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SIMULATION OF SORPTION ENHANCED CHEMICAL-LOOPING PROCESS FOR HYDROGEN PRODUCTION FROM BIOMASS

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งานวิจัยชิ้นนี้ได้ศึกษาการปรับปรุงกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับสำหรับการผลิตไฮโดรเจนจากชีวมวลด้วยวิธีทางทฤษฎี โดยใช้ซังข้าวโพดเป็นวัตถุดิบ และใช้กระบวนการไพโรไลซิสเพื่อเปลี่ยนชีวมวลเป็นน้ำมันชีวภาพก่อนป้อนเข้าสู่กระบวนการรีฟอร์มมิง งานชิ้นนี้สนใจที่จะศึกษาและพัฒนาศักยภาพในการผลิตไฮโดรเจนของกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับ ในงานชิ้นนี้ อันดับแรก เราเปรียบเทียบประสิทธิภาพในการผลิตไฮโดรเจนของกระบวนการรีฟอร์มมิง 4 กระบวนการที่แตกต่างกัน ในรูปของค่าการแปรผันของน้ำมันชีวภาพ ปริมาณผลิตไฮโดรเจนที่ผลิตได้ ความบริสุทธิ์ของไฮโดรเจน และพลังงานที่ใช้ ผลการจำลองกระบวนการแสดงให้เห็นว่า กระบวนการที่ส่งเสริมด้วยการดูดซับ และกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับ เป็นกระบวนการที่เหมาะสมสำหรับการผลิตไฮโดรเจนในสภาวะอุณหภูมิคงที่ ซึ่งให้ค่าการแปรผันของน้ำมันเท่ากับ 100 เปอร์เซ็นต์, ปริมาณการผลิตของไฮโดรเจน 169 กรัมไฮโดรเจนต่อกิโลกรัมซังข้าวโพด ความบริสุทธิ์ของไฮโดรเจน 97 เปอร์เซ็นต์ และใช้พลังงาน 11.8 กิโลวัตต์ ที่อุณหภูมิการรีฟอร์ม 550 องศาเซลเซียส, ความดัน 1 บาร์, สัดส่วนไอน้ำสมดุลเท่ากับ 5, สัดส่วนนิกเกิลออกไซด์สมดุลเท่ากับ 0.1 และสัดส่วนแคลเซียมออกไซด์สมดุลเท่ากับ 2 นอกจากนี้ เรายังศึกษาการพัฒนากระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับ เพื่อให้หน่วยให้ความร้อนและหน่วยทำความเย็นมีปริมาณน้อยที่สุด และลดการสูญเสียความร้อนจากเครื่องปฏิกรณ์ โดยดำเนินการในสภาวะไม่สูญหรือได้ความร้อน ผลการจำลองกระบวนการแสดงให้เห็นว่า การรวมความร้อนในกระบวนการเคมิคอลลูปปิงที่ส่งเสริมด้วยการดูดซับที่ดัดแปลงแล้วให้ปริมาณการผลิตของไฮโดรเจน 77.4 กรัมไฮโดรเจนต่อกิโลกรัมซังข้าวโพด ความบริสุทธิ์ของไฮโดรเจน 77 เปอร์เซ็นต์ ใช้พลังงาน 5.64 กิโลวัตต์ และลดหน่วยให้ความร้อนจาก 8 หน่วย เหลือ 3 หน่วย โดยใช้เครื่องแลกเปลี่ยนความร้อน 2 เครื่อง แทนที่หน่วยให้ความร้อนของน้ำและหน่วยให้ความร้อนของอากาศที่ป้อนเข้าสู่กระบวนการ

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ลายมือชื่อนิสิต ....
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TRIRAT UDOMCHOKE: SIMULATION OF SORPTION ENHANCED CHEMICAL-LOOPING PROCESS FOR HYDROGEN PRODUCTION FROM BIOMASS. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: SUWIMOL WONGSAKULPHASATCH, Ph.D., 146 pp.

This research focuses on improvement of sorption enhanced chemical-looping process for hydrogen production from biomass via theoretical method. Corn stover was applied as a raw material. Pyrolysis process was applied for the conversion of biomass to bio-oil before feeding to reforming process. Sorption enhanced chemical-looping is of interest in this work to investigate and develop its potential for hydrogen production. In this work, we firstly compared hydrogen production efficiency of four different reforming processes in terms of bio-oil conversion, hydrogen yield, hydrogen purity, and energy consumption. The simulation results show that sorption enhanced and sorption enhanced chemical-looping reforming processes are the optimal processes for hydrogen production, which can provide 100% bio-oil conversion, 169 g hydrogen/kg corn stover of hydrogen yield, 97% of hydrogen purity and 11.8 kW of energy consumption at reforming temperature of 550 Celsius degree, pressure of 1 bar, steam equivalence ratio (SER) of 5, NiO equivalence ratio (NER) of 0.1, and CaO equivalence ratio (CER) of 2. Furthermore, improvement of SE-CLR process was also studied with the goal to minimize amount of preheating and cooling units and reduce loss of heat from reactor by adiabatic operation. The results show that heat integration in modified SE-CLR process can provide 77.4 g hydrogen/kg corn stover of hydrogen yield, 77% of hydrogen purity and 5.64 kW of energy consumption. Moreover, preheating units used in the process were reduced from 8 to 3 and using 2 heat exchangers instead of feed water preheater and feed air preheater.

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CHAPTER 1

INTRODUCTION

1.1 Rationale

At present, energy from fossil sources, which have been widely used, tends to be insufficient to meet the future demand. Moreover, such petroleum sources leads to many pollutants as it releases greenhouse gases or acidification gases such as carbon dioxide (CO_2), carbon monoxide (CO), sulfur oxide (SO_x), etc. According to this concern, an alternative source, hydrogen, has been emerged as an attractive interest because it can be used as energy source and it does not cause pollutant. Autothermal processes of hydrogen production are mostly based on steam reforming reaction, partial oxidation reaction and water-gas shift reaction with pressure swing adsorption (PSA) to achieve more than 99.9% of hydrogen purity. However, there are many limitations for these processes, such as high cost of PSA system, high energy consumption in steam reforming reaction, or cost of oxygen separation from the air for use as reactant in the partial oxidation reaction. From these reasons, improvement of hydrogen production is essential in order to lower cost and enhance efficiency. One of interesting technologies is sorption enhanced chemical-looping method, which is the combination of sorption enhanced hydrogen production method and chemical-looping method. Sorption enhanced method for hydrogen production can be accomplished by addition of carbon dioxide adsorption in reforming unit. By applying this technique, higher purity of hydrogen as well as larger hydrogen yield can be obtained without the need of additional separation unit. The adsorbents used in this method are, for example, calcium carbonate ($CaCO_3$), hydrotalcite (HTC) and dolomite ($CaCO_3$ x $MgCO_3$). Chemical-looping method is the use of metal oxide instead of oxygen gas in the partial oxidation reaction. Reaction of metal oxide and fuel occurs in the first reactor, where metal oxide is converted to metal. After that, the metal and the air are fed to the second reactor and the metal is converted back to the metal oxide before feeding back to the first reactor for reuse. Based on this technology, an expensive oxygen purification unit is not required. The advantages of sorption enhanced chemical-looping method for hydrogen production are larger hydrogen yield without additional separation unit as well as oxygen purification unit and reusable adsorbent and metal oxide.

In this research, we are interested in investigating the use of sorption enhanced chemical-looping for hydrogen production via theoretical approach. Biomass was selected as raw materials because it is one of the interesting renewable resources which can be applied substitute for fossil fuel. Hydrogen production from sorption enhanced chemical-looping process models together with optimal operating conditions are subjects to be investigated for the goal to maximize the hydrogen yield and fuel conversion as well as minimize the energy consumption.

1.2 Objectives

1) To model sorption enhanced chemical-looping process for the production of hydrogen from biomass.
2) To determine optimal conditions for the production of hydrogen production from biomass via sorption enhanced chemical-looping process.

1.3 Scope of work

1) Aspen Plus program will be used to theoretically examined viability of hydrogen production process from biomass via sorption enhanced chemical-looping process, which will be considered from pyrolysis to sorption enhanced chemical-looping process.
2) Corn stover is selected as biomass material, which has to be converted by pyrolysis process to bio-oil before feeding to sorption enhanced chemical-looping process for hydrogen production.
3) CaO is used as adsorbent and NiO is used as oxidizing agent for hydrogen production by sorption enhanced chemical-looping process.
4) The effects of temperature, pressure, steam equivalence ratio, oxygen equivalence ratio, NiO equivalence ratio and CaO equivalence ratio on process performances will be determined in terms of conversion of bio-oil, hydrogen yield, hydrogen purity, energy consumption and amount of preheating units and cooling units used in the process.
5) Performances of the proposed sorption enhanced chemical-looping will be compared with autothermal reforming, chemical looping reforming and sorption enhanced process.

1.4 Expected Outputs

Propose a suitable process for hydrogen production from biomass.

CHAPTER 2

THEORIES

2.1 Biomass

Biomass is organic substance originated from living or newly living organisms, which are animal and vegetable derived materials. Carbon, hydrogen, and oxygen are typical organic molecules found in biomass whereas nitrogen and other atoms, such as alkali, alkaline earth and heavy metals are found in small quantities [1].

Biomass material is divided into 5 basic categories [1]:

1) Virgin wood from forestry, arboricultural activities, or from wood processing.
2) Energy crops: high yield crops grown specifically for energy applications.
3) Agricultural residues: residues from agriculture harvesting or processing.
4) Food waste from food and drink manufacture, preparation and processing, and post-consumer waste.
5) Industrial waste and co-products from manufacturing and industrial processes.

2.1.1 Conversion technologies

Characteristics and properties of different types of biomass and their sub-groups are widely diverse. Therefore, the conversion technologies to make optimal use of biomass are also various, which include thermal and chemical conversion technologies.

Thermal conversion

Thermal conversion is the process in which heat is used to convert biomass into other chemicals. The thermal conversion of biomass is divided into 3 processes:

1) Combustion

Combustion is an exothermic reaction with heat and light generation. When biomass is used as fuel, oxidation reaction occurs by reaction between carbon, hydrogen, oxygen, sulfur and nitrogen in the biomass and oxygen. Combustion process occurs by gas phase reaction, surface reaction, or both and following by fusion, evaporation and pyrolysis [2].

When fuel material of biomass is flamed up, oxidation reaction of carbon (C), hydrogen (H) and oxygen (O) in cellulose, hemicellulose, lignin, and other molecules form carbon dioxide (CO_2) and water (H_2O). The molecules within biomass contain atoms in different quantities and some of these can also be oxidized. Oxide is released as gas in the flue gases, or as solid as ash or slag [1].

Combustion of biomass is the simplest way to obtain energy and is used widely because the technology of fossil fuels can be applied with combustion. Advantages of biomass combustion are low NO_x, SO_x, HCl and dioxin formation and excellent flammability. Heat from combustion is used for power generation and heat production by recovering heat through steam and hot water using boiler and heat exchanger [2].

2) Gasification

Gasification is the process of biomass solid conversion to fuel gas or syngas [2]. In the other words, it is a partial oxidation process by conversion of a carbon source such as coal, natural gas or biomass, into carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) and possibly hydrocarbon molecules such as methane (CH_4) [1].

Fundamental gasification processes are as follows [2]:

a) Evaporation of surface moisture
b) Evaporation of inherent moisture
c) Volatilization
d) Volatilization and gasification reaction
e) Char gasification

Gasification technology can be used for [1]:

- Heating water in central heating, district heating or process heating applications.
- Steam for electricity generation or motive force.
- As part of systems producing electricity or motive force.
- Transport using an internal combustion engine.

If the gasification occurs at low temperature, such as 700-1000°C, the product gas will have a relatively high level of hydrocarbons compared to high temperature gasification. Thus, it may be used to be burned for heat or electricity generation via a steam turbine or used to be suitable gas cleanup for an internal combustion engine for electricity generation. However, the combustion chamber for a simple boiler may be close coupled with the gasifier, which the producer gas may be cleaned of longer chain hydrocarbons (tars), transported, stored and burned remotely [1].

Higher temperature gasification (1200-1600°C) leads to few hydrocarbons in the product gas, and a higher proportion of CO and H_2, which is known as synthesis gas (syngas or bio-syngas) as it can be used to synthesize longer chain hydrocarbons using techniques such as Fischer-Tropsch (FT) synthesis. If the ratio of H_2 to CO is correct (2:1), Fischer-Tropsch synthesis can be used to convert syngas into high quality synthetic diesel biofuel which is completely compatible with autothermal fossil diesel and diesel engines [1].

3) Pyrolysis

Pyrolysis is the precursor to gasification, and occurs as part of both gasification and combustion. It consists of thermal decomposition in the absence of oxygen. It is essentially based on a long established process, being the basis of charcoal burning [1].

Pyrolysis can be simply explained by Eq. 2.1 [2]

$$\underset{\text{Biomass}}{(C_6H_{12}O_6)_m} \xrightarrow{\text{Heat (500-600 }^{\circ}\text{C)}} \underset{\text{Gas}}{(H_2+CO+CH_4+\ldots+C_5H_{12})}\uparrow +\underset{\text{Liquid}}{(H_2O+\ldots+CH_3OH+CH_3COOH+\ldots)} + \underset{\text{Char}}{C} \quad \ldots(2.1)$$

During pyrolysis, the moisture evaporates at 100-110 $^{\circ}$C first, and hemicellulose is decomposed at 200-260 $^{\circ}$C, follow by the decomposition of cellulose at 240-340 °C and lignin at 280-350 °C. Finally, the pyrolysis is terminated at 500 °C. Higher heating rate results in higher vapor production rate, higher pressure and lower residence time [2].

Applications of pyrolysis include [1]:

- Biomass energy densification for transport or storage
- Co-firing for heat or power
- Feedstock for gasification

The products of pyrolysis include gas, liquid, and a sold char, with the proportions of each depending upon parameters of the process. Lower temperatures (around 400°C) tend to produce more solid char (slow pyrolysis), whereas somewhat higher temperatures (around 500°C) produce a much higher proportion of liquid (bio-oil), provided the vapor residence time is kept down to around 1second or less. After this, secondary reactions take place and increase the gas yield [1].

Chemical conversion

1) Biochemical conversion

Since biomass is material from nature, many biochemical processes have been developed to break down the molecules of biomass. Biochemical conversion is process which uses enzymes of bacteria and other micro-organisms to decompose the biomass. The biochemical conversion processes are [1]:

- Anaerobic digestion
- Fermentation
- Composting

2) Other chemical processes

Converting straight and waste vegetable oils into biodiesel [1]:

- Trans-esterification

2.1.2 Hydrogen production from biomass

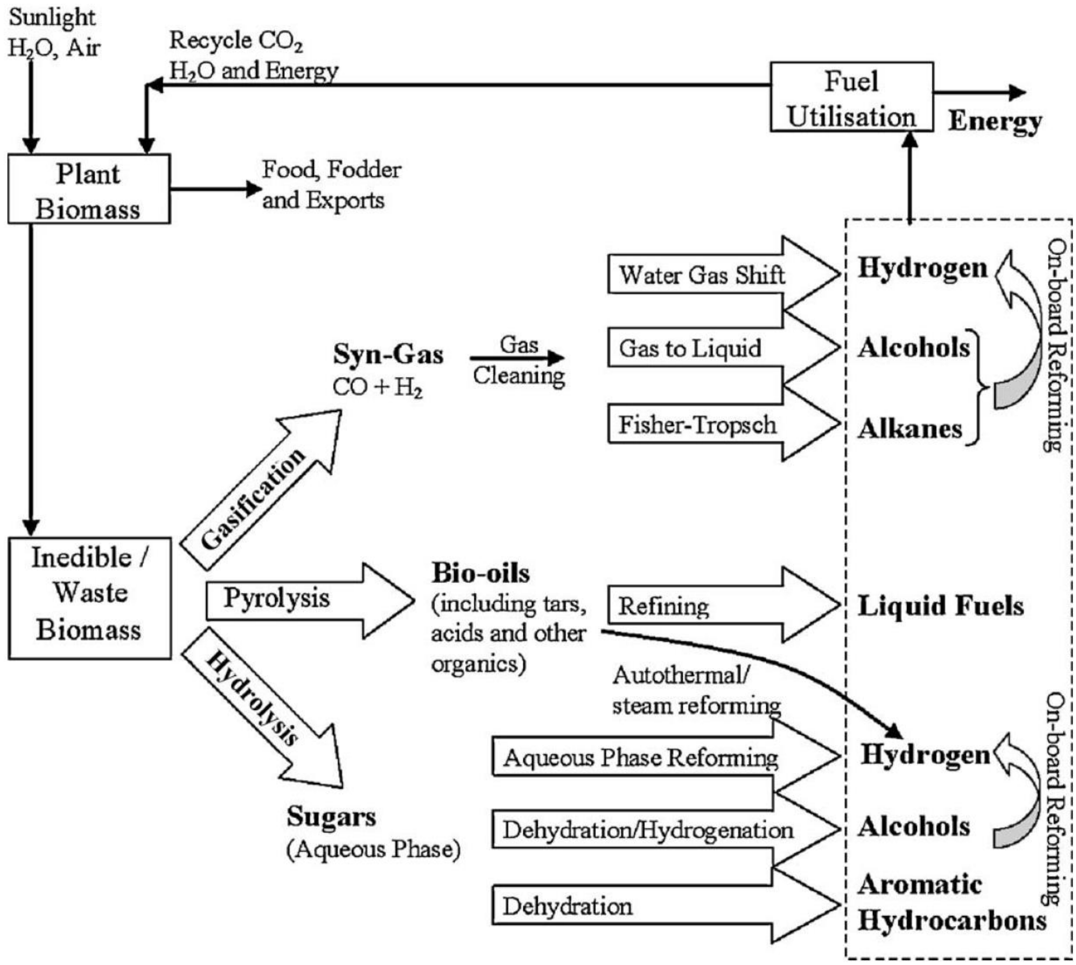


Figure 2.1: Hydrogen and liquid fuels production from biomass sources. The waste CO_2, H_2O, and energy produced from these fuels can be utilized to produce further biomass [3].

Figure 2.1 shows different ways to produce hydrogen and liquid fuels from biomass. Syn-gas can be produced by gasification and is used to produce hydrogen, alcohols and alkanes by water-gas shift (WGS), gas to liquid and Fisher-Tropsch, respectively. Bio-oils can be generated by pyrolysis and is used to produce liquid fuels by refining and to produce hydrogen by autothermal or steam reforming process with high conversion efficiency. Sugar-monomers can be produced by hydrolysis of cellulose and is used to produce hydrogen, alcohols and aromatic hydrocarbons by aqueous phase reforming, dehydration or hydrogenation and dehydration respectively [3].

2.2 Autothermal reforming process (ATR)

The principle of autothermal process for hydrogen production is conversion of many types of fuels to hydrogen gas by chemical reaction. The fuels used as raw material are divided into 2 groups, light hydrocarbons such as refinery gas, natural gas, LPG, naphtha and heavy hydrocarbon such as fuel oil, asphalt, tar, and coal [4]. There are four chemical reactions applied to convert fuels to hydrogen gas: steam reforming (SR), partial oxidation (POX), autothermal reforming (ATR), and water-gas shift reaction (WGS). The first three reactions are chemical reactions which produce carbon monoxide as a by-product. Water-gas shift reaction (WGS) is used to convert carbon monoxide to hydrogen gas. Steam reforming reaction (SR) is the most commonly used for autothermal process. The equation of this reaction is shown by Eq. 2.2

$$\text{Hydrocarbon} + aH_2O(g) \longrightarrow bCO/bCO_2 + cH_2 \quad \text{Endothermic} \qquad ...(2.2)$$

Hydrogen production by steam reforming reaction is divided into 3 steps which are shown in Figure 2.2. The first step is feeding raw material and steam into the first reactor at 500-900 ^{o}C and 0.3-2.5 MPa. Nickel oxide (NiO) is mostly used as catalyst. For this process, it is essential to remove sulfur gas from reactant (Desulfurize) because the catalysts can be deactivated by sulfur. In the first reactor, reactant is converted into hydrogen, carbon dioxide, and carbon monoxide and flow out of reactor to condenser. The temperature is reduced to 360 °C by condenser and flow to the second reactor in the second step. In this step, water-gas shift reaction is occurred and more hydrogen is obtained. In the last step, hydrogen and by-product is fed to purification unit for separation of hydrogen and by-product, which final hydrogen gas of more than 95% purity can be obtained [5].

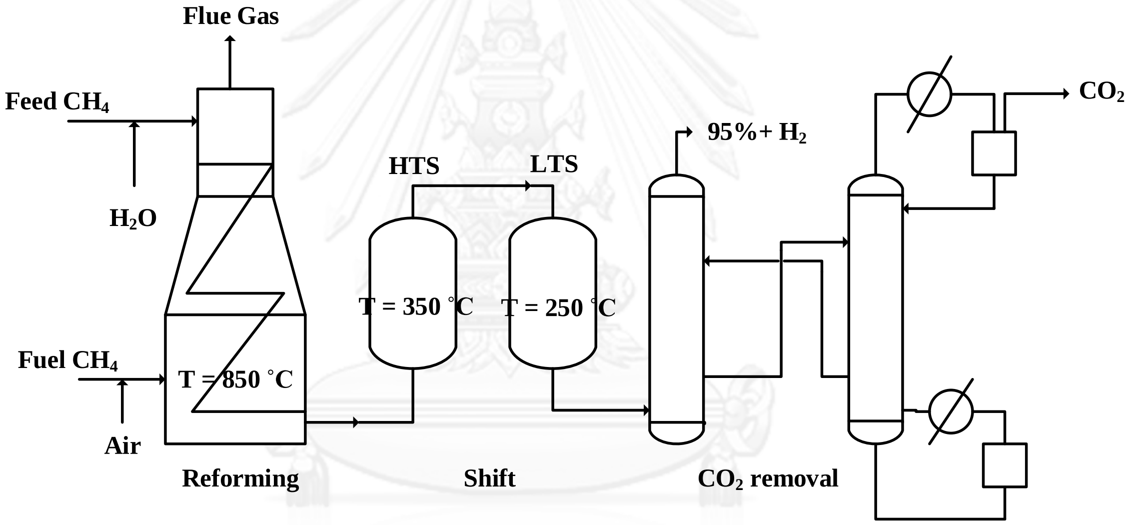


Figure 2.2: Autothermal steam methane reforming process for hydrogen production [6]

Partial oxidation reaction (POX) is the reaction which uses oxygen as oxidizing agent for convert hydrocarbon to hydrogen gas. It is shown by Eq. 2.3.

$$\text{Hydrocarbon} + aO_2(g) \rightleftharpoons bCO/bCO_2 + cH_2 \qquad \text{Exothermic} \qquad ...(2.3)$$

Autothermal reforming reaction (ATR) is the reaction which combines 2 reactions: steam reforming (SR) and partial oxidation (POX) reaction. Steam reforming and partial oxidation reaction occurs at the same time by feeding steam and oxygen to the same reactor. Heat from partial oxidation reaction will be transferred to reforming reaction, which results in reducing energy consumption by proper fraction of steam to reforming. Autothermal reforming reaction is shown by Eq. 2.4.

$$3CH_4 + H_2O(g) + O_2(g) \rightleftharpoons 3CO + 7H_2 \qquad \text{...(2.4)}$$

Water-gas shift reaction (WGS) is the reaction which is used for increasing amount of hydrogen from steam reforming, partial oxidation and autothermal reforming reaction. Carbon monoxide, a by-product of 3 reactions, is converted into hydrogen and carbon dioxide. This reaction is shown by Eq. 2.5.

$$CO + H_2O(g) \rightleftharpoons CO_2 + H_2 \qquad \Delta H^0_{298} = -41.2 \text{ kJ/mol} \qquad \text{...(2.5)}$$

Since this reaction is exothermic, hydrogen and carbon dioxide are well produced at low temperature. However, rate of reaction is low. Generally, the process of this reaction is divided into 2 steps: first step occurs at high temperature (350-370 $^{\circ}$C) with high reaction rate but conversion is limited at 90% due to reverse reaction shown by Eq. 2.6.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O(g) \qquad \Delta H^0_{298} = 41.2 \text{ kJ/mol} \qquad \text{...(2.6)}$$

For more conversion, temperature is reduced to 200-220 $^{\circ}$C and first-stage product is transferred to the second step. In this step, reaction takes place at low temperature but carbon monoxide and carbon dioxide can be converted to methane by methanation reaction as shown by Eq. 2.7 and 2.8.

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O(g) \qquad \Delta H^0_{298} = -206 \text{ kJ/mol} \qquad ...(2.7)$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O(g) \qquad \Delta H^0_{298} = -165 \text{ kJ/mol} \qquad ...(2.8)$$

From all of processes and reactions, autothermal processes for hydrogen production have many weak points that need to improve, such as

1) High pure oxygen used for partial oxidation reaction (POX), which need to separate oxygen from air and result in high energy consumption and high cost.
2) Side reaction and reverse reaction for water-gas shift reaction (WGS).
3) Cost and low productivity of pressure swing adsorption for increase hydrogen purity.
4) High energy consumption for steam reforming reaction.

As such, effective methods for hydrogen production have been developed. One of those is sorption enhanced chemical-looping method, which will be of interest and discussed in the next section.

2.3 Sorption enhanced process (SE)

Principle of sorption enhanced method for hydrogen production is using adsorbent for undesirable product adsorption, which is carbon dioxide in the most cases. Advantages of this method are reducing cost from pressure swing adsorption step, reducing reverse reaction, and increasing forward reaction for water-gas shift reaction. For these reasons, hydrogen productivity will be increased. Adsorbents used for this method should have following properties:

1) Good adsorption ability
2) Low price
3) Good stability for using in many cycles
4) Low interval between adsorption temperature and desorption temperature
5) High rate of adsorption in the operating temperature range

The reaction of calcium oxide to calcium carbonate by carbon dioxide adsorption is shown in Eq. 2.9.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H^{0}_{298} = -178 \text{ kJ/mol} \qquad \text{...(2.9)}$$

This reaction is used for carbon dioxide elimination and increasing amount and concentration of hydrogen from steam reforming, partial oxidation and water-gas shift reaction. Since this reaction is exothermic and is operated at low temperature, coke formation and sintering on catalyst decreased and cost of materials for wall construction of reactor is also reduced. Furthermore, heat from this reaction can be used in steam reforming reaction, which is endothermic. However, problems of this method are energy consumption for adsorbent regeneration and limitation of hydrogen purity lower than 99.99% at 500-650 $^{\circ}$C.

2.4 Chemical-looping reforming process (CLR)

The principle of chemical-looping method for hydrogen production is the use of metal oxide (Me_xO_y) as oxidizing agent instead of oxygen gas for partial oxidation reaction and autothermal reforming reaction, which reduces cost of oxygen separation from air. When metal oxide transfers oxygen atom to fuel for conversion to hydrogen, carbon dioxide and carbon monoxide in the reactor, it is reformed to metal (Me) and fed to another reactor with air for metal regeneration to metal oxide. After that, metal oxide is recycled to the old reactor. Flow diagram of this process can be shown in Figure 2.3.

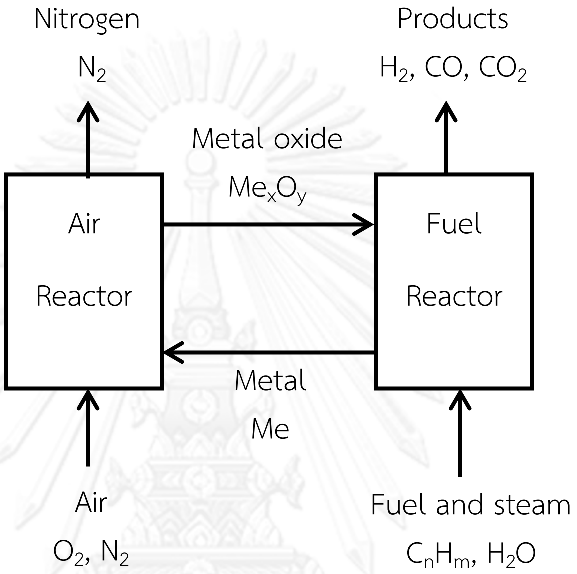


Figure 2.3: Chemical-looping for hydrogen production

The examples of main reactions for this method are shown by Eq. 2.10-2.13 (methane is used as fuel, nickel is used as metal and nickel oxide is used as metal oxide)

Fuel reactor: $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $\Delta H^0_{298} = 206$ kJ/mol ...(2.10)

$CH_4 + NiO \rightleftharpoons Ni + CO + 2H_2$ $\Delta H^0_{298} = 204$ kJ/mol ...(2.11)

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H^0_{298} = -41.1$ kJ/mol ...(2.12)

Air reactor: $Ni + 0.5O_2 \longrightarrow NiO$ $\Delta H^0_{298} = -240$ kJ/mol ...(2.13)

2.5 Sorption enhanced chemical-looping reforming process (SE-CLR)

Sorption enhanced chemical-looping method is combining of sorption enhanced method with chemical-looping method by 3 connected reactors, which are reforming reactor, calcination rector and air reactor. The principle of this method is using adsorbent and oxidizing agent in the reforming reactor for hydrogen production and carbon dioxide adsorption at the same time and using calcination reactor and air reactor for adsorbent and oxidizing agent regeneration. The 3 reactors are operated at the same time, which results in cost, step and energy reduction. Flow diagram of this process is shown in Figure 2.4.

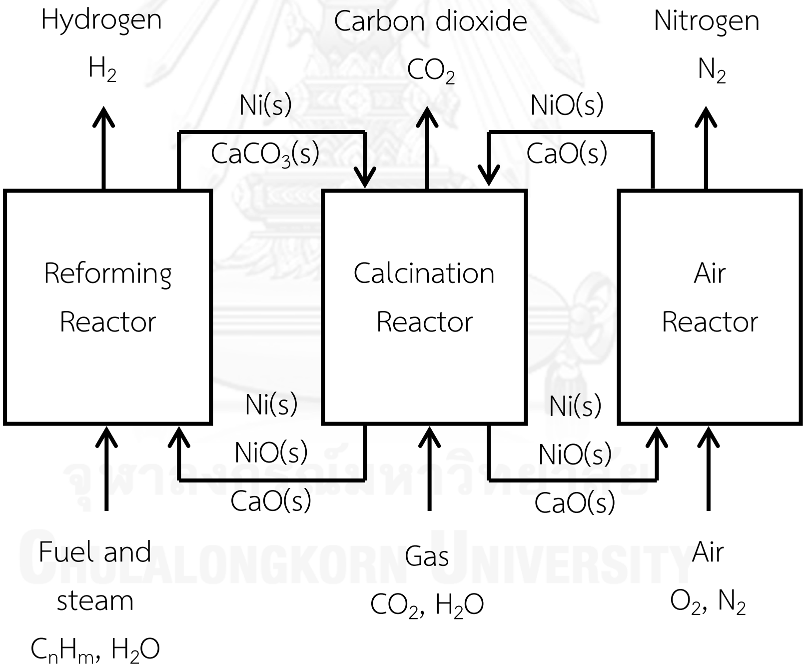


Figure 2.4: Sorption enhanced chemical-looping for hydrogen production

The example of main reaction for this method is shown in Eq. 2.14-2.19 (methane is used as fuel, nickel is used as metal and adsorbent is used as calcium oxide)

Reforming reactor: $CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H^{0}_{298} = 206\ kJ/mol$ ...(2.14)

$CH_4 + NiO \rightleftharpoons Ni + CO + 2H_2 \quad \Delta H^{0}_{298} = 204\ kJ/mol$ ...(2.15)

$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^{0}_{298} = -41.1\ kJ/mol$ ...(2.16)

$CaO + CO_2 \rightleftharpoons CaCO_3 \quad \Delta H^{0}_{298} = -177.8\ kJ/mol$ ...(2.17)

Calcination reactor: $CaCO_3 \rightleftharpoons CaO + CO_2 \quad \Delta H^{0}_{298} = 177.8\ kJ/mol$ ...(2.18)

Air reactor: $Ni + 0.5O_2 \rightleftharpoons NiO \quad \Delta H^{0}_{298} = -240\ kJ/mol$ ...(2.19)

Since exothermic reaction takes place in the air reactor, heat from this reactor can transfer to calcination reactor for endothermic reaction by nickel oxide and calcium oxide.

However, carbon formation can be performed in 4 above processes for low steam condition. Carbon solid generated in process comes from thermal cracking of fuel. Thermal cracking of CH_4 is shown in Eq. 2.20

$CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H^{0}_{298} = 74.8\ kJ/mol$ ...(2.20)

Deposited carbon can be eliminated by oxidation reaction of steam reforming of oxidation of O_2, NiO or CO_2 which are shown in Eq. 2.21-2.24

$C + H_2O \rightleftharpoons CO + H_2 \quad \Delta H^{0}_{298} = 131.3\ kJ/mol$ ...(2.21)

$C + O_2 \rightleftharpoons CO_2 \quad \Delta H^{0}_{298} = -393.5\ kJ/mol$ ...(2.22)

$C + 2NiO \rightleftharpoons CO_2 + 2Ni \quad \Delta H^{0}_{298} = 86.5\ kJ/mol$ ...(2.23)

$C + CO_2 \rightleftharpoons 2CO \quad \Delta H^{0}_{298} = 172.5\ kJ/mol$ ...(2.24)

CHAPTER 3

LITERATURE REVIEWS

Hydrogen production process has been studied by many researchers for long time. In this chapter, the literature reviews are divided into four main parts. Firstly, researches on hydrogen production by autothermal process are described. Secondly, the previous works on sorption enhanced method for hydrogen production are mentioned. Thirdly, the chemical-looping method for hydrogen production is reviewed. Lastly, the hydrogen production by sorption enhanced chemical-looping method is summarized.

3.1 Autothermal reforming process (ATR)

A raw material which has been mainly used for hydrogen production by steam reforming reaction is methane in natural gas. Researches using methane in this reaction is reported by Levent et al. [7] who used a microreactor and Go et al. [8] who used a fluidized bed reactor for this reaction. Moreover, other raw materials have been studied. Onozaki et al. [9] studied the hydrogen production by partial oxidation reaction and steam reforming reaction of tar from coke oven gas (COG) and found that carbon more than 98% in COG was converted to hydrogen and carbon monoxide. Furthermore, cost of production was lower and efficiency was higher than direct separation of hydrogen in COG. Hydrogen production from bio-ethanol was studied by Song et al. [10] using cobalt catalyst. They reported that 10 wt% of Co, 10:1:75 of H_2O: EtOH: inert and 5000 h^{-1} of gas hourly space velocity (GHSV) led to 100% of ethanol conversion and 5.5 mol H_2/mol EtOH of yield at 550 $^{\circ}C$ and atmospheric pressure. Advantages of this reaction are simple reaction, low cost, availability of various raw materials and high efficiency. However, there are many problems from this reaction such as high energy requirement (endothermic reaction), cost of sulfur elimination and cost of purification process.

Partial oxidation reaction (POX) can occur in 2 ways: with and without catalyst. Reaction with catalyst occurs at 700-1000 °C and 6-8 MPa and reaction without catalyst occurs at 1300-1500 °C and 3-8 MPa. Raw materials for this reaction are light hydrocarbons, heavy hydrocarbons and alcohol. Liguras et al. [11] investigated the hydrogen production by partial oxidation of ethanol with Ru catalyst. They found that the conversion of ethanol and selectivity of hydrogen were high. Likewise, 97% of selectivity for partial oxidation of ethanol with Pt catalyst at 97 °C was reported by Hsu et al. [12]. There are also examples of this reaction with light hydrocarbons. The research of Salazar-Villalpando and Reyes [13] and the study of Koh et al. [14] considered the hydrogen production by partial oxidation of methane. On the other hand, there are only some studies considering the use of heavy hydrocarbons. Wang et al. [15] investigated catalyst promoted by self-sustained electrochemical promotion (SSEP) for POX and SR of heavy hydrocarbons. The promoted catalyst could improve POX and SR. The partial oxidation reaction without using catalyst was studied by Marda et al. [16]. They found that conversion of bio-oil for hydrogen and carbon monoxide production was 85-95%. From the studies above, prominent points of POX are exothermic reaction and no catalyst regeneration. However, there is a weak point of this reaction, which is higher operating cost than reforming reaction, because it is essential to separate oxygen gas from air before feeding to process for high efficiency. Otherwise, purity of hydrogen is low because of the presence of nitrogen gas.

For the autothermal reforming reaction, there are many researchers studying the use of various raw materials and catalysts. Ayabe et al. [17] investigated ATR of methane and propane on metal catalysts and found that the activity of catalysts from high to low was Rh, Pd, Ni, Pt and Co respectively. Moreover, deactivation of catalysts could be occurred from oxidation reaction and carbon formation occurred from side reaction of 2 raw materials, which considerably occurred by propane but was contrary by methane and did not affect the reaction. Study on sequence of reaction was also reported, which partial oxidation of hydrocarbon occurred at entrance of reactor but steam reforming reaction occurred at surface of catalyst in the reactor. The thermodynamic analysis of this reaction was investigated by Semelsberger et al. [18]. They reported that when natural gas, methanol, ethanol, dimethylether and gasoline were used as raw materials for autothermal reforming reaction, high purity of hydrogen would be produced, which could be applied to fuel cell. For comparison, reaction temperature of oxygen-containing fuels (methanol ethanol and dimethylether) were lower than non-oxygenated fuels (natural gas and gasoline), which resulted in less carbon monoxide. Furthermore, the results showed that dimethylether had the greatest potential product content, followed by methanol, ethanol, gasoline, and natural gas. From researches above, distinctive points of this reaction are low cost due to the reduction of energy consumption and process steps, and can be used with various fuels such as alcohol, ether, natural gas and gasoline. On the contrary, there are weak points of this reaction, which are carbon formation from side reaction and deactivation of catalyst.

The studies on water-gas shift reaction (WGS) have been found with the studies of steam reforming and partial oxidation reaction. Kunkes et al. [19]

investigated hydrogen production from glycerol by steam reforming and water-gas shift reaction and reported yield of hydrogen equal to 80% and conversion of carbon of about 100%. Similarly, Chen et al. [20] studied partial oxidation and water-gas shift reaction of methane in the Swiss-roll reactor and maximum of hydrogen yield was 2.48 mol of hydrogen per mol of methane as well as 96% CH_4 conversion and 86% CO conversion were also obtained.

All of reactions above (SR, POX, ATR and WGS) can take place in the same reactor, and components of final product depend on catalyst. The catalysts generally used for autothermal reforming reaction are Ni/Al_2O_3 [17], $Cu/ZnO/Al_2O_3$ [21] and Rh/Al_2O_3 [17]. Other catalysts can be used for water-gas shift reaction such as Ru/ZrO_2-Pt/CeO_2 and Cu/ZnO-$FeCr_2O_3$. Kunkes et al. [19] studied on Pt catalyst for steam reforming reaction by adding Ru, Re and Os. They reported that it could improve the activity of catalyst and conversion of $Pt/CeO_2/ZrO_2$ catalyst for water-gas shift reaction was about 100%.

3.2 Sorption enhanced process (SE)

Various adsorbents used for hydrogen production are summarized in Table 3.1.

Table 3.1 Stoichiometric capacities and regeneration temperatures for various sorbents [6]

	Sorbent	Stoichiometric adsorption ability ($g\ CO_2/g$ sorbent)	Regeneration temperature (^{O}C)	Stoichiometric adsorption ability after 45 cycles
Natural sorbents	Calcium carbonate ($CaCO_3$)	0.79	900[a]	0.316
	Dolomyte ($CaCO_3 \times MgCO_3$)	0.46	900[a]	0.16
	Huntite ($CaCO_3 \times 3MgCO_3$)	0.25	900[a]	0.2
	Hydrotalcite, promoted K_2CO_3/hydrotalcite	0.029[b]	400[c]	stable
Synthetic sorbent	Lithium orthosilicate (Li_4SiO_4)	0.37	750[d]	Stable until 100 cycles
	Lithium zirconate (Li_2ZrO_3)	0.29	690[e]	Stable until 100 cycles
	Sodium zirconate (Na_2ZrO_3)	0.24	790[f]	Stable until 100 cycles

[a] Temperature corresponding to CO_2 equilibrium pressure of 1 bar Baker EH [22].

[b] 0.65 molCO_2/kg, from Ding and Alpay [23]

[c] Regeneration through pressure swing

[d] From Essaki and Kato [24]

[e] Experimental data from Yi and Eriksen (regeneration in nitrogen) [25]

[f] Experimental data from Lopez-Ortiz et al. (regeneration in air) [26]

Calcium carbonate ($CaCO_3$), dolomite ($CaCO_3$ x $MgCO_3$) and huntite ($CaCO_3$ x $3MgCO_3$) are available, low price, and have good adsorption ability but have low stability from sintering while regeneration by calcination. On the other hand, Anand et al. [27] reported that promoted K_2CO_3 on hydrotalcite (promoted K_2CO_3/HTC) can be used for over nearly 6000 cycles with stable performance but low adsorption capacity, which cannot be applied to industry. Abanades et al. [28] found that synthetic adsorbents can be used for a number of cycles, but they are high production cost and lower adsorption ability and lower rate of adsorption than calcium carbonate.

The reaction of calcium oxide to calcium carbonate by carbon dioxide adsorption is used for carbon dioxide elimination and increasing amount and concentration of hydrogen from steam reforming, partial oxidation and water-gas shift reaction. Since this reaction is exothermic and is operated at low temperature, coke formation and sintering on catalyst decreased and cost of materials for wall construction of reactor is reduced as well. Furthermore, heat from this reaction can be used in steam reforming reaction, which is endothermic. However, limitations of this method are energy consumption for adsorbent regeneration and limitation of hydrogen purity cannot higher than 99.99% at 500-650 $^{\circ}C$. Therefore, there are studies on improvement of this process. Andres et al. [29] investigated ultra-pure hydrogen production by steam reforming reaction and used calcium oxide as adsorbent with fluidized-bed membrane reformer on pilot scale. They reported that efficiency of carbon adsorption equal 87% and ultra-pure (99.99%) hydrogen could be produced at 550 $^{\circ}C$. Improvement of calcium oxide as adsorbent for sorption enhanced hydrogen production by adding $Ca_{12}Al_{14}O_{33}$ and nickel on calcium oxide was studied by Kim et al. [30]. They found that efficiency and conversion is high at 7% wt of Ni.

3.3 Chemical-looping reforming process (CLR)

Ryden et al. [31] studied continuous chemical-looping of natural gas with autothermal reforming reaction for hydrogen and carbon monoxide (syngas) production by 2 connected fluidized bed reactors and used $NiO/MgAl_2O_4$ as oxidizing agent. Complete conversion of natural gas and high selectivity of syngas were reported, but carbon formation occurred in some cases and was reduced by adding amount of steam in the process. Similarly, de Diego et al. [32, 33] investigated batch fluidized bed reactor and 2 connected fluidized bed reactors and found that types of supports resulted in reaction of metal oxide and preparation of metal oxide resulted in carbon formation in the process. Carbon formation from dry impregnation method is lower than deposition-precipitation method and conversion of methane is higher than 98% for 2 connected fluidized bed reactors and continuous process.

Other metals have been studied, for example, He et al. [34] used CeO_2 as oxidizing agent with iron, copper and manganese oxides by co-precipitation method and experimented on fixed bed reactor. They reported that adding transition metals (iron, copper, and manganese) could improve the reactivity and using iron with CeO_2 presented the optimal performance.

3.4 Sorption enhanced chemical-looping reforming process (SE-CLR)

This method is rarely studied because it is complicated to perform experiments with 3 reactors, which is hard to control conditions (e.g. temperature, pressure, flow, etc.) of the reactor. However, study on simulation of this method has been conducted. Pimenidou et al. [35] investigated high-pure hydrogen production by sorption enhanced chemical-looping of waste cooking oil in packed bed reactor. Nickel was used as catalyst and dolomite is used as carbon dioxide adsorbent. They reported that high purity of hydrogen (>95%) was produced at 600 ^{o}C and atmospheric pressure. However, it was found that purity of hydrogen decreased in the following cycles of using adsorbent. Rydén and Ramos [36] studied simulation of sorption enhanced chemical-looping of methane and used calcium oxide as adsorbent in fluidized bed reactor and found that hydrogen with purity of more than 98 vol.% could be produced at 600-750 ^{o}C at atmospheric pressure and more than 95% of carbon dioxide was captured. However, conversion of methane decreased when pressure in the system was increased.

3.5 Hydrogen production from biomass

Studies on hydrogen production from biomass have been carried out by many researchers. Ni et.al [37] presented an overview of hydrogen production from biomass. They reported that hydrogen production from biomass was abundant, clean and renewable. Moreover, thermochemical processes (pyrolysis and gasification) and biological processes (biophotolysis, water–gas shift reaction and fermentation) could be used to produce hydrogen. Many types of biomass were used as raw materials for hydrogen production, such as corn stover [38], waste wood [39], tar [40] and pyrolysis oil [41]. Studies on simulation of this process were reported. Shen et.al [42] investigated simulation of hydrogen production from biomass gasification in interconnected fluidized beds by Aspen Plus program and found that the favorable temperature of the gasifier should be between 750 and 800 ^{o}C, the combustor temperature should be 920 ^{o}C, and the ratio of the steam/biomass should be between 0.6 and 0.7. The steam/biomass ratio corresponding to maximal hydrogen yield declines with the increase of gasifier temperature. Ramzan et.al [43] simulated hybrid biomass gasification by using Aspen plus program and reported that temperature increases the production of CO and H_2, but increasing equivalence ratio decreases the production of CO and H_2 which decreases the cold gas efficiency. Moreover, biomass moisture content is an important parameter affecting the heating value of the gas. Similarly, experimental studies have been also reported. Sheth and Babu [39] investigated the production of hydrogen energy through waste wood gasification and found that the waste wood can be successfully converted to generate the combustible gas and the molar fraction of N_2 and CO_2 decrease with an increase in equivalent ratio. Lea-Langton et.al [41] studied pyrolysis oils for hydrogen production using chemical-looping reforming and found that maximum averaged fuel conversions of about 97% for pine oil and 89% for empty fruit bunches (EFB) oil were achieved at S/C ratios of 2.3 and 2.6, respectively, and produced H_2 with a yield efficiency of approximately 60% for pine oil and 80% for EFB oil.

CHAPTER 4

SIMULATION

In this chapter, simulation model of sorption enhanced chemical-looping for hydrogen production from corn stover is provided. Four processes for hydrogen production, including autothermal reforming (ATR), chemical-looping reforming (CLR), sorption enhanced reforming (SE) and sorption enhanced chemical-looping reforming (SE-CLR), were investigated first through computer modeling then an improvement of sorption enhanced chemical-looping reforming process were focused with the goal to minimize energy consumption.

4.1 Simulation of the 4 methods for hydrogen production by Aspen Plus program

The production of hydrogen from corn stover via typical chemical-looping reforming (CLR), sorption enhanced reforming (SE) and sorption enhanced chemical-looping reforming (SE-CLR) process with the use of NiO applied as oxidizing agent and CaO applied as CO_2 adsorbent were simulated by Aspen Plus Program. SOLIDS model modified in vapour phase by ESSRK was applied as property method for all processes because of the presence of solids in the process whereas SRK model was applied for autothermal reforming (ATR) process because of absence of solids in the process. Pyrolysis reactor, which is used to convert corn stover to bio-oil, was simulated by RYIELD unit. Reformer, calcination reactor, and air reactor were simulated by RGIBBS unit.

Main reactions occurring in the hydrogen production process is shown in Eq. 4.1-4.22 [41, 44-46]:

Pyrolysis:

Corn stover $\rightleftharpoons H_2 + CO + CO_2 + H_2O(g) + C_nH_mO_k + C_xH_y + C$ (char) ...(4.1)

$\Delta H_r^{298} > 0$

Reformer:

Steam reforming of bio-oil and hydrocarbon compounds

$C_nH_mO_k + (n - k)H_2O \rightleftharpoons nCO + (n + m/2 - k)H_2$ $\Delta H_r^{298} > 0$ ...(4.2)

$C_xH_y + xH_2O \rightleftharpoons xCO + (y + 2x)H_2$ $\Delta H_r^{298} > 0$ ...(4.3)

Oxidation of bio-oil and hydrocarbon compounds

$C_nH_mO_k + 0.5(2n + m/2 - k)O_2 \rightleftharpoons nCO_2 + (m/2)H_2O$ $\Delta H_r^{298} < 0$ ...(4.4)

$C_nH_mO_k + (2n + m/2 - k)NiO \rightleftharpoons (2n + m/2 - k)Ni + nCO_2 + (m/2)H_2O$ ...(4.5)

$\Delta H_r^{298} > 0$

$C_xH_y + 0.5(2x + y/2)O_2 \rightleftharpoons xCO_2 + (y/2)H_2O$ $\Delta H_r^{298} < 0$ ...(4.6)

$C_xH_y + (2x + y/2)NiO \rightleftharpoons (2x + y/2)Ni + xCO_2 + (y/2)H_2O$ $\Delta H_r^{298} > 0$ ...(4.7)

Oxidation of hydrogen

$H_2 + 0.5O_2 \rightleftharpoons H_2O$ $\Delta H_r^{298} = -241.8$ kJ/mol ...(4.8)

$H_2 + NiO \rightleftharpoons Ni + H_2O$ $\Delta H_r^{298} = -1.83$ kJ/mol ...(4.9)

Oxidation of carbon-monoxide

$$CO + 0.5O_2 \rightleftharpoons CO_2 \qquad \Delta H_r^{298} = -283 \text{ kJ/mol} \qquad ...(4.10)$$

$$CO + NiO \rightleftharpoons Ni + CO_2 \qquad \Delta H_r^{298} = -42.98 \text{ kJ/mol} \qquad ...(4.11)$$

Water-gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_r^{298} = -41.15 \text{ kJ/mol} \qquad ...(4.12)$$

Thermal cracking of hydrocarbon compounds

$$C_xH_y \rightleftharpoons C_{x-a}H_{y-b} + H_2 + CH_4 + C\ (s) \qquad \Delta H_r^{298} > 0 \qquad ...(4.13)$$

Water gas

$$C + H_2O \rightleftharpoons CO + H_2 \qquad \Delta H_r^{298} = 131.3 \text{ kJ/mol} \qquad ...(4.14)$$

Oxidation of carbon

$$C + O_2 \rightleftharpoons CO_2 \qquad \Delta H_r^{298} = -393.5 \text{ kJ/mol} \qquad ...(4.15)$$

$$C + 2NiO \rightleftharpoons CO_2 + 2Ni \qquad \Delta H_r^{298} = 86.5 \text{ kJ/mol} \qquad ...(4.16)$$

Boudouard

$$C + CO_2 \rightleftharpoons 2CO \qquad \Delta H^0_{298} = 172.5 \text{ kJ/mol} \qquad ...(4.17)$$

Methanation

$$C + 2H_2 \rightleftharpoons CH_4 \qquad \Delta H^0_{298} = -74.9 \text{ kJ/mol} \qquad ...(4.18)$$

$$CO + H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^0_{298} = -206.2 \text{ kJ/mol} \qquad ...(4.19)$$

Carbonation

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \Delta H_r^{298} = -177.8 \text{ kJ/mol} \qquad ...(4.20)$$

Calcination reactor:

Calcination

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad \Delta H_r^{298} = 177.8 \text{ kJ/mol} \qquad ...(4.21)$$

Air reactor:

Oxidation of nickel

$$Ni + 0.5O_2 \rightleftharpoons NiO \qquad \Delta H_r^{298} = -240 \text{ kJ/mol} \qquad ...(4.22)$$

For simulation by Aspen Plus program, ultimate and proximate analysis data is required. The ultimate values and proximate values of corn stover are shown in Table 4.1.

Table 4.1: Corn stover Ultimate and Proximate Analysis [44]

Ultimate Analysis (dry basis)	
Element	**Value (wt %)**
Ash	6
Carbon	47.28
Hydrogen	5.06
Nitrogen	0.8
Chlorine	0
Sulfur	0.22
Oxygen	40.63
Proximate Analysis (wet basis)	
Element	**Value (wt %)**
Moisture	25.0
Fixed Content	17.7
Volatile Matter	52.8
Ash	4.5

As mentioned earlier, biomass has to be converted into bio-oil before feeding into reformer. In this work, corn stover was converted into bio-oil by pyrolysis using RYIELD model. Approximated product compositions from corn stover pyrolysis are shown in Table 4.2.

Table 4.2: Pyrolysis product composition [44]

Gas Compounds	**Composition (kg/100 kg of dry corn stover)**
Carbon Dioxide	5.42
Carbon Monoxide	6.56
Methane	0.035
Ethane	0.142
Hydrogen	0.588[a]
Propane	0.152
Ammonia	0.0121
Bio-oil Compounds	
Acetic Acid	5.93
Propionic Acid	7.31
Methoxyphenol	0.61
Ethylphenol	3.80
Formic Acid	3.41
Propyl-Benzoate	16.36
Phenol	0.46
Toluene	2.27
Furfural	18.98
Benzene	0.77
Other Compounds	
Water	10.80
Char/Ash	16.39

[a] Corrected to 0.02 kg/kg of corn stover based on engineering judgment.

The processes of hydrogen production from corn stover were divided into 2 sections; pyrolysis section and hydrogen production section, of which the latter could be classified into 4 models in this work; autothermal reforming (ATR), chemical-looping reforming (CLR), sorption enhanced reforming (SE) and sorption enhanced chemical-looping reforming (SE-CLR). Process flow diagrams of those four processes are shown in Figure 4.1-4.4 and the description of streams and units for each process is presented by Table 4.3-4.10.

4.1.1 Autothermal reforming process (ATR)

1) Process flow diagram

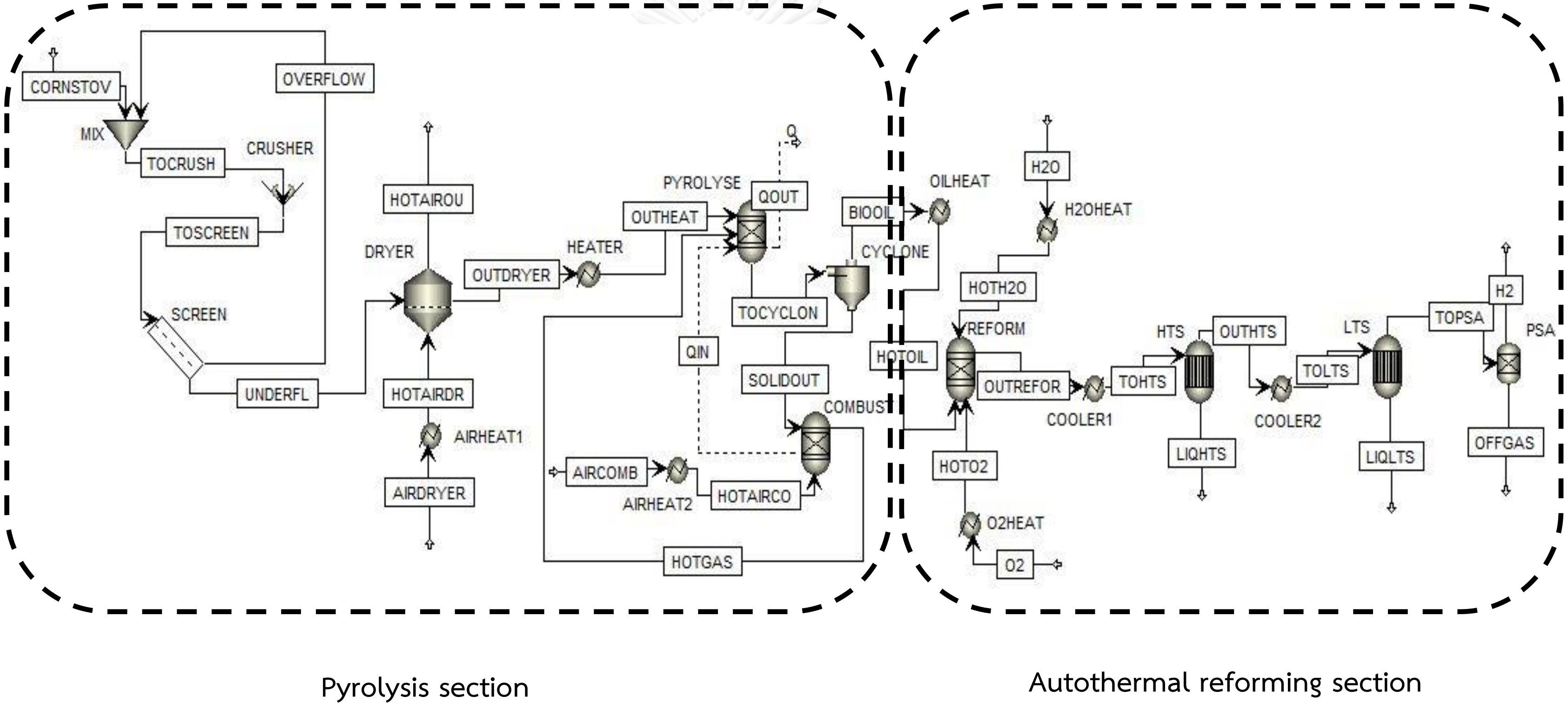


Figure 4.1: Process flow diagram of autothermal reforming (ATR) for hydrogen production from corn stover

2) Description

Table 4.3: Description of streams in Aspen Plus flowsheet presented in Figure 4.1

Stream's name	From	To	Description
			Pyrolysis section
AIRCOMB		AIRHEAT2	Air fed to heater for temperature adjustment before combustion reaction
AIRDRYER		AIRHEAT1	Air fed to heater for temperature adjustment before corn stover drying
BIOOIL	CYCLONE	OILHEAT	Bio-oil fed to reformer for hydrogen production
CORNSTOV		MIX	Corn stover fed into process
HOTAIRCO	AIRHEAT2	COMBUST	Hot air fed for combustion reaction
HOTAIRDR	AIRHEAT1	DRYER	Hot air fed for corn stover drying
HOTAIROU	DRYER		Wet air out from dryer
HOTGAS	COMBUST	PYROLYSE	Hot gas from combustion fed to pyrolysis reactor for heat supply
SOLIDOUT	CYCLONE	COMBUST	Ash and char after pyrolysis
TOCRUSH	MIX	CRUSHER	Corn stover before crushing and grinding
TOCYCLON	PYROLYSE	CYCLONE	Products from pyrolysis reactor which composes of bio-oil, ash and char
TOSCREEN	CRUSHER	SCREEN	Corn stover after crushing and grinding
OUTHEAT	HEATER	PYROLYSE	Corn stover after temperature adjustment for pyrolysis
OUTDRYER	DRYER	HEATER	Dried corn stover out from dryer to heater for temperature adjustment

Stream's name	From	To	Description
			Pyrolysis section (cont.)
OVERFLOW	SCREEN	MIX	Corn stover with more than 3 mm of particle size
QIN	COMBUST	PYROLYSE	Heat from combustor transferred to pyrolyser
QOUT	PYROLYSE		Heat from pyrolyser out of process
UNDERFL	SCREEN	DRYER	Corn stover with less than 3 mm of particle size
			Autothermal reforming section
H2	PSA		H_2 separated from gas products by pressure swing adsorption
H2O		H2OHEAT	Water fed to heater for convert to steam before feed to reformer
HOTH2O	H2OHEAT	REFORM	Hot steam fed to reformer for hydrogen production
HOTO2	O2HEAT	REFORM	Hot oxygen gas fed to reformer for hydrogen production
HOTOIL	CYCLONE	REFORM	Hot bio-oil fed to reformer for hydrogen production
LIQHTS	HTS		Liquid product out from high-temperature-shift reactor
LIQLTS	LTS		Liquid product out from low-temperature-shift reactor
O2		O2HEAT	Oxygen gas fed to heater for temperature adjustment before feed to reformer
OFFGAS	PSA		Contaminant gas separated from gas products by pressure swing adsorption
OUTHTS	HTS	COOLER2	Gas products out of high-temperature-shift reactor
OUTREFOR	REFORM	COOLER1	Products from reformer after bio-oil conversion by autothermal reforming
TOHTS	COOLER1	HTS	Gas products from reformer after cooling

Stream's name	From	To	Description
			Autothermal reforming section (cont.)
TOLTS	COOLER2	LTS	Gas products from high-temperature-shift reactor after cooling
TOPSA	LTS	PSA	Gas products fed to pressure swing adsorber for hydrogen separation

Table 4.4: Description of units in Aspen Plus flowsheet presented in Figure 4.1

Model	Name	Description
		Pyrolysis section
CRUSHER	CRUSHER	Crushes and grinds corn stover to small particles
CYCLONE	CYCLONE	Separates bio-oil and some unreacted carbon from pyrolysis (ash and char)
DRYER	DRYER	Dries corn stover
HEATER	AIRHEAT1	Heats air before feed to dryer
	AIRHEAT2	Heats air before feed to combustor
	HEATER	Heats corn stover to pyrolysis temperature
MIXER	MIX	Mixes fresh corn stover with more than 3 mm of particle size of corn stover
RGIBBS	COMBUST	Simulates combustion reaction of carbon
RYIELD	PYROLYSE	Converts corn stover to bio-oil

Model	Name	Description
		Autothermal reforming section
SCREEN	SCREEN	Screens particle with less than 3 mm size of corn stover
HEATER	COOLER1	Cools gas products from reformer
	COOLER2	Cools gas products from high-temperature-shift reactor
	H2OHEAT	Converts water to steam at reformer temperature before autothermal reforming
	O2HEAT	Heats oxygen gas at reformer temperature before autothermal reforming
	OILHEAT	Heats bio-oil at reformer temperature before autothermal reforming
REQUIL	HTS	Simulates water-gas shift reaction at high temperature (350 $^{\circ}$C)
	LTS	Simulates water-gas shift reaction at low temperature (250 $^{\circ}$C)
RGIBBS	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil
SEP	PSA	Separates hydrogen from other gas products

3) Explanation

For pyrolysis section, 3 kg/hr of corn stover was firstly fed into a mixer for combination with the overflow stream from the screen and was fed into crusher for grinding and fed to screen for screening the particle with less than 3 mm in diameter. After that, it was fed to dryer for drying and adjusted temperature to 480 °C before performing reaction in pyrolysis reactor (PYROLYSE). The products of pyrolysis reactor were fed to cyclone for solid separation. Ash and char were separated off and were fed into the combustion reactor (COMBUST) which combusted at 500 °C and were transferred heat to pyrolysis reactor. Bio-oil (BIOOIL) as vapor products from the cyclone was transferred to the sorption enhanced chemical-looping section. This section consists of 3 cyclones and 3 fluidized-bed reactors; reformer (REFORM), calcination reactor (CALCINE) and air reactor (AIRREACT). However, some CO, CO_2, H_2O, CH_4 and H_2 from pyrolysis process were also fed to this section.

For ATR process, bio-oil (BIOOIL), steam (H2O) and oxygen gas (O2) are fed to reformer (REFORM) for steam reforming and partial oxidation reaction at 400-1000°C. Products from reformer, CO, CO_2, H_2 and H_2O, are fed to high temperature shift reactor (HTS) at 350 °C and low temperature shift reactor (LTS) at 250 °C for water gas shift reaction. RGibbs model was used as reforming reactor (REFORM) and REquil model was used for both HTS and LTS. After that, H_2 and CO_2 in vapor product stream (TOPSA) were separated by pressure swing adsorption (PSA), which the model SEP was applied for this case to produce high purity hydrogen.

4.1.2 Chemical-looping reforming process (CLR)

1) Process flow diagram

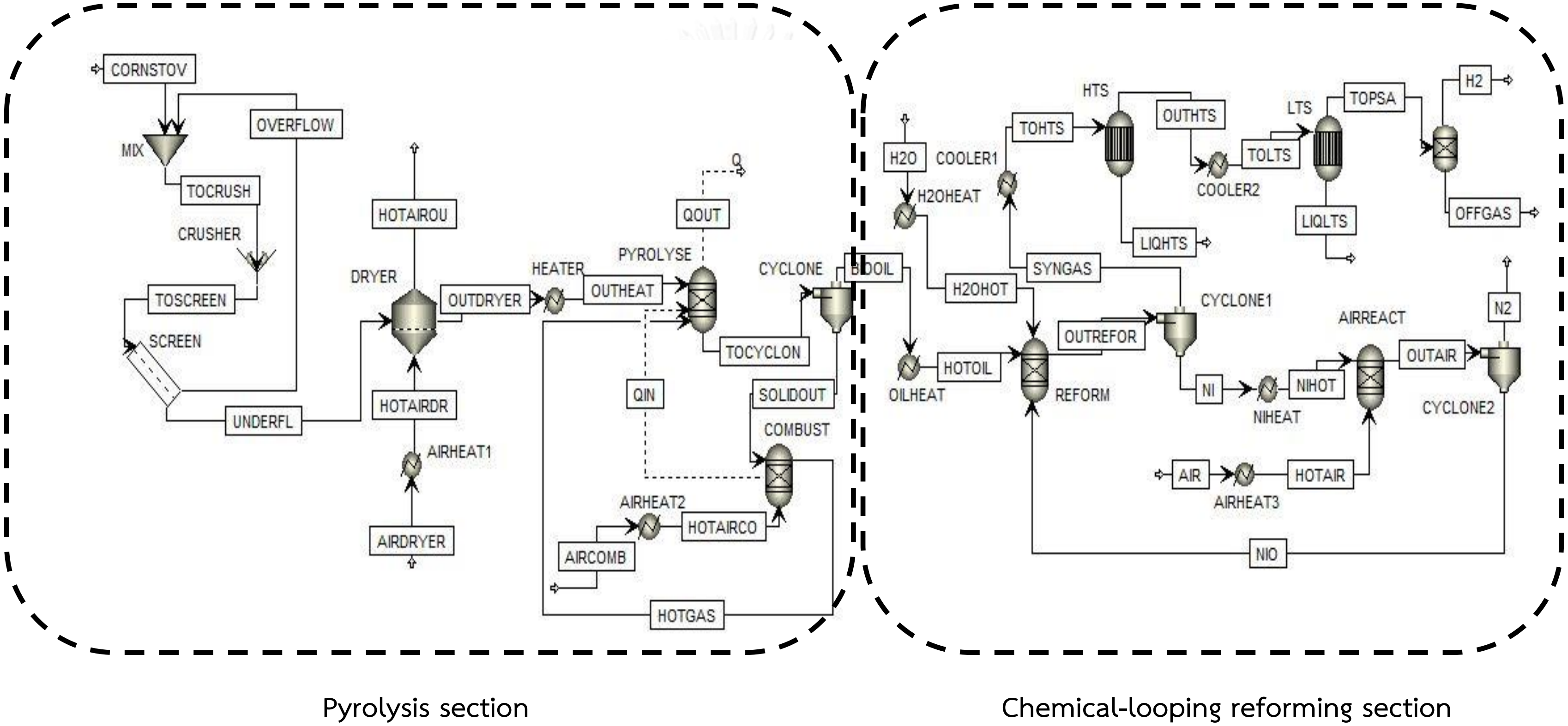


Figure 4.2: Process flow diagram of chemical-looping reforming (CLR) for hydrogen production from corn stover

2) Description

Table 4.5: Description of streams in Aspen Plus flowsheet presented in Figure 4.2

Stream's name	From	To	Description
			Pyrolysis section
AIRCOMB		AIRHEAT2	Air fed to heater for temperature adjustment before combustion reaction
AIRDRYER		AIRHEAT1	Air fed to heater for temperature adjustment before corn stover drying
BIOOIL	CYCLONE	OILHEAT	Bio-oil fed to reformer for hydrogen production
CORNSTOV		MIX	Corn stover fed into process
HOTAIRCO	AIRHEAT2	COMBUST	Hot air fed for combustion reaction
HOTAIRDR	AIRHEAT1	DRYER	Hot air fed for corn stover drying
HOTAIROU	DRYER		Wet air out from dryer
HOTGAS	COMBUST	PYROLYSE	Hot gas from combustion fed to pyrolysis reactor for heat supply
SOLIDOUT	CYCLONE	COMBUST	Ash and char after pyrolysis
TOCRUSH	MIX	CRUSHER	Corn stover before crushing and grinding
TOCYCLON	PYROLYSE	CYCLONE	Products from pyrolysis reactor which composes of bio-oil, ash and char
TOSCREEN	CRUSHER	SCREEN	Corn stover after crushing and grinding
OUTHEAT	HEATER	PYROLYSE	Corn stover after temperature adjustment for pyrolysis
OUTDRYER	DRYER	HEATER	Dried corn stover out from dryer to heater for temperature adjustment

Stream's name	From	To	Description
Pyrolysis section (cont.)			
OVERFLOW	SCREEN	MIX	Corn stover with more than 3 mm of particle size
QIN	COMBUST	PYROLYSE	Heat from combustor transferred to pyrolyser
QOUT	PYROLYSE		Heat from pyrolyser out of process
UNDERFL	SCREEN	DRYER	Corn stover with less than 3 mm of particle size
Chemical-looping reforming section			
AIR		AIRHEAT3	Air fed to heater for temperature adjustment before oxidation reaction
H2	PSA		H_2 separated from gas products by pressure swing adsorption
H2O		H2OHEAT	Water fed to heater for convert to steam before feed to reformer
HOTAIR	AIRHEAT3	AIRREACT	Hot air fed to air reactor for Ni conversion to NiO
HOTH2O	H2OHEAT	REFORM	Hot steam fed to reformer for hydrogen production
HOTO2	O2HEAT	REFORM	Hot oxygen gas fed to reformer for hydrogen production
HOTOIL	CYCLONE	REFORM	Hot bio-oil fed to reformer for hydrogen production
LIQHTS	HTS		Liquid product out from high-temperature-shift reactor
LIQLTS	LTS		Liquid product out from low-temperature-shift reactor
N2	CYCLONE2		Rich N_2 gas out of process from oxidation reaction
NI	CYCLONE1	NIHEAT	Ni out of reformer fed to heater for temperature adjustment before oxidation reaction
NIHOT	NIHEAT	AIRREACT	Hot Ni fed to air reactor to convert back to NiO

Stream's name	From	To	Description
			Chemical-looping reforming section (cont.)
NIO	CYCLONE2	REFORM	NiO regenerated to reformer
OFFGAS	PSA		Contaminant gas separated from gas products by pressure swing adsorption
OUTAIR	AIRREACT	CYCLONE2	Solid products from oxidation reaction in air reactor
OUTHTS	HTS	COOLER2	Gas products out of high-temperature-shift reactor
OUTREFOR	REFORM	CYCLONE1	Products from reformer after bio-oil conversion by autothermal reforming
SYNGAS	CYCLONE1	COOLER1	Gas products separated from solid products from reformer
TOHTS	COOLER1	HTS	Gas products from reformer after cooling
TOLTS	COOLER2	LTS	Gas products from high-temperature-shift reactor after cooling
TOPSA	LTS	PSA	Gas products fed to pressure swing adsorber for hydrogen separation

Table 4.6: Description of units in Aspen Plus flowsheet presented in Figure 4.2

Model	Name	Description
		Pyrolysis section
CRUSHER	CRUSHER	Crushes and grinds corn stover to small particles
CYCLONE	CYCLONE	Separates bio-oil and some unreacted carbon from pyrolysis (ash and char)
DRYER	DRYER	Dries corn stover
HEATER	AIRHEAT1	Heats air before feed to dryer
	AIRHEAT2	Heats air before feed to combustor
	HEATER	Heats corn stover to pyrolysis temperature
MIXER	MIX	Mixes fresh corn stover with more than 3 mm of particle size of corn stover
RGIBBS	COMBUST	Simulates combustion reaction of carbon
RYIELD	PYROLYSE	Converts corn stover to bio-oil
SCREEN	SCREEN	Screens particle with less than 3 mm size of corn stover
		Chemical-looping reforming section
CYCLONE	CYCLONE1	Separates gas and solid products from reformer
	CYCLONE2	Separates gas and solid products from air reactor
HEATER	AIRHEAT3	Heats air before feed to air reactor
	COOLER1	Cools gas products from reformer

Model	Name	Description
		Chemical-looping reforming section (cont.)
HEATER	COOLER2	Cools gas products from high-temperature-shift reactor
(cont.)	H2OHEAT	Converts water to steam at reformer temperature before autothermal reforming
	NIHEAT	Heats Ni before feed to air reactor
	OILHEAT	Heats bio-oil at reformer temperature before autothermal reforming
REQUIL	HTS	Simulates water-gas shift reaction at high temperature (350 $^{\circ}C$)
	LTS	Simulates water-gas shift reaction at low temperature (250 $^{\circ}C$)
RGIBBS	AIRREACT	Simulates oxidation reaction for Ni regeneration to NiO
	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil
SEP	PSA	Separates hydrogen from other gas products

3) Explanation

For CLR process, bio-oil (BIOOIL), steam (H2O) and Nickel oxide (NiO) (from NIO stream) were fed into reformer for bio-oil conversion at isothermal conditions. Heat used in this reactor came from hot-solid streams (NIO) which were heated by exothermic reaction in the air reactor. Solids from NIO stream is comprised of NiO. Temperature of reformer was 400-1000°C at atmospheric pressure. Steam reforming reaction and oxidation reaction occurred in this reactor, where NiO was used as the oxidizing agent. CO, CO_2, H_2, H_2O and Ni were produced from these reactions. Carbon monoxide reacts with water and produced hydrogen and carbon dioxide. Finally, gases and solids were fed to the first cyclone (CYCLONE1) for solid-gas separation and solid was fed to air reactor (AIRREACT) thereafter. Nickel metal was converted back to nickel oxide by feeding air into the air reactor (AIRREACT). This reactor operated under isothermal conditions: 1000 °C at atmospheric pressure. Oxygen in air was used to oxidize nickel metal to nickel oxide. NiO from this reactor was fed to cyclone (CYCLONE2) for solid-gas separation and was fed back to reforming reactor (REFORM) for reuse of NiO.

4.1.3 Sorption enhanced process (SE)

1) Process flow diagram

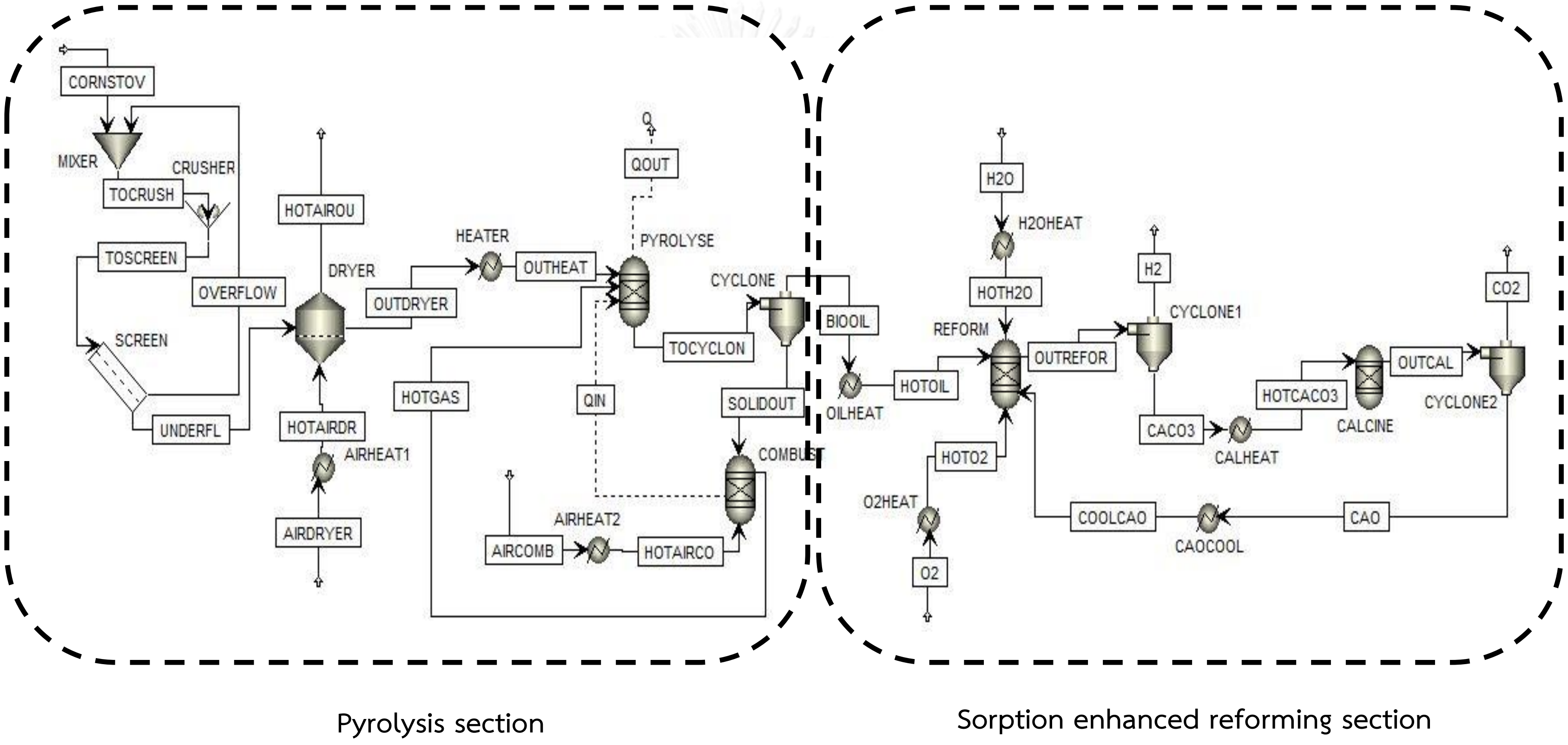


Figure 4.3: Process flow diagram of sorption enhanced reforming (SE) for hydrogen production from corn stover

2) Description

Table 4.7: Description of streams in Aspen Plus flowsheet presented in Figure 4.3

Stream's name	From	To	Description
			Pyrolysis section
AIRCOMB		AIRHEAT2	Air fed to heater for temperature adjustment before combustion reaction
AIRDRYER		AIRHEAT1	Air fed to heater for temperature adjustment before corn stover drying
BIOOIL	CYCLONE	OILHEAT	Bio-oil fed to reformer for hydrogen production
CORNSTOV		MIX	Corn stover fed into process
HOTAIRCO	AIRHEAT2	COMBUST	Hot air fed for combustion reaction
HOTAIRDR	AIRHEAT1	DRYER	Hot air fed for corn stover drying
HOTAIROU	DRYER		Wet air out from dryer
HOTGAS	COMBUST	PYROLYSE	Hot gas from combustion fed to pyrolysis reactor for heat supply
SOLIDOUT	CYCLONE	COMBUST	Ash and char after pyrolysis
TOCRUSH	MIX	CRUSHER	Corn stover before crushing and grinding
TOCYCLON	PYROLYSE	CYCLONE	Products from pyrolysis reactor which composes of bio-oil, ash and char
TOSCREEN	CRUSHER	SCREEN	Corn stover after crushing and grinding
OUTHEAT	HEATER	PYROLYSE	Corn stover after temperature adjustment for pyrolysis

Stream's name	From	To	Description
Pyrolysis section (cont.)			
OUTDRYER	DRYER	HEATER	Dried corn stover out from dryer to heater for temperature adjustment
OVERFLOW	SCREEN	MIX	Corn stover with more than 3 mm of particle size
QIN	COMBUST	PYROLYSE	Heat from combustor transferred to pyrolyser
QOUT	PYROLYSE		Heat from pyrolyser out of process
UNDERFL	SCREEN	DRYER	Corn stover with less than 3 mm of particle size
Sorption enhanced reforming section			
CACO3	CYCLONE1	CALHEAT	$CaCO_3$ fed to heater for temperature adjustment before feed to calcination reactor
CAO	CYCLONE2	CAOCOOL	Regenerated CaO fed to cooler for temperature adjustment
CO2	CYCLONE2		CO_2 separated from CaO after calcination reaction
COOLCAO	CAOCOOL	REFORM	Regenerated CaO fed to reformer for CO_2 adsorption
H2	CYCLONE1		H2 and other gas products separated from solid products from reformer
H2O		H2OHEAT	Water fed to heater for convert to steam before feed to reformer
HOTCACO3	CALHEAT	CALCINE	$CaCO_3$ fed to calcination reactor for regeneration to CaO
HOTH2O	H2OHEAT	REFORM	Hot steam fed to reformer for hydrogen production
HOTO2	O2HEAT	REFORM	Hot oxygen gas fed to reformer for hydrogen production
HOTOIL	CYCLONE	REFORM	Hot bio-oil fed to reformer for hydrogen production

Stream's name	From	To	Description
Sorption enhanced reforming section (cont.)			
O2		O2HEAT	Oxygen gas fed to heater for temperature adjustment before feed to reformer
OUTCAL	CALCINE	CYCLONE2	Products from calcination reactor
OUTREFOR	REFORM	CYCLONE1	Products from reformer after bio-oil conversion by autothermal reforming

Table 4.8: Description of units in Aspen Plus flowsheet presented in Figure 4.3

Model	Name	Description
Pyrolysis section		
CRUSHER	CRUSHER	Crushes and grinds corn stover to small particles
CYCLONE	CYCLONE	Separates bio-oil and some unreacted carbon from pyrolysis (ash and char)
DRYER	DRYER	Dries corn stover
HEATER	AIRHEAT1	Heats air before feed to dryer
	AIRHEAT2	Heats air before feed to combustor
	HEATER	Heats corn stover to pyrolysis temperature
MIXER	MIX	Mixes fresh corn stover with more than 3 mm of particle size of corn stover
RGIBBS	COMBUST	Simulates combustion reaction of carbon
RYIELD	PYROLYSE	Converts corn stover to bio-oil

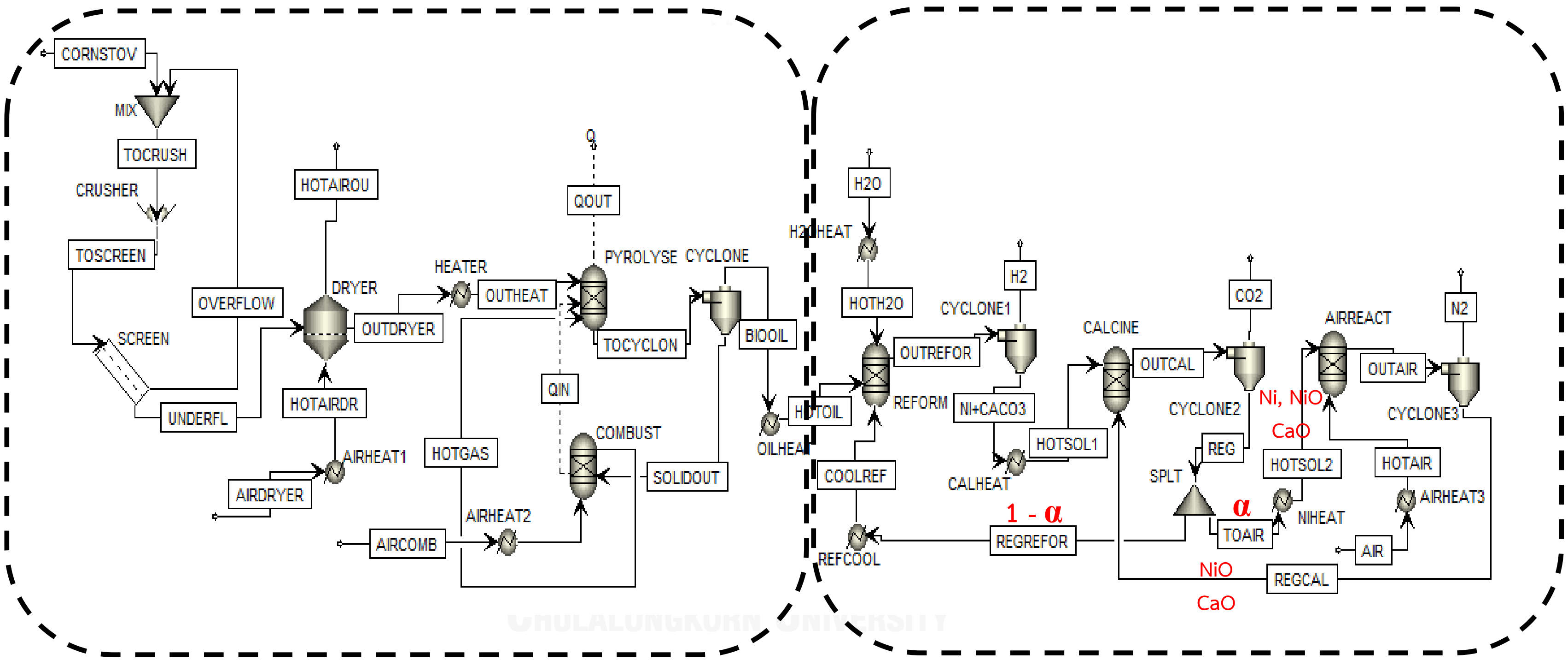
Model	Name	Description
		Pyrolysis section (cont.)
SCREEN	SCREEN	Screens particle with less than 3 mm size of corn stover
		Sorption enhanced reforming section
CYCLONE	CYCLONE1	Separates gas and solid products from reformer
	CYCLONE2	Separates gas and solid products from calcination reactor
HEATER	CALCOOL	Cools CaO before feed to reformer
	CALHEAT	Heats $CaCO_3$ before feed to calcination reactor
	H2OHEAT	Converts water to steam at reformer temperature before autothermal reforming
	O2HEAT	Heats oxygen gas before feed to reformer for bio-oil conversion
	OILHEAT	Heats bio-oil at reformer temperature before autothermal reforming
RGIBBS	CALCINE	Simulates calcination reaction for $CaCO_3$ regeneration to CaO
	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil

3) Explanation

For SE process, bio-oil (BIOOIL), steam (H2O), and Calcium oxide (CaO) (from COOLCAO stream) were fed into reformer for bio-oil conversion at isothermal conditions. Solids from COOLCAO stream is comprised of CaO. Temperature of reformer was 400-1000 °C at atmospheric pressure. Steam reforming and partial oxidation reaction occurred in this reactor. CO, CO_2, H_2 and H_2O were mainly produced from these reactions. Carbon monoxide reacted with water and produced hydrogen and carbon dioxide by water-gas shift reaction. Carbon dioxide in the system was adsorbed by adsorbent (CaO) and form $CaCO_3$. Finally, gassous and solid products were fed to the first cyclone (CYCLONE1) for solid-gas separation and solid was fed to calcination reactor (CALCINE) thereafter. Carbon dioxide was desorbed from the adsorbent by heating in calcination reactor (CALCINE). This reactor was operated under isothermal condition:T = 900°C and P = 1 atm. The endothermic desorption equation is shown by Eq.4.13. CO_2 and CaO were fed to cyclone (CYCLONE2) for gas-solid separation and fed back to reformer (REFORM) for reuse.

4.1.4 Sorption enhanced chemical looping reforming process (SE-CLR)

1) Process flow diagram



Pyrolysis section

Sorption enhanced chemical-looping reforming

Figure 4.4: Process flow diagram of sorption enhanced chemical-looping reforming (SE-CLR) for hydrogen production from corn stover

2) Description

Table 4.9: Description of streams in Aspen Plus flowsheet presented in Figure 4.4

Stream's name	From	To	Description
			Pyrolysis section
AIRCOMB		AIRHEAT2	Air fed to heater for temperature adjustment before combustion reaction
AIRDRYER		AIRHEAT1	Air fed to heater for temperature adjustment before corn stover drying
BIOOIL	CYCLONE	OILHEAT	Bio-oil fed to reformer for hydrogen production
CORNSTOV		MIX	Corn stover fed into process
HOTAIRCO	AIRHEAT2	COMBUST	Hot air fed for combustion reaction
HOTAIRDR	AIRHEAT1	DRYER	Hot air fed for corn stover drying
HOTAIROU	DRYER		Wet air out from dryer
HOTGAS	COMBUST	PYROLYSE	Hot gas from combustion fed to pyrolysis reactor for heat supply
SOLIDOUT	CYCLONE	COMBUST	Ash and char after pyrolysis
TOCRUSH	MIX	CRUSHER	Corn stover before crushing and grinding
TOCYCLON	PYROLYSE	CYCLONE	Products from pyrolysis reactor which composes of bio-oil, ash and char
TOSCREEN	CRUSHER	SCREEN	Corn stover after crushing and grinding
OUTHEAT	HEATER	PYROLYSE	Corn stover after temperature adjustment for pyrolysis
OUTDRYER	DRYER	HEATER	Dried corn stover out from dryer to heater for temperature adjustment

Stream's name	From	To	Description
			Pyrolysis section (cont.)
OVERFLOW	SCREEN	MIX	Corn stover with more than 3 mm of particle size
QIN	COMBUST	PYROLYSE	Heat from combustor transferred to pyrolyser
QOUT	PYROLYSE		Heat from pyrolyser out of process
UNDERFL	SCREEN	DRYER	Corn stover with less than 3 mm of particle size
			Sorption enhanced chemical-looping reforming section
AIR		AIRHEAT3	Air fed to heater for temperature adjustment before oxidation reaction
CO2	CYCLONE2		CO_2 separated from CaO after calcination reaction
COOLREF	REFCOOL	REFORM	Regenerated solids fed to reformer for bio-oil conversion
H2	CYCLONE1		H_2 and other gas products separated from solid products from reformer
H2O		H2OHEAT	Water fed to heater for convert to steam before feed to reformer
HOTAIR	AIRHEAT3	AIRREACT	Hot air fed to air reactor for Ni conversion to NiO
HOTH2O	H2OHEAT	REFORM	Hot steam fed to reformer for hydrogen production
HOTOIL	CYCLONE	REFORM	Hot bio-oil fed to reformer for hydrogen production
HOTSOL1	CALHEAT	CALCINE	Hot solids fed to calcination reactor for calcination reaction
HOTSOL2	NIHEAT	AIRREACT	Hot solids fed to air reactor for oxidation reaction
N2	CYCLONE2		Rich N_2 gas out of process from oxidation reaction
NI+CACO3	CYCLONE1	CALHEAT	Ni and $CaCO_3$ separated from gas products from reformer after bio-oil conversion

Stream's name	From	To	Description
Sorption enhanced chemical-looping reforming section (cont.)			
OUTAIR	AIRREACT	CYCLONE3	Products from air reactor
OUTCAL	CALCINE	CYCLONE2	Products from calcination reactor
OUTREFOR	REFORM	CYCLONE1	Products from reformer after bio-oil conversion by autothermal reforming
REG	CYCLONE2	SPLT	Regenerated solids fed to spliter
REGCAL	CYCLONE3	CALCINE	Regenerated solids fed to calcination reactor for heat supply
REGREFOR	SPLT	REFCOOL	Regenerated solids fed to cooler for temperature adjustment before feed to reformer
TOAIR	SPLT	NIHEAT	Solids fed to heater for temperature adjustment before feed to air reactor

Table 4.10: Description of units in Aspen Plus flowsheet presented in Figure 4.4

Model	Name	Description
		Pyrolysis section
CRUSHER	CRUSHER	Crushes and grinds corn stover to small particles
CYCLONE	CYCLONE	Separates bio-oil and some unreacted carbon from pyrolysis (ash and char)
DRYER	DRYER	Dries corn stover
HEATER	AIRHEAT1	Heats air before feed to dryer
	AIRHEAT2	Heats air before feed to combustor
	HEATER	Heats corn stover to pyrolysis temperature
MIXER	MIX	Mixes fresh corn stover with more than 3 mm of particle size of corn stover
RGIBBS	COMBUST	Simulates combustion reaction of carbon
RYIELD	PYROLYSE	Converts corn stover to bio-oil
SCREEN	SCREEN	Screens particle with less than 3 mm size of corn stover
		Sorption enhanced chemical-looping reforming section
CYCLONE	CYCLONE1	Separates gas and solid products from reformer
	CYCLONE2	Separates gas and solid products from calcination reactor
	CYCLONE3	Separates gas and solid products from air reactor
FSPLT	SPLT	Splits regenerated solids to reformer and to air reactor

Model	Name	Description
		Sorption enhanced chemical-looping reforming section (cont.)
HEATER	AIRHEAT3	Heats air before feed to air reactor
	CALHEAT	Heats $CaCO_3$ before feed to air reactor
	H2OHEAT	Converts water to steam at reformer temperature before autothermal reforming
	NIHEAT	Heats Ni before feed to air reactor
	OILHEAT	Heats bio-oil at reformer temperature before autothermal reforming
	REFCOOL	Cools regenerated solids before feed to reformer for bio-oil conversion
RGIBBS	AIRREACT	Simulates oxidation reaction for Ni regeneration to NiO
	CALCINE	Simulates calcination reaction for $CaCO_3$ regeneration to CaO
	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil

3) Explanation

For SE-CLR process, bio-oil (BIOOIL), steam (H2O), Nickel oxide (NiO) and Calcium oxide (CaO) (by COOLREF streams) were fed into reformer for bio-oil conversion at isothermal conditions. Solids from COOLREF stream is comprised of Ni, NiO and CaO. Temperature of reformer was 400-1000 °C at atmospheric pressure. Steam reforming reaction and oxidation reaction occurred in this reactor, where NiO was used as the oxidizing agent. CO, CO_2, H_2, H_2O and Ni were produced from these reactions. Carbon monoxide reacts with water and produced hydrogen and carbon dioxide. Carbon dioxide in the system was adsorbed by adsorbent (CaO) and form $CaCO_3$. Finally, the obtained gases and solids were fed to the first cyclone (CYCLONE1) for solid-gas separation and solid was fed to calcination reactor (CALCINE) thereafter. Carbon dioxide was desorbed from the adsorbent by heat in calcination reactor (CALCINE). The heat used in this reactor was obtained from hot-solid stream (REGCAL) which was heated by exothermic reaction in the air reactor. This reactor was operated at isothermal condition, temperature of 900 °C and pressure is 1 atm. The endothermic desorption equation is shown by Eq.4.13. Gas (CO_2) and solids (Ni, NiO and CaO) were fed to cyclone (CYCLONE2) for gas-solid separation and fed to spliter (SPLT) for division into 2 streams; REGREFOR and TOAIR. The minor solids (Ni, NiO and CaO in REGREFOR) were fed back to reforming reactor (REFORM) for reuse and heat supply whereas the major solids (Ni, NiO and CaO in TOAIR) were fed to air reactor (AIRREACT) for nickel regeneration. Nickel metal was converted back to nickel oxide by feeding air into an air reactor (AIRREACT). This reactor operated with isothermal conditions; 1000 °C at atmospheric pressure.

Oxygen in air was used to oxidize nickel metal to nickel oxide. Solids (NiO, Ni and CaO) from this reactor were fed to cyclone (CYCLONE3) for solid-gas separation. The solids (NiO and CaO in REG2CAL) were fed to calcination reactor (CALCINE) for heat supply to the calcination reaction in the calcination reactor.

The effect of reforming temperature, pressure, steam equivalence ratio (SER), oxygen equivalence ratio (OER), NiO equivalence ratio (NER) and CaO equivalence ratio (CER) on hydrogen yield, bio-oil conversion, hydrogen purity were investigated. Reforming temperature was varied between 400-1000°C, pressure was varied in the 1-25 bar of range, SER was varied between 0.5-8 by mol whereas 0.1-1 for OER and NER and 0.1-4 of CER. All reactors in sorption enhance chemical-looping process (REFORM, CALCINE, AIRREACT) were isothermal. Hydrogen yield, bio-oil conversion and hydrogen purity were calculated by Eq. 4.23-4.25.

$$\text{Hydrogen yield (g/kg)} = \frac{\text{g of H}_2\text{ produced}}{\text{kg of biomass fed (dry basis)}} \qquad \text{...(4.23)}$$

$$\text{Bio} - \text{oil conversion (\%)} = \frac{\text{Biooil fed} - \text{biooil out}}{\text{Biooil fed}} \times 100\% \qquad \text{...(4.24)}$$

$$\text{Hydrogen purity (\%)} = \frac{\text{mol of H}_2\text{ produced}}{\text{mol of dry gas out}} \times 100\% \qquad \text{...(4.25)}$$

Formula of bio-oil which was fed to reformer was represented by $CH_{1.224}O_{0.38}$. Steam equivalence ratio (SER), oxygen equivalence ratio (OER), nickel-oxide equivalence ratio (NER) and calcium oxide equivalence ratio (CER) are defined as shown in Eq. 4.26-4.29. Circulated NiO to bio-oil molar ratio (CNB) and circulated CaO to bio-oil molar ratio (CCB) were defined as shown in Eq. 4.30-4.31. For SE-CLR process, amount of solids (Ni, NiO and CaO) regenerated in the process were determined by “α” which defined in Eq. 4.32.

$$\mathrm{SER} = \frac{\text{Actual } \mathrm{H_2O} \text{ to bio−oil molar ratio}}{\text{Stoichiometric } \mathrm{H_2O} \text{ to bio−oil molar ratio}} \qquad \text{...(4.26)}$$

$$\mathrm{OER} = \frac{\text{Actual } \mathrm{O_2} \text{ to bio−oil molar ratio}}{\text{Stoichiometric } \mathrm{O_2} \text{ to bio−oil molar ratio}} \qquad \text{...(4.27)}$$

$$\mathrm{NER} = \frac{\text{Actual NiO to bio−oil molar ratio}}{\text{Stoichiometric NiO to bio−oil molar ratio}} \qquad \text{...(4.28)}$$

$$\mathrm{CER} = \frac{\text{Actual CaO to bio−oil molar ratio}}{\text{Stoichiometric CaO to bio−oil molar ratio}} \qquad \text{...(4.29)}$$

$$\mathrm{CNB} = \frac{\text{Circulated NiO in process (kmol/h)}}{\text{Bio−oil fed to process (kmol/h)}} \qquad \text{...(4.30)}$$

$$\mathrm{CCB} = \frac{\text{Circulated CaO in process (kmol/h)}}{\text{Bio−oil fed to process (kmol/h)}} \qquad \text{...(4.31)}$$

$$\alpha = \frac{\text{Solids (Ni,NiO,CaO)from splitter to air reactor(kmol/h)}}{\text{Solids (Ni,NiO,CaO) fed to splitter (kmol/h)}} \qquad \text{...(4.32)}$$

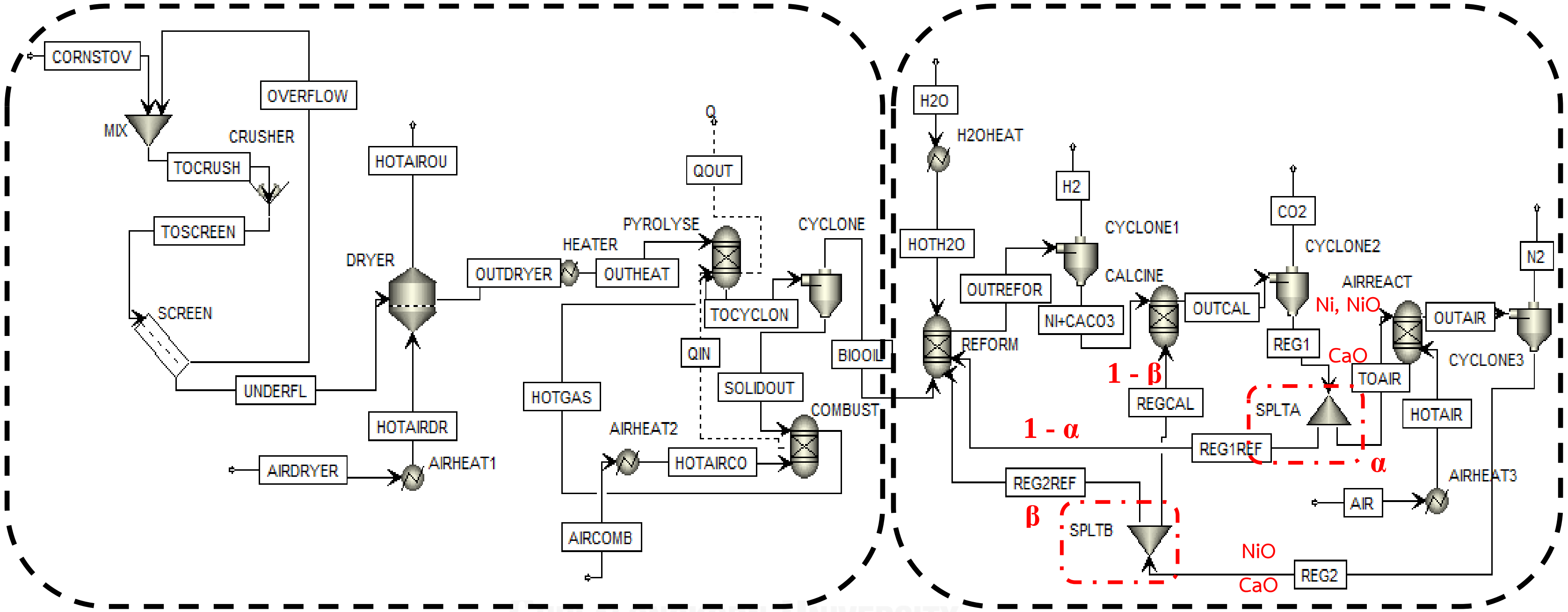
4.2 Improvement of sorption enhanced chemical-looping reforming process

Although high fuel conversion, hydrogen yield and hydrogen purity can be obtained when the sorption enhanced chemical-looping has been applied; however, external energy, preheating units and cooling units still are required. Moreover, for hydrogen production by sorption enhanced chemical-looping reforming process in fluidized bed reactors, effect of amounts of catalyst (NiO) and adsorbent (CaO) regenerated in the process on conversion, hydrogen yield and hydrogen purity has never been examined. In this section, the production of hydrogen from sorption enhanced chemical-looping reforming process was modeled together with examining optimal operating conditions under constraint of adiabatic reactors in sorption enhanced chemical-looping reforming section. Variation of amounts of catalyst (NiO) and adsorbent (CaO) regenerated in the process subject to be investigated for the goal to minimize external energy, preheating and cooling units as well as maximize bio-oil conversion, hydrogen yield and hydrogen purity.

Principle for minimize external energy, preheating and cooling units of sorption enhanced chemical-looping process is elimination of heater and cooler used in the process and sufficiently supply heat from exothermic reaction in air reactor for endothermic reaction in reformer and calcination reactor. Moreover, heat integration between hot stream out from process and cold stream fed to process will also be discussed. Process flow diagram of modified sorption enhanced chemical-looping reforming process is presented in Figure 4.5 and modified sorption enhanced chemical-looping reforming with heat integration is shown in Figure 4.6 Descriptions of streams and units for both of processes are presented by Table 4.11-4.14.

4.2.1 Modified sorption enhanced chemical-looping reforming process

1) Process flow diagram



Pyrolysis

Modified sorption enhanced chemical-looping reforming section

Figure 4.5: Process flow diagram of modified sorption enhance chemical-looping reforming for hydrogen production from corn stover

2) Description

Table 4.11: Description of streams in Aspen Plus flowsheet presented in Figure 4.5

Stream's name	From	To	Description
			Pyrolysis section
AIRCOMB		AIRHEAT2	Air fed to heater for temperature adjustment before combustion reaction
AIRDRYER		AIRHEAT1	Air fed to heater for temperature adjustment before corn stover drying
BIOOIL	CYCLONE	OILHEAT	Bio-oil fed to reformer for hydrogen production
CORNSTOV		MIX	Corn stover fed into process
HOTAIRCO	AIRHEAT2	COMBUST	Hot air fed for combustion reaction
HOTAIRDR	AIRHEAT1	DRYER	Hot air fed for corn stover drying
HOTAIROU	DRYER		Wet air out from dryer
HOTGAS	COMBUST	PYROLYSE	Hot gas from combustion fed to pyrolysis reactor for heat supply
SOLIDOUT	CYCLONE	COMBUST	Ash and char after pyrolysis
TOCRUSH	MIX	CRUSHER	Corn stover before crushing and grinding
TOCYCLON	PYROLYSE	CYCLONE	Products from pyrolysis reactor which composes of bio-oil, ash and char
TOSCREEN	CRUSHER	SCREEN	Corn stover after crushing and grinding
OUTHEAT	HEATER	PYROLYSE	Corn stover after temperature adjustment for pyrolysis

Stream's name	From	To	Description
			Pyrolysis section (cont.)
OUTDRYER	DRYER	HEATER	Dried corn stover out from dryer to heater for temperature adjustment
OVERFLOW	SCREEN	MIX	Corn stover with more than 3 mm of particle size
QIN	COMBUST	PYROLYSE	Heat from combuster transferred to pyrolyser
QOUT	PYROLYSE		Heat from pyrolyser out of process
UNDERFL	SCREEN	DRYER	Corn stover with less than 3 mm of particle size
			Sorption enhanced chemical-looping reforming section
AIR		AIRHEAT3	Air fed to heater for temperature adjustment before oxidation reaction
CO2	CYCLONE2		CO_2 separated from CaO after calcination reaction
H2	CYCLONE1		H_2 and other gas products separated from solid products from reformer
H2O		H2OHEAT	Water fed to heater for convert to steam before feed to reformer
HOTAIR	AIRHEAT3	AIRREACT	Hot air fed to air reactor for Ni conversion to NiO
HOTH2O	H2OHEAT	REFORM	Hot steam fed to reformer for hydrogen production
HOTOIL	CYCLONE	REFORM	Hot bio-oil fed to reformer for hydrogen production
N2	CYCLONE2		Rich N_2 gas out of process from oxidation reaction
NI+CACO3	CYCLONE1	CALCINE	Ni and $CaCO_3$ separated from gas products from reformer after bio-oil conversion
OUTAIR	AIRREACT	CYCLONE3	Products from air reactor
OUTCAL	CALCINE	CYCLONE2	Products from calcination reactor

Stream's name	From	To	Description
Sorption enhanced chemical-looping reforming section (cont.)			
OUTREFOR	REFORM	CYCLONE1	Products from reformer after bio-oil conversion by autothermal reforming
REG1	CYCLONE2	SPLTA	Regenerated solids from calcination reactor fed to the first spliter
REG2	CYCLONE3	SPLTB	Regenerated solids from air reactor fed to the second spliter
REG1REFOR	SPLTA	REFORM	Regenerated solids fed to reformer for bio-oil conversion
REG2REFOR	SPLTB	REFORM	Regenerated solids fed to reformer for bio-oil conversion
REGCAL	SPLTB	CALCINE	Regenerated solids fed to calcination reactor for heat supply
TOAIR	SPLTA	AIRREACT	Solids fed to air reactor for oxidation reaction

Table 4.12: Description of units in Aspen Plus flowsheet presented in Figure 4.5

Model	Name	Description
Pyrolysis section		
CRUSHER	CRUSHER	Crushes and grinds corn stover to small particles
CYCLONE	CYCLONE	Separates bio-oil and some unreacted carbon from pyrolysis (ash and char)
DRYER	DRYER	Dries corn stover
HEATER	AIRHEAT1	Heats air before feed to dryer

Model	Name	Description
		Pyrolysis section (cont.)
HEATER	AIRHEAT2	Heats air before feed to combustor
(cont.)	HEATER	Heats corn stover to pyrolysis temperature
MIXER	MIX	Mixes fresh corn stover with more than 3 mm of particle size of corn stover
RGIBBS	COMBUST	Simulates combustion reaction of carbon
RYIELD	PYROLYSE	Converts corn stover to bio-oil
SCREEN	SCREEN	Screens particle with less than 3 mm size of corn stover
		Sorption enhanced chemical-looping reforming section
CYCLONE	CYCLONE1	Separates gas and solid products from reformer
	CYCLONE2	Separates gas and solid products from calcination reactor
	CYCLONE3	Separates gas and solid products from air reactor
FSPLT	SPLTA	Splits regenerated solids to reformer and to air reactor
	SPLTB	Splits regenerated solids to reformer and to calcination reactor
HEATER	AIRHEAT3	Heats air before feed to air reactor
	H2OHEAT	Converts water to steam at reformer temperature before autothermal reforming
RGIBBS	AIRREACT	Simulates oxidation reaction for Ni regeneration to NiO
	CALCINE	Simulates calcination reaction for $CaCO_3$ regeneration to CaO
	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil

3) Explanation

For modified sorption enhanced chemical-looping reforming process which is present in Fig.4.5, one splitter was added to the process (SPLTB) to split solids from air reactor (AIRREACT) to reformer (REFORM) and calcination reactor (CALCINE) in order to transferred NiO and CaO to reformer for heat supply to reformer. This could reduce 3 heaters and 1 cooler with heat from solids was applied instead. Reformer, calcination reactor and air reactor were operated at adiabatic conditions instead of isothermal conditions. From these modifications, energy supplied to the process will significantly decrease. The effect of amounts of solids regenerated in the process determined by both splitters (SPLTA and SPLTB) on hydrogen yield, bio-oil conversion, hydrogen purity, reforming temperature, calcination temperature and oxidation temperature were investigated. Amount of solids regenerated in the process were determined by "α" which is defined in Eq. 4.33 and "β" is defined in Eq. 4.34

$$\alpha = \frac{\text{Solids (Ni,NiO,CaO)from SPLTA to air reactor(kmol/h)}}{\text{Solids (Ni,NiO,CaO) fed to SPLTA (kmol/h)}} \qquad \text{...(4.33)}$$

$$\beta = \frac{\text{Solids (NiO,CaO)from SPLTB to reformer(kmol/h)}}{\text{Solids (NiO,CaO) fed to SPLTB (kmol/h)}} \qquad \text{...(4.34)}$$

For studying effect of amounts of catalyst (NiO) and adsorbent (CaO) regenerated in the process on process performance; bio-oil conversion, hydrogen yield and hydrogen purity, α was varied from 0.95 to 1 and 0-0.05 range for β at 42.4 of CNB and 42.4 of CCB. Then, CNB, CCB and split ratios (α and β) was simultaneously varied in order to study effect of CNB and CCB on process performance and to find optimum conditions for hydrogen production by sorption enhanced chemical-looping process. CNB was varied from 12.3 to 123.2 and CCB was varied in the 31.3-125.2 range.

4.2.2 Modified sorption enhance chemical-looping reforming with heat integration

1) Process flow diagram

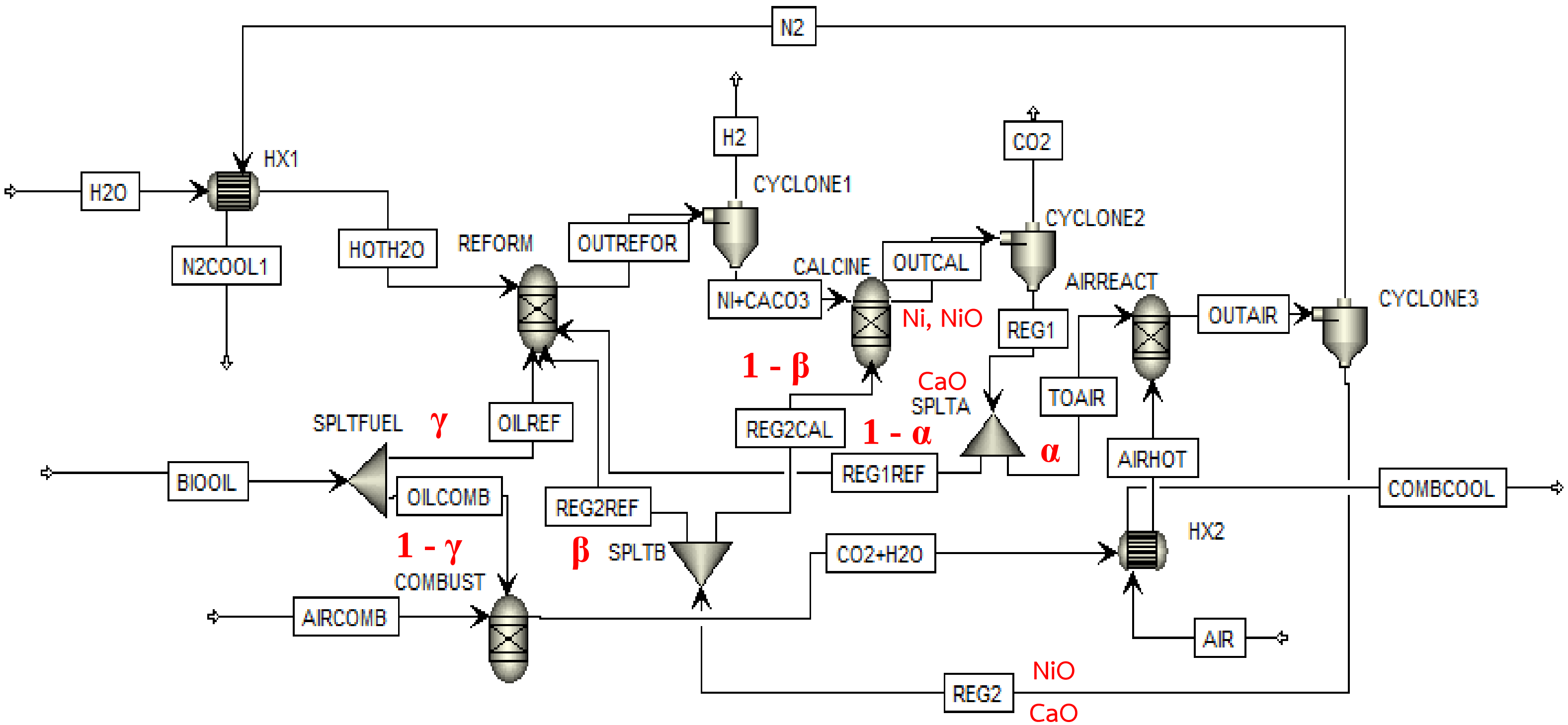


Figure 4.6: Process flow diagram of modified sorption enhance chemical-looping reforming with heat integration for hydrogen production from bio-oil

Table 4.13: Description of streams in Aspen Plus flowsheet presented in Figure 4.6

Stream's name	From	To	Description
AIR		HX3	Air fed to heat exchanger for temperature adjustment before oxidation reaction
AIRCOMB		COMBUST	Air fed to combustor for combustion reaction of bio-oil
BIOOIL		SPLTFUEL	Bio-oil fed to the first heat exchanger for preheat
CO2	CYCLONE2		CO_2 separated from CaO after calcination reaction
CO2+H2O	COMBUST	HX2	Gas products from combustor fed to heat exchanger for air preheating
H2	CYCLONE1		H_2 and other gas products separated from solid products from reformer
H2O		HX1	Water fed to heat exchanger for convert to steam before feed to reformer
HOTAIR	HX2	AIRREACT	Hot air fed to air reactor for Ni conversion to NiO
HOTH2O	HX1	REFORM	Hot steam fed to reformer for hydrogen production
N2	CYCLONE2	HX1	Rich N_2 gas out from air reactor fed to heat exchanger
N2COOL1	HX1		Cool N_2 gas out of process
NI+CACO3	CYCLONE1	CALCINE	Ni and $CaCO_3$ separated from gas products from reformer after bio-oil conversion
OILCOMB	SPLTFUEL	COMBUST	Bio-oil fed to combustor for combustion reaction
OILREF	SPLTFUEL	REFORM	Bio-oil fed to reformer for hydrogen production
OUTAIR	AIRREACT	CYCLONE3	Products from air reactor
OUTCAL	CALCINE	CYCLONE2	Products from calcination reactor

Stream's name	From	To	Description
OUTREFOR	REFORM	CYCLONE1	Products from reformer after bio-oil conversion by autothermal reforming
REG1	CYCLONE2	SPLTA	Regenerated solids from calcination reactor fed to the first spliter
REG2	CYCLONE3	SPLTB	Regenerated solids from air reactor fed to the second spliter
REG1REFOR	SPLTA	REFORM	Regenerated solids fed to reformer for bio-oil conversion
REG2REFOR	SPLTB	REFORM	Regenerated solids fed to reformer for bio-oil conversion
REGCAL	SPLTB	CALCINE	Regenerated solids fed to calcination reactor for heat supply
TOAIR	SPLTA	AIRREACT	Solids fed to air reactor for oxidation reaction

Table 4.14: Description of units in Aspen Plus flowsheet presented in Figure 4.6

Model	Name	Description
CYCLONE	CYCLONE1	Separates gas and solid products from reformer
	CYCLONE2	Separates gas and solid products from calcination reactor
	CYCLONE3	Separates gas and solid products from air reactor
FSPLT	SPLTA	Splits regenerated solids to reformer and to air reactor
	SPLTB	Splits regenerated solids to reformer and to calcination reactor
	SPLTFUEL	Splits bio-oil to reformer and combustor
HEATX	HX1	Converts water to steam and preheats before feed to reformer
	HX2	Preheats air before feed to air reactor

Model	Name	Description
RGIBBS	AIRREACT	Simulates oxidation reaction for Ni regeneration to NiO
	CALCINE	Simulates calcination reaction for $CaCO_3$ regeneration to CaO
	COMBUST	Simulates combustion reaction of bio-oil and air for heat supply in the process
	REFORM	Simulates steam reforming and oxidation reaction for hydrogen production from bio-oil

3) Explanation

For the modified sorption enhanced chemical-looping reforming process with heat integration, Bio-oil was split into 2 streams; OILREF and OILCOMB. OILREF is bio-oil, which was fed to reformer for hydrogen production whereas OILCOMB was fed to combustor for combustion reaction in order to generate heat supply for the process. Ratio of amount of bio-oil fed to reformer to amount of bio-oil from pyrolysis section was defined by "γ" as shown in Eq. 4.35

$$\gamma = \frac{\text{Bio}-\text{oil fed to reformer(kmol/h)}}{\text{Bio}-\text{oil from pyrolysis section (kmol/h)}} \qquad \text{...(4.35)}$$

Combustor was operated at adiabatic conditions and external air was fed for combustion reaction. Two heat exchangers were applied instead of heaters for preheat water and air before feed to reactors. Water was heated from 35 $^{\circ}$C to 450 $^{\circ}$C and air was heated from 35 $^{\circ}$C to 920 $^{\circ}$C. Hot streams used for exchange are N_2 which was gas products from exothermic air reactor and CO_2+H_2O from combustor which comprised of CO_2 and H_2O from exothermic combustion reaction. Therefore, the heater for conversion of water to steam and the heater for preheat air will be eliminated which results in reduction of external energy consumption.

CHAPTER 5

RESULTS AND DISCUSSION

Results of simulation studies of sorption enhance chemical-looping process for hydrogen production from biomass are presented and discussed in this chapter. It is divided into 4 parts. Firstly, validation of simulation of autothermal reforming process (ATR), chemical-looping reforming process (CLR), sorption enhanced process (SE) and sorption enhanced chemical-looping process (SE-CLR) are presented. Secondly, effect of various conditions, including reforming temperature, pressure, and steam to fuel ratio, on performance of each process are examined in terms ofconversion of fuel, yield of hydrogen produced, purity of hydrogen and energy consumption. Thirdly, the improvement of sorption enhanced chemical-looping process is performed: amounts of Ni, NiO and CaO circulated and regenerated in the process are investigated. Lastly, reduction of energy consumption in sorption enhanced chemical-looping process by heat integration is further investigated. Process performance and energy consumption are compared between sorption enhanced chemical-looping process and sorption enhanced chemical-looping process with heat integration.

5.1 Validation of different processes modeling for hydrogen production

5.1.1 Autothermal reforming process (ATR)

Autothermal reforming of ethanol was selected to validate according to the work of Graschinsky et.al [47]. In Figure 5.1 is shown the effect of reforming temperature and oxygen to ethanol molar ratio on hydrogen production at water to ethanol molar ratio of 5 reported by Graschinsky et.al [47]. “Ro” represents oxygen to ethanol molar ratio and “R” represents water to ethanol molar ratio. And in Figure 5.2 shows the effect of reforming temperature on hydrogen production obtained from our simulation by Aspen Plus program. It can be seen that that the results obtained from our model is compatible to those reported by Graschinsky et.al.

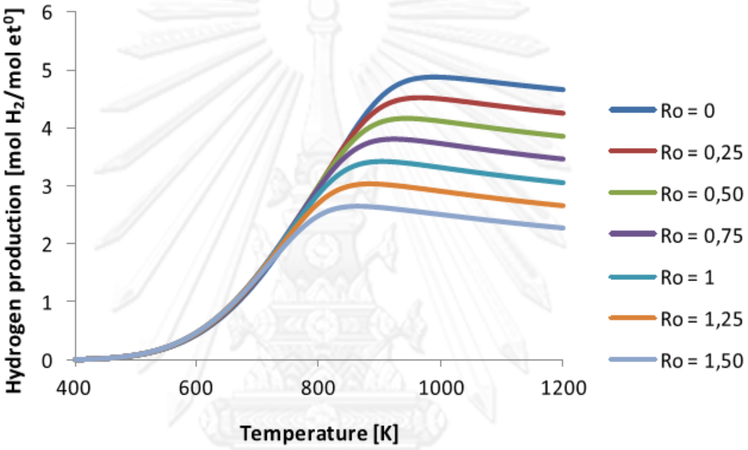


Figure 5.1: Hydrogen production vs. temperature for Ro = 0-1.5 and R=5 from Graschinsky et.al [47]

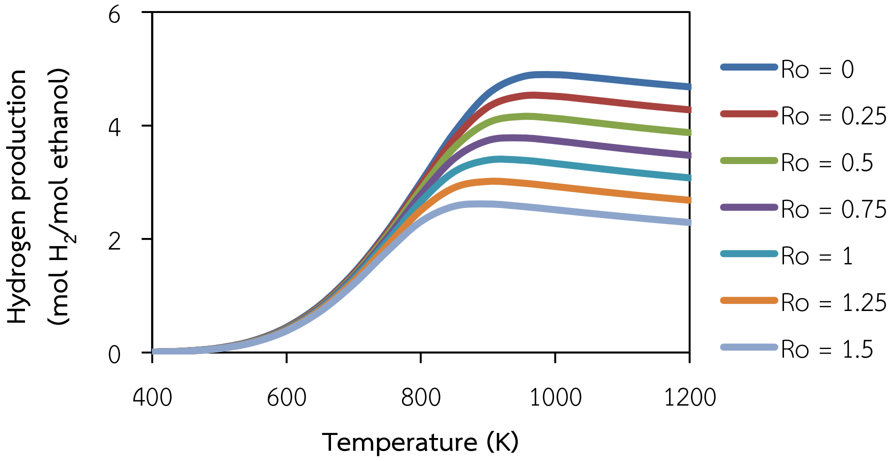


Figure 5.2: Hydrogen production vs. temperature for Ro = 0-1.5 and R = 5 from model in Figure 4.1

5.1.2 Chemical-looping reforming process (CLR)

Gas compositions at equilibrium from CLR process which used methane as reactant and NiO as oxygen carrier was investigated for validation of CLR process. Thermodynamic equilibrium gas composition for different operating pressures and temperatures is shown in Figure 5.4 compared to a thermodynamic calculation reported by Ortiz et.al [48], demonstrated in Figure 5.3. Our results are found to be similar to those presented by Ortiz et al.

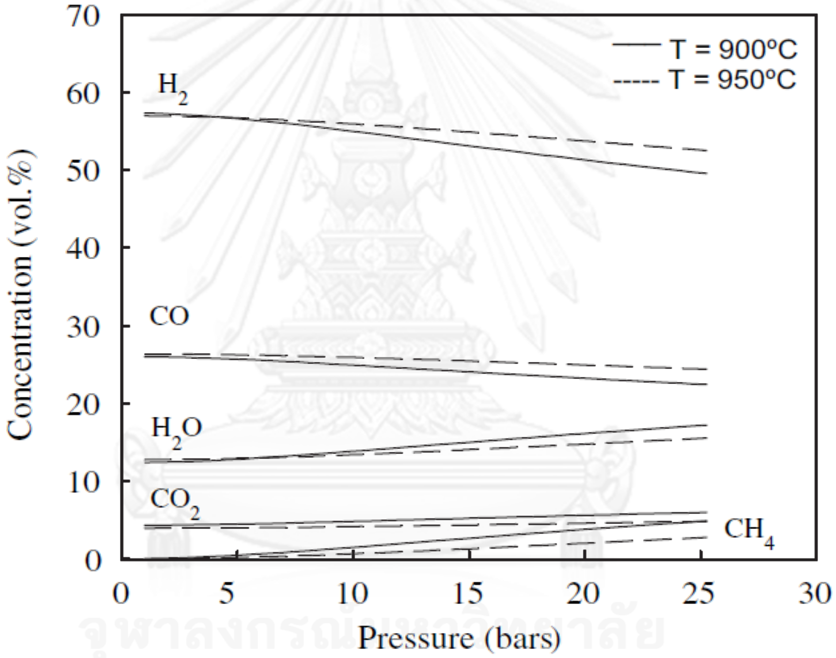


Figure 5.3: Thermodynamic equilibrium gas composition for different operating pressures and temperatures from Ortiz et.al [48]

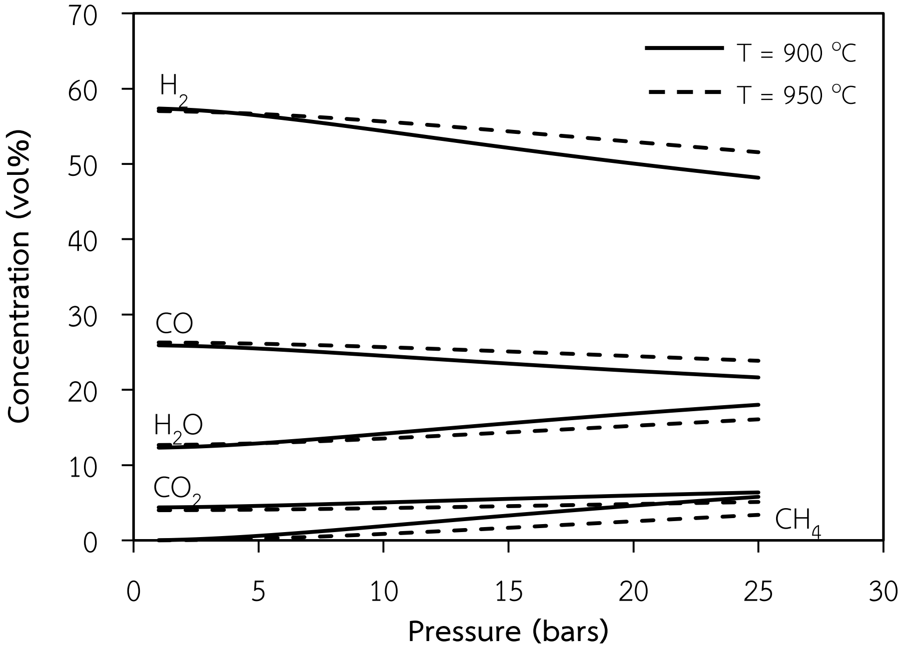


Figure 5.4: Thermodynamic equilibrium gas composition for different operating pressures and temperatures from model in Figure 4.2

5.1.3 Sorption enhanced process (SE)

Sorption enhanced process was validated by applying propane as raw material and CaO as CO_2 adsorbent for hydrogen production compared to those investigated by Wang et.al [49]. Figure 5.5 presents their results of hydrogen produced per mole of propane as a function of water to propane ratio (WPR) and temperature at atmospheric pressure. Figure 5.6 presents our simulation results of gas compositions at equilibrium for different operating pressures and temperatures. It can be confirmed that the model used for simulation can be validated. However, for low WPR (1 and 3), the difference of trends between 2 graphs (Figure 5.5 and Figure 5.6) is found because carbon formation performed and Aspen Plus program cannot simulate without errors.

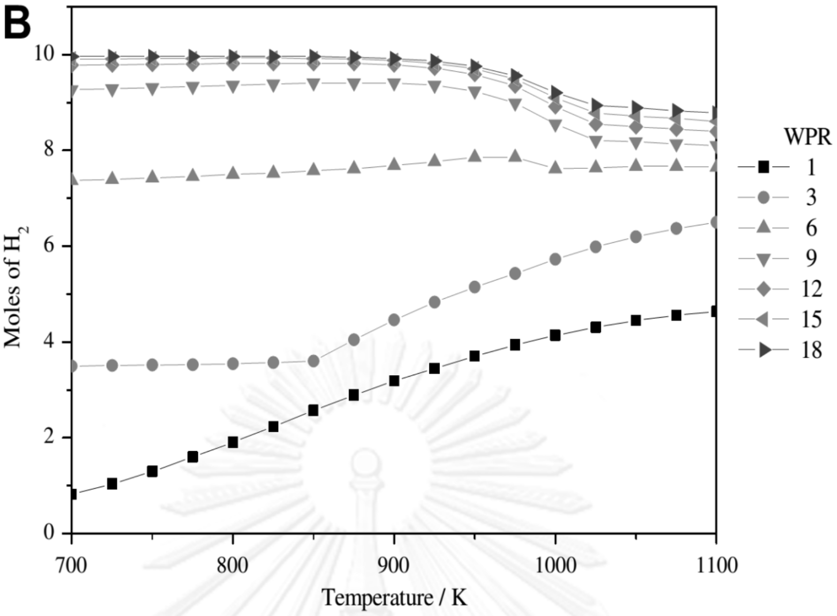


Figure 5.5: Moles of hydrogen produced per mole of propane as a function of WPR and temperature at atmospheric pressure for sorption enhanced steam reforming (SESR) from Wang et.al [49]

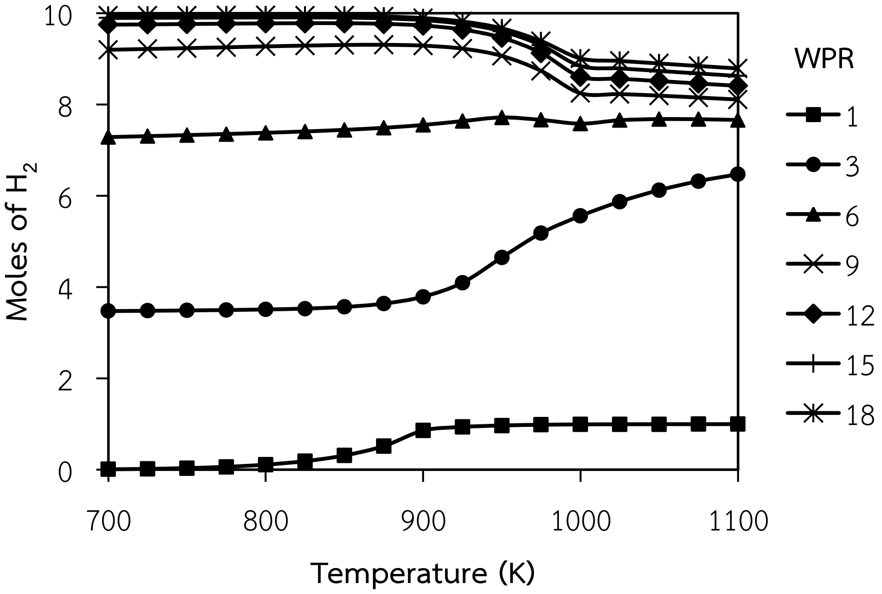


Figure 5.6: Moles of hydrogen produced per mole of propane as a function of WPR and temperature at atmospheric pressure for sorption enhanced steam reforming (SESR) from model in Figure 4.3

5.1.4 Sorption enhanced chemical-looping process (SE-CLR)

For sorption enhanced chemical-looping process, validation was performed by using methane as reactant, NiO as oxygen carrier, and CaO as CO_2 adsorbent. Process performance at thermodynamic equilibrium as a function of temperature at 1 bar, H_2O/CH_4 of 2, NiO/CH_4 of 1, and CaO/CH_4 of 1 was investigated. Our results (Figure 5.8) are in good agreement with those reported by Ryden and Ramos [36] (Figure 5.7).

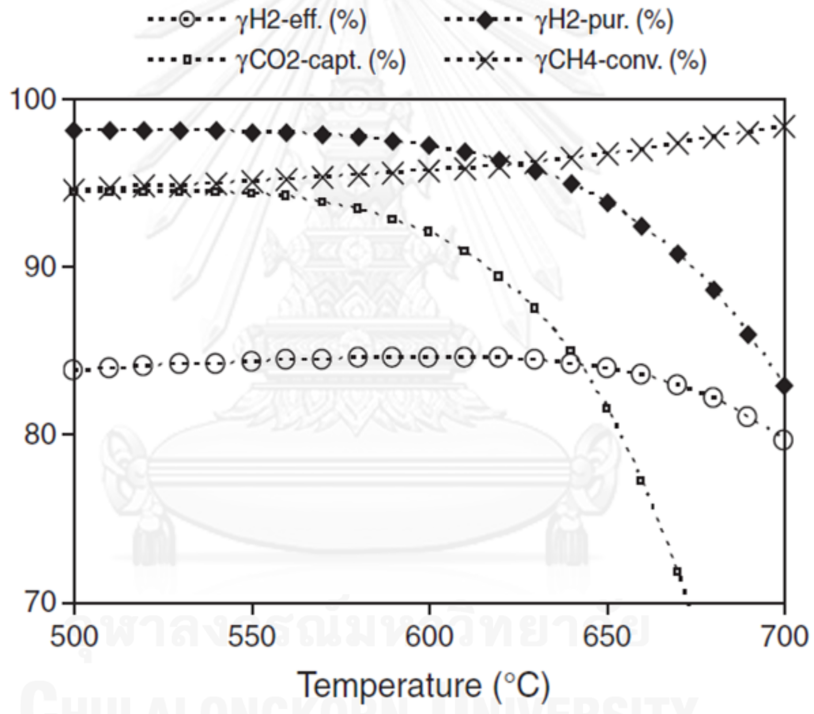


Figure 5.7: Process performance at thermodynamic equilibrium as function of temperature with P =1 bar, H_2O/CH_4=2, NiO/CH_4=1, CaO/CH_4=1 from Ryden and Ramos [36]

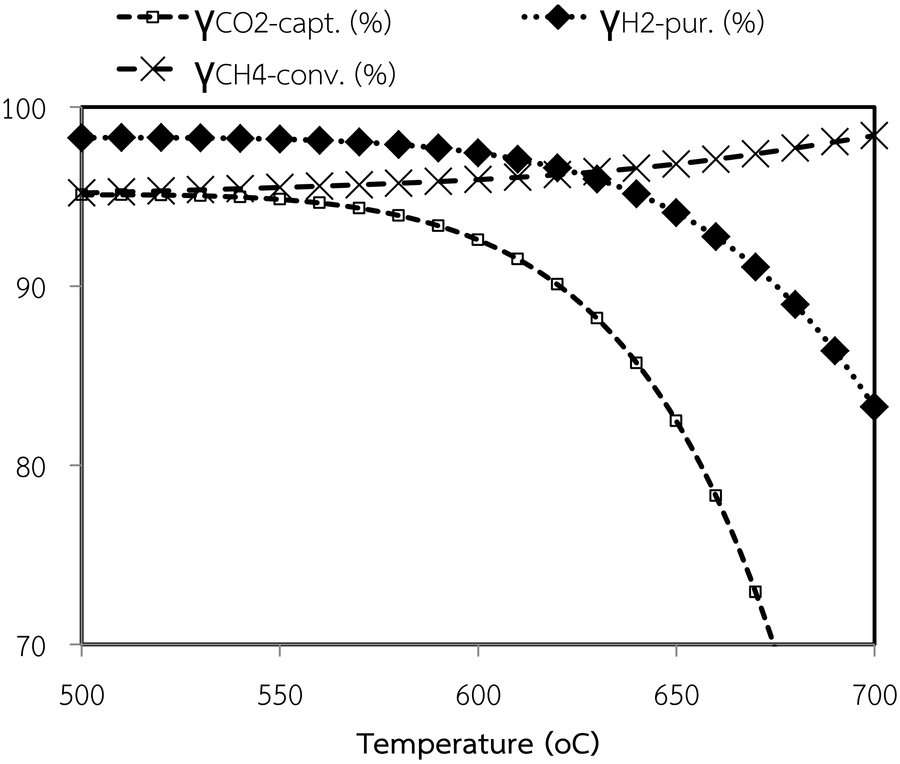


Figure 5.8: Process performance at thermodynamic equilibrium as function of temperature with P =1 bar, H_2O/CH_4=2, NiO/CH_4=1, CaO/CH_4=1 from model in Figure 4.4

5.2 Performance comparison of different processes for hydrogen production from corn stover

5.2.1 Base case condition

Process performances of autothermal reforming (ATR), chemical-looping reforming (CLR), sorption enhanced (SE) and sorption enhanced chemical-looping reforming (SE-CLR) at base case condition are summarized in Table 5.1. All processes were operated at 1 bar with 480 °C of pyrolyser and 600 °C of reformer and 3 kg/h of corn stover was fed with SER = 5. The results show that 100 % bio-oil conversion was obtained for all processes but hydrogen yield and hydrogen purity obtained from SE and SE-CLR processes are 169.2 g H_2/ kg corn stover and 95.9%, respectively, which are higher than those obtained from ATR and CLR processes of 152.7 g H_2/ kg corn stover of yield and 63.3% purity. These imply that the presence of CaO significantly results in higher hydrogen yield and hydrogen purity. However, for energy consumption, ATR and CLR processes consume similar value of ca. 8 kW whereas SE and SE-CLR process consumes greater amount of 12 kW.

Table 5.1: Process performance of different processes for hydrogen production from corn stover at base case condition

Parameters	ATR	CLR	SE	SE-CLR
Corn stover feed rate (kg/h)	3	3	3	3
Steam equivalence molar ratio (SER)	5	5	5	5
Pyrolysis temperature (°C) [Pyrolyser]	480	480	480	480
Reforming temperature (°C) [Reformer]	600	600	600	600
Calcination temperature (°C) [Calcination reactor]	-	-	900	900
Oxidation temperature (°C) [Air reactor]	-	1000	-	1000
HTS temperature (°C)	350	350	-	-
LTS temperature (°C)	250	250	-	-
Pressure (bar)	1	1	1	1
OER	0.1	-	0.1	-
NER	-	0.1	-	0.1
CER	-	-	2	2
CNB	-	0.31	-	3.05
CCB	-	-	6.2	62.0
α	-	-	-	0.9
Bio-oil conversion (%)	100	100	100	100
Hydrogen yield (g H_2/ kg corn stover)	152.7	152.7	169.2	169.2
Hydrogen purity (%)	63.3	63.3	95.9	95.9
Energy consumption (kW)	7.6	7.8	12.1	12.5

5.2.2 Investigation of carbon formation region

In this work, the effect of operating condition on process performances was considered in the area where no carbon is formed for practical criteria. As such, the effect of operating conditions on carbon formation was firstly investigated. In Figure 5.9-5.11 are shown the effect of SER, OER, NER and CER on carbon formation.

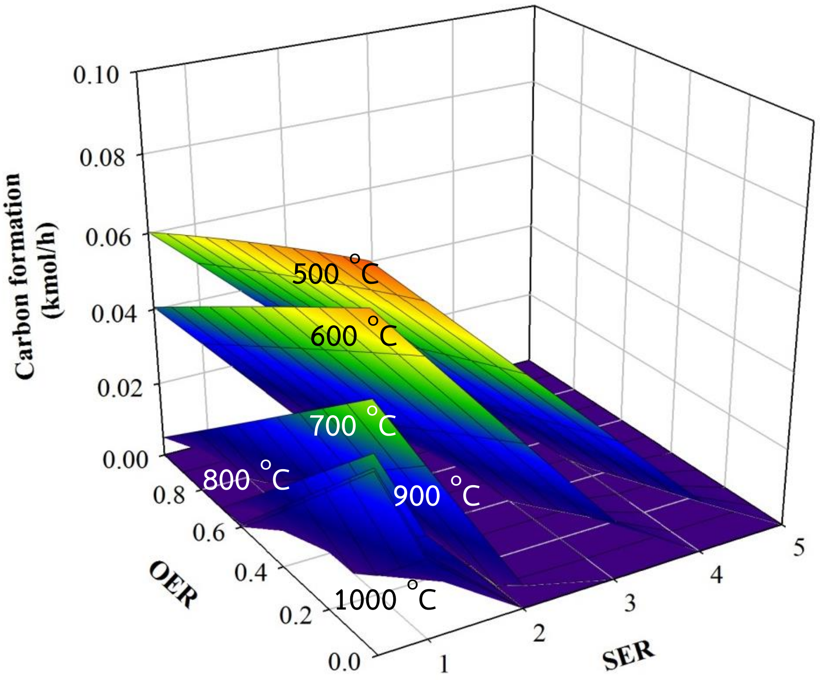


Figure 5.9: Carbon formation from various oxygen equivalence ratios (OER), steam equivalence ratios (SER) and reforming temperature for ATR process

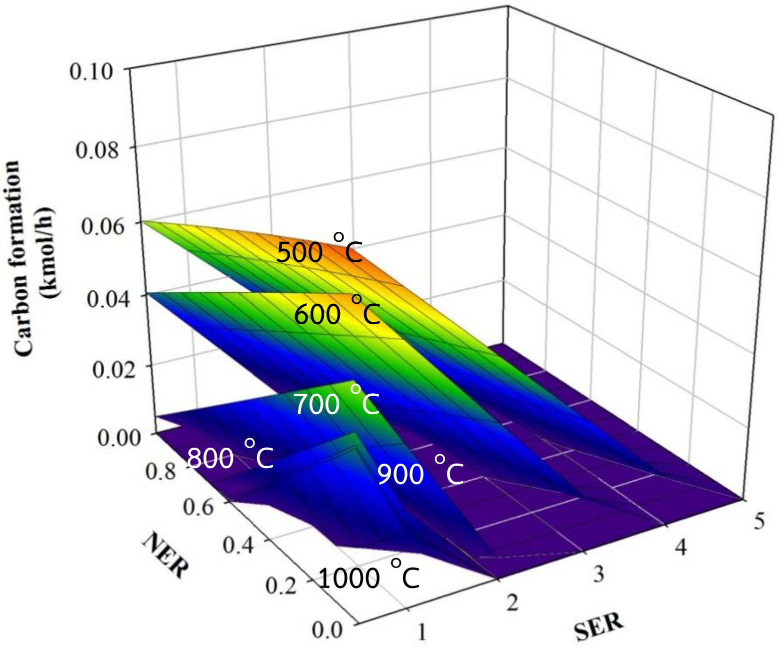


Figure 5.10: Carbon formation from various NiO equivalence ratios (NER), steam equivalence ratios (SER) and reforming temperature for CLR process

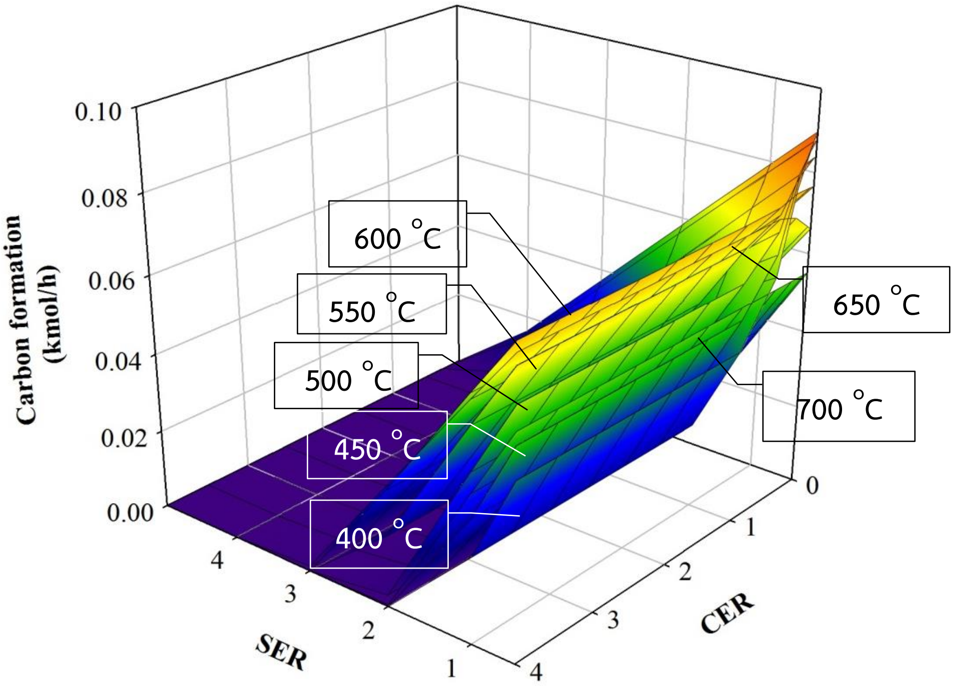


Figure 5.11: Carbon formation from various CaO equivalence ratios (CER), steam equivalence ratios (SER) and reforming temperature for SE process

As seen in Figure 5.9-5.10, higher SER decreases the carbon formation due to higher amount of steam shift equilibrium of water gas reaction (Eq. 4.14). Similarly, increase of OER and NER results in lower carbon formation due to oxidation reaction of carbon in Eq. 4.15 and Eq. 4.16. Increase of reforming temperature also leads to lower carbon formation because endothermic water gas reaction (Eq. 4.14) shifts forward.

Figure 5.11 presents the effects of SER, CER and reforming temperature on carbon formation. Lower carbon formation is observed at higher CER because higher amount of CaO shifts CO_2 adsorption by carbonation reaction (Eq. 4.20), which results in oxidation of carbon (Eq. 4.15) shifts forward. For SER = 0-4, carbon formation is found in the temperature range of 400-600 $^{\circ}$C increasing temperature leads to an increase of carbon formation in this temperature range. This shows that temperature affects less on endothermic water gas reaction (Eq. 4.14) and steam reforming of hydrocarbon compounds (Eq. 4.3) than shift backward by reducing CO_2 in Boudouard reaction (Eq. 4.17) which results in increasing of carbon for 400-600 $^{\circ}$C. On the other hand, lower amount of carbon was observed at temperature higher than 600 $^{\circ}$C, indicating that water gas reaction (Eq. 4.14) and endothermic steam reforming of hydrocarbon compounds (Eq. 4.3) are predominant rather than shifted backward by CO_2 adsorption (Eq. 4.20) in Boudouard reaction (Eq. 4.17) for temperature above 600 $^{\circ}$C.

As such, for the remaining of this study, the operating temperature was considered at above 4 of SER (SER = 5-8) and temperature higher than 400 $^{\circ}$C.

5.2.2.1 Effect of operating conditions on autothermal reforming process (ATR)

The effects of OER and SER on hydrogen yield, hydrogen purity and energy consumption are shown by Figure 5.12-5.14, respectively. The reforming reaction was operated at 600 °C and 1 bar. At fixed OER, increase of SER results in higher hydrogen yield and hydrogen purity because higher amount of steam shift equilibrium of endothermic steam reforming (Eq. 4.2-4.3) forward. However, this leads to higher energy consumption because more heat is required for overall endothermic reaction in reformer and preheating-steam unit. For SER above 5, hydrogen yield and purity slightly increases because of limited of bio-oil. At fixed of SER, increase of OER results in lower hydrogen yield and hydrogen purity (Figure 5.12-5.13). This shows that when bio-oil was limited, higher amount of oxygen feed to process causes higher conversion of H_2 and CO to other gaseous products (CO_2, H_2O) by oxidation reactions (Eq. 4.8 and 4.10). This leads to lower energy consumption (Figure 5.14) because of highly exothermic oxidation reaction of H_2 and CO occurred with excess oxygen. The range of hydrogen yield is 128-172 g H_2/ kg corn stover and maximum hydrogen yield is 172 g H_2/ kg corn stover at 0.1 of OER and 8 of SER. For hydrogen purity, 59-66% of purity is obtained and maximum purity is 66% at OER of 0.1 and SER of 8. Energy consumption is in the range of 6.4-11.5 kW and minimum of energy consumption is 6.4 kW at SER of 5 and OER of 1.

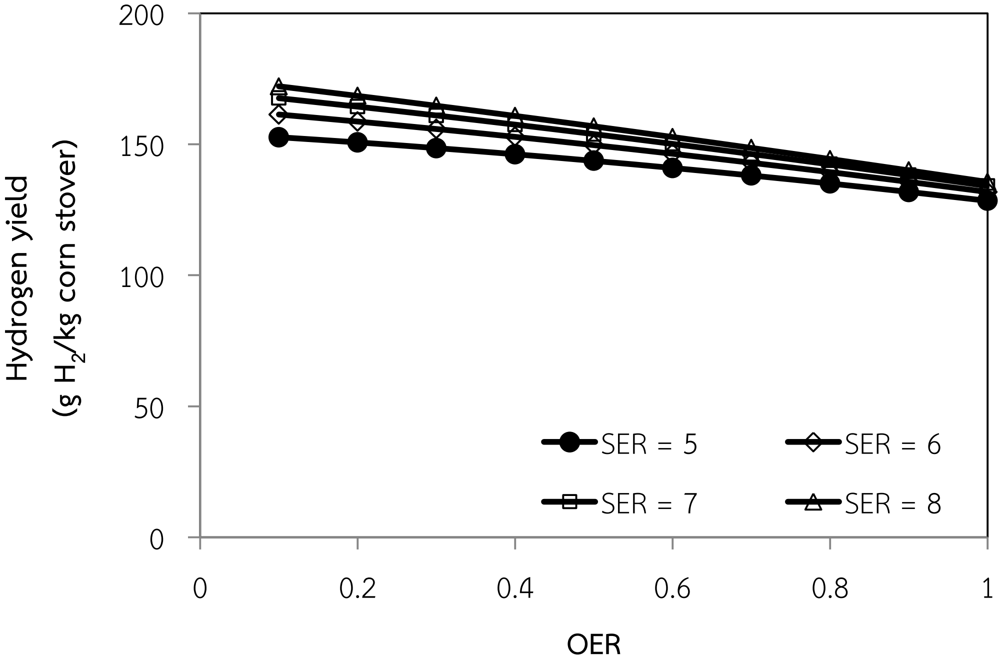


Figure 5.12: Hydrogen yield from various oxygen equivalence ratios (OER) and steam equivalence ratios (SER) for ATR process at 600 °C, 1 bar

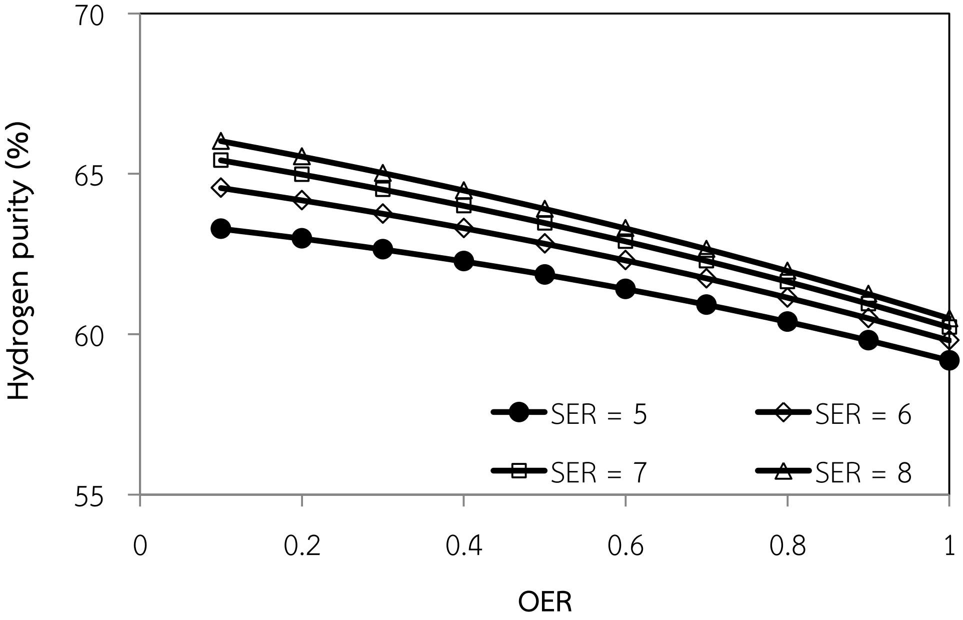


Figure 5.13: Hydrogen purity from various oxygen equivalence ratios (OER) and steam equivalence ratios (SER) for ATR process at 600 °C, 1 bar

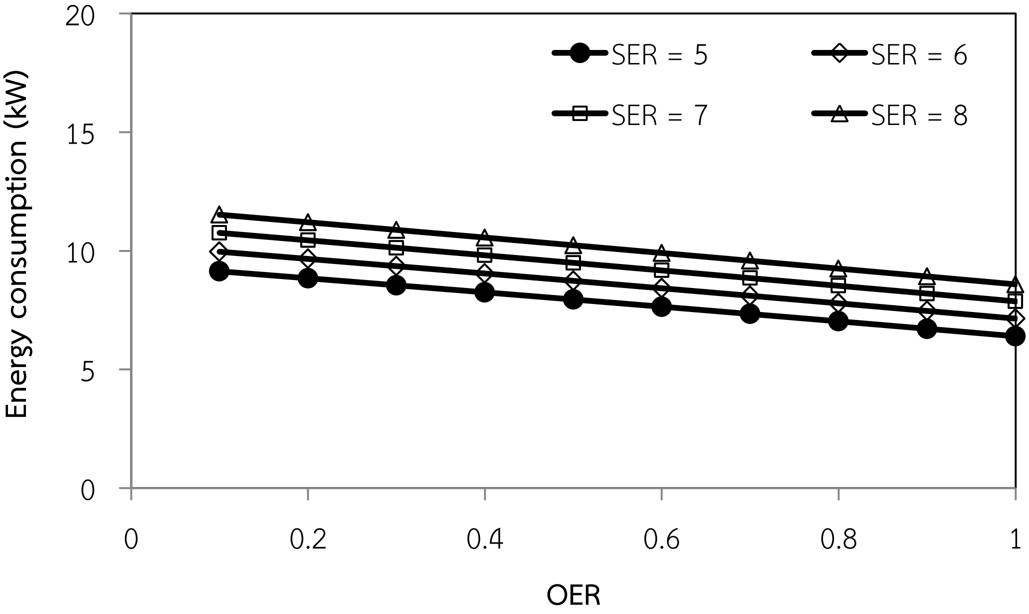


Figure 5.14: Energy consumption from various oxygen equivalence ratios (OER) and steam equivalence ratios (SER) for ATR process at 600 °C, 1 bar

5.2.2.2 Effect of operating conditions on chemical-looping reforming process (CLR)

Hydrogen yield, hydrogen purity and energy consumption from various NERs and SERs for CLR process operated at 600 °C and 1 bar are presented in Figure 5.15-5.17, respectively. At constant SER, increase of NER results in lower hydrogen yield, hydrogen purity, and energy consumption because higher amount of NiO shifts the equilibrium of oxidation reactions of H_2 and CO (Eq. 4.9 and Eq. 4.11), which are exothermic. On the other hand, higher SER leads to higher hydrogen yield and hydrogen purity because increase amount of steam results in shift equilibrium of Eq. 4.2-4.3 forward. SER slightly effects on energy consumption because oxidation of bio-oil by NiO is more prominent than steam reforming reaction. However, for SER above 5, hydrogen yield and hydrogen purity slightly increase because of limited bio-oil.

The range of hydrogen yield is 128-172 g H_2/ kg corn stover and maximum hydrogen yield is 172 g H_2/ kg corn stover at NER of 0.1 and SER of 8. For hydrogen purity, 59-66% of purity is obtained and maximum purity is 66% at OER of 0.1 and SER of 8. Energy consumption is in the range of 1.5-5 kW and minimum of energy consumption is 1.5 kW at SER = 8 at NER = 1.

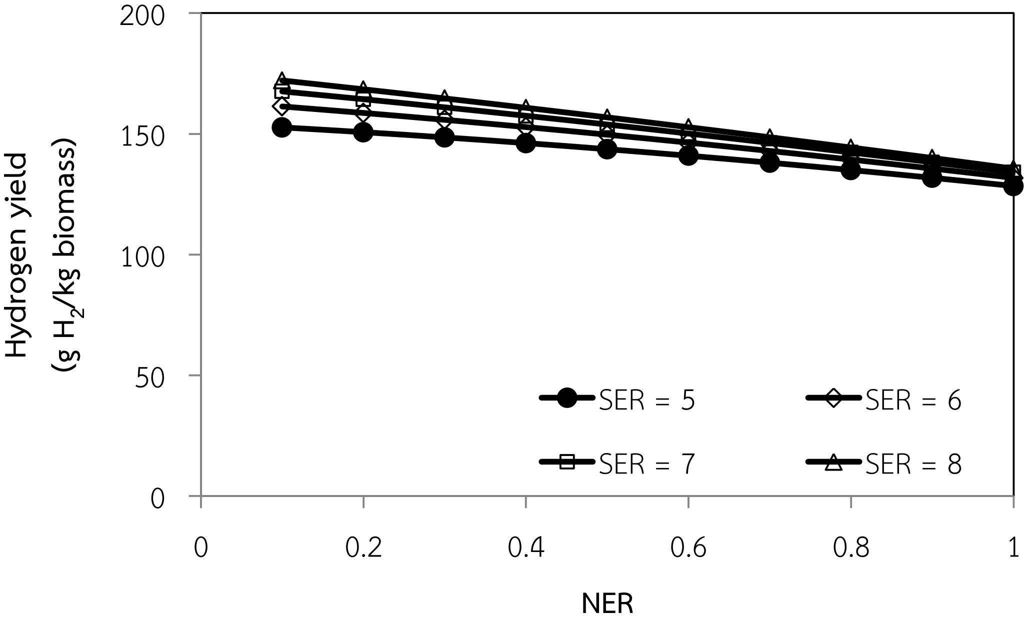


Figure 5.15: Hydrogen yield from various NiO equivalence ratios (NER) and steam equivalence ratios (SER) for CLR process at 600 °C, 1 bar

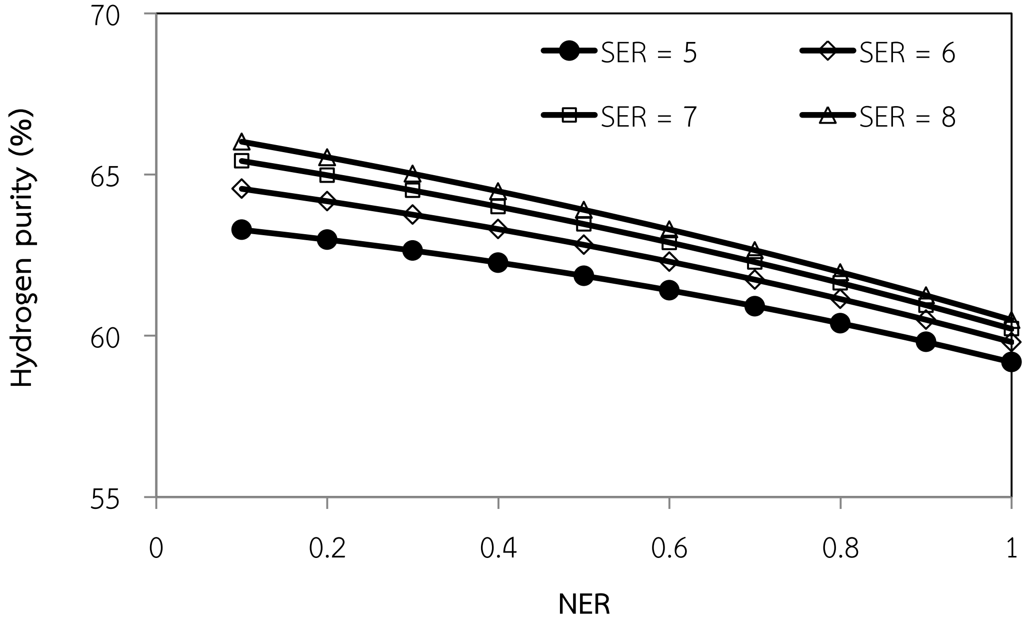


Figure 5.16: Hydrogen purity from various NiO equivalence ratios (NER) and steam equivalence ratios (SER) for CLR process at 600 °C, 1 bar

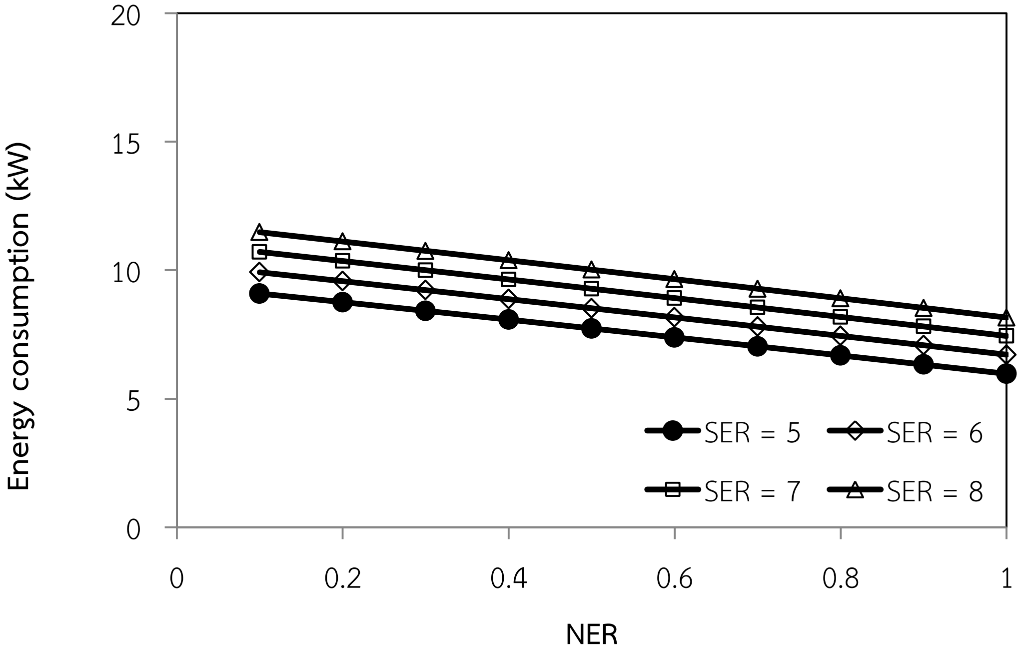


Figure 5.17: Energy consumption from various NiO equivalence ratios (NER) and steam equivalence ratios (SER) for CLR process at 600 °C, 1 bar

5.2.2.3 Effect of operating conditions on sorption enhanced process (SE)

Figure 5.18-5.20 show the process performances of SE for various CERs and SERs at 600 °C and 1 bar. Higher CER at constant SER results in higher hydrogen yield and hydrogen purity only below CER of 2. This result shows that excess amount of CaO insignificantly affect hydrogen yield and hydrogen purity because of limited carbon dioxide in the reformer. Energy consumption tends to increase for higher CER because higher energy for calcination is required for higher amount of CaO. For constant CER, increase of SER leads to higher hydrogen yield and energy consumption due to the endothermic steam reforming reactions (Eq. 4.2-4.3) are shifted forward. However, higher SER insignificantly effects on hydrogen purity at constant amount of CER because carbonation reaction of CaO (Eq. 4.20) predominantly effects on hydrogen purity. The range of hydrogen yield is 126-183 g H_2/ kg corn stover and maximum hydrogen yield is 183 g H_2/ kg corn stover at CER = 2-4 and SER = 6-8. Hydrogen purity of 61-98% is obtained and maximum purity is 98% at CER = 2-4 and SER = 5-8. Energy consumption is in the range of 11.7-16.5 kW and minimum of energy consumption is 11.7 kW at SER = 5 and CER = 0.05.

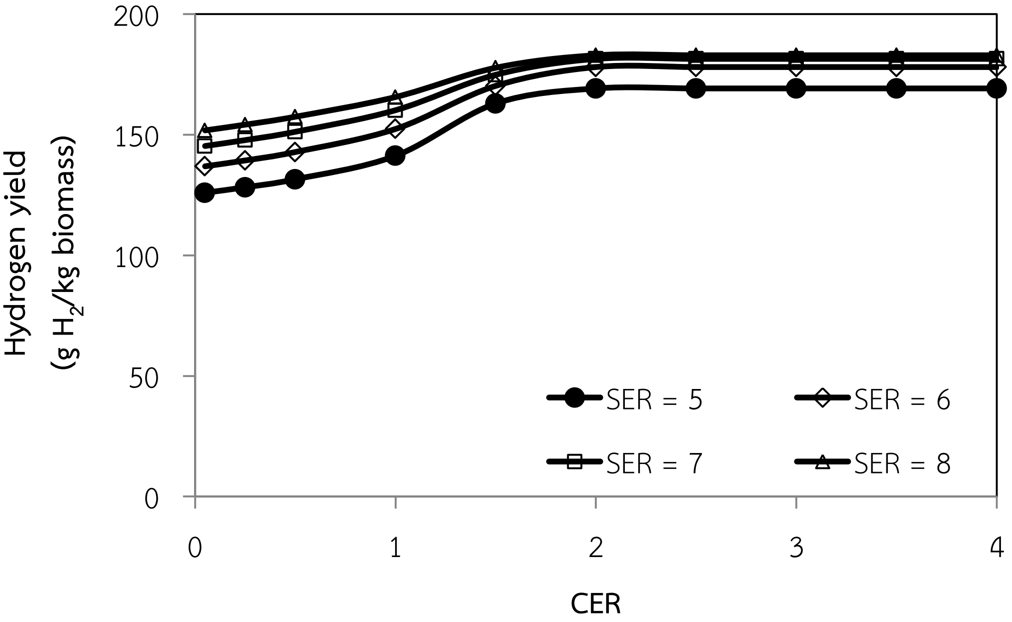


Figure 5.18: Hydrogen yield from various CaO equivalence ratios (CER) and steam equivalence ratios (SER) for SE process at 600 °C, 1 bar

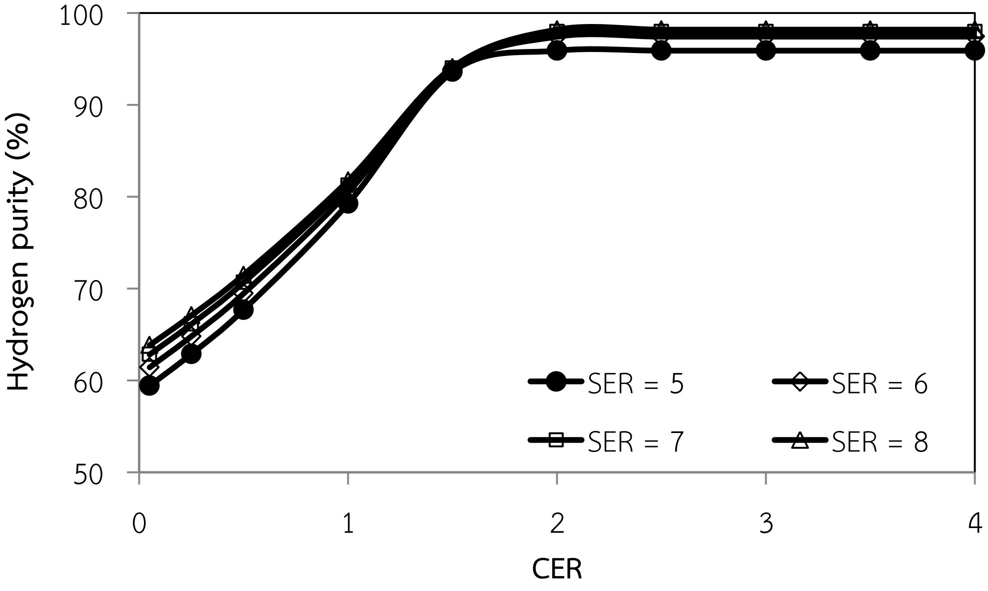


Figure 5.19: Hydrogen purity from various CaO equivalence ratios (CER) and steam equivalence ratios (SER) for SE process at 600 °C, 1 bar

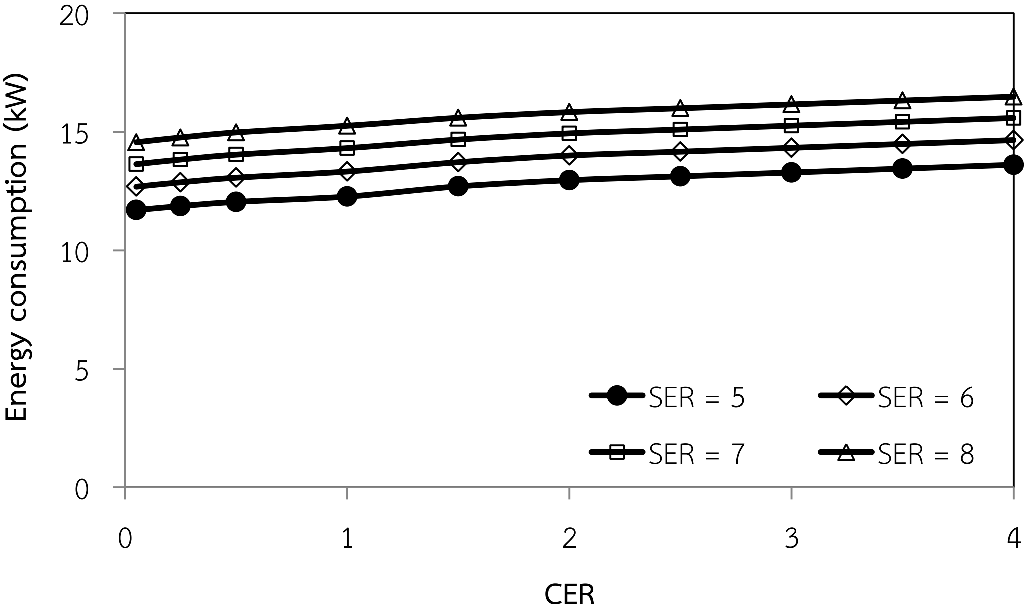


Figure 5.20: Energy consumption from various CaO equivalence ratios (CER) and steam equivalence ratios (SER) for SE process at 600 °C, 1 bar

5.2.3 Effects of temperature and pressure on process performances

5.2.3.1 Autothermal reforming process (ATR)

Effects of reforming temperature and pressure on hydrogen yield, hydrogen purity and energy consumption for ATR process at SER = 5 and OER = 0.1 are presented in Figure 5.21-5.23. Hydrogen yield, hydrogen purity and energy consumption are found to decrease with increasing pressure for temperature range of 500-800 °C. But over 800 °C, hydrogen yield, hydrogen purity and energy consumption are insignificantly affected by pressure as reactants were completely reacted at temperature above 800 °C. For the range of 500-800 °C, increasing pressure leads to a reduction of hydrogen yield and purity and energy consumption due to the equilibrium shifts backward according to Le Chartelier’s principle for steam reforming (Eq. 4.2-4.3) and oxidation reaction (Eq. 4.4 and 4.6) in autothermal reformer. This shows that overall reaction in reformer is endothermic. At the same pressure, higher temperature results in higher hydrogen yield and purity and energy consumption because of endothermic reaction occurs well at high temperature. Maximum hydrogen yield and hydrogen purity of ATR process are 181 g H_2/kg corn stover and 67 %, respectively. These values are observed at operating pressure of 1 bar for temperature range of 800-1000 °C. Minimum energy consumption of 5.2 kW is obtained at 25 bars and 500 °C. Hydrogen yield of 20-181 g H_2/kg corn stover, hydrogen purity of 18.5-67 %, and energy consumption of 5.2-8.2 kW are obtained in the temperature range of 500-1000 °C and pressure 1-25 bars.

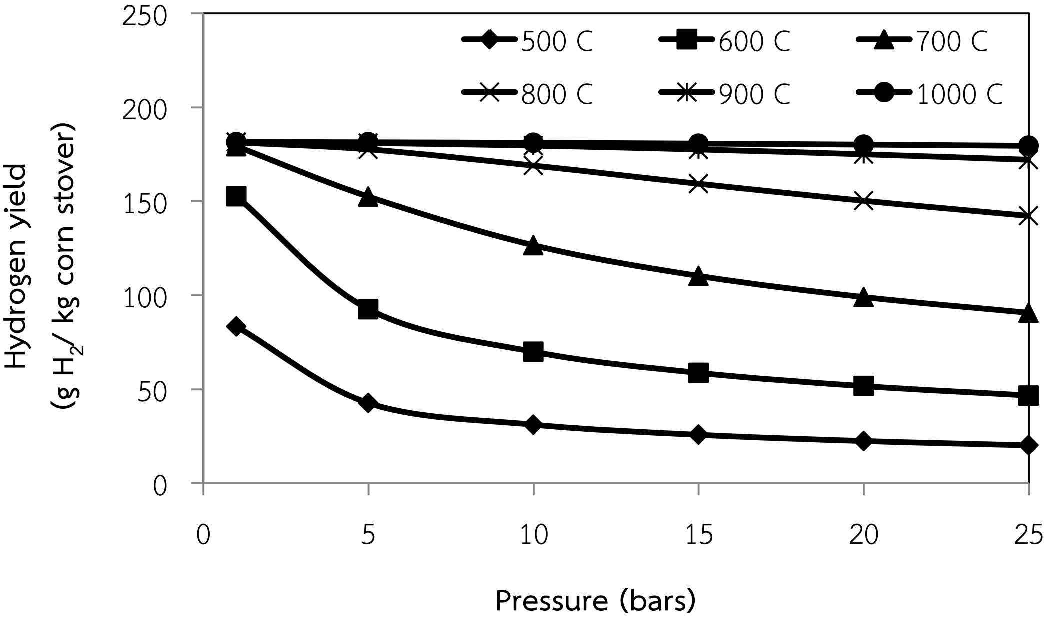


Figure 5.21: Hydrogen yield from various reforming temperature and pressure for ATR process at SER = 5, OER = 0.1

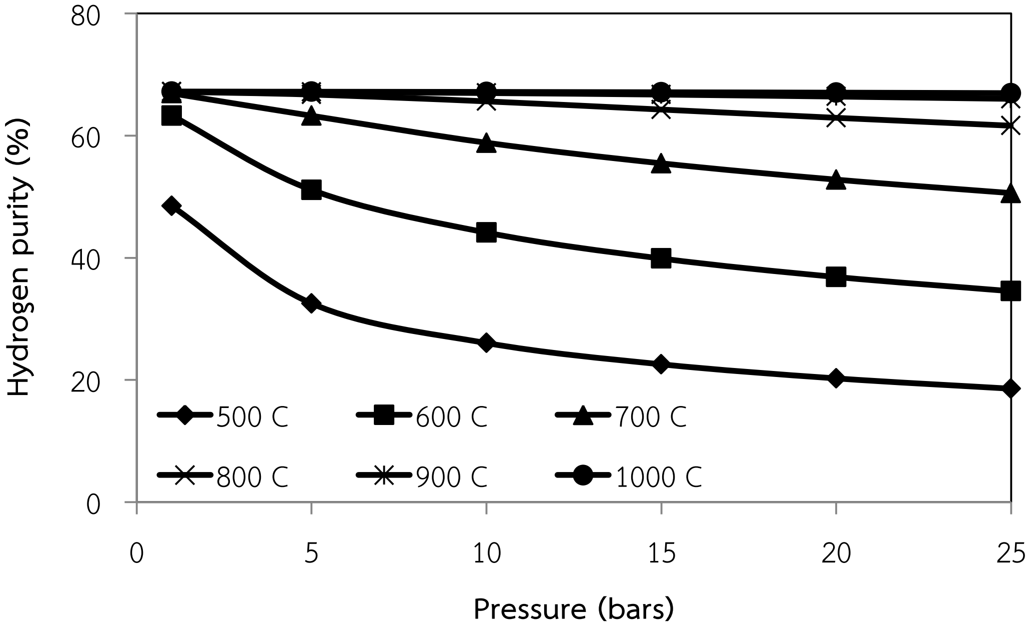


Figure 5.22: Hydrogen purity from various reforming temperature and pressure for ATR process at SER = 5, OER = 0.1

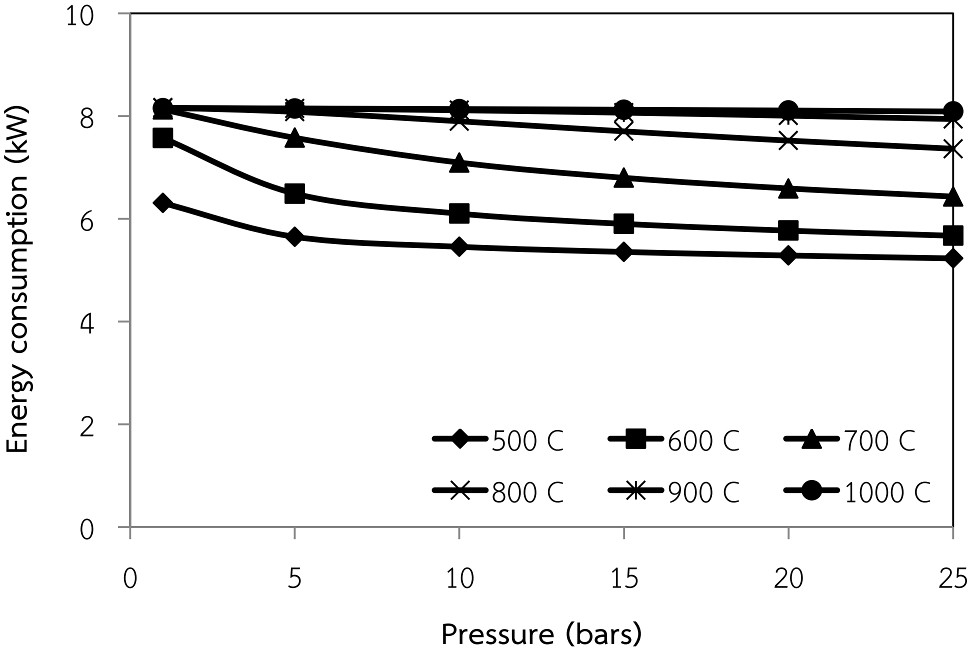


Figure 5.23: Energy consumption from various reforming temperature and pressure for ATR process at SER = 5, OER = 0.1

5.2.3.2 Chemical-looping reforming process (CLR)

Figure 5.24-5.26 show the effect of reforming temperature and pressure on hydrogen yield, hydrogen purity and energy consumption for CLR process at SER = 5 and NER = 0.1. Similar trend of hydrogen yield, hydrogen purity and energy consumption to that of ATR process is observed in case of CLR. The values of hydrogen yield, hydrogen purity and energy consumption are found to decrease with increasing pressure for 500-800 ^{o}C but are insignificantly affected by pressure as reactants were completely reacted at temperature above 800 ^{o}C. For the temperature range of 500-800 ^{o}C, increasing pressure leads to a reduction of hydrogen yield, hydrogen purity, and energy consumption due to the equilibrium shifts backward according to Le Chartelier's principle for steam reforming (Eq. 4.2-4.3) and oxidation reaction (Eq. 4.5 and Eq. 4.7) in reformer. This shows that overall reaction in reformer is endothermic. At the same pressure, higher temperature results in higher hydrogen yield and purity and energy consumption because of endothermic reaction occurs well at high temperature. Maximum hydrogen yield and hydrogen purity of ATR process are 181 g H_2/kg corn stover and 67 % which are observed at 1 bar for 800-1000 ^{o}C. Minimum energy consumption 4.95 kW is obtained at 25 bars and 500 ^{o}C. The 20-181 g H_2/kg corn stover of hydrogen yield, 18.5-67 % of hydrogen purity and 4.95-9.7 kW of energy consumption are obtained in the range of 500-1000 ^{o}C and 1-25 bars. For comparison, CLR consumes less energy than ATR at low temperature (< 600 ^{o}C) and consumes more energy at high temp (> 600 ^{o}C). This is because energy generated from air reactor in CLR reactor is insufficient at high reforming temperature.

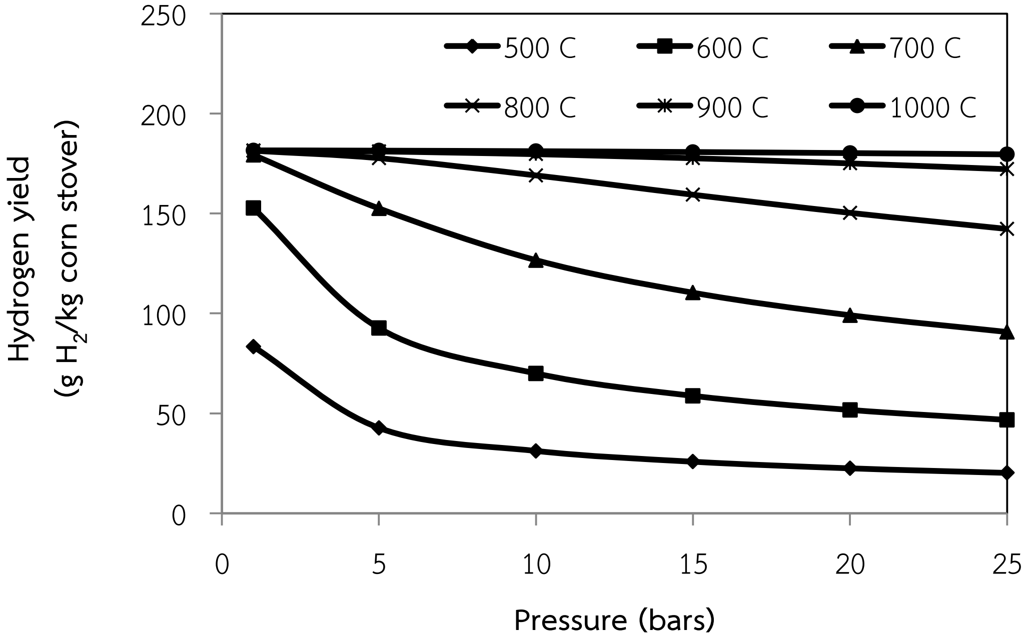


Figure 5.24: Hydrogen yield from various reforming temperature and pressure for CLR process at SER = 5, NER = 0.1

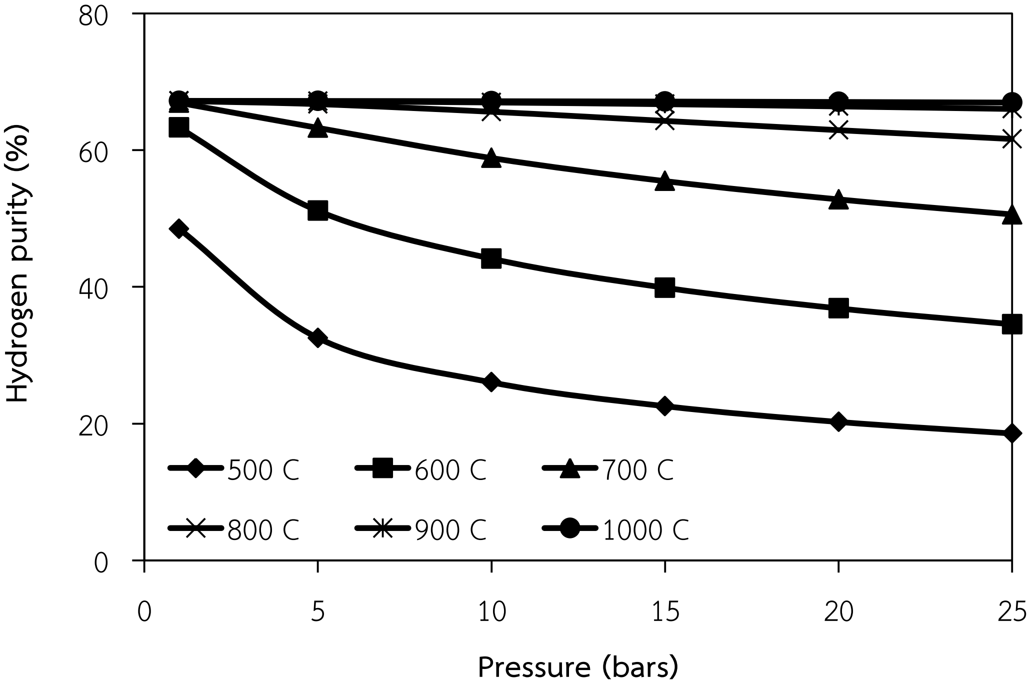


Figure 5.25: Hydrogen purity from various reforming temperature and pressure for CLR process at SER = 5, NER = 0.1

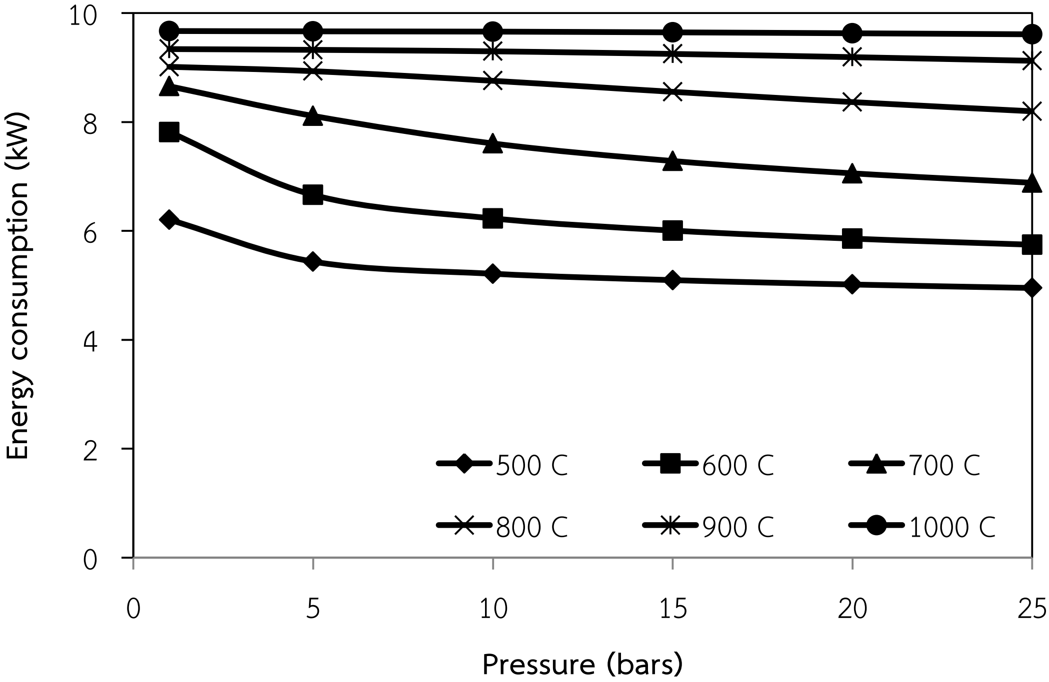


Figure 5.26: Energy consumption from various reforming temperature and pressure for CLR process at SER = 5, NER = 0.1

5.2.3.3 Sorption enhanced process (SE)

For SE process, Figure 5.27-5.29 present the effects of reforming temperature and pressure on hydrogen yield, hydrogen purity and energy consumption at SER = 5 and CER = 2. Operating conditions of this process were studied in the range of 400-700 °C and 1-25 bars. Hydrogen yield found to decrease with increasing pressure due to the equilibrium shifts backward according to Le Chartelier's principle for steam reforming (Eq. 4.2-4.3) and oxidation reaction (Eq. 4.4 and 4.6) in reformer, which are predominant compared to shift equilibrium of water-gas shift reaction (Eq. 4.12) by CO_2 adsorption (Eq. 4.20). However, at 700 °C and 1 bar, hydrogen yield is lower because exothermic carbonation reaction (Eq. 4.20) is reverse at this condition. At the same pressure, higher temperature results in higher hydrogen yield because of endothermic reaction preferable occurs at high temperature. Maximum hydrogen yield of SE process is 169 g H_2/kg corn stover observed at 1 bar for 550-600 $^{\circ}$C.

Lower hydrogen purity is obtained from increasing pressure at 400-600 $^{\circ}$C by the same reason described in the trend of hydrogen yield. At the same pressure, increasing temperature insignificantly affects hydrogen purity because CO_2 adsorption occurs well at high pressure (> 5 bars). Nevertheless, hydrogen purities at 650-700 $^{\circ}$C and 1 bar are lower than other conditions because CO_2 desorption tends to occur at high temperature and low pressure (reverse of Eq.4.12). Maximum hydrogen purity of 97 % is achieved by 400-550 $^{\circ}$C and 1 bar.

Since endothermic reaction in reformer unfavorable occurs according to Le Chartelier's principle, energy consumption was found to decrease with increasing pressure. Furthermore, higher reforming temperature leads to higher energy consumption at the same pressure because endothermic reaction in reformer occurs well at high temperature. Minimum energy consumption 9.3 kW is obtained at 25 bars and 500 $^{\circ}$C.

The 103-169 g H_2/kg corn stover of hydrogen yield, 75-97 % of hydrogen purity and 9.3-13 kW of energy consumption are obtained in the temperature range of 400-700 $^{\circ}$C and pressure 1-25 bars. For comparison in the same range of reforming temperature and pressure (500-700 $^{\circ}$C, 1-25 bars), SE process produces more hydrogen yield and hydrogen purity than those of ATR and CLR processes and consumes more energy consumption than those of ATR and CLR processes at the same conditions (Table 5.1).

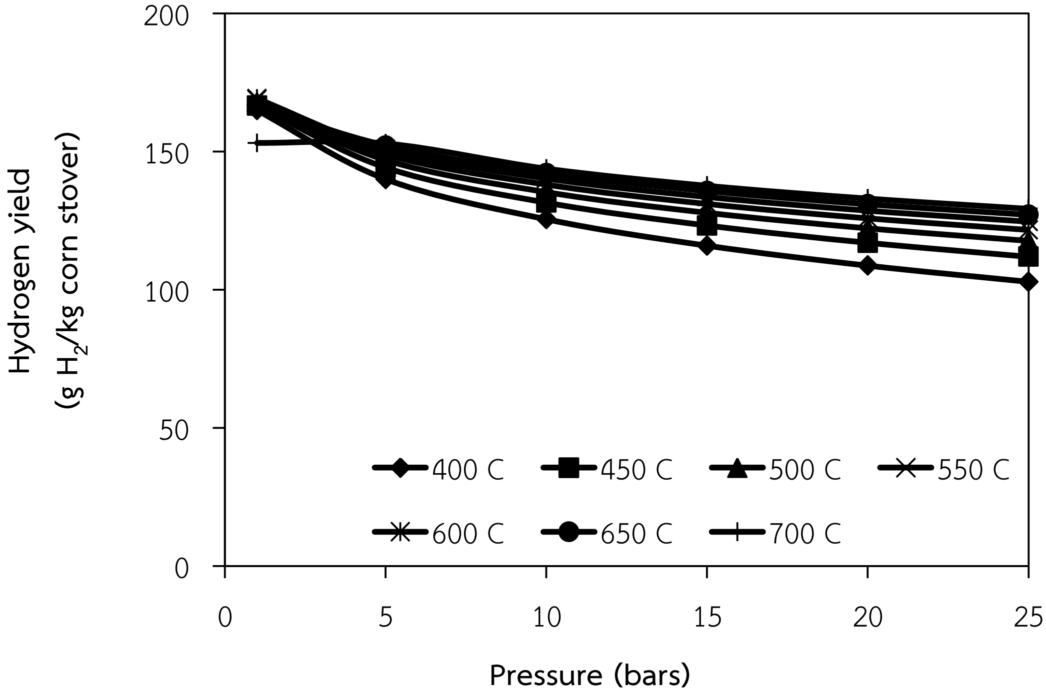


Figure 5.27: Hydrogen yield from various reforming temperature and pressure for SE process at SER = 5, CER = 2

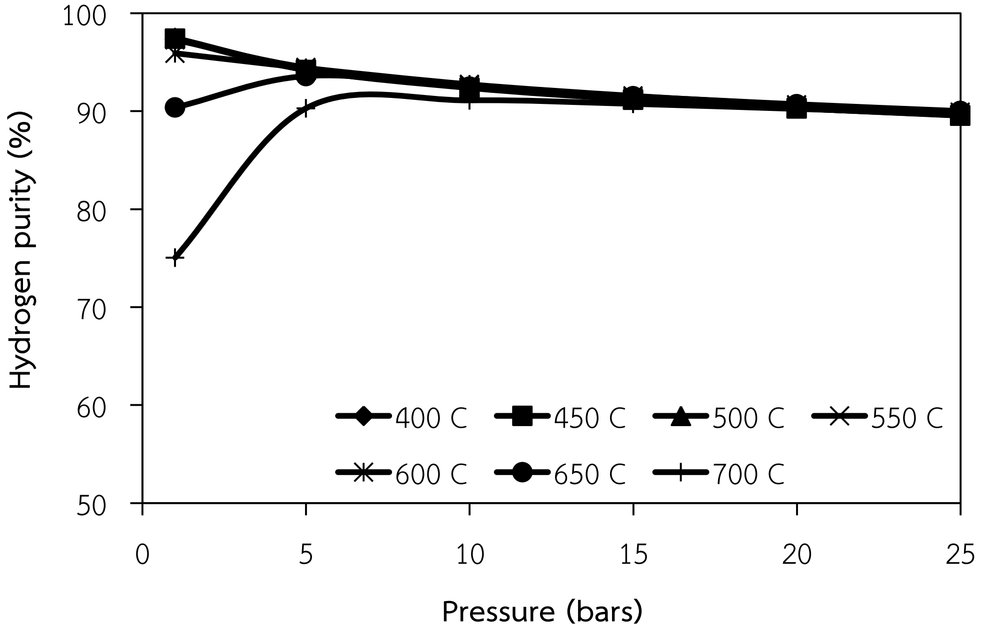


Figure 5.28: Hydrogen purity from various reforming temperature and pressure for SE process at SER = 5, CER = 2

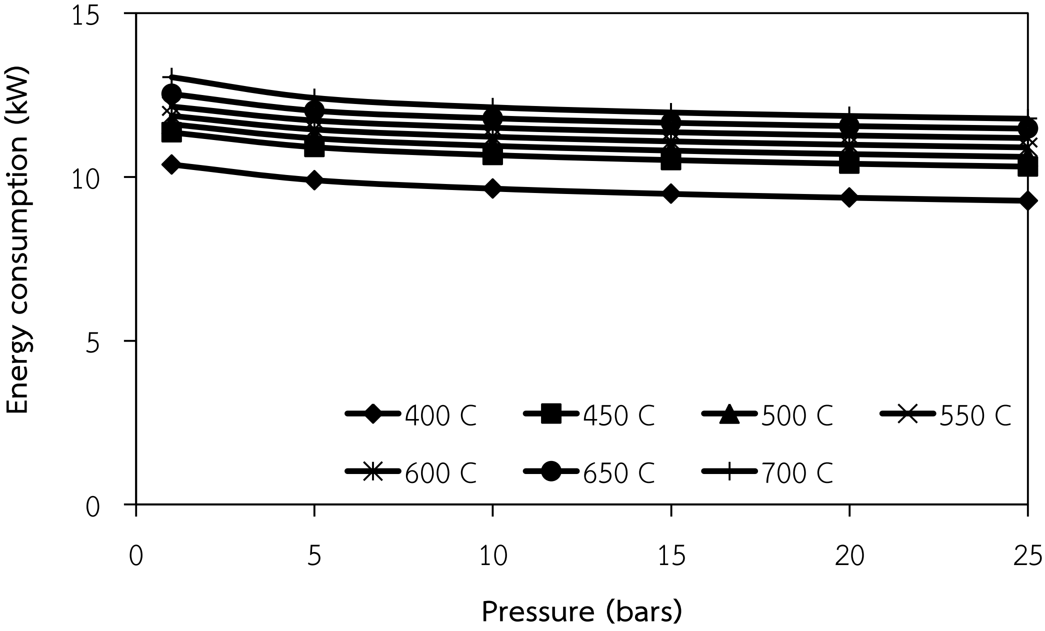


Figure 5.29: Energy consumption from various reforming temperature and pressure for SE process at SER = 5, CER = 2

5.2.3.4 Sorption enhanced chemical-looping reforming process (SE-CLR)

Figure 5.30-5.32 show the effects of reforming temperature and pressure on hydrogen yield, hydrogen purity and energy consumption at SER = 5, NER = 0.1, CER = 2 and α = 0.8 for SE-CLR process. Operating conditions of this process were studied in the range of CO_2 adsorption occurs: T = 400-700 $^{\circ}$C and P = 1-25 bars. Similar fashion of hydrogen yield, hydrogen purity and energy consumption to those observed with SE process is presented and can be described by the same reason. Equilibrium of shifts backward according to Le Chartelier's principle for steam reforming (Eq. 4.2-4.3) and oxidation reaction (Eq. 4.5 and 4.7) in reformer is applied to explain the reason of decreasing hydrogen yield and purity with increasing pressure, which can overcome shift equilibrium of water-gas shift reaction (Eq. 4.12) by CO_2 adsorption (Eq. 4.20). However, low hydrogen yield and purity at 650-700 $^{\circ}$C and 1 bar are obtained since exothermic carbonation reaction (Eq. 4.20) is reversed at this condition. At the same pressure, higher temperature results in higher hydrogen yield because of endothermic reaction occurs at high temperature but higher temperature insignificantly results in hydrogen purity because CO_2 adsorption occurs at high pressure (> 5 bars). Maximum hydrogen yield of SE-CLR process is 169 g H_2/kg corn stover which is observed at 1 bar for 550-600 $^{\circ}$C and maximum hydrogen purity is 97.5 % at 1 bar and 400-550 $^{\circ}$C.

Similarly, energy consumption was found to decrease with increasing pressure due to endothermic reaction in reformer does not likely occur according to Le Chartelier's principle. Moreover, higher reforming temperature results in higher energy consumption at the same pressure because endothermic reaction in reformer occurs at high temperature. Minimum energy consumption 9 kW is obtained at 25 bars and 500 $^{\circ}$C.

The 103-169 g H_2/kg corn stover of hydrogen yield, 75-97 % of hydrogen purity and 9-12 kW of energy consumption are obtained in the range of 400-700 $^{\circ}$C and 1-25 bars. For comparison in the same range of reforming temperature and pressure (500-700 $^{\circ}$C, 1-25 bars), SE-CLR process produces more hydrogen yield and hydrogen purity than those obtained from either ATR or CLR processes but performs the equivalent values with SE process. Furthermore, SE-CLR process consumes more energy consumption than one of ATR, CLR and SE processes due to heat for preheating more solids is required for SE-CLR process. This can be noticed from the base case conditions (Table 5.1).

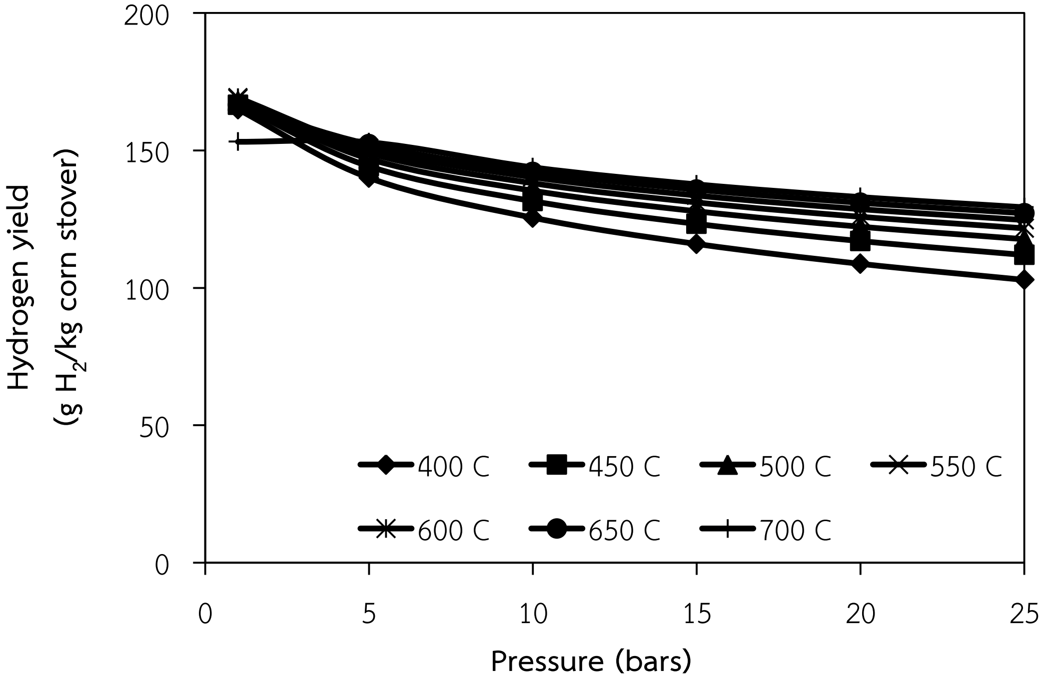


Figure 5.30: Hydrogen yield from various reforming temperature and pressure for SE-CLR process at SER = 5, NER = 0.1, CER = 2, α = 0.8

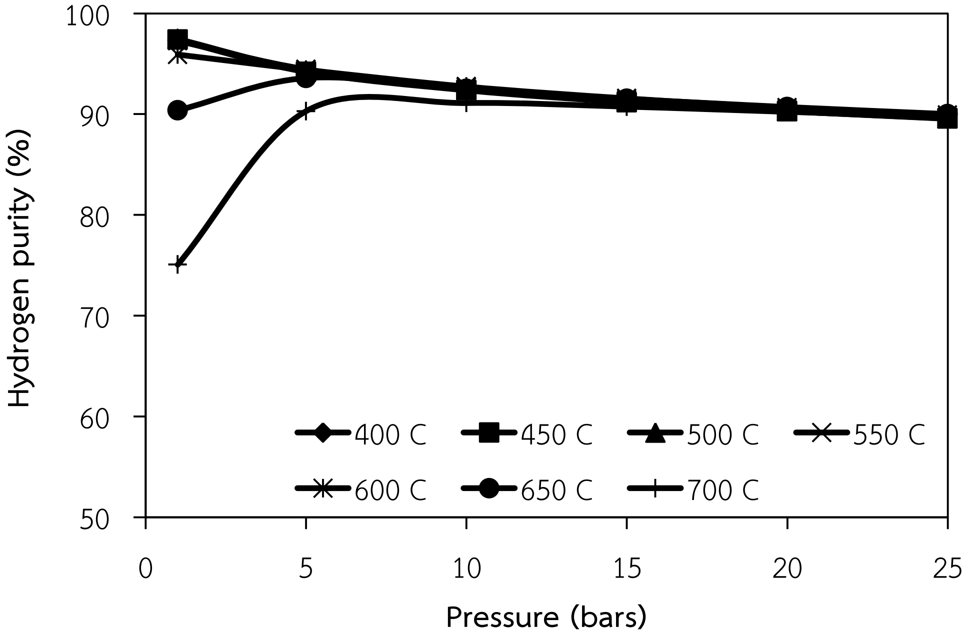


Figure 5.31: Hydrogen purity from various reforming temperature and pressure for SE-CLR process at SER = 5, NER = 0.1, CER = 2, α = 0.8

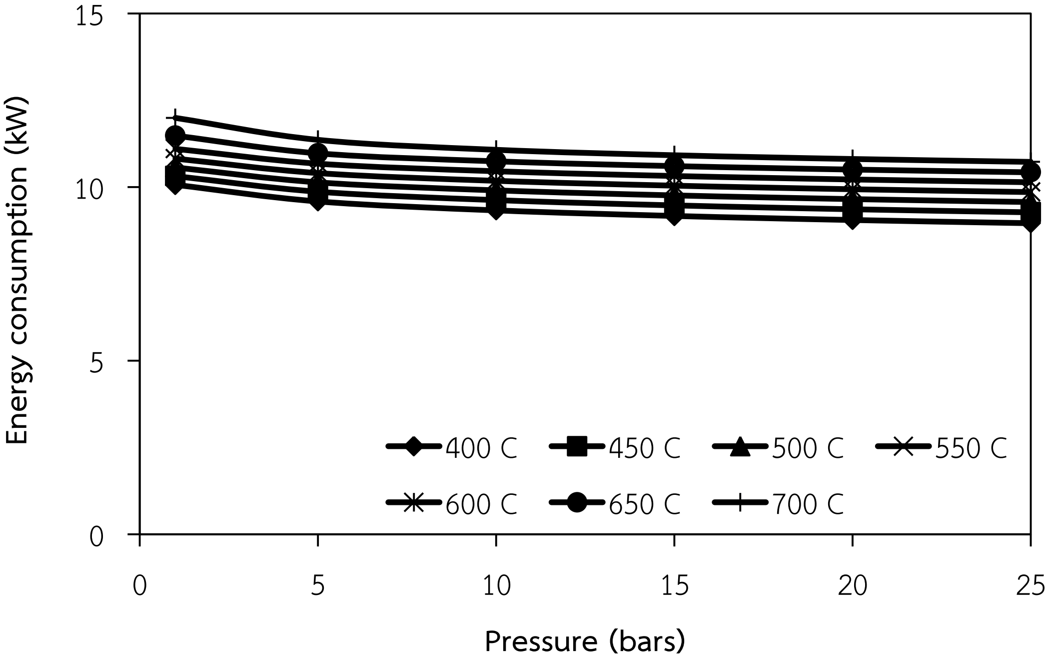


Figure 5.32: Energy consumption from various reforming temperature and pressure for SE-CLR process at SER = 5, NER = 0.1, CER = 2, α = 0.8

Table 5.2: Process performances comparison between SE and SE-CLR processes for hydrogen production from corn stover at optimal conditions

Parameter	SE	SE-CLR
Corn stover feed rate (kg/h)	3	3
Steam equivalence molar ratio (SER)	5	5
Pyrolysis temperature (°C) [Pyrolyser]	480	480
Reforming temperature (°C) [Reformer]	550	550
Calcination temperature (°C) [Calcination reactor]	900	900
Oxidation temperature (°C) [Air reactor]	-	1000
Pressure (bars)	1	1
NER	-	0.1
CER	2	2
CNB	-	1.55
CCB	6.2	31.0
α	-	0.8
Bio-oil conversion (%)	100	100
Hydrogen yield (g H_2/ kg corn stover)	169	169
Hydrogen purity (%)	97	97
Energy consumption (kW)	11.9	11.8

From the above results, sorption enhanced (SE) reforming and sorption enhanced chemical-looping reforming (SE-CLR) process likely to be more suitable processes for hydrogen production than others in terms of producing high hydrogen yield and hydrogen purity. The optimal conditions for both of these processes are

550 °C and 1 bar with SER = 5, NER = 0.1 (for SE-CLR) and CER = 2. The 169 g H_2/ kg corn stover of hydrogen yield and 97 % of hydrogen purity are obtained from the optimal conditions of SE and SE-CLR processes. However, for energy consumption consideration, SE-CLR process is more interesting than SE process (11.9 kW for SE and 11.8 kW for SE-CLR at optimal conditions (Table 5.2)

Although sorption enhanced (SE) reforming process provides high hydrogen yield and high hydrogen purity, oxygen separation unit, external energy, preheating units and cooling units still be required. Moreover, further reduction of energy consumption cannot be performed for SE process because exothermic reactor which produces hot solids does not present in the sorption enhanced section. On the other hand, sorption enhanced chemical-looping (SE-CLR) process can be operated without oxygen separation unit and with less preheating and cooling units by varying the amounts of hot solids from calcination reactor (Ni, NiO and CaO) and air reactor (NiO and CaO) fed to reformer and ones circulated in the process under adiabatic conditions. This can reduce external energy by transferred heat in the process from circulated hot solids among 3 adiabatic reactors instead of 3 isothermal reactors which were applied for previous simulation. Therefore, improvement of hydrogen production process with the goal to eliminate the oxygen separation unit and reduce preheating and cooling units as well as energy consumption by variation of amounts of solids regenerated in the SE-CLR process will be discussed in the next section.

5.3 Improvement of sorption enhanced chemical-looping process by variation of amounts of solids regenerated in the process

In this section, variation amounts of solids: Ni, NiO and CaO regenerated in the process for improvement of sorption enhanced chemical-looping (SE-CLR) will be discussed. The values of NER and CER are adjusted for adiabatic operation.

5.3.1 Modified sorption enhanced chemical-looping process for hydrogen production from corn stover (base case)

Process performance of modified sorption enhanced chemical-looping for hydrogen production from corn stover at base case condition is shown in Table 5.3. The results show that 99.5% bio-oil conversion was observed with the production of 113.2 g H_2/kg corn stover. However, only 65.1% hydrogen purity can be achieved. This might be due to CO_2 cannot be adsorbed by CaO at high temperature more than 700 °C (evidence will be shown later in the following investigation) and excess of NiO leads to more CO_2 production from complete oxidation reaction (see Eq. 4.5 and 4.7). Energy consumption is much higher than SE and SE-CLR process because higher amount of air fed to process is required for higher amount of NiO. The values of α and β represent the amounts of solid regenerated in the process, which could affect reforming temperature in the reformer.

Table 5.3: Process performance of modified sorption enhanced chemical-looping process for hydrogen production from corn stover at base case condition

Parameter	Value
Corn stover feed rate (kg/h)	3
SER	5
Reforming temperature (°C) [Reformer]	723
Calcination temperature (°C) [Calcination reactor]	961
Oxidation temperature (°C) [Air reactor]	1033
Pressure (bar)	1
NER	1
CER	4
CNB	30.8
CCB	125.2
α	0.95
β	0.05
Bio-oil conversion (%)	99.5
Hydrogen yield (g H_2/kg corn stover)	113.2
Hydrogen purity (%)	65.1
Energy consumption (kW)	29.9

5.3.2 Effect of catalyst (Ni, NiO) and adsorbent (CaO) regeneration

For practical applications, it is necessary to minimize energy usage. In this work, we consider an alternative flow process to improve process performances. Varying amount of NiO and CaO in regeneration streams was performed to investigate bio-oil conversion, hydrogen yield and hydrogen purity. Figure 5.33 is shown bio-oil conversion for different ratios of amount of solids, Ni, NiO and CaO, fed to air reactor to solids out of the second cyclone (α) and ratios of amount of solids (NiO and CaO) fed to reformer to solids out of the third cyclone (β) at CNB = 42.4 and CCB = 42.4. The results show that bio-oil conversion increase with increasing amount of NiO and CaO fed back to reformer (lower α and higher β). This phenomenon is due to higher amount of hot solids NiO and CaO fed back into the reformer, resulted in higher reforming temperature as is evidenced by the results shown in Figure 5.34. This leads to higher hydrogen yield (Figure 5.37) and hydrogen purity (Figure 5.38) due to the process is endothermic (Eq. 4.2-4.3).

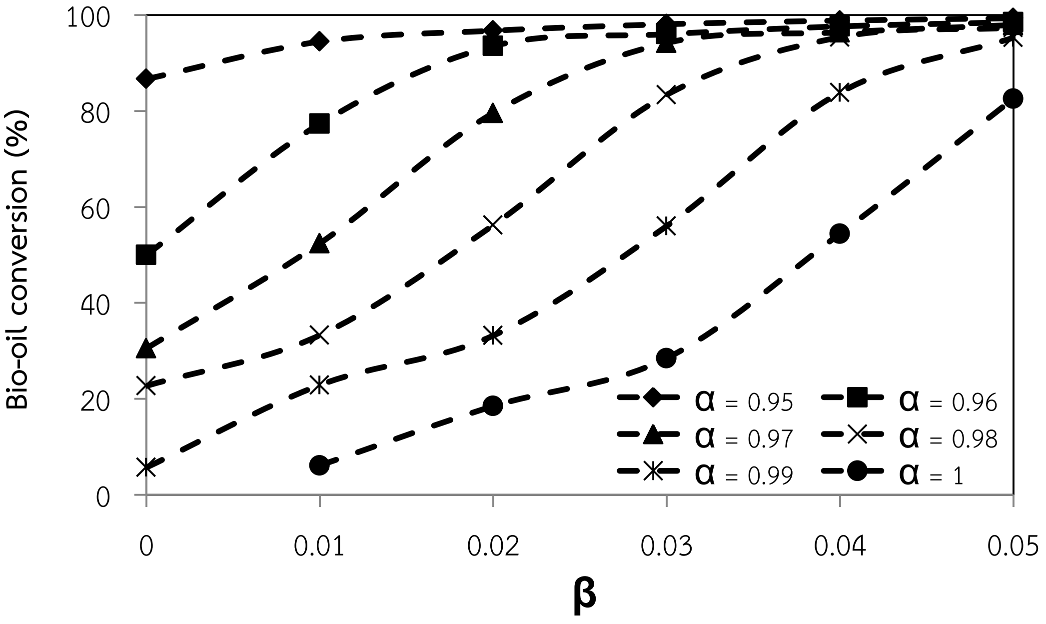


Figure 5.33: Effect of catalyst (NiO) and adsorbent (CaO) regeneration ratios on bio-oil conversion at CNB = 42.4 and CCB = 42.4

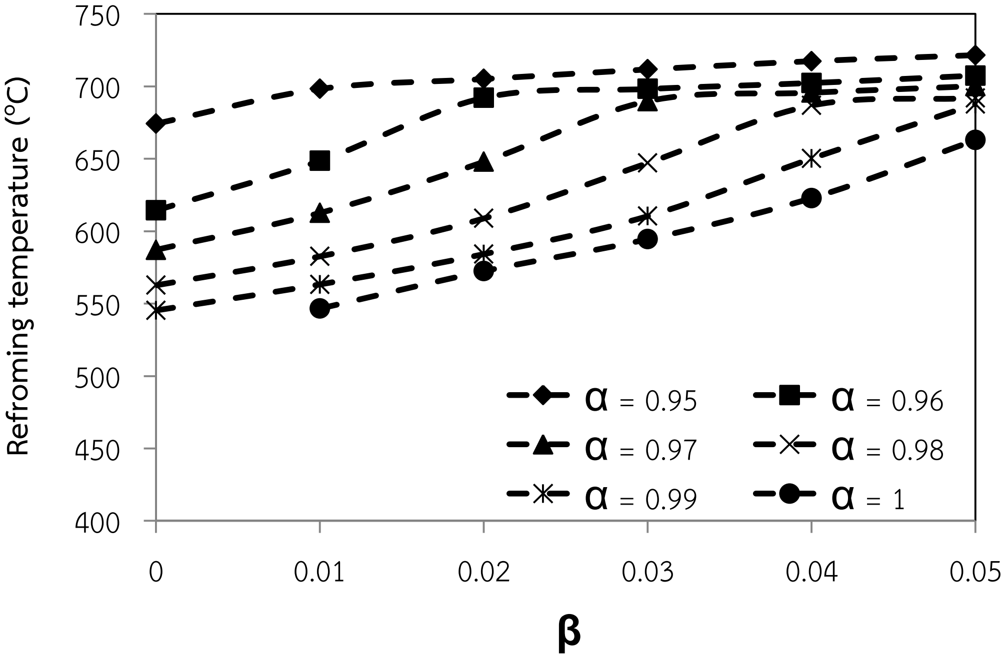


Figure 5.34: Effect of catalyst (NiO) and adsorbent (CaO) regeneration ratios on reforming temperature at CNB = 42.4 and CCB = 42.4

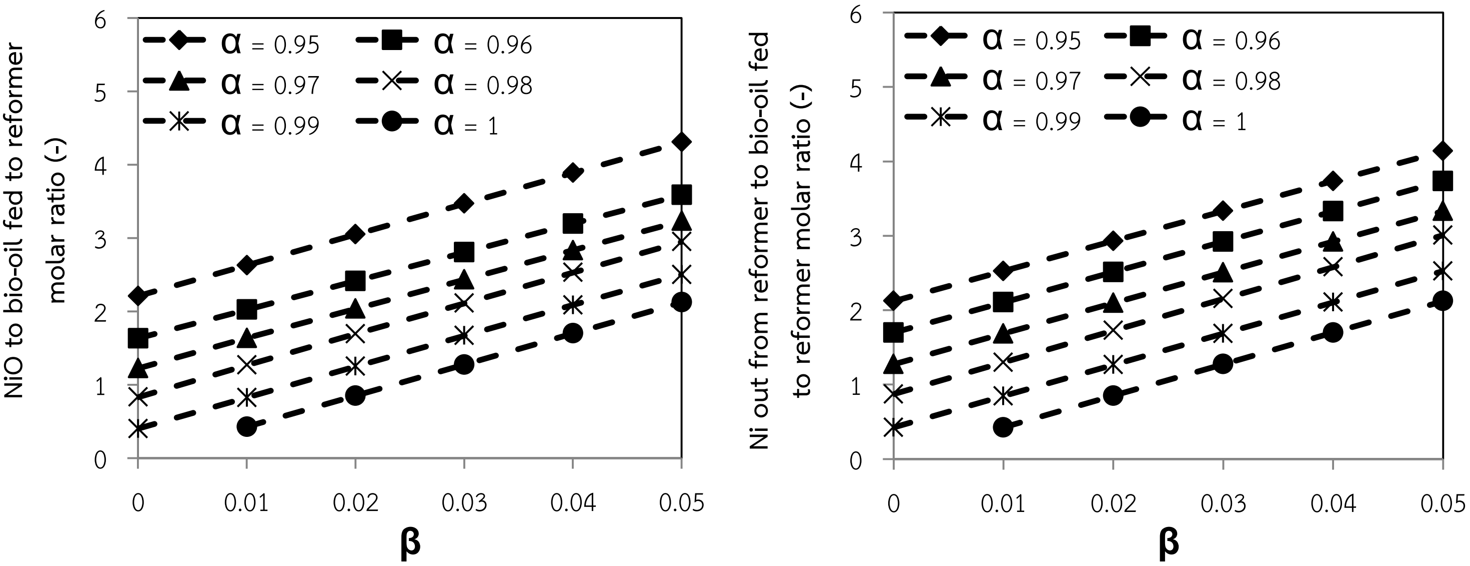


Figure 5.35: Nickel oxide (NiO) fed and Nickel metal (Ni) out from reformer to bio-oil fed molar ratio for various catalyst (NiO) and adsorbent (CaO) regeneration ratios at CNB = 42.4 and CCB = 42.4

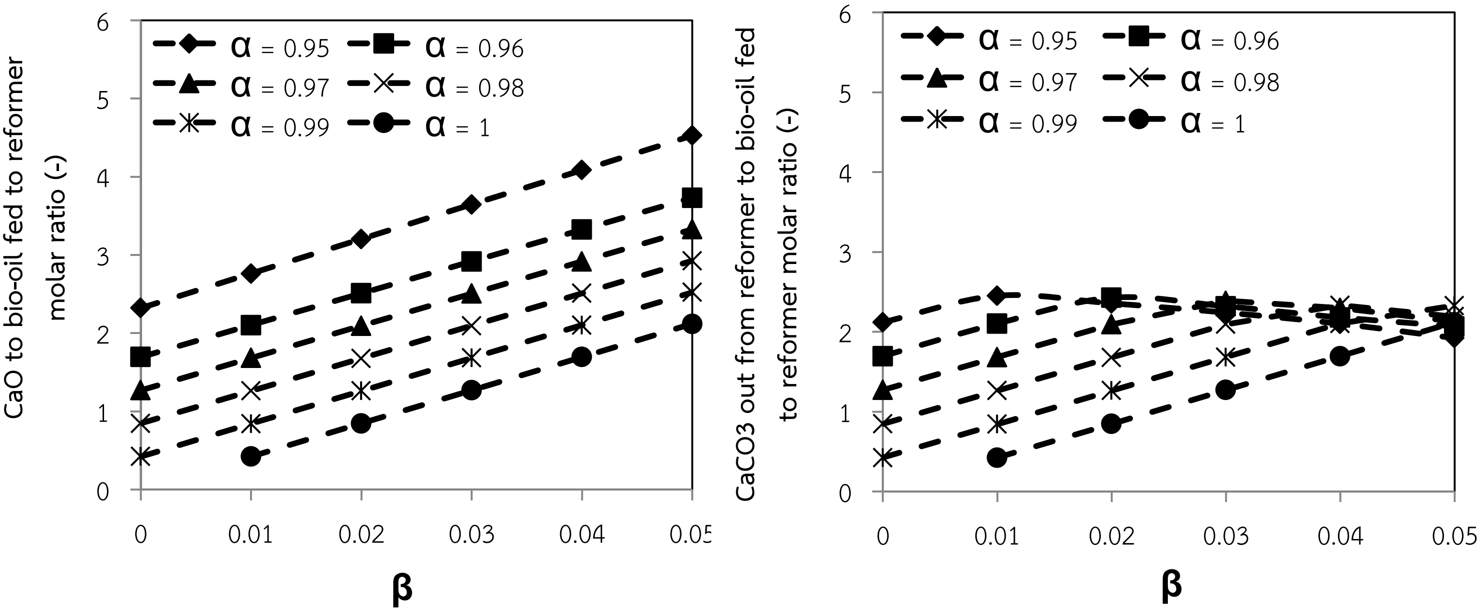


Figure 5.36: Calcium oxide (CaO) fed and calcium carbonate (CaCO3) out from reformer to bio-oil fed molar ratio for various catalyst (NiO) and adsorbent (CaO) regeneration ratios at CNB = 42.4 and CCB = 42

Note that, bio-oil reaches maximum conversion of 96% and does not change at any value of α lower than 0.98 at β higher than 0.03 due to the limit of bio-oil feed. Figure 5.35-5.36 illustrate amount of solids NiO, Ni, CaO and $CaCO_3$ fed to and out from reformer. This indicates that all of NiO were converted to Ni but some of CaO did not adsorb CO_2 and were not converted to $CaCO_3$. CaO cannot adsorb CO_2 at higher 680 $^{\circ}$C of temperature and reverse reaction of Eq. 4.20 occurs. Moreover, amount of CaO does not affect bio-oil conversion which can notice from lower amount of $CaCO_3$ does not cause a decrease of conversion.

For constant β, bio-oil conversion decreases when α increases because lower amount of solids results in lower reforming temperature. On the other hand, bio-oil conversion increases when β increases because higher amount of solids causes higher reforming temperature for constant α. Maximum conversion of bio-oil is 99.3% at 0.95 of α and 0.05 of β.

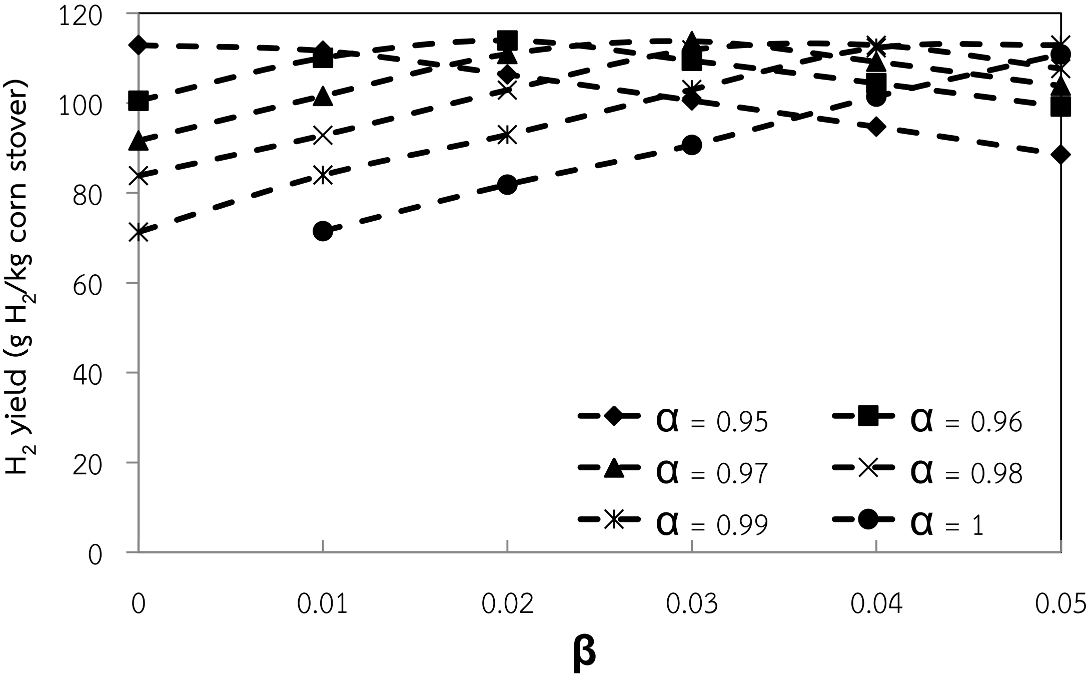


Figure 5.37: Effect of catalyst (NiO) and adsorbent (CaO) regeneration ratios on hydrogen yield at CNB = 42.4 and CCB = 42.4

Figure 5.37 shows hydrogen yield obtained from different amounts of solid (Ni, NiO and CaO) separation. Hydrogen yield is found to increase for higher amounts of solid fed to reformer (lower α and higher β) because of higher reforming temperature evidenced by Figure 5.34. However, hydrogen yield decreases at any value of α lower than 0.98 and β higher than 0.01 due to hydrogen and carbon-monoxide are oxidized to CO_2 and H_2O by NiO according to Eq. 4.9 and 4.11, which are more prominent than hydrogen production by Eq. 4.2 when bio-oil is limited. For constant β at high values (0.02-0.05), hydrogen yield found to increase before decrease when α value increases because lower amount of solids fed to reformer results in higher hydrogen yield from reduction of excess of NiO which leads to oxidation of H_2 and CO (Eq. 4.9 and 4.11), but it results in lower yield when amount of solids is too low (too high α value) because of lower reforming temperature and amount of CaO. This trend was not found at low β values (below 0.02) because amount of solids still be low and excess NiO was not provided. Maximum of hydrogen yield is 113.9 g H_2/kg corn stover at (0.96, 0.02) and minimum of hydrogen yield is 71.3 g H_2/kg corn stover at (0.99, 0).

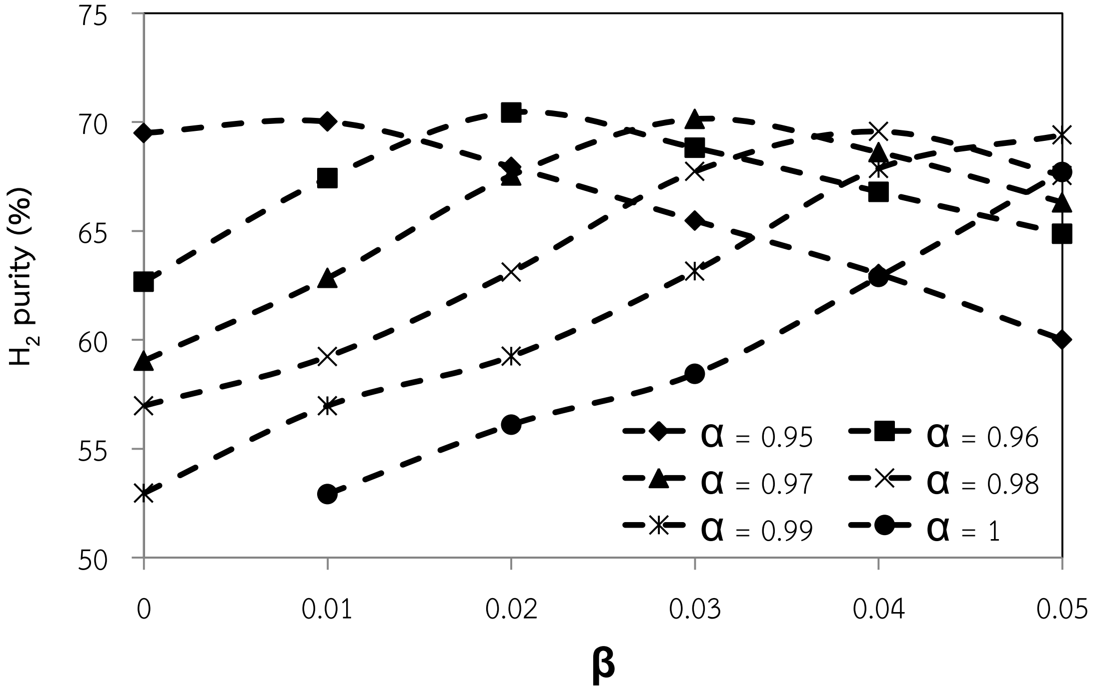


Figure 5.38: Effect of catalyst (NiO) and adsorbent (CaO) regeneration ratios on hydrogen purity at CNB = 42.4 and CCB = 42.4

Figure 5.38 presents the effect of amounts of Ni, NiO and CaO separation on hydrogen purity. Higher hydrogen purity is found when amounts of solid fed to reformer increase (lower α and higher β) because CO_2 adsorption well occurs in higher amount of CaO conditions. Nevertheless, purity is found to decrease at any value of α lower than 0.98 at β higher than 0.01 due to hydrogen and carbon-monoxide are oxidized to CO_2 and H_2O by NiO from Eq. 4.9 and 4.11, which are more predominant than hydrogen production by Eq.4.2 when bio-oil is limited. For constant β at high values (0.02-0.05), hydrogen purity found to increase before decrease when α value increases because lower amount of solids (higher α value) fed to reformer results in higher hydrogen purity from reduction of excess of NiO which leads to oxidation of H_2 and CO (Eq. 4.9 and 4.11), but it results in lower purity when amount of solids is too low (too high α value) because of lower reforming temperature and amount of CaO. This trend was not found at low β values (below 0.02) because amount of solids still be low and excess NiO was not provided. Maximum of hydrogen purity is 70.4% at (0.96, 0.02) and minimum of hydrogen yield is 52.9% at (1, 0.01). In comparison, hydrogen purity obtained from thermodynamic analysis for chemical-looping reforming is only 4.3%, our results show significantly improvement in purity of hydrogen.

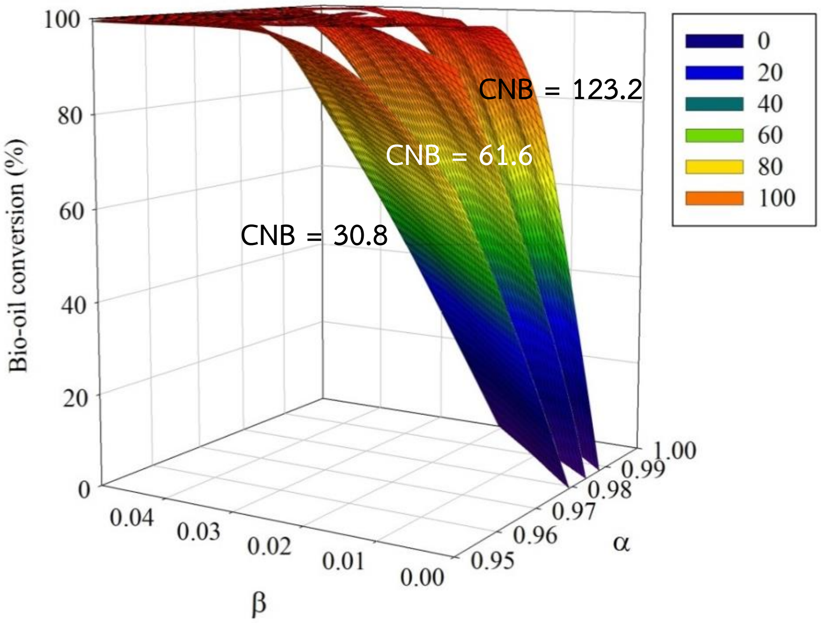


Figure 5.39: Bio-oil conversion from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 31.3

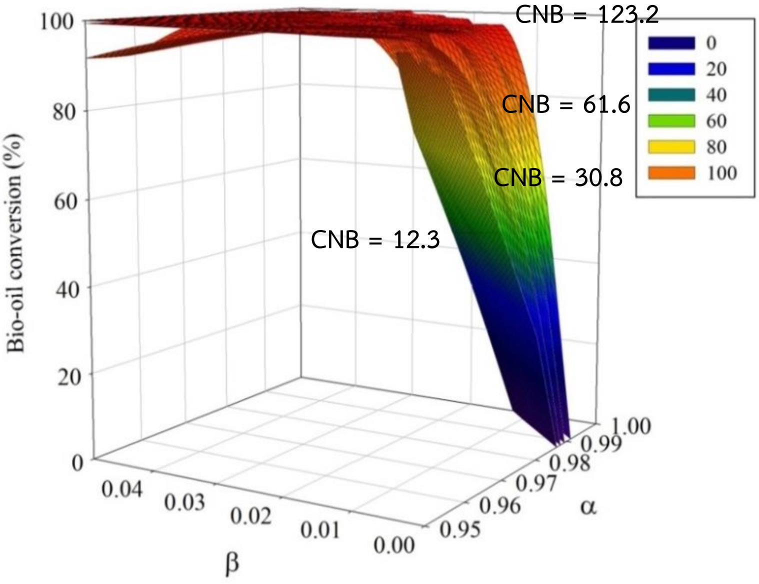


Figure 5.40: Bio-oil conversion from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 62.6

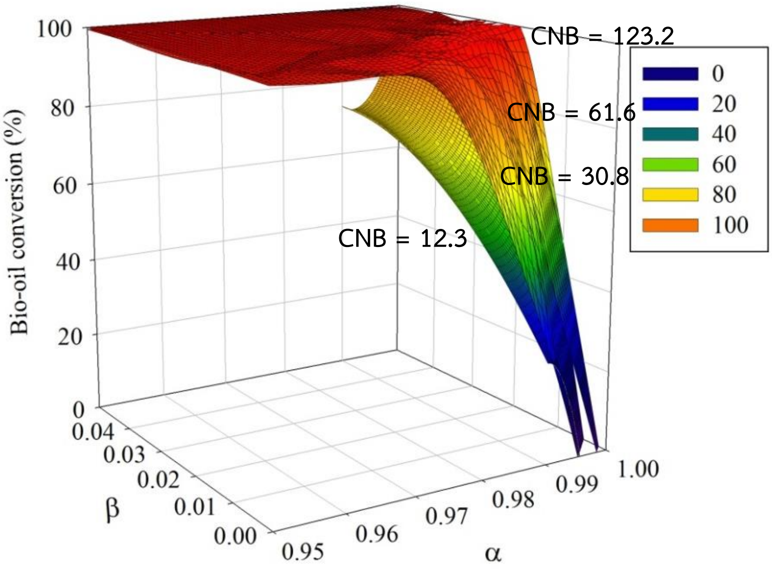


Figure 5.41: Bio-oil conversion from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 125.2

Bio-oil conversion for various catalyst (NiO) and adsorbent (CaO) regeneration ratios (α and β) at different circulated NiO to bio-oil molar ratios (CNB) and circulated CaO to bio-oil molar ratios (CCB) are shown in Figure 5.39-5.41. Data at CCB = 31.3 and CNB = 12.3 cannot be obtained because circulating solids are not enough to supply heat for adiabatic process. From these graphs, increase of CNB results in higher bio-oil conversion which approaches 100% for all CCBs because more NiO results in shift equilibrium of oxidation of NiO from Eq. 4.5 and 4.7. Moreover, higher CCB results in higher bio-oil conversion because the presence of more CaO results in shift equilibrium of Eq. 4.5 and 4.7 by CO_2 adsorption to $CaCO_3$ (Eq. 4.20). Maximum of bio-oil conversion is more than 99.9% for CNB value is above 61.6 at all CCBs.

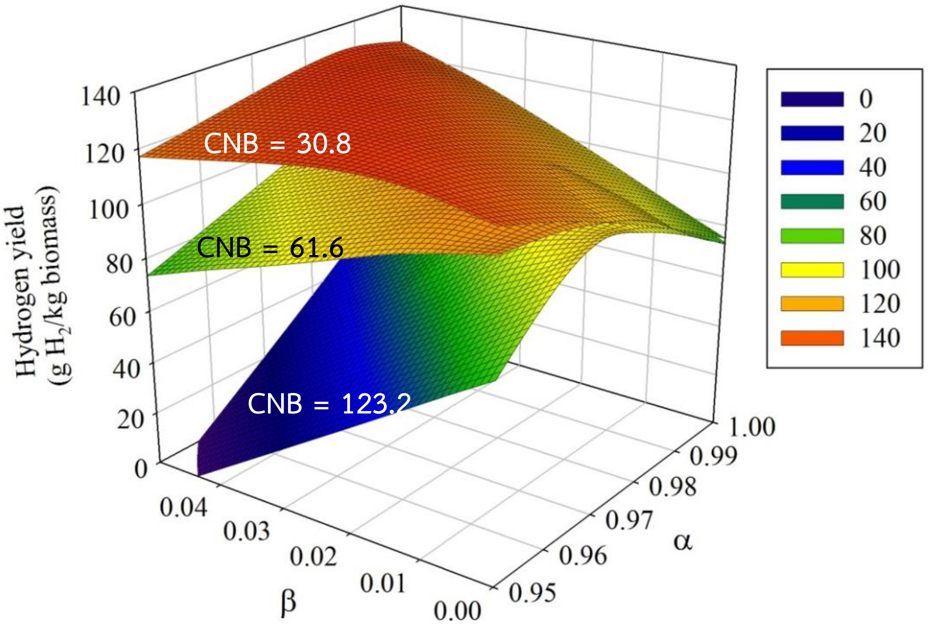


Figure 5.42: Hydrogen yield from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 31.3

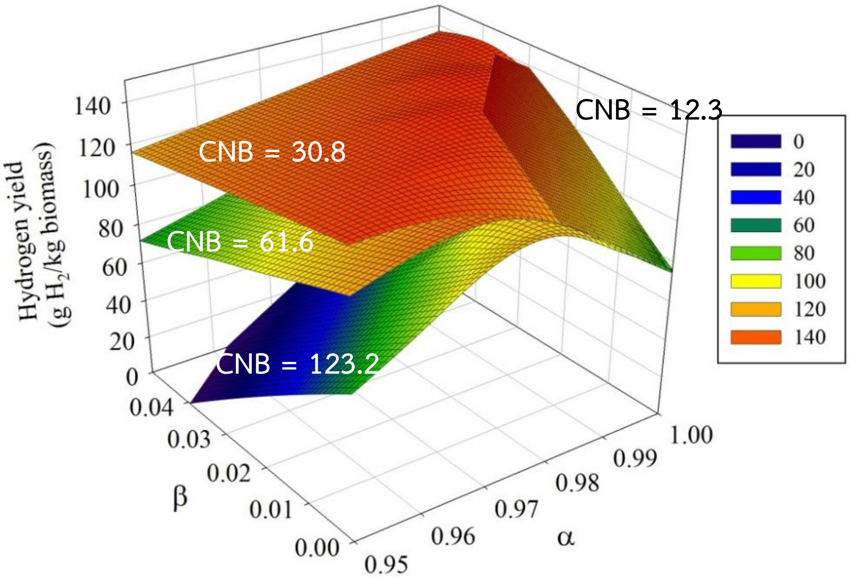


Figure 5.43: Hydrogen yield from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 62.6

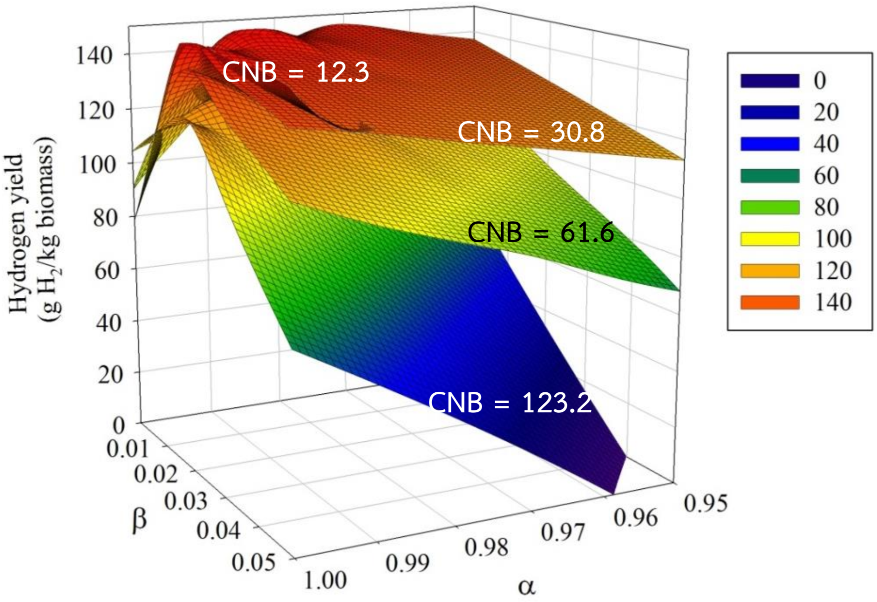


Figure 5.44: Hydrogen yield from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 125.2

Figure 5.42-5.44 show hydrogen yield from sorption enhanced chemical-looping process for various catalyst (NiO) and adsorbent (CaO) regeneration ratios (α and β) at different circulated NiO to bio-oil molar ratios (CNB) and circulated CaO to bio-oil molar ratios (CCB). More CNB results in less hydrogen yield due to more NiO leads to oxidation of bio-oil in Eq. 4.5, which produced CO_2 and H_2O but H_2. On the other hand, at CCB higher than 62.6, more H_2 and CO can be converted to H_2O and CO_2 by NiO from Eq. 4.9 and 4.11. For constant CNB, increase of CCB causes more hydrogen yield due to shift equilibrium of Eq. 4.12 by CO_2 adsorption (Eq. 4.20). However, yield of hydrogen is limited to about 153 g H_2/kg biomass by amount of bio-oil. Maximum hydrogen yield is 153.4 g H_2/kg biomass at 12.3 of CNB and 125.2 of CCB.

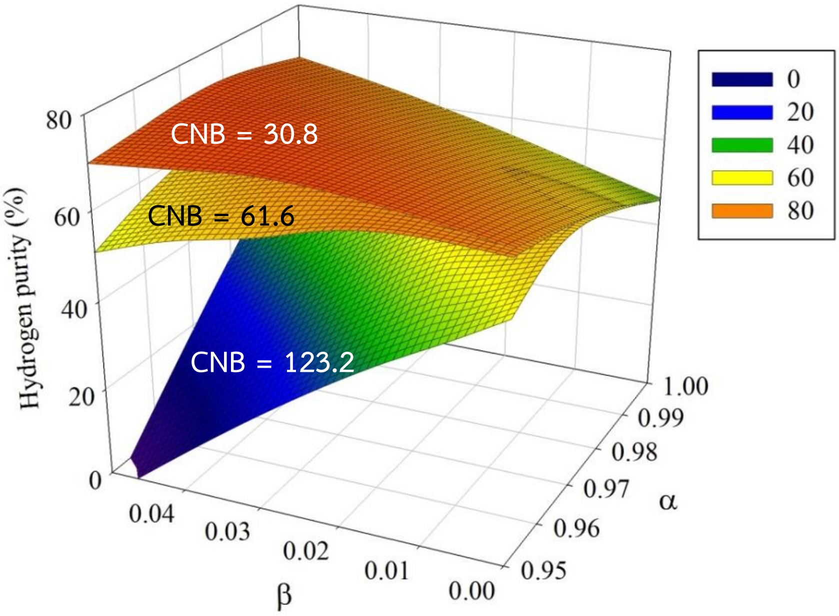


Figure 5.45: Hydrogen purity from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 31.3

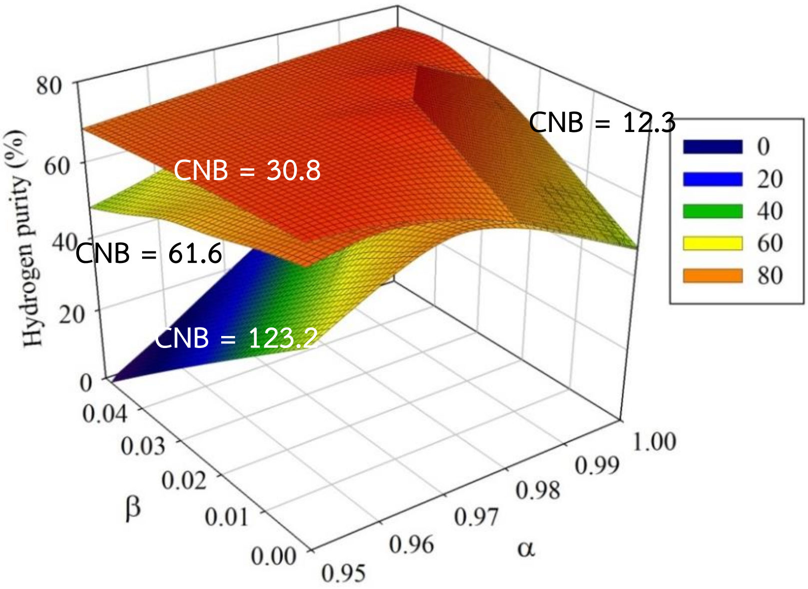


Figure 5.46: Hydrogen purity from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB =62.6

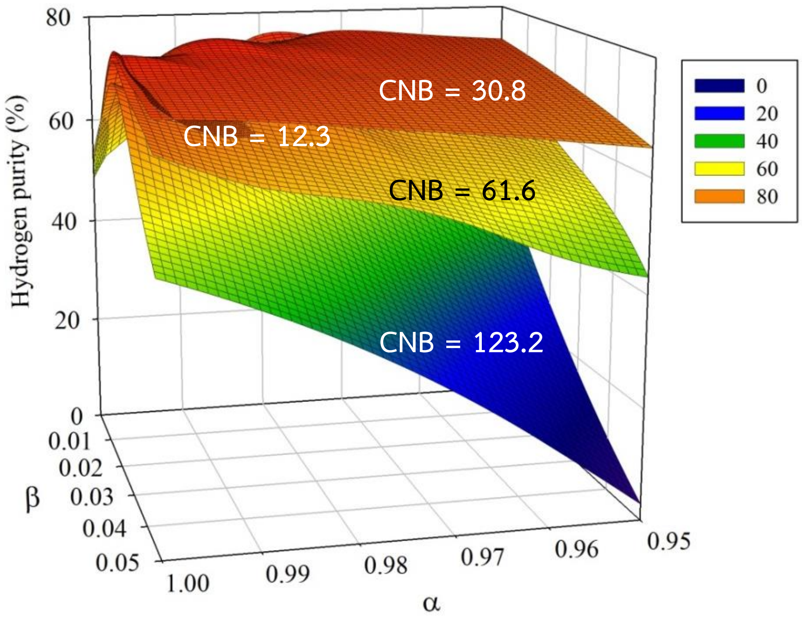


Figure 5.47: Hydrogen purity from different catalyst (NiO) and adsorbent (CaO) regeneration ratios and different circulated NiO to bio-oil molar ratios (CNB) at CCB = 125.2

Hydrogen purity for various catalyst (NiO) and adsorbent (CaO) regeneration ratios (α and β) at different circulated NiO to bio-oil molar ratios (CNB) and circulated CaO to bio-oil molar ratios (CCB) are presented in Figure 5.45-5.47. Trends of hydrogen purity are similar to hydrogen yield as shown in Figure 5.42-5.44. Therefore, the same reason can be applied in this case; more CNB results in less hydrogen purity since more prominence of Eq. 4.5, Eq. 4.9 and Eq. 4.11 and higher CCB results in more hydrogen purity due to CO_2 adsorption (Eq. 4.20) can shift equilibrium of Eq. 4.12 and reduce the CO_2 in gas products. Maximum hydrogen purity is 77 % at 12.3 of CNB and 125.2 of CCB.

Modified sorption enhanced chemical-looping reforming (SE-CLR) process can be applied for reduction of preheating and cooling units, which is shown by comparison with SE and SE-CLR process in Table 5.4. However, lower hydrogen yield and hydrogen purity and high energy consumption are drawbacks from this improvement. The optimal conditions for modified SE-CLR process are CNB = 12.3 and CCB = 125.2 with α = 1 and β = 0.02 which leads to 680 °C of reforming temperature, 891 °C of calcination temperature 929 °C oxidation temperature, NER = 0.094 and CER = 0.82. These conditions results in 92% bio-oil conversion, 153.4 g H_2/kg corn stover of hydrogen yield, 77% of hydrogen purity and 29.9 kW of energy consumption. In case of amounts of preheating and cooling units, modified SE-CLR requires 5 preheating units and none of cooling units and oxygen separation units but 7 preheating units, 1 cooling unit and 1 oxygen separation unit are required in SE process and 8 preheating units, 1 cooling unit and none of oxygen separation units are required in SE-CLR process (Table 5.4).

Table 5.4: Process performance comparison of SE, SE-CLR and modified SE-CLR processes at optimal conditions

Parameter	SE	SE-CLR	Modified SE-CLR
Corn stover feed rate (kg/h)	3	3	3
SER	5	5	5
Pyrolysis temperature (^{o}C) [Pyrolyser]	480	480	480
Reforming temperature (^{o}C) [Reformer]	550	550	678
Calcination temperature (^{o}C) [Calcination reactor]	900	900	851
Oxidation temperature (^{o}C) [Air reactor]	1000	1000	944
Pressure (bar)	1	1	1
NER	-	0.1	0.094
CER	2	2	0.82
CNB	-	1.55	12.3
CCB	6.2	31.0	125.2
α	-	0.8	1
β	-	-	0.02
Bio-oil conversion (%)	100	100	92
Hydrogen yield (g H_2/kg corn stover)	169	169	153.4
Hydrogen purity (%)	97	97	77
Energy consumption (kW)	11.9	10.8	29.9
Oxygen separation unit (count)	1	-	-
Preheating unit (count)	7	8	5
Cooling unit (count)	1	1	-

Since the energy consumption of modified SE-CLR still be high, further reduction of energy consumption is still required. We further investigated the reduction of external energy and preheating and cooling units by heat integration among hot streams and cold streams in the process which is presented in the next section.

5.4 Improvement of sorption enhanced chemical-looping process by heat integration

Heat integration of hot and cold streams in sorption enhanced chemical-looping (SE-CLR) process was performed in this section. Hot streams in this process consist of hydrogen product stream (H2), CO_2 stream from desorption of $CaCO_3$ (CO2), and depleted air which composes of nitrogen gas (N2). Cold streams in this process consist of water feed (H2O) and air feed (AIR) at environmental temperature assumed by 35 ^{o}C. However, energy in hot streams is not enough to supply cold streams. Therefore, bio-oil stream (BIOOIL) was necessary to be splitted into 2 streams; one was fed to reformer for hydrogen production and another was fed to adiabatic combuster with air for heat generation by combustion reaction.

For energy consumption reduction approach, CNB, CCB, α and β values were fine tuned to suitable values, which were 30.8 of CNB, 62.6 of CCB, 0.99 of α and 0.03 of β. This led to variation of reforming temperature, calcination temperature, oxidation temperature, NER and CER from modified SE-CLR process. Ratio of bio-oil fed to reformer to bio-oil from pyrolyser (γ) was varied to determine optimal condition. Bio-oil conversion, hydrogen yield and hydrogen purity for various γ values were presented in Figure 5.48-5.50.

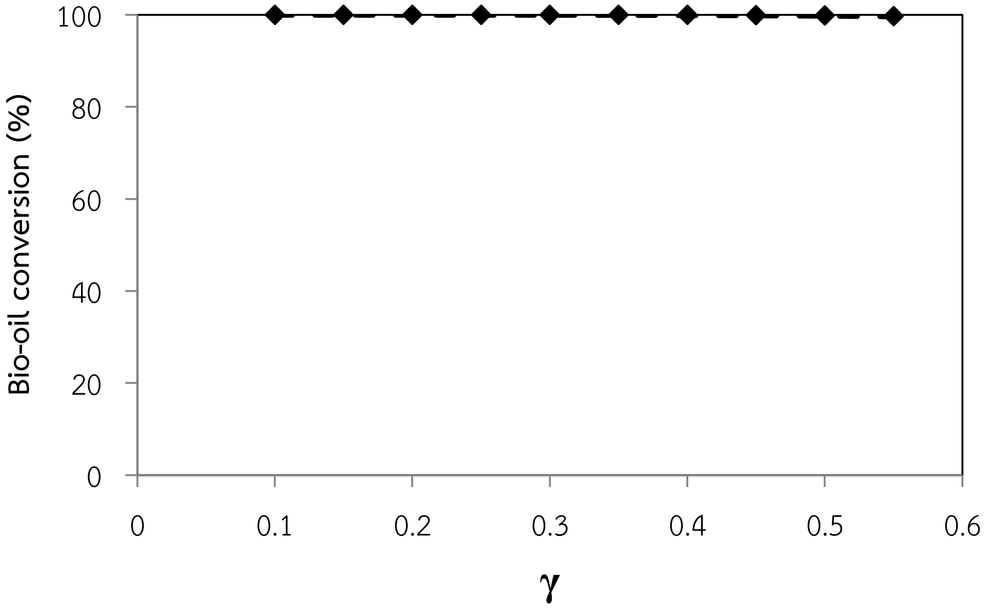


Figure 5.48: Bio-oil conversion for various γ values at CNB = 30.8, CCB = 62.6, α = 0.99 and β = 0.03

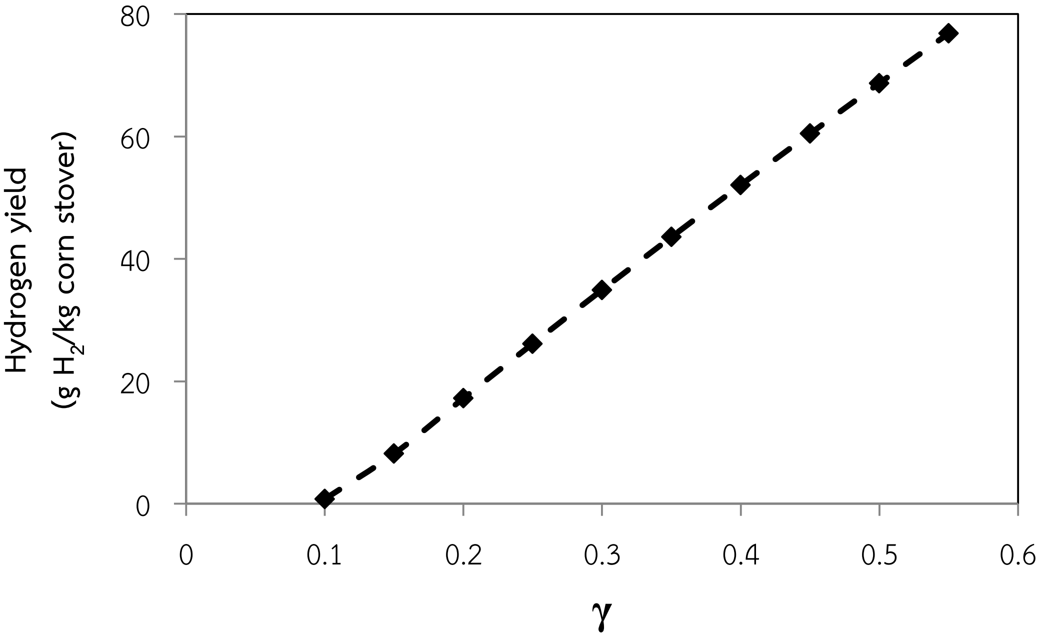


Figure 5.49: Hydrogen yield for various γ values at CNB = 30.8, CCB = 62.6, α = 0.99 and β = 0.03

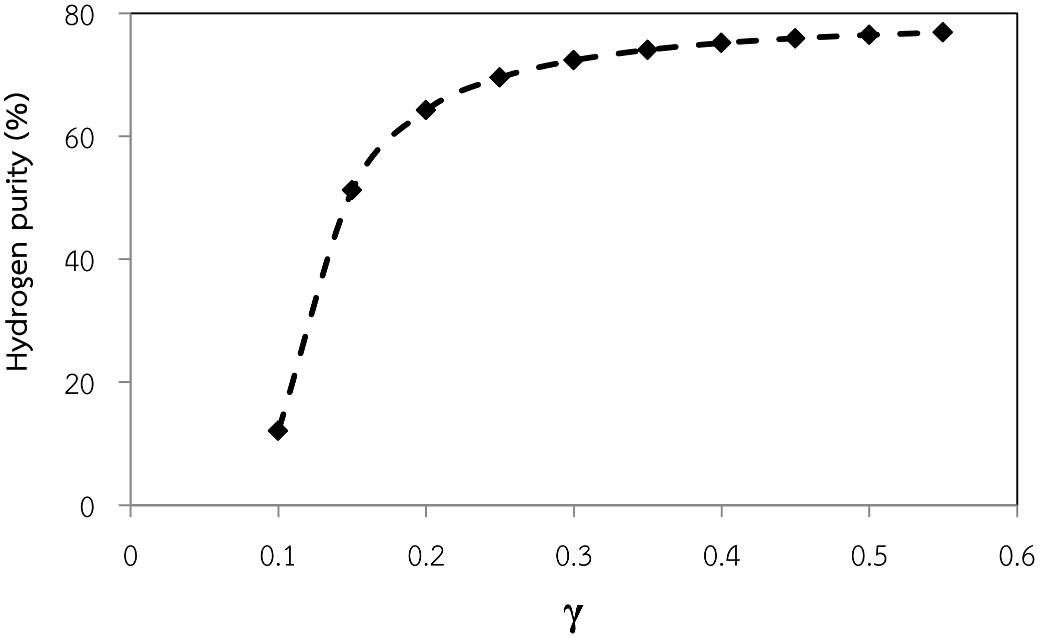


Figure 5.50: Hydrogen purity for various γ values at CNB = 30.8, CCB = 62.6, α = 0.99 and β = 0.03

Figure 5.48-5.50 show the effects of γ values on bio-oil conversion, hydrogen yield and hydrogen purity. The higher γ values result in higher hydrogen yield and hydrogen purity because higher amount of bio-oil was fed to reformer. However, γ values insignificantly affect on bio-oil conversion which approach 100% because conditions as mentioned above (CNB = 30.8, CCB = 62.6, α = 0.99 and β = 0.03) lead to high temperature (above 700 °C) which results in complete conversion of bio-oil. Optimal value of γ is 0.55 which leads to 99.8% of bio-oil conversion, 77.4 g H_2/kg corn stover of hydrogen yield, 77% of hydrogen purity and 5.64 kW of energy consumption. Moreover, preheating units are reduce to 3 by using 2 heat exchangers instead of air preheater and steam preheater. Process performance for above 0.55 of γ cannot be obtained because amount of bio-oil fed to combuster for heat generation is not enough to generate sufficient heat supplied for the process.

Table 5.5: Process performance comparison of SE, SE-CLR, modified SE-CLR and modified SE-CLR with heat integration processes at optimal conditions

Parameter	SE	SE-CLR	Modified SE-CLR	Modified SE-CLR with heat integration
Corn stover feed rate (kg/h)	3	3	3	3
SER	5	5	5	5
Pyrolysis temperature (°C) [Pyrolyser]	480	480	480	480
Reforming temperature (°C) [Reformer]	550	550	678	717
Calcination temperature (°C) [Calcination reactor]	900	900	851	857
Oxidation temperature (°C) [Air reactor]	1000	1000	944	919
Pressure (bar)	1	1	1	1
NER	-	0.1	0.094	0.4
CER	2	2	0.82	0.8
CNB	-	1.55	12.3	30.8
CCB	6.2	31.0	125.2	62.6
α	-	0.8	1	0.99
β	-	-	0.02	0.03
γ	1	1	1	0.55
Bio-oil conversion (%)	100	100	92	99.8
Hydrogen yield (g H_2/kg corn stover)	169	169	153.4	77.4
Hydrogen purity (%)	97	97	77	77.1
Energy consumption (kW)	11.9	10.8	29.9	5.64
Oxygen separation unit (count)	1	-	-	-
Preheating unit (count)	7	8	5	3
Cooling unit (count)	1	1	-	-
Heat exchanger unit (count)	-	-	-	2

Process performances comparison of SE, SE-CLR, modified SE-CLR and modified SE-CLR with heat integration processes are presented in Table 5.5. SE-CLR with heat integration processes can reduce external energy, preheating units and cooling units used in the process. The 5.64 kW of energy consumption derived from pyrolysis section in modified SE-CLR with heat integration process is lower than other processes. Furthermore, preheating unit used in the process is less than other processes and 2 heat exchangers were applied instead of 2 preheating units. This leads to lower amount of utilities consumed in the process than other processes. However, low hydrogen yield and hydrogen purity are obtained because of division of bio-oil stream. These drawbacks should be improved and the process should be more developed in the future.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The simulation results of sorption enhanced chemical-looping for hydrogen production from biomass derived from corn stover are summarized. The sorption enhanced chemical-looping reforming (SE-CLR) process was simulated using NiO as oxidizing agent and CaO as CO_2 adsorbent for improvement the process performance comparing with autothermal (ATR), chemical-looping reforming (CLR) and sorption enhanced (SE) processes. Comparison of process performances which comprise of bio-oil conversion, hydrogen yield, hydrogen purity and energy consumption is performed at various conditions under isothermal constraint. Moreover, modified SE-CLR and modified SE-CLR with heat integration were also simulated for minimization of energy consumption and preheating and cooling units in the SE-CLR process under adiabatic constraint. Finally, the optimal conditions and suitable process for hydrogen production from corn stover are provided.

6.1.1 Comparison of ATR, CLR, SE and SE-CLR processes

From the simulation results in the part of comparison of ATR, CLR, SE and SE-CLR, the conclusion can be drawn as follows;

1) Increase of SER results in higher hydrogen yield, hydrogen purity and energy consumption for all processes because steam reforming and water-gas shift reaction are shifted forward.

2) Increase of OER results in lower hydrogen yield, hydrogen purity and energy consumption for ATR process because oxidation reaction of bio-oil, hydrogen and carbon-monoxide are shifted forward.

3) Increase of NER results in lower hydrogen yield, hydrogen purity and energy consumption for CLR process because oxidation reaction of bio-oil, hydrogen and carbon-monoxide are shifted forward.

4) Increase of CER results in higher hydrogen yield, hydrogen purity and energy consumption for SE processes because carbonation reaction is shifted forward.

5) Higher reforming temperature leads to higher hydrogen yield, hydrogen purity and energy consumption for all processes because overall reaction in reformer is endothermic.

6) Higher pressure leads to lower hydrogen yield, hydrogen purity and energy consumption for all processes according to Le Chartelier's principle but insignificantly affects ones at high temperature (above 800 ^{o}C) for ATR and CLR processes because bio-oil is completely converted.

7) At SER = 5, OER = 0.1 (for ATR), NER = 0.1 (for CLR and SE-CLR) and CER = 4 (for SE and SE-CLR), bio-oil conversion reaches 100 %.

8) For SE and SE-CLR processes, reforming temperature above 650 ^{o}C at pressure of 1 bar leads to low hydrogen yield and hydrogen purity because CO_2 adsorption shifts backward at high temperature and low pressure.

9) Favorable processes for hydrogen production are SE and SE-CLR processes due to high hydrogen yield, high hydrogen purity and low energy consumption can be obtained.

10) Optimal conditions for hydrogen production by SE and SE-CLR processes are 550 °C and 1 bar with SER = 5, NER = 0.1 (for SE-CLR) and CER = 4 which provides the 169 g H_2/ kg corn stover of hydrogen yield, 97 % of hydrogen purity and 11.9 kW of energy consumption for SE and 11.8 kW of energy consumption for SE-CLR.

6.1.2 Improvement of sorption enhanced chemical-looping process by variation of amounts of solids regenerated in the process

For reduction of energy consumption, improvement of SE-CLR is required. From the simulation results in the part of improvement of sorption enhanced chemical-looping process by variation of amounts of solids (Ni, NiO and CaO) regenerated in the process, the conclusion can be drawn as follows;

1) Higher value of α leads to lower bio-oil conversion, hydrogen yield and hydrogen purity for modified SE-CLR process because lower amounts of NiO and CaO are fed to reformer for hydrogen production.

2) Higher value of β leads to higher bio-oil conversion because of higher amounts of NiO and CaO are fed to reformer but hydrogen yield and hydrogen purity decreases at any value of α lower than 0.98 at β higher than 0.01 due to excess of NiO leads to oxidation reaction of bio-oil, hydrogen and carbon-monoxide.

3) Increase of CNB results in higher bio-oil conversion but lower hydrogen yield and hydrogen purity because excess of NiO leads to oxidation reaction of bio-oil, hydrogen and carbon-monoxide.

4) Increase of CCB results in higher bio-oil conversion, hydrogen yield and hydrogen purity because carbonation reaction is shifted forward.

5) Optimal conditions for hydrogen production by modified SE-CLR process are CNB = 12.3 and CCB = 125.2 with α = 1 and β = 0.02 which leads to 678 °C of reforming temperature, 851 °C of calcination temperature 944 °C oxidation temperature, NER = 0.094 and CER = 1.64. These conditions results in 92% bio-oil conversion, 153.4 g H_2/kg corn stover of hydrogen yield, 77% of hydrogen purity and 29.9 kW of energy consumption.

6) Modified SE-CLR requires 5 preheating units and none of cooling units and oxygen separation units but 7 preheating units, 1 cooling unit and 1 oxygen separation unit are required in SE process and 8 preheating units, 1 cooling unit and none of oxygen separation units are required in SE-CLR process.

6.1.3 Improvement of sorption enhanced chemical-looping process by heat integration

For further reduction of energy consumption, utilities, preheating and cooling units, heat integration of SE-CLR process was required. From the simulation results in the part of improvement of sorption enhanced chemical-looping process by heat integration, the conclusion can be drawn as follows;

1) For energy consumption reduction approach, CNB, CCB, α and β values were modified to suitable values which were 30.8 of CNB, 62.6 of CCB, 0.99 of α and 0.03 of β.

2) Higher value of γ results in higher hydrogen yield and hydrogen purity due to higher amount of bio-oil is fed to reformer but insignificantly affect bio-oil conversion which approach 100% at the mentioned conditions.

3) Optimal value of γ is 0.55 which leads to 99.8% of bio-oil conversion, 77.4 g H_2/kg corn stover of hydrogen yield, 77% of hydrogen purity and 5.64 kW of energy consumption.

4) Preheating units can be reduced to 3 by using 2 heat exchangers instead of air preheater and steam preheater.

6.2 Recommendations

1) Modified SE-CLR with heat integration still provides lower hydrogen yield and hydrogen purity than other processes. Therefore, operating conditions (reforming temperature, pressure, SER, CNB, CCB, α and β values) should be further studied.

2) Comparison of cost or amount of utilities for 6 processes (ATR, CLR, SE, SE-CLR, modified SE-CLR and modified SE-CLR with heat integration) should be further investigated.

3) Dividing of bio-oil for combustion in modified SE-CLR with heat integration process should be compared with dividing of corn stover in the future process performance study.

4) Combination of isothermal reactors and adiabatic reactors for the goal to maximize hydrogen yield and hydrogen purity should be further investigated.

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APPENDIX

APPENDIX

1. Calculation of SER, OER, NER and CER

SER, OER, NER and CER can be calculated by Eq. 4.26-4.29 from Chapter 4

$$\mathrm{SER} = \frac{\text{Actual } H_2O \text{ to bio−oil molar ratio}}{\text{Stoichiometric } H_2O \text{ to bio−oil molar ratio}} \qquad ...(4.26)$$

$$\mathrm{OER} = \frac{\text{Actual } O_2 \text{to bio−oil molar ratio}}{\text{Stoichiometric } O_2 \text{ to bio−oil molar ratio}} \qquad ...(4.27)$$

$$\mathrm{NER} = \frac{\text{Actual NiO to bio−oil molar ratio}}{\text{Stoichiometric NiO to bio−oil molar ratio}} \qquad ...(4.28)$$

$$\mathrm{CER} = \frac{\text{Actual CaO to bio−oil molar ratio}}{\text{Stoichiometric CaO to bio−oil molar ratio}} \qquad ...(4.29)$$

Bio-oil fed to reformer with CO_2, CO, H_2, H_2O and CH_4 produced by pyrolyser in pyrolysis section. The empirical formula of bio-oil is $CH_{1.224}O_{0.38}$. Moles of bio-oil and contaminant gas are performed as follows;

Components	Mole flow rate (kmol/hr)	Stoichiometric No. based on bio-oil
Bio-oil	0.02477	1
CH_4	8.28E-05	0.003
H_2O	0.022739	0.918
CO	0.008883	0.359
CO_2	0.004671	0.189
H_2	0.011064	0.447

Stoichiometric number based on bio-oil was calculated by dividing mole flow rate of contaminant gas by mole flow rate of bio-oil.

Example

Stoichiometric No. of CO = $\frac{\mathbf{0.008883}}{\mathbf{0.02477}}$ = 0.359

Therefore, the equation of steam reforming, complete oxidation by O_2 and complete oxidation by NiO of bio-oil are shown as Eq. A1-A3.

Steam reforming of bio-oil

$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.918H_2O + 0.447H_2 + x_1H_2O \rightleftharpoons$

$y_1CO + z_1H_2$ ....(A1)

Complete oxidation of bio-oil and O_2

$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.918H_2O + 0.447H_2 + x_2O_2 \rightleftharpoons$

$y_2CO_2 + z_2H_2O$ ....(A2)

Complete oxidation of bio-oil and NiO

$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.918H_2O + 0.447H_2 + x_3NiO \rightleftharpoons$

$y_3CO_2 + z_3H_2O + x_3Ni$ ....(A3)

x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3 and z_3 were calculate by balance of the Eq. A1-A3 presented by Table A1.

Table A1: Stoichiometric number of Eq. A1, A2 and A3

Equation A1		Stoic No.	**Equation A2**		Stoic No.	**Equation A3**		Stoic No.
Left	$CH_{1.224}O_{0.38}$	1	**Left**	$CH_{1.224}O_{0.38}$	1	**Left**	$CH_{1.224}O_{0.38}$	1
	CH_4	0.003		CH_4	0.003		CH_4	0.003
	H_2O	0.918		H_2O	0.918		H_2O	0.918
	CO	0.359		CO	0.359		CO	0.359
	CO_2	0.189		CO_2	0.189		CO_2	0.189
	H_2	0.447		H_2	0.447		H_2	0.447
	H_2O	**-0.483**		**O_2**	**1.525**		**NiO**	**3.051**
Right	**CO**	**1.551**	Right	**CO_2**	**1.551**	Right	**CO_2**	**1.551**
	H_2	**1.5**		**H_2O**	**1.983**		**H_2O**	**1.983**
							Ni	**3.051**

Substitute values in the Table A1 in the Eq. A1-A3 and get Eq. A4-A6 as follows

Steam reforming of bio-oil

$$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.435H_2O + 0.447H_2 \rightleftharpoons$$

$$1.551CO + 1.5H_2 \quad \text{....(A4)}$$

Complete oxidation of bio-oil and O_2

$$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.918H_2O + 0.447H_2 + 1.525O_2 \rightleftharpoons$$

$$1.551CO_2 + 1.983H_2O \quad \text{....(A5)}$$

Complete oxidation of bio-oil and NiO

$$CH_{1.224}O_{0.38} + 0.003CH_4 + 0.359CO + 0.189CO_2 + 0.918H_2O + 0.447H_2 + 3.051NiO \rightleftharpoons 1.551CO_2 + 1.983H_2O + 3.051Ni \qquad \text{....(A6)}$$

Water-gas shift reaction and carbonation reaction are also applied for SER and CER calculation shown as Eq. 4.11-4.12.

Water-gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \text{...(4.12)}$$

Carbonation

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \text{...(4.20)}$$

Stoichiometric numbers of H_2O are 0.435 plus 1.551 because H_2O was used in Eq. A4 and Eq.4.11 and stoichiometric number of CaO is 1.551 plus 1.551 because CaO adsorbs CO_2 from Eq.A5 or A6 and Eq.4.11. Since there is some amount of water in bio-oil feed stream to reformer (0.022739 kmol/h), this amount of water is needed to add in calculation of SER. Calculation of SER, OER, NER and CER was shown in following example.

<u>Example</u>

Feed 0.2232 kmol/h of H_2O, 0.00378 kmol/h of O_2, 0.0151 kmol/h of NiO and 0.1536 kmol/h of CaO with 0.02477 kmol/h of bio-oil into reformer. SER, OER, NER and CER are calculated by

$$\mathrm{SER} = \frac{0.2232+0.0227}{(0.435+1.551)\times0.02477} = 5$$

$$\mathrm{OER} = \frac{0.00378}{1.525\times0.02477} = 0.1$$

$$\mathrm{NER} = \frac{0.0151}{3.051 \times 0.02477} = 0.2$$

$$\mathrm{CER} = \frac{0.1536}{(1.551+1.551) \times 0.02477} = 2$$

2. Calculation of CNB and CCB

CNB and CCB can be calculated by Eq. 4.30-4.31 in Chapter 4

$$\mathrm{CNB} = \frac{\textbf{Circulated NiO in process (kmol/h)}}{\textbf{Bio−oil fed to process (kmol/h)}} \quad \text{...(4.30)}$$

$$\mathrm{CCB} = \frac{\textbf{Circulated CaO in process (kmol/h)}}{\textbf{Bio−oil fed to process (kmol/h)}} \quad \text{...(4.31)}$$

Example

Feed 0.02477 kmol/h of bio-oil in the reformer. 0.763 kmol/h of NiO and 1.55 kmol/h of CaO are circulated in the process. CNB and CCB are calculated by

$$\mathrm{CNB} = \frac{0.763}{0.02477} = 30.8$$

$$\mathrm{CCB} = \frac{1.55}{0.02477} = 62.6$$

VITA

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