

# PERFORMANCE ANALYSIS OF CHEMICAL LOOPING HYDROGEN PRODUCTION SYSTEM DRIVEN BY SOLAR ENERGY

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## ABSTRACT

Taking methane as fuel gas, nickel oxide as oxygen carrier and calcium oxide as carbon dioxide adsorbent, a solar-driven chemical-looping hydrogen production system was established and the hydrogen production performance of the system under different reaction conditions was explored. The results showed that, if the concentrating solar energy was used as the heat source of the fuel reactor, the ratio of nickel to methane was 2.25, the ratio of water to methane was 1, the temperature of the fuel reactor was between 450 and 600 °C, the pressure of the fuel reactor was at atmospheric pressure, and the ratio of calcium oxide to methane was 1, a better system performance could be achieved. The key process experiments are carried out in the honeycomb reactor. The results show that the separation of CO<sub>2</sub> generated in the reaction process is an important way to improve the efficiency of chemical looping hydrogen production. Using CaO to capture and separate CO<sub>2</sub> in the reaction process could improve the effect of hydrogen production. Also, the huge energy consumption caused by gas separation could be avoided. This study presents a method for efficiently using low-temperature solar energy for hydrogen production.

**Keywords:** solar energy; hydrogen production; chemical looping cycle; honeycomb reactor.

## NONMENCLATURE

### Abbreviations

$n_{CH_4}$	The methane flow at fuel reactor inlet
$n'_{CH_4}$	The methane flow at fuel reactor outlet

$n_{H_2}$	The hydrogen flow at fuel reactor inlet
$n'_{H_2}$	The hydrogen flow at fuel reactor outlet
$Q_H^{net}$	Low calorific value of hydrogen
$E_H^{net}$	Exergy value of hydrogen
$Q_F^{net}$	Low calorific value of methane
$E_F^{net}$	Exergy value of methane
$V_F$	Volume flow of hydrogen
$Q_S$	Solar heat per unit time
$E_S$	Solar exergy per unit time
$\eta_{Fuel}$	Conversion rate of fuel gas
$Y$	Hydrogen generation rate
$\eta_{EN}$	Thermal efficiency of hydrogen
$\eta_{EX}$	Exergy efficiency of hydrogen

## 1. INTRODUCTION

Due to many problems caused by traditional energy, renewable energy has gradually become a hotspot in the field of energy research. As the most abundant renewable energy on earth surface, solar has some issues including decentralization and discontinuity[1]. Concentrated solar thermochemistry is an effective way to overcome these difficulties, which converts solar energy into the chemical energy of CO or H<sub>2</sub> and stores it [2]. Direct solar thermal decomposition of water to H<sub>2</sub> usually need an extremely high temperature requirement of more than 2200 °C [3]. The excessive temperature not only has the large number of thermal radiation losses, but also present a challenge to the reactor materials [4]. To reduce reaction temperature of hydrogen production process, an alternative approach is

to employ hydrocarbon materials as reactant [5, 6]. Methane steam reforming is another way to produce H<sub>2</sub>, which is carried out over Ni-based catalyst at no less than a temperature of 800 °C and a pressure of 14 atm [7]. The limitation of working conditions restricts the combination with concentrated solar energy. A promising way to produce hydrogen using concentrated solar energy is the chemical-looping cycles [8].

During the chemical-looping cycles, a variety of metal oxides have been tested as the oxygen carriers (OC) [9]. Among the rest, nickel oxide is considered as a dramatic OC material for chemical-looping cycles, due to it exhibits a lower reaction temperature with methane and good catalytic effect of its reduction products on the reaction of methane and steam [10], which could improve the performance of hydrogen production. The reduction reaction is highly endothermic, so solar energy could be employed to meet the requirement as input. Nickel oxide, as the partial oxidant of methane, needs to react with air to regenerate after losing oxygen. The reaction could release a large amount of heat at high temperature of 1200 °C steadily and continuously [11].

In our previous work, a novel honeycomb fixed-bed reactor for chemical-looping cycles was constructed [11, 12]. In this reactor, OC was integrated into the honeycomb chamber, which could improve the reaction rate and the conversion of the reactants [11]. In previous experiments, it was found that in the hydrogen production process of methane and nickel oxide, there is still a lot of carbon dioxide at the outlet of the reactor, which maybe limit further conversion of methane to hydrogen. Based on this, the performances of chemical-looping cycles hydrogen production under different conditions are analyzed.

## 2. METHODOLOGY

### 2.1 System design

The process flowsheet of this proposed scenario is developed and simulated by Aspen Plus software. Various thermodynamic methods have been existed in Aspen Plus, and the built-in PR-BM (Peng - Robinson with Boston-Mathias) function is chosen as general thermodynamic method to calculate individual and binary physical properties.

The schematic diagram of solar syngas production via chemical-looping cycle from redox cycling is displayed in Figure. 1. The system is mainly divided into four parts, including concentrated solar collector, fuel reactor, calcium carbonate decomposition reactor and air

reactor. The fuel gas used in the reaction system is CH<sub>4</sub>, the oxygen carrier is nickel oxide, and the carbon dioxide adsorbent is CaO. After certain preheating, CH<sub>4</sub> is sent into the fuel reactor to undergo chemical looping cycles with the oxidized oxygen carrier, and CaO, as a CO<sub>2</sub> adsorbent, is also sent into the fuel reactor for simultaneous reaction. In the reaction process of the fuel reactor, the heat required to be absorbed by the reaction is provided by the concentrated solar energy collector. The solar energy absorbed in the reaction process is transferred into the reaction products in the fuel reactor, which effectively improves the maximum available energy of solar energy. The reaction products of the fuel reactor are divided into two streams. The gaseous products are mainly H<sub>2</sub>, H<sub>2</sub>O and trace amounts of CO<sub>2</sub>, CO and CH<sub>4</sub>. After condensation by the condenser, H<sub>2</sub> with high purity can be obtained. The solid products in the fuel reactor are mainly the reduced oxygen carrier Ni and CaCO<sub>3</sub> generated after CO<sub>2</sub> absorption. The solid products are sent into the calcium carbonate decomposition reactor for thermal decomposition reaction. During the reaction, CO<sub>2</sub> is generated as the only gas product, which could eliminate the additional energy consumption of gas separation. This reaction needs to absorb a large amount of reaction heat, which is provided by the exothermic oxidation reaction between Ni and air in the air reactor. In the air reactor, a large amount of high temperature heat could be released, which can not only meet the reaction heat required for calcium carbonate decomposition, but also provide temperature heat to the power generation system, so as to realize the efficient utilization of energy. After the two reactions, NiO and CaO are regenerated and sent into the fuel reactor again, so as to realize the circulation of oxygen carrier and CO<sub>2</sub> absorbent.

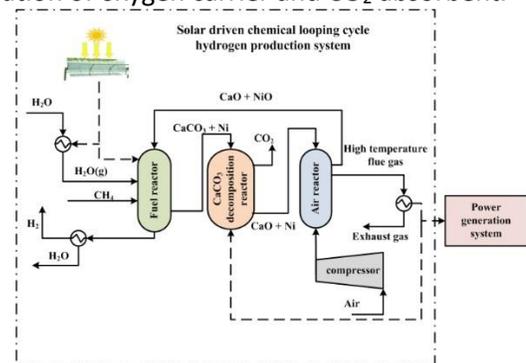
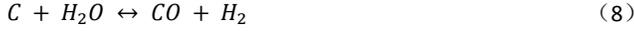
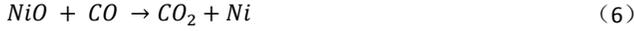
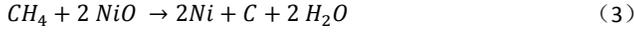
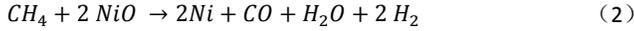
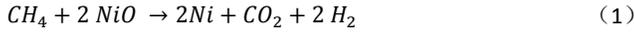


Figure 1 The schematic diagram of solar syngas production via chemical-looping cycle from redox cycling

The hydrogen generation process occurs primarily in the fuel reactor. The main reactions that occur in the fuel reactor are as follows:



Eq. (1) is the main reaction in the fuel reactor and other reactions are side reaction.

The main reaction that occurs in the air reactor is as follow:



The CaO/CaCO<sub>3</sub> cycle is added to absorb CO<sub>2</sub> generated in the reaction process of the fuel reactor, so as to ensure the high purity of H<sub>2</sub> in the gas phase logistics separated by the separator after the fuel reactor, and at the same time to achieve CO<sub>2</sub> capture at a higher concentration. The main cycle reactions of CaO/CaCO<sub>3</sub> are as follows:



## 2.2 Process assessment

In the thermodynamic analysis of the chemical looping hydrogen production system driven by solar energy, the factors that affect the system performance mainly include the ratio of nickel oxide to methane, the ratio of water to methane, the ratio of carbon dioxide adsorbent to methane that is directly inputted into the fuel reactor, the temperature of the fuel reactor and the pressure of the fuel reactor. There are several main evaluation indexes, including the composition of gas generation in the fuel reactor, the content of hydrogen, the conversion rate of fuel gas ( $\eta_{Fuel}$ ), gas generation rate ( $Y$ ), thermal efficiency of hydrogen ( $\eta_{EN}$ ) and exergy efficiency of hydrogen ( $\eta_{EX}$ ). The definitions are as follows:

$$\eta_{Fuel} = 1 - \frac{n'_{CH_4}}{n_{CH_4}} \quad (12)$$

$$Y = n'_{H_2}/n_{H_2} \quad (13)$$

$$\eta_{EN} = \frac{Q_H^{net} V_H}{Q_F^{net} V_F + Q_S} \quad (14)$$

$$\eta_{EX} = \frac{E_H^{net} V_H}{E_F^{net} V_F + E_S} \quad (15)$$

Where  $n'_{CH_4}$  and  $n'_{H_2}$  are the methane flow and hydrogen flow at fuel reactor outlet, and  $n_{CH_4}$  and  $n_{H_2}$  are the methane flow and hydrogen flow at fuel reactor inlet.  $Q_H^{net}$  and  $E_H^{net}$  are the low calorific value and exergy value of hydrogen, separately.  $Q_F^{net}$  and  $E_F^{net}$  are the low calorific value and exergy value of methane, separately.  $V_F$  is the volume flow of hydrogen.  $Q_S$  and  $E_S$  are solar heat and exergy absorbed by the

concentrated solar energy collector per unit time, separately.

According to the existing research results of the same type and the analysis of system characteristics, it is necessary to preliminarily determine the optimal range of operating conditions in the process of system performance evaluation. The main specifications are shown in Table. 1.

Table. 1 Main specifications in this proposed process.

Item	Specifications
Fuel reaction temperature (°C)	450 - 750
Mole ratio of CaO/CH <sub>4</sub>	0 - 1.5
Mole ratio of NiO/CH <sub>4</sub>	1.25 - 4
Mole ratio of H <sub>2</sub> O/CH <sub>4</sub>	0-2
Methane inlet flow (kmol/hr)	1
Fuel reactor inlet temperature (°C)	25
Reaction pressure (MPa)	0.101325

## 2.3 Experimental section

The active component of OC is NiO, with Al<sub>2</sub>O<sub>3</sub> doped into the iron oxide as an inert support material. The preparation and processing of honeycomb oxygen carriers have been described in our previous literature. NiO/Al<sub>2</sub>O<sub>3</sub> powders could be obtained by the coprecipitation method. Then the reactor and OC can be integrated by molding the powder into a honeycomb structure [11, 12].

The oxygen carrier is regarded as not only the solid reactant but also the composition material of the honeycomb chamber. The configuration diagram for the honeycomb fixed-bed reactor is shown in Figure. 2. As shown, the oxygen carriers and support materials are made into a cylindrical monolithic block with a series of axial microchannels. In this way, the integration of the oxygen carrier and reaction chamber is achieved.



Figure 2 The configuration diagram for the honeycomb reactor and the honeycomb oxygen carrier.

The solar energy is collected by the parabolic concentrator and transferred to the reactor through the heat-conducting oil to provide the heat required for the endothermic reaction. During the endothermic, methane is introduced into the honeycomb reactor at 300-600 ml/min, and the reaction temperature is maintained at 600 °C. During the OC regeneration stage,

air is fed at 1200 °C. The processes are all controlled an integrated controller and operated at an atmospheric pressure.

### 3. RESULT AND DISCUSSION

#### 3.1 Effect of material ratio of NiO/CH<sub>4</sub>

Figure 3 (a) (b) shows the quantities of each component at the outlet of the fuel reactor and the parameters used to evaluate the hydrogen production performance of the system under different ratios of NiO/CH<sub>4</sub>. It could be seen that, the outlet flows of CO<sub>2</sub> and CO are always almost 0 with the ratio of NiO/CH<sub>4</sub> is increased from 1.25 to 4.0, which due to CaO is introduced into the fuel reactor. The equilibrium of the reactions is destroyed and the reactions are pushed towards the direction of producing CO<sub>2</sub>. The methane at the outlet gradually decreased to nearly zero. Because it is difficult to make all CH<sub>4</sub> to be reacted in the reactor as the amount of NiO is not big enough. H<sub>2</sub> appears a trend of increasing first and decreasing then with the increase of the NiO/CH<sub>4</sub> ratio. This is because when the NiO/CH<sub>4</sub> ratio is too low, the conversion of CH<sub>4</sub> is not high enough, resulting in a small amount of H<sub>2</sub> generated. When the NiO/CH<sub>4</sub> ratio is too high, the ratio of fully oxidized CH<sub>4</sub> to H<sub>2</sub>O increases due to the sufficient amount of oxygen carrier, resulting in a decreasing trend of H<sub>2</sub> production.

It could be seen that the values of  $Y$ ,  $\eta_{EN}$  and  $\eta_{EX}$  show a change trend of first increasing and then decreasing from (b). The values all reach the peak when the NiO/CH<sub>4</sub> ratio is about 2.25. In the meantime, the hydrogen purity and the conversion of CH<sub>4</sub> both tend to be stable, approaching higher than 90%. According to the above results, the optimal NiO/CH<sub>4</sub> ratio is around 2.25.

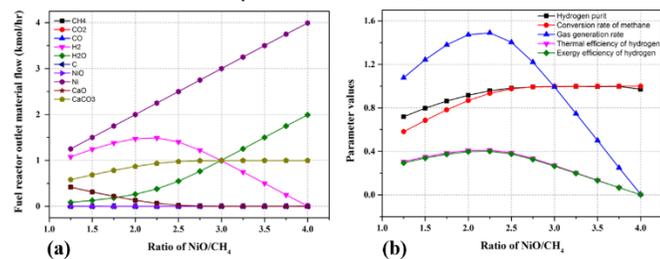


Figure 3 Effect of material ratio of NiO/CH<sub>4</sub>.

#### 3.2 Effect of material ratio of H<sub>2</sub>O/CH<sub>4</sub>

Figure. 4 (a), (b) show the quantities of each component at the outlet of the fuel reactor and the parameters used to evaluate the hydrogen production performance of the system under different ratios of H<sub>2</sub>O/CH<sub>4</sub>. With the continuous input of water in the fuel reactor, most of the gas composition changes little,

except the flow of H<sub>2</sub> showing a slight upward trend and CH<sub>4</sub> showing a slight downward trend respectively until the H<sub>2</sub>O/CH<sub>4</sub> ratio reaching 1.0. All of evaluation parameters also have a slight increase and then tend to be stable. It means that, the gradual increase of water on the reactor has a promoting effect on hydrogen production, but the effect is weak. The proper amount of water is necessary to be inputted into the reactor to avoid the formation of carbon deposition.

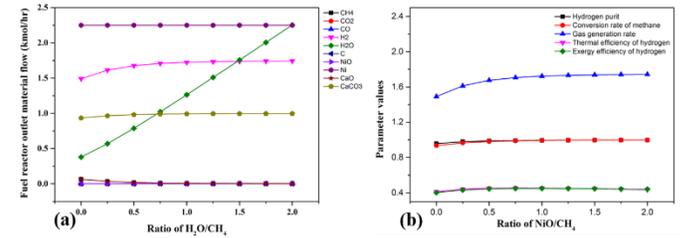


Figure 4 Effect of material ratio of H<sub>2</sub>O/CH<sub>4</sub>.

#### 3.3 Effect of reaction temperature

Figure. 5 (a), (b) show the quantities of each component at the outlet of the fuel reactor and the parameters used to evaluate the hydrogen production performance of the system under different reaction temperatures. During the temperatures are between 450 and 600 °C, the output flow of each gas component has little changes. The flow of CH<sub>4</sub>, CO<sub>2</sub>, CO are closed to 0 and the flow of H<sub>2</sub> maintains at a high value, which means that temperature has little effect in this area. The hydrogen purity is always maintained around 1, which indicates that there is no need to conduct separation of the output gas. It could avoid the high additional energy consumption caused by gas separation. The hydrogen generation rate is about 1.8, which means almost H from CH<sub>4</sub> could be transferred into H<sub>2</sub>. When the temperature is higher than 600 °C, the flow of H<sub>2</sub> starts to decreasing and the flow of H<sub>2</sub>O starts to increasing gradually. As the temperature gradually increases, the reactivity of NiO and CH<sub>4</sub> increases, which causes the CH<sub>4</sub> is more easily oxidized by NiO to water rather than H<sub>2</sub>. The evaluation parameters are all also trend to be decrease. Besides that, the flows of CO<sub>2</sub> and CaO present an obvious rising trend, while the flow of CaCO<sub>3</sub> decreases significantly. It means that high temperature could limit the ability of CaO to absorb CO<sub>2</sub>. When the temperature reaches 750 °C, the flow of CaCO<sub>3</sub> is close to 0, which indicates that CO<sub>2</sub> can no longer be absorbed at this temperature and the carbon capture effect is significantly reduced. Therefore, too high temperature will limit the hydrogen production performance of the system, and a lower fuel reactor temperature should be appropriately selected.

Considering that the reaction temperature range of the fuel reactor is 450 ~ 600 °C, the trough solar energy collector can be combined as heat source. As a mature way of solar energy concentrating, trough solar energy can make full use of low and medium temperature solar energy and match the fuel reactor well.

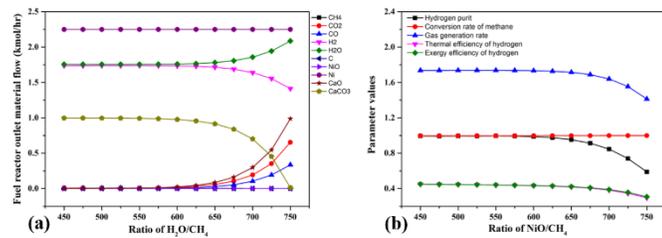


Figure 5 Effect of reaction temperature.

### 3.4 Effect of CaO input

Figure. 6 (a), (b) show the quantities of each component at the outlet of the fuel reactor and the parameters used to evaluate the hydrogen production performance of the system under different ratios of CaO/CH<sub>4</sub>. During the CaO/CH<sub>4</sub> ratio gradually increases from 0 to 1, the flow of H<sub>2</sub> shows an obvious trend of gradually increasing, while the flow of CO<sub>2</sub> shows an trend of decreasing. When the CaO/CH<sub>4</sub> ratio is greater than 1, it will not change any more. It is due to the fact that the increasing incoming CaO absorbs more CO<sub>2</sub>. According to Eq. (1) and (7), CO<sub>2</sub> in the reaction product is absorbed so that the reaction is continuously promoted towards H<sub>2</sub>, leading to the increase of H<sub>2</sub> flow and the decrease of CO<sub>2</sub> flow. After the CaO/CH<sub>4</sub> ratio exceeds 1, CO<sub>2</sub> could be completely absorbed, and the excess CaO will no longer affect the reactions. Also, the trend of methane could be explained for the same reason. It could be seen from (b), the values of  $\eta_{Fuel}$ ,  $Y$ ,  $\eta_{EN}$  and  $\eta_{EX}$  also increase with the increasing of CaO/CH<sub>4</sub> ratio. Based on the results above, the optimal CaO/CH<sub>4</sub> ratio is around 1.

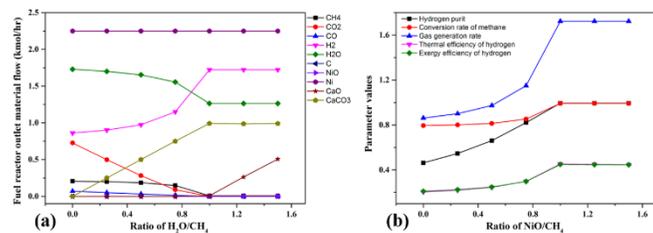


Figure 6 Effect of CaO input.

### 3.5 Experimental results

Based on the proposed hydrogen production system, key process experiments are carried out in the honeycomb reactor. In order to study the performance

improvement of the proposed system, the oxygen carrier is selected as NiO without CaO, the reaction pressure is 0.101325 MPa, and the reaction temperature is set as 600 °C. Figure. 7 (a) shows the outlet gas flow rate and oxygen transfer rate at different methane inlet flow rates. It could be seen that, as methane flow increases, hydrogen production and CO content increases obviously. Also, the oxygen transfer rate increases as a direct proportion function. The flow of CO<sub>2</sub> is steady but high, and the flow of unreacted CH<sub>4</sub> also increases. It means that a large amount of CO<sub>2</sub> produced by the reaction is an important factor restricting the effect of hydrogen production without adding CaO. Therefore, the separation of CO<sub>2</sub> generated in the reaction process is an important and significant way to improve the efficiency of chemical looping hydrogen production. High cyclic stability is an essential requirement for the application of the chemical-looping cycles. Figure. 7 (b) illustrates the stability of oxygen carrier and chemical-looping cycles hydrogen production process for 15 cycles. Throughout the circulation process, oxygen carrier keeps almost complete conversion and the reaction performance is hardly affected. In the meantime, the conversion rate of methane, the yield of hydrogen and the oxygen transfer rate of oxygen carrier are almost brought into correspondence in each cycle reaction. All these result show that the chemical-looping hydrogen production process of honeycomb NiO has excellent stability. The proposed honeycomb chamber is formed by oxygen carrier, which allows oxygen carrier to be uniformly distributed in the honeycomb chamber. And the structure plays an important role in improving the stability.

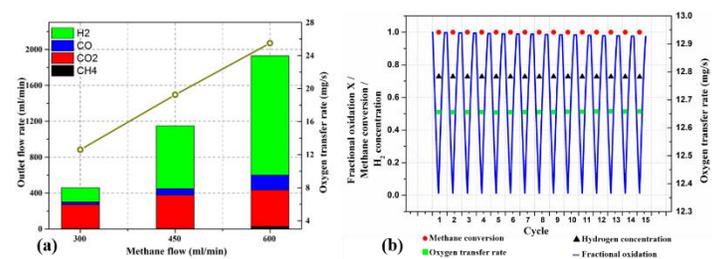


Figure 7 (a) Effect of CH<sub>4</sub> flow rate on measured outlet gas components and oxygen transfer rate. (b) Cyclic stability of methane conversion, hydrogen yield, oxygen transfer rate and fractional oxidation during the chemical-looping cycle hydrogen production process.

## 4. CONCLUSION

This paper built a solar - chemical looping hydrogen production system. The simulation and performance

analysis are carried out mainly for the reaction of hydrogen production process. The influence factors of affecting hydrogen production system performance are discussed, and the fuel reactor operating conditions are optimized. At the same time, key process experiments are carried out in the honeycomb reactor. The following conclusion could be got:

(1) For the NiO/CaO - CH<sub>4</sub> chemical looping hydrogen production system, the fuel reaction temperature within the range of 450 ~ 600 °C can obtain better reaction performance, and other optimized reaction conditions include: the NiO/CH<sub>4</sub> ratio is 2.25, the H<sub>2</sub>O/CH<sub>4</sub> ratio is 1, and the CaO/CH<sub>4</sub> ratio is 1.

(2) The reaction temperature of the hydrogen production process is low, and the reaction pressure is ambient pressure, which can effectively cooperate with the trough concentrated solar energy collector. The trough concentrated solar energy collector provides heat for the reaction process in the fuel reactor, and makes full use of the low and medium temperature solar energy for chemical looping hydrogen production, improving the energy utilization efficiency of solar energy.

(3) The enrichment of CO<sub>2</sub> in the reactor is an important factor restricting the effect of hydrogen production. The separation of CO<sub>2</sub> generated in the reaction process is and significant way to improve the efficiency of chemical looping hydrogen production. Using CaO to capture and separate CO<sub>2</sub> in the reaction process not only improves the effect of hydrogen production, but also avoids the huge energy consumption caused by gas separation.

## ACKNOWLEDGEMENT

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