

Simulation of Modified Sorption Enhanced Chemical Looping Reforming for Hydrogen Production from Biogas

A. Phluanglue, W. Khaodee, S. Wongsakulphasatch, W. Kiatkittipong, A. Arpornwichanop, and S. Assabumrungrat

Abstract—Process simulation of modified sorption enhanced chemical looping reforming (SECLR) for hydrogen production was presented in this work. Biogas consisting of 50% CH₄ and 50% CO₂ by mole was fed to the process, where NiO and CaO were used as an oxidizing agent and CO₂ adsorbent, respectively. The system performances including methane conversion, hydrogen purity and energy consumption were investigated. The simulation results show that methane conversion and hydrogen purity were close to the values at equilibrium condition of steam reforming (SR). It is found that high CO₂ content in the feed stream resulted in high energy consumption at reforming reactor.

Keywords—Chemical looping reforming, Hydrogen production, Process simulation, Sorption enhanced chemical looping reforming.

I. INTRODUCTION

At present, the energy supply mostly comes from fossil sources therefore consumption of fossil sources has continuously increased year by year. However, the fossil sources, which are dead animals and plants accumulated for very long times, are non-renewable resources because they are being depleted much faster than the new ones are being formed. Moreover, the use of fossil fuels such as coal, crude oil and natural gas emits CO₂ to the atmosphere, leading to global warming problem. Therefore, the use of alternative fuels is becoming an important issue.

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Hydrogen is considered as the future potential energy carrier because it has high heating value and contains no carbon atom. The heating value of hydrogen is higher than that of natural gas and coal approximately 3 and 4 times, respectively. Nowadays, there are many hydrogen production processes which have been invented.

Steam reforming (SR) process has been widely used for hydrogen production. It is considered to be the most economical way to produce hydrogen. The SR process with general feedstock i.e., natural gas, which its main component is methane, is called steam methane reforming (SMR). Several units are involved in this process which mainly consists of pretreatment unit to purify feed, steam reforming reactor, water-gas shift reactor, and purification unit to produce the purified hydrogen. A conventional SMR process is illustrated in Fig. 1. The reactions occurred in the reforming reactor are listed below.

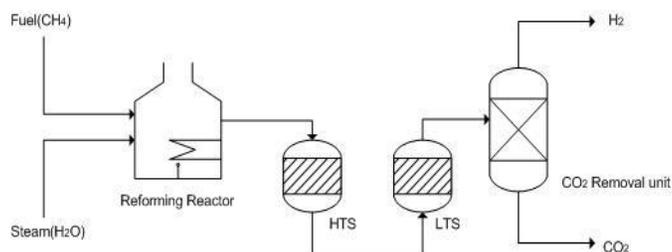


Fig. 1 Flowsheet for a conventional SMR process

Reaction (1) is steam methane reforming, (2) is water-gas shift and (3) is a global steam methane reforming, combination between (1) and (2). In the reforming reactor, high temperature and pressure are required for highly endothermic reaction and limiting the reactor size, respectively. Therefore, this reactor is typically carried out at temperature of 800–1000°C and pressure of 14–20 atm. From previous researches, various catalysts can be applied in SMR process such as Ni/ α -Al₂O₃ [1], Ni/Ce-ZrO₂ [2], Ni/ZrO₂ [3], Ni/SiO₂ [4], Ru/ α -Al₂O₃ [5], BaRh_xZr_(1-x)O₃ [6], and Rh/Al₂O₃ [7]. Although Ni is active lower than noble metal such as Rh and Ru; however, it is still more attractive due to its lower cost. The effluent gas from the reforming reactor contains about 76% H₂, 5% CH₄, 9% CO, and 10% CO₂ on a molar dry basis. The effluent gas from reforming reactor is routed to the

water-gas shift reactors including high temperature shift reactor (HTS) and low temperature shift reactor (LTS). In these reactors, (2) is favored. The role of these reactors is to convert the remaining CO into more H₂. Lastly, the hydrogen purification unit is equipped to produce high purified H₂. For this unit, either absorption via amine scrubber or adsorption via pressure swing adsorption (PSA) can be processed.

Apart from SR process, partial oxidation (POX) and autothermal reforming (ATR) processes can be also used to produce hydrogen. However, oxygen acting as an oxidizing agent needs to be separated from air to take place the oxidation in these processes, leading to high cost. In order to overcome this disadvantage, chemical looping reforming (CLR) process is developed. This process involves both steam reforming reaction and partial oxidation. The metal oxide is selected as an oxidizing agent instead of pure oxygen, resulting in the reduction in cost. A basic chemical looping reforming system composes of two reactors, one for fuel to produce hydrogen and another one for air to regenerate the metal (Fig. 2).

Hydrocarbon and steam are fed to the fuel reactor, which is filled with metal oxides. The metal oxides have been investigated by several researchers such as NiO/SiO₂, CuO/SiO₂, Mn₂O₃/SiO₂ and Fe₂O₃/SiO₂ from [8], Ce-Fe-O, Ce-Cu-O and Ce-Mn-O from [9], and La_{0.7}Sr_{0.3}Cr_{0.1}Fe_{0.9}O₃ from [10]. The most widely-used metal oxide is nickel oxide. The related reactions within fuel reactor are as follows:

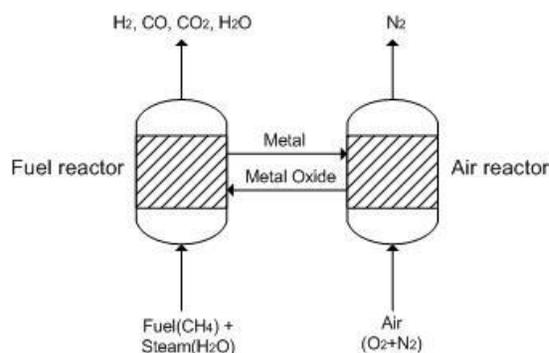
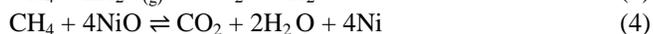
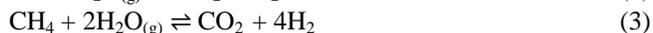
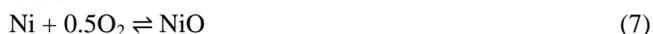


Fig. 2 The principle of chemical looping reforming



Reactions (4)-(6) are complete oxidation, partial oxidation and CO₂ reforming, respectively. NiO is reduced to Ni²⁺ when the reaction takes place, transferring oxygen to the fuel. For re-use, Ni²⁺ is converted back into metal oxide form by passing it to the air reactor, where air is fed to provide oxygen for oxidation. The regeneration occurs through the following reaction.



After the regeneration process, metal oxide is recycled to the fuel reactor.

Even though SMR is considered to be the most economical way to produce hydrogen, it still has some disadvantages such as high energy requirement in reforming reactor and having several downstream units. To improve the SMR process, novel hydrogen production processes have been invented such as sorption enhanced steam reforming (SESR) and sorption enhanced chemical looping reforming (SECLR) process.

The SESR is carried out by adding CO₂ adsorbent into the reforming reactor. According to (3), equilibrium is shifted forward due to the removal of CO₂. Consequently, more CH₄ conversion and higher H₂ purity are achieved. Therefore, the CO₂ adsorbent is the crucial part of this process. The desired properties of the adsorbents can be summarized by the following lists.

1. High CO₂ adsorption capacity and selectivity to the CO₂
2. Fast adsorption kinetics
3. Major part of the adsorption capacity occurring through physisorption.
4. Good cyclic stability
5. Reasonable cost

The examples of the CO₂ adsorbents from previous studies are CaO [11], CaO/Ca₁₂Al₁₄O₃₃ [12], CaO-Ca₉Al₆O₁₈ [13], HTCS [14], MgO [15], Al₂O₃ [15], Li₂O [16], Li₂ZrO₃ [17], Li₄SiO₄ [18], Li₂CuO₂ [19], Li₅AlO₄ [20], and Na₂ZrO₃ [21]. The promising CO₂ adsorbent is Ca-based sorbent because it fulfills most of the above requirements. This sorbent adsorbs CO₂ through (8) as expressed below.



The reaction (8), so-called carbonation, is exothermic; therefore, it can provide heat to the endothermic reaction (3). This sorbent continues to adsorb CO₂ until it reaches saturation point. Regeneration process is required to reuse the adsorbent. Regeneration occurs through calcination as shown in the following reaction.



Reaction (9) is typically operated at about 800-1000°C. SESR could be considered as future potential process for hydrogen production. However, there are still some problems of this process which are energy consumption for adsorbent regeneration and limitation of hydrogen purity lower than 99.99% at 500-650°C.

For the process of sorption enhanced chemical looping reforming (SECLR), this is the combined process between sorption enhanced steam reforming (SESR) and chemical looping reforming (CLR) process. SECLR is composed of three connected reactors including reforming reactor, air reactor and calcination reactor as illustrated in Fig. 3.

Metal oxide and CO₂ adsorbent are employed in SECLR. The CO₂ formation from SMR, water-gas shift and oxidation in reforming reactor is captured by CO₂ adsorbent via (8), leading to more fuel conversion and higher hydrogen purity. The interesting metal oxide and CO₂ adsorbent are NiO and CaO, respectively. The main reactions take place in reforming reactor, air reactor and calcination reactor are (1)-(9).

Reoxidation to metal oxide form (7) is highly exothermic. Heat from this reaction can be provided to the calcination reactor and reforming reactor which is possible to reach thermo neutral. Therefore, this process has potential to carry out under self-sufficient condition.

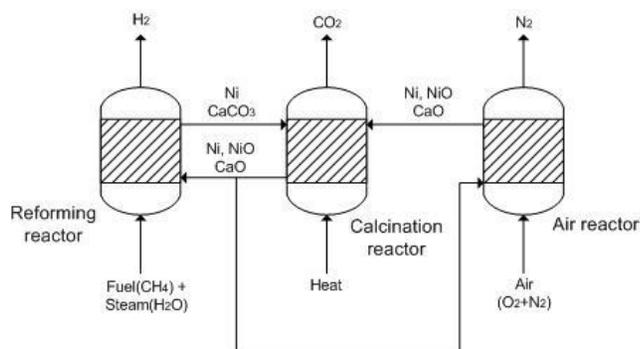


Fig. 3 The principle of sorption enhanced chemical looping reforming

As reported by [23], SECLR process has been modified by splitting a part of recycled solids from air reactor to reforming reactor. The purpose of this modification was to manage the heat integration of three adiabatic reactors.

Feed for hydrogen production process is typically natural gas, which is non-renewable energy source. For environmental impact, the use of renewable energy source is of interest and one of those is biogas. Although the combustion of biogas releases CO_2 as same as the case of using natural gas; however, the CO_2 released from biogas is a part of the carbon cycle and therefore is carbon neutral.

In this work, simulation of modified SECLR for hydrogen production was examined. The feedstock, biogas with 50% mol CH_4 and 50% mol CO_2 , was used for this process. NiO and CaO were employed as an oxidizing agent and CO_2 adsorbent, respectively. The process performances including hydrogen purity, methane conversion and energy consumption were determined.

II. SIMULATION OF SECLR

The hydrogen production processes via sorption enhanced chemical looping reforming (SECLR), which NiO and CaO was used in the system, were simulated by ASPEN Plus Program. The methods and units applied for this simulation are shown as follows:

- prediction property model: SOLIDS model with modified vapor phase of ESSRK
- reforming reactor, calcination reactor and air reactor: RGIBBS
- fluid/solid separator: CYCLONE

The SOLIDS model was used due to the presence of solid in this process. The feed stream is biogas composed of 50% CH_4 and 50% CO_2 by mole. The assumption was that the formation of other compounds, except for CH_4 , H_2O , H_2 , CO_2 , CO , Ni, NiO, CaCO_3 , CaO, N_2 , and O_2 , was thermodynamically unfavored at relevant process conditions.

III. RESULTS AND DISCUSSION

A. Model Validation

In this work, our simulation was firstly validated with the results from [22], where the feed is pure methane. Fig. 4 shows the flowsheet of SECLR system used for model validation. The block components and streams are summarized in Tables I and II, respectively.

The validation was divided into two cases consisting of SECLR at pressure of 1 and 5 bar. Table III exhibits the SECLR validation results for both cases.

TABLE I
SUMMARY OF BLOCK COMPONENTS FOR THE MODEL

Model	Name	Description
RGIBBS	REFORM	Simulates steam reforming and oxidation reaction
	CALCINE	Simulates calcination reaction of CaCO_3
	AIRREACT	Simulates oxidation reaction of Ni
CYCLONE	CYCLONE1	Separates gas and solid products from reforming reactor
	CYCLONE2	Separates gas and solid products from calcination reactor
	CYCLONE3	Separates gas and solid products from air reactor
FSPLT	SPLT	Splits regenerated solids to reforming reactor and to air reactor

TABLE II
SUMMARY OF STREAMS FOR THE MODEL

Stream	Description
CH4	Pure methane feed
H2O	H_2O feed
OUTREFOR	Products from reforming reactor
H2	Hydrogen product
NI+CACO3	Solid to calcination reactor for CaCO_3 calcination
OUTCAL	Products from calcination reactor
CO2	CO_2 desorbed from regeneration
OUTCY2	Regenerated solids before splitting to reforming reactor and air reactor
NINIOCAO	Regenerated solids to reforming reactor
TOAIR	Regenerated solids to air reactor
AIR	Air used for oxidation of Ni
OUTAIR	Products from air reactor
N2	N_2 gas (inert)
NIOCAO	Regenerated solids to calcination reactor to provide heat

As seen in Table III, the results from this work were in good agreement with those reported by [22]; H_2 purity and CH_4 conversion were found that deviated only 0.3% for 1 bar operation case and 0.2% and 0.4% for 5 bar operation case. Therefore, this simulation model is used for further investigation on SECLR and modified SECLR processes.

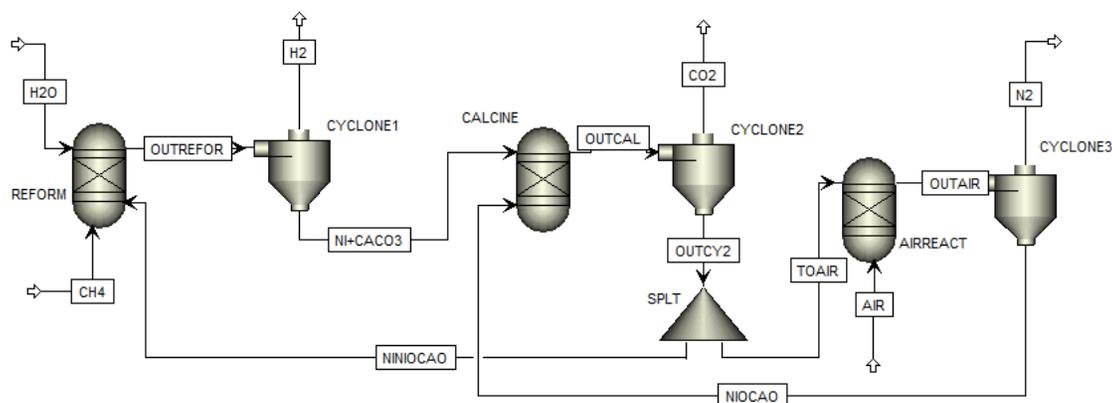


Fig. 4 The simulated diagram of SECLR for model validation

TABLE III
SECLR VALIDATION RESULTS

Parameter	@ 1 bar		@ 5 bar	
	This work	[22]	This work	[22]
CH ₄ feed	0.1 kmol/h	1 mol	0.1 kmol/h	1 mol
H ₂ O feed	0.22 kmol/h	2.2 mol	0.26 kmol/h	2.6 mol
O ₂ feed	0.053 kmol/h	0.53 mol	0.055 kmol/h	0.55 mol
N ₂ feed	0.2 kmol/h	2 mol	0.207 kmol/h	2.07 mol
CH ₄ feed T.(°C)	321	321	340	340
Air feed T.(°C)	576	576	630	630
Reformer T.(°C)	580	580	630	630
Cal. T.(°C)	880	880	980	980
Air reactor T.(°C)	1000	1000	1050	1050
Solid CR to AR(%)	92.2	92.2	95.2	95.2
CH ₄ conversion(%)	97.3	97	95	94.6
H ₂ purity (%)	98.4	98.7	97.6	97.8

B. System Performance Analysis

In this part, the modified SECLR process fed by biogas (50% mol CH₄ and 50% mol CO₂) was investigated. The configuration of modified SECLR was based on the system proposed by [23], of which some recycled solids were partially split from the air reactor to the reforming reactor. The flowsheet of modified SECLR is shown in Fig. 5. The block components and streams are similar to those in Tables II and III, except for the additional information as listed below.

FSPLT (SPLT2): To split regenerated solids to reforming reactor and to calcination reactor

RETOCAL: Regenerated solids to calcination reactor

RETREFOR: Regenerated solids to reforming reactor

The analysis was considered at system pressure of 1 bar. The simulation results of modified SECLR fed by biogas are shown in Table IV.

TABLE IV
THE SIMULATION RESULTS OF MODIFIED SECLR FROM BIOGAS

Parameter	Values
CH ₄ feed (kmol/h)	0.1
CO ₂ feed (kmol/h)	0.1
CaO:(CH ₄ +CO ₂ feed)	0.5
H ₂ O feed (kmol/h)	0.22
O ₂ feed (kmol/h)	0.053
N ₂ feed (kmol/h)	0.2
CH ₄ feed Temp. (°C)	321
Air feed Temp. (°C)	576
Reformer Temp. (°C)	580
Calcination reactor Temp. (°C)	880
Air reactor Temp. (°C)	1000
Solid CR to AR (%)	92.2
Solid AR to CR (%)	90
CH ₄ conversion (%)	83.2
H ₂ purity (%)	66.2
RR energy consumption (kW)	2.35
CR energy consumption (kW)	3.31

*AR = Air reactor; CR = Calcination reactor; RR = Reforming reactor

From Table IV, the results show that methane conversion and hydrogen purity were close to those of SR equilibrium values which are about 80% and 72%, respectively. It was presumed that CO₂ did not tend to react with CH₄ to form CO and H₂ via (6) or dry reforming but it can be adsorbed by CaO to form CaCO₃ via (8) or carbonation. Owing to the condition at adsorbent saturation, CaO could not adsorb CO₂ so the shift of (3) toward H₂ was not favored. Therefore, methane conversion and hydrogen purity of modified SECLR from biogas with 50% mol CH₄ and 50% mol CO₂ were limited to equilibrium value of SR.

In terms of energy consumption, comparing with pure methane feed, higher energy was consumed at reforming reactor as a result of high CO₂ content in the feed stream. This was because the heat provided to reforming reactor partially divided to heat up CO₂ in the feed.

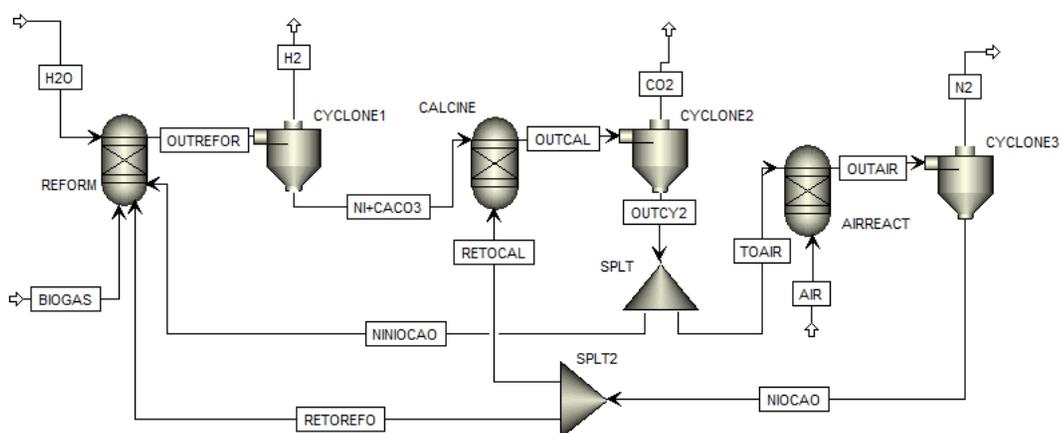


Fig. 5 The simulated diagram of modified SECLR

IV. CONCLUSION

The SECLR and modified SECLR processes for hydrogen production were simulated by Aspen Plus Program. The SECLR process was firstly validated and found that the use of SOLIDS model with modified vapor phase of ESSRK for property method and RGIBBS for the three reactors including reforming reactor, calcination reactor and air reactor was a good choice for process simulation like SECLR.

The modified SECLR process fed by biogas (50% mol CH₄ and 50% mol CO₂) was also studied. The results showed that the methane conversion and hydrogen purity were close to those of SR equilibrium values because of adsorbent saturation condition. Moreover, the increase in CO₂ content in feed caused higher energy consumption at reforming reactor because a portion of heat supplied to reforming reactor was necessary to be heated up CO₂ in the feed stream.

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