Korean J. Chem. Eng., **31**(2), 230-239 (2014)
DOI: 10.1007/s11814-013-0196-3

pISSN: 0256-1115
eISSN: 1975-7220

Hydrogen production via sorption enhanced chemical looping reforming of glycerol using Ni-based oxygen carrier and Ca-based sorbent: Theoretical and experimental study

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(*Received 11 June 2013 • accepted 1 October 2013*)

Abstract−The sorption enhanced chemical looping reforming of glycerol (SECLRG) was proposed. This process can produce high purity H_2 without need for additional gas separation equipment. Thermodynamic analysis on the reformer of SECLRG was conducted based on the minimization of Gibbs free energy. The results show that the favorable operation conditions for reformer are pressures around 1-20 atm, temperatures around 800 K, oxygen excess number of 1, and sorbent excess number of 1. The thermal efficiency with steam addition is higher than that without steam addition. The SECLRG was also examined in a fixed bed reactor, with NiO/Al_2O_3 and CaO particles as bed material and glycerol as fuel. Experimental results showed that the H_2 molar fraction was higher with CaO than without it. Initially, high purity hydrogen (>95%) was obtained by SECLR of glycerol at 800 K and 1 atm.

Keywords: Hydrogen, Sorption Enhanced Chemical Looping Reforming (SECLR), CO_2 Capture, Glycerol, Thermodynamic Analysis

INTRODUCTION

Hydrogen (H_2) has been perceived as an ideal future energy carrier as a clean and sustainable energy [1]. When H_2 is burned, the only emission is water vapor. Clearly, H_2 is less of a pollutant in the air because it omits little tail pipe pollution. It has the potential to run a fuel cell engine with greater efficiency over an internal combustion engine [2]. Hydrogen is not an energy source, but a carrier, while it can be produced from not only fossil fuels, but also biomass and water [3].

Glycerol ($C_3H_8O_3$) is a by-product of the biodiesel process from biomass [4]. The glycerol-to-hydrogen system could be regarded as nearly CO_2 neutral as carbon dioxide released into the atmosphere during glycerol conversion can be absorbed in the growth of biomass. In addition, from thermodynamic point of view, glycerol can be effectively converted into H_2 [5,6]. Glycerol produces H_2 via steam reforming (SRG) [7-10], partial oxidation (POG) [11, 12], dry reforming (DRG) [13] and autothermal reforming (ATRG) [14]. Of these four ways, SRG provides the highest hydrogen yield and lower side reactions rate. However, SRG is a highly endothermic reaction; it is necessary to supply O_2 for SRG. Chemical looping technology can separate O_2 from air by introducing a suitable metal oxide as oxygen carrier to circulate between the air reactor and fuel reactor [15-18]. By this way, gas products are not diluted with nitrogen (N_2) from air, eliminating the need for costly air separation. The chemical looping concept is of interest for CO_2 capture during H_2 generation [19,20]. The calcium looping combines carbonation of calcium oxide (CaO) with calcination of calcium carbonate ($CaCO_3$).

To integrate the oxygen looping with the calcium looping, the CO_2 removal from the gas phase will push the equilibrium to H_2 production [21]. The process is known as “sorption enhanced chemical looping reforming” (SECLR). SECLR could be used to produce H_2 with inherent CO_2 capture without a need for water gas shift (WGS) reactors and air separation operations. The concept of unmixed reforming, proposed by Kumar et al. [22], and Lyon and Cole [23], utilizes in situ CO_2 sorption within the reformer. They showed that a nearly pure hydrogen stream could be generated by cycling feed flows in a single reactor, effectively carrying out chemical looping reforming in a packed bed reactor. Dupont et al. [24] proposed the production of H_2-rich gas from methane and sunflower oil using the unmixed reforming, with CaO addition, in a packed bed reactor. The experimental results reported in this aforementioned work were thermodynamically modeled by da Silva et al. [25]. Unmixed steam reforming makes use of the chemical looping of an oxygen carrier, which in its reduced form also acts as a steam reforming catalyst. Oxidation of the reduced catalyst under air feed allows the separation of N_2 and introduces ‘unmixed combustion’ [23] as a means to operate near autothermally, that is, with reduced or little heat input.

To date, there have been a few studies on SECLR of methane, ethanol and waste cooking oil [26-29]; however, little has been found in the literature on SECLR of glycerol (SECLRG). Here, we will focus on the optimal operation conditions of the reformer using Gibbs free energy minimization method. This is done in two ways. Firstly, the theoretical challenges and opportunities are examined by means of a thermodynamic study. Secondly, the reaction of reformer is examined experimentally in a fixed bed reactor. However, the experiment using the catalyst only, i.e., without sorbent, is also carried

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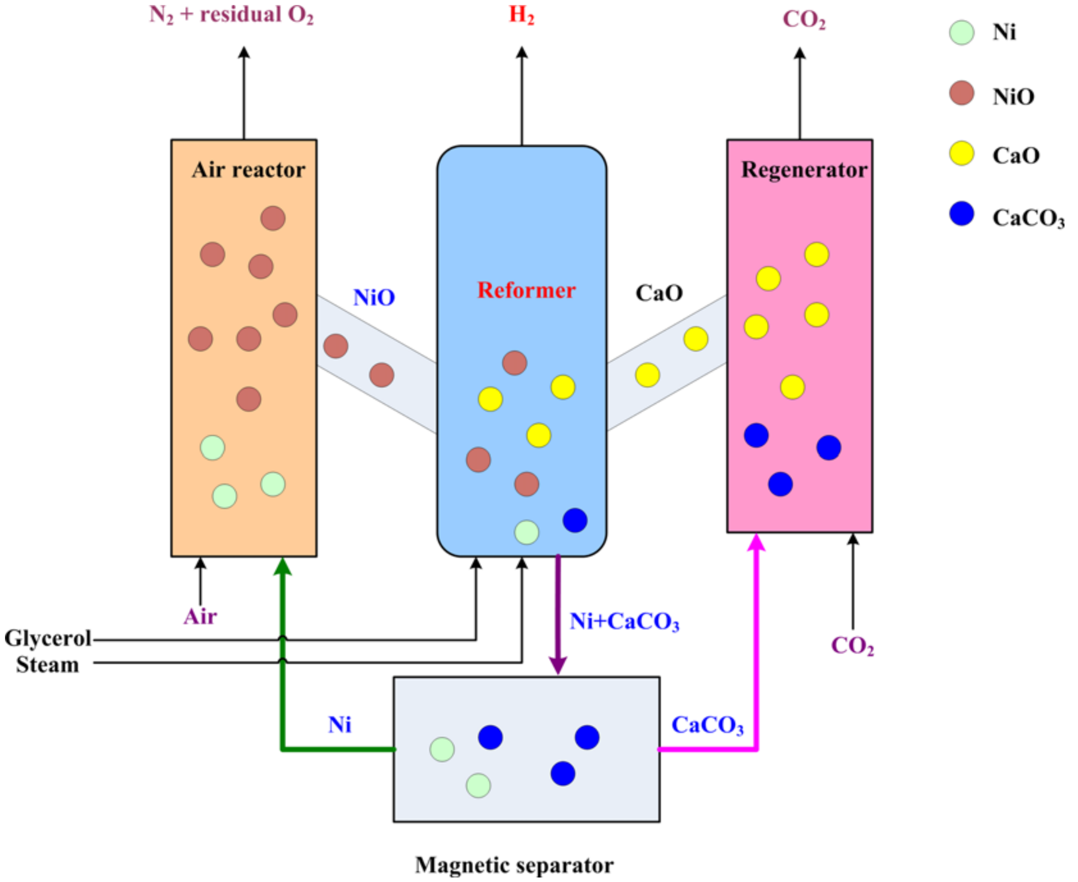

Fig. 1. Flow sheet of sorption enhanced chemical looping reforming (SECLR) of glycerol.

out for comparison.

SORPTION ENHANCED CHEMICAL LOOPING REFORMING

As shown in Fig. 1, SECLR consists of an air reactor, a reformer, a regenerator and a magnetic separator. A mixture of solid oxygen carrier particles (NiO) and CO_2 sorbent (CaO) is used as bed material. Possible reactions of SECLRG are summarized in Table 1.

Oxidation reactions in air reactor are listed in Eqs. (1)-(3); they are all exothermic. The first type is oxidation of Ni, which can be described as Eq. (1) [16,17]. The second type is oxidation of carbonaceous deposits, which can be described as Eqs. (2) and (3) [26].

In the reformer, glycerol is partially oxidized with O provided by the oxygen carrier. Simultaneously, any CO_2 produced in the process is absorbed by CaO, resulting in sorption enhanced steam reforming. All reactions in the reformer can be summarized with Eqs. (4)-(12). In Eqs. (4), (5) and (6), Ni acts as a catalyst, rather than as a reactant or product. However, in Eqs. (7) and (8), NiO or Ni acts as a product and reactant, respectively. Solid carbon may be deposited on the surface of an oxygen carrier or sorbent under certain conditions through the Boudouard reaction [Eq. (9)] or methane decomposition [Eq. (10)]. CO_2 and steam can be absorbed by CaO according to Eqs. (11) and (12). When Ni and $CaCO_3$ and/or $Ca(OH)_2$ come out of the reformer, they can be separated by magnetic separator based on the magnetism Ni. Then Ni is transported into the air reactor. It is oxidized with air and returned to the reformer. Similarly, $CaCO_3$ is transported into the regenerator. It is split into CaO and CO_2 and introduced into the reformer. The H_2 from the

Table 1. Key reactions of SECLRE

Equations	$\Delta_r H^\theta/(kJ\cdot mol^{-1})$	
$Ni+\frac{1}{2}O_2\rightarrow NiO$	−239.7	(1)
$C+O_2\rightarrow CO_2$	−393.5	(2)
$C+\frac{1}{2}O_2\rightarrow CO$	−110.5	(3)
$C_3H_8O_3\rightarrow 3CO+4H_2$	251.2	(4)
$CO+H_2O\rightarrow CO_2+H_2$	−41.1	(5)
$CO+3H_2\rightarrow CH_4+H_2O$	−205.9	(6)
$CO+NiO\rightarrow Ni+CO_2$	−43.3	(7)
$H_2+NiO\rightarrow Ni+H_2O$	−2.1	(8)
$CO_2\rightarrow\frac{1}{2}C+\frac{1}{2}CO_2$	−86.2	(9)
$CH_4\rightarrow C+2H_2$	74.6	(10)
$CaO+CO_2\rightarrow CaCO_3$	−178.2	(11)
$CaO+H_2O\rightarrow Ca(OH)_2$	−109.2	(12)
$C_3H_8O_3+3NiO+3CaO\rightarrow 3CaCO_3+4H_2+3Ni$	−413.2	(13)
$CaCO_3\rightarrow CaO+CO_2$	178.2	(14)
$Ca(OH)_2\rightarrow CaO+H_2O$	109.2	(15)

outlet of the reformer also accompanied with H_2O, which can easily be separated out by cooling. These reactions, mainly catalyzed by the reduced state of the metals or lower-valence metal oxides, are considered undesirable and can be suppressed by adjusting reaction parameters such as temperature, pressure and/or oxygen/fuel ratios in the reformer. The overall reaction in the reformer should be just about thermo neutral.

The reduction potential of $C_3H_8O_3$ is therefore 3 mol of NiO as indicated by Eq. (13). It is clear that both C and H content play a role in the reduction, while the O content in the fuel hampers this reaction. While NiO undergoes reduction to Ni, significant coking occurs from fuel thermal decomposition reactions. Once Ni is sufficiently reduced, steam reforming occurs on the Ni-catalyst. So steam could be added to enhance the relative importance of steam reforming. However, steam reforming cannot be allowed to dominate the process since this would make the reformer endothermic.

The regenerator produces a stream of steam and CO_2 according to Eqs. (14) and (15). Both are endothermic. A small flow of sweep gas may be needed to facilitate fluidization. In the regenerator, $CaCO_3$ decomposes at 973-1,223 K, depending on the CO_2 partial pressure, according to Eq. (14) [21]. Simultaneously, $Ca(OH)_2$ [Eq. (15)] also decomposes. The regenerator requires the input of energy.

The SECLR technology combines chemical looping reforming (CLR) with carbon dioxide separation. SECLR can directly convert $C_3H_8O_3$ into H_2, rather than syngas. Furthermore, this process also eliminates the need for the expensive cryogenic air separation. Obviously, pure carbon dioxide can be obtained and stored.

METHODOLOGY

1. Calculation Method

The equilibrium composition is calculated using the Gibbs energy minimization method, which was described in our previous work [27,28]. The program finds the most stable phase combination and seeks the phase composition where the Gibbs energy of the system reaches its minimum at a fixed mass balance, pressure and temperature. One assumption made is that all substances in the solid phase are in pure form and not mixtures. Further, it is assumed that $C_3H_8O_3$ is converted to the gaseous components (e.g., H_2, H_2O, CO, CH_4 and CO_2). Solid C, NiO, Ni, CaO, $CaCO_3$ and $Ca(OH)_2$ are also included in the equilibrium calculations. The predominant equilibrium compositions in SECLR of glycerol were simulated at various pressures (1-100 atm), temperatures (500-1,500 K), oxygen excess numbers (Φ, 0-2) and sorbent excess numbers (Ψ, 0-2).

The H_2 concentration on a dry basis is defined as the fraction of H_2 in the outlet (except H_2O) of reformer. Similarly, the CO, CH_4 or CO_2 concentration on a dry basis is defined as the fraction of CO, CH_4 or CO_2 in the outlet (except H_2O), respectively.

The H_2 yield is defined as the number of moles of H_2 in the outlet of reformer divided by 4 (the maximum number of moles of H_2 produced from $C_3H_8O_3$ theoretically). Similarly, the CO, CH_4, CO_2 or C yield is defined as the number of moles of CO, CH_4, CO_2 or C in the outlet divided by 3 (the maximum number of moles of CO, CH_4, CO_2 or C produced from $C_3H_8O_3$ theoretically).

The oxygen excess number (Φ) is defined as the actual amount of O(n_{OA}), added with the oxide except steam, over the stoichiometric amount (n_{OS}) needed for full conversion of $C_3H_8O_3$ by Eq. (16).

$$\Phi = n_{OA}/n_{OS} \tag{16}$$

The sorbent excess number (Ψ) is defined as the actual amount of CaO (n_{CA}) over the stoichiometric amount needed for CaO (n_{CS}), which can completely convert C atom from $C_3H_8O_3$ to $CaCO_3$, through Eq. (17).

$$\Phi = n_{CA}/n_{CS} \tag{17}$$

The energy efficiency (η) is calculated according to Eq. (18) by dividing the energies output (E_{out}) by the total energy input of glycerol (E_{in}), which is 1.56×10^6 J·mol^{-1}.

$$\eta(\%) = \frac{E_{out}}{E_{in}} \times 100 = \frac{E_{H_2}}{E_{in}} \times 100 \tag{18}$$

where E_{H_2} are the energy of H_2 in the outlet, respectively.

2. Experimental

2-1. Preparation of Oxygen Carrier and Sorbent Particles

Nickel-based oxygen carrier particles were prepared by impregnation method. The support particles (Al_2O_3) were heated at 523 K for 2 h to evaporate the moisture completely. Then these particles were exposed to a warm (333 K) and highly concentrated aqueous solution of nickel nitrate [$Ni(NO_3)_2$]. A volume of $Ni(NO_3)_2$ solution was added to the sample. Then it was dried at 383 K for 3 h to remove the pore water. This was followed by calcination at 773 K for 3 h to remove NO_2 and form NiO. The NiO/Al_2O_3 was sintered for 6 h at 1,223 K to increase the mechanical strength of the particles, prior to sieving to a size range of 40-60 mesh. The NiO content was 60 wt%. The CO_2 sorbent was $CaCO_3$ particles, which were calcined for 2 h at 1,273 K in order to obtain CaO. After that, the resulting particles were also sieved to a size of 40-60 mesh. Both them were thoroughly mixed with each other prior to the SECLR experiment. A CLR experiment without CO_2 sorbent was also conducted as reference, in which silica sand was used rather than CaO. The silica sand also had a particle size of 40-60 mesh.

2-2. Experimental Procedure

As shown in Fig. 2, the SECLRG was carried out in a quartz tube fixed bed reactor (Inside diameter=10 mm; Length=300 mm) at the atmospheric pressure. The whole fixed bed reactor was placed in a temperature-controlled oven. In a typical run, 6.22 g of NiO/Al_2O_3 and 1.87 g of CaO were used. The glycerol (0.05 ml/min) was fed into a vaporizer held at 573 K. Then, the gaseous glycerol was passed through the reactor. The liquid components in the outlet stream were condensed in an ice trap, and the gaseous components were fed into gas bags. Gas analysis was performed with the thermal conductivity detection (TCD). H_2, CO, CH_4 and CO_2 were separated with a TDX-1 column and high-purity Ar as carrier gas. For the reported runs, experimental errors of product mole fraction were lower than 1%.

RESULTS AND DISCUSSION

1. Thermodynamic Study

1-1. Temperature Effect

In Fig. 3, the influence of temperature on the reaction performance is plotted at 1 atm. It can be seen that H_2 and CH_4 are favored at low temperature. This could be expected because Eqs. (5), (6) and (11) are dominated at low temperature. The highest H_2 concentra-

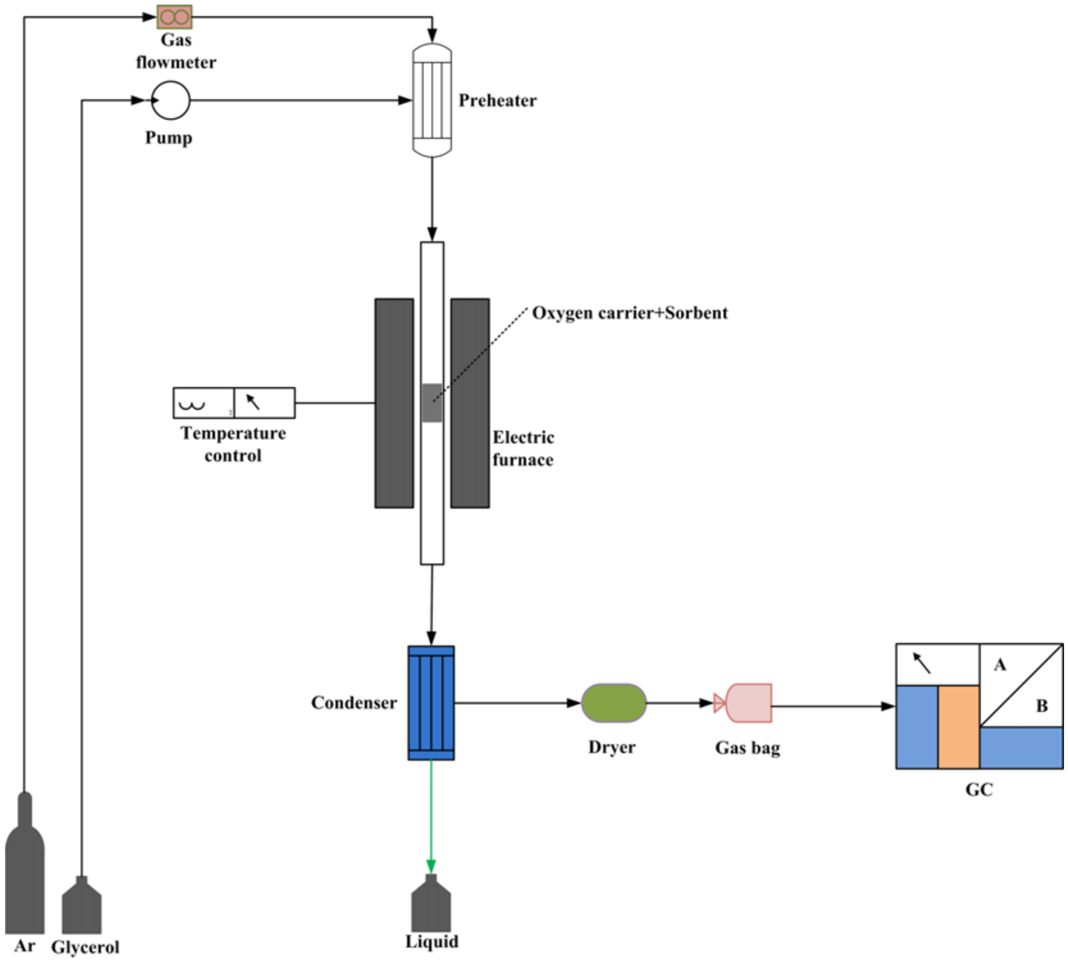

Fig. 2. Flow diagram of fixed bed test system.

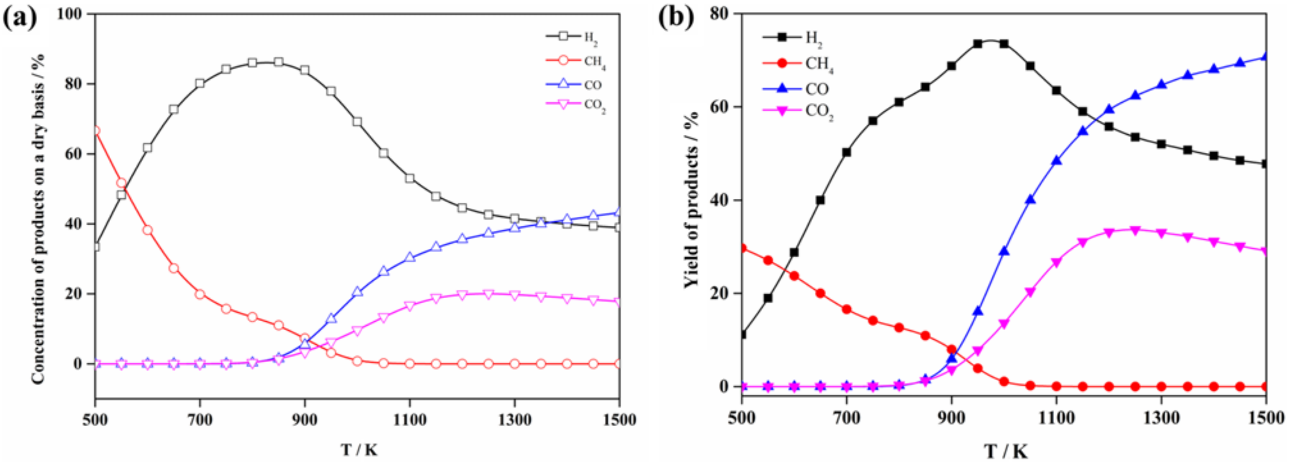

Fig. 3. The concentrations (a) and yields (b) of H_2, CH_4, CO and CO_2 as a function of temperature at 1 atm, Φ=1 and Ψ=1.

tion (86.03%) and yield (73.50%) can be obtained at 800 K and 950 K, respectively. However, the CO concentration is 0.27% and 12.74% at 800 K and 950 K, respectively. High H_2 concentration, and low CO, CH_4, CO_2 concentrations are the most important characteristics desirable for SECLR of glycerol. It is necessary to choose lower T (800 K rather than 950 K) in order to avoid CO formation.

1-2. Oxygen Excess Number Effect

The high oxygen excess number (Φ) is an advantage for CO_2 and H_2O formation since more oxygen can be transported per mass unit of added material [30]. As shown in Fig. 4, both the H_2 concentration and yield first rise and then weaken, with increasing Φ from 0 to 2. Moreover, the highest H_2 concentration and yield can be ob-

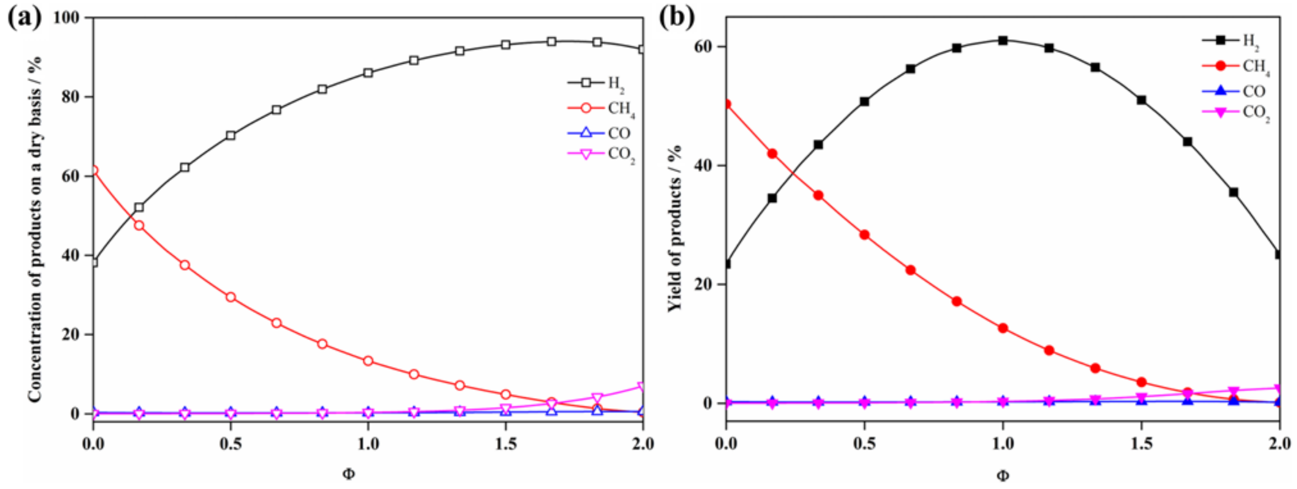

Fig. 4. The concentrations (a) and yields (b) of H_2, CH_4, CO and CO_2 as a function of Φ at 800 K, 1 atm and Ψ=1.

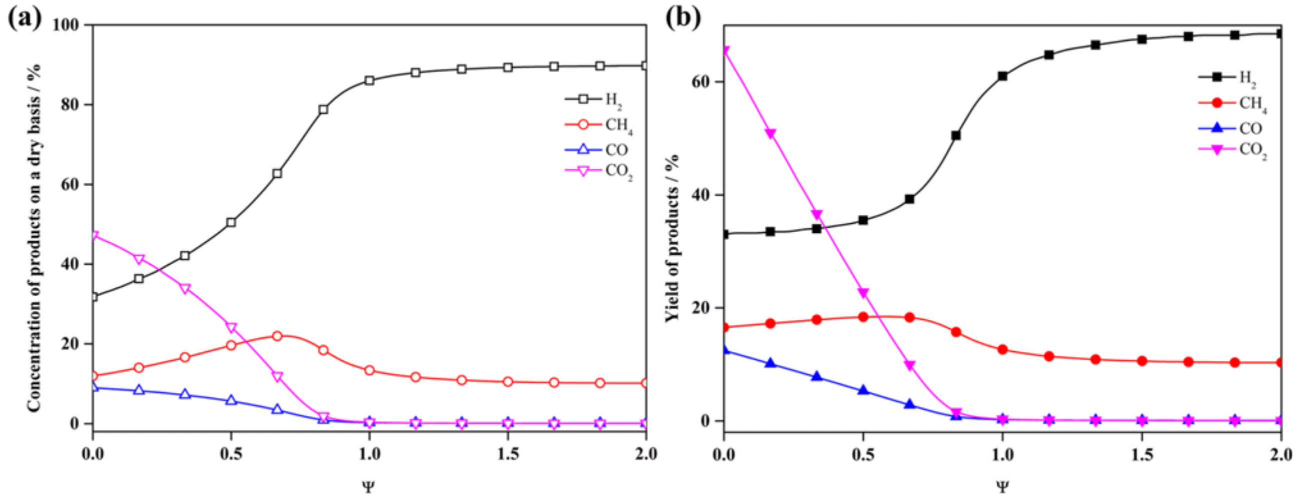

Fig. 5. The concentrations (a) and yields (b) of H_2, CH_4, CO and CO_2 as a function of Ψ at 800 K, and Φ=1 and 1 atm.

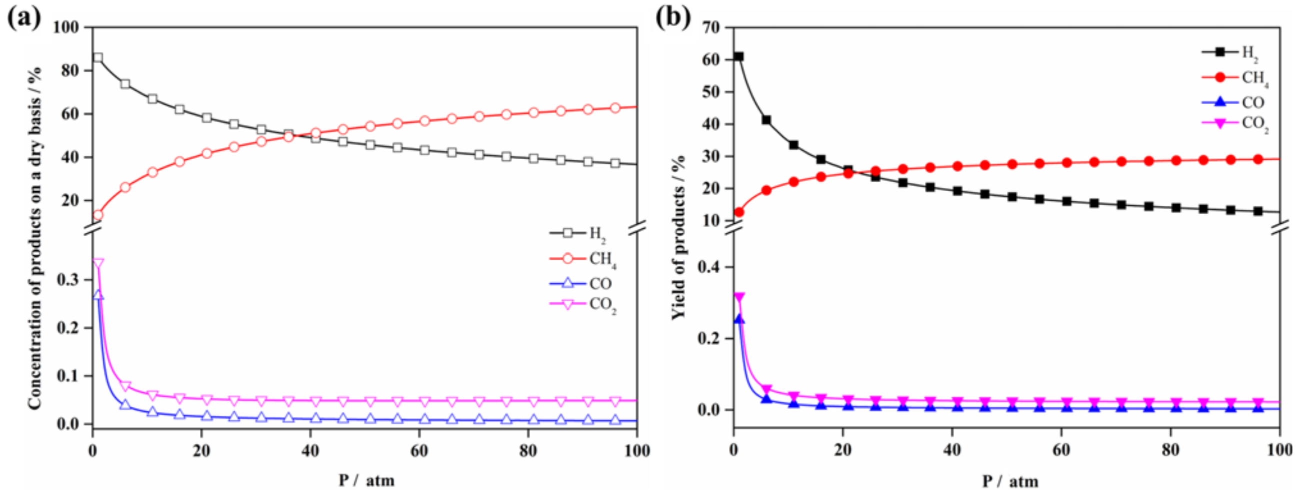

Fig. 6. The concentrations (a) and yields (b) of H_2, CH_4, CO and CO_2 as a function of P at Φ=1, Ψ=1, and 800 K.

tained at Φ=1.6 and 1.0, respectively. However, the 53% of H atom from glycerol is oxidized to form H_2O at Φ=1.6. Considering the H_2 yields, Φ=1.0 is chosen as the best oxygen excess number.

1-3. Sorbent Excess Number Effect

The advantage of using CaO is that the exit composition of the SECLR process has a high H_2 concentration and a lower CO or CO_2

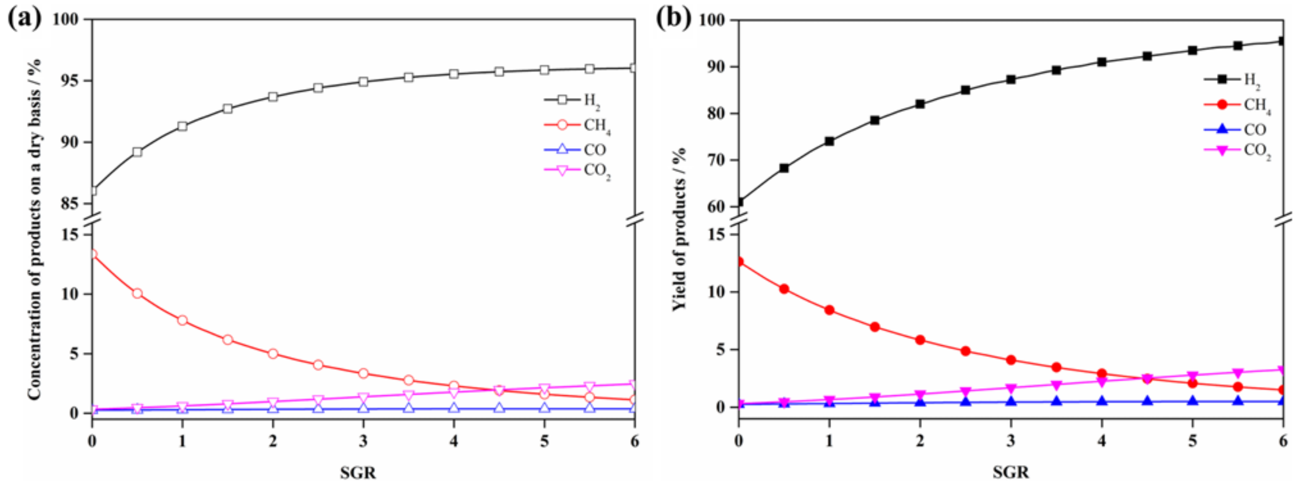

Fig. 7. The concentrations (a) and yields (b) of H_2, CH_4, CO and CO_2 as a function of SGR at 800 K, 1 atm, Φ=1 and Ψ=1.

concentration, both that are better for the operation of the fuel cells, especially proton exchange membrane fuel cell (PEMFC) [30]. To determine the influence of the sorbent (CaO), the Ψ was varied from 0 to 2. In Fig. 5, the predicted H_2, CH_4, CO and CO_2 concentrations (on a dry basis) and yields as a function of Ψ are displayed. With the increase of Ψ from 0 to 1, the H_2 concentration sharply rises from 31.73% to 86.03%, but CO_2 output concentration is reduced from 47.35% to 0.34%, correspondingly. It is attributed to the carbonation reaction with CaO, Eq. (11). The CO concentration decreases from 8.99% to 0.27% with increasing Ψ from 0 to 1 at 800 K. Then the H_2 and CO_2 concentrations remain steady with a further increase in the Ψ above 1. In light of the above discussion, the Ψ of 1 should be viewed as the optimal conditions based on the thermodynamic calculation, i.e., assuming that the mass transfer and kinetic limitations have a negligible effect on the effective capture of CO_2.

1-4. Pressure Effect

Fig. 6 shows the H_2, CH_4, CO and CO_2 concentrations (on a dry basis) and yields at different pressures. The H_2, CO and CO_2 concentrations and yields reduce with increasing the pressure from 1 to 100 atm; it is attributed to the methanation reaction [Eq. (6)], Boudouard reaction [Eq. (9)] and carbonation reaction [Eq. (11)]. There is a quick rise in the CH_4 concentration with increasing the pressure from 1 to 100 atm due to the methanation reaction [Eq. (6)]. It reveals that the increased pressure hampers the formation of H_2. Since SECLR of glycerol involves a volumetric increase, this is in accordance with Le Chatelier's principle. Increasing pressure improves the CO_2 uptake efficiency. However, it has a negative effect on the H_2 production, because the absolute amount of H_2 decreases with the pressure increasing. The increase of CH_4 produced can also dilute H_2 in the product gas at the same time. In addition, high pressure also brings other problems like manufacture and safety. However, from an engineering and industrial point of view, a normal reaction is usually conducted at 1-20 atm in order to make the transport of oxygen carrier particles easier, especially the continuous loop cycle. The previous studies found the steam gasification of carbonaceous fuels coupled with CO_2 capture should be operated at elevated pressures [31-34]. The selection of the operating pressures (1-20 atm) is likely due to the predicted decomposition pressure of $CaCO_3$ as a function of temperature.

A more sophisticated analysis gives consideration to the formation of $Ca(OH)_2$, which is enhanced at elevated pressures (when high-pressure steam is present). The CaO also reacts with the steam to produce $Ca(OH)_2$, according to Eq. (12), and an increase in the system pressure corresponds to an increase in the conversion of CaO to $Ca(OH)_2$. This is consistent with the thermodynamic studies conducted by Feng et al. [35], Kinoshita and Turn [36]. The H_2 concentration is on the decrease at higher pressures due to the H_2O formation. However, the CO_2 concentration in on the decrease due to the low decomposition pressure of the $CaCO_3$, as discussed above.

1-5. Steam Effect

The use of steam restrains the solid carbon formation and promotes the H_2 formation via Eqs. (19) and (20), respectively. As shown in Fig. 7, the H_2 and CO_2 concentrations and yields increase, but CH_4 concentration and yield decrease, with increasing SGR from 0 to 6. The addition of steam facilitates water gas shift (WGS), Eq. (5). Also, increasing the SGR increases the amount of H_2 produced. Since the H_2 concentration changes slightly while SGR is higher than 3, the SGR of 3 is selected as the best. It indicates that the SECLRG mimics the conventional oxidative reforming of glycerol, and it seems reasonable to believe that this is the best way to design an SECLRG process.

$$C+2H_2O \rightarrow CO_2+2H_2 \quad (19)$$

$$C_3H_8O_3+NiO+2H_2O+3CaO \rightarrow 3CaCO_3+Ni+6H_2 \quad (20)$$

1-6. Carbon Formation

Carbon formation is a possible side reaction in SECLRG. The Boudouard reaction [Eq. (9)] or methane decomposition [Eq. (10)] are amongst the most probable reactions leading to carbon formation [37]. Methane decomposition is an endothermic reaction, thermodynamically favored at high temperatures. The exothermic Boudouard reaction takes place at low temperature. Kinetically, both Eq. (9) and Eq. (10) are known to have a limited importance in the absence of a catalyst. Transition metals, such as Ni and Fe catalysts, can catalyze carbon formation. Carbon formation also depends on reaction conditions, such as the availability of oxygen, fuel conversion, reaction temperature and pressure [38]. The carbon deposition on the CaO surface may limit the efficiency of the total CO_2 capture

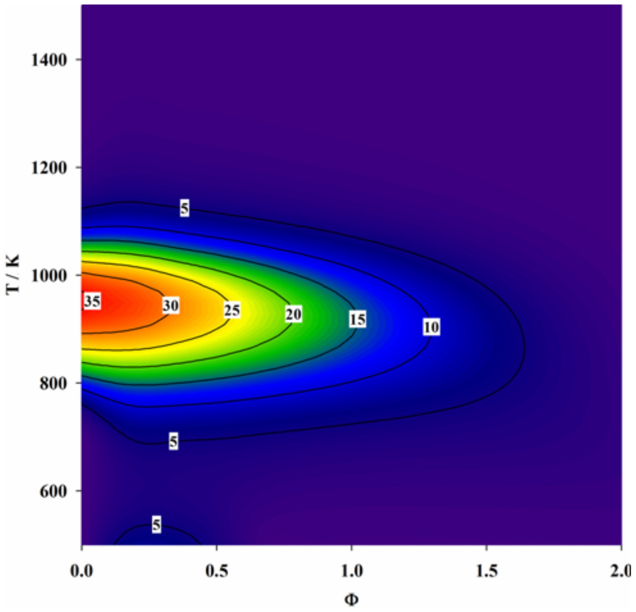

Fig. 8. The carbon yield as a function of Φ and T at 1 atm and Ψ=1.

[39]. Therefore, it is important to understand the possible carbon formation mechanisms and to investigate the operating strategies that need to be implemented to minimize or avoid carbon formation.

Carbon formation mainly depends on temperature and Φ. As shown in Fig. 8, the carbon yield diminishes sharply with increasing Φ from 0 to 2 at a fixed Ψ of 1 and 1 atm. The increase of oxygen carrier restrains the formation of solid carbon via Eq. (21).

$$NiO+C\rightarrow Ni+CO \tag{21}$$

As shown in Fig. 9, the carbon yield falls with the rise of SGR from 0 to 3, showing that the addition of steam restrains the carbon formation. It is attributed to the steam reforming of carbon via Eq. (19).

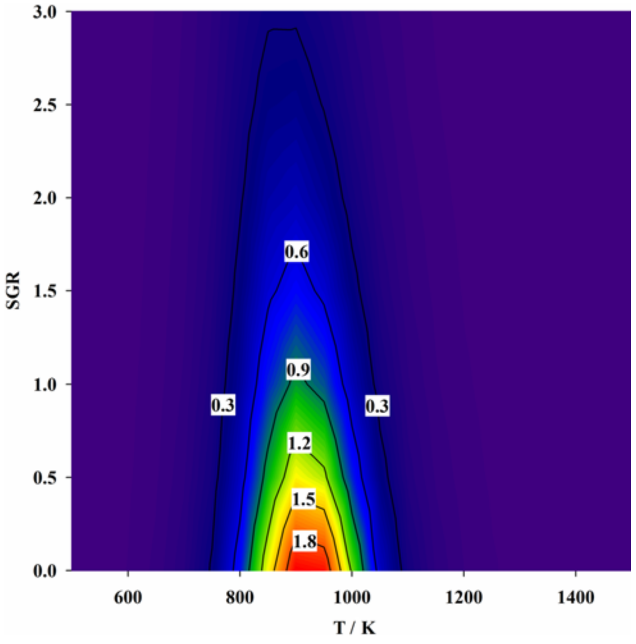

Fig. 9. The carbon yield as a function of SGR and T in reformer at 1 atm.

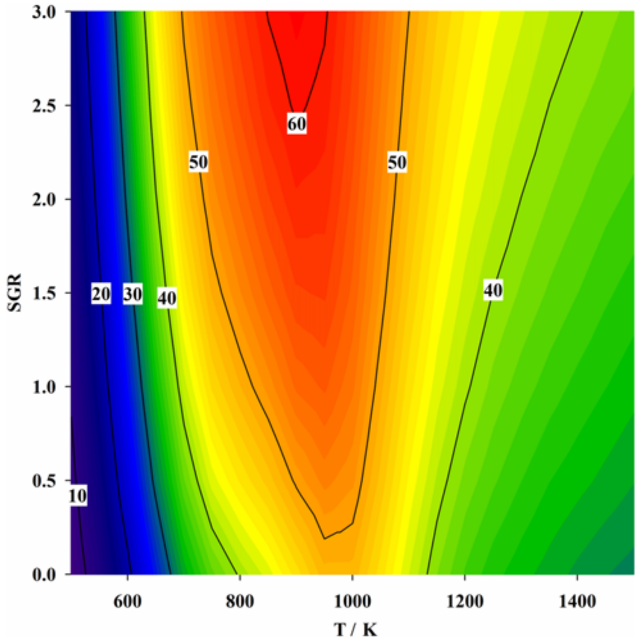

Fig. 10. The effect of SGR and T on the thermal efficiency (%) of SECLR of glycerol at 1 atm, Φ=1 and Ψ=1.

1-7. Thermal Efficiency

Fig. 10 shows the effect of SGR and T on the thermal efficiency (η) at 1 atm, Φ=1 and Ψ=1. In SECLR of glycerol, the addition of steam leads to a higher efficiency (meaning a higher hydrogen flow at the outlet of reformer). Obviously, the efficiency of the process with steam addition is higher than that without steam. It is attributed to H_2 formation from steam through Eq. (20). However, the disadvantage of using steam is that the water evaporation process consumes a great deal of energy.

1-8. Summary of the Best Operational Conditions for SECLRG

Table 2 shows the optimal conditions for the SECLRG process with and without CaO sorbent. As can be seen, high H_2 concentrations can be reached under thermo-neutral conditions, with no carbon deposition during fuel flow. In absence of CaO, the reformate composition is suitable to feed the anode of solid oxide fuel cells (SOFC) or molten carbonate fuel cells (MCFC), which are more tolerant to CO, and H_2 purity may not be so critical. For PEMFCs application, whose anode must be fueled by a high purity hydrogen stream containing CO at concentrations lower than 20 ppm to avoid platinum catalyst poisoning, the SECLRG process should be operated with CaO in order to produce a H_2-rich gas. Besides, an additional step, including a preferential CO oxidation reactor, is also needed. It is possible to obtain H_2 at concentrations of about 95% at 800 K, using an inlet SGR of 3.

2. Experimental

Two experimental series were performed in the fixed bed reactor. In the first, the sample consisted of 6.22 g NiO/Al_2O_3 and 1.87 g silica sand. In the second, the solid sample was composed of 6.22 g of NiO/Al_2O_3 and 1.87 g of CaO. A comparison between experiments with and without CaO added to the sample can be found in Figs. 11 and 12.

Table 2. Process outputs under optimized conditions

	CLRG			SECLRG			SECLRG		
T (K)	700	800	900	700	800	900	700	800	900
Φ		1			1			1	
Ψ		0			1			1	
SGR		0			0			3	
Concentration on a dry basis									
H_2 (%)	16.35	31.77	43.03	80.15	86.03	83.92	92.65	94.88	89.06
CH_4 (%)	22.6	11.93	2.65	19.83	13.38	7.3	7.21	3.36	0.82
CO (%)	1.82	8.99	21.12	0	0.26	5.42	0.02	0.37	3.45
CO_2 (%)	59.24	47.29	33.18	0.01	0.33	3.37	0.1	1.38	6.67
ΔH ($kJ\cdot mol^{-1}$, based on $C_3H_8O_3$)	108.90	203.60	337.50	–239.70	–154.80	–36.80	–182.70	–89.61	48.73

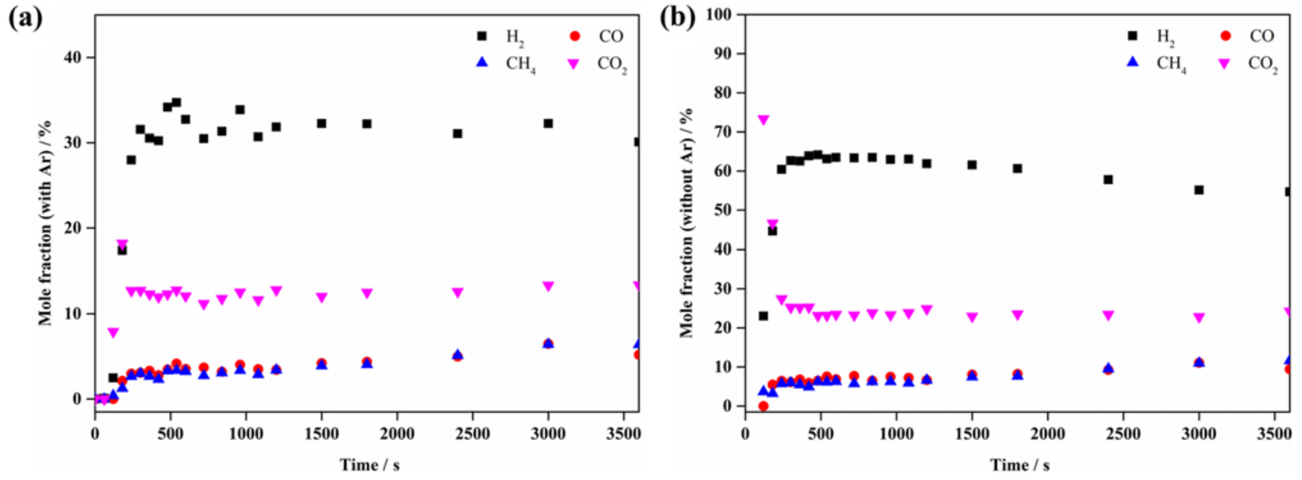

Fig. 11. Measured dry gas concentrations during reduction of 6.22 g NiO/Al_2O_3 and 1.87 g sand at 800 K with 0.05 ml/min $C_3H_8O_3$. (a) With Ar; (b) Without Ar.

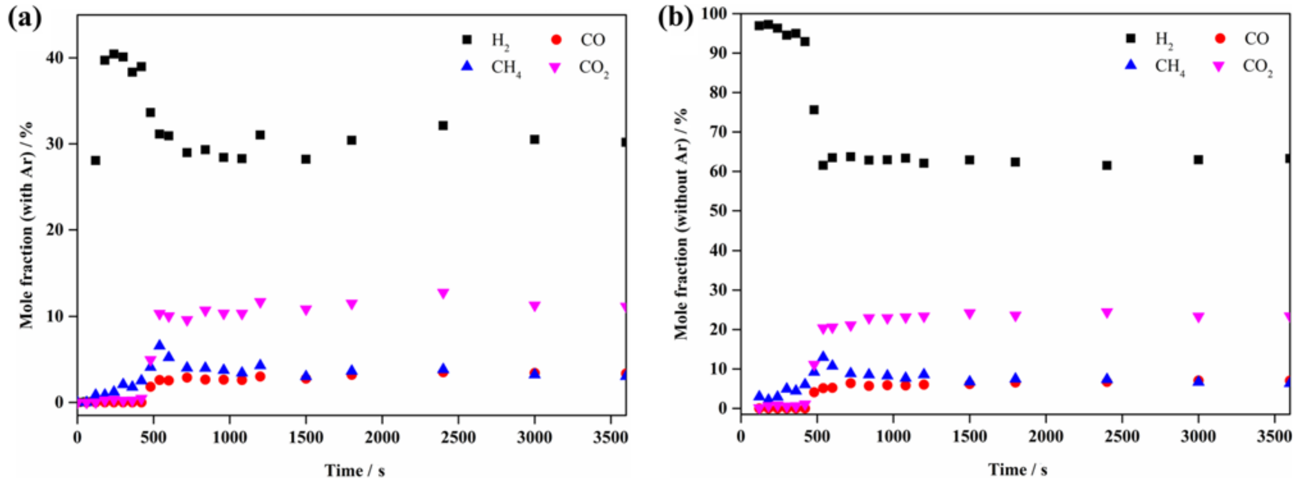

Fig. 12. Measured dry gas concentrations during reduction of 6.22 g NiO/Al_2O_3 and 1.87 g CaO at 800 K with 0.05 ml/min $C_3H_8O_3$. (a) With Ar; (b) Without Ar.

In Fig. 11(a), it can be seen that the reduction process could be divided into two periods. During the first period, when the oxygen carrier had a high NiO content, converted $C_3H_8O_3$ was to a large extent subject to full oxidation. This can be seen from the early CO_2 peak at t=120 s in Fig. 11(a). Little H_2 is produced here, so H atom in glycerol is converted mostly into H_2O, which is not seen since the analyzers measure on dry gas. When CaO is present, CO_2 will be captured in the bed as $CaCO_3$ and instead there is an early peak of H_2 at t=120 s in Fig. 12(a). This peak does not describe a large volumetric flow of H_2, but since CO_2 produced is captured in the bed as $CaCO_3$ this small amount of H_2 produced early constitutes a considerable volumetric concentration on dry basis. Once the most readily available O atom in the oxygen carrier is consumed, the share of unconverted $C_3H_8O_3$ is increased as well as the volumetric production of H_2. Eventually, the stable reforming conditions with high H_2 production were achieved. For the case where CaO was present, CO_2 would be captured as $CaCO_3$, thus enhancing the WGS [Eq. (5)], producing H_2 of considerably higher purity than for experiments without CaO.

As of Figs. 11(b) and 12(b), the experimental data suggests that the amount of O provided by the oxygen carrier for the reforming period was in the order of 1 mol NiO per 3 mol converted $C_3H_8O_3$; this number may vary slightly during the reduction period. Despite these uncertainties, the generation of H_2 and CO_2 fitted reasonably well to the expected. The positive effect of adding CaO to the reactor is obvious. Based on the experiments conducted, it can be concluded that the SECLR of glycerol should be feasible. The H_2 concentration on a dry basis (without Ar) of more than 95% was produced at 800 K. About 500 seconds after reaction, the concentration to H_2 was hampered with time, and showed a tendency to deactivate. Therefore, as expected from sorption enhancement, during this period the effect of the sorbent was to not only fully chemisorb CO_2, but also to cause nearly complete conversion of CO and CH_4. It should be possible to improve it by increasing the residence time or using an oxygen carrier optimized for $C_3H_8O_3$ conversion at low temperatures.

CONCLUSIONS

It can be concluded that sorption enhanced chemical looping reforming (SECLR) of glycerol could be an attractive process for H_2 production with CO_2 capture. The concept is straightforward compared to conventional technology such as steam reforming, for which excessive heat transfer operations, separate water gas shift reactors and multiple gas separation steps are necessary. In contrast, SECLR only requires its three adiabatic reactor vessels to produce reasonably pure streams of H_2, CO_2 and N_2. A theoretical analysis of SECLRG is carried out by minimizing the Gibbs free energy of the system. The temperature, Φ, Ψ and pressure have pronounced influences on the reformer of SECLR. The maximum H_2 concentration is 86.03% at 800 K, Φ of 1, Ψ of 1 and 1 atm. High pressure has negative effect on the H_2 formation; however, increased pressure could add other benefits such as small equipment size and reduced energy consumption for H_2 compression. Favorable operation conditions are: Pressures around 1-20 atm, reactor temperatures around 800 K, $\Phi=1$, and $\Psi=1$. The efficiency of the process with steam addition was higher than that without steam addition, showing that the addition of steam is beneficial for the H_2 generation.

The experimental results showed that the H_2 molar fraction was higher with the CaO present than without it. It can be concluded that it is possible to utilize oxygen from NiO to oxidize $C_3H_8O_3$, while at the same time enhancing the chemical looping reforming reaction by capturing CO_2 as $CaCO_3$. Initially, the high purity hydrogen (>95%) was produced by SECLRG at 800 K and 1 atm.

ACKNOWLEDGEMENTS

This work is financially supported by the National Natural Science Foundation of China with Grant No. 21206074, the Natural Science Foundation of Jiangsu province with Grant No. BK2012406, the Research Fund for the Doctoral Program of Higher Education of China with Grant No. 20123219120033, the Fundamental Research Funds for the Central Universities with Grant No. 30920130111012, the Zijin Intelligent Program of Nanjing University of Science and Technology with Grant No. 2013-ZJ-0103.

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