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SIMULATION AND PROCESS DESIGN FOR HYDROGEN PRODUCTION USING SORPTION-ENHANCED CHEMICAL LOOPING REFORMING OF METHANE

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A Thesis Submitted in Partial Fulfillment of the Requirements
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เอกชน ผู้เลื่องลือ : การจำลองและการออกแบบกระบวนการสำหรับการผลิตไฮโดรเจนด้วยเคมิคอลลูปปิงรีฟอร์มมิงของมีเทนที่ส่งเสริมด้วยการดูดซับ (SIMULATION AND PROCESS DESIGN FOR HYDROGEN PRODUCTION USING SORPTION-ENHANCED CHEMICAL LOOPING REFORMING OF METHANE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.วัชรพงษ์ ขาวดี, 99 หน้า.

งานวิจัยนี้เป็นการศึกษาและปรับปรุงกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับสำหรับการผลิตไฮโดรเจน โดยกระบวนการนี้จะใช้มีเทนเป็นวัตถุดิบ แคลเซียมออกไซด์เป็นตัวดูดซับคาร์บอนไดออกไซด์ และนิกเกิลออกไซด์เป็นตัวออกซิไดซ์ สำหรับงานวิจัยนี้จะทำการศึกษาผลของอุณหภูมิของเครื่องปฏิกรณ์รีฟอร์มมิง อัตราการป้อนของไอน้ำ และอัตราการไหลของของแข็งต่อสมรรถนะที่ได้ของกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับเป็นอันดับแรก จากนั้นจะทำการเปรียบเทียบสมรรถนะที่ได้จากสภาวะที่ดีที่สุดของกระบวนการนี้กับกระบวนการผลิตไฮโดรเจนอีกสองกระบวนการ นั่นคือ กระบวนการรีฟอร์มมิงด้วยไอน้ำ และกระบวนการรีฟอร์มมิงด้วยไอน้ำที่ส่งเสริมด้วยการดูดซับ ซึ่งพบว่ากระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับมีสมรรถนะที่ดีที่สุด ต่อมาได้ทำการพิจารณาถึงความเป็นไปได้ในการดำเนินการโดยไม่มีการถ่ายเทความร้อนของเครื่องปฏิกรณ์สำหรับกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับ พบว่าเครื่องปฏิกรณ์ทุกเครื่องของกระบวนการนี้สามารถดำเนินการโดยไม่มีการถ่ายเทความร้อนได้โดยทำการปรับสภาวะบางอย่าง ได้แก่ อุณหภูมิไอน้ำสายป้อน อุณหภูมิอากาศสายป้อน อัตราส่วนของแข็งที่ส่งจากเครื่องปฏิกรณ์แคลซิเนชันไปยังเครื่องปฏิกรณ์อากาศ และอัตราส่วนของแข็งที่ส่งจากเครื่องปฏิกรณ์อากาศไปยังเครื่องปฏิกรณ์แคลซิเนชัน จากนั้นได้ทำการศึกษาเพิ่มเติมถึงผลของคาร์บอนไดออกไซด์ในสายป้อนต่อการดำเนินการโดยไม่มีการถ่ายเทความร้อนของเครื่องปฏิกรณ์ของกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับ ซึ่งพบว่าคาร์บอนไดออกไซด์ในสายป้อนที่มากขึ้นนั้นส่งผลเสียต่อสมรรถนะได้จากกระบวนการ เช่น อัตราการผลิตไฮโดรเจนและความบริสุทธิ์ของไฮโดรเจนที่ผลิตได้น้อยลง สำหรับเครื่องปฏิกรณ์ที่ใช้ในกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับนั้นได้มีการคำนึงถึงการออกแบบเบื้องต้นด้วยเช่นกัน ซึ่งสามารถระบุได้ว่าเครื่องปฏิกรณ์จะเป็นเครื่องปฏิกรณ์แบบฟลูอิดไดซ์เบดสามเครื่องต่อกัน ซึ่งเครื่องปฏิกรณ์รีฟอร์มมิงและแคลซิเนชันจะดำเนินการในช่องเกิดฟองอากาศ ในขณะที่เครื่องปฏิกรณ์อากาศจะดำเนินการในช่วงช่วงฟลูอิดไดซ์แบบเร็ว โดยเส้นผ่านศูนย์กลางของแต่ละเครื่องปฏิกรณ์นั้นจะมีความแตกต่างกันขึ้นอยู่กับช่วงการดำเนินการของแต่ละเครื่องปฏิกรณ์

ภาควิชา วิศวกรรมเคมี

สาขาวิชา วิศวกรรมเคมี

ปีการศึกษา 2558

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AGACHON PHULUANGLUE: SIMULATION AND PROCESS DESIGN FOR HYDROGEN PRODUCTION USING SORPTION-ENHANCED CHEMICAL LOOPING REFORMING OF METHANE. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: WATCHARAPONG KHAODEE, D.Eng., 99 pp.

This research focuses on the investigation and improvement of sorption enhanced chemical-looping reforming process for hydrogen production. Methane, CaO and NiO were employed as a raw material, CO_2 adsorbent, and oxidizing agent, respectively. In this work, the effects of reforming temperature, steam flow rate, and solid circulation rate on the process performances of sorption enhanced chemical-looping reforming process were firstly studied. Subsequently, its process performances at the optimal condition were compared with those from other two hydrogen production processes i.e., steam reforming and sorption enhanced steam reforming processes. It was found that the sorption enhanced chemical-looping reforming process showed the best performance. In addition, the feasibility of adiabatic operation of reactors for sorption enhanced chemical-looping reforming process was considered. It was found that all reactors of this process could be adiabatically operated by adjusting some parameters such as steam feed temperature, air feed temperature, solid ratio from calcination reactor to air reactor, and solid ratio from air reactor to calcination reactor. Moreover, the influence of CO_2 content in feed stream on an adiabatic operation of sorption enhanced chemical-looping reforming process was investigated. Higher in CO_2 content in feed stream exhibited the negative effects on the SECLR process that was operated adiabatically such as less H_2 productivity and H_2 purity. For the reactors of sorption enhanced chemical-looping reforming process, their preliminary design was also taken into account. It could be reasonably indicated that the reactors of SECLR process would be 3-connected fluidized bed reactor which reforming and calcination reactors were carried out in bubbling regime while air reactor was operated in fast fluidization regime. The difference in diameter of each reactor depending on its operating regime was observed.

Department:	Chemical Engineering	Student's Signature ....
Field of Study:	Chemical Engineering	Advisor's Signature ....
Academic Year:	2015	Co-Advisor's Signature ....

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CHAPTER 1

INTRODUCTION

1.1 Rationale

At present, the consumption of fossil sources has continuously increased year by year since the energy supply mostly comes from fossil fuels such as coal, crude oil, and natural gas. However, these sources, which are dead animals and plants accumulated for very long time, are non-renewable because they are being depleted much faster than the new ones being formed. Moreover, the global warming issue is seriously concerned as a result of CO_2 emission to atmosphere from the uses of fossil fuels. Therefore, switching from fossil fuels to alternative fuels has been necessarily taken into account. According to no carbon atom in gaseous hydrogen, it can be considered as clean energy and the future potential energy carrier due to its high heating value. The heating value of hydrogen is higher than that of natural gas and coal approximately 3 and 4 times, respectively. With regard to hydrogen production processes, the steam reforming (SR) has been operated conventionally. Although SR is practically used in various industries, it still has some limitations in terms of thermodynamic limitation, high energy demand, catalyst deactivation and consisting of several units such as reforming reactor, water-gas shift reactor and purification unit. To modify and improve the SR process, novel hydrogen production processes have been invented such as sorption enhanced steam reforming (SESR) and sorption enhanced chemical looping reforming (SECLR) processes. The SESR is carried out by filling CO_2 adsorbent into the reforming reactor. According to Le Chatelier’s principle, the equilibrium of reforming reaction is shifted forward due to the removal of CO_2, resulting in higher in CH_4 conversion and H_2 purity. This sorbent continues to adsorb CO_2 until reaching the saturation point. The regeneration process is subsequently required for the reuse purpose. The interesting adsorbents used for this process are CaO, hydrotalcite (HTC) and Li_2CO_3. For the process of sorption enhanced chemical looping reforming (SECLR), it has been developed through a combination of sorption enhanced steam reforming (SESR) and chemical looping reforming (CLR) process. Typically, metal oxide and CO_2 adsorbent are employed in SECLR. The metal oxide is used as an oxidizing agent instead of pure oxygen, leading to the reduction in cost due to the absence of air separation unit. The metal oxide is reduced to its metal form when the reaction takes place in the reforming reactor. However, the metal is converted back into metal oxide form by passing it to the air reactor, where air is fed to provide oxygen for oxidation. The metal oxides such as NiO/SiO_2, CuO/SiO_2, Mn_2O_3/SiO_2 and Fe_2O_3/SiO_2 have been proposed to employ in SECLR.

In this research, SR, SESR and SECLR processes fed by methane or methane-containing gas mixture such as the mixture of methane and carbon dioxide are of particular interest. NiO and CaO are selected as an oxidizing agent and CO_2 adsorbent, respectively. The optimal process by examining the process performances in terms of hydrogen purity, methane conversion, hydrogen production rate, and energy requirement are considered. In addition, the energy self-sustained operation is also concerned for comparative study among hydrogen production processes i.e., SR, SESR and SECLR.

1.2 Objectives

1) To model and determine optimal operating condition of SECLR processes for hydrogen production from methane.

2) To determine the process performances including hydrogen purity, methane conversion, hydrogen production rate, and energy requirement for SR and SESR process, compared with SECLR processes.

3) To study the feasibility of adiabatic operation of SECLR process compared with the process under isothermal operation.

4) To investigate the effect of CO_2 content in feed stream on adiabatic operation of SECLR process.

5) To design reactor configuration for SECLR process.

1.3 Scope of Works

1) Aspen Plus program will be used to simulate the processes of SR, SESR and SECLR for hydrogen production. The processes are based on no external fuel supplied.

2) Methane is selected as a feedstock for SR, SESR and SECLR processes.

3) NiO and CaO are considered as an oxidizing agent and CO_2 adsorbent, respectively.

4) The process performances including hydrogen purity, methane conversion, hydrogen production rate and energy consumption for SR, SESR and SECLR processes will be determined and compared by varying the operating conditions such as operating temperature, steam feed flow rate and solid circulation rate.

5) Solid circulation rate and feed pre-heating temperature are adjusted for adiabatic operation of SECLR process.

6) The effect of CO_2 content in feed stream on adiabatic operation is also investigated.

7) The reactor configuration of SECLR process is lastly designed.

1.4 Expected Output

Propose a suitable process for hydrogen production from methane.

CHAPTER 2

THEORY

This chapter presents the essential information for various hydrogen production processes including the steam methane reforming (SMR), sorption enhanced steam methane reforming (SESMR), partial oxidation (POX) and catalytic partial oxidation (CPOX), chemical looping reforming (CLR) and sorption enhanced chemical looping reforming (SECLR).

2.1 Hydrogen Production Processes

Hydrogen is considered as the future potential energy carrier because it has high heating value and contains no carbon atom. Presently, there are many hydrogen production processes that have been proposed. The description of hydrogen production processes concerned in this work is concluded below.

2.1.1 Steam Methane Reforming (SMR)

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 Figure 2.1.

The reactions occurred in the reforming reactor are listed below.

$$CH_4 + H_2O_{(g)} \rightleftharpoons CO + 3H_2 \qquad \Delta H^0_{298} = 206.2 \text{ kJ/mol} \tag{2.1}$$

$$CO + H_2O_{(g)} \rightleftharpoons CO_2 + H_2 \qquad \Delta H^0_{298} = -41.2 \text{ kJ/mol} \tag{2.2}$$

$$CH_4 + 2H_2O_{(g)} \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H^0_{298} = 165 \text{ kJ/mol} \qquad (2.3)$$

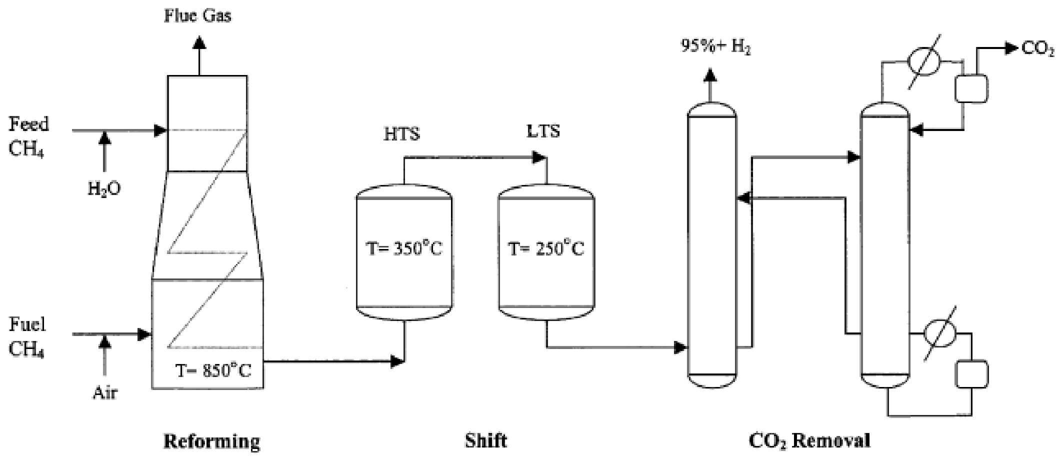

Figure 2.1 Flowsheet for a conventional SMR process [1]

The reactions (2.1) to (2.3) are steam methane reforming, water-gas shift and global steam methane reforming, combination between (2.1) and (2.2). In this reactor, high temperature and pressure are required for highly endothermic reaction and limiting the reactor size, respectively. 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, reaction (2.2) is favored. The role of these reactors is to convert the remaining CO into more H_2. Lastly, the hydrogen purification unit is equipped to produce high purified H_2. For this unit, either absorption via amine scrubber or adsorption via pressure swing adsorption (PSA) can be processed.

2.1.2 Sorption Enhanced Steam Methane Reforming (SESMR)

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, sorption enhanced steam methane reforming (SESMR) has been invented. The SESR is carried out by adding CO_2 adsorbent into the reforming reactor. According to reaction (2.3), equilibrium is shifted forward due to the removal of CO_2. Consequently, more CH_4 conversion and higher H_2 purity are achieved. Therefore, the CO_2 adsorbent is the crucial part of this process. The promising CO_2 adsorbent is Ca-based sorbent. This sorbent adsorbs CO_2 through reaction (2.4) as expressed below.

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \Delta H^0_{298} = -178 \text{ kJ/mol} \qquad (2.4)$$

The reaction (2.4), so-called carbonation, is exothermic; therefore, it can provide heat to the endothermic reaction (2.3). This sorbent continues to adsorb CO_2 until it reaches saturation point. Regeneration process is required to reuse the adsorbent. Regeneration occurs through calcination as shown in the following reaction.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad \Delta H^0_{298} = 178 \text{ kJ/mol} \qquad (2.5)$$

The reaction (2.5) is typically operated at about 800-1000°C.

The SESMR process can be carried out as batch process using two or more parallel externally heated fixed bed reactors. One is operated in adsorption mode whereas the other is processed in desorption mode. In addition, SESMR is also operated as an interconnected fluidized bed system which sorbent is circulated between reformer and regenerator. However, the mechanical stability of the sorbent is the additional requirement for fluidized bed system. Figure 2.2 illustrates the example of SESMR carried out as batch process using two fixed bed reactor [2].

2.1.3 Partial Oxidation (POX) and Catalytic Partial Oxidation (CPOX)

The partial oxidation (POX) is the process which methane is reacted with oxygen. The POX occurs through reaction (2.6) as shown below.

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H^0_{298} = -35.7 \text{ kJ/mol} \qquad (2.6)$$

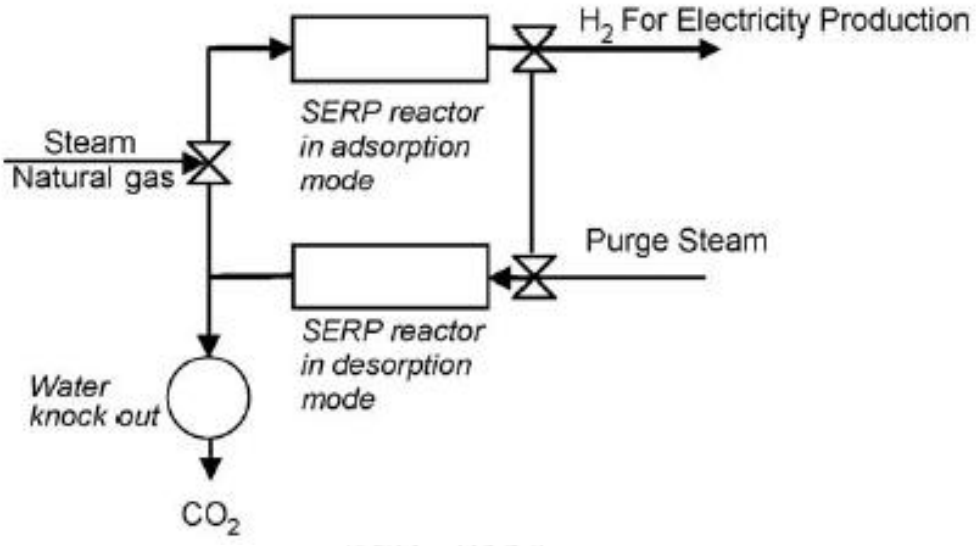

Figure 2.2 SESMR in power generation plants: adsorption and desorption modes [2]

However, the side reactions as listed in reactions (2.7)-(2.9) are possible to take place in this process.

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \qquad \Delta H^0_{298} = -890.3 \text{ kJ/mol} \qquad (2.7)$$

$$CO + 0.5O_2 \rightleftharpoons CO_2 \qquad \Delta H^0_{298} = -283 \text{ kJ/mol} \qquad (2.8)$$

$$H_2 + 0.5O_2 \rightleftharpoons H_2O \qquad \Delta H^0_{298} = -285.8 \text{ kJ/mol} \qquad (2.9)$$

The exothermic POX typically conducts at a temperature range of 1423-1773 K (1150-1500°C) and a pressure range of 25-80 bar. However, this process still requires an additional heat for operating the equipment.

Unlike POX, the catalytic partial oxidation (CPOX) is conducted in the reactor filled with catalyst bed, causing lower in operating temperature. Ni-based catalyst is widely used for CPOX. However, CPOX is still at the stage of catalyst development.

The syngas ratio (H_2:CO) obtained from this process is around 2 which is lower than from SMR. Moreover, another disadvantage of POX and CPOX is oxygen plant requirement. Hence, CPOX is not applied as much as SMR for hydrogen production.

2.1.4 Chemical Looping Reforming (CLR)

The chemical looping reforming (CLR) process involves both steam reforming reaction and partial oxidation. Unlike POX, 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 is composed of two reactors, one for fuel to produce hydrogen and another one for air to regenerate the metal (Figure 2.3).

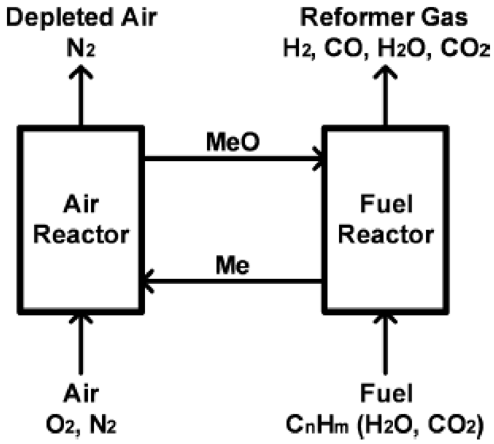

Figure 2.3 The principle of chemical looping reforming [3]

Hydrocarbon and steam are fed to the fuel reactor, which is filled with metal oxides. The most widely-used metal oxide is nickel oxide. The related reactions within fuel reactor include reactions (2.1)-(2.3) and (2.10)-(2.12) as shown below.

$$CH_4 + 4NiO \rightleftharpoons CO_2 + 2H_2O + 4Ni \qquad \Delta H^0_{1200} = 136 \text{ kJ/mol} \tag{2.10}$$

$$CH_4 + NiO \rightleftharpoons CO + 2H_2 + Ni \qquad \Delta H^0_{1200} = 211 \text{ kJ/mol} \tag{2.11}$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^0_{1200} = 259 \text{ kJ/mol} \tag{2.12}$$

Reactions (2.10)-(2.12) are complete oxidation, partial oxidation and CO_2 reforming, respectively. NiO is reduced to Ni^{2+} when the reaction takes place, transferring oxygen to the fuel. For re-use, Ni^{2+} 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.

$$Ni + 0.5O_2 \rightleftharpoons NiO \qquad \Delta H^0_{1200} = -234 \text{ kJ/mol} \qquad (2.13)$$

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

2.1.5 Sorption Enhanced Chemical Looping Reforming (SECLR)

The sorption enhanced chemical looping reforming (SECLR) is the combined process between sorption enhanced steam reforming (SESR) and chemical looping reforming (CLR) processes. SECLR is composed of three connected reactors including reforming reactor, air reactor, and calcination reactor as illustrated in Figure 2.4.

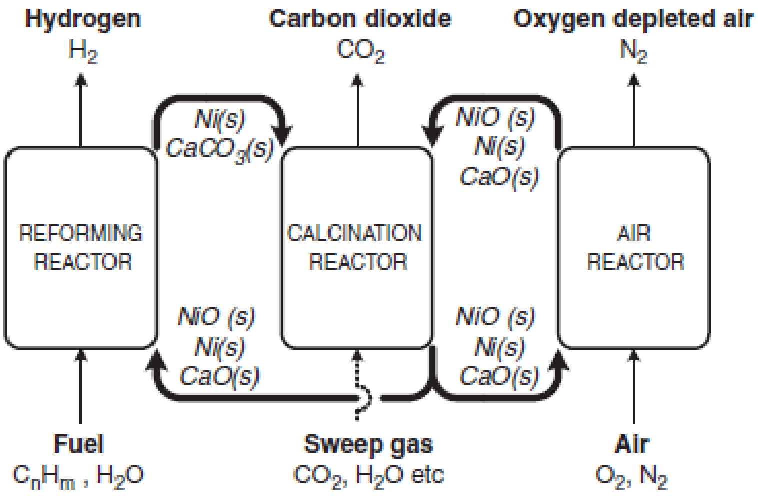

Figure 2.4 The principle of sorption enhanced chemical looping reforming [4]

Metal oxide and CO_2 adsorbent are employed in SECLR. The CO_2 formation from SMR, water-gas shift and oxidation in reforming reactor is captured by CO_2 adsorbent via reaction (2.4), leading to more fuel conversion and higher hydrogen purity. The interesting metal oxide and CO_2 adsorbent are NiO and CaO, respectively. The main reactions taken place in reforming reactor, air reactor, and calcination reactor are reactions (2.1)-(2.5), and (2.10)-(2.13).

Reoxidation to metal oxide form (reaction (2.13)) 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.

CHAPTER 3

LITERATURE REVIEWS

Hydrogen production processes have been studied for decades. There are many interesting processes, especially sorption enhanced steam methane reforming (SESMR) and sorption enhanced chemical looping reforming (SECLR) processes which high purity of hydrogen can be provided. In this chapter, the literature reviews are mainly divided into four parts. The first part considers the researches of steam methane reforming processing with support and catalyst system. Regarding the second part, the catalysts and CO_2 adsorbents that are widely used in sorption enhanced steam methane reforming (SESMR) for CO_2 removal are mentioned. The advantages and drawbacks of adsorbents such as calcium-based adsorbent (CaO), hydrotalcite sorbent and ceramic adsorbent are also indicated in this part. For the SESMR operation, its background is provided in the third part. In addition, the researches of this process focus on different types of reactor. The study of each reactor type is further described in terms of cyclic stability of sorbents and suitable operating condition. For the last part, chemical looping reforming (CLR) and sorption enhanced chemical looping reforming (SECLR) processes are reviewed.

3.1 Steam Methane Reforming

Steam methane reforming (SMR) has been widely used for hydrogen production. The catalysts in this reaction have to process at severe operating conditions which are temperatures in the range of 823-1223 K, pressures up to 4 MPa and the presence of large amount of steam. Therefore, a durability of steam reforming catalysts is one of the most important factors to be considered. A suitable steam reforming catalyst should resist the coking or carbon deposition [5] and the decomposition by steam, provide high selectivity, retard to side reactions, maintain the activity at high temperature and pressure, and have high mechanical stability. In the laboratory and industrial scale for hydrogen production, the commonly used steam reforming catalyst is nickel (nickel supported on alumina), although its activity is lower than other active metals such as palladium, platinum, rhodium. Moreover, it usually has less stability than those active metals due to carbon formation or oxidation problem. However, Ni is more attractive due to its lower cost.

Not only the catalyst, but also the support needs to be considered as one of the important factors. Various supports used for SMR such as α- and γ-Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, ZrO_2, and TiO_2 are gathered from several works. Many researchers have studied the effect of different supports on SMR reaction. Dong *et al.* (2002) studied the effects of Nickel (Ni) content and the role of support via Ni/Ce-ZrO_2 as a catalyst/support on the SMR reaction. They claimed that the conversion of methane increased with the increasing nickel content up to 15 wt.%. Furthermore, the stability was found to be affected and 15 wt.% of Ni showed the remarkable stability. It can be concluded that Ce-ZrO_2 support played an important role in the catalytic activity and stability of Ni/Ce-ZrO_2 catalysts [6]. Liu *et al.* (2002) investigated the performance of Ni/Ce-ZrO_2-θ-Al_2O_3 at low temperature SMR. Good performance of Ni/Ce-ZrO_2-θ-Al_2O_3 was found in terms of the catalytic activity and stability toward SMR at the temperature range of 400-650°C. They also revealed that at temperature of 650°C, increase in O_2/CH_4 or H_2O/CH_4 ratio led to higher methane conversion while increasing of H_2O/CH_4 ratio resulted in increasing H_2 content in dry tail gas [7]. Ni catalyst was still continuously studied. Matsumura and Nakamori (2003) investigated the effects of different kinds of supports such as silica, ɤ-alumina, and zirconia (Ni/SiO_2, Ni/Al_2O_3, Ni/ZrO_2) at low temperature SMR (500°C). The effect of reducing temperature was also examined. They claimed that nickel was oxidized by steam during the reaction, leading to the decreased activity of nickel supported on silica (Ni/SiO_2) which was reduced with hydrogen at 500°C. However, the catalyst reduced at 700°C was fairly active although nickel was partially oxidized during the reaction. Among the examined supports, nickel supported on zirconia (Ni/ZrO_2) was the most effective catalyst in the SMR process at 500°C [8]. Takahashi *et al.* (2004) further investigated the effect of ZrO_2 support. Ni/SiO_2 and Ni/SiO_2-ZrO_2 catalysts prepared by homogeneous precipitation in sol–gel-derived wet silica gel were employed as the catalyst/support in order to study the effect of ZrO_2 on steam resistance. The results showed that Ni/SiO_2-ZrO_2 was more stable to steam than Ni/SiO_2. They claimed that the lost activity was attributed to the coarsening of silica that occurred in the presence of high-temperature steam hindered the active surface of Ni [9]. Beside the effects of catalyst and support, the effect of promoter was also investigated by some researchers. Maluf and Assaf (2009) studied the effect of different loadings of Mo oxide as promoter (0.05, 0.5, 1.0 and 2.0 wt.%) on catalytic performance of NiO/Al_2O_3 catalyst. High stability could be obtained for the catalysts with all Mo oxide contents with steam/methane feed ratio of 4:1. However, only the catalyst with 0.05 wt.% Mo could be stable throughout 500 min of the test with the steam/methane feed ratio of 2:1. They revealed that the addition of Mo to Ni catalysts caused the decrease in the metal surface area, but increase in the specific activity of the active sites [10]. From the catalyst development, the SMR process has searched for other suitable catalysts. For example, Zeppieri *et al.* (2010) investigated the performances of an innovative rhodium-perovskite catalyst ($BaRh_xZr_{(1-x)}O_3$) and nickel-based catalyst in SMR reaction. The rhodium-perovskite catalyst was found to be higher activity and methane conversion than the nickel-based catalyst [11].

The reactions in SESMR process, steam methane reforming accompanied with CO_2 adsorption, are not significantly different from conventional steam reforming process except for the addition of CO_2 adsorption or adsorbent. Therefore, the high activity and stability of catalyst/support that is already proven by SMR reaction can also be used in this process.

3.2 CO_2 Adsorbents in Sorption Enhanced Steam Methane Reforming (SESMR) Process

Steam methane reforming is widely used process for hydrogen production. However, this process still has some limitations as listed below.

1. Thermodynamic limitation
2. High energy demand
3. Expensive alloy reformer tubes
4. Catalyst deactivation

Since steam methane reforming reaction is the reversible reaction limited by its thermodynamic equilibrium, the reaction temperature has to be operated in the range of 800-900°C in order to achieve complete methane conversion for the conventional steam methane reforming. At this elevated temperature, reformer tube reactors have to be constructed from an expensive alloy. In addition, the catalyst is deactivated by carbon formation, resulting in blockage of reformer tubes and increased pressure drops [12, 13]. To overcome these drawbacks of conventional steam methane reforming process, novel technique for hydrogen production, so-called sorption enhanced steam methane reforming (SESMR) which CO_2 adsorbent is added to the conventional steam methane reforming, has been proposed. The addition of CO_2 adsorbent causes simultaneous reactions of steam methane reforming and CO_2 adsorption, leading to shifting the equilibrium of steam methane reforming reaction beyond its thermodynamic equilibrium. The effect of the addition of adsorbent into SESMR has been widely investigated on various adsorbents such as activated carbons, zeolites, metal-organic frameworks (MOFs), calcium oxide, zirconates, orthosilicates, hydrotalcites, alumina, etc. However, activated carbons, zeolites, and MOFs are not suitable for SESMR reaction because they show poor CO_2 adsorption performance when the temperature and humidity increase. Moreover, the presence of nonpolar species leads to lower CO_2 selectivity of zeolites while the MOFs are adsorbing through molar weight and decomposed at temperatures over 400°C which is quite low temperature for SESMR reaction [14].

The adsorbents used for sorption enhanced steam methane reforming (SESMR) should have high selectivity to CO_2 and high CO_2 adsorption capacity. However, the adsorbent regeneration cannot be avoided in SESMR process. The adsorbents have to operate with multi-cycle operation. Therefore, the cyclic stability is a factor to be concerned. A cheap adsorbent with high selectivity to CO_2 and high CO_2 adsorption capacity may not be preferred if its stability is low. An expensive adsorbent may be more interesting if it has higher stability for a longer time using. The desired properties of the adsorbents can be summarized as follows:

1. High CO_2 adsorption capacity and selectivity to CO_2
2. Fast adsorption kinetics
3. Major part of the adsorption capacity occurred through physisorption
4. Good cyclic stability

5. Reasonable cost

From many researches, the adsorbents that follow major of the properties mentioned above and can be used in SESMR process are summarized into the following 3 categories.

(1) Calcium-based sorbent

(2) hydrotalcite-like compound

(3) Ceramic sorbent such as Na_2ZrO_3 and Li_4SiO_4

At present, there are no adsorbents that meet all requirements including high CO_2 adsorption capacity and selectivity to CO_2, fast adsorption kinetics, good cyclic stability, reasonable cost, and etc. Tables 3.1 and 3.2 show the stoichiometric capacities/regeneration temperatures and the summarized advantages/disadvantages for various sorbents, respectively.

3.3 Sorption Enhanced Steam Methane Reforming Operation

For the SESMR, reactors are generally divided into 2 types including fixed bed reactor and fluidized bed reactor. Surprisingly, the original proposed patents and early works on sorption enhanced reforming were based on fluidized bed reactors but in the recent studies, majority of experiments, for example, to study cyclic stability, reaction rate, catalyst, and sorbent configuration and suitable operating conditions for SESMR (e.g. S/C ratios, sorbent-to-catalyst ratios, temperature, etc.) have been done on fixed bed reactor. Although these data are useful, in the industrial point of view, fixed bed reactors are not suitable for SESMR process on an industrial because of the synchronization of two reactors in different modes, first for reaction-sorption and another one for regeneration mode where continuous regeneration of sorbent is required.

Table 3.1 Stoichiometric capacities and regeneration temperatures for various sorbents [12]

Sorbent	**Stoich. capacity [g CO_2/g sorbent]**	**Regeneration temperature [°C]**
Limestone	0.79	900[a]
Dolomite	0.46	900[a]
Huntite($CaCO_3 \times 3MgCO_3$)	0.25	900[a]
Hydrotalcite	0.029[b]	400[c]
Lithium orthosilicate	0.37	750[d]
Lithium zirconate	0.29	690[e]
Sodium zirconate	0.24	790[f]

[a] Temperature at which CO_2 equilibrium pressure is 1 bar [15]

[b] A capacity of 0.65 mole CO_2/kg, reported by Ding and Alpay [16]

[c] Regeneration is performed using pressure swing

[d] Reported by Essaki and Kato [17]

[e] Experimental findings of Yi and Eriksen [18] (regenerated in pure nitrogen)

[f] Experimental findings of L´opez-Ortiz *et al.* [19] (regenerated in air)

Table 3.2 Summarized advantages and disadvantages for various sorbents

Sorbents	Advantages	Disadvantages
CaO (limestone)	-Low cost -High CO_2 sorption capacity -Medium kinetic rate	-Use high temperature for CO_2 adsorption -Poor stability(cyclic operation) -Required high temperature for regeneration
CaO (Dolomite)	-Low cost -High CO_2 sorption capacity -Medium kinetic rate -Medium stability	- Use high Temperature for CO_2 adsorption - Required high temperature for regeneration
CaO-$Ca_9Al_6O_{18}$ CaO-$Ca_{12}Al_{14}O_{33}$ CaO/Al_2O_3 [20] $CaCeZrO_x$ [21] CaO-$KMnO_4$	-High CO_2 sorption capacity -Medium kinetic rate -Good stability	- Use high Temperature for CO_2 adsorption - Required high temperature for regeneration
HTC K_2CO_3-HTC (for improving CO_2 sorption capacity)	-Fast kinetic rate -Good stability -Use medium temperature for CO_2 adsorption	-Very low CO_2 sorption capacity

Sorbents	Advantages	Disadvantages
	-Use medium temperature for regeneration	
Li_2ZrO_3 K_2CO_3-Li_2ZrO_3 (for improving carbonation rate)	-High CO_2 sorption capacity -Good stability	-High cost -Very slow adsorption rate - Use high Temperature for CO_2 adsorption
Li_4SiO_4 K_2CO_3-Li_2ZrO_3 (for improving sorption capacity)	-High CO_2 sorption capacity -Good stability	-High cost - Slow adsorption rate - Use high Temperature for CO_2 adsorption
Na_2ZrO_3	-High CO_2 sorption capacity -Good stability	-High cost - Quite slow adsorption rate - Use high temperature for CO_2 adsorption
Ba_2TiO_4 [22] BaO [2]	-Low CO_2 equilibrium pressurewhich good for polishing (combine with CaO)	-Poor kinetics and capacity compared with CaO -Required very high temperature for regeneration

The decay of sorbent during multi-cycle operation leads to difficulty in matching between the production time and the regeneration time. Therefore, to be applied for the industrial scale SESMR process, fluidized bed reactor seems to be more suitable than fixed bed reactor. However, the additional required property of sorbent used for fluidized bed is the mechanical stability of the sorbent. This is because the fluidization will cause particle attrition and generation of fines. Table 3.3 shows the comparison of fluidized beds relative to fixed bed reactors.

Table 3.3 Comparison between fluidized beds and fixed bed reactors [23]

Advantages relative to fixed beds	Disadvantages relative to fixed beds
Temperature uniformity (no hot spots)	Gas by-passing (limited gas-solid contacting)
Excellent bed-to-surface heat transfer	Substantial backmixing
Able to add/remove particles continuously	Attrition (wear/erosion)
Low pressure drops	Entrainment
Wide size distribution of particles	Design and scale-up are more complex

3.3.1 Fixed Bed Reactors

Because of the advantages of fluidized bed reactor as mentioned above, the experimental investigation for enhancement of steam methane reforming by in situ removal of CO_2 has been conducted in small-scale fixed bed reactors. For example, Balasubramanian *et al.* (1999) performed the SESMR with CaO as a CO_2 acceptor in fixed bed reactor. The results showed that at temperature above 550°C, the reaction rate was high and the reactions reached the equilibrium at all studied reaction conditions. They also showed that the H_2 concentration over 95% could be obtained in a single-step process by the addition of a calcium-based CO_2 acceptor to commercial steam methane reforming catalyst [24]. A Lithium zirconate and hydrotalcite derived Ni catalyst were used as sorbent and catalyst, respectively, for SESMR experiment in fixed bed reactor from Fernandez *et al.* (2005)'s work. They claimed that the process could directly produce H_2 product purity over 95 mol% with less than 0.2 mol% of CO [25]. Li *et al.* (2006) tested two parallel fixed-bed reactors operated in a cyclic manner which Ni and $CaO\text{-}Ca_{12}Al_{14}O_{33}$ were used as a catalyst and adsorbent, respectively. They showed that this process continuously produced hydrogen with purity higher than 90%. In addition, the suitable parameters (temperature, pressure, steam/carbon and etc.) for determining the feed switchover time for high purity hydrogen production were investigated [26]. Fernandez *et al.* (2007) still studied with the fixed bed reactor which Ni supported HTCs was used as a catalyst and different sorbents, Li_2ZrO_3 and Na_2ZrO_3, were used in this study. The results showed that H_2 concentration at least 95% could be achieved by using Na_2ZrO_3 as acceptor. However, due to the low carbonation rate of Li_2ZrO_3, effect of CO_2 adsorption on SESMR was not observed when Li_2ZrO_3 was employed [27].

3.3.2 Fluidized Bed Reactors

Fluidized bed reactor has advantageous properties for applying to the industrial scale of SESMR such as good mixing of solids, good temperature control, and transfer of particles between reactors making continuous operation possible. However, fluidized bed seems to be a relatively immature technology.

Fluidization occurs when solid particles are suspended in an upward flowing stream of fluid, which is either a liquid or a gas (only fluidizing gas is considered for

SESMR). In fluidized bed, there is a distributor plate which its function is to distribute the gas over the reactor cross section and to act as a support for the bed material. Fluidizing gas velocity in fluidized bed can be adjusted to give different flow regimes in fluidized bed. Fluidized beds can be operated in different flow regimes such as in bubbling, turbulent or fast fluidization, depending on the reaction rate. At high reaction rate, high-velocity fluidization, the fast fluidized regime, is tended to be used. At slow reaction rate, operation in the low-velocity bubbling fluidization regime should be used. Both low and high velocity operations of fluidized beds can be conducted in a variety of reactor configurations [28].

For SESMR, there are two potential fluidized bed configurations including bubbling bed-bubbling bed configuration (dual bubbling bed) and fast fluidization-bubbling bed configuration (circulating fluidized bed) as illustrated in Figure 3.1.

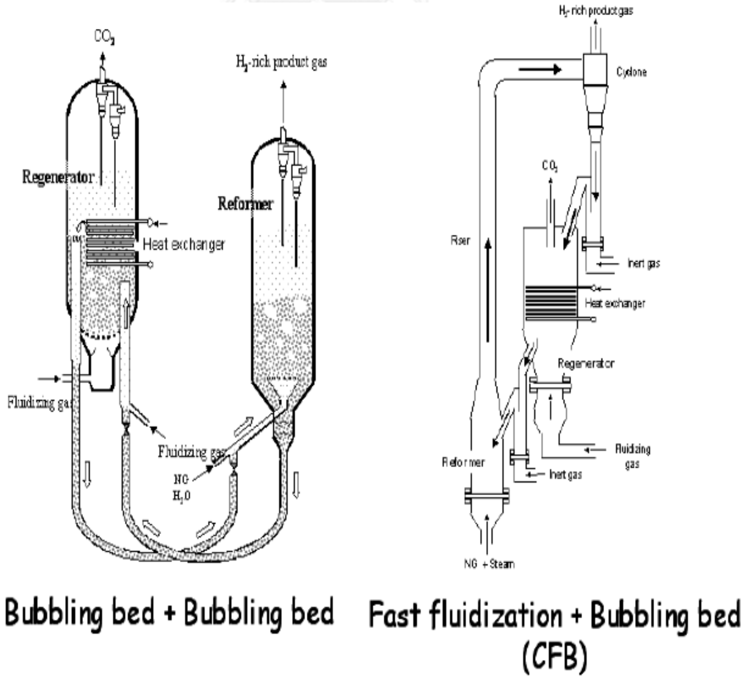

Figure 3.1 Proposed reactor configurations [29]

In the bubbling bed-bubbling bed configuration, both reactors are operated in bubbling regime. The superficial gas velocity is normally about 0.1-1 m/s. In this type of reactor, solids are transferred between each reactor by utilizing the difference in static pressure. Another configuration is fast fluidization-bubbling bed configuration or circulating fluidized bed (CFB). This configuration utilizes the concept of replacing one bubbling bed by a riser. In the reformer (riser section), reactor is operated in fast fluidization regime. Typical gas velocity in the riser is in the range of 2-10 m/s. As a result of high gas velocity, solids are transferred to the regenerator which operated in bubbling regime. The higher gas velocity in the reformer (riser) leads to lower residence time than that in regenerator (bubbling bed). This is a result of requiring high reaction rate of reaction-sorption. Furthermore, the high velocity in the reformer (riser) also causes mechanical degradation of the particles (catalysts and adsorbents) by attrition. It can be concluded that CFB reactors are easier to operate and the gas throughput is much higher than for the bubbling bed but some additional requirements are needed such as the required catalyst and adsorbent with higher mechanical stability. Table 3.4 shows the comparison between bubbling bed-bubbling bed configuration (dual bubbling bed) and fast fluidization-bubbling bed configuration (circulating fluidized bed)

Table 3.4 Comparison between bubbling bed-bubbling bed configuration (dual bubbling bed) and fast fluidization-bubbling bed configuration (circulating fluidized bed) [23]

Parameters	**Bubbling bed-Bubbling bed configuration**	**Fast fluidization-Bubbling bed configuration**
Operation	Difficult	Easy
Attrition	Low	High
Gas throughput	Low	High
Reaction rate	Available at low reaction rate	High reaction rate required in riser

There are many researches which SESMR was conducted in fluidized bed reactors. For example, Hildenbrand *et al.* (2006) investigated the SESMR performance in fluidized bed reactor which operated in bubbling regime by using $Ni/NiAl_2O_4$ and CaO as a catalyst and an adsorbent, respectively. They reported that hydrogen product purity over 90 mole% were obtained at temperatures below 600 °C [30]. Johnsen *et al.* (2006) also investigated fluidized bed reactor which operated in bubbling regime. Catalyst and adsorbent were Ni and CaO, respectively. They showed that the equilibrium of H_2 concentration could reach more than 98% at 600°C and 1.013×10^5 Pa. However, due to poor stability of dolomite, the total production time decreased with increasing number of cycles but the reaction rate seemed unaffected [12]. To develop fluidized bed reactor for applying to the industrial scale, Arstad *et al.* (2009) performed SESMR in two bubbling bed reactors operated continuously which $Ni/NiAl_2O_3$ and CaO were used as a catalyst and adsorbent, respectively. SMR and CO_2

adsorption were carried out in one reactor while regeneration was carried out in another reactor. Although the results were far from the optimum point, the reactor system showed the promising results concerning SESMR process using calcined dolomite as a sorbent with a CO_2 separation efficiency of ca. 65% [31]. Arstad *et al.* (2012) also carried out SESMR in two bubbling bed reactors operated continuously to investigate the effect of sorbent on the catalyst ratio (20/80 and 50/50). Catalyst and adsorbent used in this study were $Ni/NiAl_2O_4$ and CaO, respectively. They reported that the outlet of H_2 concentration could gain 97-98% at steam to methane ratio of 4, temperature of 575°C and ambient pressure when using 50/50 sorbent to catalyst ratio while another ratio gave lower outlet H_2 concentration and quickly dropped after only a few hours. Moreover, they also found that only small fraction of the CO_2 adsorption capacity was used in this experiment [32].

3.4 Chemical Looping Reforming (CLR) and Sorption Enhanced Chemical Looping Reforming (SECLR) Process for Hydrogen Production

3.4.1 Chemical Looping Reforming (CLR) Process

Chemical looping reforming (CLR) is a process involving steam reforming reaction and partial oxidation of metal oxides. The influence of metal oxides (Ni, Cu, Mn, and Fe) on SiO_2 support as catalyst and oxidizing agent for hydrogen production from natural gas via CLR has been reported by Zafar *et al.* (2005). Among the examined catalysts, the NiO/SiO_2 catalyst showed high reduction reactivity and selectivity toward H_2. However, the reaction rate decreased as a function of a cycle due to the formation of irreversible metal silicates, which did not react at a sufficient rate [33]. Ryden *et al.* (2006) claimed that complete conversion of natural gas and high selectivity toward H_2 and CO could be achieved by using $NiO/MgAl_2O_4$ in laboratory reactors consisting of two interconnected fluidized beds. Furthermore, the addition of 25 vol% steam into the natural gas could reduce or eliminate the carbon formation [3]. In terms of the support effect, Ryden *et al.* (2008) reported the catalytic performances of NiO catalysts with different supports including $MgAl_2O_4$, α-Al_2O_3 and γ-Al_2O_3. They found that NiO supported on $MgAl_2O_4$ and α-Al_2O_3 showed good stability with unchanged physical and chemical structure while another one lost its porosity but remained highly reactive [34]. He *et al.* (2009) found that the addition of transition-metal oxides (Fe, Cu and Mn) into cerium oxide to prepare composite oxygen carrier by co-precipitation method could improve the reactivity of Ce-based oxygen carrier in terms of H_2 production and CO selectivity at above 800 °C. However, Ce-Fe-O showed the best performance for CLR [35]. Except for NiO and CeO_2, Nalbandian *et al.* (2011) studied the syngas production from methane by using the Perovskites with the general formula $La_{1-x}Sr_xM_yFe_{1-y}O_3$ (M = Ni, Co, Cr, Cu) as oxygen carriers. The results showed that $La_{0.7}Sr_{0.3}Cr_{0.1}Fe_{0.9}O_3$ sample mixed with 5% NiO gave the best results and H_2 yield up to 90% [36].

3.4.2 Sorption Enhanced Chemical Looping Reforming (SECLR) Process

Sorption enhanced chemical looping reforming (SECLR) is a process which combines between CLR and CO_2 adsorption of the adsorbent. Therefore, good metal oxides used for CLR and good adsorbents used for SESMR as mentioned in the earlier part can be used in this process. Unfortunately, it is difficult to perform the experiment of this process due to complexity and difficulty to control all of 3 reactors, consisted of chemical looping reformer, regenerator, and air reactor. There are only a few studies have been done about SECLR on laboratory and simulation. Pimenidou *et al.* (2010) conducted simulation for SECLR with using NiO and CaO as metal oxide and adsorbent, respectively. The results showed that 98% purity hydrogen could be achieved from this process. However, the carbonation decreased to about 56% in the following cycles due to low stability of CaO. Furthermore, the experimental studies of SECLR were also investigated by using waste cooking oil as feedstock. They revealed that this process could be operated for 6 cycles at 600°C and steam to carbon ratio of 4 without obvious deterioration in fuel and steam conversion, H_2 purity, and carbon products selectivity [37]. More than 98% purity hydrogen produced from SECLR could be achieved in accordance with Ryden and Ramos (2012)'s simulation work at 600 °C when using of NiO and CaO as metal oxide and adsorbent, respectively [4].

CHAPTER 4

SIMULATION AND DESIGN

In this chapter, simulation model of sorption enhanced chemical-looping reforming process for hydrogen production from pure methane was considered. Other two processes for hydrogen production, including steam reforming (SR) and sorption enhanced steam reforming (SESR), were also investigated through computer modeling. The optimal operating condition and process performances including methane conversion, hydrogen purity, energy requirement, and hydrogen productivity were then examined and compared. A further study of sorption enhanced chemical-looping reforming process focused on the adiabatic operation of all three reactors. Moreover, the effects of CO_2 in content in feed stream on the adiabatic operation were investigated. Lastly, the basic design of reactors for sorption enhanced chemical-looping reforming process including regime of operation and pipe line system of three reactors consisting of reforming reactor, calcination reactor, and air reactor were performed.

4.1 Simulation of Sorption Enhanced Chemical-Looping Reforming Process for Hydrogen Production by Aspen Plus Program

The hydrogen production process via sorption enhanced chemical-looping reforming process which NiO and CaO were used in the system, was simulated by ASPEN Plus Program. The process was based on no external fuel supplied. 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

- furnace: RStoic
- fluid/solid separator: CYCLONE

For this process, the SOLIDS model was used due to the presence of solid in this process. The feed stream was methane with a trace of H_2S as an impurity. 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. The process flow diagram of SECLR is illustrated in Figure 4.1 and the description of streams and units are presented in Tables A.1 and A.2 (See Appendix A), respectively.

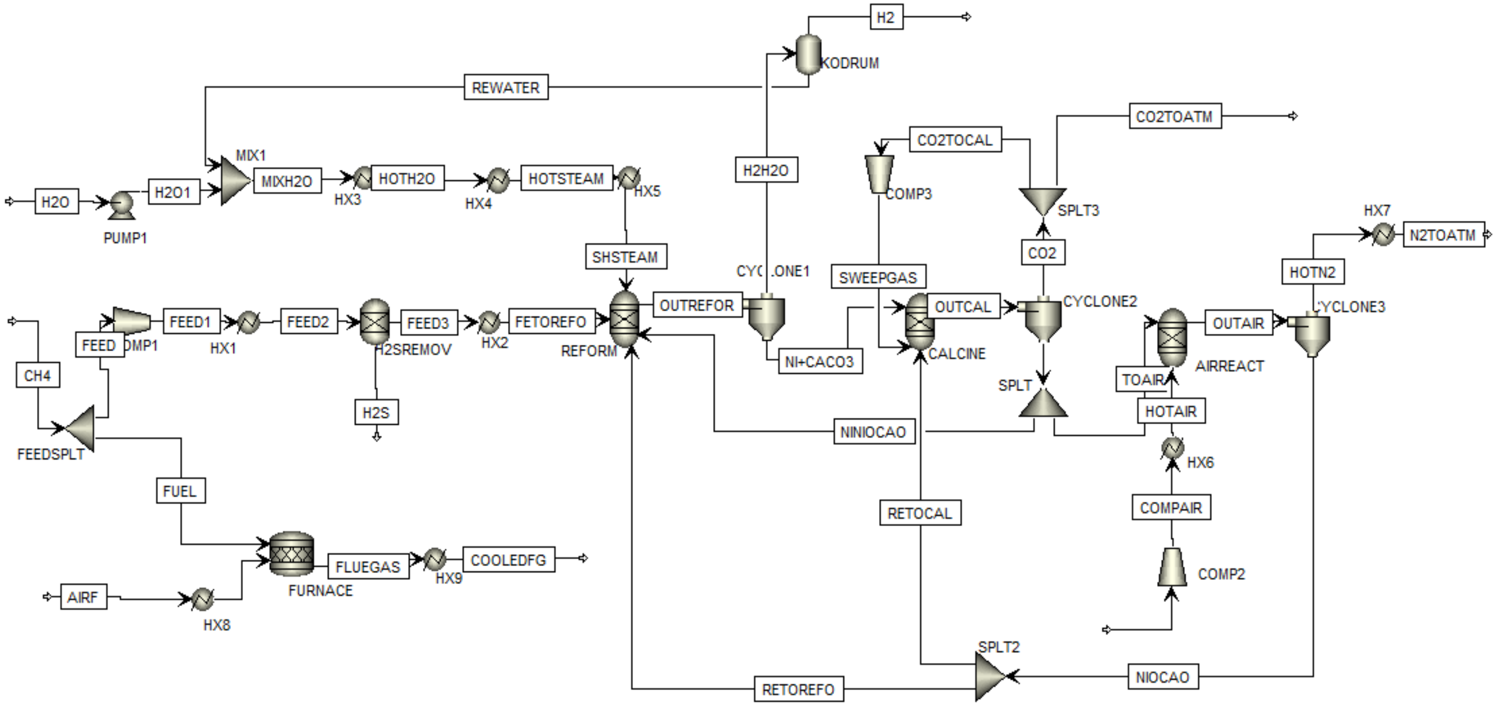

Figure 4.1 Process flow diagram of sorption enhanced chemical-looping reforming process

Process description: Sorption enhanced chemical looping reforming process

For the process of sorption enhanced chemical looping reforming, firstly, the feed stream was partly divided into two parts, which one part was used for hydrogen production and another one was used as fuel. For a fuel, the splitted stream were burned with air in the furnace and had to provide the sufficient heat for the reforming reactor, calcination reactor, air reactor, and boiler. For hydrogen production, the feed stream was necessary to be pretreated before sending to the reforming reactor because the impurity, especially H_2S, was the steam reforming catalyst poisoning. The feed stream was compressed and then heated to the suitable condition for the H_2S removal unit. After pretreatment process, the pretreated feed stream was heated and then routed to the reforming reactor along with the steam which was produced by the boiler. Due to the presence of CO_2 adsorbent and metal oxide, the main reactions taking place in the reforming reactor were reactions (2.1)-(2.4) and (2.10)-(2.12). The products from the reforming reactor mostly consisted of H_2, CO, and the remaining steam. As mentioned in Chapter 2, this process did not require the temperature shift reactor. Thus, the products were then routed to the water removal unit. The water was removed and recycled back for reuse purpose while another stream of high purity hydrogen product could be obtained from this unit. However, there was not only the requirement of calcination reactor but also air reactor to regenerate the metal. The solids from the reforming reactor including saturated adsorbent and metal were sent to the calcination reactor for adsorbent regeneration. The main reaction taking place in the calcination reactor was reaction (2.5). After that the solids from calcination reactor were divided into 2 parts which one was sent back to the reforming reactor while another one was routed to the air reactor. The CO_2 which was the byproduct from regeneration process of the calcination reactor was partially splitted for using as sweep gas while the remaining was emitted to the atmosphere. In the air reactor where the air was fed for metal regeneration, the metal was converted back to its metal oxide form. The reaction occurring in this reactor was reaction (2.13). During regeneration process, N_2 was obtained as a byproduct. These N_2 could be used to preheat the feed to the reforming reactor and feed to the H_2S removal unit, respectively, before emitting to the atmosphere.

4.2 Simulation of Steam Reforming and Sorption Enhanced Steam Reforming Process

These processes were also simulated by ASPEN Plus Program. CaO was applied as a CO_2 adsorbent for SESR process. Both processes were based on no external fuel supplied. The methods and units applied for these processes were almost as same as the sorption enhanced chemical-looping reforming process. The difference was that only the vapor phase of SRK model would be used for SR process.

Similar to the SECLR process, the SOLIDS model was used for SESR process due to the presence of solid. The feed stream and assumption were also similar to the SECLR process. The process flow diagrams of SR and SESR are illustrated in Figures 4.2 and 4.3, respectively, and the description of streams and units are presented in Tables A.3 and A.4, and A.5 and A.6 (See Appendix A), respectively.

The main reactions taking place in reforming reactor of SR process were reactions (2.1)-(2.3) but the main reactions taking place in reforming reactor and calcination reactor of SESR process were reactions (2.1)-(2.4), and (2.5), respectively.

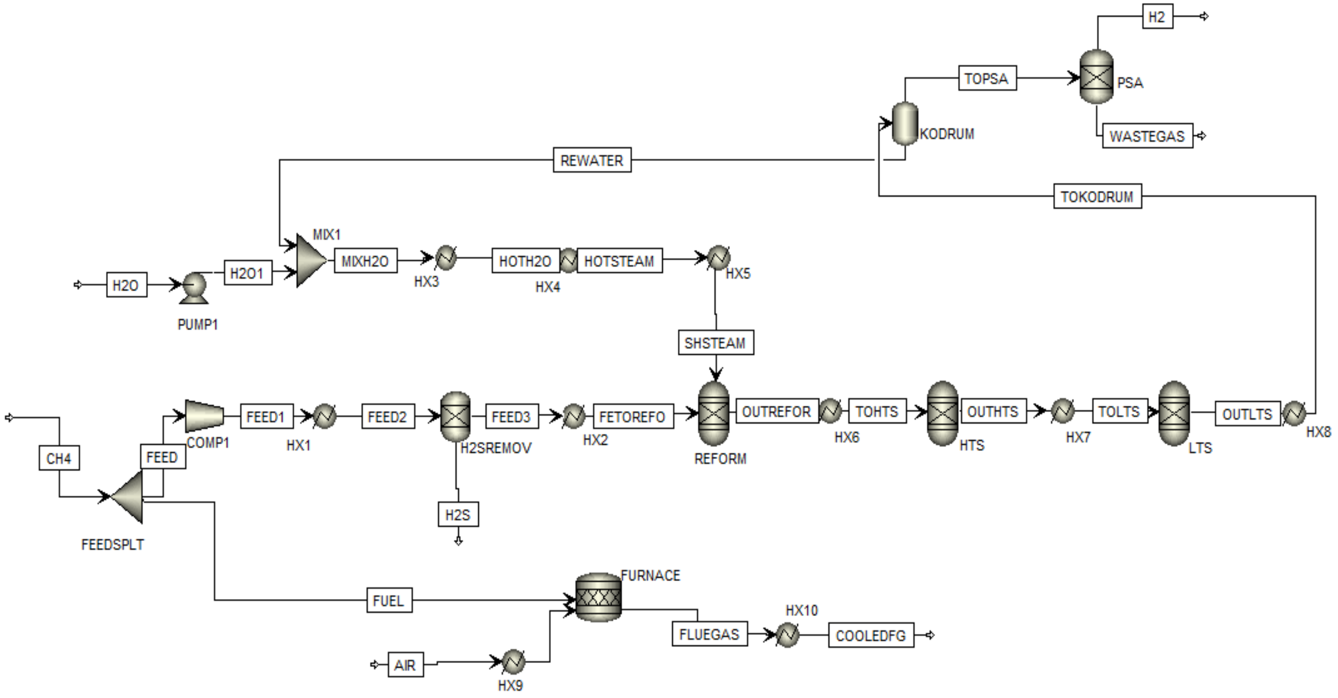

Figure 4.2 Process flow diagram of steam reforming process

Process description: Steam reforming process

For the process of steam reforming, firstly, the feed stream was splitted and pretreated in the same way as SECLR process. After H_2S removal, the pretreated feed stream was heated and then routed to the reforming reactor along with the steam. The steam was produced at the boiler which the production steps were preheating the feed water and then vaporizing/superheating. There was no solid involved in this process. Therefore, the main reactions taking place in the reforming rector were reactions (2.1)-(2.3). The products from the reforming reactor which mostly consisted of H_2, CO, CO_2, and the remaining steam could be used to provide heat to preheat the feed to the reforming reactor and H_2S removal unit before sending to high temperature shift reactor. After that the products from high temperature shift reactor could also be used to preheat the water then were routed to low temperature shift reactor. The main reaction occurring in both high and low temperature shift reactors was reaction (2.2). The products from low temperature shift reactor were cooled down and the remaining water was then removed and recycled back at the water removal unit. Finally, the gaseous products were sent to the pressure swing adsorption unit to remove the impurities such as CO, CO_2, and unconverted CH_4 for producing high purity hydrogen product.

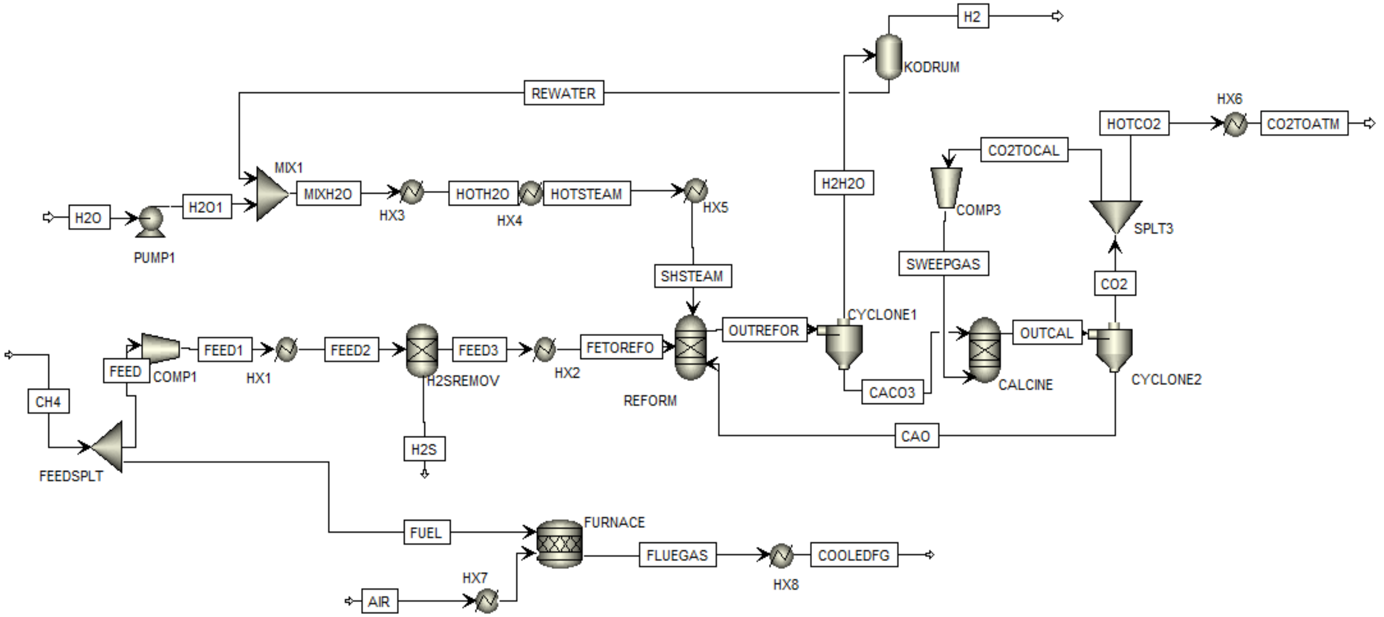

Figure 4.3 Process flow diagram of sorption enhanced steam reforming process

Process description: Sorption enhanced steam reforming process

For the process of sorption enhanced steam reforming, the feed stream was also first separated and pretreated to use as fuel and fed to the reforming reactor in the similar way to SECLR process. After the impurities removal process, the pretreated feed stream was heated and then sent to the reforming reactor along with the steam. The main reactions occurring in the reforming reactor were not only reactions (2.1)-(2.3) but also reaction (2.4) due to the presence of CO_2 adsorbent in this reactor. The products from the reforming reactor mostly consisted of H_2, CO, and the remaining steam. In contrast to the steam reforming process, this process did not require the temperature shift reactor because high hydrogen purity could be produced by only one step. Therefore, the gaseous products were routed to the water removal unit. The water was removed and recycled back to combine with the feed water. The stream of high purity hydrogen product could be obtained at this unit. However, another reactor which was calcination reactor was required for this process to regenerate CO_2 adsorbent. Hence, the saturated adsorbents from the reforming reactor were routed to the calcination reactor for regeneration. The main reaction taking place in the calcination reactor was reaction (2.5). After the regeneration process, the adsorbents were sent back to the reforming reactor. During regeneration process, CO_2 was obtained as a byproduct. One part of CO_2 were used as sweep gas while the others could be used to preheat the feed to the reforming reactor and feed to the H_2S removal unit before emitting to the atmosphere.

4.3 Simulation of Adiabatic Operation of SECLR Process and the Study of Effects of CO_2 Content in Feed Stream on the Adiabatic Operation

For the SECLR operated under adiabatic condition, the methods, units applied for this simulation, feed stream, and assumption were similar to the isothermal SECLR process. Moreover, the process flow diagram and the description of streams and units were as same as the SECLR process presented in Section 4.1. However, in this part, the effects of CO_2 in feed stream including 10%, 20%, 30%, 40%, and 50% (by mole) on the process performances for the adiabatic operation of SECLR process were also investigated.

4.4 Preliminary Reactor Design for SECLR Process

In this part, the study focused on the basic design of reactors for sorption enhanced chemical-looping reforming process including regime of operation and pipe line system of three reactors consisting of reforming reactor, calcination reactor, and air reactor. All three reactors were considered as three connected fluidized bed reactor. Therefore, solids had to be able to be transferred among these reactors. The design was based on the simulation results from the sorption enhanced chemical-looping reforming with adiabatic operation. The necessary parameters for fluidization calculation were minimum fluidization velocity (U_{mf}) and terminal settling velocity (U_t). The minimum fluidization velocity and terminal settling velocity could be calculated by the equations reported by Wen and Yu [38] and Pinchbeck and Popper [39] as shown below.

For finding U_{mf}

$$\frac{DU_{mf}\rho_f}{\mu} = \sqrt{(33.7^2 + 0.0408Ar)} - 33.7 \qquad (4.1)$$

where $$Ar = \frac{D_e^3 \rho_f (\rho_p - \rho_f) g}{\mu^2}$$

and $$D = \emptyset_s D_e$$

For finding U_t

For $N_{RE} < 1$ $$\frac{U_t}{U_{mf}} = 91.7 \quad (4.2)$$

For $N_{RE} > 500$ $$\frac{U_t}{U_{mf}} = 8.72 \quad (4.3)$$

CHAPTER 5

RESULTS AND DISCUSSION

The simulation results of various hydrogen production processes can be discussed and divided into five sections. The validation of simulation results from sorption enhanced chemical-looping reforming (SECLR), steam reforming (SR), and sorption enhanced steam reforming process (SESR) is firstly investigated as indicated in Section 5.1. For Section 5.2, the effects of various parameters, including reforming temperature, steam flow rate, and solid circulation rate, on each process performance are examined in terms of CH_4 conversion, purity of hydrogen produced, hydrogen productivity and energy consumption. Moreover, a comparative study of process performance at optimal condition among sorption enhanced chemical-looping reforming (SECLR), steam reforming (SR), and sorption enhanced steam reforming process (SESR) is studied and the appropriate process is further proposed in Section 5.3. In addition, Section 5.4 further investigated the viable sorption enhanced chemical-looping reforming process under an adiabatic operation. The effects of CO_2 content in the feed stream on the adiabatic operation of sorption enhanced chemical-looping reforming process are also taken into account. Lastly, the preliminary design of reactors for sorption enhanced chemical-looping reforming is carried out.

5.1 Validation of Hydrogen Production Processes

Since this work studied the simulation model for several hydrogen production processes i.e., sorption enhanced chemical-looping reforming (SECLR), steam reforming (SR), and sorption enhanced steam reforming process (SESR), the validation part of these processes was necessary to confirm the feasibility of the simulation model. Therefore, this section is evidently presented the validation of these processes with previously published papers as shown in Sections 5.1.1-5.1.3.

5.1.1 Sorption Enhanced Chemical-Looping Reforming (SECLR) Process

For this process, the simulation results were validated with the results from [4]. This published data was obtained under the condition of pure methane feed stream and NiO and CaO acting as an oxidizing agent and an adsorbent, respectively. The SECLR system for model validation consists of several units as illustrated in Figure 5.1. Furthermore, there are two cases of operating condition i.e., pressures of 1 and 5 bar for model validation. Hence, the simulation results for SECLR process with different operating pressures compared with the available data are exhibited in Table 5.1.

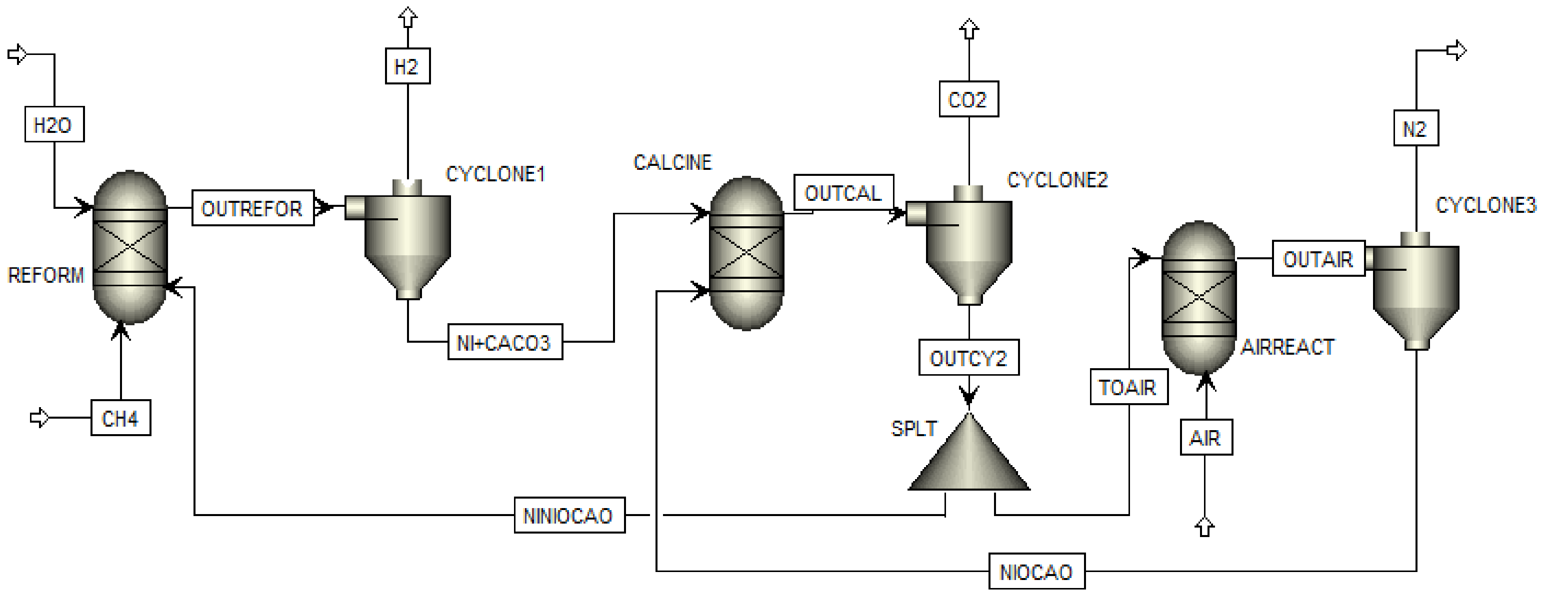

Figure 5.1 Process flow diagram of sorption enhanced chemical-looping reforming process for the model validation

Table 5.1 SECLR validation results

Parameter	@ 1 bar		@ 5 bar	
	This work	[4]	This work	[4]
CH_4 feed	0.1 kmol/h	1 mol	0.1 kmol/h	1 mol
H_2O 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 Temperature (°C)	321	321	340	340
Air feed Temperature (°C)	576	576	630	630
Reformer Temperature (°C)	580	580	630	630
Calcination Temperature (°C)	880	880	980	980
Air reactor Temperature (°C)	1000	1000	1050	1050
Solid CR to AR[a] (%)	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

[a] Solid CR to AR refers to the ratio of solid from calcination reactor to air reactor to total solid from calcination reactor.

According to the results presented in Table 5.1, the results from this work were in good agreement with those data reported by [4]. The process output such as H_2 purity and CH_4 conversion was deviated only 0.2-0.4% for both cases of different operating pressures. Therefore, this simulation model was acceptable for further investigation on SECLR process.

However, the simulation model of SECLR for validation was a bit different in recycle solid among three reactors, compared to that of SECLR for further studies in this work. The modeling for validation referred to the system that the outlet solid from air reactor was sent back to calcination reactor only, while it was recycled to both reforming reactor and calcination reactor in case of the SECLR system considered in this research.

5.1.2 Sorption Enhanced Steam Reforming (SESR) Process

In order to validate the modeling for this process, there is the published report from [40], providing the necessary data. That research studied the sorption enhanced steam reforming system operated with fluidized bed reactors fed by methane. The validation results in terms of product distribution are provided in Table. 5.2.

Table 5.2 Validation results of SESR process

Gaseous product species	Product distribution (%)	
	This work	[40]
H_2	97	98.7
CO_2	0.6	0.8
CH_4	1.8	0.2
CO	0.6	0.3

From the results reported by [40], the process was carried out at the operating temperature of 600°C, pressure of 1 bar, and steam to carbon ratio of 3. As seen the results in Table 5.2, it was found that the product distribution obtained from this work showed some minor deviation, compared to the reference. Nevertheless, this simulation model could be fairly used for further studies on SESR process.

5.1.3 Steam Reforming (SR) Process

The results from the simulation model for this process were compared to those from the available data as indicated in [41] in order to validate the modeling of this work. The steam reforming of methane processed with fixed bed reactor at the operating temperature of 700°C, pressure of 3 bar and steam to carbon ratio of 3 was employed as a reference system. The published data and the simulation results are tabulated in Table 5.3.

Table 5.3 Validation results of SR process

Gaseous product species	Product distribution (%)	
	This work	[41]
H_2	74.8	75
CO_2	10.4	10
CH_4	3.7	3.7
CO	11.1	11.3

From Table 5.3, the product distribution simulated from this work was in good agreement with the reference's results. Thus, this simulation model was reasonable to use for studying the effects of parameters on SR process performance.

5.2 Effects of Operating Conditions on Process Performances

Regarding three hydrogen production processes studied in this research, there were several process parameters such as process conditions affected the process performance. In addition, the operating conditions investigated in this work were composed of the reforming temperature, steam flow rate, and solid circulation rate. Each operating condition for sorption enhanced chemical-looping reforming, steam reforming, and sorption enhanced reforming processes was varied in the simulation model. The simulation results caused by different operating conditions are mentioned and described in Sections 5.2.1-5.2.3.

5.2.1 Sorption Enhanced Chemical-Looping Reforming Process

From the study of various operating conditions, the influence of the reforming temperature on H_2 productivity, energy provided by the combustion of splitted CH_4 feed stream, CH_4 conversion, and H_2 purity are illustrated in Figures 5.2 and 5.3.

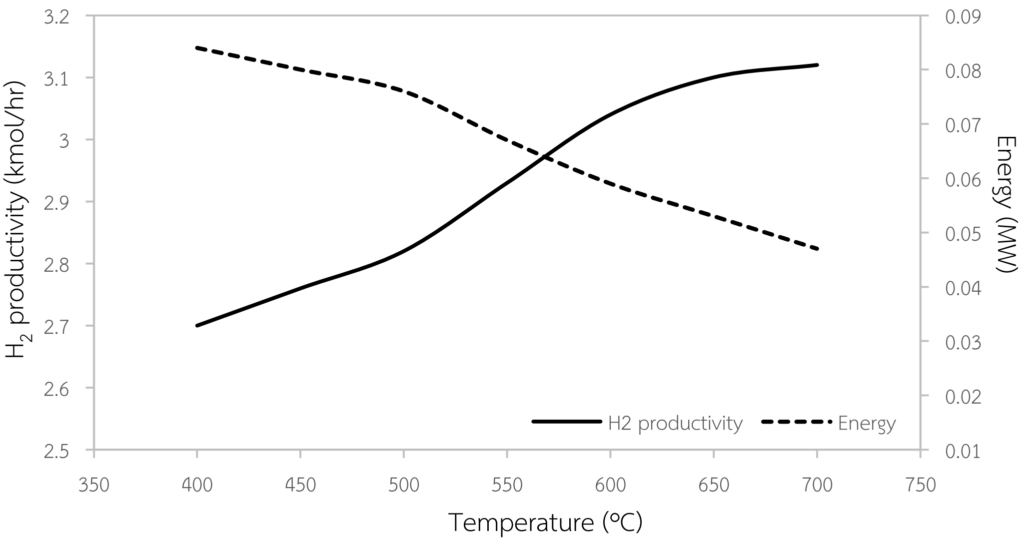

Figure 5.2 The effect of reforming temperature on H_2 productivity and energy from the furnace of SECLR process

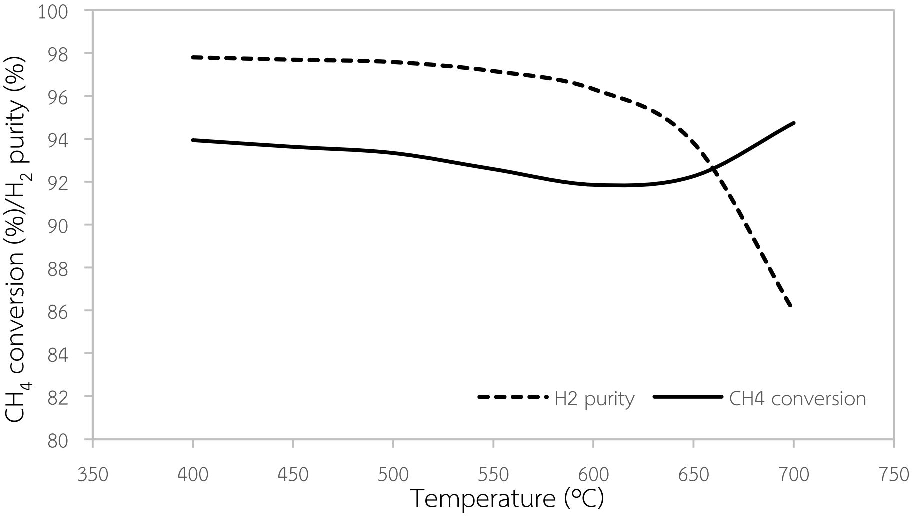

Figure 5.3 The effect of reforming temperature on CH_4 conversion and H_2 purity of SECLR process

As the results shown in Figure 5.2, H_2 productivity increased with increasing of reforming temperature. Because of the endothermic reaction of partial oxidation and steam reforming, it thermodynamically converted methane into higher amount of the desired hydrogen product at higher reforming temperatures. However, the increase in H_2 productivity was smaller at higher reforming temperatures, compared to lower reforming temperatures. This was probably due to the exothermic reaction of carbonation. It was revealed that the adsorption of CO_2 by CaO at the temperatures of 400-575°C was better than that at the temperatures of 575-700°C. This apparently resulted in less shifted equilibrium of main reactions for the temperature of 575-700°C. Moreover, the reverse water gas shift reaction could also affect lower in H_2 productivity at higher reforming temperatures. In contrast with H_2 productivity results, the opposite trend was observed for energy provided from the furnace. Although, higher energy was required as the reforming temperature increased, CaO adsorbed less CO_2, leading to less $CaCO_3$ production. Consequently, lower energy was required for calcination reactor due to less $CaCO_3$ regeneration. Taking into account the total energy requirement from all reactors, it reduced when reforming temperature increased because less energy required at calcination reactor dominated more energy required at reforming reactor.

For CH_4 conversion (Figure 5.3), the conversion decreased as the reforming temperature increased in the range of 400-575°C. This was because the reduction in carbonation conversion was more pronounced than the increase in the conversion from partial oxidation and steam reforming reactions. Therefore, less shifted equilibrium of main reactions was occurred in the temperature range of 400-575°C, leading to less CH_4 conversion. Even though CH_4 conversion decreased in this temperature range, H_2 productivity still increased because the steam reforming reaction, which gave higher H_2 yield than the partial oxidation reaction, would gradually dominate at higher temperatures as shown in Figure 5.2. For the reforming temperature in the range of 575-700°C, the effect of endothermic reaction of steam reforming would be obvious. Furthermore, the decreasing of carbonation conversion was presented at high temperature. For this case, the increase in partial oxidation and steam reforming conversion would overcome the decrease in the carbonation conversion at this temperature range. Therefore, it led to the increased CH_4 conversion at the reforming temperature above 575°C. For H_2 purity, it almost remained stable until the reforming temperature of 575°C. This was because CaO could still adsorb all CO_2 produced from the reactions although the carbonation conversion decreased. Nevertheless, all CO_2 could not be adsorbed by CaO at the temperature above 575°C due to lower capability to adsorb CO_2 at higher temperatures. Consequently, higher in amount of CO_2 remained in the product stream caused the decreasing of H_2 purity.

For another operating condition, the effects of steam flow rate were investigated. The results of process performances are presented in Figures 5.4 and 5.5.

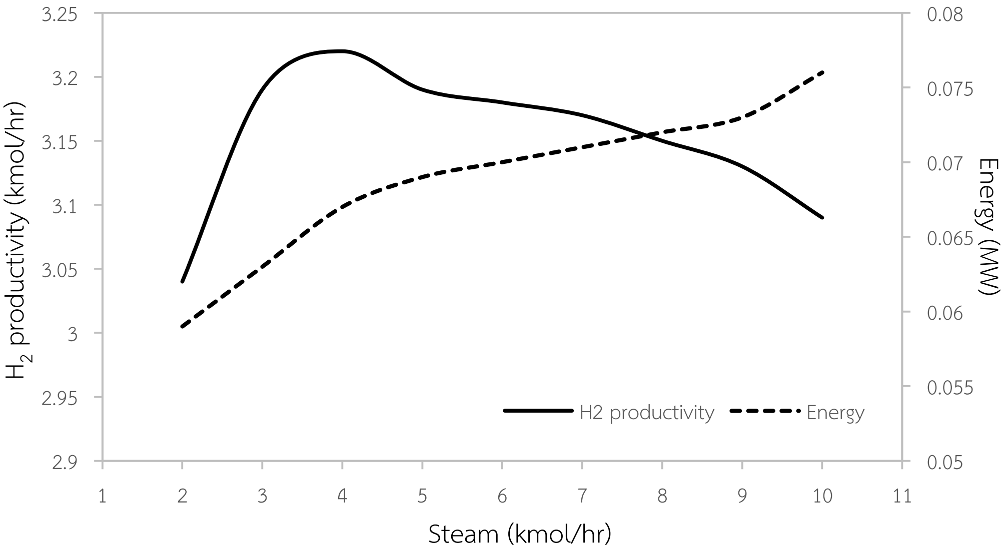

Figure 5.4 The effect of steam flow rate on H_2 productivity and energy from the furnace of SECLR process

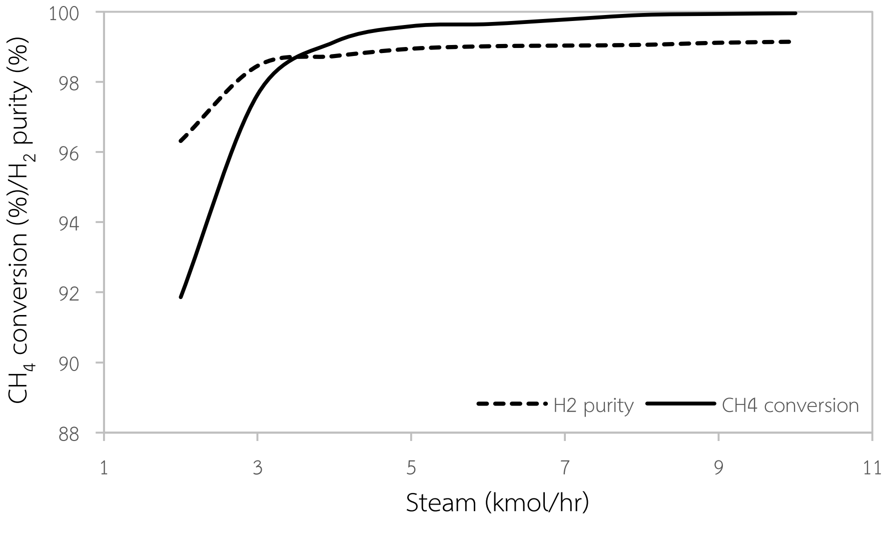

Figure 5.5 The effect of steam flow rate on CH_4 conversion and H_2 purity of SECLR process

From the results in Figures 5.4 and 5.5, H_2 productivity increased at the steam flow rate in the range of 2-4 kmol/hr. The increasing of steam flow rate shifted forward the equilibrium of steam reforming reaction to generate more hydrogen. Since higher energy was required to produce steam, it was necessary to separate more CH_4 feed stream to combust in the furnace to meet the heat requirement. Thus, less CH_4 remaining was fed to reforming reactor, resulting in lower H_2 productivity obtained. However, at low steam flow rate (below 4 kmol/hr), the effect of shifted equilibrium overcame the effect of less CH_4 feed stream, leading to obtaining higher H_2 productivity. On the other hand, less CH_4 fed to reforming reactor as a result of higher energy requirement was more pronounced at high steam flow rate. The H_2 productivity then showed the reduction trend at steam flow rate more than 4 kmol/hr. In the case of energy provided from the furnace, it required more heat when higher steam flow rate was operated because more energy was consumed at the boiler for producing steam. In Figure 5.5, the reaction in reforming reactor shifted by adding more steam affected higher in CH_4 conversion. However, it was not different at high steam flow rate. For the H_2 purity, it was significantly affected by the steam flow rate, especially at low steam flow rate. In addition, it was stable at steam flow rate more than 4 kmol/hr. Its profile was similar to the CH_4 conversion profile.

Lastly, the effect of solid circulation rate was studied. Due to the complexity of the simulation model for SECLR process, it met the limitation and then could not be simulated. However, it could be estimated by considering the CaO balance for the reforming reactor. From the basic knowledge, it was presumed that the amount of CaO required for this process should be equal to its amount at saturation point which was at the ratio of CH_4 to CaO of 1:1. From the calculation, the CaO balance was performed around the reforming reactor as shown the values in Table 5.4.

Table 5.4 The CaO balance around reforming reactor of SECLR process

CaO from AR (kmol/hr)	CaO from CR (kmol/hr)	CaO outlet from RR (kmol/hr)	Converted CaO[a] (kmol/hr)
3.468	2.934	5.357	1.045

[a] CaO were converted to $CaCO_3$ then $CaCO_3$ would be sent to calcination reactor along with excess CaO.

The results in Table 5.4 were estimated under the optimal condition of SECLR process, which was at steam flow rate of 4 kmol/hr and reforming temperature of 600°C, and CH_4 fed to reforming reactor of 1.08 kmol/hr. From the results, it was found that the amount of CaO at least 1.045 kmol/hr should be used in this process. The excess amount of CaO would not affect the process performances such as H_2 productivity, total energy requirement, CH_4 conversion and H_2 purity. Although the total energy requirement did not change, the heat required for each reactor would be different. However, the excess amount of CaO would affect larger sizes of reactor and pipeline, leading to higher cost for this process.

5.2.2 Steam Reforming Process

For this process, it was investigated only two operating conditions including the reforming temperature and steam flow rate that influenced on the process performances. The simulation results for this process are shown in Figures 5.6 and 5.7.

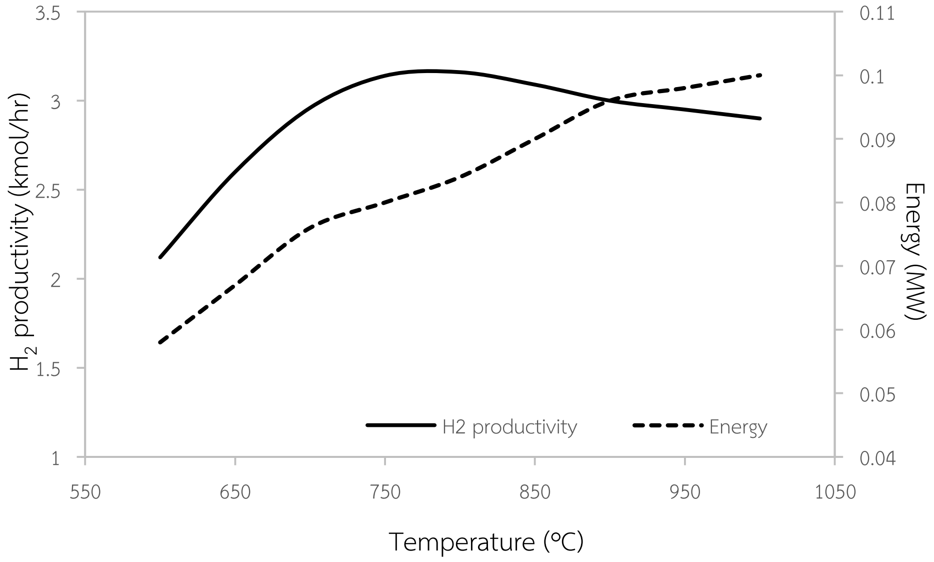

Figure 5.6 The effect of reforming temperature on H_2 productivity and energy provided from the furnace of SR process

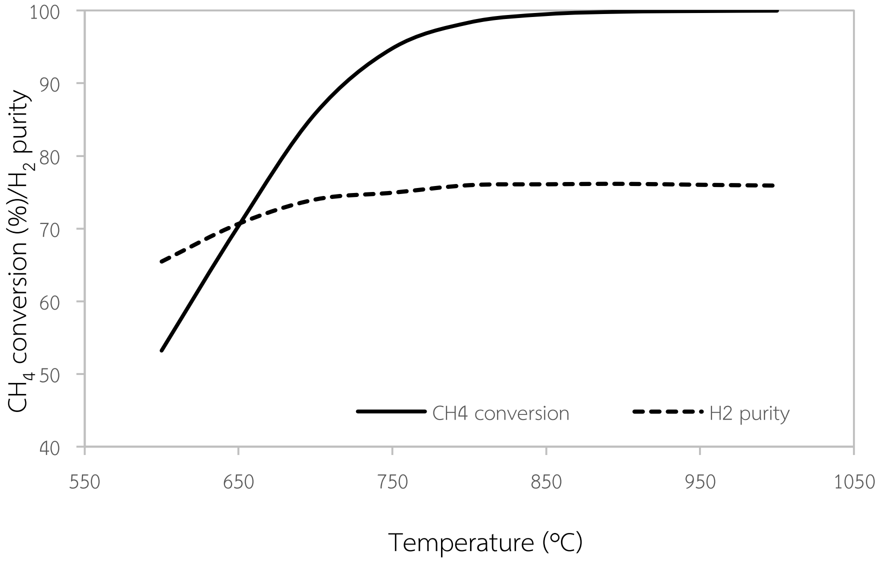

Figure 5.7 The effect of reforming temperature on CH_4 conversion and H_2 purity of SR process

Typically, the steam reforming process required higher heat at higher reforming temperature due to highly endothermic reaction as illustrated in Figure 5.6. Moreover,

H_2 productivity also increased with increasing reforming temperature. However, it started to decline at the reforming temperature of 800°C. This reduction resulted from less CH_4 fed to the reactor as mentioned in Section 5.2.1. In addition, the reverse water gas shift reaction that consumed H_2 at high temperature also affected the decrease in H_2 productivity. It was further found that H_2 produced was less than the maximum of H_2 yield. For CH_4 conversion, according to the endothermic reaction in reforming reactor, this profile was generally presented as indicated in Figure 5.7. The conversion obviously increased until it was almost constant at the reforming temperature around 850°C. In case of H_2 purity, it showed the similar trend to the CH_4 conversion profile. However, it was stable at ca. 75%, indicating low H_2 purity achieved. This was due to the formation of several by-products such as CO and CO_2.

For further studies, Figures 5.8 and 5.9 show the simulation results of process performances obtained from varied steam flow rates.

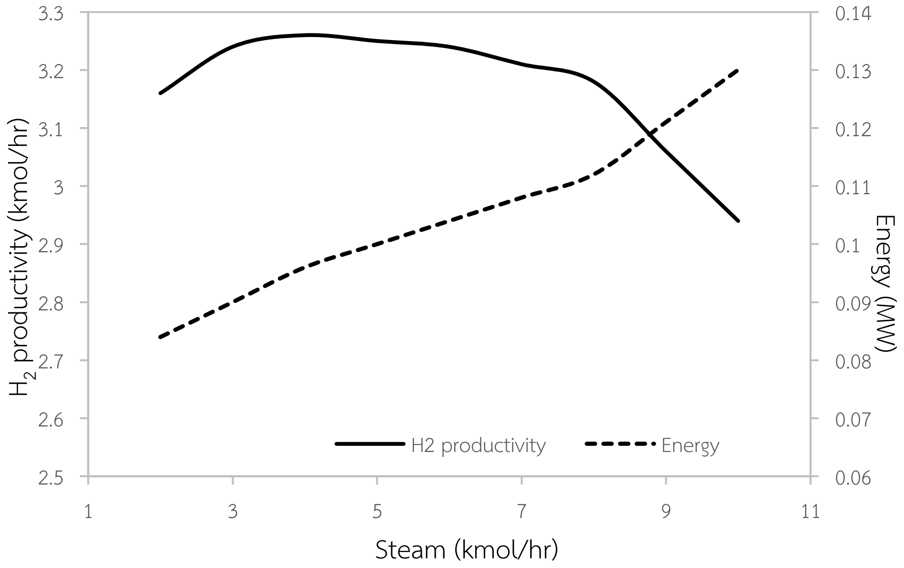

Figure 5.8 The effect of steam flow rate on H_2 productivity and energy provided from the furnace of SR process

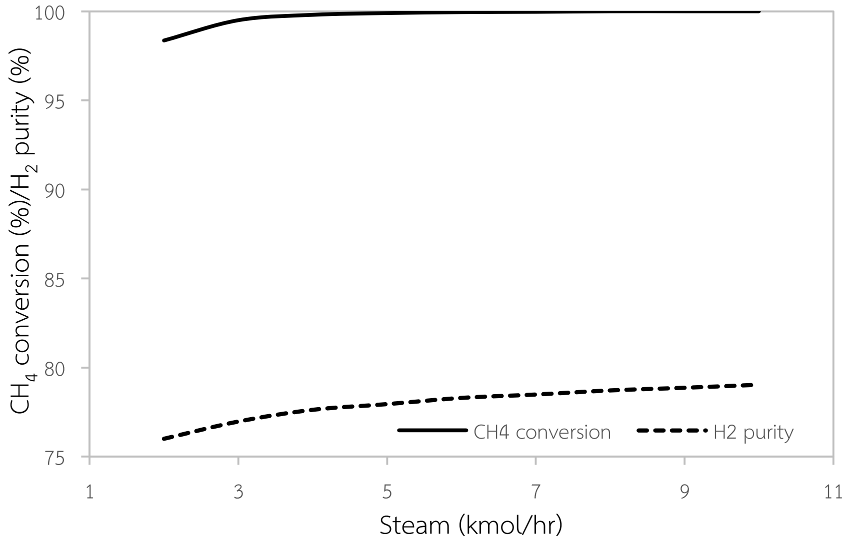

Figure 5.9 The effect of steam flow rate on CH_4 conversion and H_2 purity of SR process

In case of SR process, it was obviously seen that H_2 productivity profile was similar to that of SECLR process. The major factors affected the process performances involved the main reaction shifted forward by adding steam into the reforming reactor and less CH_4 fed to the reactor caused by higher in heat requirement. The former played an important role on H_2 productivity for the steam flow rate in the range of 2-4 kmol/hr, while the steam flow rate more than 4 kmol/hr relied on the latter. Like the SECLR process, the energy required from the furnace increased because the steam was added to the reactor. Owing to the endothermic reaction in the reactor, CH_4 conversion increased with increasing the steam flow rate until it reached ca. 100% at the steam flow rate of 5 kmol/hr. For H_2 purity of this process, the profile was different from the profile of SECLR process. In this case, the increase in H_2 purity was appeared for all of steam flow rate studied. Without CO_2 adsorption in SECLR process, higher amounts of by-products such as CO and CO_2 were presented at higher steam flow rate, leading to lower in H_2 purity as illustrated in Figures 5.5 and 5.9.

5.2.3 Sorption Enhanced Steam Reforming Process

For the last process, the effects of reforming temperature, steam flow rate and solid circulation on performance of sorption enhanced steam reforming process were examined. The results of process performances including H_2 productivity, energy requirement, CH_4 conversion, and H_2 purity are presented in Figures 5.10 and 5.11.

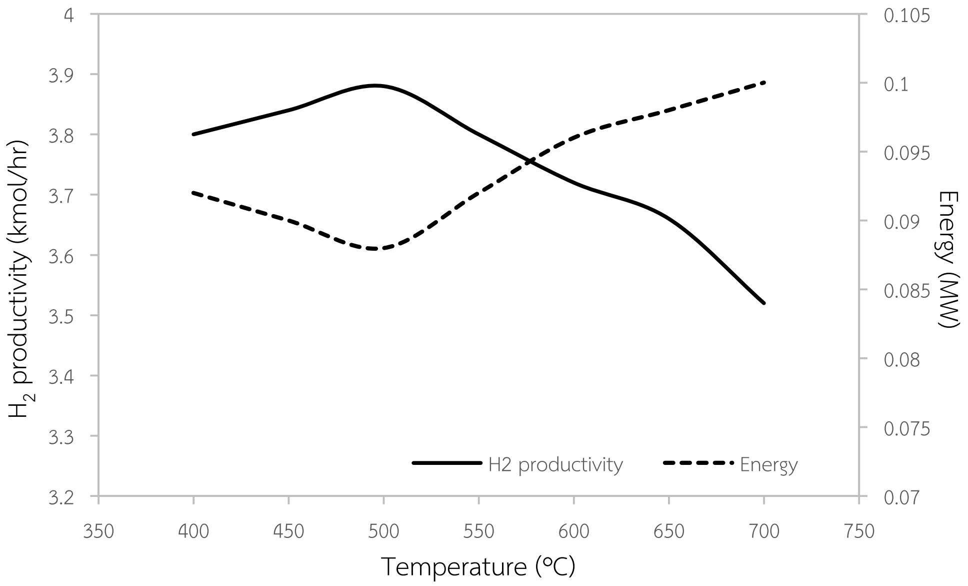

Figure 5.10 The effect of reforming temperature on H_2 productivity and energy provided from the furnace of SESR process

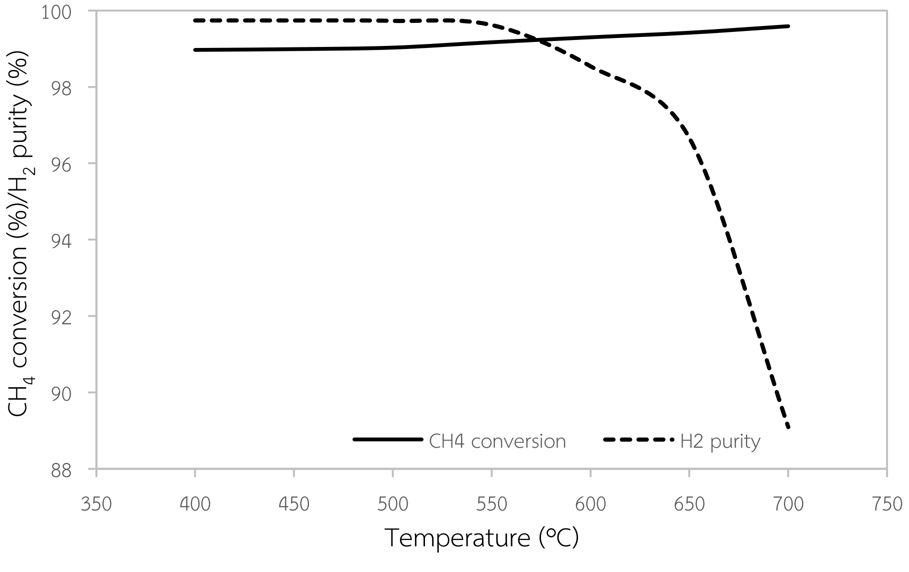

Figure 5.11 The effect of reforming temperature on CH_4 conversion and H_2 purity of SESR process

In Figure 5.10, at the reforming temperature in the range of 400-500°C, the capability of CaO to adsorb CO_2 via carbonation reaction was better than that at higher reforming temperatures. In addition, the exothermic reaction of carbonation could provide heat to the system. Although the main reaction for producing H_2 was endothermic, resulting in increasing of H_2 productivity with increased reforming temperature, the total heat requirement was still presented in lower values. This was probably due to the importance of carbonation reaction in this temperature range. Moreover, the reduction in energy required led to higher amount of CH_4 fed to the reforming reactor. Eventually, H_2 productivity obtained was higher at higher reforming temperature. At the reforming temperature higher than 500°C, the opposite trend was observed. Since the carbonation reaction was evidently dropped at high temperatures, heat provided from this exothermic reaction was less than the heat requirement from the endothermic of main reaction. The energy requirement in total then increased with increasing reforming temperature. Less CH_4 fed to the reforming reactor was subsequently reduced and resulted in less H_2 productivity. For CH_4 conversion, the conversion tended to increase as the reforming temperature increased for all reforming temperature range as shown in Figure 5.11. However, their values were insignificantly different and approached 100%. This was because of the endothermic reaction of steam reforming coupled with CO_2 adsorption. For H_2 purity, it almost unchanged until the reforming temperature of 550°C because CaO could still adsorb all of CO_2 produced from the reactions. Nonetheless, the adsorption ability of CaO was drastically decreased at higher reforming temperature. Hence, CO_2 remaining in the product stream was higher at the temperatures above 550°C, leading to the reduction in H_2 purity produced as seen in Figure 5.11.

For the effect of steam flow rate on the process performances, the simulation results are provided in Figures 5.12 and 5.13.

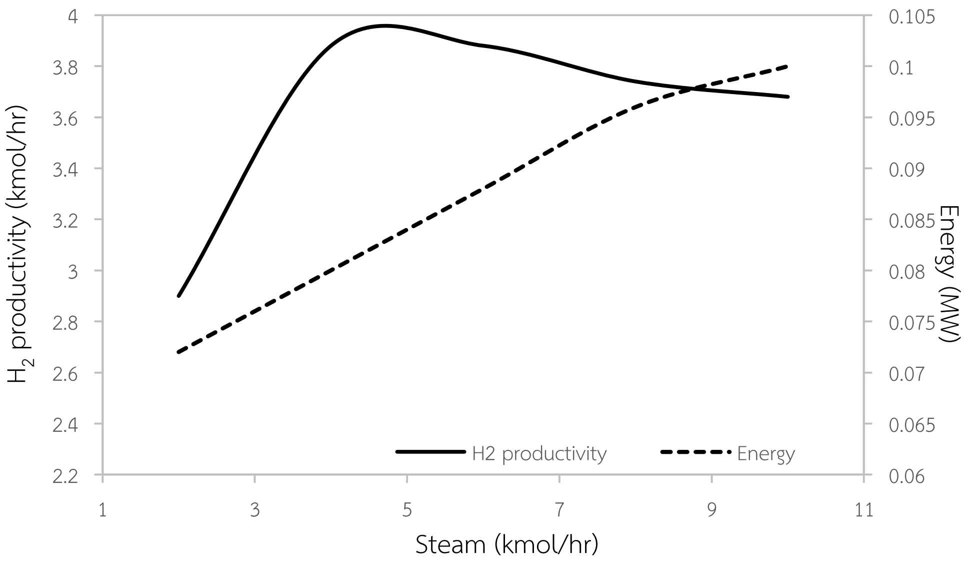

Figure 5.12 The effect of steam flow rate on H_2 productivity and energy provided from the furnace of SESR process

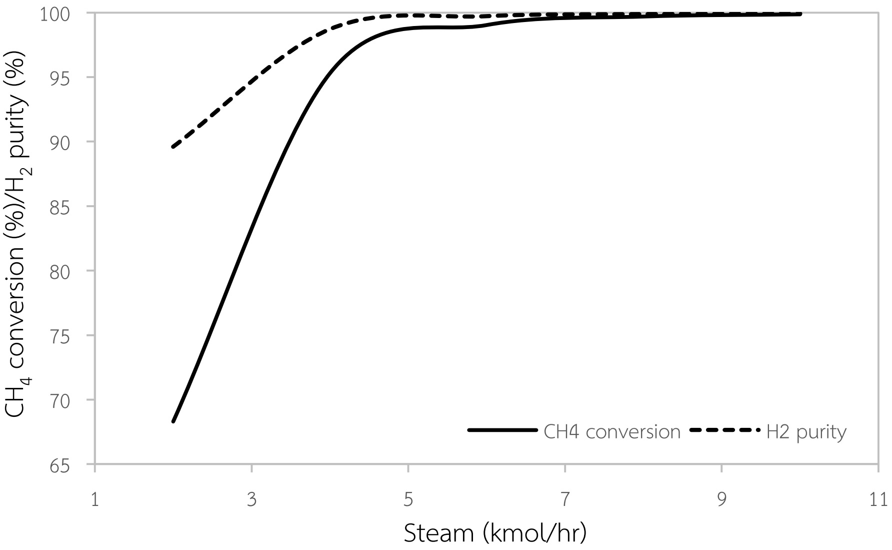

Figure 5.13 The effect of steam flow rate on CH_4 conversion and H_2 purity of SESR process

Since the SESR process was not different from the SECLR process, the profiles of process performances as shown in Figures 5.12 and 5.13 were similar to those from

SECLR process. These phenomena could be explained like the description of Figures 5.4 and 5.5 in Section 5.2.1.

For this process, the investigation of solid circulation rate on process performances was also taken into account. The results are then displayed in Figures 5.14 and 5.15.

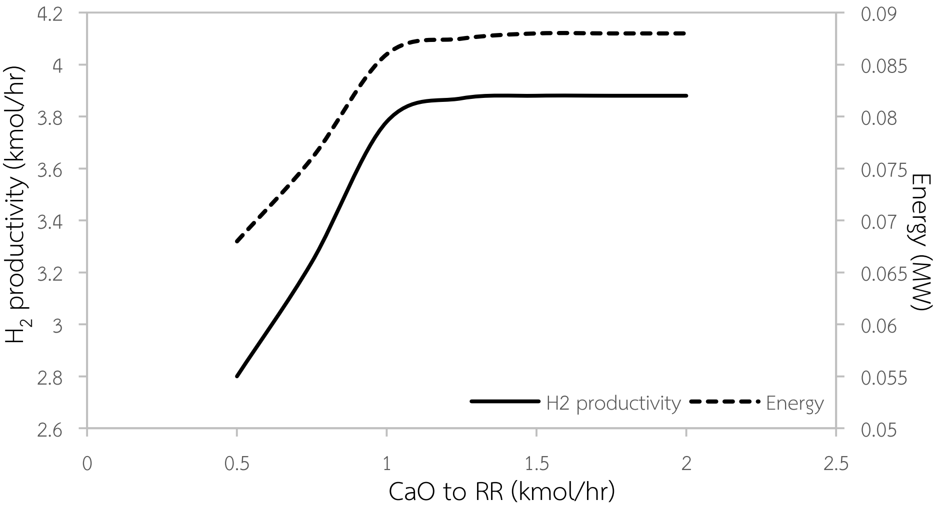

Figure 5.14 The effect of solid circulation rate on H_2 productivity and energy provided from the furnace of SESR process

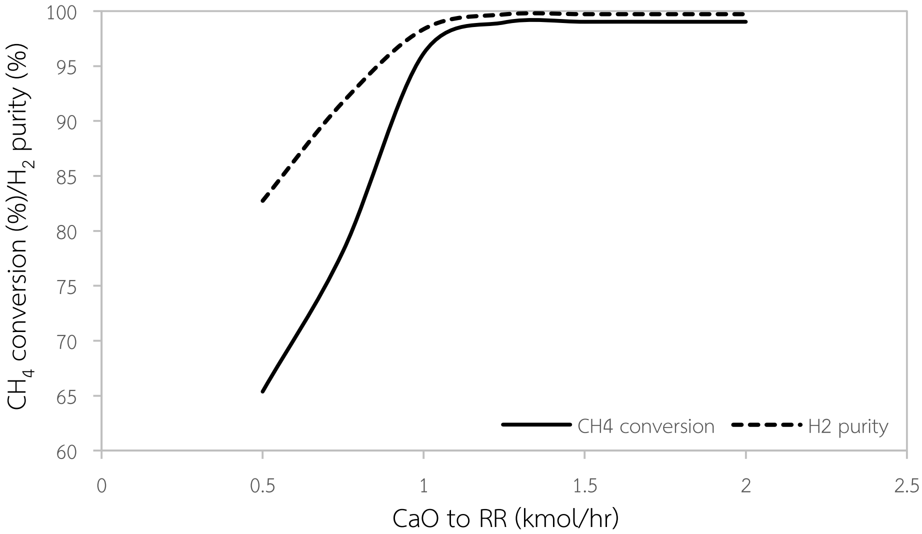

Figure 5.15 The effect of solid circulation rate on CH_4 conversion and H_2 purity of SESR process

From this simulation results, all performances including H_2 productivity, energy requirement, CH_4 consumption, and H_2 purity were affected by the solid circulation rate with the similar trend. These profiles indicated that it rapidly increased as the solid circulation rate increased in the range of 0.5-1.1 kmol/hr and remained stable at higher values. This was reasonable that some portions of CO_2 could not be adsorbed at low solid circulation rate as a result of insufficient amount of CaO. Even though the equilibrium of steam reforming reaction was shifted forward, it could not reach the saturation point. Therefore, all process performances could not be approached their possible maximum values. For this process, the amount of CaO required at least 1.1 kmol/hr should be processed at the optimal condition i.e., the reforming temperature of 500°C and the steam flow rate of 6 kmol/hr. At amount of CaO more than 1.1 kmol/hr, all process performances could reach the maximum values which were H_2 productivity of 3.88 kmol/hr, energy requirement of 0.088 MW, CH_4 consumption of

99.03%, and H_2 purity of 99.73%. Although the excess amount of CaO would not affect the process performances including H_2 productivity, total energy requirement, CH_4 conversion, and H_2 purity, the energy requirement of each reactor could be different. For this process, the energy requirement at reforming reactor was lower, whereas its value at calcination reactor was higher. However, the sizes of reactor and pipeline could be larger in case of the excess amount of CaO, causing higher cost.

5.3 Optimal Operations for Hydrogen Production Processes

In this section, all process performances of three processes including SR, SESR and SECLR were compared at their optimal conditions. The optimal conditions of each process were considered from the results as illustrated in Figures 5.2-5.15 by means of thermodynamic approach. For all processes, CH_4 feed to the process of 2 kmol/hr and no external fuel supplied were assumed. The simulation results at the optimal conditions of SR, SESR and SECLR are summarized in Table 5.5.

Table 5.5 Simulation results at optimal conditions of SR, SESR and SECLR

Parameter	Process		
	SR	SESR	SECLR
CH_4 feed to RR[a] (kmol/hr)	0.9	0.98	1.08
CH_4 feed temperature to RR (°C)	300	300	300
Steam feed to RR (kmol/hr)	6	6	4
Steam feed temperature to RR (°C)	150	150	150
Air feed to AR[b] (kmol/hr)	-	-	2.53
Air feed temperature to AR (°C)	-	-	250
Temperature @RR (°C)	800	500	600
Temperature @CR[c] (°C)	-	900	900
Temperature @AR (°C)	-	-	950
Pressure @RR (bar)	1.5	1.5	1.5
Pressure @CR (bar)	-	1.5	1.5
Pressure @AR (bar)	-	-	1.5
H_2 productivity (kmol/hr)	3.24	3.88	3.22
CH_4 conversion (%)	99.95	99.03	99.14
H_2 yield	3.6	3.96	2.98
Theoretical H_2 yield	4	4	3-4
H_2 purity (% on dry basis)	78.29	99.93	98.74
Steam consumption (kmol/hr)	1.44	1.94	1.07
Total energy requirement for boiler and reactors (MW)	0.104	0.088	0.067

[a] RR is reforming reactor

[b] AR is air reactor

[c] CR is calcination reactor

From the results in Table 5.5, the SR process gave H_2 productivity of 3.24 kmol/hr that could be expressed in terms of H_2 yield of 3.6 while the SESR process exhibited H_2 productivity of 3.88 kmol/hr or H_2 yield of 3.96. As expected, higher in H_2 yield for SESR process, which closed to the maximum theoretical H_2 yield of 4, came from the presence of CO_2 adsorbents in the reforming reactor. The adsorbents adsorbed CO_2 through the reaction (2.4). According to Le Chatelier's principle, the reaction (2.3) can be shifted forward by removing CO_2, leading to higher in steam consumption of SESR process. For SECLR process, H_2 productivity of 3.22 kmol/hr or H_2 yield of 2.98 was obtained. It was clearly found that the H_2 productivity from SECLR process was lower than that from SESR process. This was because the main reaction taking place in reforming reactor was reaction (2.11) instead of reaction (2.3) for SESR process. Therefore, less steam was required for SECLR process. As seen in Table 5.5, this process exhibited the lowest steam consumption. For the theoretical H_2 yield for SECLR process, it could be indicated in the range of 3-4. In case of the theoretical H_2 yield of 3, it was probably due to the combination of partial oxidation and water gas shift reactions. For the value of 4, it was considered as mentioned earlier for the SESR process. For CH_4 conversion and H_2 purity, SR process had to be operated at the temperature of 800°C of reforming reactor in order to achieve high CH_4 conversion as obtained from SESR and SECLR processes. Furthermore, the H_2 purity of 78.29% from SR process exhibited very low when compared to the values of 99.93% and 98.74% from SESR and SECLR processes, respectively, due to the thermodynamic limitation. In addition, CH_4 conversion and H_2 purity from SECLR process were similar to those from SESR process whereas less steam was consumed. This was because the main reaction taking place in the reforming reactor of SECLR process was the partial oxidation reaction followed by the steam reforming reaction at the studied condition.

Considering the energy requirement for each process, SR process required the highest one. It subsequently caused the lowest CH_4 fed to the reforming reactor of SR process, compared to other processes. For the SESR process, although high energy was required at calcination reactor as a result of the endothermic calcination reaction, less energy was required at reforming reactor because heat of reaction from carbonation could provide to the endothermic reaction of steam reforming. Moreover, the additional heat could also be transferred to the reforming reactor via solid circulation from the calcination reactor. Thus, lower in energy requirement was observed, compared to SR process. However, the lowest energy requirement was found from the SECLR process. Like the SESR process, heat generated from carbonation could supply to the reforming reactor, leading to the reduction in energy requirement. Furthermore, solid circulation from air reactor could provide to both reforming reactor and calcination reactor. Consequently, both reactors required low energy for processing SECLR operation.

5.4 Sorption Enhanced Chemical-Looping Reforming Process under Adiabatic Operation

As mentioned in Section 5.3, SECLR was the efficient process for producing H_2 under isothermal operation. In order to operate this process practically, it would be considered the reactors operated adiabatically. However, some parameters consisting of steam feed temperature, air feed temperature, solid ratio from calcination reactor to air reactor and solid ratio from air reactor to calcination reactor had to be adjusted for the process operated under adiabatic condition. Under this opearation, CH_4 feed stream was splitted to combust for producing and super-heating steam and air pre-heating only. The comparison in operating condition and process performance between SECLR and SECLR under adiabatic operation is presented in Table 5.6.

Table 5.6 Simulation results of SECLR and SECLR under adiabatic operation

Parameter	Process	
	SECLR	SECLR under adiabatic operation
CH_4 feed to RR (kmol/hr)	1.08	1.28
CH_4 feed temperature to RR (°C)	300	300
Steam feed to RR (kmol/hr)	4	4
Steam feed temperature to RR (°C)	150	300
Air feed to AR (kmol/hr)	2.53	2.53
Air feed temperature to AR (°C)	250	985
Temperature @RR (°C)	600	610
Temperature @CR (°C)	900	883
Temperature @AR (°C)	950	950
Pressure @RR (bar)	1.5	1.5
Pressure @CR (bar)	1.5	1.5
Pressure @AR (bar)	1.5	1.5
H_2 productivity (kmol/hr)	3.22	3.95
CH_4 conversion (%)	99.14	98
H_2 yield	2.98	3.09
Theoretical H_2 yield	3-4	3-4
H_2 purity (% on dry basis)	98.74	98.37
Steam consumption (kmol/hr)	1.07	1.44
Solid ratio from CR to AR[a]	0.922	0.945
Solid ratio from AR to CR[b]	0.9	0.992
Total energy requirement for boiler and reactors (MW)	0.067	0.026

[a] Solid ratio from CR to AR refers to the ratio of solid from calcination reactor to air reactor to total solid from calcination reactor.

[b] Solid ratio from AR to CR refers to the ratio of solid from air reactor to calcination reactor to total solid from air reactor.

From the results in Table 5.6, the process performances especially CH_4 conversion and H_2 purity of SECLR process operated under adiabatic condition insignificantly differed from those of SECLR process. However, H_2 productivity obtained from the process under adiabatic operation was higher than that obtained from SECLR process because less CH_4 was splitted for combustion as a result of the reduction in heat requirement of all reactors. As expected, in terms of energy requirement, SECLR process operated adiabatically was lower than the SECLR one. Under the adiabatic operation, heat combustion of CH_4 splitted was used only for producing steam and air pre-heating. In case of H_2 yield, its value was higher than 3 for the process with adiabatic operation. As mentioned in Section 5.3, it could be implied that the steam reforming reaction was more pronounced. This was probably due to higher in steam consumption for SECLR under adiabatic operation, compared to SECLR process. In order to operate the process adiabatically, steam feed temperature, air feed temperature, solid ratio from calcination reactor to air reactor, and solid ratio from air reactor to calcination reactor were changed from 150°C, 250°C, 0.922, and 0.9 to 300°C, 985°C, 0.945 and, 0.992, respectively. It was found that steam feed temperature and air feed temperature were increased in order to reduce the energy requirement at reforming reactor and air reactor, respectively. Furthermore, more solids were sent to calcination reactor to provide heat to this reactor via the solid circulation.

5.5 Effect of CO_2 Content in Feed Stream on Process Performances for SECLR under Adiabatic Operation

From the simulation results for this effect, it significantly affected the operating condition and process performance as summarized in Table 5.7. In this case, several parameters such as steam feed temperature, solid ratio from calcination reactor to air reactor, and solid ratio from air reactor to calcination reactor were necessary to change in order to suit SECLR process under adiabatic operation. All studied conditions were based on steam feed and air feed flow rate of 4 and 2.53 kmol/hr, respectively.

Table 5.7 Simulation results of SECLR process operated under adiabatic condition with different CO_2 content in feed stream

Parameter	CO_2 content in feed stream					
	0%	10%	20%	30%	40%	50%
CH_4 feed to RR (kmol/hr)	1.28	1.274	1.269	1.264	1.259	1.254
CH_4 feed temperature to RR (°C)	300	300	300	300	300	300
Steam feed temperature to RR (°C)	300	370	430	495	535	578
Air feed temperature to AR (°C)	985	985	985	985	985	985
Temperature @RR (°C)	610	643	666	683	695	705
Temperature @CR (°C)	883	883	883	883	883	883
Temperature @AR (°C)	950	950	950	950	950	950
H_2 productivity (kmol/hr)	3.95	3.91	3.87	3.81	3.75	3.69
CH_4 conversion (%)	98	98.24	98.47	98.67	98.83	98.97
H_2 yield	3.09	3.07	3.05	3.01	2.98	2.94
Theoretical H_2 yield	3-4	3-4	3-4	3-4	3-4	3-4
H_2 purity (% on dry basis)	98.37	96.94	94.92	92.59	90.32	87.96
Steam consumption (kmol/hr)	1.44	1.41	1.37	1.32	1.26	1.21
Solid ratio from CR to AR	0.945	0.9449	0.9447	0.9445	0.9444	0.9443
Solid ratio from AR to CR	0.992	0.993	0.9935	0.9937	0.9939	0.9941
Total energy requirement (MW)	0.026	0.026	0.026	0.026	0.026	0.026

As seen the results in Table 5.7, the CO_2 content in feed stream showed the negative effect on the SECLR process operated adiabatically. More CO_2 content in feed stream resulted in more CH_4 splitted because heat of combustion was partially provided to heat CO_2 up. Therefore, lower in H_2 productivity was obtained when CO_2 content in feed stream increased. In addition, H_2 purity and CH_4 conversion were also significantly influenced by CO_2 content in feed stream. H_2 purity tended to decrease as CO_2 content in feed stream increased. Unlike the H_2 purity, CH_4 conversion showed the opposite trend which gradually increased with increasing of CO_2 content in feed stream because of higher in reforming temperature. This trend was similar to the profile as indicated in Figure 5.3 at the reforming temperature more than 600°C.

As considered the increase in CO_2 content in feed stream, the operating conditions were adjusted. The steam feed temperature and solid ratio from air reactor to calcination reactor were increased, whereas the solid ratio from calcination reactor to air reactor was reduced. In addition, more energy requirement at calcination reactor was needed due to the influence of calcination reaction taking place in this reactor. Therefore, more solids were routed to the calcination reactor to provide heat via solid circulation. However, it was found that heat obtained from solid circulation was not enough, causing the solid outlet at the reforming reactor having higher temperatures to decrease the energy requirement of calcination reactor. The reforming temperature could be higher by increasing of the carbonation reaction taking place in reforming reactor. Nonetheless, steam feed temperature had to be increased and more solids were also sent to the reforming reactor to provide more heat to the reforming reactor, leading to increase the solid temperature at the reforming reactor outlet in order to carry out the adiabatic operation for all reactors in the process.

5.6 Basic Design of Reactors of Sorption Enhanced Chemical-Looping Reforming

According to the results from Section 5.3, SESR and SECLR processes were the promising process for hydrogen production. Both processes could achieve high CH_4 conversion and H_2 purity with lower energy consumption, compared to the conventional SR process. However, due to the requirement of solid regeneration, fixed bed reactor as typically used in the conventional SR process was not suitable. This was because it required the synchronization of two reactors for different modes i.e., one for reaction-sorption and another one for regeneration mode for SESR process. For this purpose, at least two fixed bed reactors would be employed for two different modes. The decay of sorbent during multi-cycle operation led to difficulty in matching between production time and regeneration time. The example of reactor configuration for SESR is illustrated in Figure 5.16. The fluidized bed reactor operated in fast fluidization regime (superficial gas velocity of 2-10 m/s) was used for the reforming reactor because high gas throughput could be achieved and reaction kinetics of steam reforming and carbonation were fast enough [42, 43]. For the calcination reactor, the fluidized bed reactor operated in bubbling regime (superficial gas velocity of 0.1-1 m/s) was used instead due to lower reaction rate of calcination reaction [44]. It could be applied this concept for designing the reactor configuration for SECLR process. However, there were some different reactor configurations between SESR and SECLR due to the difference in number of reactors in the process with concerning about the solid transportation. The reactor design was based on Figure 5.17 which was composed of three reactors including reforming reactor, calcination reactor, and air reactor. The proposed reactor configuration for SECLR is illustrated in Figure 5.18. The feed stream consisting of pure methane and steam were supplied to the riser inlet. For this reactor configuration, the riser was used only for solid transportation. The solids including metal, metal oxide, and adsorbent then were sent to the reforming reactor which was fluidized bed reactor operated in bubbling regime. This was because the major reactions taking place in this reactor were partial oxidation and carbonation which were slower than that of steam reforming [45]. After that, solids were circulated to the calcination reactor which was also fluidized bed reactor operated in bubbling regime for adsorbent regeneration. The CO_2 product from calcination reactor was partially splitted to use as sweep gas at calcination reactor. The sweep gas had to be sufficient for causing bubbling fluidization or having superficial gas velocity between minimum fluidization velocity (U_{mf}) and terminal settling velocity (U_t). The minimum fluidization velocity and terminal settling velocity could be calculated by the equations reported by Wen and Yu [38] and Pinchbeck and Popper [39] as mentioned in the Chapter 4. After the adsorbent regeneration, some solids were sent back to the reforming reactor via riser while the remaining solids were sent to the air reactor. For the air reactor, the fluidized bed reactor was operated in fast fluidization regime instead due to high reaction rate of oxidation reaction [45] and the requirement of solid circulation to both reforming and calcination reactors. As seen from Figure 5.18, there was an inlet for inert gas at intervals along the length of each standpipes. This inert gas would give an external aeration to ensure that the catalyst remained fluidized phenomenon. A gas medium could be air, steam, or nitrogen.

With classifying the flow regime for the reactors, the reforming reactor, calcination reactor, and air reactor were considered to be fluidized bed reactor operated in bubbling, bubbling, and fast fluidization regime, respectively. However, the different regimes resulted from the difference in gas velocity. The gas velocity in the range of minimum fluidization velocity (U_{mf}) and terminal settling velocity (U_t) was used to indicate the bubbling regime, whereas the gas velocity exceeding the terminal settling velocity (U_t) caused the fast fluidization regime. For the calculation, owing to the lack of researches about fluidization, the results reported Ryden and Ramos [4] which was the closest work to this research could be used as the basis. Nonetheless, some parameters were not reported in their work. For example, the report provided only the bulk density of NiO and $CaCO_3$ which were 2,600 and 1,200 kg/m^3, respectively, with the diameter range of 90-212 µm, while the bulk density of other solids were unknown. The bulk density and particle density had a relationship as shown in the following equation.

$$\rho_{bulk} = \rho_{particle}(1 - \phi) \tag{5.1}$$

where ϕ = bed porosity

From the bulk density reported by Ryden and Ramos, the calculated average bed porosity was calculated and then obtained the value of 0.58. For this study, this bed porosity was then assumed for all reactors. Thus, the bulk density of solids by weight average for each reactor could be calculated which were 1,800, 1,790, and 1,801 kg/m^3 for reforming reactor, calcination reactor, and air reactor, respectively. For designing the reactor basically, the important and calculated parameters were based on the simulation results from Section 5.4. The crucial parameters are presented and summarized in Table 5.8.

Table 5.8 Important and calculated parameters for basic reactor design

Reactor	Stream	Flow rate (kg/hr)	Solid mass fraction	Density/ Particle density (kg/m^3)	Cal. Bulk density (kg/m^3)	Viscosity (kg/ms)
Reforming reactor (610°C)	Gas and steam fed to RR	92.6	-	0.358	-	$3.27\text{x}10^{-5}$
	Ni	3.59	0.012	8,908	3,741	-
	NiO	78.51	0.264	6,670	2,801	-
	CaO	215.28	0.724	3,340	1,403	-
	$CaCO_3$	-	-	2,710	1,138	-
Calcination reactor (883°C)	CO_2 sweep gas to CR	5.94	-	0.686	-	$4.40\text{x}10^{-5}$
	Ni	65.28	0.014	8,908	3,741	-
	NiO	1,244.83	0.259	6,670	2,801	-
	CaO	3,373.08	0.702	3,340	1,403	-
	$CaCO_3$	121.55	0.025	2,710	1,138	-
Air reactor (950°C)	Air fed to AR	72.99	-	0.425	-	$4.91\text{x}10^{-5}$
	Ni	61.69	0.014	8,908	3,741	-
	NiO	1,176.37	0.262	6,670	2,801	-
	CaO	3,251.93	0.724	3,340	1,403	-
	$CaCO_3$	-	-	2,710	1,138	-

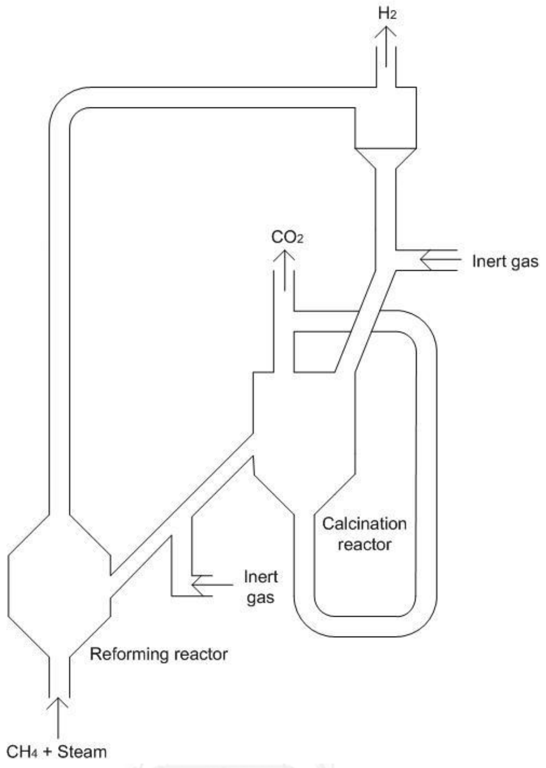

Figure 5.16 Reactor configuration of SESR process

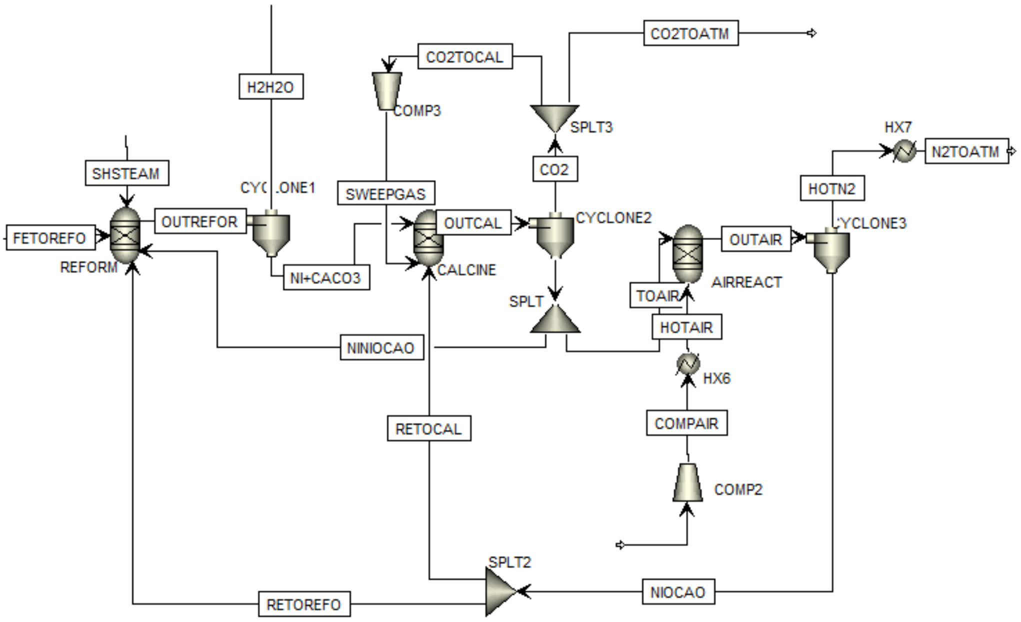

Figure 5.17 The scheme of SECLR process for reactor design

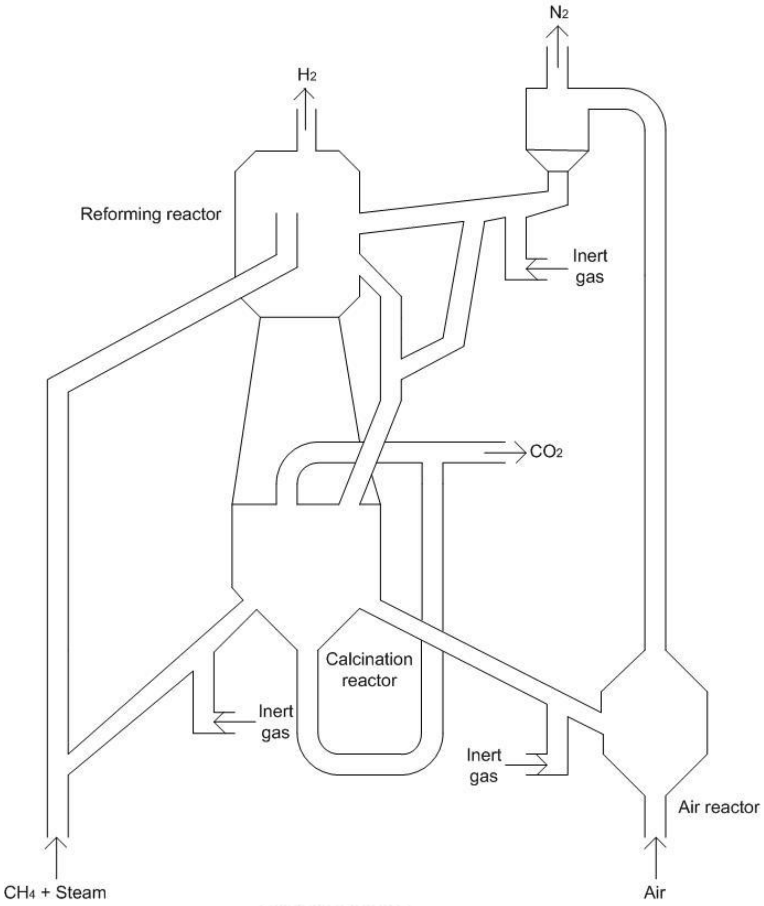

Figure 5.18 Reactor configuration of SECLR process

From the information indicated in Table 5.8, U_{mf} and U_t could then be calculated from the equations (4.1) to (4.3), respectively. The calculation procedure was listed as follows:

1. Calculating Ar
2. Substituting Ar from 1) into equation (4.1) to find U_{mf}
3. Finding Reynolds number using U_{mf} obtained from 2)
4. Calculating U_t from equations (4.2) or (4.3) which was dependent on Reynolds number
5. Checking Reynolds number with U_t obtained from 4)

6. Calculating volumetric gas flow rate from the data reported in Table 5.8
7. Estimating the range of reactor diameter
8. Estimating the reactor volume and height from equations (5.2) and (5.3)

$$Reactor\ volume = Volumetric\ flow\ rate\ x\ residence\ time \quad (5.2)$$

$$Reactor\ height = \frac{4\ x\ Reactor\ volume}{\pi\ x\ Reactor\ diameter^2} \quad (5.3)$$

The assumptions were that all solid particles in the process were spherical with average diameter of 100 μm. From the above calculation procedure, the results are presented in Table 5.9.

As indicated in Table 5.9, the diameters of reforming reactor and calcination reactor should be in the range of 0.55-5.3 m, and 0.12-1.13 m, respectively. In these diameter ranges, gas velocities were in the range of minimum fluidization velocity (U_{mf}) and terminal settling velocity (U_t) which caused bubbling fluidization regime. On the other hand, the diameter had to be less than 0.55 m for air reactor because of the gas velocity higher than terminal settling velocity (U_t) which was essential for causing fast fluidization regime. For estimating the reactor volume and height, the residence time inside the reactor was taken into account. Since the residence time could not be obtained from Aspen Plus program, the information from the previous researches would be considered instead. The calculated reactor volume and height equations (5.2) and (5.3) are summarized in Table 5.10.

Table 5.9 The calculation results of basic design for each reactor

Reactor	Ar	Cal. U_{mf} (m/s)	Re with U_{mf}	Cal. U_t (m/s)	Re with U_t	Vol. gas flow rate (m^3/s)	Cal. Diameter (m)
Reforming reactor	5.91	3.27×10^{-3}	3.27×10^{-3}	0.3	0.328	0.072	0.55-5.3
Calcination reactor	6.22	2.41×10^{-3}	3.76×10^{-3}	0.22	0.343	2.41×10^{-3}	0.12-1.13
Air reactor	3.11	2.17×10^{-3}	1.88×10^{-3}	0.20	0.173	0.048	Less than 0.55

Table 5.10 The calculated reactor volume and height for each reactor

Reactor	The slowest reaction taking place	Vol. gas flow rate (m^3/s)	Residence time (s)	Reactor volume (m^3)	Reactor height (m)
Reforming reactor	Carbonation	0.072	150 [43]	10.8	0.49-45.48
Calcination reactor	Calcination	2.41×10^{-3}	360 [44]	0.87	0.87-76.96
Air reactor	Oxidation	0.048	7.5 [45]	0.36	More than 1.52

From Table 5.10, the reactor volume of reforming reactor, calcination reactor, and air reactor were 10.8 m^3, 0.87 m^3, and 0.36 m^3, respectively. The height of reforming reactor, calcination reactor, and air reactor were in the range of 0.49-45.48 m, 0.87-76.96 m, and more than 1.52 m, respectively. For these reactor sizes, the process performances including H_2 productivity, energy requirement, CH_4 conversion, and H_2 purity were achieved as presented in the second column of Table 5.6.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The simulation results of sorption enhanced chemical-looping for hydrogen production from methane are summarized in this chapter. The sorption enhanced chemical-looping reforming (SECLR) process was simulated using NiO and CaO as oxidizing agent and CO_2 adsorbent, respectively. The other hydrogen production processes, which were steam reforming (SR) process and sorption enhanced steam reforming (SESR) process, were also simulated. The effects of various parameters including reforming temperature, steam flow rate and solid circulation rate on process performances were studied. The optimal conditions of all processes were considered and then the process performances which were composed of hydrogen productivity, energy requirement, methane conversion, and hydrogen purity were examined and compared. Moreover, the possibility of SECLR process operated adiabatically was analyzed by varying the solid circulation ratio and steam/air pre-heating temperature. The effects of CO_2 content in feed stream on the SECLR under adiabatic operation were also investigated. Finally, the preliminary design of reactors for sorption enhanced chemical-looping reforming process was carried out.

6.1.1 Effects of Various Parameters

6.1.1.1 SECLR Process

1. A change in reforming temperature showed the significant effect on H_2 productivity, energy consumption, CH_4 conversion, and H_2 purity with the different trends.
2. The increase in steam flow rate led to increasing of hydrogen productivity, CH_4 conversion, and H_2 purity only at low steam flow rate range. Higher steam flow was not necessary to be operated because it insignificantly affected those parameters and caused higher energy requirement.
3. Increasing of solid circulation rate resulted in higher hydrogen productivity, energy requirement, CH_4 conversion, and H_2 purity until reaching the saturation point. After this point, their values remained constant.

6.1.1.2 SR Process

1. The increase in reforming temperature showed the positive effect on H_2 productivity, CH_4 conversion, and H_2 purity at low temperature range. At high temperature range, the effects of reverse water gas shift reaction and energy required were more dominant and showed the unsatisfied results for all process performances.
2. A change in steam flow rate exhibited significant effect on hydrogen productivity, CH_4 conversion, and H_2 purity only at low steam flow rate range as same as the SECLR process.

6.1.1.3 SESR Process

1. Increasing of reforming temperature showed good results of H_2 productivity, energy requirement, CH_4 conversion, and H_2 purity only at low

temperature range. Higher reforming temperature showed the negative effect on all process performances except for CH_4 conversion.

2. A change in steam flow rate showed the similar trend to the SECLR process for all process performances.

3. The increase in solid circulation rate exhibited the similar trend to the SECLR process for all process performances.

6.1.2 Process Performance for Hydrogen Production Processes at Optimal Conditions

6.1.2.1 Optimal Conditions

The different optimal conditions were found for each process. For the SECLR process, the optimal conditions were at the reforming temperature of 600°C, steam flow rate of 4 kmol/hr and CaO circulation rate at least 1.045 kmol/hr. The optimal operations of SR process were at the reforming temperature of 800°C and steam flow rate of 6 kmol/hr. Lastly, for the SESR process, the reforming temperature of 500°C, steam flow rate of 6 kmol/hr and CaO circulation rate at least 1.1 kmol/hr were carried out at its optimal conditions.

6.1.2.2 The Comparison in Process Performances

1. Although lower in H_2 productivity and H_2 yield was obtained from SECLR process when compared to the SESR process, the lowest steam consumption was found for SECLR process due to the difference in main reaction taking place in the reforming reactor.

2. SR process showed the lowest CH_4 conversion and H_2 purity because of the thermodynamic limitation. Moreover, CH_4 conversion and H_2 purity obtained from

SECLR process were close to those obtained from SESR process with lower steam consumption.

3. SECLR process showed the lowest energy requirement because heat of carbonation reaction could be used within the reforming reactor. Furthermore, heat could also provide to both reforming and calcination reactors via the solid circulation from air reactor.

6.1.3 Adiabatic Operation of SECLR Process

1. The SECLR process operated under adiabatic condition showed insignificantly different CH_4 conversion and H_2 purity for the SECLR process. Moreover, H_2 productivity obtained from adiabatic operation of SECLR process was more than that obtained from SECLR process due to lower in CH_4 splitted to combust.

2. The energy requirement of SECLR process operated adiabatically was lower than that of SECLR process.

3. Steam feed temperature, air feed temperature, solid ratio from calcination reactor to air reactor, and solid ratio from air reactor to calcination reactor were adjusted to process with adiabatic operation.

6.1.4 Effect of CO_2 Content in Feed Stream on Adiabatic Operation of SECLR Process

1. The CO_2 content in feed stream showed the negative effect on H_2 productivity because heat of combustion had to be partially provided to heat CO_2 up.

2. Negative effect of CO_2 content was also found on H_2 purity. On the other hand, CH_4 conversion was gradually increased when CO_2 content in feed stream increased.

3. Increasing of CO_2 content in feed stream resulted in increasing, decreasing and increasing of steam feed temperature, solid ratio from calcination reactor to air reactor, and solid ratio from air reactor to calcination reactor, respectively, to maintain the adiabatic operation of SECLR process.

6.1.5 Basic Design of Reactors of Sorption Enhanced Chemical-Looping Reforming

1. Reactors for SECLR process would be 3-connected fluidized bed reactor which reforming reactor, calcination reactor, and air reactor were operated in bubbling, bubbling, and fast fluidization regime, respectively, because it was dependent on the reaction rate and solid transportation.

2. The diameter of reforming reactor, calcination reactor, and air reactor should be in the range of 0.55-5.3 m, 0.12-1.13 m, and less than 0.55 m, respectively. In these diameter ranges, gas velocity would be compatible with the operating regime of each reactor.

3. Rector volume and height could be estimated via the residence time obtained from the previous researches. The reactor volume of reforming reactor, calcination reactor, and air reactor were 10.8 m^3, 0.87 m^3, and 0.36 m^3, respectively. The height of reforming reactor, calcination reactor, and air reactor were in the range of 0.49-45.48 m, 0.87-76.96 m, and more than 1.52 m, respectively.

6.2 Recommendations

1. Other feeds such as natural gas and ethanol should be further studied and compared with methane feed.
2. The cost including capital and operating cost and the amount of utilities for 4 processes (SR, SESR, SECLR, and adiabatic operation of SECLR) should be further investigated.
3. Combination of isothermal reactors and adiabatic reactors for hydrogen production processes in order to achieve the maximum hydrogen productivity and hydrogen purity should be taken into account in further study.
4. The effects of CaO characteristics such as pore diameter, pore volume, and particle diameter on process performances should be further investigated.
5. The attrition rate of solids and cyclone efficiency should be taken into account for more accurate calculation.

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APPENDIX

APPENDIX A

Table A.1 Summary of streams for SECLR process

Stream	Description
CH4	Methane feed
FEED	Splitted methane feed
FEED1	Compressed methane feed
FEED2	Hot feed to H_2S removal unit
FEED3	Purified methane feed
FUEL	Fuel feed to furnace
AIRF	Air feed to furnace
FLUEGAS	Hot flue gas from furnace
COOLEDFG	Cooled flue gas
FETOREFOR	Hot methane feed to reforming reactor
H2O	H_2O feed
H2O1	Pumped H_2O feed
MIXH2O	Mixed H_2O feed
HOTH2O	Hot H_2O feed
HOTSTEAM	Hot steam feed
SHSTEAM	Superheated steam feed
H2S	Removed H_2S from methane feed
OUTREFOR	Products from reforming reactor
H2H2O	Feed to water removal unit
REWATER	Recycled water
H2	Hydrogen product
NI+CACO3	Spent metal oxide and adsorbent to calcination reactor
OUTCAL	Products from calcination reactor
CO2	CO_2 from regeneration process
CO2TOCAL	CO_2 for being sweep gas
SWEEPGAS	Compressed CO_2 sweep gas
CO2TOATM	CO_2 to atmosphere

Stream	Description
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
COMPAIR	Compressed air
HOTAIR	Hot air feed to air reactor
OUTAIR	Products from air reactor
HOTN2	Hot N_2 from regeneration process
N2TOATM	N_2 to atmosphere
NIOCAO	Regenerated solids before splitting to reforming reactor and calcination reactor
RETOCAL	Regenerated solids to calcination reactor
RETOREFOR	Regenerated solids to reforming reactor

Table A.2 Summary of block components for SECLR process

Model	Name	Description
RGIBBS	REFORM	Simulates steam reforming 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	FEEDSPLT	Splits CH_4 feed to furnace
	SPLT	Splits regenerated solids to reforming reactor and to air reactor

Model	Name	Description
	SPLT2	Splits regenerated solids to reforming reactor and to calcination reactor
	SPLT3	Splits CO_2 for being sweep gas
MIXER	MIX1	Simulates mixing between water and recycled water
SEP	H2SREMOV	Simulates feed purification
FLASH2	KODRUM	Simulates removal of water
HEATER	HX1	Simulates feed preheating
	HX2	Simulates feed preheating
	HX3	Simulates water preheating
	HX4	Simulates steam production
	HX5	Simulates steam production
	HX6	Simulates air preheating
	HX7	Simulates CO_2 cooling down
	HX8	Simulates air preheating
	HX9	Simulates flue gas cooling down
COMPR	COMP1	Simulates feed compression
	COMP2	Simulates air compression
	COMP3	Simulates sweep gas compression
RStoic	FURNACE	Simulates combustion
PUMP	PUMP1	Simulates water compression

Table A.3 Summary of streams for SR process

Stream	Description
CH4	Methane feed
FEED	Splitted methane feed
FEED1	Compressed methane feed
FEED2	Hot feed to H_2S removal unit
FEED3	Purified methane feed
FUEL	Fuel feed to furnace
AIRF	Air feed to furnace
FLUEGAS	Hot flue gas from furnace
COOLEDFG	Cooled flue gas
FETOREFOR	Hot methane feed to reforming reactor
H2O	H_2O feed
H2O1	Pumped H_2O feed
MIXH2O	Mixed H_2O feed
HOTH2O	Hot H_2O feed
HOTSTEAM	Hot steam feed
SHSTEAM	Superheated steam feed
H2S	Removed H_2S from methane feed
OUTREFOR	Products from reforming reactor
TOHTS	Feed to high temperature shift reactor
OUTHTS	Products from high temperature shift reactor
TOLTS	Feed to low temperature shift reactor
OUTLTS	Products from low temperature shift reactor
TOKODRUM	Feed to water removal unit
REWATER	Recycled water
TOPSA	Feed to PSA unit
H2	Hydrogen product
WASTEGAS	Waste gas from PSA unit

Table A.4 Summary of block components for SR process

Model	Name	Description
RGIBBS	REFORM	Simulates steam reforming reaction
	HTS	Simulates water-gas shift reaction
	LTS	Simulates water-gas shift reaction
SEP	PSA	Simulates hydrogen purification
	H2SREMOV	Simulates feed purification
MIXER	MIX1	Simulates mixing between water and recycled water
FLASH2	KODRUM	Simulates removal of water
HEATER	HX1	Simulates feed preheating
	HX2	Simulates feed preheating
	HX3	Simulates water preheating
	HX4	Simulates steam production
	HX5	Simulates steam production
	HX6	Simulates product cooling down
	HX7	Simulates product cooling down
	HX8	Simulates product cooling down
	HX9	Simulates air preheating
	HX10	Simulates flue gas cooling down
FSPLT	FEEDSPLT	Splits CH_4 feed to furnace
RStoic	FURNACE	Simulates combustion
COMPR	COMP1	Simulates feed compression
PUMP	PUMP1	Simulates water compression

Table A.5 Summary of streams for SESR process

Stream	Description
CH4	Methane feed
FEED	Splitted methane feed
FEED1	Compressed methane feed
FEED2	Hot feed to H_2S removal unit
FEED3	Purified methane feed
FUEL	Fuel feed to furnace
AIRF	Air feed to furnace
FLUEGAS	Hot flue gas from furnace
COOLEDFG	Cooled flue gas
FETOREFOR	Hot methane feed to reforming reactor
H2O	H_2O feed
H2O1	Pumped H_2O feed
MIXH2O	Mixed H_2O feed
HOTH2O	Hot H_2O feed
HOTSTEAM	Hot steam feed
SHSTEAM	Superheated steam feed
H2S	Removed H_2S from methane feed
OUTREFOR	Products from reforming reactor
H2H2O	Feed to water removal unit
REWATER	Recycled water
H2	Hydrogen product
CACO3	Spent adsorbent to calcination reactor
OUTCAL	Products from calcination reactor
CO2	CO_2 from regeneration process
CO2TOCAL	CO_2 for being sweep gas
SWEEPGAS	Compressed CO_2 sweep gas
HOTCO2	Hot CO_2 before cooling down
CO2TOATM	CO_2 to atmosphere
CAO	Regenerated solids to calcination reactor

Table A.6 Summary of block components for SESR process

Model	Name	Description
RGIBBS	REFORM	Simulates steam reforming reaction
	CALCINE	Simulates calcination reaction of $CaCO_3$
CYCLONE	CYCLONE1	Separates gas and solid products from reforming reactor
	CYCLONE2	Separates gas and solid products from calcination reactor
FSPLT	FEEDSPLT	Splits CH_4 feed to furnace
	SPLT3	Splits CO_2 for being sweep gas
MIXER	MIX1	Simulates mixing between water and recycled water
SEP	H2SREMOV	Simulates feed purification
FLASH2	KODRUM	Simulates removal of water
HEATER	HX1	Simulates feed preheating
	HX2	Simulates feed preheating
	HX3	Simulates water preheating
	HX4	Simulates steam production
	HX5	Simulates steam production
	HX6	Simulates CO_2 cooling down
	HX7	Simulates air preheating
	HX8	Simulates flue gas cooling down
RStoic	FURNACE	Simulates combustion
COMPR	COMP1	Simulates feed compression
	COMP3	Simulates sweep gas compression
PUMP	PUMP1	Simulates water compression

VITA

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