A solar assisted polygeneration system integrating methane reforming and chemical looping combustion with zero carbon emission

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Abstract
The capture and utilization of CO₂ is aimed at conserving fossil fuels and reducing greenhouse gas emissions by providing an alternative carbon feedstock and closing the carbon cycle. This paper combines chemical-looping combustion (CLC) and methane reforming with CO₂ to accomplish CO₂ capture and utilization and proposes a novel polygeneration system to produce syngas, electricity, chilled water for cooling, and hot water. In this cycle, CLC, assisted by solar thermal energy, is employed to drive turbines to produce electricity and to separate CO₂ after the recovery of waste heat from high temperature gas. The reaction in the reformer of separated CO₂ and methane is driven by solar thermal energy to produce syngas. A part of the produced syngas fuel is sent to CLC such that CLC and methane reforming are coupled in this polygeneration system. The thermodynamic performance of the polygeneration system, including the energy and exergy efficiencies, are analyzed and compared on the basis of design conditions. In addition, the energy utilization diagram (EUD) analysis reveals the mechanism for the improvement and enhancement of the system performance in the novel system. The results indicate that the energy and exergy efficiencies approach 71% and 56%, respectively. Meanwhile, the instantaneous solar share is approximately 46%, and the net solar-to-exergy efficiency approaches 25%. The maximum exergy destruction of the system occurred in the chemical reaction sub-system.

Key words: Polygeneration system, Chemical-looping combustion (CLC), Methane reforming, Thermodynamic analysis

1. Introduction

Carbon dioxide (CO₂) emission through the combustion of fossil fuels is the main contributor to global warming and climate change. CO₂ capture and utilization is regarded as a possible way to prevent carbon emission and is a medium-term solution to stabilize atmospheric CO₂ concentrations (Pans et al. 2013). However, conventional CO₂ capture technologies including post-combustion separation, pre-combustion and oxy-fuel combustion require additional energy consumption and economic cost. Compared to these capture technologies, chemical-looping combustion (CLC) is an advanced combustion technology for the separation of CO₂ with a low energy consumption (Adanez et al. 2012). Additionally, the methane reforming process with CO₂ used to produce synthesis gas (syngas), is regarded as a valuable transformative way to utilize CO₂ (Ashcroft et al. 1991; Schuurman et al. 1998; Wei and Iglesia 2004). Achieving CO₂ separation, utilization and integration in energy systems is one of the alternative ways to control the greenhouse effect.

As a CO₂ capture technology, the CLC concept was initially proposed by Richter and Knoche to improve thermal efficiency in fuel combustion systems in 1983. In the past three decades, many researchers studied the CLC cycle including oxygen carriers (Gayán et al. 2012; Arjmand et al. 2014), gaseous and solid fuels (Anthony 2008), and reactor (Harichandan and Shamim 2014; Wang et al. 2014), or integrated CLC and power cycles to construct new
energy systems (Pans et al. 2013; Ozcan and Dincer 2014). In the investigations on CLC power cycle, CLC is employed to separate and capture CO₂ and achieve high thermal efficiency as much as possible. Ishida integrated CLC to construct a new gas turbine power-generation system to reduce the exergy loss caused by the conversion of fuel energy in 1987, and the expected thermal efficiency reaches to 50.2% (Ishida 1987). With the development and research of the CLC technology, there are many kinds of CLC power cycles driven by sygas (mainly carbon monoxide (CO) and hydrogen) (Spallina et al. 2014), hydrogen or methanol (Zhang et al. 2009), etc. These studies reported that conventional power cycles integrated with CLC could achieve lower energy destruction and higher efficiency in the capture of CO₂. From the current study status and trend, it can be concluded that renewable energy integrated into the CLC coupled power cycle is more widely utilized to reduce the exergy destruction of reaction process and decrease the energy consumption of CO₂ separation.

As a CO₂ utilization technology, CO₂ reforming of methane was proposed by Fischer and Tropsch, in 1928, to produce syngas. To achieve the goals of high transformation rate and energy efficiency, many researchers have investigated different aspects of the process such as the reforming mechanism, reaction catalyst, supporting effect and carbon deposition. The active catalyst is needed to improve the transformation rate of the reactant. The results based on large numbers of experiments indicate that the Ni metal is a relatively ideal reaction catalyst (Bradford and Vannice 1996; Tsipouria V 1999; Jing et al. 2004; Jing et al. 2004). Additionally, the supporting effect of catalysts dramatically influences the CO₂ reforming of methane, and in particular, the acidity and basicity of the carrier material directly affects the structure and activity of catalyst. The experiments from Bradford and Vannice (Bradford and Vannice 1996) have indicated that solid MgO with high basicity is an ideal carrier to absorb gases. However, the industrialization of CO₂ methanol reforming has not been realized. The main reasons for this are the formation of coke and deactivation of the catalyst. The effective methods for decreasing coke formation include the utilization of compound catalysts and adoption of a reasonable temperature for coke elimination. In general, CO₂ reforming of methane can occur continuously and achieve a higher transformation rate by controlling the reaction temperature and adopting effective catalysts and reaction carriers.

The additional energy may be needed to assist the reduction reaction of oxygen carriers in CLC and the CO₂ reforming of methane (Jafarian et al. 2014a). Solar thermal energy is a type of renewable energy that has been integrated and applied in many energy systems, in recent years, to tackle the worldwide energy and environmental problems (Behar et al. 2013). Consequently, studies on utilizing solar energy to drive reactors in the CLC and the CO₂ reforming of methane have become a research hotspot.

For the integration of CLC with solar thermal energy, many researchers focused on different aspects from metal oxide, key parameters, integration structure, and so on. The hybrid solar CLC system was first proposed by Hong et al. (Hong and Jin 2005), and then further developed by Jafarian et al (Jafarian et al. 2013a). Hong et al. designed the integrated CLC system with metal oxide (NiO) as an oxygen carrier, the exergy efficiency of the proposed cycle with solar thermal energy with the temperature of about 500-600°C is expected to be 4 percentage points higher than the conventional gas turbine combined cycle at a turbine inlet temperature of 1200°C (Hong and Jin 2005), and the exergy efficiency of the cycle with the 450-550°C solar thermal energy is more than 60% and the system is approximately 9–15 percentage points higher efficiency than the conventional combined cycle with CO₂ separation (Hong et al. 2006). Moreover, Hong et al. proposed a novel solar-hybrid gas turbine combined cycle integrated with methanol-fueled CLC (Hong et al. 2010). Solar thermal energy with 150-300°C is utilized to drive the reduction in Fe₂O₃ with methanol in the reduction reactor, and the exergy efficiency may reach 58.4% at a turbine inlet temperature of 1400°C. Differently, Jafarian et al. (Jafarian et al. 2013a) focused the temperature variations during the conversion of an oxygen carrier particle exposed to high intensity solar heat flux. The effects on the particle conversion and maximum temperature of various operating parameters i.e. particle size, external heat and mass transfer, radiation heat flux intensity, methane mole fraction and surrounding temperature. Jafarian et al. (Jafarian et al. 2013b) proposed a novel solar–CLC hybrid system for steady base-load power production, despite diurnal fluctuations in solar input. The simulation predicts that 70% of the absorbed solar energy in solar fuel reactor is stored in the particles, while 14.25% of the total energy is lost due to re-radiation through solar fuel reactor aperture. The solar energy is also used efficiently, with the exergy efficiency of the proposed solar hybrid CLC being 7% higher than the reference CLC system without solar input when averaged over the 24 h day.

At the aspects of integration system structure, Zhang et al. (Zhang et al. 2016) designed a trigeneration system that the concentrated solar heat at approximately 350°C is utilized to drive the CLC, and the annually average efficiency of
solar-fuel-power can be about 21%, with approximately 5 percentage points higher than that of solar thermal power system. Jafarian et al. (Jafarian et al. 2014b) proposed a novel hybrid solar CLC, in which the oxygen carrier particles in the CLC system is utilized to provide solar thermal energy storage, and it achieve a solar fraction of up to 60% while providing sufficient storage to achieve continuous base-load power generation. Moreover, Jafarian et al. (Jafarian et al. 2014c) designed two integrated configurations with CLC and solar energy, one case is that the outlet from the air reactor is fed directly to a gas turbine while in another case an after-burner, also firing methane, is added to increase the gas turbine inlet temperature. The compared results show that the first law efficiency of the cycle employing an after-burner is higher 6.0% than the cycle without the after-burner. However, this is achieved at the cost of decreasing the solar share from 60.0%, without the after-burner, to 41.4% with it.

In addition, for the integration of solar thermal energy with CO₂ reforming of methane, Anikeev et al. (Anikeev et al. 1998) designed a solar volumetric thermochemical reactor/receiver with a catalytic absorber, tested the thermochemical conversion efficiency of the CO₂ reforming of methane in the high flux solar furnace and achieved a 30% overall efficiency with the Ni–Cr catalytic absorber. Wang et al. (Wang et al. 2015) constructed a metallic foam solar thermochemical reactor with a parabolic dish concentrator and analyzed the thermochemical performance of a solar driven CO₂ methane reforming process using a joint inversion method based on chemical process software and the finite volume method. Kodama et al. (Kodama et al. 2002) utilized solar thermal energy to drive the reforming reaction with Ni catalyst and achieved a 90% transformation rate of methane.

The originality of this work lies in proposing a novel polygeneration system that integrates solar-assisted CO₂ reforming of methane and CLC, and achieves the both CO₂ capture and utilization in a distributed energy system. Its thermodynamic performance is analyzed and compared to that of a solar-hybrid trigeneration system with CLC. The exergy destructions are also analyzed to find the sources and locations of irreversibility. Furthermore, an energy utilization diagram (EUD) analysis is presented as a point of comparison between the novel system and the referenced system and to reveal the mechanism of the improvement in system performance in the novel system.

2. System description

We proposed a solar-hybrid trigeneration system integrated methane CLC shown in Fig. 1 in literature (Wang and Fu 2016). The CLC reactions driven by solar heat produce the high-temperature (HT) gas to drive gas turbine to generate electricity. The waste heat accompanied of the HT gas is then entered into the absorption chiller and heat exchanger to produce chilled water and domestic hot water sequentially. Finally, the mixture gas of CO₂ and water vapor through CLC reaction is cooled down and CO₂ is separated.

Fig. 1 The reference trigeneration system (Wang and Fu 2016)
Fig. 2 The novel polygeneration system that couples solar-assisted CO\(_2\) reforming of methane with chemical looping combustion

The studied boundary is ended at the CO\(_2\) separation in the reference trigeneration system (Wang and Fu 2016), and the CO\(_2\) storage and utilization are not considered. To enlarge and improve the reference system, we designed a novel polygeneration system that couples solar-assisted CO\(_2\) reforming of methane with CLC in Fig. 2. The novel system includes a methane reforming sub-system, a solar-assisted CLC sub-system, a power generation sub-system, a waste heat utilization sub-system and a CO\(_2\) separation sub-system. The CO\(_2\) reforming of methane in the reformer is an endothermic reaction driven by the solar thermal energy to generate syngas. Then, the generated syngas fuel is introduced into the solar-hybrid CLC sub-system to produce power, and the waste heat of exhaust gas from the turbine is recovered to produce chilled water for cooling and domestic hot heat. Finally, the mixed gas of CO\(_2\) and H\(_2\)O is cooled, and CO\(_2\) is separated and again introduced into the reformer as the material for the reforming reaction.

The CLC sub-system coupled with the CO\(_2\) reforming of methane is mainly employed to generate HT gas to drive gas turbine. This sub-system consists of reforming reactor, fuel reactor and air reactor, and the main reactions involved in the system are described below:

(1) Reforming reactor

\[
CO_2 + CH_4 \rightarrow 2CO + 2H_2, \quad \Delta H = 246.9 \text{kJ/mol} \tag{1}
\]

Methane (stream 1) reacts with the separated CO\(_2\) (stream 13) from the CO\(_2\) separator (Sep) in the reformer, which the solar heat collected from the solar tower provides the necessary heat to the endothermic reaction. The generated HT syngas including CO and H\(_2\) (stream 2) is cooled down the normal temperature (stream 3), and then is split to two flows (stream 4 and stream 5). One half of syngas (stream 4) being fuel is introduced into the fuel reactor in the CLC sub-system, and another half of syngas (stream 5) being one kind of product in the polygeneration is collected and stored.

(2) Fuel reactor

Ca-based oxygen carriers have shown high reactivity and good performance working at high temperature, therefore, the solid CaSO\(_4\) (steam 20) being the oxygen carrier is cyclically between the fuel reactor and the air reactor in the CLC sub-system, the solid CaSO\(_4\) (steam 20) is utilized as an oxygen carrier. Consequently, the syngas (stream 4) is pressurized (stream 6), and then is heated by solar heat and reacts with the CaSO\(_4\) particles in the reduction reactor (Red) as follows:
\[
\frac{1}{4} \text{CaSO}_4 + \text{CO} \rightarrow \frac{1}{4} \text{CaS} + \text{CO}_2, \quad \Delta H = -43.54 \text{kJ/mol} \tag{2}
\]

\[
\frac{1}{4} \text{CaSO}_4 + \text{H}_2 \rightarrow \frac{1}{4} \text{CaS} + \text{H}_2\text{O}, \quad \Delta H = -6.13 \text{kJ/mol} \tag{3}
\]

The generated solid CaS (stream 22) is entered into the oxidation reactor (Oxd) to participate the reaction, and the generated gas including CO$_2$ and water vapor (stream 7) is again heated by the HT CaSO$_4$ (stream 20) in the gas-solid heat exchanger to drive gas turbine (GT2).

### (3) Air reactor

\[
\frac{1}{2} \text{CaS} + \text{O}_2 \rightarrow \frac{1}{2} \text{CaSO}_4, \quad \Delta H = -478.99 \text{kJ/mol} \tag{4}
\]

The ambient air (stream 14) is compressed to the air with the HT and high-pressure (stream 15), and then is transported to the oxidation reactor (Oxd). The O$_2$ in the air reacts with the solid CaS (stream 20) to generate the HT CaSO$_4$ (stream 20). The generated HT gas including mainly N$_2$ and unreacted O$_2$ (stream 16) is entered to gas turbine (GT1) to produce electricity.

The two stream flows of gas with the HT and high-pressure (stream 7 and stream 16) are introduced into gas turbines (GT2 and GT1) respectively to drive generator to produce electricity. The HT exhausted gas (stream 9 and stream 17) is used to drive absorption chiller (AC) to produce chilled water for space cooling. The middle-grade heat is recovered and utilized through the AC. The exhausted gas from the AC (stream 10 and stream 18) is cooled in the separator and CO$_2$ (stream 13) and H$_2$O (stream 14) are separated. Thus, the separated CO$_2$ is introduced into the reforming reactor and it realizes a whole cycle.

### 3. Simulation methodology

#### 3.1 Assumptions

The polygeneration system coupled with CLC and methane reforming is simulated by Aspen Plus™. The following assumptions are made:

i) Gaseous species are considered to be ideal gases.

ii) There is no gas or material loss in the system during the operation process.

iii) The system is assumed to be at steady-state and under a steady flow.

iv) All the reactors are modeled as a RGibbs unit, which uses minimization of the Gibbs free energy when the phase and chemical equilibrium for the process are achieved without any specification of possible reactions.

The design states and operational conditions are listed in Table 1.

#### 3.2 Mathematical equations

##### 3.2.1 Performance indicators

### (1) Energy efficiency

From the viewpoint of the first law of thermodynamics, energy efficiency is employed to evaluate the performance of energy utilization of the polygeneration system. It can be written to:

\[
\eta_{en} = \frac{W_{net} + Q_c + Q_h + Q_{sol}}{Q_c + Q_h + Q_{sol}}
\tag{5}
\]

where $\eta_{en}$ is the energy efficiency of the polygeneration system, $W_{net}$ is the net power output; $Q_c$, $Q_h$ and $Q_{sol}$ are energy outputs of cooling, domestic hot water and syngas respectively, $Q_c$ and $Q_{sol}$ are the energy inputs of methane and solar heat respectively.

### (2) Exergy efficiency

From the viewpoint of the second law of thermodynamics, exergy efficiency is expressed to:
\[ \eta_{ex} = \frac{E_{x_f} + E_{x_c} + E_{x_h} + E_{x_{sy}}}{E_{x_f} + E_{x_{sol}}} \]  

(6)

where \( \eta_{ex} \) is the energy efficiency of the polygeneration system, \( E_{x_f} \) is the exergy of net power output; \( E_{x_c} \), \( E_{x_h} \) and \( E_{x_{sy}} \) are exergy outputs of cooling, domestic hot water and syngas respectively, \( E_{x_f} \) is the exergy input of methane. \( E_{x_{sol}} \) is the exergy of solar thermal energy input of the novel hybrid system and:

\[ E_{x_{sol}} = Q_{sol} \cdot \eta_{s,ex} \]  

(7)

where \( \eta_{s,ex} \) is the maximum exergy efficiency of solar radiation at earth surface. In the standard atmospheric conditions, \( \eta_{s,ex} = 0.9171 \) (Chu and Liu 2009) when the solar zenith angle is 0. The chemical exergy of syngas is calculated as:

\[ E_{x_{sy}} = \sum x_i e_{x_{sy,i}}^0 + R T_0 \sum x_i \ln(x_i) \]  

(8)

where \( x_i \) is the mass fraction of syngas, \( T_0 \) is the reference temperature, \( e_{x_{sy,i}}^0 \) is the standard chemical exergy of gas species, and \( R \) is the gas constant.

| Table 1 Main design states | Operating conditions | Source |
|---------------------------|----------------------|--------|
| Ambient temperature (°C)  | 25                   |        |
| Ambient pressure (bar)    | 1                    |        |
| Direct solar radiation (W/m²) | 1000           |        |
| Solar heat collection efficiency (%) | 59     | (Hong et al. 2010) |
| Optical efficiency of solar collector field (%) | 65     | (Hong et al. 2010) |
| Isentropic efficiency of the air compressor (%) | 88     | (Hong et al. 2010) |
| Chilled water temperature (T_{ch}/T_{sw}; °C) | 9/14 |        |
| Hot water temperature (°C) | 65                   |        |
| COP (coefficient of performance) of the AC | 1.3   | (Marcos et al. 2011) |
| Gas outlet temperature of the AC (°C) | 180   |        |
| Gas outlet temperature of the heat exchanger (°C) | 110   |        |
| LHV of methane (MJ/Nm³) | 35.88     |        |
| LHV of CO (MJ/Nm³) | 12.64     |        |
| LHV of H₂ (MJ/Nm³) | 10.79     |        |
| Mole of input methane (kmol/h) | 10     |        |
| **Reformer**               |                      |        |
| Operating temperature (°C) | 1100                 | (Kodama et al. 2002) |
| Operating pressure (bar)  | 1                    |        |
| **Reduction reactor**     |                      |        |
| Operating temperature (°C) | 900                  | (Tian 2010) |
| Operating pressure (bar)  | 20                   |        |
| **Oxidation reactor**     |                      |        |
| Operating temperature (°C) | 900                  | (Tian 2010) |
| Operating pressure (bar)  | 20                   |        |

(3) Instantaneous solar share

The instantaneous solar share (ISS) is employed to measure the contribution of the solar thermal energy in the polygeneration system, and it is defined the solar ratio of the total energy inputs. Consequently, it is expressed to:
\[
ISS = \frac{Q_{sol}}{Q_{sol} + Q_f}
\]  

(9)

(4) Solar-to-exergy efficiency
To compare the contribution difference of solar heat in the new and reference systems, the solar-to-exergy efficiency is defined to:
\[
\eta_{ex,sol} = \frac{Ex_{poly} - Ex_{ref}}{Ex_{sol}}
\]

(10)

where \( \eta_{ex,sol} \) is the solar-to-exergy efficiency, \( Ex_{poly} \) and \( Ex_{ref} \) are the exergy outputs of the new polygeneration system and the solar reference system, respectively.

### 3.2.2 Balance equations

(1) Mass balance
The mass balance for the new system can be expressed to:
\[
\sum m_{in} = \sum m_{out}
\]

(11)

where \( m_{in} \) and \( m_{out} \) denote the inlet and outlet mass flow rate of all streams, respectively.

(2) Energy balance
The overall energy balance for the polygeneration system can be presented to:
\[
\sum Q_{in} = \sum Q_{out} + \sum Q_{loss}
\]

(12)

where \( Q_{in} \), \( Q_{out} \) and \( Q_{loss} \) denote the inlet, outlet and loss of energy, respectively. During the calculation of energy efficiency, the following energy equations are used:
\[
W_{net} = W_{GT1} + W_{GT2} - W_{comp1} - W_{comp2}
\]

(13)

\[
Q_f = m_{CH4} LHV_{CH4}
\]

(14)

\[
Q_{ch} = m_{syngas} (x_{CO} LHV_{CO} + x_{H2} LHV_{H2})
\]

(15)

\[
Q_{sol} = \frac{G_f q_{sol,th}}{\eta_{col}}
\]

(16)

where \( W_{GT1} \) and \( W_{GT2} \) are the power outputs of gas turbine 1 and gas turbine 2, respectively, \( W_{comp1} \) and \( W_{comp2} \) are the power consumptions of compressor 1 and compressor 2, respectively, \( LHV_{CH4} \), \( LHV_{CO} \) and \( LHV_{H2} \) are the lower heating value (LHV) of methane, CO and H\(_2\), respectively, \( m_{CH4} \) and \( m_{syngas} \) are the mass of methane and syngas respectively, \( x_{CO} \) and \( x_{H2} \) denote the mass fractions of CO and H\(_2\) in the syngas respectively, \( G_f \) denotes the mole flow of fuel, \( q_{sol,th} \) is the absorption solar heat of 1 mole of fuel in the chemical reaction; \( \eta_{col} \) is the solar heat collection efficiency.

(3) Exergy balance
Similarly, the overall exergy balance can be presented to:
\[
\sum Ex_{in} = \sum Ex_{out} + \sum Ex_{dest}
\]

(17)

where \( Ex_{in} \), \( Ex_{out} \) and \( Ex_{dest} \) denote the inlet, outlet and destruction of exergy, respectively.

### 3.3 EUD methodology
The energy utilization diagram (EUD) proposed by Ishida (Ishida et al. 1987) is adopted as an effective method of graphical exergy analysis to reveal the mechanism of the key processes in the complex cycles, especially the complicated chemical/thermal processes. The EUD methodology is based on the definition of energy level.
\( A = \Delta E/\Delta H = 1 - T_0 \Delta S/\Delta H \), and the variation in both the energy level and energy quantity are shown graphically using \( A-\Delta H \) coordinates. In the EUD diagram, the \( x \)-coordinate is the energy change (\( \Delta H \)) and the \( y \)-coordinate is the energy level (\( A \)). The energy donor and acceptor are involved in an energy transformation process and the shaded area surrounded by their curves is the exergy destruction. The EUD methodology is employed to analyze and compare the exergy destructions of the novel system and the reference system, which consists of the chemical reaction sub-system, the power generation sub-system and the heat exchange sub-system.

4 Results and discussions

4.1 Thermodynamic performances

The calculated results of the state points are summarized in Table 2.

| State point | \( T \) (\(^\circ\)C) | \( P \) (bar) | \( G \) (kmol/h) | Mole composition |
|-------------|-----------------|--------------|----------------|-----------------|
| 1           | 20              | 1            | 10             | 1               |
| 2           | 1100            | 1            | 40             | 0.5 0.5         |
| 3           | 25              | 1            | 40             | 0.5 0.5         |
| 4           | 25              | 1            | 20             | 0.5 0.5         |
| 5           | 25              | 1            | 20             | 0.5 0.5         |
| 6           | 563             | 20           | 20             | 0.5 0.5         |
| 7           | 900             | 20           | 20             | 0.5 0.5         |
| 8           | 1240            | 20           | 20             | 0.5 0.5         |
| 9           | 517             | 1            | 20             | 0.5 0.5         |
| 10          | 181             | 1            | 20             | 0.5 0.5         |
| 11          | 106             | 1            | 20             | 0.5 0.5         |
| 12          | 70              | 1            | 10             | 1               |
| 13          | 70              | 1            | 10             | 1               |
| 14          | 20              | 1            | 50             | 0.79 0.21       |
| 15          | 548             | 20           | 50             | 0.79 0.21       |
| 16          | 1290            | 20           | 40             | 0.83 0.17       |
| 17          | 589             | 1            | 40             | 0.83 0.17       |
| 18          | 184             | 1            | 40             | 0.83 0.17       |
| 19          | 106             | 1            | 40             | 0.83 0.17       |
| 20          | 1300            | 20           | 5              | 1               |
| 21          | 1053            | 20           | 5              | 1               |
| 22          | 900             | 20           | 5              | 1               |

The energy and exergy efficiencies of the polygeneration system and the reference system are listed in Table 3. The total energy efficiency of the new system is approximately 71.69\%, which is 4.40\% larger than the reference system. The exergy efficiency of the new system is approximately 56.58\%, which is 1.13\% larger than the reference system. Compared to the products of the reference system, the syngas and electricity are the main products of the polygeneration system and they account for 54.32\%. For the same methane inputs, the electricity, chilled water and hot water of the reference system have larger values than those in the polygeneration system because only half of syngas from the methane reformer is utilized to drive the CLC sub-system while the other half of syngas is collected as the product.

| Efficiency | Syngas | Power | Cooling | Hot water |
|------------|--------|-------|---------|-----------|
| Polygeneration system | Energy | 71.69 | 29.18 | 25.14 | 15.77 | 1.60 |
| Exergy | 56.58 | 29.58 | 26.03 | 28.90 | 2.24 |
| Reference system (Wang and Fu 2016) | Energy | 67.29 | - | 36.15 | 28.90 | 2.24 |
| Exergy | 55.45 | - | 53.04 | 2.02 | 0.39 |
Table 4  Exergy performance of the new system and reference system

| Units                  | Parameters        | New system  | Ratio (%) | Reference system | Ratio (%) |
|------------------------|-------------------|-------------|-----------|------------------|-----------|
|                        |                   | Exergy      |           | Exergy           |           |
|                        |                   | (kJ/kmol-CH₄) |           | (kJ/kmol-CH₄)    |           |
| Input                  | Total input       | 1418928.20  | 100.00    | 1203246.26       | 100.00    |
|                        | Methane fuel      | 843836.60   | 59.47     | 843836.60        | 70.13     |
|                        | Solar thermal energy | 575091.60  | 40.53     | 359409.66        | 29.87     |
| Output                 | Total output      | 802829.58   | 56.58     | 667200.05        | 55.45     |
|                        | Syngas            | 419718.96   | 29.58     | —                | —         |
|                        | Net power         | 369347.01   | 26.03     | 638201.81        | 53.04     |
|                        | Cold exergy       | 13763.60    | 0.97      | 24305.57         | 2.02      |
|                        | Heat exergy       | 1418.93     | 0.10      | 4692.66          | 0.39      |
| Loss                   | Total destruction | 616098.62   | 43.42     | 536046.21        | 44.55     |
| Chemical reaction      | Reformer          | 76338.34    | 5.38      | —                | —         |
|                        | Reduction reactor | 43844.88    | 3.09      | 64975.30         | 5.40      |
|                        | Oxidation reactor | 100885.79   | 7.11      | 129830.27        | 10.79     |
| Heat exchange          | Heat exchanger    | 46257.06    | 3.26      | —                | —         |
|                        | Splitter          | 10216.28    | 0.72      | —                | —         |
|                        | Gas-solid heat exchanger | 10925.75 | 0.77     | 10107.27         | 0.84      |
|                        | Absorption chiller | 29655.60   | 2.09      | 45001.41         | 3.74      |
|                        | Heat water exchanger | 27810.99 | 1.96     | 34292.52         | 2.85      |
|                        | CO₂ Separation    | 14614.96    | 1.03      | 19973.89         | 1.66      |
|                        | Exhaust gas       | 31358.31    | 2.21      | 48250.17         | 4.01      |
| Power                  | Compressor 1      | 45973.27    | 3.24      | 52100.56         | 4.33      |
|                        | Compressor 2      | 55905.77    | 3.94      | —                | —         |
|                        | Gas turbin1       | 82439.73    | 5.81      | 85430.48         | 7.10      |
|                        | Gas turbin2       | 39871.88    | 2.81      | 45964.01         | 3.82      |
| Efficiency             | Energy (%)        | 71.69       |           | 67.07            |           |
|                        | Exergy (%)        | 56.58       |           | 55.45            |           |
|                        | ISS (%)           | 46.35       |           | 31.89            |           |
|                        | Solar-to-exergy (%) | 25.38     |           | 24.65            |           |

Table 4 shows the exergy utilization and destruction of the novel system and the reference system. Compared to their inputs, the solar thermal energy input in the new polygeneration system is about 1.6 times than that in the reference system at the same methane input, and more solar energy is utilized in the new polygeneration system. At the higher solar proportion, the polygeneration system has the higher energy and exergy efficiencies. This point indicates that the input middle-grade solar heat more effectively assists the chemical reactions to transfer the heat energy into the chemical energy in the new polygeneration system. The net solar-to exergy efficiency of the novel system is higher 0.73% than that of the reference system and approaches 25.38%; and the instantaneous solar share in the poly-generation system, 46.35% is much larger than that of the reference system, 31.89%.

Analyzed the mechanism of efficiency improvement from the exergy destructions, the total exergy destruction at the same methane input in the new polygeneration system is more than in the reference system while the total exergy efficiency of the polygeneration system is higher. The methane chemical energy, assisted by the solar thermal energy, is utilized to produce syngas by the reforming reaction in the polygeneration system, however, half of syngas is collected as product, and the other half is used to produce power, cooling and heat. Consequently, the energy loss during syngas...
utilization becomes less. Compared to the exergy destructions of components between the two systems, the largest exergy destructions both occur in the chemical reaction units, which are approximately 15.58% and 16.19%, respectively. The exergy destruction of the chemical reaction unit in the new system including three reactors is less than the reference system. It shows that the methane reforming achieves efficient energy utilization through the substitution syngas for methane in the CLC process.

4.2 Graphical exergy analysis of the system

4.2.1 Chemical reaction sub-system

The chemical reaction sub-system consists of the methane reforming reaction and the reactions in the CLC. Figure 3 shows the reforming process in the polygeneration system. In the methane reforming reaction, the solar thermal energy acts as the energy donor, which is illustrated by the $A_{ed}$ curve. The average solar thermal energy level is 0.78, corresponding to a reforming reaction temperature of 1100°C. The $A_{ea}$ curve stands for the energy acceptor, which depends on the reforming reaction, including the preheating reactant and chemical reaction processes. The shaded area between the $A_{ed}$ and $A_{ea}$ curves, 76.3 kJ/mol-CH$_4$, is the exergy destruction of the methane reforming process.

![Fig. 3 EUD for the methane reforming in the polygeneration system](image1)

![Fig. 4 EUD for the chemical looping combustion in the polygeneration system](image2)
Figure 4 displays the EUD of the CLC reactions in the polygeneration system. The shaded area on the left side stands for the exergy destruction of the reduction reaction, in which the $A_{ed1}$ curve represents the energy level of solar thermal energy that acts as the energy donor to supply the heat of the endothermic reaction. The average solar thermal energy level is 0.74, corresponding to a reduction reaction temperature of 900°C. In addition, the energy level of the reduction reaction is represented by $A_{ea1}$. The exergy loss in the reduction process is approximately 43.8 kJ/mol-CH$_4$. The shaded area on the right side stands for the exergy destruction of the oxidation reaction, in which the $A_{ed2}$ curve acts as the energy donor. The heating processes of CaS and air illustrated by the $A_{ea2}$ and $A_{ea3}$ curves, respectively, act as the energy acceptors. CaS and air are heated to the turbine inlet temperature (1200°C). The shadow area between the energy donor and the energy acceptors is 100.9 kJ/mol-CH$_4$, representing the exergy destruction in the oxidation reaction process. As a result, the total exergy destruction of the CLC process is 144.7 kJ/mol-CH$_4$, and the overall exergy destruction of the chemical reaction sub-system in the polygeneration system is 221.0 kJ/mol-CH$_4$.

Compared to the polygeneration system, the EUD for the methane-fueled CLC reactions in the reference system is shown in Fig. 5. The EUD for the CLC in the reference system is similar to that in the polygeneration system. The shaded area on the left side stands for the exergy destruction of the reduction reaction. The solar thermal energy acting as the energy donor is represented by the $A_{ed1}$ curve, and its level is 0.74. In addition, the energy level of the reduction reaction is represented by $A_{ea1}$. The exergy loss in the reduction process is 64.9 kJ/mol-CH$_4$. The shaded area on the right side stands for the exergy destruction of the oxidation reaction and the exergy destruction in the oxidation reaction process is 129.8 kJ/mol-CH$_4$. Hence, the total exergy destruction of the CLC process in the reference system is 194.7 kJ/mol-CH$_4$. Comparing between the two systems, the exergy destruction of the CLC process in the polygeneration system (144.7 kJ/mol-CH$_4$) is lower than that in the reference system (194.7 kJ/mol-CH$_4$) because only half of the syngas is used in the reaction in the CLC sub-system for the polygeneration system. However, the overall exergy destruction of the chemical reaction sub-system in the polygeneration system (221.0 kJ/mol-CH$_4$) is higher than that in the reference system because of the extra exergy loss caused by the reformer.

4.2.2 Power sub-system

Figure 6 shows the EUD for the power sub-system in the polygeneration system. The power produced by the two gas turbines acts as the energy donor, as illustrated by the $A_{ed,GT}$ curve in Fig. 7. The width of the $A_{ed,GT}$ curve stands for the output power of the gas turbines. A part of the generated power is used to drive the two compressors ($A_{ea,comp1}$ and $A_{ea,comp2}$), and the rest is the net power output ($W_{net}$). The exergy destruction in the power sub-system is mainly caused by the gas turbines and compressors and is approximately 224.0 kJ/mol-CH$_4$.

Figure 7 shows the exergy destruction of the power sub-system in the reference system, which is from the compressors and two turbines. The energy donor and acceptors are similar to those in Fig. 6. The total exergy destruction in the power sub-system, including the gas turbines and compressor, is approximately 183.4 kJ/mol-CH$_4$. 
For the two power sub-systems, the exergy destruction in the polygeneration system (161.9 kJ/mol-CH$_4$) is approximately 22% higher than that in the reference system (132.5 kJ/mol-CH$_4$). This happens because of the following two points: 1) only half of the syngas produced from the methane reforming is utilized in the power sub-system in the polygeneration system, and 2) the net output power in the polygeneration system ($W_{\text{net}} = 369.3$ kJ/mol-CH$_4$) is lower than that in the reference system ($W_{\text{net}} = 638.2$ kJ/mol-CH$_4$) because of higher power consumption by the extra compressor.

![Fig. 6 EUD for the power sub-system in the polygeneration system](image1)

![Fig. 7 EUD for the power sub-system in the reference system](image2)

**4.2.3 Heat exchanger sub-system**

Figure 8 shows the energy transformation in the heat exchangers and the exergy waste to the environment in the polygeneration system. The $A_{\text{exd}}$ curve represents the syngas cooling process from the methane reformer outlet, in which the thermal exergy loss is 56.4 kJ/mol-CH$_4$. The $A_{\text{exd}}$ and $A_{\text{exa}}$ curves stand for the energy transformation in the gas-solid heat exchanger in the CLC; here, the high temperature solid CaSO$_4$ acts as the energy donor. The CO$_2$/H$_2$O mixture from the reduction reaction, acting as the energy acceptor, is re-heated to the gas turbine inlet temperature by the solid CaSO$_4$. The exergy destruction of the gas-solid heat exchanger is 10.9 kJ/mol-CH$_4$. The $A_{\text{exd}}$ and $A_{\text{exa}}$ curves represent the waste heat utilization of the system and act as the energy donor. The released thermal energy is used to drive the absorption chiller and heat the water exchanger. The exergy destruction of the waste heat utilization process is
57.5 kJ/mol-CH₄. Then, the flue gas from the oxidation reaction side, illustrated by the \( A_{ed5} \) curve, is discharged into the ambient environment and the exergy loss is 31.3 kJ/mol-CH₄. The flue gas from the reduction reaction side, as illustrated by the \( A_{ed6} \) curve, is cooled by the CO₂ separator to separate CO₂ and the exergy destruction is 14.6 kJ/mol-CH₄. As a result, the total exergy destruction of the heat exchanger sub-system in the polygeneration system is 170.7 kJ/mol-CH₄.

On the other hand, the EUD for the heat exchanger sub-system in the reference system is shown in Fig. 9. Similarly, the \( A_{ed1} \) and \( A_{ea1} \) curves represent the energy transformation in the gas-solid heat exchanger, and its exergy destruction is 10.1 kJ/mol-CH₄. The exergy destruction of the waste heat utilization of the system, denoted as \( A_{ed2} \) and \( A_{ed3} \), is 79.3 kJ/mol-CH₄. The exergy loss of flue gas is 68.2 kJ/mol-CH₄ including the diffuse exergy of the oxidation reaction side flue gas (48.2 kJ/mol-CH₄) and the CO₂ separator (20.0 kJ/mol-CH₄). The total exergy destruction of the heat exchanger sub-system in the reference system is 157.6 kJ/mol-CH₄.

It is clearly observed that the exergy destruction for each process of the heat exchanger sub-system is lower in the polygeneration system than the reference system, which is caused by the lower flue gas flow rate in the polygeneration system. However, the total exergy destruction of the heat exchanger sub-system in the polygeneration system (170.7 kJ/mol-CH₄) is more than that in the reference system (157.6 kJ/mol-CH₄) because of the extra heat exchanger used to cool the syngas.

![Fig. 8 EUD for the heat exchangers in the polygeneration system](image)

![Fig. 9 EUD for the heat exchangers in the reference system](image)
According to the above EUD analysis, the maximum exergy destruction of the polygeneration system occurs in the chemical reaction sub-system, which accounts for 15.58% of the total input exergy. The total exergy destruction in the polygeneration system is larger than that in the reference system because the CO$_2$ reforming process of methane is integrated into the polygeneration system. However, the utilized solar energy in the polygeneration system is more than that in the reference system. Consequently, the exergy destruction ratio in the polygeneration system reduces due to the increasing solar thermal energy input. Specifically, the energy level of methane at the energy donor side is decreased to increase the energy level of solar thermal energy. Finally, the exergy efficiency of the polygeneration system is improved.

5. Conclusions

A novel polygeneration system is proposed; this system couples solar-hybrid methane reforming with CLC and achieves the integration of CO$_2$ separation and utilization. The solar thermal energy is integrated with the fuel chemical energy through the methane reforming and the CLC.

The thermodynamic performances of the new polygeneration system are evaluated. On the basis of design operating parameters, the overall system energy and exergy efficiencies are approximately 71.69% and 56.58%, respectively, which is 4% and 1% higher than the efficiencies of the reference trigeneration system. When the instantaneous solar share is approximately 46.35%, the net solar-to-exergy efficiency can approach 25.38%. According to the graphical exergy analysis for the system, the maximum exergy destruction of the polygeneration system occurred in the chemical reaction sub-system, which accounts for 16% of the total input exergy. The syngas not only is output as a product but it also decreases the exergy destruction of the power sub-system and the heat exchanger sub-system. In addition, the novel system achieves zero carbon emission.

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