downstream the reactor by taking advantage of endothermic reactions of certain fossil fuels (e.g. CH_4). Such comprehensive utilization and the syngas produced enable the establishment of a polygeneration system for simultaneous power and methanol production with the possibility of eliminating the self-generation power-plant that is conventionally needed for methanol production. A scheme is conceptually proposed based on the type of splitting reaction in isothermal TC, and optimization of the polygeneration system is discussed with solar conversion efficiency as the objective. Fossil fuel consumption for the production of a unit mass of methanol is about 22GJ/ton, lower than typical values in current industrial processes. Compared with direct solar reforming or direct combustion of the same fossil fuels, this new approach features lower carbon emissions per unit calorific value of fuel obtained due to the incorporation of the isothermal TC upstream.

Keywords:
Isothermal, Polygeneration, Solar Fuel, Syngas, Thermochemical Cycling, Methanol.

1. Introduction

Thermochemical cycling (TC) is a technology for solar energy storage via the synthesis of chemical fuels by utilizing concentrated solar heat to drive endothermic chemical reactions. Two-step TC of ceria and its derivatives attracts much attention for efficient splitting of H_2O (or CO_2) for H_2 (or CO), a valuable feedstock to product ammonia, methanol, or liquid hydrocarbon. Ceria-based H_2O and CO_2 splitting processes are described as follows: oxygen is first released when solar energy is used to reduce the metal oxide at a high temperature T_{Re}; then the reduced metal/metal oxide is re-oxidized with water or CO_2 at a lower temperature T_{Ox}, yielding H_2 or CO.

Reduction (at T_{Re}): $\Delta\delta^{-1}\text{CeO}_{2\text{-}\delta_f} \rightarrow \Delta\delta^{-1}\text{CeO}_{2\text{-}\delta_i} + 0.5\,\text{O}_2$, (R1)

Oxidation (at T_{Ox}): $\Delta\delta^{-1}\text{CeO}_{2-\delta_i} + \text{H}_2\text{O} \rightarrow \Delta\delta^{-1}\text{CeO}_{2-\delta_f} + \text{H}_2$, or (R2a)

$$\Delta\delta^{-1}\text{CeO}_{2-\delta_i} + \text{CO}_2 \rightarrow \Delta\delta^{-1}\text{CeO}_{2-\delta_f} + \text{CO},$$ (R2b)

Combined: $\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\,\text{O}_2$, or (3a)

$$\text{CO}_2 \rightarrow \text{CO} + 0.5\,\text{O}_2,$$ (3b)

where δ stands for oxygen nonstoichiometry; δ_i and δ_f correspond to δ values at the beginning and the end of the oxidation step, respectively ($\delta_i > \delta_f$); T_{Ox} and T_{Re} are the temperatures at which oxidation and reduction reactions occur, respectively.

Low solar-to-fuel efficiency has been the bottleneck for solar-driven TC in general. In 2012, Seinfeld [1] achieved 1.73% (average) and 3.53% (peak) solar-to-fuel efficiency with RPC foam made of pure CeO_2. Heat recovery from solid oxygen carrier and reactor is a key issue to improve the efficiency. A typical two-step TC works with a large temperature difference which cause a big thermal shock within the reactor and a large fraction of heat lost to the environment. In 2013, a few groups [2-4] reported isothermal water splitting, in which reduction and oxidation occur at identical temperatures. The elimination of temperature difference makes high-efficiency heat recovery easier, for heat is carried away by the fluid phase instead of the solid phase.
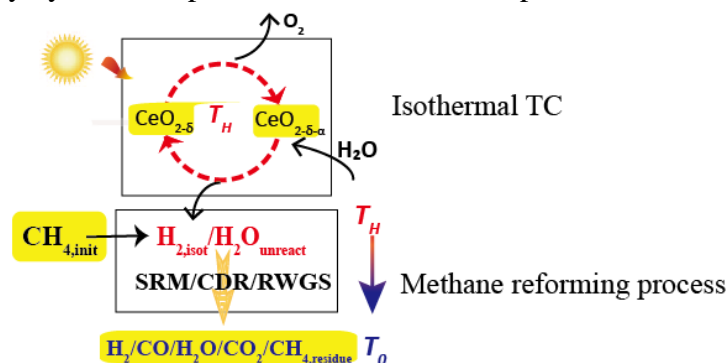

Fig. 1. Simplified scheme for H_2O splitting isothermal TC integrated with methane

Effective heat recovery and energy cost reduction are essential for isothermal TC, which is a potentially high-efficiency method for producing solar fuels. The solar-to-fuel efficiency of isothermal splitting of CO_2 is much higher (e.g. three times higher at 1500°C without heat recovery) than isothermal water splitting process [5] due to the favorable thermodynamic nature of CO_2 and the lack of phase change. Direct use of oxidation products and unreacted CO_2 can reduce additional energy consumption for CO_2 separation which finally cut down the solar energy input to the system. The gas mixture downstream the oxidation process contains a large amount of sensible heat, the heat recovery of which can be used to heat the fresh CO_2 or H_2O on the feed side. However, heat exchangers are immature above the temperature of 1100°C [6]. Instead of direct heat recovery via a heat exchanger, we propose a novel approach of simultaneously recovering waste heat and unreacted gas (e.g. H_2O or CO_2) downstream the reactor by taking advantage of endothermic reactions of certain fossil fuels [7] (e.g. CH_4). The temperature of the gaseous exhaust of isothermal oxidation reaction can be reduced to 600-850°C and the calorific value of which can also be improved. The scheme is shown in Fig. 1, taking H_2O splitting isothermal TC for example. Isothermal co-splitting of CO_2 and H_2O can obtain syngas, while the integration with fossil fuel can improve the syngas production and the utilization of solar energy. Compared with direct solar reforming or direct combustion of the same fossil fuels, this new approach features lower carbon emissions per unit calorific value of fuel obtained due to the incorporation of the isothermal TC upstream. At the end of this paper, a solar thermochemical polygeneration system integrated with methane for methanol synthesis is proposed to further prove the benefit of this approach. H_2O/CO_2 ratio for co-splitting with isothermal TC, CH_4/H_2O and CH_4/CO_2 ratio are compared and optimized for optimum solar to methanol efficiency.

2. Analytical Methodology

The thermodynamic efficiency of the two-step TC [5] for converting solar energy and H_2O (or CO_2) to H_2 (or CO) can be defined as:
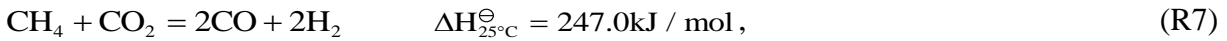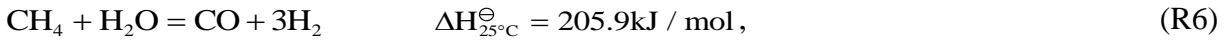
$$\eta_{HHV} = \frac{HHV}{(Q_{redu} + Q_{heat} + Q_{ceria})/\eta_{abs}}, \tag{4}$$

where HHV is the higher heating value of one mole of H_2 (or CO), the denominator represents the total solar energy input consisting of re-radiation losses and three enthalpy terms Q_{redu}, Q_{heat} and Q_{ceria} for extracting 1 mole of O atoms from ceria: that required to reduce ceria from $CeO_{2-\delta_i}$ to $CeO_{2-\delta_f}$ at T_{Re}, that to heat water (or CO_2) from 25°C to T_{Ox}, and that to heat ceria from T_{Ox} to T_{Re}. For isothermal TC, Q_{ceria} vanishes for $T_{Re}=T_{Ox}=T_H$; The denominator is the solar energy needed for producing one mole of H_2 (or CO).

$$\eta_{abs} = 1 - \frac{\sigma \cdot T^4}{I \cdot C}, \tag{5}$$

is the solar absorption efficiency of an ideal blackbody reactor [8] in which the cycling reactions are assumed to take place, σ is Stefan-Boltzmann's constant, T is the temperature of the reactor, I is solar irradiation, and C is concentration ratio;

The newly proposed approach recovers waste heat and utilizes unreacted gas (e.g. H_2O or CO_2) downstream the isothermal TC reactor by taking advantage of endothermic reactions of certain fossil fuels (e.g. CH_4), mainly the steam reforming of methane (SRM) , the carbon dioxide reforming of methane reaction (CDR) and the reverse water gas shift reaction (RWGS):

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H^{\ominus}_{25°C} = 205.9 kJ/mol, \tag{R6}$$

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad \Delta H^{\ominus}_{25°C} = 247.0 kJ/mol, \tag{R7}$$

$$H_2 + CO_2 = CO + H_2O \qquad \Delta H^{\ominus}_{25°C} = 41.1 kJ/mol. \tag{R8}$$

Therefore, through the combination of these reactions, the unreacted gases in the exhaust and its high temperature sensible heat are rationally used, and the final products after reforming are a mixture of H_2, CO, CO_2, H_2O (with residual CH_4). The conversion efficiency of solar energy into chemical energy for an isothermal TC integrated with fossil fuels [9] is represented by the solar to syngas efficiency:

$$\eta_{sol\text{-}to\text{-}syngas} = \frac{n_{H_2} HHV_{H_2} + n_{CO} HHV_{CO} - n_{CH_4,react} HHV_{CH_4}}{Q_{solar}}, \tag{9}$$

where Q_{solar} is the total solar energy delivered through the receiver's aperture considering the solar absorption efficiency. $n_{CH4,react}$, n_{H2} and n_{CO} are the amounts of CH_4 reacted, H_2 and CO produced after the reforming process, respectively. HHV_{H2}, HHV_{CO} and HHV_{CH_4} are the higher heating values of H_2, CO and CH_4, respectively. The energetic upgrade factor is defined as the ratio of the higher heating value of syngas to that of feedstock processed in a similar form [9] (but with HHV instead of LHV):

$$U = \frac{n_{syngas} HHV_{syngas}}{n_{feedstock} HHV_{feedstock}}, \tag{10}$$

The calorific value per mole of the gas mixture downstream the oxidation reactor is defined by:

$$HHV_{mix} = \frac{(X_{CO} HHV_{CO} + X_{H_2} HHV_{H_2} + X_{CH_4,residue} HHV_{CH_4})}{X_{CO} + X_{H_2} + X_{CO_2} + X_{H_2O} + X_{CH_4,residue}}, \tag{11}$$

where X_{CO}, X_{H2}, X_{CO2}, X_{H2O}, $X_{CH_4,residue}$ are the mole fractions of CO, H_2, CO_2, H_2O and the remaining CH_4, respectively.

Another important parameter is the net carbon emissions per unit calorific value, defined as:

$$C = \frac{(n_{CH_4,feed} - n_{CH_4,residue}) \times 44g/mol}{n_{H_2} HHV_{H_2} + n_{CO} HHV_{CO}}, \tag{12}$$

where $n_{CH_4,feed}$ and $n_{CH_4,residue}$ are the amounts of CH_4 input and residue for SRM or CDR process, respectively; The SRM and CDR processes include the RWGS and many other reactions. The carbon elements released are traced back to the reacted CH_4 instead of CO_2 input of the isothermal TC for that CO_2 are released again after it participates in the total process.

3. Results and Discussion

3.1. Isothermal splitting of CO_2 or H_2O

For the convenience of discussion, the ratios of CO_2 and H_2O to available oxygen vacancies in ceria upon reduction are defined as $r_{CO_2} = n_{CO_2} / (\delta_i n_{Ceria})$ and $r_{H_2O} = n_{H_2O} / (\delta_i n_{Ceria})$, respectively.
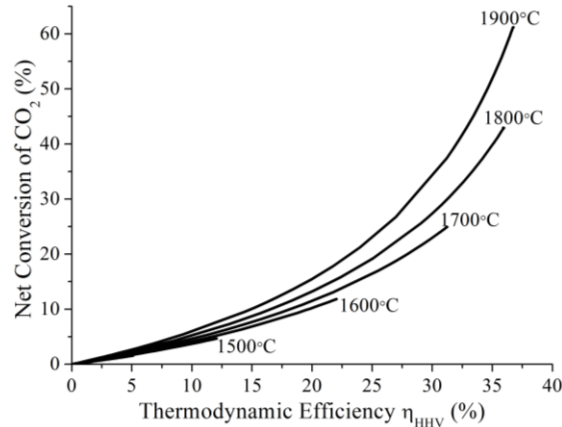

Fig. 2. Percentage of CO_2 converted to CO and η_{HHV} for different T_H from 1500 to 1900°C.
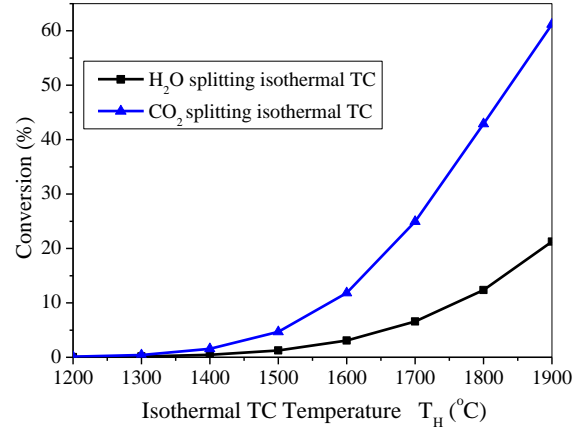

Fig. 3. The conversion of CO_2 and H_2O for isothermal oxidation reaction, T_H in the range from 1200-1900°C:

The high temperature thermolysis of CO_2 or H_2O will lead to a higher oxygen partial pressure, which will be a higher driving force for the oxidation step of the splitting cycle. The net conversion of CO_2 to CO is shown in Fig. 2 for different isothermal reaction temperature T_H. For CO_2 splitting isothermal TC at 1600°C, the net conversion of CO_2 is 11.4% while the HHV efficiency is 21.5% (without heat recovery) for r_{CO2}=0.01.

The output of the oxidation reaction of isothermal TC is a mixture of CO and unreacted CO_2 (at T_H) for CO_2 splitting process, while for H_2O splitting process, the output is a mixture of H_2 and unreacted H_2O (at T_H). The conversions of CO_2 to CO and H_2O to H_2 for CO_2 and H_2O splitting isothermal TC are shown in Fig. 3 in which r_{CO2}=r_{H2O}=0.01. Physical condensation is possible for the separation of H_2 and H_2O to obtain pure hydrogen only, while for the separation of CO and CO_2, extra energy is needed to obtain pure CO. For a fixed amount of H_2O or CO_2 input, a specific H_2 or CO will be obtained, and the total solar energy for the part of isothermal TC is calculated by (4).

3.2. Isothermal TC integrated with downstream methane reforming

The molar percentage of CO and CO_2 downstream the reactor are 11.4% and 88.6%, respectively, assuming that the initial gas flow rate of CO_2 is 1000 kmol/h and the temperature of isothermal CO_2 splitting process is 1600°C. Then CH_4 is added into the mixture of CO and CO_2 downstream the isothermal oxidation reactor to lower the temperature, and unreacted CO_2 is converted to CO and H_2 with the major endothermic reaction of CDR, shown in (R7). With the continuous increase of the amount of methane, the gas mixture achieves thermodynamic equilibrium with no extra entering heat, and the mole fraction of the gas mixture is shown in Fig. 4. CH_4/CO_2 ratio is the molar ratio of CH_4 to CO_2 input of isothermal TC. The mixing temperature decreases rapidly until the remaining CH_4 begin to appear with a noticeable amount (i.e. mole fraction $> 10^{-3}$ is chosen) at a CH_4/CO_2 ratio of 0.1562 (marked as CH_4/CO_2 ratio-x). It is worth mentioning that the reverse water gas reaction and other chemical reactions occur simultaneously to gain a minimum Gibbs free energy.
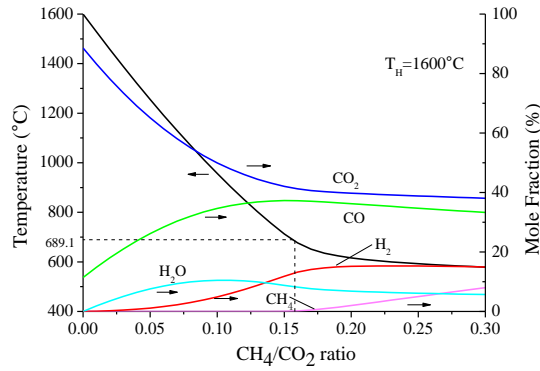
Fig. 4. Isothermal CO_2 splitting process integrated with downstream CDR at $T_H=1600°C$.

For each temperature of isothermal splitting TC of CO_2 ranging from 1200-1900°C, there is an optimal CH_4/CO_2 ratio-x to reach the point where the mole fraction of CH_4 is 10^{-3}, shown in Fig. 5(a). With the increase of T_H, the CH_4/CO_2 ratio-x increases mainly because the sensible heat of the oxidation products of isothermal TC does. The mole fraction of CO is twice more than H_2 when T_H is in a range of 1200-1900°C, for which the main reactions are CDR (R7) and RWGS (R8). The reaction of CDR has a trend to occur easily because the large percentage of CO_2 existing downstream the oxidation reactor and the equilibrium constant is the largest among CDR, SRM and RWGS. The H_2 produced in the CDR reacts with CO_2 to obtain CO and H_2O in the following step above the equilibrium temperature of 817°C, and only a small amount of produced water reacts with methane because of the larger equilibrium constant for CDR than SRM and that the content of CO_2 in the gas mixture is larger than H_2O. With the increase of temperature, the equilibrium constant for both CDR and RWGS increase but the former grows faster, such that the ratio of CO/H_2 decrease (The mole fractions of CO and H_2 after a reforming process without recovery of CO from an isothermal TC are shown in dashed line in Fig. 5(a)). The gap between CO and H_2 content enlarges with the increase of isothermal temperature due to higher CO_2 to CO conversion by isothermal TC. More CO from the isothermal TC is added into the methane reforming process, which slightly influences the RWGS reaction.
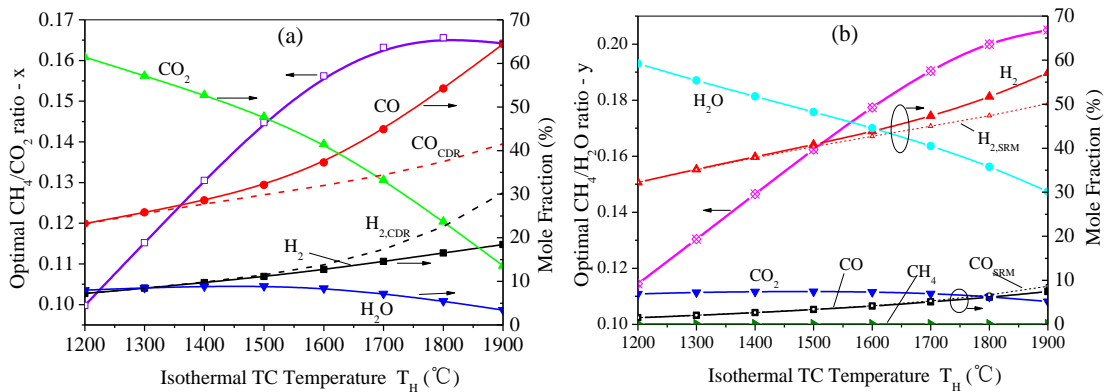

Fig. 5. CH_4/CO_2 ratio-x or CH_4/H_2O ratio-y and the mole fractions of various gas species after methane reforming process (a)Isothermal CO_2 splitting process integrated with CDR, $T_H=1200-1900°C$; (b) Isothermal H_2O splitting process integrated with SRM, $T_H=1200-1900°C$

As for water splitting with isothermal TC, the H_2 content in the oxidation reaction vary with respect to T_H at fixed r_{H2O}. SRM and RWGS are the main endothermic reactions when methane is added to the oxidation products. Fig. 5(b) shows the optimal CH_4/H_2O ratio-y and the equilibrium mole fraction of each component after the reforming process, and hydrogen takes a large portion in the gas mixture. Here, CH_4/H_2O ratio-y is the optimal molar ratio of CH_4 to H_2O input of the isothermal TC when the mole fraction of CH_4 is 10^{-3} after the reforming process. The red solid and dashed lines represent the contents of H_2 in the gas mixture of the proposed system and that of the methane reforming only system at the same temperature, respectively. More H_2 will be produced in the isothermal TC with the increase of T_H and it will influence the component ratio of the proposed

system. The mole fraction of H_2 of the proposed system has a larger increase trend than that of a methane reforming only system with the increase of T_H. Fig. 6 shows the comparison of H_2 and CO for T_H ranging from 1200 to 1900°C where the dashed and solid lines represent CO_2 splitting and water splitting isothermal TC integrated with methane, respectively. We assume that the initial inputs of CO_2 and H_2O for isothermal TC are both 1000kmol/h. The sensible heat of the gas mixture after H_2O splitting isothermal oxidation reaction is larger than CO_2 and the enthalpy change of SRM is larger than CDR for the same amount of methane. That is why the CO_2 splitting process needs less CH_4 input than water splitting process and the mixing temperature T_0 is higher.
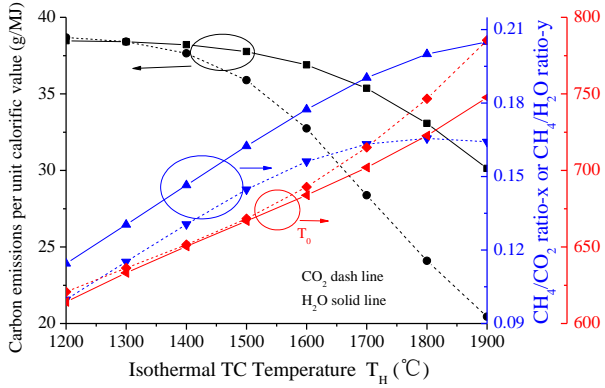

Fig. 6. Isothermal CO_2 and H_2O splitting process integrated with downstream methane reforming at T_H=1200-1900°C.
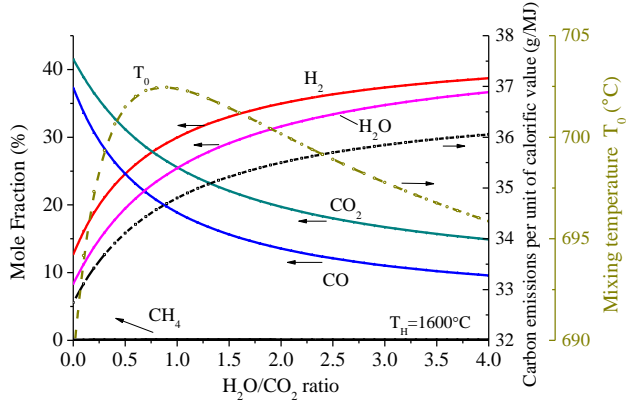
Fig. 7. Isothermal co-splitting CO_2 and H_2O splitting process integrated with methane.

At a given isothermal splitting temperature of CO_2 or H_2O alone, the percentage of each gas species in the mixture after the refoming process is fixed, but co-splitting of CO_2 and H_2O can obtain varying molar ratios of CO/H_2. Fig. 7 shows the mole fraction of the gas mixture after the reforming process. The CH_4/CO_2 ratio-x and CH_4/H_2O ratio-y are optimal values shown in Fig. 5 and the isothermal TC temperature is 1600°C. No H_2O exists when H_2O/CO_2 ratio is 0, and the mole fraction of the gas mixture is the same as that shown in Fig. 5 (a) when the isothermal temperature is 1600°C. With the increase of H_2O/CO_2 ratio, the percentage of H_2 increases rapidly, for SRM plays an increasingly important role, producing more H_2. The mole fraction of H_2 is lower than CO before the H_2O/CO_2 ratio reaches 0.56. The mixing temperature T_0 after reforming is in the range of 685°C to 705°C. When the H_2O/CO_2 ratio is about 1.39, the CO/H_2 ratio is about 0.5, which is an important parameter for many chemical synthesis processes, such as methanol and dimethyl ether.

Both the isothermal TC and methane reforming process store part of the concentrated solar energy. To reveal the proportion of storage capability by isothermal TC, we define $R_{iso,st}$ as the isothermal TC heat storage rate:

$$R_{iso,st} = \frac{n_{CO,iso}HHV_{CO} + n_{H_2,iso}HHV_{H_2}}{n_{CO}HHV_{CO} + n_{H_2}HHV_{H_2} - n_{CH_4,react}HHV_{CH_4}}, \tag{13}$$

where $n_{CO,iso}$ and $n_{H2,iso}$ are the amounts of CO and H_2 produced during isothermal TC, respectively, with subscript 'iso' standing for products of isothermal TC (rather than those of downstream methane reforming); $n_{CH_4,react}$ is the amount of CH_4 consumed in the methane reforming process. The isothermal TC stores energy in the form of chemical energy of CO or H_2, while the reforming process convert sensible heat of the gas mixture downstream the oxidation reactor into the promoted chemical energy by the enthalpy change of SRM or CDR and RWGS. Fig. 8(a) shows the isothermal heat storage rate of isothermal TC, where the capacity of CO_2 splitting process is higher than that of water splitting process. The calorific value per mole of the gas mixture is an important parameter indicating the ability of gas mixture in converting chemical potential to internal energy when burning, which has been defined in (11) and showed in Fig. 8(a). According to the calorific value of the gas mixture, a proper combined-cycle power plant can be established to generate electricity. To get a higher calorific value per mole gas mixture, physical condensation can be used

to remove H_2O. The calorific value is also an important parameter for the modification of existing combined cycle power plants. Extra fossil fuels can be directly added into the combustion chamber of a gas turbine in order to improve the calorific value per mole if the power generated from the newly proposed system is not enough for methanol synthesis.
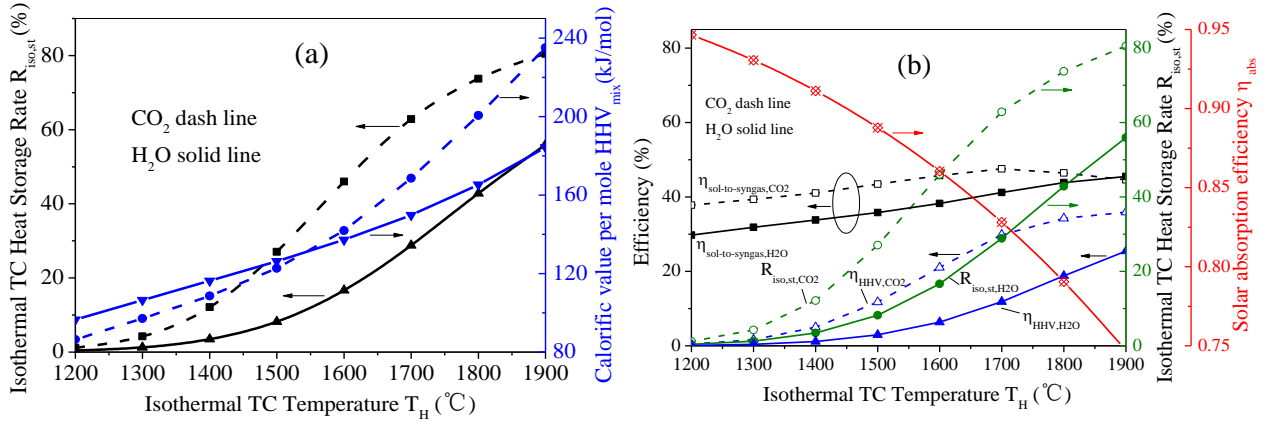

Fig. 8. (a)Isothermal TC heat storage rate and the calorific value per mole of gas mixture for CO_2 and H_2O splitting integrated with methane reforming downstream. (b)The efficiency, isothermal TC heat storage rate and solar absorption efficiency varied with T_H.

The solar-to-syngas efficiency of the solar-driven isothermal TC integrated with methane is shown in Fig. 9(a). It is worth mentioning that the product of $R_{iso,st}$ and $\eta_{sol-to-syngas}$ is just η_{HHV} .With the increase of T_H, the solar-to-syngas efficiencies of the newly proposed system for both CO_2 and H_2O splitting are higher than the η_{HHV} of isothermal TC without heat recovery (Fig. 8(b)), because the rational use of waste heat from T_0 to T_H . After 1700°C, the solar-to-syngas efficiency of CO_2 splitting system integrated with methane begins to decrease mainly because of the rapidly decreased solar absorption efficiency. The maximum upgrade factors of R6 and R7 driven by solar energy are 1.281 and 1.277 (ratio of the heating value of products to reactants), respectively and the values are close to the ugrade factors of isothermal H_2O and CO_2 splitting TC at 1200°C (Fig. 9(a)), for only a small amount H_2 or CO is produced in the isothermal TC. With the increase of the isothermal TC temperature, the upgrade factor of CO_2 splitting process integrated with methane has a larger growth trend than H_2O for the conversion of CO_2 to CO is larger than that of H_2O to H_2 in an isothermal TC at the same T_H (Fig. 3).
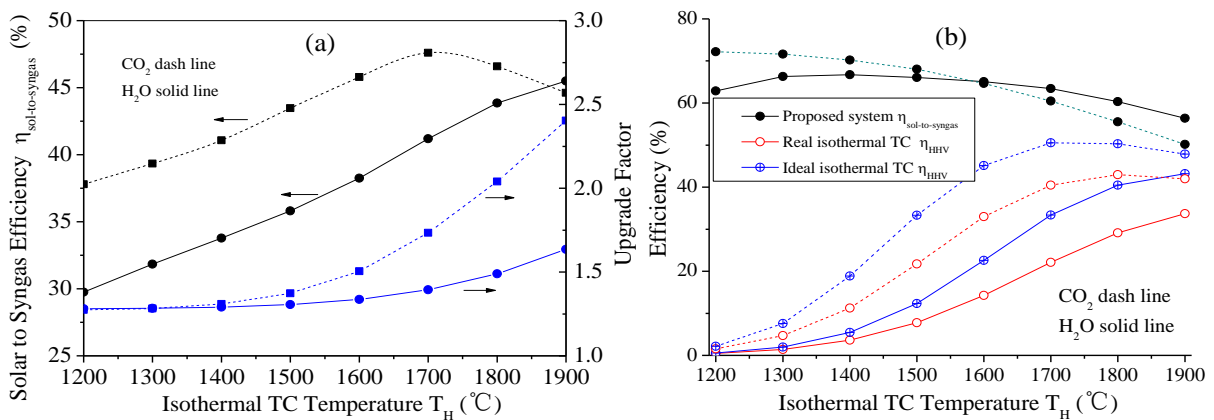

Fig. 9. (a) Solar-to-syngas efficiency $\eta_{sol-to-syngas}$ and Upgrade Factor for isothermal TC integrated with methane as a function of T_H (b) Efficiency of isothermal TC and proposed system with different heat recovery varied with isothermal TC temperature

After methane reforming process, the heat of the gas mixture ranging from 25°C to T_0 is recovered with a 80% rate. The solar to syngas efficiency for the proposed system is shown in black lines with solid symbols in Fig. 9(b), where the dashed and solid lines represent CO_2 and H_2O splitting isothermal TC integrated with methane, respectively. The efficiencies of isothermal TC with an

ideal 80% heat recovery of the mixed gases (CO/CO_2 or H_2/H_2O) downstream the oxidation reactor (i.e. ideal isothermal TC efficiencies) are shown in blue lines with half open symbols, in the mean time, the mixed gases are cooled from T_H to room temperature. Because of the immaturity of heat exchanger for temperatures above 1100°C, only 80% heat recovery of the mixed gases from 1100°C to 25°C is calculated, and the efficiencies of which (i.e. real isothemal TC efficiencies) are shown in red lines with open symbols (Fig. 9 (b)). The efficiencies of the proposed system for both CO_2 and H_2O splitting isothermal TC integrated with CH_4 are higher than the real and ideal efficiencies of isothermal TC.

This new approach has the potential to produce high-quality syngas and lower specific CO_2 emissions per mole of feedstock at the same time. The carbon emission per unit calorific value of fuels obtained after the reforming process of this new approach is calculated according to (12), compared with direct combustion of methane or direct combustion of syngas after solar reforming (Fig. 10). The heat needed for the enthalpy change of the CDR and SRM reactions is from the waste heat downstream the oxidation reactor, and then the products are combusted to calculate the carbon emissions per unit calorific value. Both the isothermal splitting of CO_2 and H_2O integrated with methane lower the specific CO_2 emissions as the isothermal TC is carbon-neutral and the calorific value of the methane is upgraded through the solar energy input by the enthalpy change of endothermic reactions (SRM, CDR and RWGS). The proportion of CO in the isothermal oxidation gas mixture and the isothermal TC heat storage rate increases with the increase of isothermal temperature, that's why the specific CO_2 emissions of this new system decrease. The carbon emissions per calorific value is lower for CO_2 splitting than that of H_2O splitting isothermal TC integrated with methane although the value of CDR is a bit higher than SRM shown in Fig. 10, mainly because of a higer conversion of CO_2 to CO than H_2O to H_2 at the same T_H.

The specific CO_2 emissions of the CO_2 and H_2O co-splitting isothermal TC process integrated with methane are also calculated in Fig. 7. The carbon emissions per unit calorific value of fuel obtained are in the range of 32.7 to 36.1 g/MJ for T_H=1600°C, which is between those of the splitting of H_2O and CO_2 integrated with methane independently. With the increase of H_2O/CO_2 ratio, the specific CO_2 emissions increase, for the H_2O splitting isothermal TC integrated with methane has a much larger specific CO_2 emission (Fig. 10(a)) than CO_2 (Fig. 10(b)) and more methane is needed to obtain nearly the same calorific value of syngas.
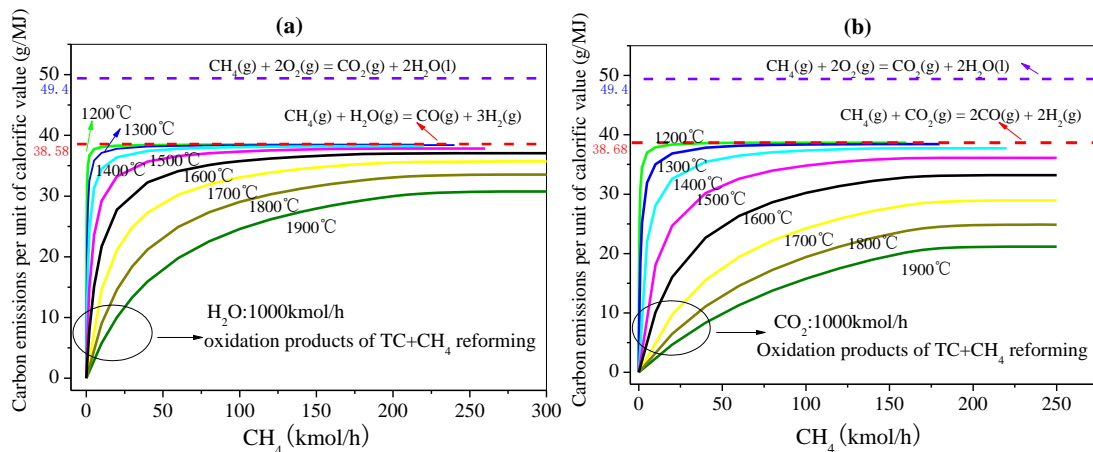

Fig. 10. Carbon emissions per unit calorific value of fuel obtained of the polygeneration system with isothermal TC splitting water (a) or CO_2 (b) TC integrated with CH_4 heat and gas recovery downstream.

3.3. Solar thermochemical polygeneration system integrated with CH_4

Recovery of waste heat and utilization of unreacted gas (e.g. H_2O or CO_2) downstream the reactor integrated with fossil fuels enable the establishment of a polygeneration system for simultaneous power and methanol production with the advantage of eliminating self-generation power plant which is conventionally needed for methanol production.
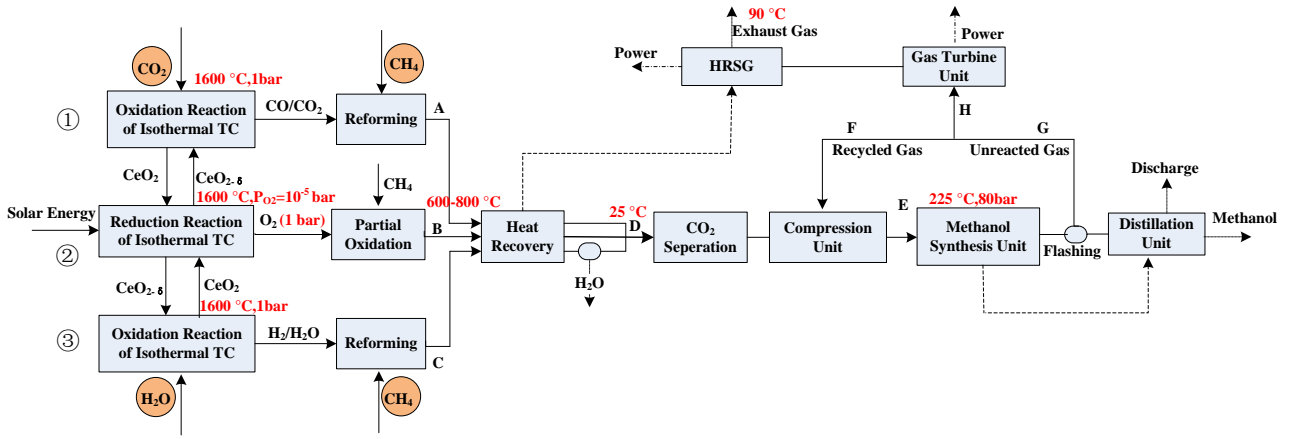
Fig. 11. Simplified process of solar thermochemical polygeneration system integrated with methane

A scheme [10] is conceptually proposed based on the splitting reaction in isothermal TC (Fig. 11), of which solar energy and methane are the main input energy and the purpose of the system is to generate power and methanol. The polygeneration system mainly consists of four parts: isothermal splitting of CO_2 and H_2O, methane reforming process, methanol synthesis reaction and combined cycle for power. The isothermal oxidation reaction of CO_2 or H_2O splitting TC produces CO or H_2 respectively with a large amount of CO_2 or H_2O remaining, while the reduction reaction produces pure oxygen. SRM, partial oxidation of methane and CDR are the main reactions occurring when methane is added to the products of isothermal TC, shown as A, B and C in Fig. 11, respectively. Before the mixing of these three streams (point D in Fig. 11), the latent heat is recovered and water is removed independently. Selexol method [11] is used to absorb CO_2 and the syngas is then compressed to a pressure of 80 bar. Methanol is synthesized at 225°C and purified in the distillation unit. The unreacted gas and exhaust gas are then combusted to produce power in a gas and steam combined cycle.

The inputs of the polygeneration system are the concentrated solar energy and complementary CH_4 and the outputs of which are power and methanol. We define a series of formulas to evaluate the performance and energy consumptions in the following part:

The Solar Energy Consumption is the ratio of solar energy to the mass of synthesized methanol:

$$E_{sol} = \overset{\cdot}{Q}_{solar} / \overset{\cdot}{m}_{CH_3OH} , \tag{14}$$

where $\overset{\cdot}{m}_{CH_3OH}$ is the mass flow rate of synthesized methanol, $\overset{\cdot}{Q}_{solar}$ (kW) is the solar energy input considering the solar absorption efficiency in (5).

The Fossil Fuel Consumption is the ratio of lower heating value of methane to the mass of synthesized methanol without considering the solar energy input, which is an important index indicating the utilization of CH_4 input:

$$E_{fos} = (\overset{\cdot}{n}_{CH_4,init} LHV_{CH_4,init} - W / \eta_0) / \overset{\cdot}{m}_{CH_3OH} , \tag{15}$$

where W is the net power output of the system, more methane will be directly added into the combined cycle to make sure that the value of W is positive; η_0 is the heat to power efficiency of the gas and steam combined cycle; If W / η_0 is positive, it represents the superfluous methane for the polygeneration system and if it is negative it represents the extra needed methane to produce enough power for methanol production except the initial input methane for reforming process.

The power generated of the polygeneration system is much smaller than the heating value of synthesized methanol from the calculation of the system in Fig. 11. First, we assume that the power of the polygeneration system comes from the CH_4 input (extra CH_4 is needed to make sure that the power output of the system is enough for the methanol production) instead of solar energy. Therefore, the system can be simplified to one output (methanol) and two inputs (solar energy and

CH_4 deducted the portion to generate power) system. Then the system is compared with state-of-the-art industrial methanol energy consumption making a further simplification to obtain a one input (solar energy) and one output (methanol deducted the portion from CH_4) system. Then we defined $\eta_{Solar-CH_3OH}$ as the heating value of methanol to the solar energy input of this one input and one output model:

$$\eta_{Solar-CH_3OH} = (\overset{\square}{R}_{CH_3OH} - (\overset{\square}{Q}_{CH_4} - \frac{W}{\eta_0}) \times \frac{3.6}{E}) \times LHV_{CH_3OH} / (\overset{\square}{Q}_{solar} \times 3600), \quad (16)$$

where $\overset{\square}{R}_{CH_3OH}$ (kg/h) is methane productivity; $\overset{\square}{Q}_{CH_4}$ (kW) is the total heating value of CH_4 input; E (GJ/ton), is the industrial energy consumption of CH_4 to produce methanol. LHV_{CH_3OH} (kJ/kg) is the lower heating value of methane. The Net Solar Energy Consumption is defined as the ratio of the solar energy to the mass of methanol of the simplified one input and one output model:

$$E_{sol,net} = \overset{\square}{Q}_{solar} \times 3600 / [\overset{\square}{Q}_{CH_3OH} - (\overset{\square}{Q}_{CH_4} - \frac{W}{\eta_0}) \times \frac{3.6}{E}], \quad (17)$$

In the configuration of water spliting and CO_2 splitting oxidation reaction, the ratio of CO_2 to H_2O is adjusted so that the optimal CO/H_2 ratio (usually 1:2) at point D in Fig. 11 is produced to synthesize methanol. Note that the CO/H_2 ratio at equilibrium of partial oxidation of methane ($CH_4+0.5O_2=CO+2H_2$) is exactly 1:2 at point B in Fig. 11. The temperature of isothermal oxidation products is 1600°C, which decreases to 600-850°C after the reforming process of methane. WGS reaction ($CO+H_2O=CO_2+H_2$) occurs and more hydrogen will be generated at the expense of CO with the decrease of the temperature. The three pathways are not mixed before heat recovery process, for the reason that there is still a large amout of water after SRM (pathway ③), which will react with the produced CO in pathway ①. The separation of water before mixing at point D in Fig. 11 is necessary to improve the yield of methanol. An advantage of the polygeneration system is that syngas is produced from the isothermal TC and methane reforming process without either WGS or RWGS reactors.
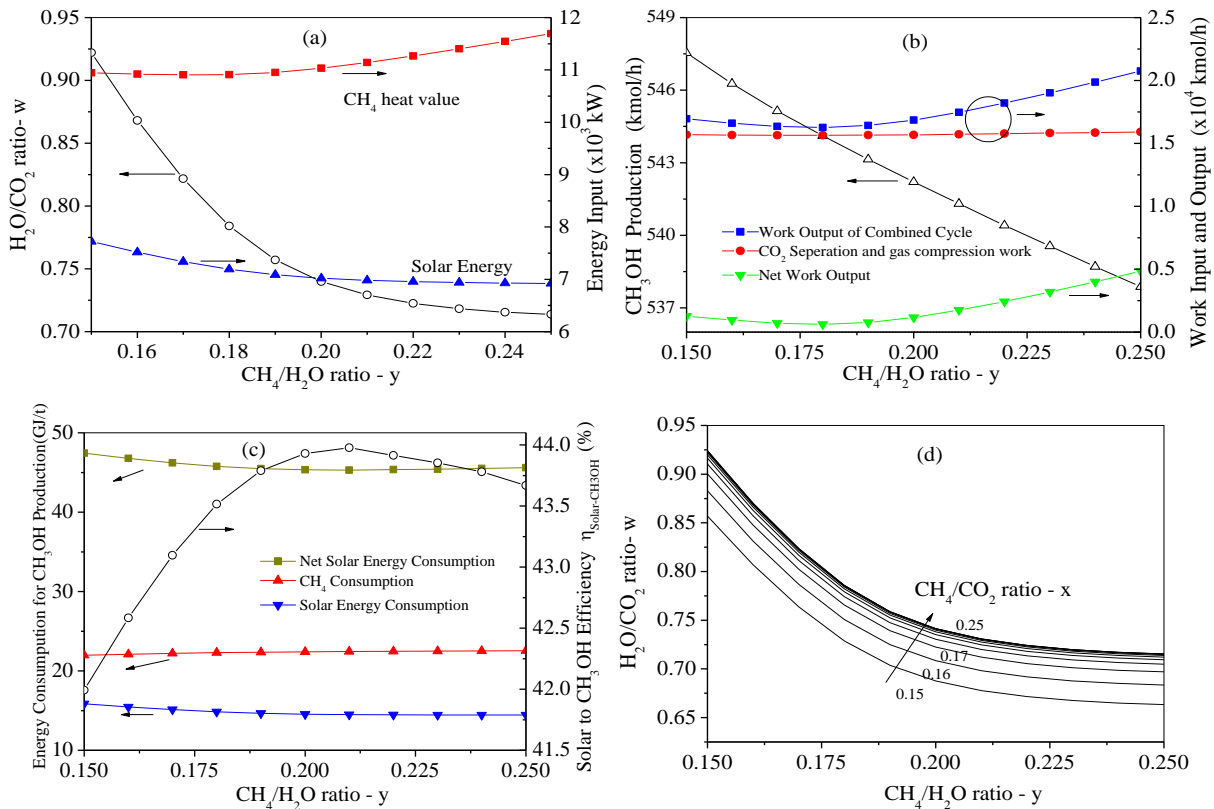
Fig. 12. (a) The optimal H_2O/CO_2 ratio and energy input varied with CH_4/H_2O ratio-y (b) Methanol production and work output varied with CH_4/H_2O ratio-y (c) Energy consumption for CH_3OH production varied with CH_4/H_2O ratio-y (d) The optimal H_2O/CO_2 ratio-w for various CH_4/H_2O ratio-y and CH_4/CO_2 ratio-x. The CH_4/CO_2 ratio-y of (a)(b)(c) is fixed to 0.21.

We assume that the CH_4/CO_2 ratio (pathway①) is fixed to 0.21 and the molar amount of CO_2 is 1000 kmol/h, while the CH_4/H_2O ratio (pathway ③) changes from 0.15 to 0.25, therefore a series of H_2O/CO_2 ratio will be obtained to make sure that the CO/H_2 ratio before methanol synthesis at point D in Fig. 11 is 1:2, shown in Fig. 12(a). The heating value of CH_4 and concentrated solar energy needed by the polygeneration system are also shown. The methanol production and work output are shown in Fig. 12(b), where the net work output is the work output of combined cycle unit deducting the CO_2 separation work and the compression work of the gas mixture before methanol synthesis. The net work output may be negative because the exhaust gas is not enough for the combined cycle to produce a large amount of power and it will be positive with the increase of CH_4/CO_2 ratio-x. The minimum net solar energy consumption of methanol is about 42.7 GJ/ton and maximum $\eta_{Solar-CH_3OH}$ is about 45% (Fig. 12(c)). The net solar energy consumption is much higher than solar energy consumption because the conversion of fossil fuel to methanol synthesis is deducted. The Fossil Fuel Consumption is about 22 GJ/ton, lower than typical values (about 28-40 GJ/ton) [12] in current industrial processes.
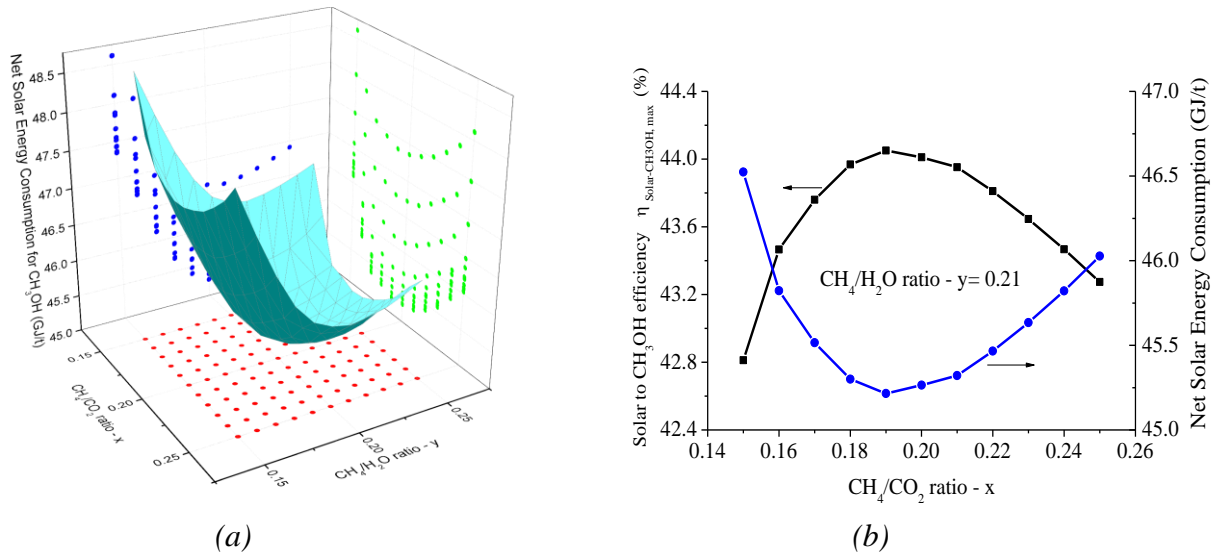

| (a) | (b) |

Fig. 13. (a)The Net Solar Energy Consumption for CH_3OH with CH_4/CO_2 ratio-x and CH_4/H_2O ratio-y ranging from 0.15-0.25 (b) The maximum $\eta_{Solar-CH_3OH}$ and minimum Net Solar Energy Consumption for CH_3OH production

CH_4/CO_2 ratio-x is changed from 0.15 to 0.25 with CH_4/H_2O ratio-y being changed simultaneously, and the H_2O/CO_2 ratio-w is optimized to make sure that the CO/H_2 ratio of the syngas before methanol synthesis is 0.5 (Fig. 12 (d)). The net solar energy consumption for CH_3OH is shown in Fig. 13(a) with a variety of CH_4/H_2O ratio-y and CH_4/CO_2 ratio-x. For each point of CH_4/CO_2 ratio-x from 0.15 to 0.25, the solar to CH_3OH efficiency reaches the maximum value when CH_4/H_2O ratio-y is around 0.21. Note that the operational and optical losses are not taken into account when calculating the solar to CH_3OH efficiency.

5. Conclusions

In this paper, we proposed a novel approach of simultaneously recovering waste heat and unreacted gas (e.g. H_2O or CO_2) downstream the reactor of isothermal thermochemical cycling (TC) by taking advantage of endothermic reactions of certain fossil fuels (e.g. CH_4). It has the potential to produce high-quality syngas and lower the temperature of isothermal oxidation products to the region of 600-850°C where mature heat exchangers are widely used. The solar-to-syngas efficiencies of the

proposed system for CO_2 and H_2O splitting at 1600°C are 45.7% and 38.1%, respectively, while the efficiencies of isothermal TC without CH_4 integration are only 21.0% and 6.4% without heat recovery. The isothermal TC heat storage rates of the proposed system for CO_2 and H_2O splitting processes are 46.1% and 15.7% at 1600°C, respectively. Compared with direct solar reforming or direct combustion of the same fossil fuels, this new approach features lower carbon emissions per unit calorific value of fuel obtained due to the incorporation of the isothermal TC upstream. Co-splitting of CO_2 and H_2O integrated with methane can obtain adjustable CO/H_2 ratio for various chemical synthesis process. A scheme of polygeneration of methane and power system is proposed as an example of this novel approach. It is possible to eliminate the self-generation power-plant which is conventionally needed for methanol production and no WGS or RWGS reactor is needed. Fossil fuel consumption for the production of a unit mass of methanol is about 22GJ/ton, lower than typical values in current industrial processes and the optimal solar to methane efficiency can be more than 44%.

Acknowledgments

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