การผลิตไฮโดรเจนโดยเคมิคอลลูปปิงรีฟอร์มมิงบนตัวเร่งปฏิกิริยา NiO/CeO_2

นางสาวอภิชญา ยาหอม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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HYDROGEN PRODUCTION VIA CHEMICAL LOOPING REFORMING ON NiO/CeO_2

Miss Apichaya Yahom

A Thesis Submitted in Partial Fulfillment of the Requirements
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Department of Chemical Engineering
Faculty of Engineering
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อภิชญา ยาหอม: การผลิตไฮโดรเจนโดยเคมิคอลลูปปิงรีฟอร์มมิงบนตัวเร่งปฏิกิริยา NiO/CeO_2 (HYDROGEN PRODUCTION VIA CHEMICAL LOOPING REFORMING ON NiO/CeO_2) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. วรงค์ ปวราจารย์,120 หน้า.

งานนี้ได้ศึกษาการผลิตไฮโดรเจนจากมีเทนด้วยกระบวนการเคมิคอลลูปปิงรีฟอร์มมิงบนตัวเร่งปฏิกิริยา NiO โดยการจำลองด้วยโปรแกรมแอสเพน พลัส และการทดลอง ในส่วนของการใช้โปรแกรมได้มีการจำลองกระบวนการเคมิคอลลูปปิงและกระบวนการเคมิคอลลูปปิงรีฟอร์มมิงแบบมีการดูดซับเพื่อหาช่วงปฏิบัติการทดลองที่จะได้ไฮโดรเจนที่มีความบริสุทธิ์สูง มีการต้องการพลังงานในระบบที่ต่ำ ในส่วนของการทดลอง ได้ใช้ NiO บนตัวรองรับสองชนิด ได้แก่ CeO_2 และ Al_2O_3 ในการศึกษากระบวนการเคมิคอลลูปปิงคอมบัสชันแบบธรรมดา กระบวนการเคมิคอลลูปปิงคอมบัสชันแบบมีการดูดซับ กระบวนการเคมิคอลลูปปิงรีฟอร์มมิงแบบธรรมดาและกระบวนการเคมิคอลลูปปิงรีฟอร์มมิงแบบมีการดูดซับ โดยได้ทำการทดลองในเครื่องปฏิกิริยาแบบแพ็ค ที่ความดัน 1 บาร์ และที่ 600 องศาเซลเซียส NiO ประพฤติตัวเป็นของแข็งที่ถ่ายโอนออกซิเจนซึ่งจะถูกรีดิวซ์โดยแก๊สมีเทน และจะถูกออกซิไดซ์โดยอากาศ ในงานนี้ได้เลือก NiO เพราะมีความสามารถในการผลิตไฮโดรเจนได้สูง มีราคาไม่สูงมากและหาได้ง่าย ในกระบวนการเคมิคอลลูปปิงคอมบัสชัน จะใช้แก๊สมีเทน 2×10^{-6} โมล/วินาที (3 มล.(ที่อุณหภูมิห้อง)/นาที) เป็นสารตั้งต้นทำปฏิกิริยา ส่วนกระบวนการเคมิคอลลูปปิงรีฟอร์มมิง จะใช้แก๊สมีเทน 2×10^{-6} โมล/วินาที (3 มล.(ที่อุณหภูมิห้อง)/นาที) และน้ำ 4×10^{-6} โมล/วินาที (6 มล.(ที่อุณหภูมิห้อง)/นาที)เป็นสารตั้งต้นทำปฏิกิริยา ผลการทดลองพบว่า NiO/CeO_2 จะผลิตไฮโดรเจนได้ปริมาณมากกว่า NiO/Al_2O_3 เพราะ CeO_2 มีปริมาณออกซิเจนที่สามารถถ่ายเทได้สูงซึ่งจะช่วยในการทำปฏิกิริยานอกจากออกซิเจนบนนิกเกิลได้ นอกจากนี้ แคลเซียมออกไซด์ที่อยู่ในเครื่องปฏิกิริยาจะทำให้ผลิตภัณฑ์มีไฮโดรเจนที่มีความบริสุทธิ์สูงขึ้น และแก๊สมีเทนถูกทำปฏิกิริยามากขึ้นเนื่องจากแคลเซียมออกไซด์จะดูดซับแก๊สคาร์บอนไดออกไซด์ซึ่งจะทำให้ในระบบมีการทำปฏิกิริยามากขึ้นและยังทำให้ไฮโดรเจนมีความบริสุทธิ์สูงขึ้น

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APICHAYA YAHOM: HYDROGEN PRODUCTION VIA CHEMICAL LOOPING REFORMING ON NiO/CeO2.
ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D.
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This work focuses on the production of hydrogen from methane via the chemical looping reforming process, where NiO was used as the oxygen storing species. The study involved simulation of this process using a simulation package, Aspen Plus and laboratory experiments. The simulation work considered a conventional chemical looping process and a sorption enhanced chemical looping process, with the aim of finding appropriate operating conditions for the production of high purity hydrogen gas with low energy process requirements. The experimental work involved the loading of NiO on two different supports, CeO_2 and Al_2O_3, used in conventional chemical looping and sorption enhanced chemical looping operated under both combined combustion as well as reforming processes. Experiments were conducted in a fixed-bed reactor operating at 1 bar and 600°C. NiO was used as a solid oxygen carrier which in this process is reduced by methane and subsequently oxidized by air in a cyclic process. In the chemical looping combustion experiments, methane was fed as a reactant at a rate of $2x10^{-6}$ mol/s (3 cm^3(NTP)/min), and in the chemical looping reforming experiments, methane was fed at a rate of $2x10^{-6}$ mol/s (3 cm^3(NTP)/min) and steam at a rate of $4x10^{-6}$ mol/s (6 cm^3(NTP)/min). The results show a higher production rate of hydrogen with NiO/CeO_2 than for NiO/Al_2O_3. This result is explained by the higher oxygen storage capacity of CeO_2 which promotes the partial oxidation of methane. In addition, a higher hydrogen gas purity and a higher methane conversion were observed in the presence of CaO.

Department :…Chemical Engineering...	Student's Signature ……………..…………
Field of Study :..Chemical Engineering.	Advisor's Signature ……………..…………
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CHAPTER I
INTRODUCTION

1.1 Rationale

Hydrogen is an important feedstock for many chemical and petrochemical industries. It is used to produce various chemicals such as ammonia, methanol and hydrochloric acid. Currently hydrogen has been considered as a new clean and renewable energy source since 2000s to surpass shortage of petroleum, natural gas and coal, and to suppress pollution problems. Doll and Wietschel (2008) concluded that using hydrogen in transportation could significantly reduce carbon dioxide emissions. Hydrogen can be produced by several routes such as conversion from various primary fuels (e.g. natural gas, biomass and coal) and electrolysis process of water (Andrews and Shabani, 2012). Presently, natural gas whose main composition is methane is the major source for hydrogen production. The reactions can take place via three main routes: partial oxidation, steam reforming and autothermal reforming. Partial oxidation is an exothermic process in which a fuel is partially combusted with oxygen in a reformer (using less oxygen than a complete combustion) to generate hydrogen and carbon monoxide. An additional unit of air separation is required to generate oxygen-rich gas. Practically, direct feeding of air in the reform is not advisable due to presence of nitrogen in product gas. This is particularly important when carbon dioxide sequestration is of concern. Steam reforming is a process using steam to react with a fuel at high temperature. This reaction has several advantages. For example, no nitrogen is present in the process. However, the reaction is highly endothermic and thus requires large heat transfer area. Autothermal reforming is the process that combines partial oxidation and steam reforming together, so that this process needs less or no energy in operation because heat from partial oxidation reaction can be utilized for the steam reforming.

Chemical looping reforming is a hydrogen production technology which has attracted attention of many researchers nowadays. The process usually needs two reactors: a fuel reactor and an air reactor. In the fuel reactor, a primary fuel reacts with an oxygen carrier, and the products are hydrogen, carbon monoxide, carbon dioxide, water and oxygen-depleted solid material which can be subsequently regenerated by oxidation with air in the air reactor. Carbon monoxide can react with steam, yielding the products of hydrogen and carbon dioxide. Under the chemical looping reforming, the need for installing a nitrogen separation unit is no longer required. It is also possible to operate the hydrogen production under sorption-enhanced chemical looping reforming in which an adsorbent is mixed with an oxygen carrier to adsorb carbon dioxide, enabling the carbon dioxide capture for later sequestration.

In chemical looping reforming, solid materials including an oxygen carrier (metal oxide) and a support must be selected properly to get the highest activity, selectivity, conversion of fuel, and hydrogen production. Many oxygen carriers have been used such as Fe_2O_3, NiO, CuO, CoO and perovskites. Developments and synthesis of various metal oxides for chemical looping have been widely studied. It was reported that, to get high hydrogen production, NiO is the most interesting and promising oxygen carrier since it has high reactivity and high oxygen transport capacity. Support also plays an important role on the performances and, therefore, various supports such as Al_2O_3, TiO_2 and ZrO_2 have been tested in chemical looping reforming studies. Although there have been many studies focusing on development of solid materials for chemical looping reforming, many problems have been reported, for example, deactivation by carbon formation, sintering of metallic phases from the limited thermal resistance. The research on the development of solid materials for chemical looping reforming is still an important topic. The desired properties of solid materials are, for example, long useful life and less carbon formation.

In this work, NiO oxygen carrier supported on CeO_2 is proposed as a potential solid material for chemical looping reforming and sorption-enhanced chemical looping reforming. CeO_2 is well-known as a material with high oxygen storage and good redox properties. It is expected that when applied as a support of NiO, the solid material could perform well on the chemical looping reforming. Experimental study was carried out to compare the performance of NiO/CeO_2 with that of a conventional Ni/Al_2O_3 under various operating conditions.

1.2 Objective

To synthesize NiO/CeO_2 as a potential solid material for hydrogen production via chemical looping reforming and sorption-enhanced chemical looping reforming.

1.3 Scope of works

1. NiO was selected as an oxygen carrier for the hydrogen production from chemical looping reforming of methane.
2. Wetness impregnation technique was employed for loading NiO on two selected supports including Al_2O_3 and proposed CeO_2.
3. Reaction tests were carried out to compare catalytic performances of the two solid materials under chemical looping reforming and sorption-enhanced chemical looping reforming (with CaO as CO_2 adsorbent).
4. The effects of various operating variables (e.g. steam per methane, NiO per methane, temperature) on the reaction performances were considered.
5. Various techniques (XRD, BET, XPS and SEM-Edx) were employed to characterize properties of the synthesized materials.

1.4 Organization of the thesis

Beside Introduction chapter, the thesis is divided into five chapters: Theory, Literature reviews, Experimental and Simulation, Results and discussion, and Conclusions and Recommendations.

Theory (Chapter 2) presents various hydrogen production technologies which are developed to get high hydrogen purity and low energy requirement. Chemical looping reforming process is focused as one of the most promising technologies.

Literature reviews (Chapter 3) summarize previous studies of chemical looping reforming. The focus was on metal oxides used in experiments, supports, carbon dioxide sorption, and fixed bed reactor study.

In part of Experimental and Simulation (Chapter 4), simplified block flow diagrams and operating conditions of conventional chemical looping reforming and chemical looping reforming with CO_2 sorbent are shown. Furthermore, experimental setup, chemicals and gases, metal oxides preparation, and operating condition for experimental are presented.

Next, results and discussion (Chapter 5) describe the results of both conventional chemical looping reforming and chemical looping reforming with CO_2 sorbent from simulations to determine the appropriate operating condition for getting high hydrogen purity and low energy requirement, and from experiments by comparing different supports for NiO. Performance of carbon dioxide sorption enhanced chemical looping reforming is compared to that of conventional chemical looping reforming. Moreover, a metal oxides after the reaction experiments are also focused.

Finally, conclusion and recommendation (Chapter 6) is provided to determine the operating condition which would get high hydrogen purity and low energy requirement, moreover, recommendation is also described for future work.

CHAPTER II

THEORY

2.1 Hydrogen production

Hydrogen is a promising and renewable fuel. Combustion of this gas does not emit greenhouse gas, moreover, it produces large amount of energy per unit weight, and easily converted to electricity by fuel cells. Besides, hydrogen is a main feedstock in ammonia production, oil refinery, and methanol production (10.0%).

Hydrogen has average atomic weight of 1.00794 g. At standard pressure and temperature, this gas is colorless, non-toxic, odorless, and highly combustible. Naturally occurring atomic hydrogen is rare on earth because hydrogen readily forms covalent compounds with most elements and is present in a water molecule and in organic compounds.

Hydrogen can be produced by several ways from fossil resources, such as natural gas coal, as well as renewable resources, such as biomass and water with renewable energy sources like sunlight, wind, wave or hydro-power (process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical). The first hydrogen production was the electrolysis of water since the late 1920s.

RXN.1 $H_2O + \text{electricity} \rightarrow H_2 + 1/2O_2$ $\Delta H_{298K} = 241.8$ kJ/mol

Since 1960s, hydrogen from fossil-based feedstocks has been the main industrial hydrogen production. At present, hydrogen production is focused on:

1. Hydrogen production from fossil energy sources.

2. Hydrogen production in large scale, with CO_2 capture and storage
3. Hydrogen production in small scale from biomass.
4. Photo-electrolysis (photolysis). This is the process that uses light to split water directly into hydrogen and oxygen.
5. Photo-biological hydrogen production (biophotolysis). This method is based on photosynthesis and being catalyzed by hydrogenases such as cyanobacteria, green algae, etc.

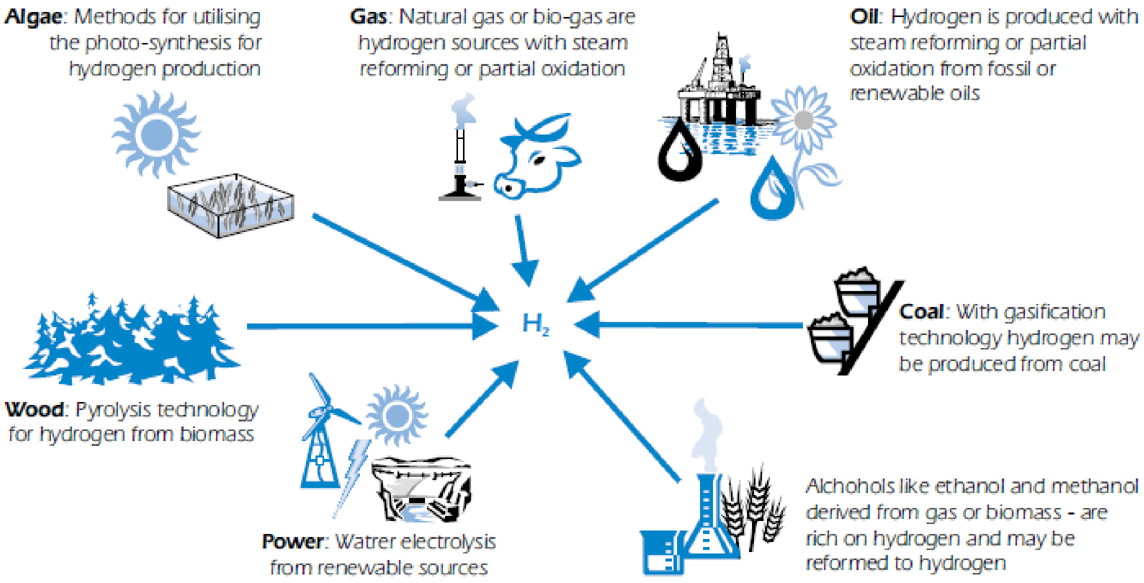


Figure 2.1 Hydrogen production

Hydrogen is generally produced from fossil fuels because they are easy to find and can produce a large amount of hydrogen compared to other sources. Hydrogen can be produced from fossil fuel by three main ways:

1. Partial oxidation

A fuel is partially combusted in a reformer to generate a hydrogen-rich syngas. Partial oxidation of natural gas (99% Methane) is as follow:

RXN.2 $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ $\Delta H_{298K} = -35.7$ kJ/mol

2. Steam reforming

Steam reforming is always a typical route of hydrogen production. The reaction is always accompanied with "water gas shift reaction" having carbon monoxide reacted with steam to form hydrogen and carbon dioxide.

RXN.3 $CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H_{298K} = 206.1$ kJ/mol

RXN.4 $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{298K} = -41.2$ kJ/mol

3. Autothermal reforming

Autothermal reforming is a combination of both steam reforming and partial oxidation

RXN.2 $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ $\Delta H_{298K} = -35.7$ kJ/mol

RXN.3 $CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H_{298K} = 206.1$ kJ/mol

RXN.4 $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{298K} = -41.2$ kJ/mol

A life cycle assessment (LCA) is a method that shows the environmental impacts of overall processes and compares the full range of environmental effects assignable to products and services. In order to quantify the emissions, resource consumption, and energy use, material and energy balances are performed in a cradle-to-grave manner on the operations required to transform raw materials into useful products. LCA of hydrogen production via natural gas steam reforming was performed to examine the net emissions of greenhouse gases.

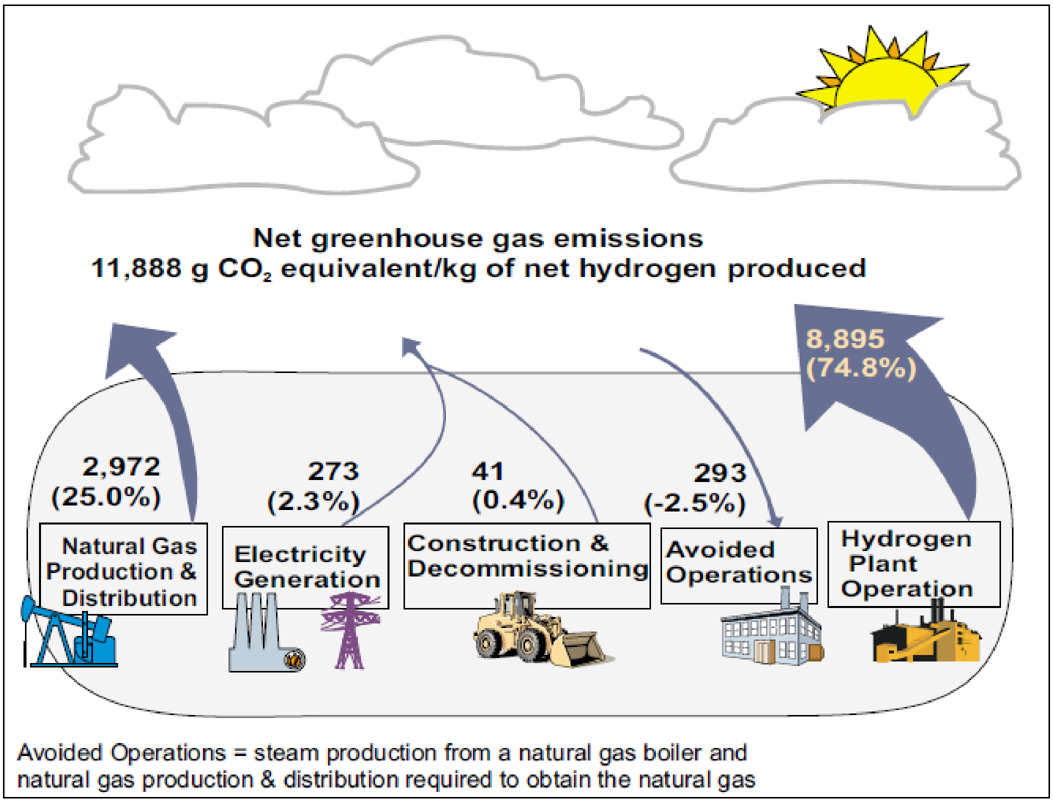


Figure 2.2 Life cycle assessment of hydrogen production via natural gas steam reforming

2.2 Chemical looping

The objective of development of carbon dioxide capture technologies is to reduce the cost of processes. Chemical looping Combustion (CLC) is suggested as the best alternatives to reduce the economic cost of carbon dioxide capture which is developed from Carbon Capture and Storage or CCS. A European project “Enhanced Capture of CO_2” (ENCAP) focused on the research in the development of cost efficient pre-combustion and oxy-fuel processes for carbon dioxide capture, including chemical looping combustion. Chemical looping combustion is the cheapest technologies for carbon dioxide capture.

Chemical looping is an interesting technology which has no direct contact between fuel and air. No separation unit is required for separation of nitrogen and carbon dioxide. An oxygen carrier (metal oxide) is employed as a media for transferring oxygen for the reactions. Chemical looping has two main options: chemical looping combustion and chemical looping reforming.

Chemical looping combustion which produces carbon dioxide and steam as main products has two reactions: Reduction reaction and Oxidation reaction.

RXN.5 $CH_4 + 4MeO \rightarrow CO_2 + 2H_2O + Me$ Reduction reaction

RXN.6 $Me + \frac{1}{2}O_2 \rightarrow MeO$ Oxidation reaction

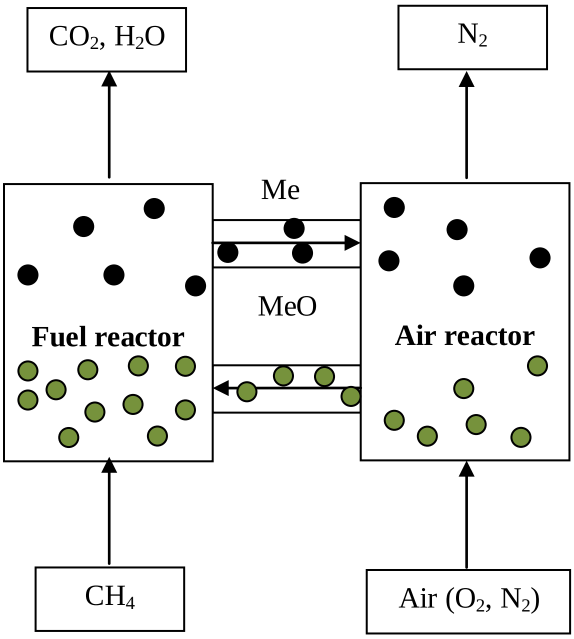


Figure 2.3 Chemical looping combustion

Chemical looping reforming is like chemical looping combustion but uses less metal oxide to react with fuel and forms hydrogen and carbon monoxide as main products.

RXN.7	$CH_4 + MeO \rightarrow CO + 2H_2 + Me$	Reduction reaction
RXN.6	$Me + ½O_2 \rightarrow MeO$	Oxidation reaction

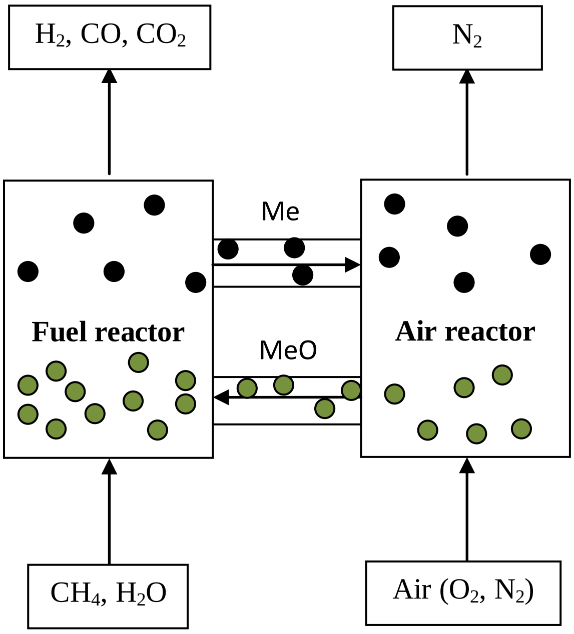


Figure 2.4 Chemical looping reforming

2.3 Oxygen Carrier

Oxygen carrier, always metal oxide, is a solid which is circulated in chemical looping operation. In process, solid material as oxygen-carrier containing oxygen is used to combust the fuel and get oxygen depleted solid material or only metal. To close the loop, the metal must be re-oxidized in air to form metal oxide before starting a new cycle. Oxygen carrier should have high reactivity with fuel and oxygen, in addition, it can convert a large amount of fuel to CO_2 and H_2O (or CO and H_2) (Rydén et al., 2008). Moreover reactivity of the carrier, cost, toxicity, thermal stability, and attrition resistance (in case of using fluidized bed reactor) should be considered (Najera et al., 2011).

Oxygen carriers used in chemical looping are, for example, Fe_2O_3, CuO, CoO and NiO. Each metal oxide has different equilibrium constant and, consequently, different conversion of a reducing gas. The higher the equilibrium constant, the higher reducing gas is converted. The selectivity towards CO_2 and H_2O which is affected by the equilibrium constant for CO and H_2, respectively, depends on the redox system.

Nickel oxide (NiO) is an interesting oxygen carrier that is often used in chemical looping reforming because nickel is a catalyst most widely used in hydrogen production and has high oxygen transport capacity.

There are many reactions taking place in chemical looping reforming:

RXN.8 $CH_4 + 4NiO \rightarrow CO_2 + 2H_2O + 4Ni$ $\Delta H_{298K} = 174.9$ kJ/mol

RXN.9 $CH_4 + NiO \rightarrow CO + 2H_2 + Ni$ $\Delta H_{298K} = 208.6$ kJ/mol

RXN.10 $CH_4 + 2NiO \rightarrow CO_2 + 2H_2 + 2Ni$ $\Delta H_{298K} = 169.9$ kJ/mol

RXN.3 $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H_{298K} = 206.1$ kJ/mol

RXN.11 $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ $\Delta H_{298K} = 357.8$ kJ/mol

RXN.4 $H_2O + CO \leftrightarrow CO_2 + H_2$ $\Delta H_{298K} = -41.2$ kJ/mol

RXN.12 $Ni + ½O_2 \rightarrow NiO$ $\Delta H_{298K} = -244.3$ kJ/mol

The oxygen transport capacity of the material (R_{OC}) is a characteristic of the oxygen-carrier which is important for process design and operation. Furthermore, it is an indicator of the amount of oxygen that can be transferred by the oxygen carrier between reactors. R_{OC} depends on the oxygen transport capability of oxide, R_O, and the fraction of the active compound for oxygen transport, x_{OC}.

$$R_{OC} = x_{OC}R_O \qquad (2.1)$$

Considering that the metal oxides are combined with an inert. Thus, the effective value of oxygen transport capacity of an oxygen-carrier depends on the fraction of active material for oxygen transport, x_{OC}. The oxygen transport capability, R_O, defined by Eq. (2), depends on the metal oxide and redox reactions. Where m is the instantaneous mass and the denominator is the maximum oxygen transport between the masses of fully oxidized, m_{ox}, and masses of reduced, m_{re}, oxygen-carrier, respectively.

$$R_O = (m_{ox} - m_{re})/m_{ox} \qquad (2.2)$$

2.4 Carbon dioxide sorption

Carbon dioxide can be absorbed by amine solutions. Solution mostly used is Ethanolamine but usually mono ethanolamine or MEA. MEA is a colorless, viscous, toxic, flammable, corrosive liquid with an odor similar to ammonia. MEA which absorbs carbon dioxide can be separated from gas by using a stripping column, then MEA can be used again.

Besides absorption, carbon dioxide can be adsorbed by solid materials called sorbents. Various sorbents such as CaO, Li_4SiO_4 and Li_2ZrO_3 are available for adsorption of carbon dioxide gas. The reactions are as follows:

The sorption reactions of sorbents are:

RXN.13 $CaO + CO_2 \leftrightarrow CaCO_3$ $\Delta H_{298K} = -178.8$ kJ/mol

RXN.14 $Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3$ $\Delta H_{298K} = -142.0$ kJ/mol

RXN.15 $Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$ $\Delta H_{298K} = -160.0$ kJ/mol

And the sorbents can be heated to desorb gas and the solids can be used again.

2.5 Carbon activity

In chemical looping process, carbon formation may occur. There are four reactions that carbon may occur:

$2CO \leftrightarrow CO_2 + C$ (C 1)

$CH_4 \leftrightarrow 2H_2 + C$ (C 2)

$CO+H_2 \leftrightarrow H_2O+C$ (C 3)

$CO_2+2H_2 \leftrightarrow 2H_2O+C$ (C 4)

The carbon activities, α, is the indicator for the presence of carbon in the system. It does not give the information regarding the amount of carbon formed. Carbon activities were defined in Equations 1–4 to determine the possibility of carbon formation.

$$\alpha_{C,CO} = K_I \frac{P_{CO}^2}{P_{CO_2}}$$ equation 1

$$\alpha_{C,CH_4} = K_{II} \frac{P_{CH_4}}{P_{H_2}^2}$$ equation 2

$$\alpha_{C,CO-H_2} = K_{III}\frac{P_{CO}P_{H_2}}{P_{H_2O}} \qquad \text{equation 3}$$

$$\alpha_{C,CO_2-2H_2} = K_{IV}\frac{P_{CO_2}P_{H_2}^2}{P_{H_2O}^2} \qquad \text{equation 4}$$

Where K_I, K_{II} and K_{III}, and K_{IV} represent the equilibrium constants of the reactions I, II, III and IV, respectively, and P_n is the partial pressure of component n. When $\alpha_c > 1$, the system is not in equilibrium and carbon formation occurred. If $\alpha_c = 1$, the system is at equilibrium, and if $\alpha_c < 1$, carbon formation is thermodynamically not preferable.

CHAPTER III

LITERATURE REVIEWS

Chemical looping has been investigated and studied since 1980s. The literature reviews are divided into three topics. Firstly, previous works on metal oxides used in chemical looping is described. Secondly, supports used for metal oxides are reviewed. Then, carbon dioxide sorption for enhancing hydrogen production is summarized.

3.1 Metal oxides

Many metal oxides have been used in chemical looping such as Fe_2O_3, CuO, CoO, Mn_3O_4, NiO, etc. Each of them has various advantages. For example, Fe_2O_3, or Iron oxide, is observed to offer the highest conversion of syngas to combustion products such as CO_2, H_2O, etc. (Gnanapragasam et al., 2009). It is an attractive metal oxide for chemical looping combustion because of its low cost and environmental compatibility, low tendency to form carbon, no risk of sulphide or sulphate formation from any gases containing sulfur, moreover it is cheaper than other metal oxides. It is not toxic in spite of its weak redox characteristics, low methane conversion and oxygen transport capacity so that most of the works used materials with contents of higher than 60 wt% of this metal oxide. Fe_2O_3 can be reduced in form of Fe_3O_4 (Magnetite), FeO (Wustite), or Fe when reacting with fuel. However, Cho et al. (2006) and Rydén et al. (2010) reported agglomeration problems in the bed as a result of the phase change from wustite to magnetite when metal oxide is oxidized in air.

Copper oxide (CuO) shows high reaction rates with all the supports and preparation methods, high oxygen transport capacity, and no thermodynamic restrictions for complete fuel conversion to carbon dioxide and water. In addition, it is cheaper than other materials such as nickel and cobalt and has less environmental problems. But this metal oxide has disadvantages in high tendency to defluidization because of its low melting temperature while a higher operating temperature is preferred to obtain high efficiencies in the system, and cannot be made by mechanical mixing and wet impregnation because it is easily agglomerated (Adanez et al., 2012). de Diego et al. (2004), Cao et al. (2006), Roux et al. (2006), Tian et al. (2008), Siriwardane et al. (2009), and Rubel et al. (2009) investigated pure CuO carried out thermogravimetric analysis during reaction with fuel gases or directly with coal. The result showed that CuO has high reactivity, even at low temperatures but the oxidation reaction rate of pure CuO decreased quickly with the increasing number of cycles.

NiO, or nickel oxide, is commonly used in chemical looping reforming because nickel is a catalyst used in hydrogen production. Furthermore, it can be easily reduced to metallic Ni at low temperature, has high reactivity with methane and other hydrocarbons (Rydén et al., 2008), low attrition rate, and Ni can react slightly with steam to give low concentration of hydrogen (Svoboda et al., 2008). Nearly complete methane conversion was obtained in a chemical looping combustion process at low attrition rate. Moreover, using Ni-based oxygen-carriers may require safety measures because of its toxicity and nickel is more expensive than other metal oxides (Adanez et al., 2012).

Abad et al. (2007) investigated mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. This study used fluidized bed reactor. A mapping of the range of operational conditions, design values, and oxygen carrier characteristics were studied for the most usual metal oxides (CuO, Fe_2O_3, and NiO) and different fuel gases (methane, hydrogen, and carbon monoxide). Oxides of these metals supported on several inert solids showed low attrition rates and high reaction rates during many reduction–oxidation cycles.

Table 3.1 Comparison of Cu-, Fe-, and Ni-oxides at standard pressure and temperature (Abad et al., 2007)

Materials	R_O	Reactions	ΔH (kJ/mol)
CuO/Cu	0.2	$CH_4 + 4CuO \leftrightarrow 4Cu + CO_2 + 2H_2O$	-178
		$H_2 + CuO \leftrightarrow Cu + H_2O$	-85.8
		$CO + CuO \leftrightarrow Cu + CO_2$	-126.9
		$O_2 + 2Cu \leftrightarrow 2CuO$	-312.1
Fe_2O_3/Fe_3O_4	0.03	$CH_4 + 12Fe_2O_3 \leftrightarrow 8Fe_3O_4 + CO_2 + 2H_2O$	141.6
		$H2 + 3Fe_2O_3 \leftrightarrow 2Fe_3O_4 + H_2O$	-5.8
		$CO + 3Fe_2O_3 \leftrightarrow 2Fe_3O_4 + CO_2$	-47
		$O_2 + 4Fe_3O_4 \leftrightarrow 6Fe_2O_3$	-471.9
NiO/Ni	0.21	$CH_4 + 4NiO \leftrightarrow 4Ni + CO_2 + 2H_2O$	156.5

3.2 Supports

The objectives of using a support are to improve metal oxide performance, to provide a higher surface area for reaction and to increase the mechanical strength and attrition resistance (Abad et al., 2007).

NiO particle has low reaction rate because of its low porosity. Using of alumina-based compounds as support has been studied. Compared with other metal oxides, most of the oxygen-carriers supported on Al_2O_3 compounds show high reactivity with all fuel gases, no agglomeration problems, low attrition rates during operation in fluidized beds, and avoidance of carbon deposition. However, Ryu et al. (2003) and Copeland et al. (2001) reported that reduction of NiO/Al_2O_3 particles is limited by the partial transformation of NiO into $NiAl_2O_4$ spinel compound. Villa et al. (2003) showed that it has poor reactivity. Moreover, Adánez et al. (2004) and Son et al. (2006) investigated that metal oxide prepared by mechanical mixing has low crushing strength. As consequence of $NiAl_2O_4$ formation, excess of NiO should be used during particle preparation to get free NiO inside the particle. Consequently, NiO particle over $NiAl_2O_4$ support has high reactivity if the Ni content in the particle is very high up to 80 wt% to have a NiO free content of 60 wt%. Using δ-Al_2O_3 support leads to formation of important amounts of $NiAl_2O_4$ because the formation of the spinel depends on the crystalline nature of the support. To minimize the interaction of NiO with Al_2O_3, there must be some modifications of the support via thermal treatment or chemical deactivation. By thermal treatment of δ-Al_2O_3 at 1150°C, the support forms α-Al_2O_3. Gayán et al. (2008) showed that Ni-based oxygen-carrier prepared by impregnation on α-Al_2O_3 has very high reactivity, low attrition rates and agglomeration avoidance problems during operation in fluidized beds. They concluded that about 80% of the Ni reduced in the fuel-reactor was oxidized in air reactor to form free NiO while the remaining Ni was oxidized to form $NiAl_2O_4$.

Iriondo et al. (2010) investigated glycerol steam reforming over Ni catalysts supported on ceria (CeO_2), alumina (Al_2O_3) and ceria-promoted alumina to produce hydrogen in a fixed bed reactor.

RXN.16 $HOCH_2\text{-}CHOH\text{-}CH_2OH + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad \Delta H_{298K} = 123.0\ kJ/mol$

Garcia et al. (2000) observed that Al_2O_3 support is usually used in catalytic steam reforming because of its good chemical and mechanical resistance, and its high specific area. Alberton et al. (2007) observed that these characteristics can improve metal dispersion. However, this catalytic system has problem with deactivation under the steam reforming due to the formation of coke and the sintering of the metallic phase. Ni et al. (2007) summarized that coke formation is usually related to the dehydration, cracking which takes place in the acid sites of the alumina support. Seo et al. (2009) concluded that limited thermal resistance of Al_2O_3 can cause the metal sintering. To avoid the deactivation of the catalyst from coke formation, the support can be modified with a rare-earth oxide as ceria (CeO_2). Alberton et al. (2007) and Liguras et al. (2003) observed the advantages of CeO_2 that this support is favoring the coke gasification and De Lima et al. (2008) and Diagne et al. (2004) concluded that ceria is also favoring water gas shift reaction.

In this study, there are five catalysts used in experiments: Ni/CeO_2, Ni/(95% Al_2O_3 + 5% CeO_2), Ni/(90% Al_2O_3 + 10% CeO_2), Ni/(80%Al_2O_3+20% CeO_2), and Ni/Al_2O_3, these are noted for short as NiCe, NiAl5Ce, NiAl10Ce, NiAl20Ce, and NiAl, respectively.

Table 3.2 Chemical compositions in weight percent and textural properties for calcined catalysts (Iriondo et al., 2010)

Catalysts	S_{BET}	Pore V	Pore D_m
Ni/CeO_2	23	0.039	6.7
Ni/Al_2O_3	207	0.767	14.8
Ni/(95%Al_2O_3+5%CeO_2)	225	0.806	14.3
Ni/(90%Al_2O_3+10%CeO_2)	219	0.768	14
Ni/(80%Al_2O_3+20%CeO_2)	206	0.714	13.9

From Table 3.2, the Ni/CeO_2 (NiCe) catalyst showed the lowest BET surface area, pore volume and diameter. But when the ceria was used as a modifier with alumina, the surface area of the Ni catalysts supported on ceria-promoted alumina was higher than for the Ni/Al_2O_3 (NiAl for short) catalyst, excluding the Ni/(80%Al_2O_3+20% CeO_2) (NiAl20Ce for short) catalysts. Wang et al. (1998) reported that low or medium ceria contents on alumina can increase catalysts surface area.

Thermogravimetric analyses (TGA) of the spent catalysts were carried out to determine the amount and the type of carbonaceous species deposited on the catalysts after glycerol steam reforming. As shown in Table 3.3, when the ceria content was increased, amount of carbon deposited on the catalysts were lower. In general, low amount of coke were formed during glycerol steam reforming. This could be attributed to the CeO_2 capacity to store and transfer oxygen and as a result to promote the gasification of the coke deposits.

Table 3.3 Amount of carbonaceous species deposited on Ni/CeO_2, Ni/(95% Al_2O_3 + 5% CeO_2), Ni/(90% Al_2O_3 + 10% CeO_2), Ni/(80% Al_2O_3 + 20% CeO_2) (Iriondo et al., 2010)

Catalysts	g Carbon/g Catalyst
Ni/CeO_2	0.01
Ni/(95% Al_2O_3 + 5% CeO_2)	0.04
Ni/(90% Al_2O_3 + 10% CeO_2)	0.03
Ni/(80%Al_2O_3+20% CeO_2)	0.03

The catalytic activity results for the Ni/(95% Al_2O_3 + 5% CeO_2) and Ni/(90% Al_2O_3 + 10% CeO_2) catalysts showed that the incorporation of low ceria loadings enhances the activity of the Ni/Al_2O_3 catalyst prepared using a similar composition to the commercial Ni/Al_2O_3 catalysts. The catalyst surface characterization revealed that the good behaviour of the Ni/(95% Al_2O_3 + 5% CeO_2) and the Ni/(90% Al_2O_3 + 10% CeO_2) catalysts depends on the stabilization of Ni-particles which is promoted by the formation of nickel ceria interactions. The increase of ceria content reduced the capacity of the Ni/(80%Al_2O_3+20% CeO_2) catalyst to convert intermediate oxygenated hydrocarbons into hydrogen.

3.3 Carbon dioxide sorption

Chen et al. (2011) investigated calcium looping for high concentration hydrogen production with CO_2 capture in a novel compact fluidized bed. Steam reforming of coal using calcium oxide (CaO) in one of the coal technologies developed for enhancing hydrogen production by separating carbon dioxide. CaO which can be regenerable is used to remove carbon dioxide from flue gas. There are three main parts: a gasifier, a riser and a regenerator. In the gasifier, the reaction occurs with carbon dioxide removal by carbonation reaction:

RXN.13 $CaO + CO_2 \leftrightarrow CaCO_3$ $\Delta H_{298K} = -178.8$ kJ/mol

The removal of carbon dioxide favored the gasification and water shift reaction equilibrium and get hydrogen-rich gas product. CaO was regenerated in a regenerator by burning the unreacted char with oxygen, and a pure stream of carbon dioxide was separated from gas by cyclone. The regenerated CaO then flowed into a riser above a gasifier, and removed the carbon dioxide in the outlet gases from the gasifier and drived the water-gas shift reaction forward, further improving the hydrogen purity. From the results, hydrogen purity reached 96 vol% at a steam flow of 80 mol/s and CaO recycle rate of 30 mol/s when the carbon conversion rate was 0.50. Increasing the steam flow and CaO recycle rate can enhance the hydrogen yield and purity. With the increasing of operation pressure from 1 to 10 bar, the hydrogen yield and purity decrease and methane yield increases. High pressure leads to higher calcination temperature. But at high pressure, it must be operated at high temperature for decomposition of $CaCO_3$ (1100^{o}C) that leads to deactivate the sorbent.

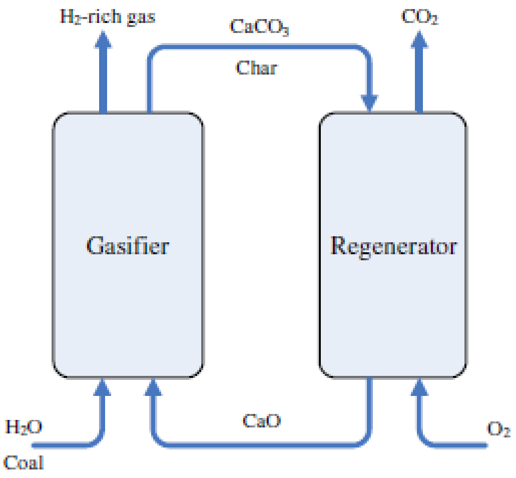


Figure 3.1 Schematic description of the coal/CaO/steam process (Chen et al., 2011)

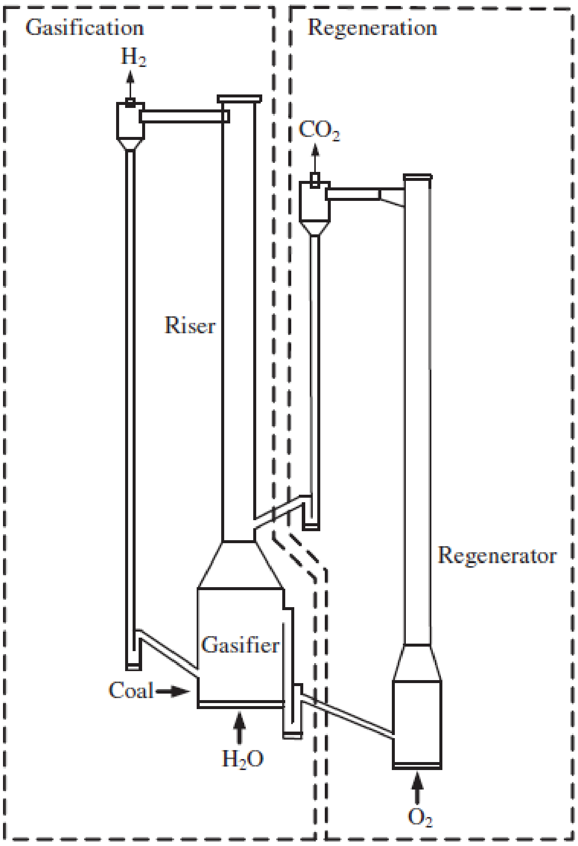


Figure 3.2 Proposed compact fluidized bed for the coal/CaO/steam process (Chen et al., 2011)

Rydén and Ramos (2012) investigated H_2 production with CO_2 capture by sorption enhanced chemical looping reforming using NiO as oxygen carrier and CaO as CO_2 sorbent. In this study, CaO was used in chemical looping reforming for enhancing hydrogen production and making more purity of main product (hydrogen).

There were three reactors used in this case: Reforming reactor, Calcination reactor, and Air reactor. Reforming reactor and Air reactor were the same as an ordinary Chemical looping, Calcination reactor was added to regenerate the $CaCO_3$ to form CaO.

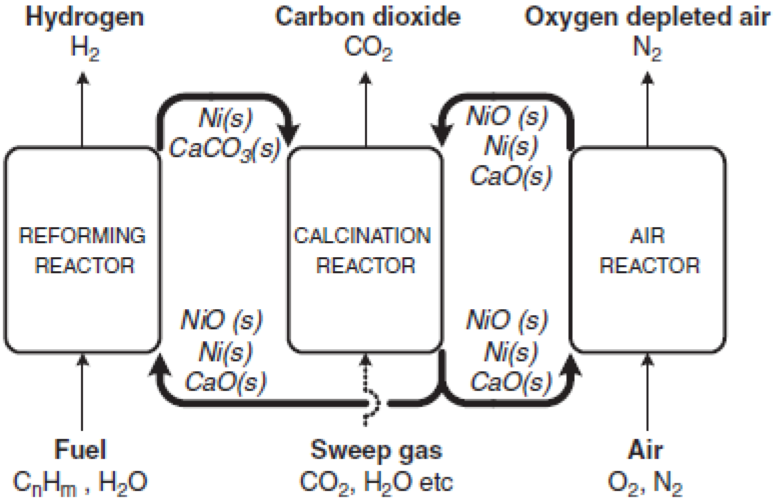


Figure 3.3 Schematic description of sorption-enhanced chemical-looping reforming (Rydén and Ramos, 2012)

In this experiment, nickel oxide was produced by freeze granulation. The particles of metal oxide had size range of 90–212 µm, bulk density was 2.6 g/cm. The NiO content was 40 wt%. CaO as a carbon dioxide sorbent had a bulk density of 1.2 g/cm and size range of 90–212 µm. Chemical looping reforming experiments without sorbent was observed by using silica instead of CaO. The silica sand had a particle size of 90–212 µm and a bulk density of 1.6 g/cm. The experiments were operated in fluidized bed quartz reactor. The solid sample was composed of 5 g of NiO and 10 g of CaO compared with the sample consisted of 5 g of NiO and 10 g silica sand. Reduction was performed with a mixture of 1.36x10^{-4} mol/s (0.20 L (NTP)/min) methane and 2.45x10^{-4} mol/s (0.36 L (NTP)/min) steam. The oxidation was performed with a mixture of 3.41x10^{-5} mol/s (0.05 L (NTP)/min) oxygen and 6.47x10^{-4} mol/s (0.95 L (NTP)/min) nitrogen. Two reactions were operated at four temperatures (600^{o}C, 650^{o}C, 700^{o}C, and 750^{o}C).

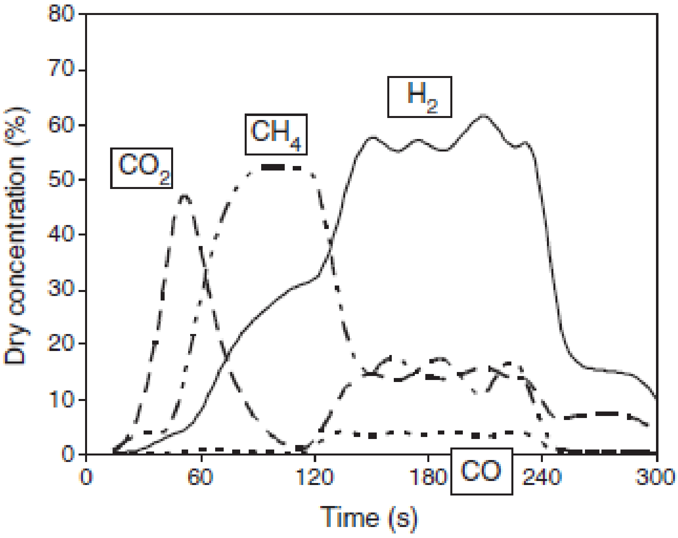


Figure 3.4 Measured dry gas concentrations during reduction of 5 g NiO and 10 g sand at 600 °C with 1.36x10^{-4} mol/s (0.20 L (NTP)/min) methane and 2.45x10^{-4} mol/s (0.36 L (NTP)/min) steam (Rydén and Ramos, 2012)

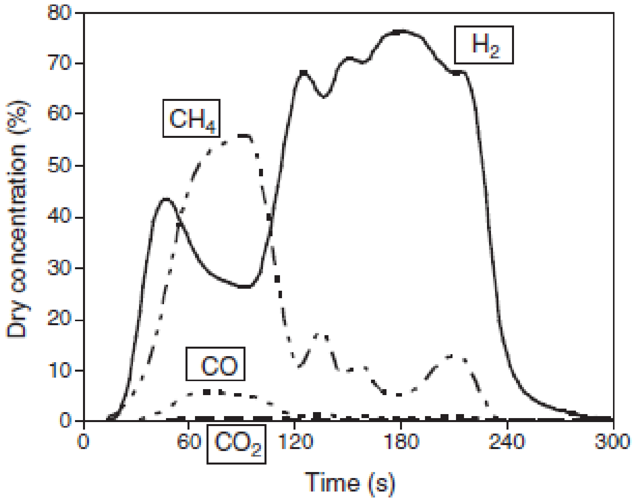


Figure 3.5 Measured dry gas concentrations during reduction of 5 g NiO and 10 g CaO at 600 °C with 1.36x10^{-4} mol/s (0.20 L (NTP)/min) methane and 2.45x10^{-4} mol/s (0.36 L (NTP)/min) steam (Rydén and Ramos, 2012)

Table 3.4a Gas concentrations for the reforming periods for conducted 5 g of NiO and 10 g of sand experiments (Rydén and Ramos, 2012)

Temperature ^{o}C	5 g of NiO and 10 g of sand			
	X_{CO} %	X_{CO2} %	X_{CH4} %	X_{H2} %
600	4.4	15.6	17.8	62.2
650	7.6	14.1	15.2	15.2
700	12.2	13.3	10	10
750	15.9	10.2	9.1	9.1

Table 3.4b Gas concentrations for the reforming periods for conducted 5 g of NiO and 10 g of CaO experiments (Rydén and Ramos, 2012)

Temperature ^{o}C	5 g of NiO and 10 g of CaO			
	X_{CO} %	X_{CO2} %	X_{CH4} %	X_{H2} %
600	1.1	0.5	14.8	83.6
650	3.5	1.7	15	79.8
700	5.9	4.7	16.5	72.9
750	16.1	9.2	6.9	67.8

From Table 3.4, CaO was found to improve the hydrogen concentration at lower temperatures, at the expense of carbon monoxide and carbon dioxide.

3.4 Fixed bed reactor

Using interconnected fluidized bed technology in chemical looping plants is very popular but may have some difficulties to maintain a stable solid circulation between the reactors, moreover, there can be problem from attrition of solid that makes metal oxide having lower activity. Thus, operating in fixed bed (or packed bed) reactors has been proposed. The main advantages of fixed bed reactor are that the separation of gas and particles is intrinsically avoided and working under pressure is possible. The disadvantages are that it must be operated at high temperature and high flow gas switching system.

CHAPTER IV

EXPERIMENTAL AND SIMULATION

This chapter provides details of experimental and simulation of chemical looping reforming. In part of simulation, chemical looping reforming and chemical looping reforming with CO_2 sorbent were simulated using Aspen plus program. In part of experimental, chemicals and gases used in the experiments, metal oxides preparation method (incipient wetness impregnation), experimental set-up and reaction testing, and characterization of materials for chemical looping reforming are presented.

4.1 Simulation

Figure 4.1 shows the block flow diagram of chemical looping reforming that was simulated using Aspen plus program. The system consists of a fuel reactor, an air reactor, cyclones and heat exchangers. The reactant stream containing 1 mol of methane and 2 mol of steam at 35^{o}C and atmospheric pressure was heated by heat exchangers and introduced to the fuel reactor at atmospheric pressure to react with NiO solid. The products were hydrogen as a major product, some fractions of methane, unreacted steam, carbon dioxide, carbon monoxide, and Ni solid that was a reduced form of NiO. The fuel reactor was assumed to operate under isothermal condition. Then, all of products were transported to the cyclone to separate Ni solid from gas. Ni was then transferred to the air reactor for combustion with air and NiO was formed. The air reactor was assumed to operate under adiabatic condition. After that, NiO was separated from nitrogen gas by cyclone before being sent to the fuel reactor. Note that part of combustion energy from the combustion in the air reactor was absorbed by the NiO solid (usually temperature higher than 1000^{o}C) and this was utilized in the fuel reactor. The product gas from fuel reactor and air reactor were cooled to 150^{o}C by heat exchangers to get energy for use within the process. The solid thermodynamic option set was used in the simulation.

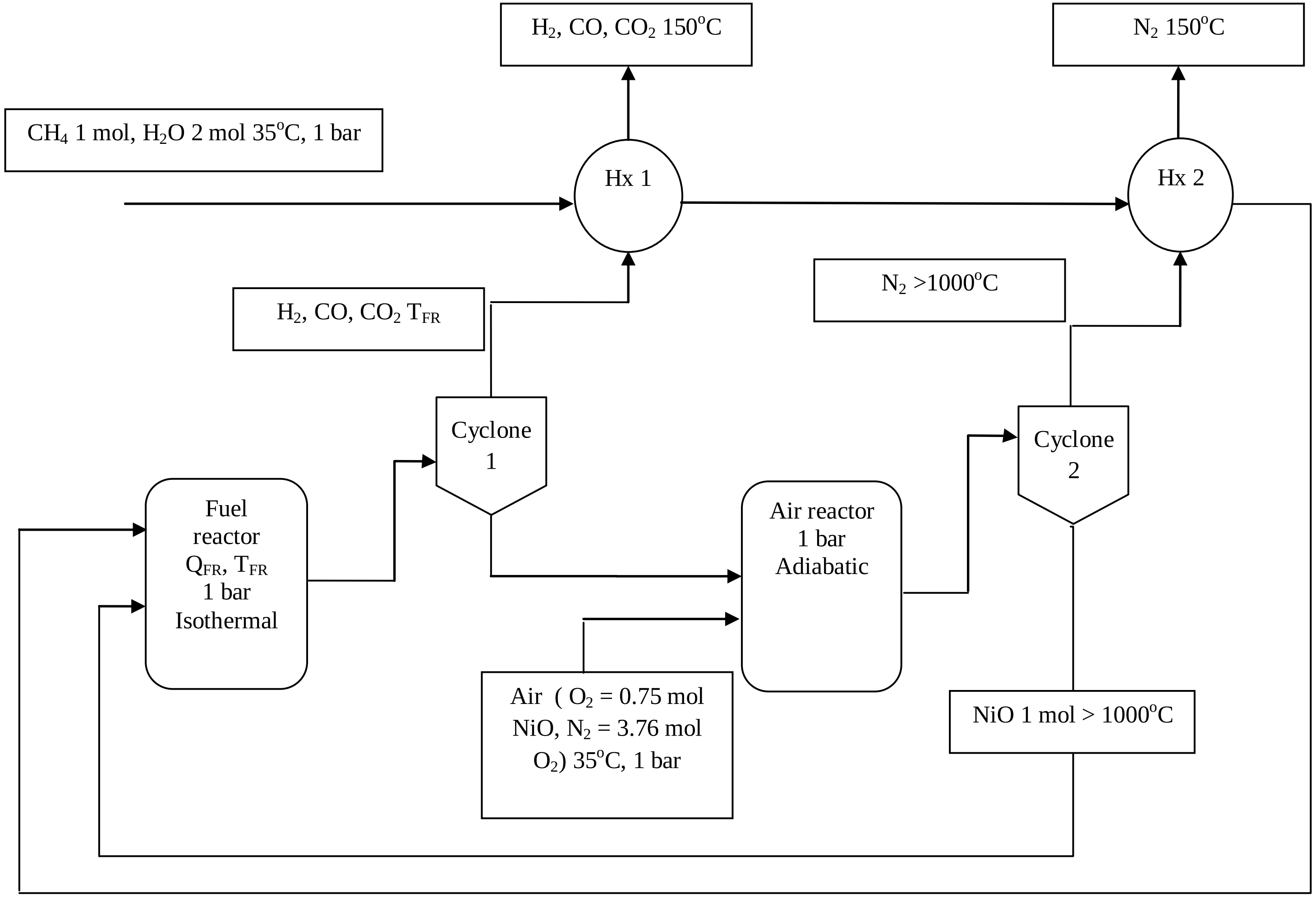


Figure 4.1 Chemical looping reforming block flow diagram

Sorption enhanced chemical looping reforming system (Figure 4.2) was also examined via Aspen plus program. The system consists of fuel reactor, calcination reactor, air reactor, cyclones, and heat exchangers. The reactant stream containing 1 mol of methane and 2 mol of steam at 35°C and atmospheric pressure was heated by heat exchangers and introduced to fuel reactor at isothermal condition (500, 600, 700, and 800°C) and atmospheric pressure to react with NiO solid and CaO as CO_2 sorbent, the products were hydrogen as a major product, some fractions of methane, unreacted steam, carbon monoxide, calcium carbonate, and Ni solid that was a reduced form of NiO. Then, all of products were transported to cyclone to separate Ni and $CaCO_3$ solids from gas. $CaCO_3$ was calcined in the calcination reactor to release carbon dioxide and there was a cyclone to separate gas from CaO and Ni solid. Ni and CaO were then transferred to air reactor to combust with air in air reactor which was operated at adiabatic condition, and NiO was formed. After that, NiO and CaO were separated from nitrogen gas by cyclone and then fed to the fuel reactor. NiO and CaO solids were at high temperature (more than 1000°C) due to the exothermic combustion in the air reactor. The product gas from the fuel reactor, the calcination reactor, and the air reactor were cooled to 150°C by heat exchangers to get energy for use within the process.

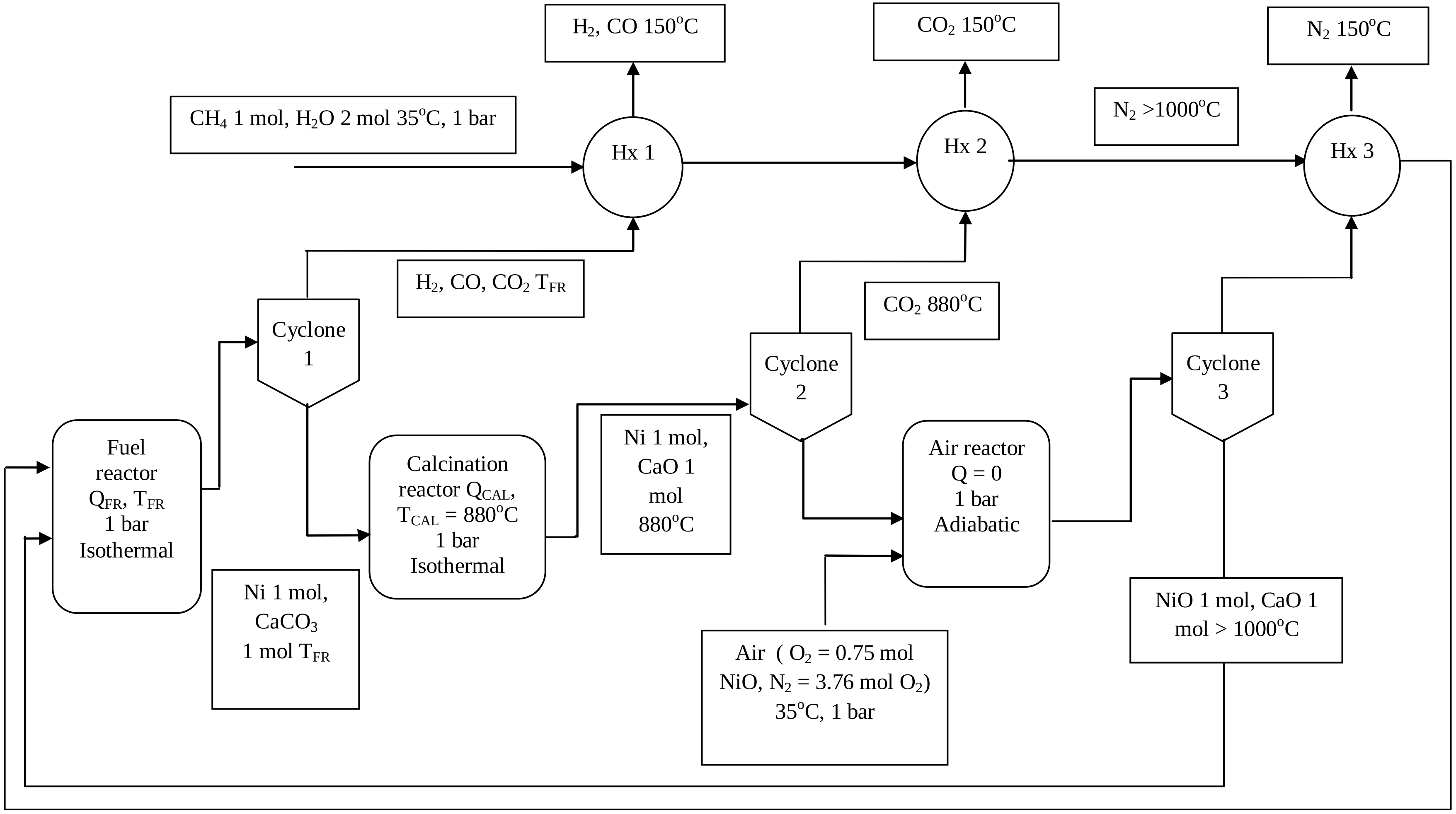


Figure 4.2 Chemical looping reforming with CO_2 sorbent block flow diagram

Table 4.1 Summary of block component for model in Aspen plus program

Component	Assumptions	Pressure (bar)	Temperature	Energy
Fuel reactor	Thermodynamic equilibrium is reached (Rgibbs)	1	T_{FR}	Q_{FR}
Calcination reactor	Thermodynamic equilibrium is reached (Rgibbs)	1	T_{CAL}	Q_{CAL}
Air reactor	Thermodynamic equilibrium is reached (Rgibbs)	1	$T > 1000^{o}C$	0
Cyclone 1	Perfect separation between solids and gas	1	T_{FR}	-
Cyclone 2	Perfect separation between solids and gas	1	T_{CAL}	-
Cyclone 3	Perfect separation between solids and gas	1	$T > 1000^{o}C$	-
Heat exchanger 1	Outlet hot stream is $150^{o}C$	1	-	-
Heat exchanger 2	Outlet hot stream is $150^{o}C$	1	-	-
Heat exchanger 3	Outlet hot stream is $150^{o}C$	1	-	-

4.2 Experimental

In part of experimental, there are comparisons between alumina (Al_2O_3) support and ceria (CeO_2) support, and between sorption experiment and no sorption experiment.

4.2.1 Chemicals and gases

1. Commercial alumina (γ-Al_2O_3, Sigma Aldrich)
2. Ceria (CeO_2) (10% Gd_2O_3 in CeO_2 (CGO) from MTEC, Thailand)
3. Calcium oxide (99.0 %, APS AJAX Finechem Co., Ltd.)
4. Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich)
5. Silicon carbide (SiC, Sigma Aldrich)
6. Nitrogen gas 99.999% (N_2)
7. Methane 99.999% (CH_4)
8. Oxygen 99.99% (O_2)
9. Argon gas 99.999% (Ar)
10. Deionized water

4.2.2 Metal oxides preparation

13wt%NiO/Al_2O_3 and 13wt%NiO/CeO_2 were used as metal oxides for hydrogen production via chemical looping reforming. Alumina (Al_2O_3) and ceria (CeO_2) are used as supports. Nickel nitrate hexahydrate (Aldrich) was used as precursor for impregnation on support. Firstly, $Ni(NO_3)_2{\cdot}9H_2O$ was dissolved in DI water to get Ni solution. After that, Ni solution was dropped over on a support (Al_2O_3 for NiO/Al_2O_3 preparation and CeO_2 for NiO/CeO_2 preparation). Then, it was dried at 100 °C over night and calcined at 800 °C for 4 h with air to form 13wt%NiO on support.

4.2.3 Experimental setup

Figure 4.3 shows the experimental setup for the chemical looping reforming of methane.

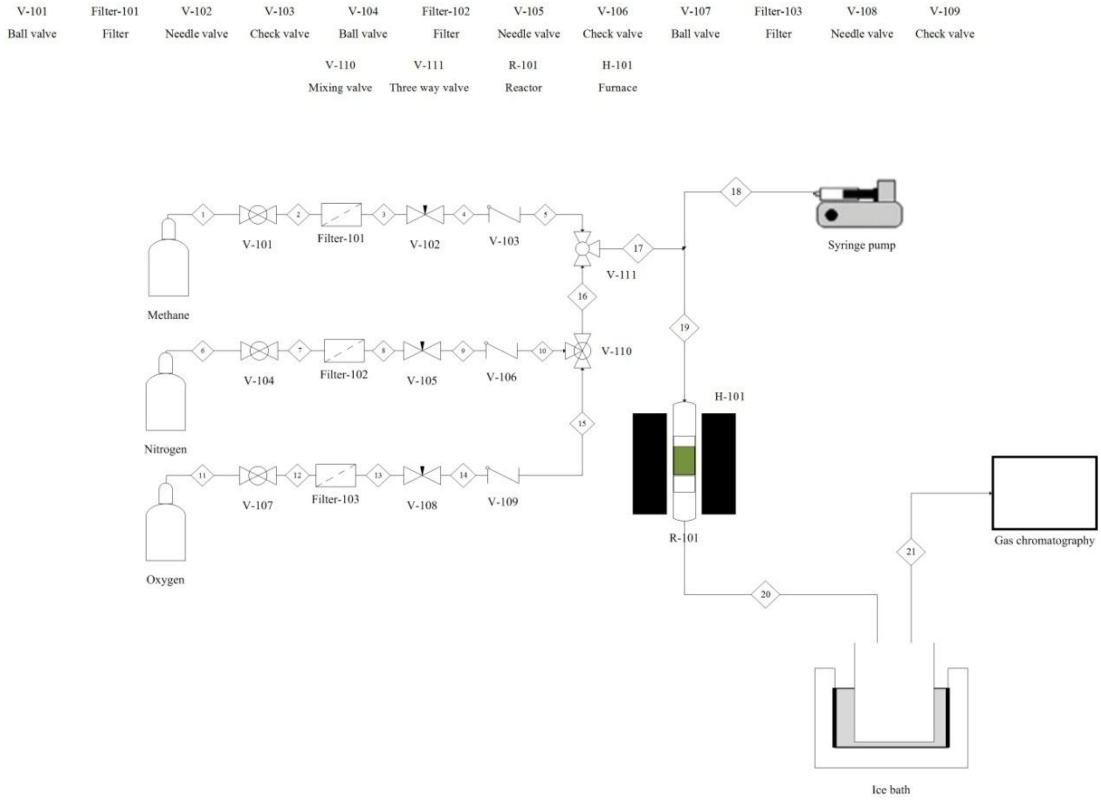


Figure 4.3 Experimental setup for the chemical looping reforming of methane

4.2.4 Reaction testing

Hydrogen production via chemical looping reforming was tested in the fixed bed quartz reactor having inner diameter of 10 mm, outer diameter of 12 mm and length of 500 mm. There were four types of experiments: 13 wt% NiO/Al_2O_3 without sorbent, 13 wt% NiO/Al_2O_3 with sorbent, 13 wt% NiO/CeO_2 without sorbent, and 13 wt% NiO/CeO_2 with sorbent. For the cases without sorbent, the experiments used silicon carbide that had the same weight instead. The objective was to compare between 1 g of metal oxide and 1 g of silicon carbide and 1 g of metal oxide physically mixed with 1 g of CaO was packed and supported by quartz wool. The reactions were tested at reaction temperature of 600 °C. The total flow rate of inlet stream was 50 ml/min. Nitrogen was used as a carrier gas. Methane which was used as a fuel in the reduction reaction was 6vol% ($2x10^{-6}$ mol/s) and steam was 18vol% ($4x10^{-6}$ mol/s) in nitrogen. The oxidation reaction was carried out in $14x10^{-6}$ mol/s (21vol%) oxygen in nitrogen. The product stream was trapped using an ice bath and analyzed by gas chromatography. This Gas Chromatograph (Shimadzu GC-8A), uses argon as carrier gas. The molecular sieve can separate H_2, O_2, CH_4, N_2 and CO. while Chromosorb 101 can separate CO_2 and higher hydrocarbons. The injection port temperature is set at 70°C and two of column oven temperatures are set at 50°C. Gas Chromatograph is preset by pressing the blue button marked INJ & COL, beneath the temperature display that can check these values.

4.2.5 Metal oxides characterization

X-ray diffraction (XRD)

X-ray diffraction (XRD) was used for metal oxide characterization. XRD pattern was used by D8 Advance of Bruker AXS, equipped with long fine focus ceramic as X-ray source (using Cu K_α source). The pattern was recorded in range of $10° < 2\theta < 80°$.

Nitrogen adsorption desorption Multipoint

The surface area of metal oxide on support was measured by using nitrogen adsorption desorption technique. It was carried out by using Micromeritics Chemisorp 2750. The nitrogen adsorption desorption isotherm was tested at 77 K with 0.2 g of metal oxide on support.

Energy-dispersive X-ray spectroscopy (EDX)

Samples were analyzed to find their elemental or chemical characterization by Energy-dispersive X-ray spectroscopy (EDX). It relies on the investigation of an interaction of some source of X-ray excitation and a sample. SEM/EDX can analyze high resolution image observation and element detection which detector system is FF Wavelength Dispersive X-ray Spectrometer (WDX). In this study, EDX was used to identify carbon left after oxidation reaction by zooming only sample's surface.

Scanning electron microscope (SEM)

The surface of metal oxide on support was scanned by using scanning electron microscope (SEM) S-3400N from Hitachi.

CHAPTER V

RESULTS AND DISCUSSION

This chapter presents results and discussion of experimental and simulation studies of chemical looping reforming systems. In part of simulation, chemical looping reforming and chemical looping reforming with CO_2 sorbent of methane were simulated using Aspen plus program, The results of interest are hydrogen production, hydrogen purity, energy requirement, carbon activity, and carbon formation at various ratios of steam per methane and ratios of NiO per methane. For the experimental study, comparison between alumina support and ceria support, and sorption enhanced chemical looping reforming are discussed.

5.1 Performance evaluation of different chemical looping reforming systems by Aspen plus

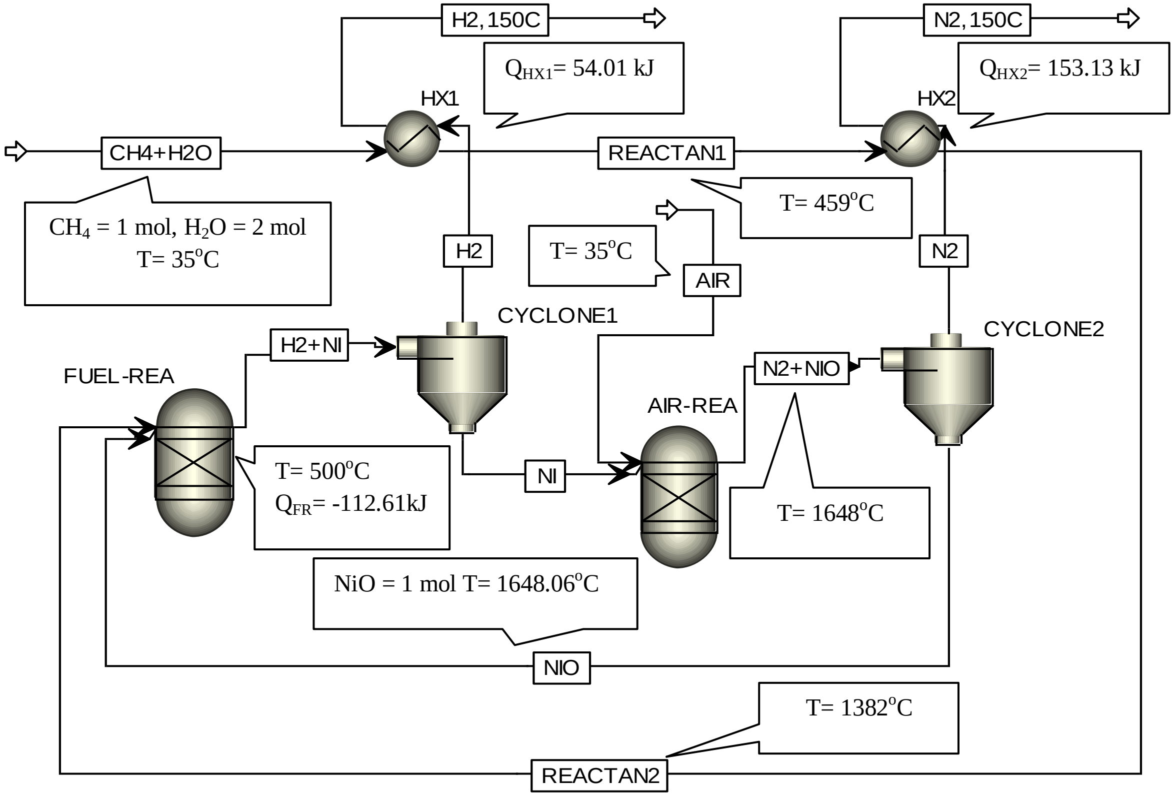
5.1.1 Performance of conventional chemical looping at base condition

In the simulation study using Aspen plus program, methane and steam at atmospheric pressure and 35^{o}C were fed to fuel reactor. In the fuel reactor the reactions between methane, steam and NiO solid took place and the product gas contained were hydrogen, carbon monoxide, carbon dioxide, some fraction of methane that did not react, and Ni which was reduced from NiO. Then, there was a cyclone for separating product gas stream from Ni solid. After that, solid was oxidized by air in the air reactor. Ni was oxidized, forming NiO. Finally, NiO which was separated from air by using another cyclone, transported to the fuel reactor to close the loop. Hydrogen concentration after condensing to trap water was calculated for hydrogen purity. To enhance the system performance, internal useful heat sources within the system by cooling product streams from the cyclone 1 and cyclone 2 to 150^{o}C, and heated NiO solid from the air reactor were utilized. The utilization of

HX1, and HX2 (heat exchanger 1, and heat exchanger 2, respectively) duties was for preheating the incoming methane and steam.

At base case condition (Figure 5.1) , there were 1 mol of methane and 2 mols of steam as reactant gas (fed to process at 35^{o}C) and 1 mol of NiO solid fed to the fuel reactor which was operated at 500^{o}C and 1 bar. The products from this reactor were 1.27 mol of hydrogen, 0.52 mol of carbon dioxide, 0.07 mol of carbon monoxide, 1.90 mol of water, 0.42 mol of unconverted methane, and 1 mol of Ni solid that was reduced from NiO. Hydrogen purity after condensation water was 55.93%. After that the gas product was completely separated from Ni solid by the cyclone 1 and cooled down to 150^{o}C that would preheat reactant stream from 35^{o}C at HX1 with heat duty of 54.01 kJ to 459^{o}C. Ni solid that was separated from product stream was oxidized with air (35^{o}C) to form NiO and get nitrogen gas, then the product from air reactor was transferred to the cyclone 2 to separate NiO solid from nitrogen gas. The air reactor was operated at 1 bar under adiabatic condition. The result showed that the temperature of reactor was 1648^{o}C. Therefore, nitrogen gas from the air reactor was at 1648.06^{o}C was used to further preheat the reactants from 459^{o}C to 1382^{o}C with heat duty 153.13 kJ. Then, the reactants at 1382^{o}C and NiO from the cyclone 2 were sent to the fuel reactor where the reaction took place at 500^{o}C. The heat duty of the fuel reactor was -112.61 kJ. It is observed that under this operation the system could be operated with demanding external heat sources. However, it should be noted that to startup the operation, some energy is required to preheat the feed gases and NiO.

From the gas compositions from the fuel reactor, the following values carbon activity of reaction (C 1), (C 2), (C 3), and (C 4) could be calculated. The values were 0.512, 0.416, 0.481, and 0.409, respectively. The result of carbon activity of four reactions less than 1 indicates that there is no carbon formation.



Q_{HX1}= 54.01 kJ

Q_{HX2}= 153.13 kJ

CH_4 = 1 mol, H_2O = 2 mol
T= 35^{o}C

T= 459^{o}C

T= 35^{o}C

T= 500^{o}C
Q_{FR}= -112.61kJ

T= 1648^{o}C

NiO = 1 mol T= 1648.06^{o}C

T= 1382^{o}C

Figure 5.1 Chemical looping reforming when feeding 1 mol of methane, 2 mol of steam and 1 mol of NiO at 500^{o}C simulated by Aspen plus

5.1.2 Effect of operation parameters of conventional chemical looping reforming

The effects of steam/methane ratio and NiO/methane ratio on hydrogen production, hydrogen purity, net energy required, and carbon activity were determined to find appropriate condition for hydrogen production via chemical looping reforming

1) Effect of steam/methane ratio

Figure 5.2 shows the effect of steam/methane ratio on hydrogen production at four temperatures. Hydrogen production is found to increase with increasing temperature. This is because the steam reforming is a highly endothermic reaction. Hydrogen production is also increased with increasing amount of steam. F_{H2} is represented for mol of hydrogen produced, $F_{CH4,0}$ is represented for mol of methane feed, S/M ratio is represented for steam/methane ratio. It can be noticed that hydrogen production at 800^{o}C at high steam per methane is slightly increased and lower than at 700^{o}C that because at high temperature obstruction of the reaction of chemical looping reforming occurred.

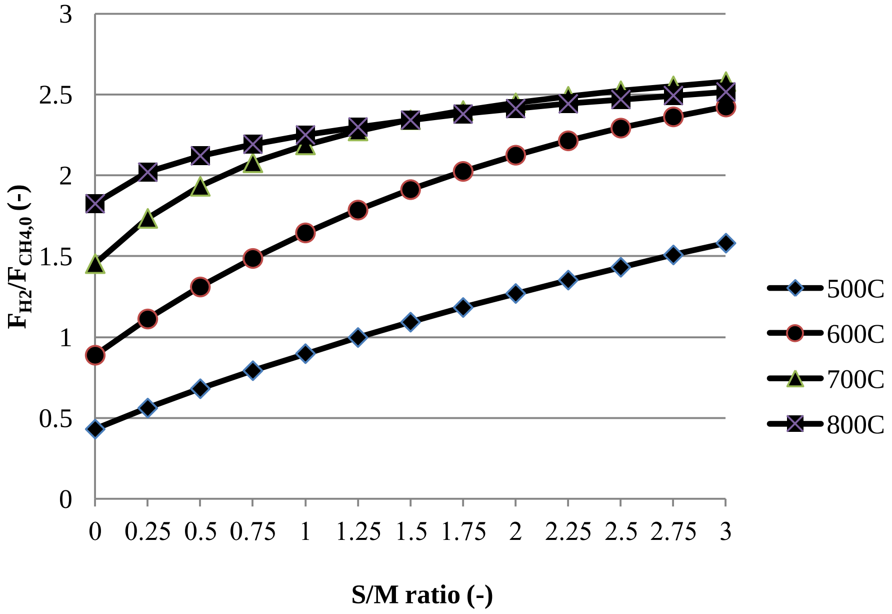


Figure 5.2 Mol of hydrogen produced per mol of methane feed at various ratios of steam per methane at different temperatures for Chemical looping reforming simulated by Aspen plus

From Figure 5.3, hydrogen purity is increased with increasing temperature and amount of steam, like the hydrogen production. Highest hydrogen purity are 61%, 70%, 71%, and 71.5% at 500^{o}C, 600^{o}C, 700^{o}C, and 800^{o}C, respectively, and other gas compositions are water, carbon dioxide, carbon monoxide, and some unconverted methane. It can be seen that at high temperature hydrogen purity levels off at high steam/methane ratio because steam fed to the reactor was excessive for the reaction with methane.

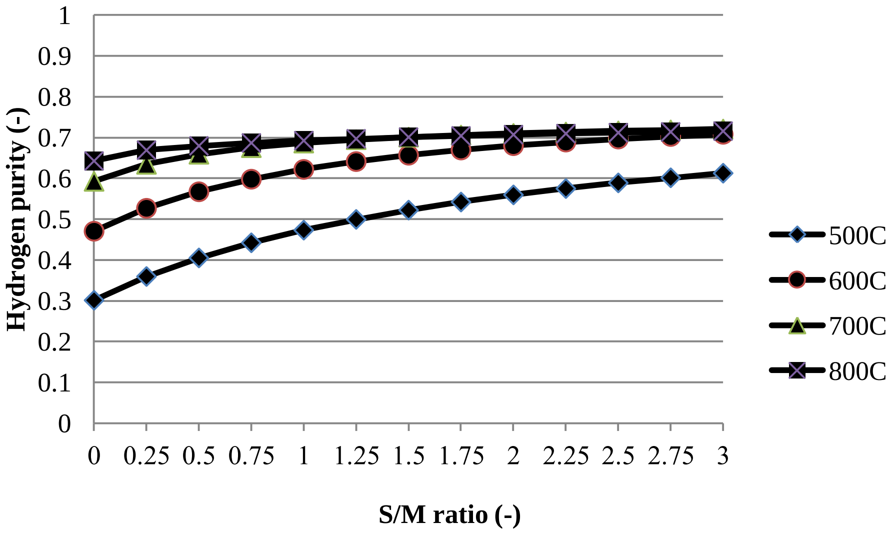


Figure 5.3 Hydrogen purity produced at various ratios of steam/methane at different temperature via Chemical looping reforming simulated by Aspen plus

The values of net energy in chemical looping reforming, as shown in Figure 5.4, become less negative with increasing temperature and ratio steam per methane. This is because when adding more steam or operating at higher temperature, more energy is consumed to generate steam and to raise the temperature. It should be noted that the negative values indicate that the process can be operated without demanding heat from outside except at the start up when some energy is required to preheat reactant gases and solid.

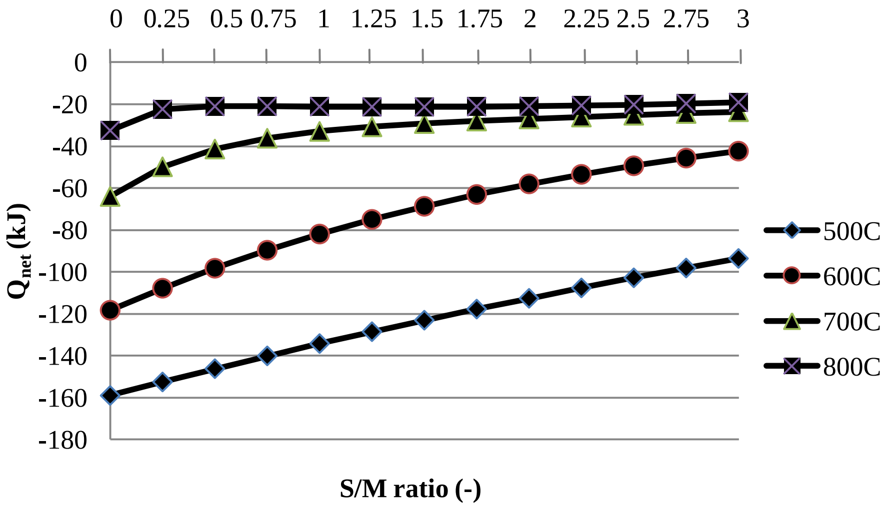


Figure 5.4 Energy requirement at various ratios of steam/methane at different temperature via Chemical looping reforming simulated by Aspen plus

Figure 5.5 shows carbon activity of reaction (C 1), reaction (C 2), reaction (C 3), and reaction (C 4) below:

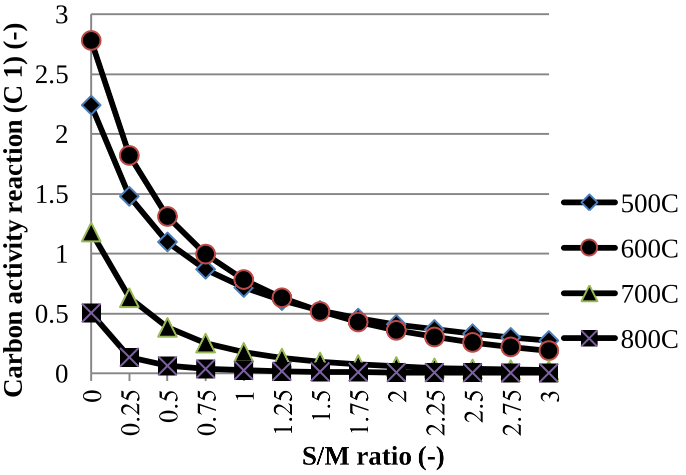
$2CO \leftrightarrow CO_2 + C$ (C 1)

$CH_4 \leftrightarrow 2H_2 + C$ (C 2)

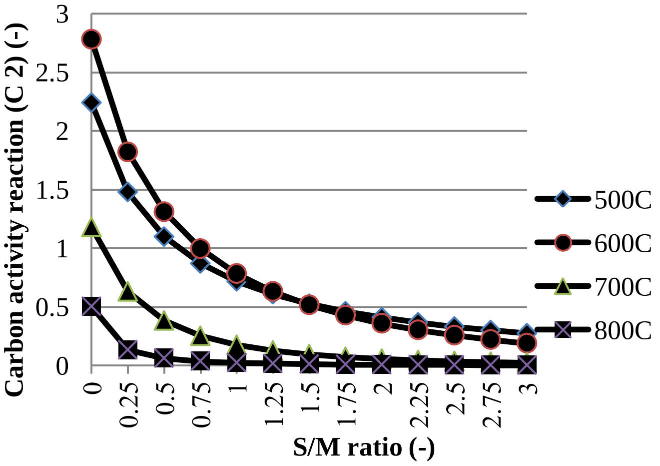
$CO+H_2 \leftrightarrow H_2O+C$ (C 3)

$CO_2+2H_2 \leftrightarrow 2H_2O+C$ (C 4)

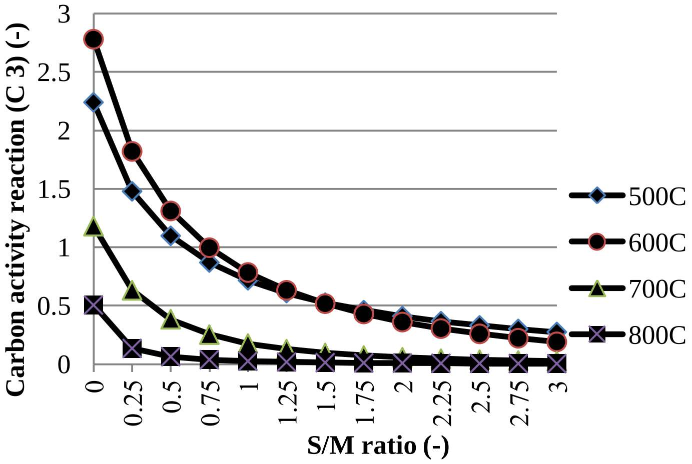
The carbon activity represents the possibility of carbon formation. At low temperature and low ratio of steam/methane, high tendency to form carbon solid was observed because steam could react with carbon monoxide and the products are carbon dioxide and hydrogen.


Carbon activity reaction (C 1) (-)
3
2.5
2
1.5
1
0.5
0
0
0.25
0.5
0.75
1
1.25
1.5
1.75
2
2.25
2.5
2.75
3
S/M ratio (-)
500C
600C
700C
800C

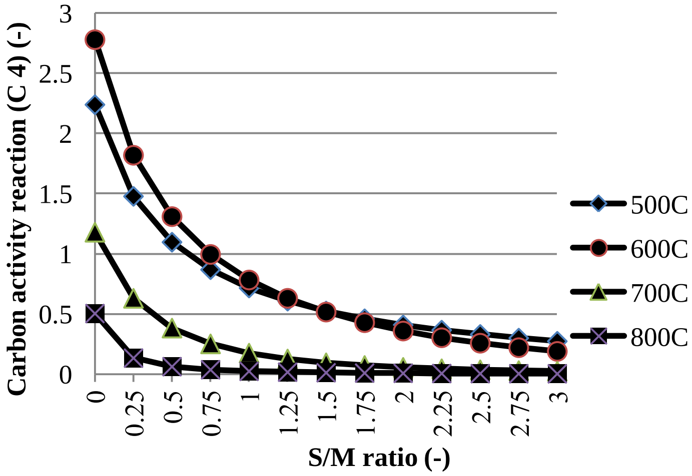
a.


Carbon activity reaction (C 2) (-)
3
2.5
2
1.5
1
0.5
0
0
0.25
0.5
0.75
1
1.25
1.5
1.75
2
2.25
2.5
2.75
3
S/M ratio (-)
500C
600C
700C
800C

b.



c.



d.

Figure 5.5 Carbon activity of each reaction at various ratios of steam/methane at different temperature via Chemical looping reforming simulated by Aspen plus (a: Carbon activity of reaction (C 1), b: Carbon activity of reaction (C 2), c: Carbon activity of reaction (C 3), d: Carbon activity of reaction (C 4))

Moles of solid carbon at different steam/methane ratios and temperature summarized in Table 5.1 also confirm this tendency. Based on the results on hydrogen production, energy required, and carbon formation operation at 600°C and ratio steam/methane of 2 is an interesting operating condition for hydrogen production in chemical looping reforming.

Table 5.1 Carbon solid occurred in Chemical looping reforming (mol) at various ratios of steam/methane at different temperature

steam/methane	T = 500°C	T = 600°C	T = 700°C	T = 800°C
0	0.36924	0.37577	0.22359	6.64E-02
0.25	0.26657	0.2501	0.045883	0
0.5	0.16126	0.12287	0	0
0.75	0.054218	0	0	0
1	0	0	0	0
1.25	0	0	0	0
1.5	0	0	0	0
1.75	0	0	0	0
2	0	0	0	0
2.25	0	0	0	0
2.5	0	0	0	0
2.75	0	0	0	0
3	0	0	0	0

2) Effect of NiO/methane ratio

When varying ratio of NiO/methane while keeping the steam/methane ratio at 2 (Figure 5.6 and Figure 5.7), it was found that increasing NiO shows less hydrogen production and hydrogen purity because the combustion of methane to carbon dioxide and water becomes more favorable with the presence of more NiO. It is noted that at NiO/methane ratio of 0, the methane steam reforming becomes the predominant reaction, and the highest mol of hydrogen per mol of methane feed and highest hydrogen purity achieved. NiO/M ratio represents NiO/methane ratio.

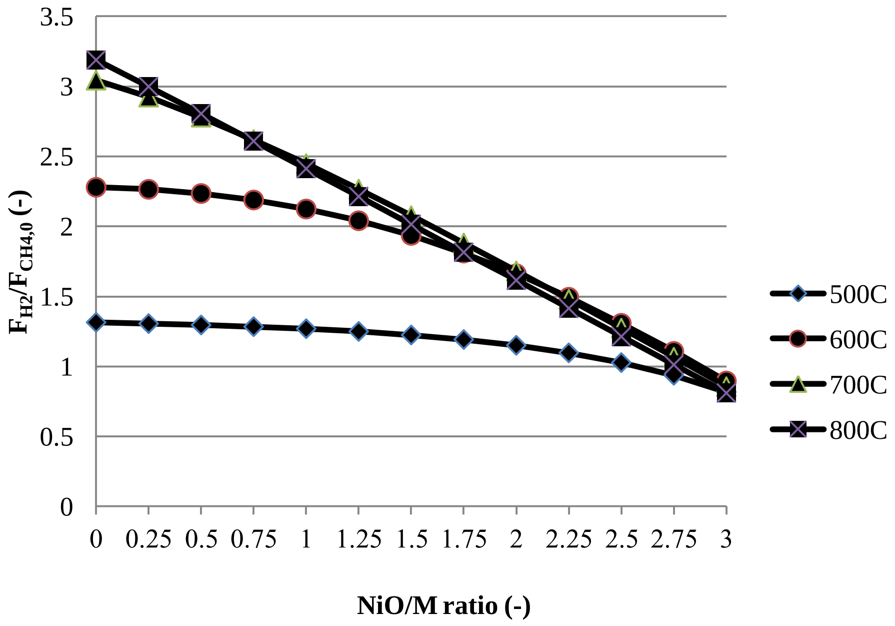


Figure 5.6 Mol of hydrogen produced per mol of methane feed at various ratios of NiO/methane at different temperature via Chemical looping reforming simulated by Aspen plus

Figure 5.7 shows highest hydrogen purity are 58.5%, 69.5%, 75.3%, and 76% at 500°C, 600°C, 700°C, and 800°C, respectively, and other gas compositions are water, carbon dioxide, carbon monoxide, and some unconverted methane.

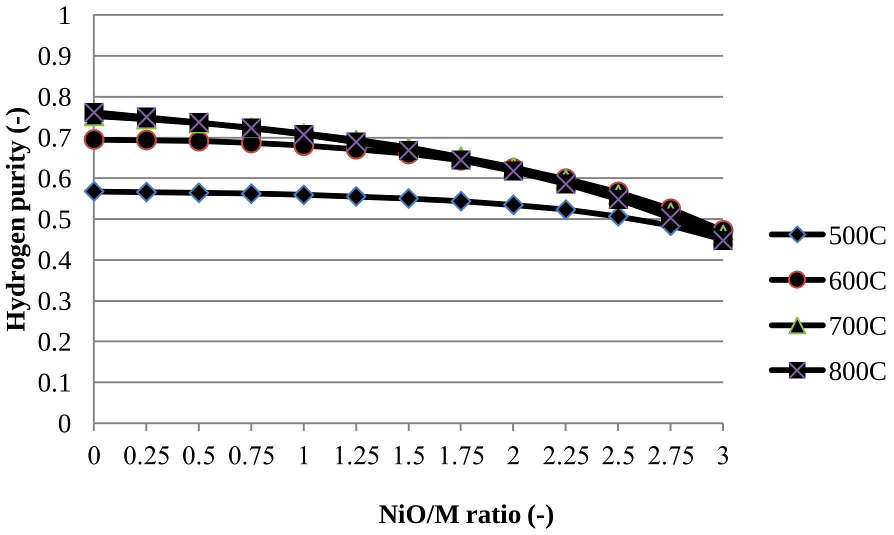


Figure 5.7 Hydrogen purity produced at various ratios of NiO/methane at different temperature via Chemical looping reforming simulated by Aspen plus

However, when considering the net energy (Q_{net}) involved in the system (shown in Figure 5.8), it was found that at low NiO/methane ratio, the net energy (Q_{net}) becomes positive, indication, that the system demands additional energy from external sources. Considering the conditions which offer Q_{net} = 0 (thermally neutral condition), the values of the corresponding NiO/methane and maximum hydrogen/methane feed at different temperatures are summarized in Table 5.2. It was found that at 500, 600, 700, 800^{o}C, hydrogen productions at Q_{net} = 0 are 1.30, 2.21, 2.55, and 2.29, respectively.

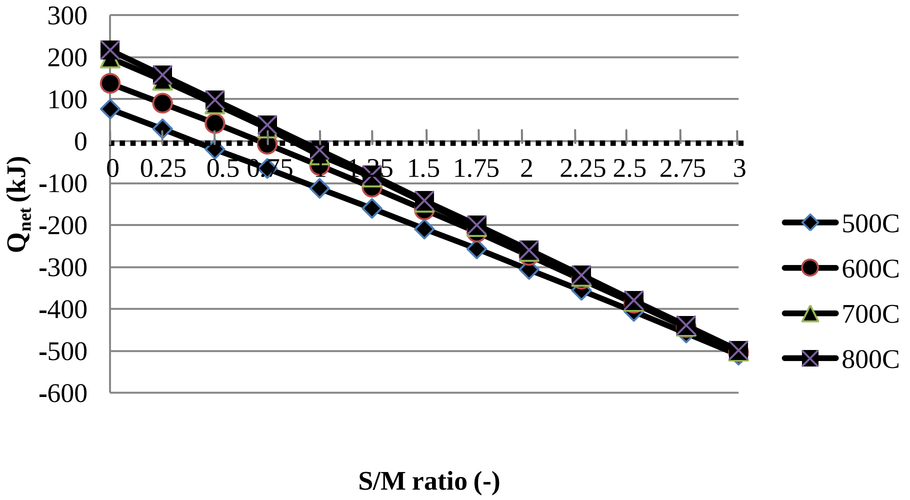


Figure 5.8 Energy requirement at various ratios of NiO/methane at different temperature via Chemical looping reforming simulated by Aspen plus (···: $Q_{net} = 0$)

Table 5.2 Mol hydrogen produced per mol methane feed when $Q_{net} = 0$ at different temperature via Chemical looping reforming

Temperature °C	NiO/methane that let $Q_{net} = 0$	Mol hydrogen produced/mol methane feed
500	0.39	1.30
600	0.65	2.21
700	0.85	2.55
800	1.16	2.29

Figure 5.9 shows carbon acitivity of reaction (C 1), reaction (C 2), reaction (C 3), and reaction (C 4) as followed:

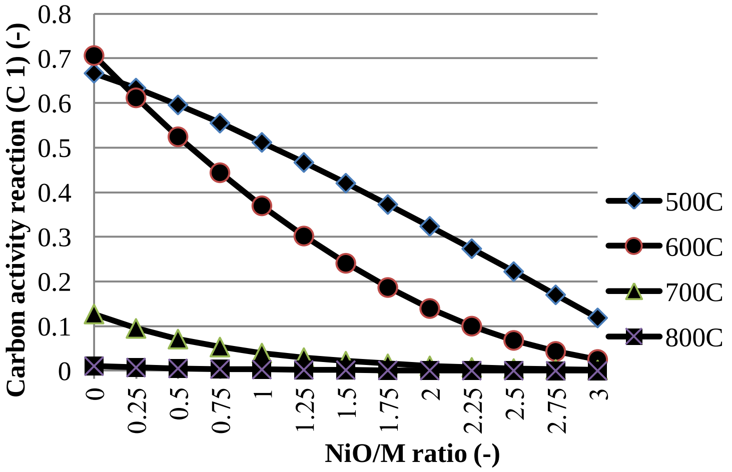
$2CO \leftrightarrow CO_2 + C$ (C 1)

$CH_4 \leftrightarrow 2H_2 + C$ (C 2)

$CO+H_2 \leftrightarrow H_2O+C$ (C 3)

$CO_2+2H_2 \leftrightarrow 2H_2O+C$ (C 4)

Within the range studied, there is no possibility of carbon formation at any ratio of NiO/methane. It is because the system was operated at a sufficient by high steam/methane ratio. It was also observed that the increasing NiO/methane ratio lowers the tendency for carbon formation because high amount of NiO would combust with methane to get more complete combustion that carbon monoxide and hydrogen would be less. From the results of Figure 5.5 and Figure 5.9, steam is the important key of carbon formation.



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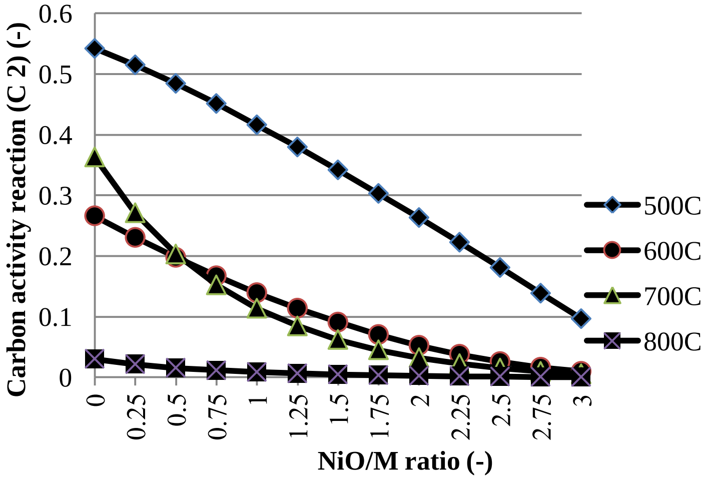

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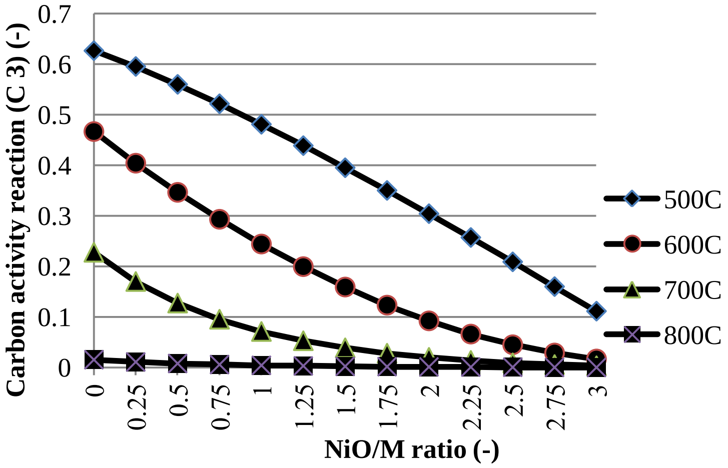

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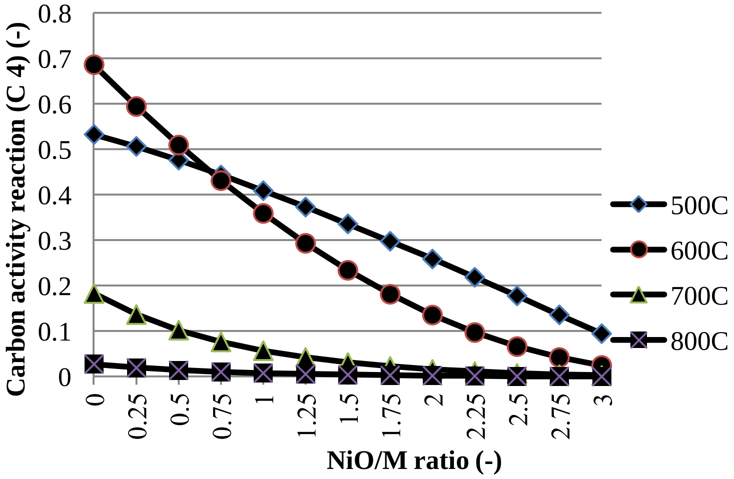


d.

Figure 5.9 Carbon activity of each reaction at various ratios of NiO/methane at different temperatures via Chemical looping reforming simulated by Aspen plus (a: Carbon activity of reaction (C 1), b: Carbon activity of reaction (C 2), c: Carbon activity of reaction (C 3), d: Carbon activity of reaction (C 4))

Table 5.3 shows that every case of at various ratios of NiO/methane at 1 mol of methane and 2 mol of steam showed no carbon formation. From the results, concerning of hydrogen production, energy requirement, and carbon formation, at 600°C and ratio of NiO/methane of 1 is an interesting operating condition for hydrogen production in chemical looping reforming.

NiO/methane ratio affects the net energy in the process. Therefore, selection of an appropriate ratio of NiO/methane can help the process operating well. However, high NiO/methane ratio suppresses hydrogen production and hydrogen purity because more NiO could react with methane, generating carbon dioxide and water.

Table 5.3 Carbon solid occurred in Chemical looping reforming (mol) at various ratios of NiO/methane at different temperatures

NiO/methane	T = 500°C	T = 600°C	T = 700°C	T = 800°C
0	0	0	0	0
0.25	0	0	0	0
0.5	0	0	0	0
0.75	0	0	0	0
1	0	0	0	0
1.25	0	0	0	0
1.5	0	0	0	0
1.75	0	0	0	0
2	0	0	0	0
2.25	0	0	0	0
2.5	0	0	0	0
2.75	0	0	0	0
3	0	0	0	0

5.1.3 Performance of chemical looping reforming with CO_2 sorbent at base condition

Chemical looping reforming with CO_2 sorbent was operated like ordinary chemical looping reforming but 1 mol of CaO was fed as CO_2 sorbent with NiO solid. CO_2 sorbent was used to adsorb carbon dioxide gas to purify hydrogen gas as main product. There were three reactors: fuel reactor, calcination reactor, and air reactor. Both fuel reactor and air reactor were like in the chemical looping reforming whereas a calcinaion reactor was added to calcine $CaCO_3$ from the fuel reactor to release carbon dioxide from CaO. Therefore, there must be more cyclone to separate carbon dioxide from solids. Calcination reactor was assumed to operate at 880^{o}C (Rydén and Ramos, 2012) and atmospheric pressure. To enhance the performance, like chemical looping reforming process, utilization of internal useful heat sources from within the system by cooling product stream from the cyclone 1, cyclone 2, and cyclone 3 to 150^{o}C, and heated NiO and CaO solid from air reactor. The utilization of HX1, HX2, and HX3 (heat exchanger 1, heat exchanger 2, and heat exchanger 3, respectively) duties is for preheating the incoming methane and steam.

At base case condition, there were 1 mol of methane and 2 mol of steam as reactant gases (fed to process at 35^{o}C), 1 mol of NiO, and 1 mol of CaO solids fed to the fuel reactor which was operated at 500^{o}C, 1 bar. The products from this reactor were 2.81 mol of hydrogen, 0.00075 mol of carbon dioxide, 0.00037 mol of carbon monoxide, 1.10 mol of water, 0.05 mol of unconverted methane, and 1 mol of Ni solid and 1 mol of $CaCO_3$ that was reduced from NiO. Hydrogen purity after condensing water was 98.29%. After that the gas product was completely separated from Ni and $CaCO_3$ solids by cyclone 1 and cooled down to 150^{o}C that would preheat reactant stream (35^{o}C) with heat duty of 43.68 kJ. Ni and $CaCO_3$ solid were calcined by calcinations reactor at 1 bar, 880^{o}C to release 1 mol of carbon dioxide from CaO and then sent to cyclone 2 to separate Ni and CaO solids from carbon dioxide that was at 880^{o}C. Net heat duty of calcination reactor was 228.81 kJ. After that, carbon dioxide was cooled down to 150^{o}C to preheat the reactants from heat exchanger 1 which was at 381^{o}C, with heat duty of 34.99 kJ. Ni and CaO solids that were separated from product stream were oxidized with air (35^{o}C) to form NiO and get nitrogen gas, then the product from the air reactor was transferred to the cyclone to separate NiO solid from nitrogen gas. The air reactor was operated at 1 bar and adiabatic condition, the result showed that when temperature of the reactor was 1153^{o}C. Therefore, nitrogen gas from the air reactor was at 1153^{o}C that would preheat the reactants from heat exchanger 2, which was at 632^{o}C, with heat duty of 142.64 kJ. Then, reactants were transferred to the fuel reactor, at 1457^{o}C, and NiO and CaO from cyclone 3 were sent to the fuel reactor whose heat duty was -281.23 kJ. However, to start the process, there must be some energy fed to preheat the reactant gas and solid during the startup similar to the conventional chemical looping reforming.

Net heat duties of process (Qnet) were summed values of the net heat duty of all reactors (fuel reactor, calcination reactor, and air reactor which was adiabatic), that was -52.42 kJ.

From the gas compositions from the fuel reactor, the following values carbon activity of reaction (C 1), (C 2), (C 3), and (C 4) could be calculated. The values were 0.011, 0.009, 0.011, and 0.009, respectively. The result of carbon activity of four reactions less than 1 indicates that there is no carbon formation.

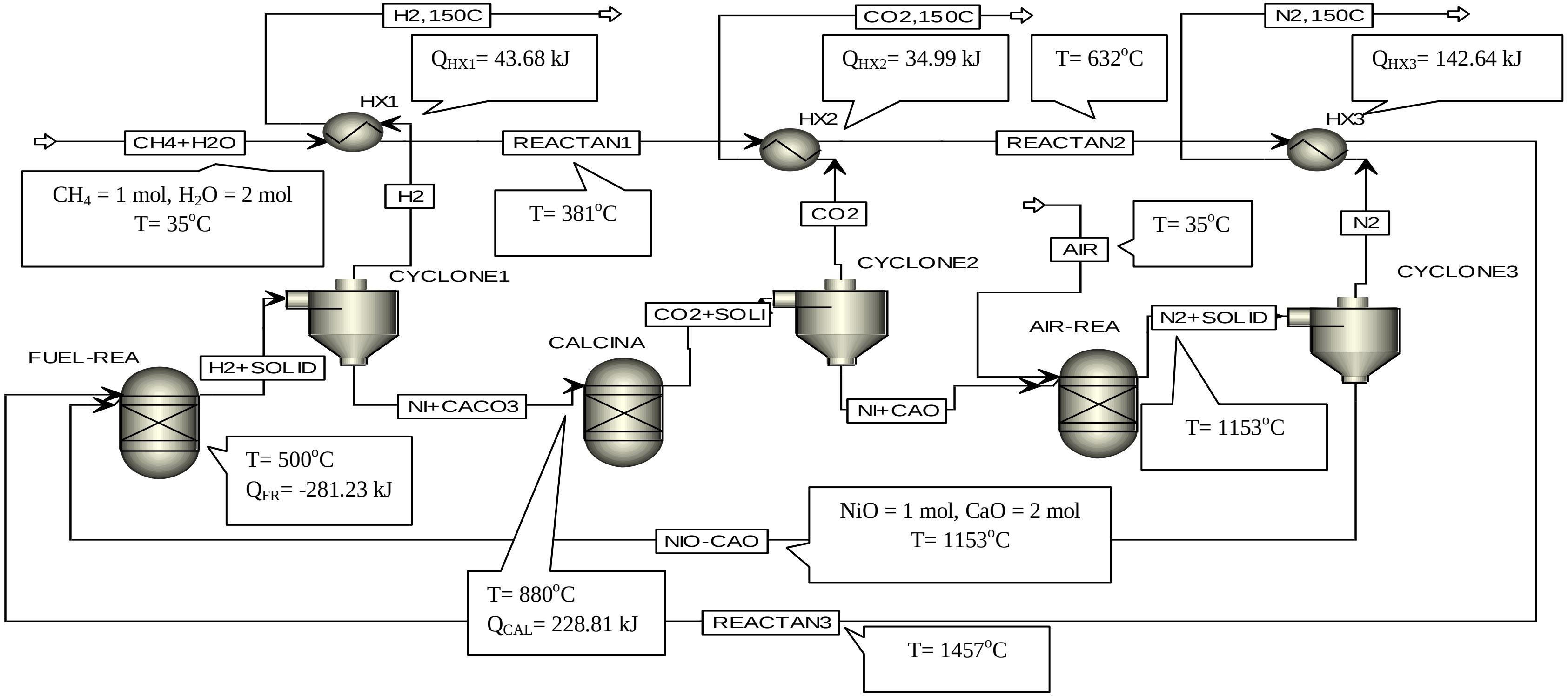


Figure 5.10 Chemical looping reforming with CO_2 sorbent simulated from Aspen plus

5.1.4 Effect of operation parameters of chemical looping reforming with CO_2 sorbent

The effects of steam/methane ratio and NiO/methane ratio on hydrogen production, hydrogen purity, net energy requirement, carbon activity were determined in order to find an appropriate condition for hydrogen production via chemical looping reforming with CO_2 sorbent.

1) Effect of steam/methane ratio

From Figures 5.11 and 5.12, hydrogen production and hydrogen purity are decreased when increasing operating temperature, despite hydrogen production is increased with higher temperature which response to theory of hydrogen production from steam reforming that the reactions were highly endothermic. Moreover, CaO that was used in process adsorbed carbon dioxide gas that shifted the reaction. Sorption reaction is an exothermic reaction; therefore, increasing operating temperature will change trend line of hydrogen production.

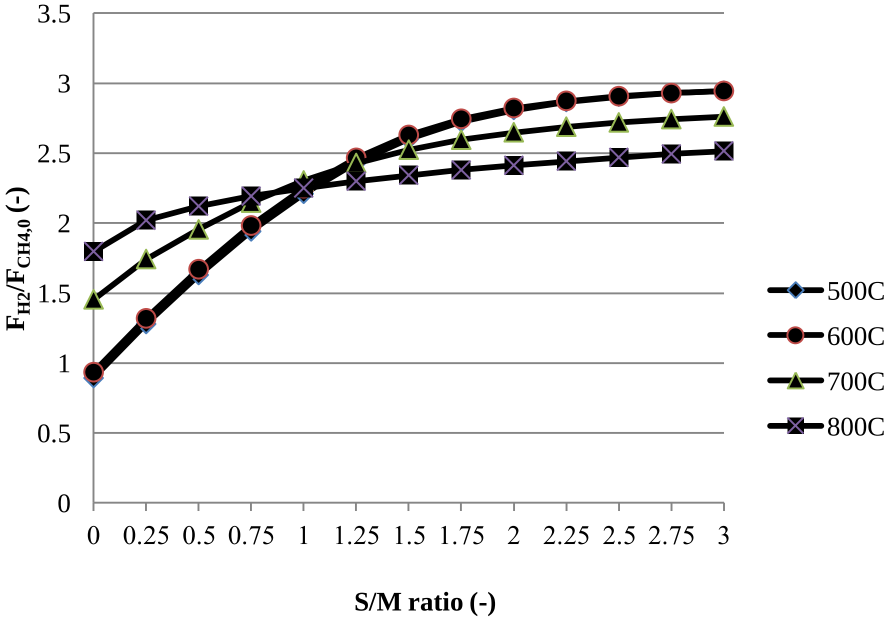


Figure 5.11 Mol of hydrogen produced per mol of methane feed at various ratios of steam/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus

Figure 5.12 shows that the highest hydrogen purity are 99.5%, 98.5%, 84.5%, and 71.5% at $500^{o}C$, $600^{o}C$, $700^{o}C$, and $800^{o}C$, respectively, and other gas compositions are water, carbon dioxide, carbon monoxide, and some unconverted methane. Using CO_2 sorbent shifts the reaction to get more hydrogen purity which is favorable at low temperature. Therefore, at high temperature especially at $800^{o}C$, hydrogen production and hydrogen purity in this case are similar to those from the case with no CO_2 sorbent because adsorption reaction is exothermic, so CaO would not adsorb gas at very high temperature. At temperature $700^{o}C$, at ratio steam/methane = 0, CaO would not adsorb carbon dioxide gas until increasing ratio steam/methane that carbon dioxide is more adsorbed. That is because CaO reacted with steam to form calcium hydroxide ($Ca(OH)_2$)as below;

RXN.17 $CaO + H_2O \leftrightarrow Ca(OH)_2 \qquad \Delta H_{298K} = -109.3$ kJ/mol

$Ca(OH)_2$ could adsorb carbon dioxide and get calcium carbonate and water as below;

RXN.18 $Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O \qquad \Delta H_{298K} = -68.7$ kJ/mol

$Ca(OH)_2$ can adorb carbon dioxide gas better than CaO (Nikulshina et al., 2006), however, at temperature $800^{o}C$ is very high so that carbon dioxide cannot be adsorbed.

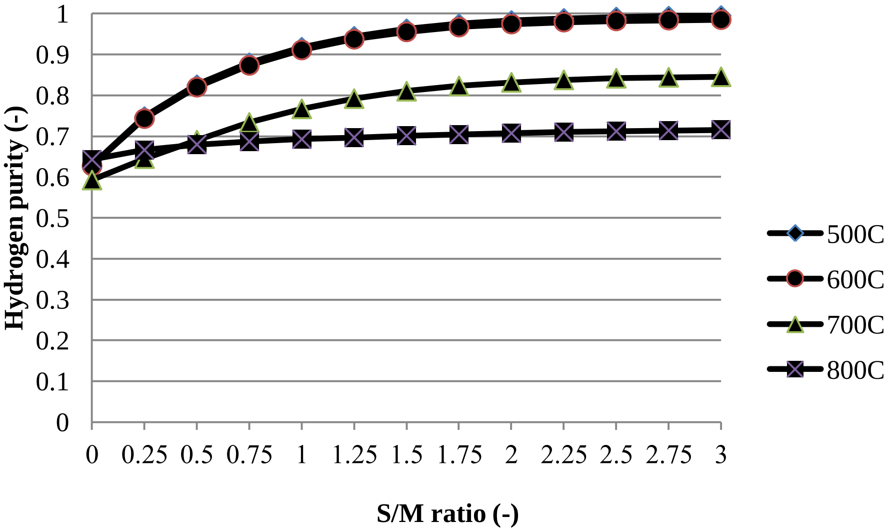


Figure 5.12 Hydrogen purity produced at various ratios of steam/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus

When using CO_2 sorbent, energy requirement (Figure 5.13) is higher than the result shown in Figure 5.4 because some fraction of energy required came from the energy used for calcinations of $CaCO_3$. Net energy in chemical looping reforming with CO_2 sorbent was calculated from summation of energy requirement for reactant (methane and steam) preheating, the fuel reactor (reduction of NiO), calcination of $CaCO_3$ (to release CO_2 from CaO) and exothermic heat from product stream and the air reactor (oxidation of Ni). However, the tendency of energy required in using CO_2 sorbent case is close to the results shown in Figure 5.4.

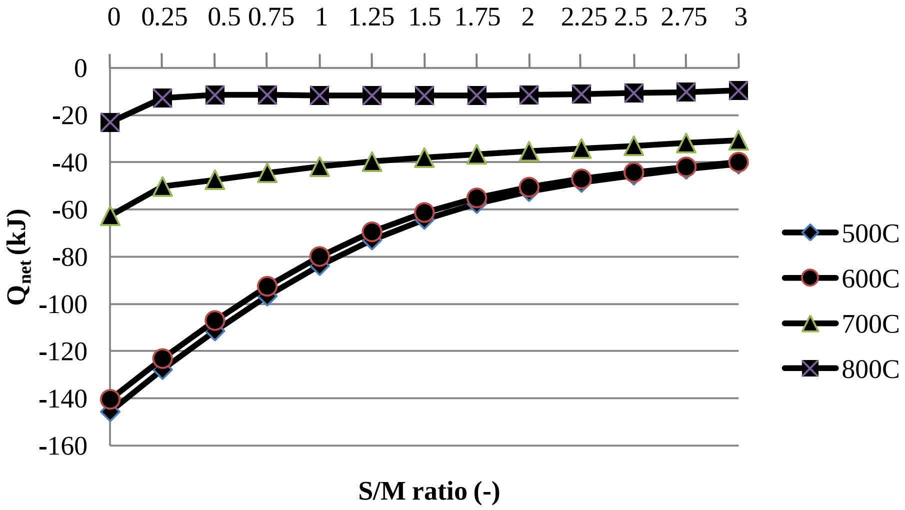


Figure 5.13 Energy requirement varying ratio steam/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus

Figure 5.14 shows carbon acitivity of reaction (C 1), reaction (C 2), reaction (C 3), and reaction (C 4)

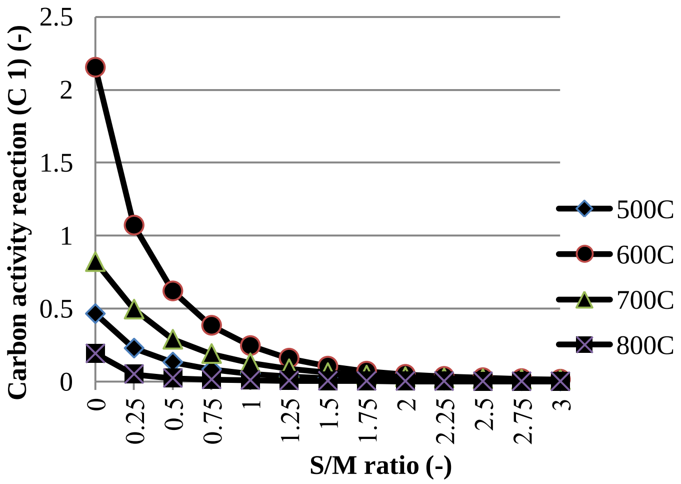
$2CO \leftrightarrow CO_2 + C$ (C 1)

$CH_4 \leftrightarrow 2H_2 + C$ (C 2)

$CO+H_2 \leftrightarrow H_2O+C$ (C 3)

$CO_2+2H_2 \leftrightarrow 2H_2O+C$ (C 4)

At low steam/methane ratio shows high tendency to form carbon solid and high ratio of steam/methane shows less tendency to formation of carbon solid because steam could react with carbon monoxide and the products were carbon dioxide and hydrogen. The results in Figure 5.14 were like the result shown in Figure 5.5. All carbon activity reactions at temperature 500 and 600°C show fewer tendencies to formation of carbon solid than case of no CaO as CO_2 sorbent because CaO adsorbed carbon dioxide which is reactant of carbon formation reactions, moreover, carbon dioxide adsorption would let methane was more consumed, therefore, there was less methane to be cracked. While at temperature 700 and 800^{o}C are high which CaO would not effective, so all carbon activity's trends in this case are not much different from case of no CaO.



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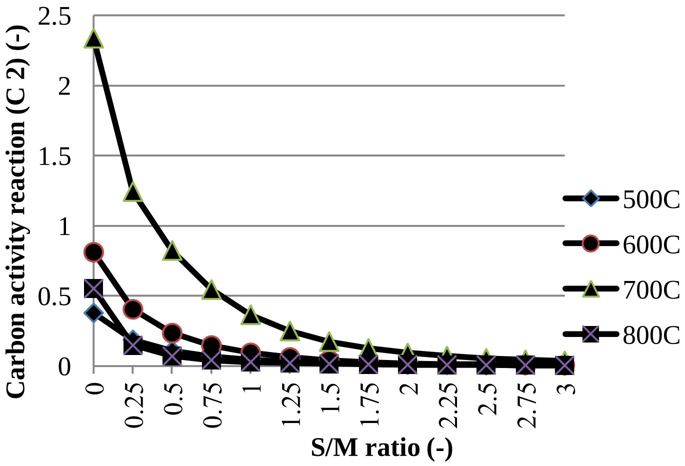

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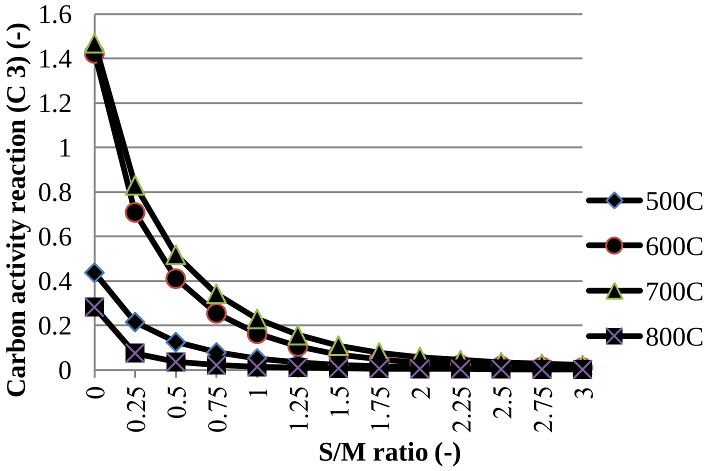

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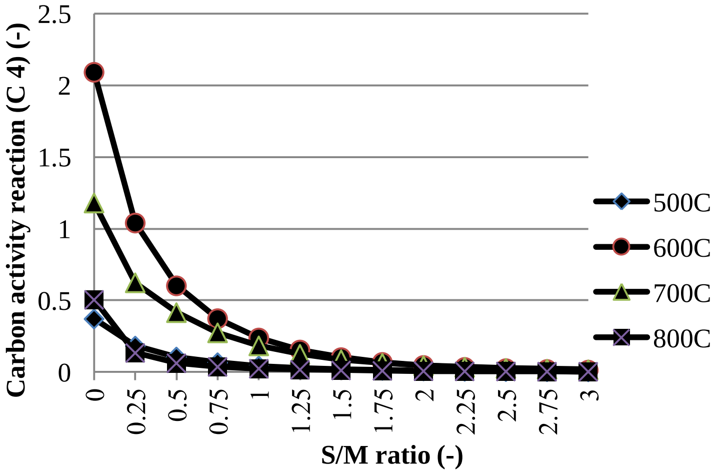

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Figure 5.14 Carbon activity of each reaction at various ratios of steam/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus (a: Carbon activity of reaction (C 1), b: Carbon activity of reaction (C 2), c: Carbon activity of reaction (C 3), d: Carbon activity of reaction (C 4))

From Table 5.4 it was found that within the range of study, no carbon formation was observed. Therefore, the use of CaO as CO_2 sorbent could help prevent carbon formation in chemical looping reforming.

Table 5.4 Carbon solid occurred in Chemical looping reforming with CO_2 sorbent (mol) at various ratios of steam/methane at different temperature

steam/methane	T = 500°C	T = 600°C	T = 700°C	T = 800°C
0	0	0	0	0
0.25	0	0	0	0
0.5	0	0	0	0
0.75	0	0	0	0
1	0	0	0	0
1.25	0	0	0	0
1.5	0	0	0	0
1.75	0	0	0	0
2	0	0	0	0
2.25	0	0	0	0
2.5	0	0	0	0
2.75	0	0	0	0
3	0	0	0	0

2) Effect of NiO/methane ratio

Figures 5.15 and 5.16 show the effect of NiO/methane ratio on hydrogen production and hydrogen purity, respectively. Increasing NiO showed less hydrogen production and purity because more NiO would be more combusted with methane to get more complete combustion whose the products were carbon dioxide and water. For the case of no NiO, only steam reforming reaction was occurred. The results in

Figure 5.15 show similar trend as those shown in Figure 5.6 but higher mol of hydrogen was produced.

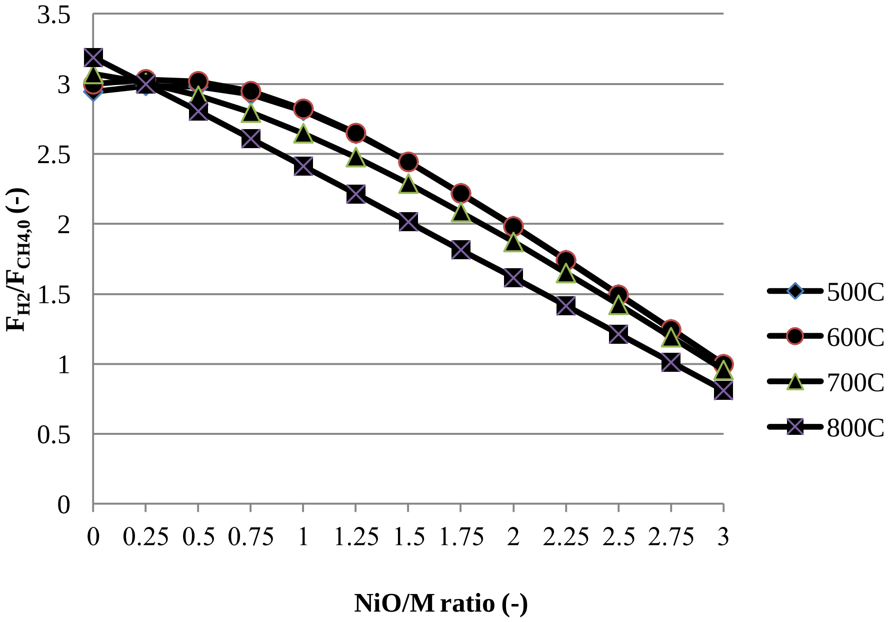


Figure 5.15 Mol of hydrogen produced per mol of methane feed at various ratios of NiO/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus

From Figure 5.16, shows highest hydrogen purity are 99.9%, 98.7%, 84.5%, and 76.1% at 500°C, 600°C, 700°C, and 800°C, respectively, and other gas compositions are water, carbon dioxide, carbon monoxide, and some unconverted methane. At 800°C, hydrogen purity in this case is close to the case with no CO_2 sorbent case because adsorption reaction is exothermic and therefore, CaO would not adsorb gas at very high temperature.

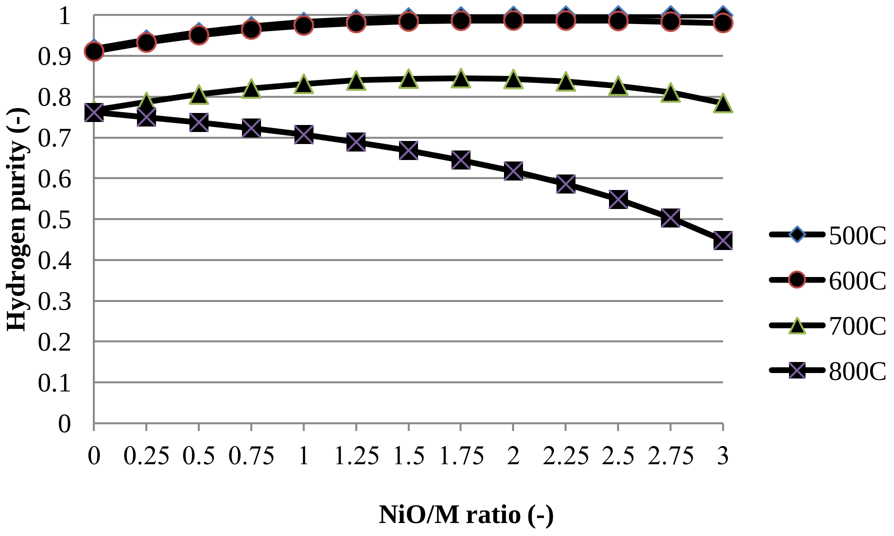


Figure 5.16 Hydrogen purity produced at various ratios of NiO/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus

Figure 5.17 shows that NiO could help to produce energy in chemical looping process because when Ni was oxidized in air reactor which was adiabatic, it produced very high amount of energies. From table 5.5, at 500, 600, 700, and 800^{o}C, NiO/methane ratios higher than 0.66, 0.67, 0.84, and 0.94, respectively, the system can be operated under thermally self sufficient condition. It can be noted from Table 5.5 that at temperature 600^{o}C, hydrogen produced per methane feed is highest.

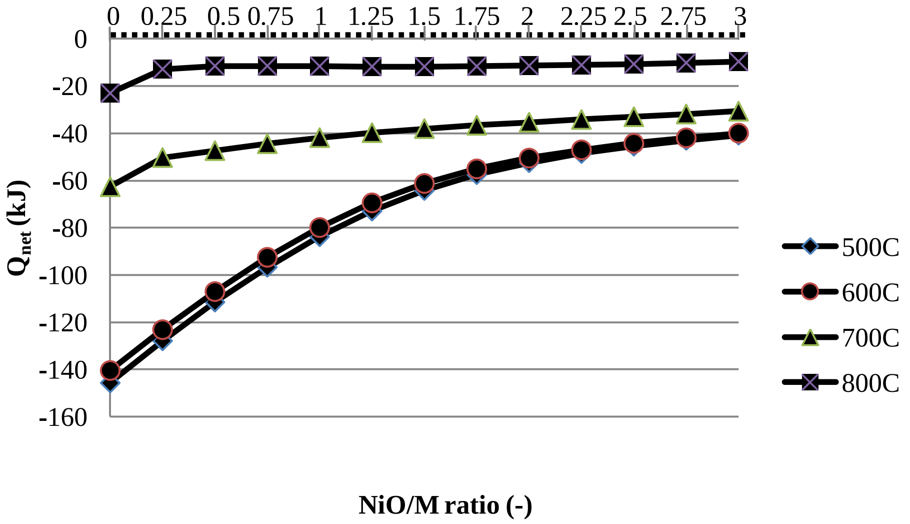
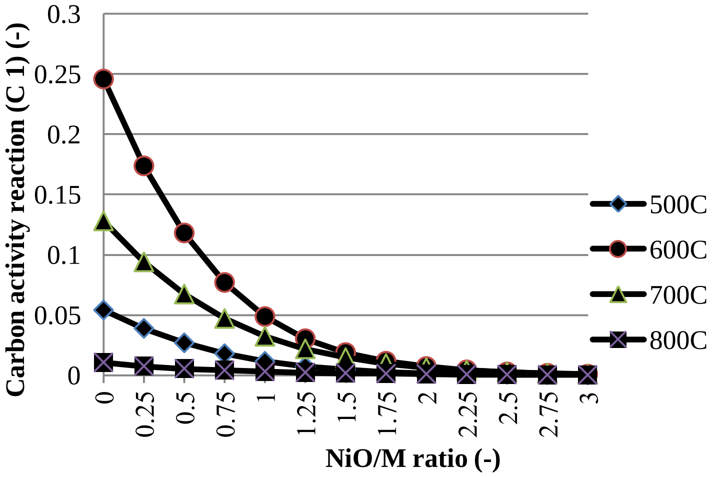


Figure 5.17 Energy requirement at various ratios of NiO/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus (▪▪▪▪ : $Q_{net} = 0$)

Table 5.5 Mol hydrogen produced per mol methane feed when $Q_{net} = 0$ at different temperature via Chemical looping reforming with CO_2 sorbent

Temperature ^{o}C	NiO/methane that let $Q_{net} = 0$	Mol hydrogen produced/mol methane feed
500	0.66	2.95
600	0.67	2.97
700	0.84	2.74
800	0.94	2.46

Carbon acitivity of reaction (C 1), reaction (C 2), reaction (C 3), and reaction (C 4) are shown in Figure.5.18 There is no possibility of carbon formation at every ratio of NiO/methane because high amount of NiO would combust with methane to get more complete combustion that carbon monoxide and hydrogen would be less. All carbon activity reactions at temperature 500 and 600^{o}C show fewer tendencies to formation of carbon solid than case of no CaO as CO_2 sorbent, and at temperature 700 and 800^{o}C all carbon activity's trends in this case are not much different from case of no CaO, like as shown in Figure 5.14 because CaO adsorbed carbon dioxide which is reactant of carbon formation reactions, moreover, carbon dioxide adsorption would let methane was more consumed, therefore, there was less methane to be cracked. While at temperature 700 and 800^{o}C are so high that CaO would not effective.



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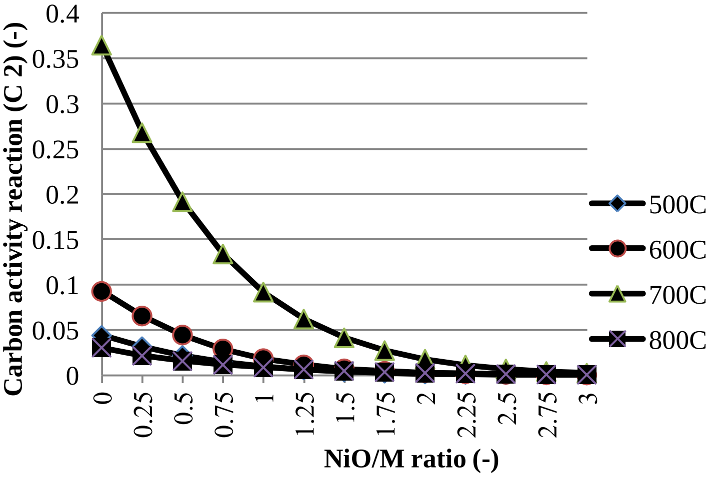

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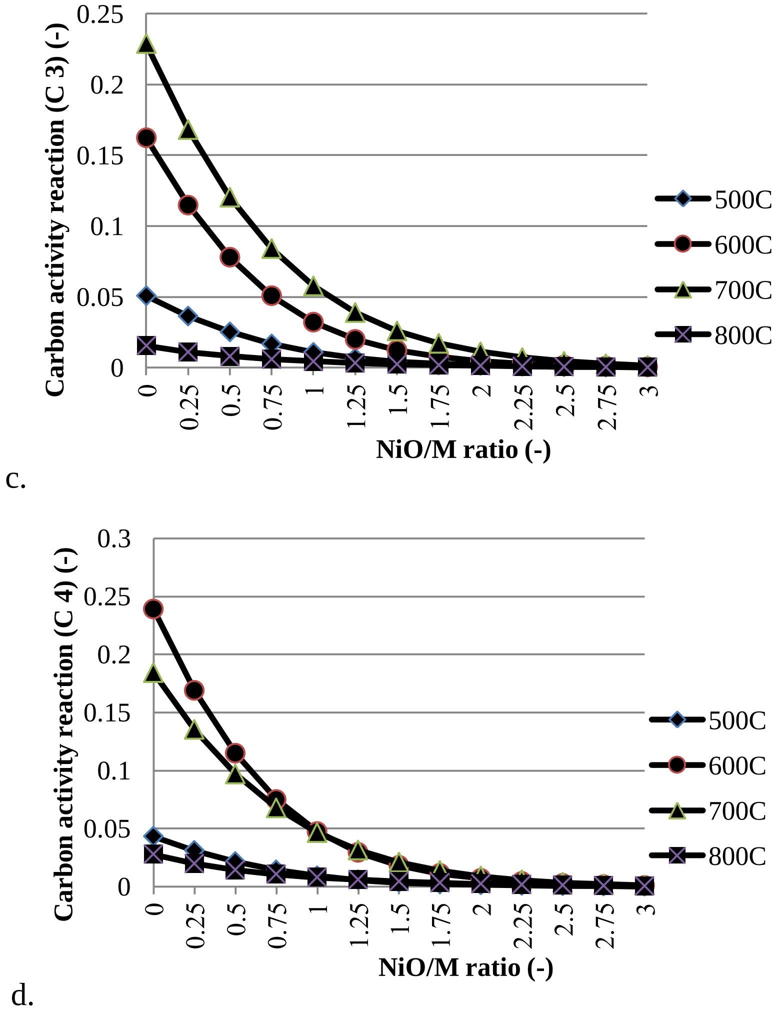

Figure 5.18 Carbon activity of each reaction at various ratios of NiO/methane at different temperature via Chemical looping reforming with CO_2 sorbent simulated by Aspen plus (a: Carbon activity of reaction (C 1), b: Carbon activity of reaction (C 2), c: Carbon activity of reaction (C 3), d: Carbon activity of reaction (C 4))

Table 5.6 Carbon solid occurred in chemical looping reforming with CO_2 sorbent (mol) varying ratio NiO per methane at different temperature

NiO/CH_4	T = 500°C	T = 600°C	T = 700°C	T = 800°C
0	0	0	0	0
0.25	0	0	0	0
0.5	0	0	0	0
0.75	0	0	0	0
1	0	0	0	0
1.25	0	0	0	0
1.5	0	0	0	0
1.75	0	0	0	0
2	0	0	0	0
2.25	0	0	0	0
2.5	0	0	0	0
2.75	0	0	0	0
3	0	0	0	0

From chemical looping reforming using CO_2 sorbent, hydrogen production and hydrogen purity can be enhanced by the carbon dioxide adsorption by CaO when a suitable operating temperature was selected. The result from the operation at 500°C was close to the result from the operation at 600°C, that showed highest hydrogen purity and low energy required. For sake of hydrogen purity, carbon dioxide adsorption, energy required, and carbon activity, temperature at 600°C, ratio steam/methane =2 and ratio NiO/methane =1 is an interesting operating condition for hydrogen production in chemical looping reforming and chemical looping reforming with CO_2 sorbent.

Comparison between conventional chemical looping reforming with chemical looping reforming with CO_2 sorbent, CaO as CO_2 sorbent helps not only to adsorb carbon dioxide gas to purify hydrogen gas as primary product but also to shift the reaction to produce more hydrogen. However, carbon dioxide adsorption is an exothermic reaction that CaO cannot adsorb gas well at high temperature. So, the appropriate condtion is the most important for chemical looping reforming with CO_2 sorbent to produce high amount of hydrogen and high hydrogen purity.

5.2 Experimental studies

In Experimental studies, two supports, Al_2O_3 support and CeO_2 support, were studied in chemical looping combustion and chemical looping reforming. In chemical looping combustion, NiO/Al_2O_3 physically mixed with silicon carbide (SiC) was compared with NiO/Al_2O_3 physically mixed with calcium oxide (CaO), and NiO/CeO_2 physically mixed with silicon carbide (SiC) was compared with NiO/CeO_2 physically mixed with calcium oxide (CaO). For all of chemical looping combustion experiments, $2x10^{-6}$ mol/s (3 ml/min) of methane was fed to the systems. In chemical looping reforming, the solids used in studies were the same as those in chemical looping combustion, but reactants of all of chemical looping reforming experiments were $2x10^{-6}$ mol/s (3 ml/min) of methane and $4x10^{-6}$ mol/s (6 ml/min) of steam. The reactions of experiments were reduction of NiO and oxidation of Ni. The results of experiments are shown as mol of product gas per mol of methane feed and mol fractions of product.

5.2.1 Catalyst characterization

NiO/Al_2O_3 and NiO/CeO_2 were characterized using SEM-EDX, XRD, and BET. The morphology of NiO/Al_2O_3 is shown in Figure 5.19 and NiO/CeO_2 is shown in Figure 5.20. The surface of NiO/Al_2O_3 reveals a crystallize aspect while NiO/CeO_2 reveals that the surface presents a granulated aspect.

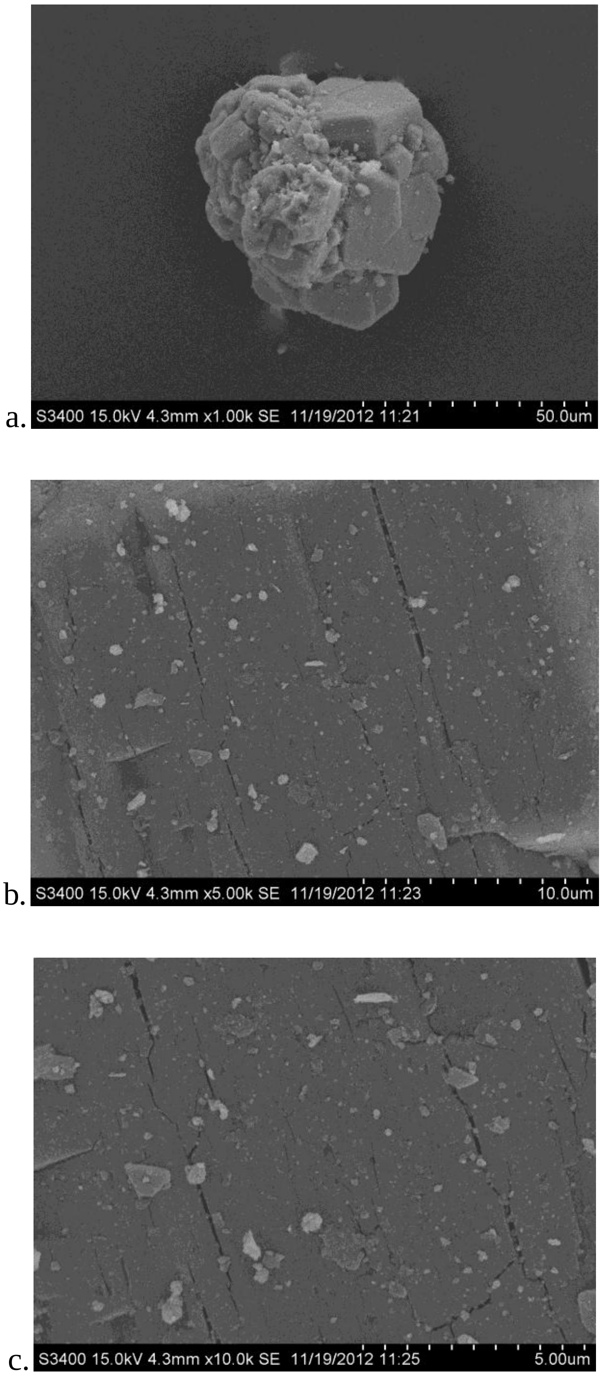

Figure 5.19 SEM of NiO/Al_2O_3 (a: 50 micrometre, b: 10 micrometre, C: 5 micrometre)

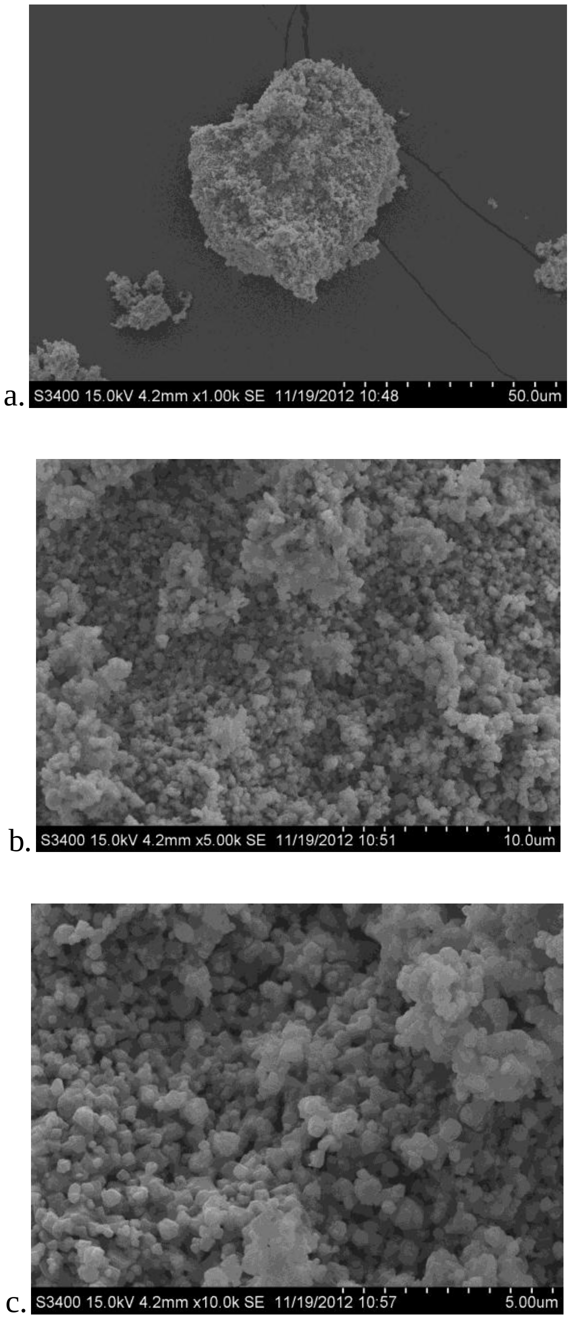

Figure 5.20 SEM of NiO/CeO_2 (a: 50 micrometre, b: 10 micrometre, C: 5 micrometre)

The XRD diffraction patterns for Al_2O_3, CeO_2, NiO/Al_2O_3, and NiO/CeO_2 are displayed in Figures 5.21and 5.22. In Figure 5.21, the sample is in the gamma crystallite phase (γ - Al_2O_3). There are four peaks located at 2θ =37.5°, 39.5°, 46.0° and 69.0°. Figure.5.21 shows three phase of γ - Al_2O_3, NiO/Al_2O_3, and $NiAl_2O_4$. $NiAl_2O_4$ is the combination of NiO and Al_2O_3 support. After impregnation of NiO on γ - Al_2O_3 support, XRD of sample shows peak of NiO and $NiAl_2O_4$ which is the combination of NiO and Al_2O_3. Peaks of NiO are located at 2θ = 37.0°, 43.0°, and peaks of $NiAl_2O_4$ are located at 2θ =19.0° and 60.0°, and 69.0°.

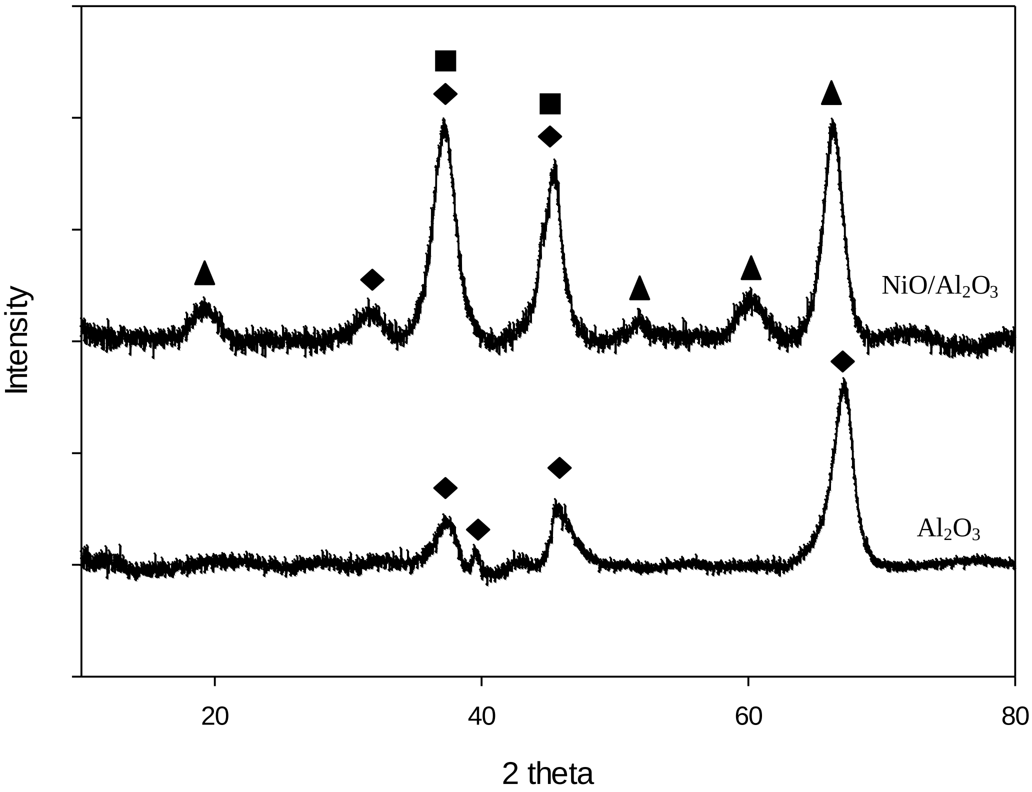

Figure 5.21 XRD of γ -Al_2O_3 and NiO/Al_2O_3 (◆: Al_2O_3, ■: NiO, ▲: $NiAl_2O_4$)

Figure 5.22 shows the typical patterns of the CeO_2 and NiO/CeO_2. There are eight peaks of CeO_2 located at 2θ =29.0°, 33.0°, 47.5°, 56.5°, 59.0°, 69.5°, 77.0° and 79.0°. After impregnation of NiO on CeO_2 support, XRD of sample shows two peaks of NiO located at 2θ =37.0°and 43.0°.

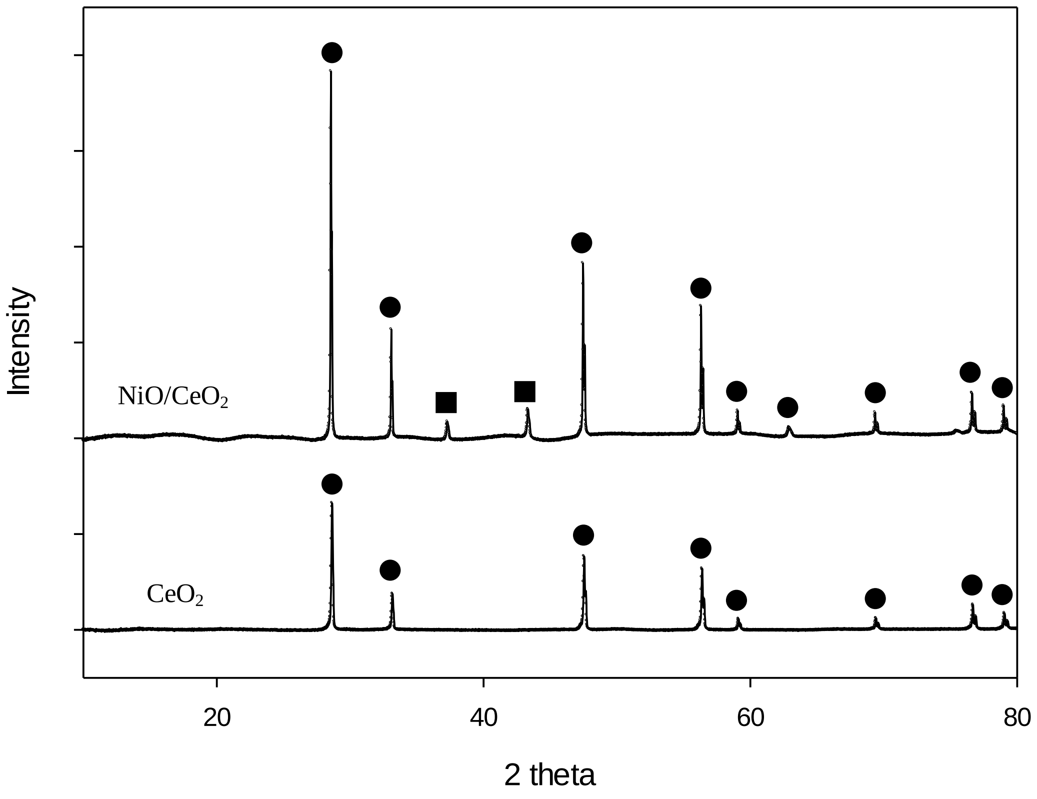

Figure 5.22 XRD of CeO$_2$ and NiO/CeO$_2$ (■: NiO,●: CeO$_2$)

From examining samples of alumina support (Al_2O_3), ceria support (CeO_2), NiO/Al_2O_3, and NiO/CeO_2, the alumina support has much more surface area than the ceria support.

Table 5.7 BET surface areas of samples

Oxygen carrier	BET surface area (m^2/g)
Al_2O_3	151.1
CeO_2	2.5
NiO/Al_2O_3	96.3
NiO/CeO_2	2.8

From Table 5.7, alumina support has a good advantage of dispersion of metal oxide on support, therefore, when loading NiO on supports, NiO can be impregnated in pores of alumina support, this loss of surface area of the alumina support after impregnation of NiO causes the encapsulation of highly expensive noble-metal catalysts usually supported on gamma-alumina, while in the ceria support, NiO just only covers on it. As shown in Table 5.7 and Table 5.8, peak of Ni (Ni 2p1, Ni 2p2, Ni 2p3) can be seen in NiO/Al_2O_3 less than NiO/CeO_2. It can be seen that surface area of NiO/CeO_2 is more than ceria support. That is due to the loading NiO followed by calcinations that pores produced from liberation of nitrogen oxides gas during thermal decomposition of nickel nitrate were occurred (Deraz, 2012) and impregnation of NiO on ceria makes sample has more crystallinity (Zhang et al., 2012).

Table 5.8 XPS of NiO/Al_2O_3

Peak	Position BE (eV)	FWHM (eV)	Atomic mass	% Atomic concentration	% Mass concentration
Ni 2p1	858.4	2.369	58.702	0.705081	1.903269
Ni 2p2	876	1.994	58.702	0.206662	0.570981
Ni 2p3	864.3	2.203	58.702	0.170192	0.459024
O 1s1	23.9	3.357	15.999	50.80233	37.56158
O 1s2	26.2	1.218	15.999	0.972526	0.716525
Al 2s	121	2.926	26.982	23.43788	29.22078
Al 2p1	76.2	2.341	26.982	23.21906	28.95208
Al 2p2	74.7	0.8	26.982	0.486263	0.615764

Table 5.9 XPS of NiO/CeO_2

Peak	Position BE (eV)	FWHM (eV)	Atomic mass	% Atomic concentration	% Mass concentration
Ni 2p1	854.7	3.99	58.702	17.92786	30.06797
Ni 2p2	861.2	3.505	58.702	7.408062	12.42612
Ni 2p3	872.7	2.116	58.702	3.748232	6.279551
O 1s1	529.7	2.382	15.999	60.53748	27.65957
O 1s2	532.3	1.792	15.999	5.056577	2.304965
Ce 3d1	882	3.227	140.115	2.280764	9.101655
Ce 3d2	899.2	3.783	140.115	2.369165	9.500591
Ce 3d3	915.8	1.954	140.115	0.671853	2.659574

5.2.2 Carbon dioxide adsorption

When $5.3x10^{-6}$ mol/s (8vol %) CO_2 at a total flow 50 ml/min was fed on 1 g CaO at 600, 700, and 800^{o}C. The results were found that CaO adsorbed least amount carbon dioxide at 800^{o}C, and highest amount carbon dioxide at 600^{o}C, because adsorption reaction of CaO is an exothermic reaction. However, hydrogen production will be favor when operating at high temperature (more than 500^{o}C). Therefore, all chemical looping experiments would be operated at 600^{o}C.

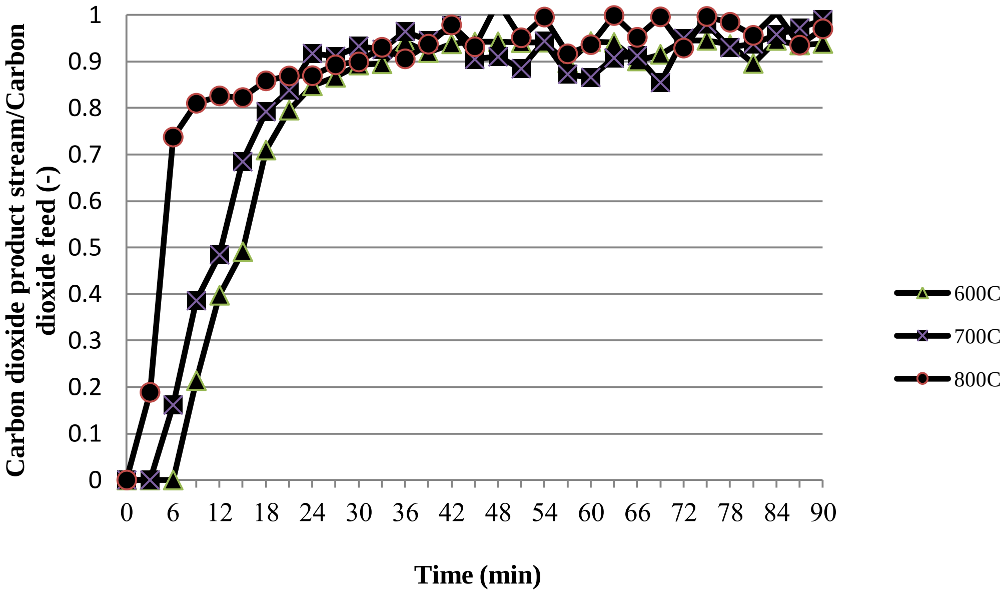

Figure 5.23 Carbon dioxide adsorption on 1 g CaO ($5.3x10^{-6}$ mol/s (8vol %) CO_2, total flow 50 ml/min)

5.2.3 Chemical looping combustion

Chemical looping combustion is the process that only fuel is fed. At the beginning of the experiment, complete combustion is occurred and only that carbon dioxide is found because there are plenty of oxygen atoms from nickel oxide. Then oxygen atom are fewer, incomplete combustion is occurred along with complete combustion. Hydrogen is found later and much more, until nickel oxide is totally reduced. At last, there is only methane cracking occurred at high temperature.

In these experiments, $2x10^{-6}$ mol/s (3 ml/min) of methane was fed along with nitrogen gas which was carrier gas. Total flow of gas transporting through the bed reactor was 50 ml/min. All of the experiments were operated at atmospheric pressure, 600°C. In case of using CaO as CO_2 sorbent, after reduction reaction, the solid bed in the reactor was calcined at 900°C to release carbon dioxide. In oxidation reaction, which had the same operating condition as reduction reaction, total flow of gas transporting through the bed reactor was 50 ml/min consisted of nitrogen as carrier gas and 14x10^{-6} mol/s (21vol%) of oxygen.

From Figure 5.24, NiO/Al$_2$O$_3$ physicallly mixed with SiC (no sorbent) was reduced by methane. There were many reactions occurred: complete combustion, incomplete combustion, and dry reforming reaction, and methane cracking.

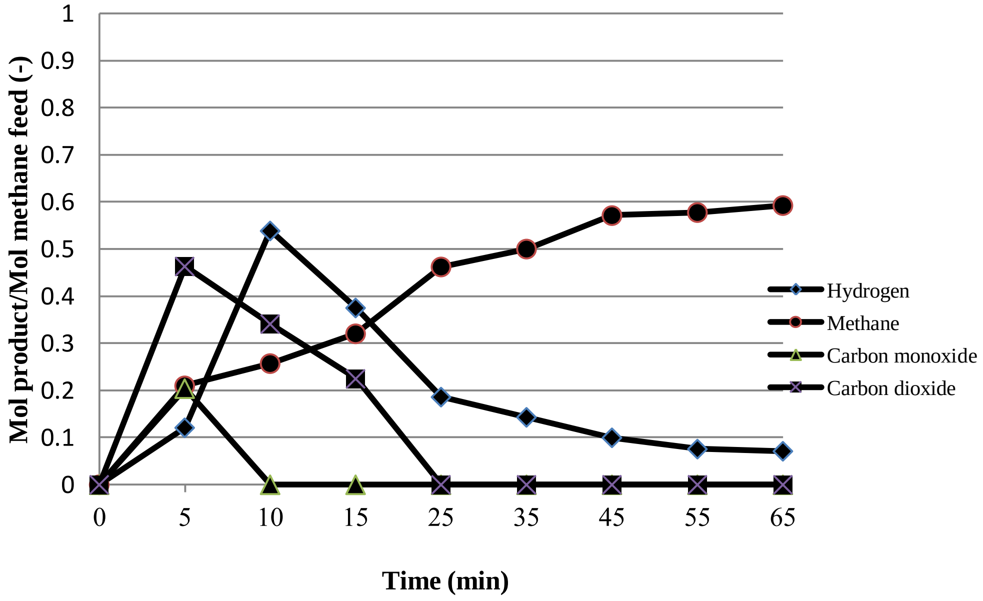

Figure 5.24 Reduction reaction in chemical looping combustion on NiO/Al$_2$O$_3$ with SiC

From Figure 5.25, NiO/Al$_2$O$_3$ physically mixed with SiC (no sorbent) produced hydrogen at a maximum purity of 47.39%.

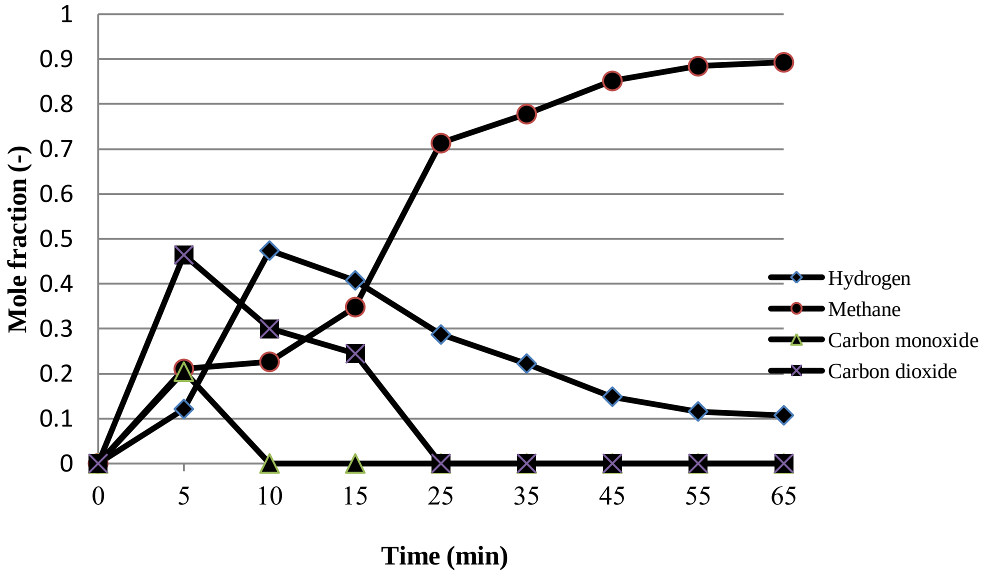

Figure 5.25 Mole fraction of Reduction reaction in chemical looping combustion on NiO/Al_2O_3 with SiC

To complete the chemical looping cycle, the Ni metal was oxidized by air to form NiO. Carbon deposited on metal was also oxidized to carbon monoxide and carbon dioxide, as shown in Figure 5.26. Then, until Ni was completely oxidized, NiO/Al_2O_3 was formed, and the product stream would be the same of the feed stream.

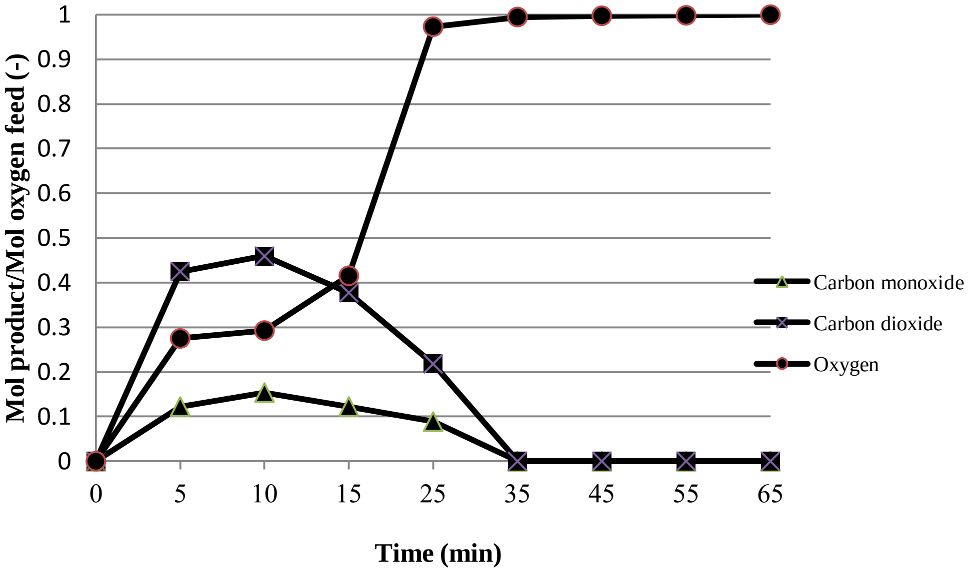

Figure 5.26 Oxidation reaction in chemical looping combustion on NiO/Al_2O_3 with SiC

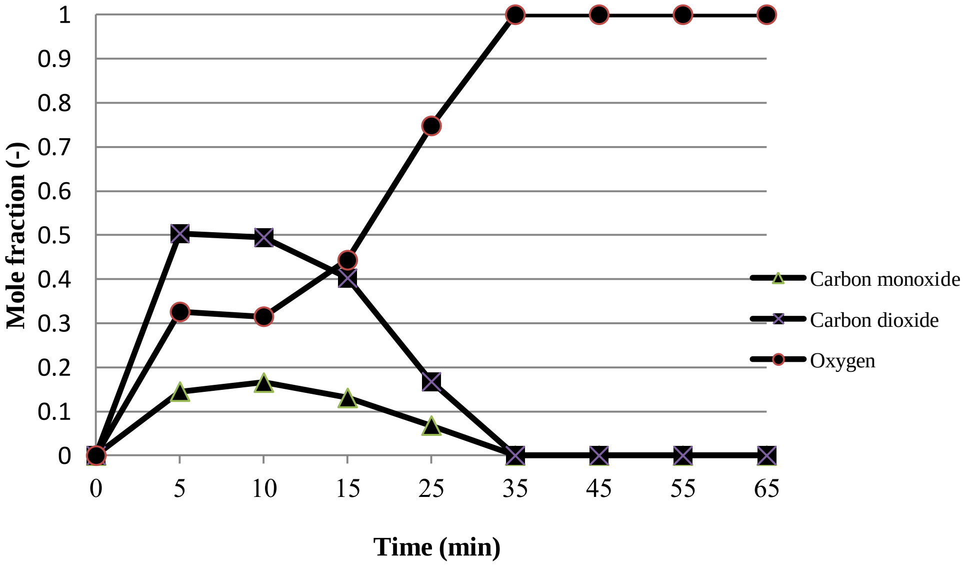

Figure 5.27 Mole fraction of Oxidation reaction in chemical looping combustion on NiO/Al_2O_3 with SiC

From Figure 5.28, NiO/Al_2O_3 physicallly mixed with CaO (CO_2 sorbent) was reduced by methane. Hydrogen purity was less than the case of no CaO (CO_2 sorbent) case. Because CaO adsorbed carbon dioxide, the dry reforming reaction would be unlikely.

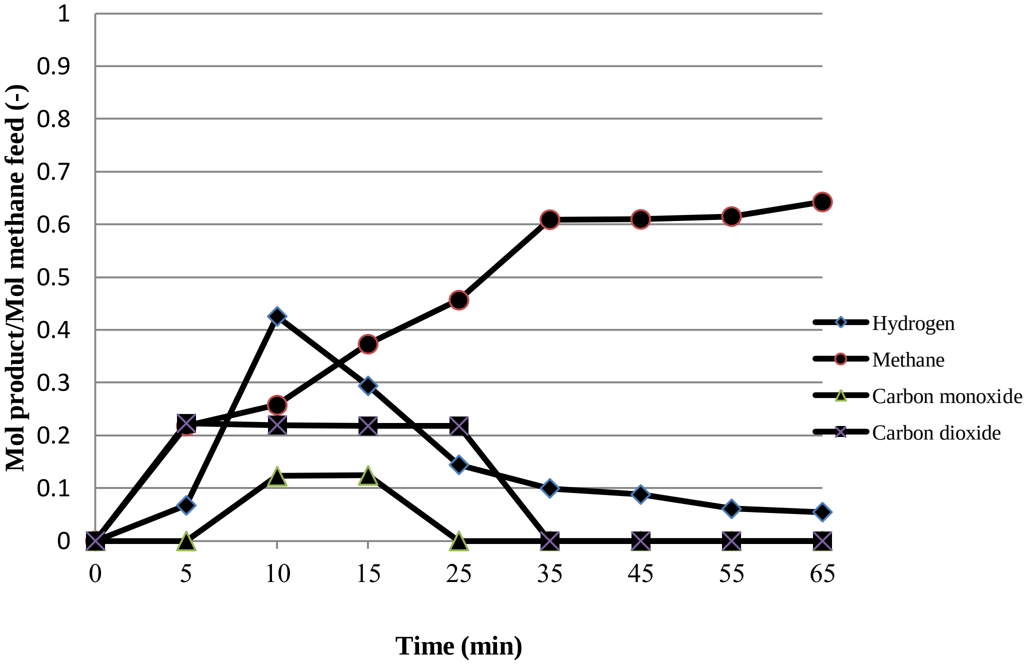

Figure 5.28 Reduction reaction in chemical looping combustion on NiO/Al_2O_3 with CaO

As shown in Figure 5.29, NiO/Al_2O_3 physically mixed with CaO produced hydrogen at a maximum purity of 41.51%.

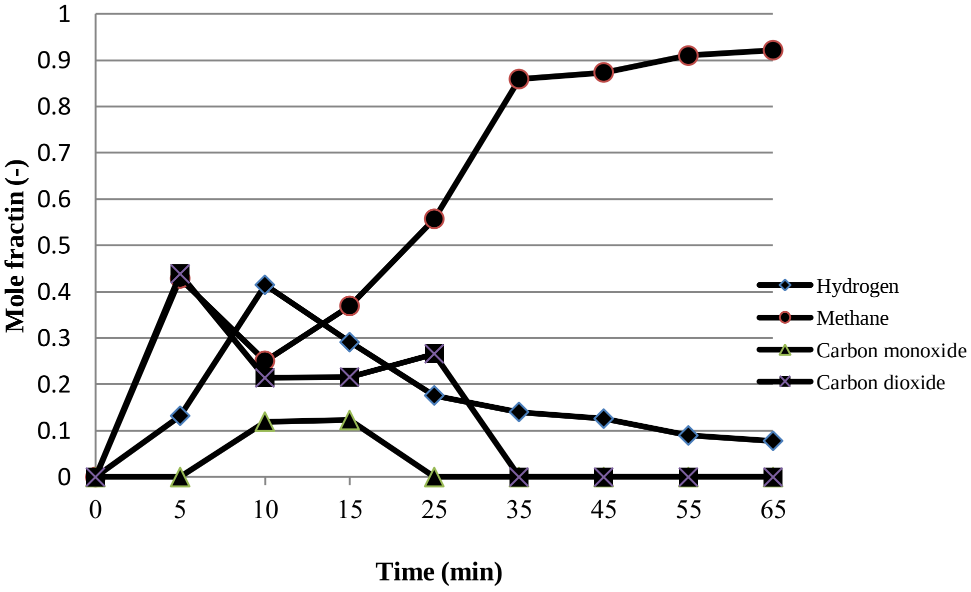

Figure 5.29 Mole fraction of Reduction reaction in chemical looping combustion on NiO/Al_2O_3 with CaO

From Figure 5.30, the oxidation reaction on NiO/Al_2O_3 with CaO was similar with the reaction on NiO/Al_2O_3 with SiC, but the product stream had less amount of carbon dioxide than the case of no sorbent because carbon dioxide that occurred at the beginning of reaction was adsorbed by CaO and formed $CaCO_3$. Therefore, before second loop of reduction, the solids should be calcined to desorb CO_2 from CaO.

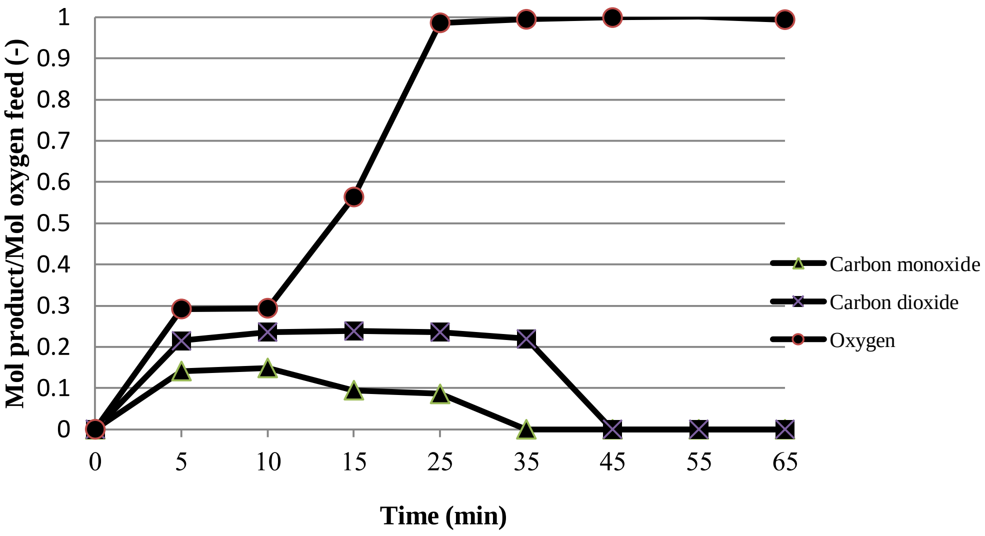

Figure 5.30 Oxidation reaction in chemical looping combustion on NiO/Al_2O_3 with CaO

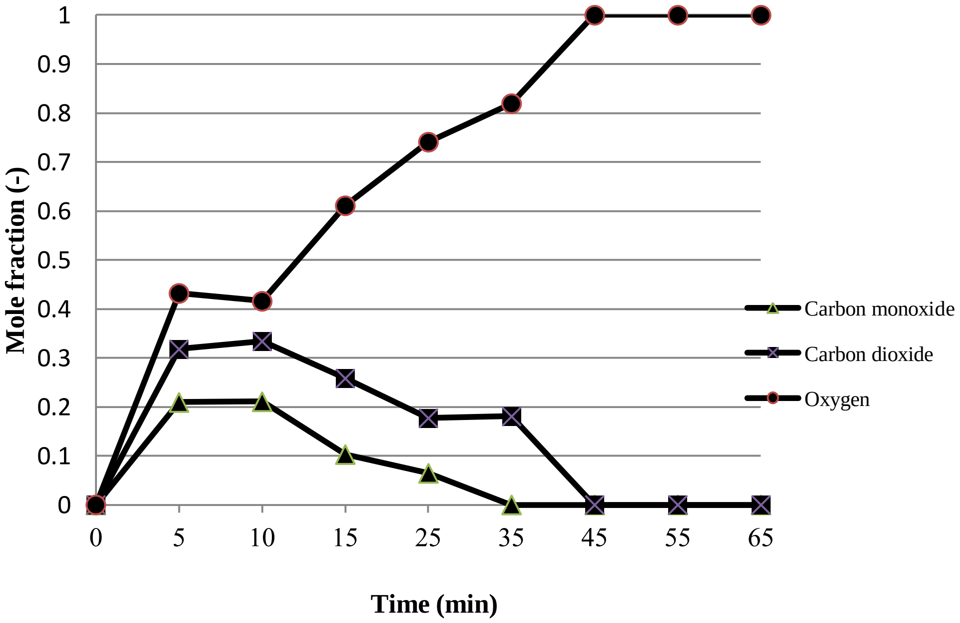

Figure 5.31 Mole fraction of Oxidation reaction in chemical looping combustion on NiO/Al_2O_3 with CaO

From Figure 5.32, NiO/CeO_2 reacted with methane producing hydrogen at higher purity than NiO/Al_2O_3 because ceria support had high oxygen storage capacity that could oxidize methane together with nickel oxide.

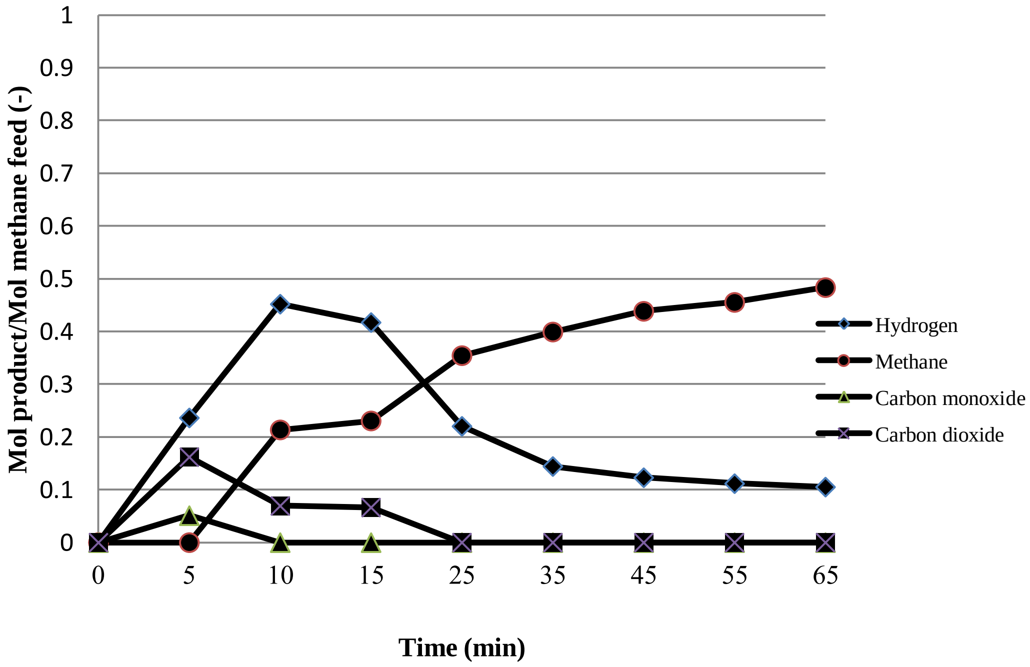

Figure 5.32 Reduction reaction in chemical looping combustion on NiO/CeO_2 with SiC

From Figure 5.33, NiO/CeO_2 physically mixed with SiC produced hydrogen at a maximum purity of 61.49%.

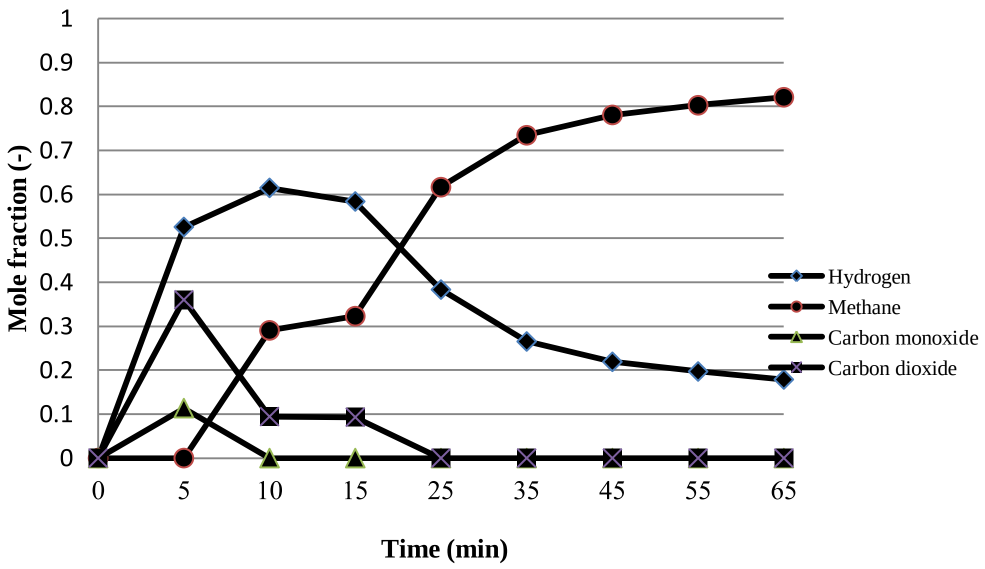

Figure 5.33 Mole fraction of Reduction reaction in chemical looping combustion on NiO/CeO_2 with SiC

When Ni/CeO_2 the from reduction reaction was oxidized by air, carbon solid which was formed on the solid packed in the reactor was oxidized and formed carbon monoxide and carbon dioxide, as shown in Figure 5.34, like the case of Ni/Al_2O_3.

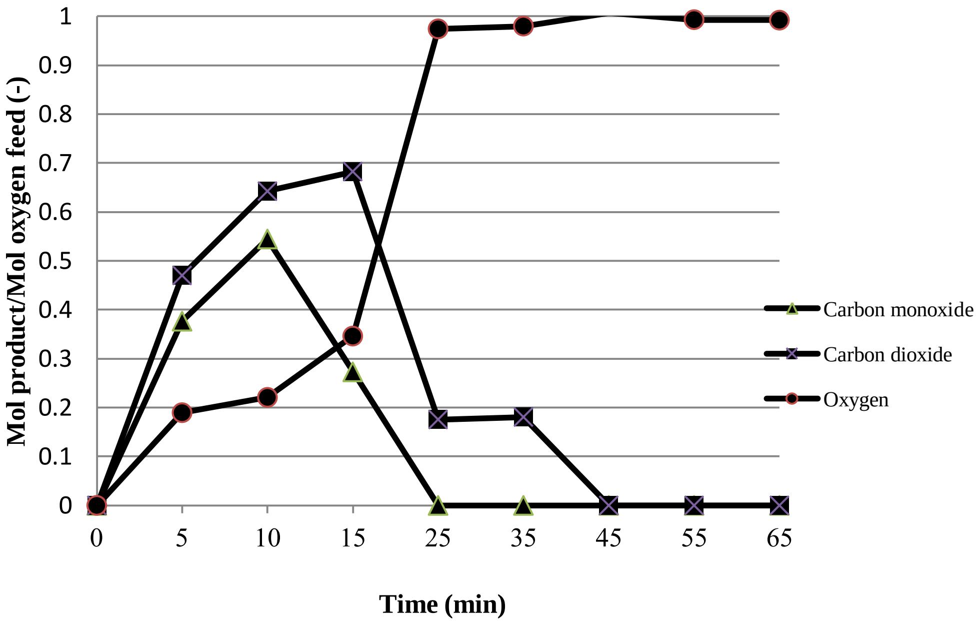

Figure 5.34 Oxidation reaction in chemical looping combustion on NiO/CeO_2 with SiC

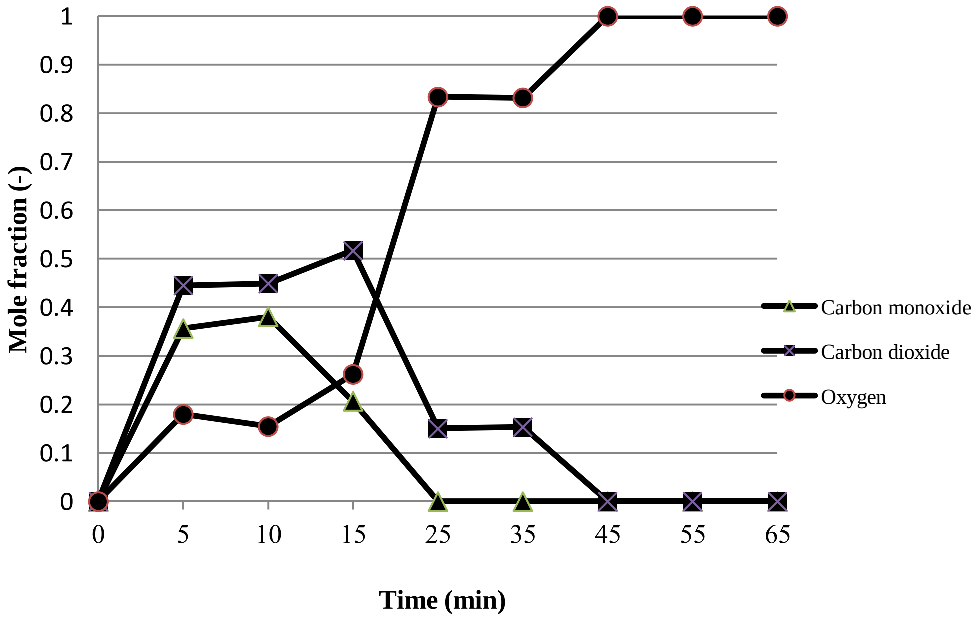

Figure 5.35 Mole fraction of Oxidation reaction in chemical looping combustion on NiO/CeO_2 with SiC

From Figure 5.36, NiO/CeO_2 physically mixed with CaO (CO_2 sorbent) was reduced by methane. Hydrogen purity was less than no CaO (CO_2 sorbent) case, like case of NiO/Al_2O_3 physically mixed with CaO.

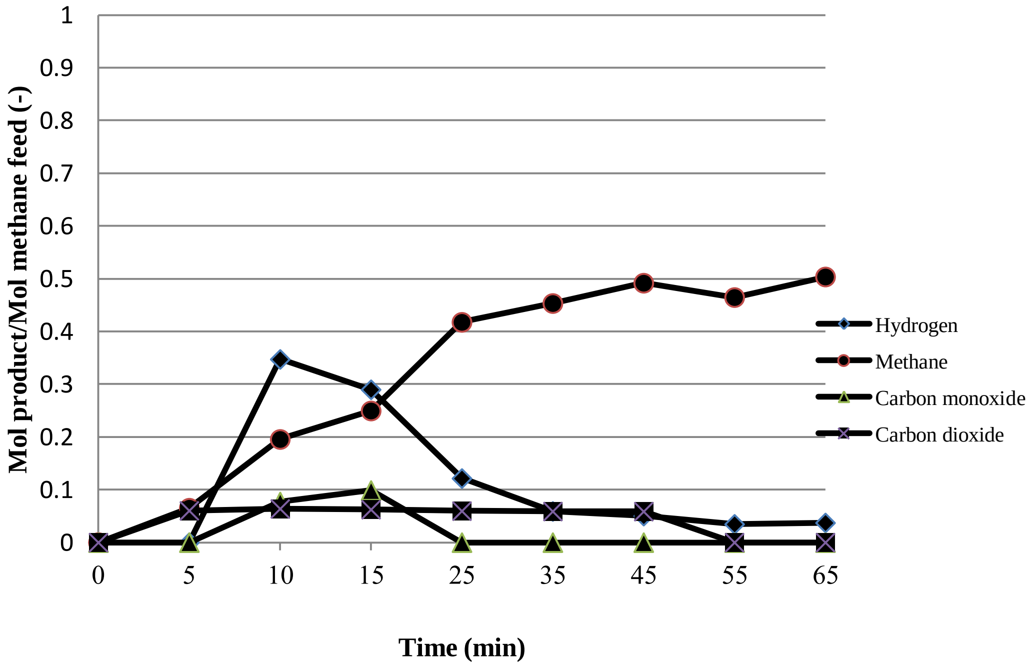

Figure 5.36 Reduction reaction in chemical looping combustion on NiO/CeO_2 with CaO

As shown in Figure 5.37, NiO/Al_2O_3 physically mixed with CaO produced hydrogen at a maximum purity of 50.79%.

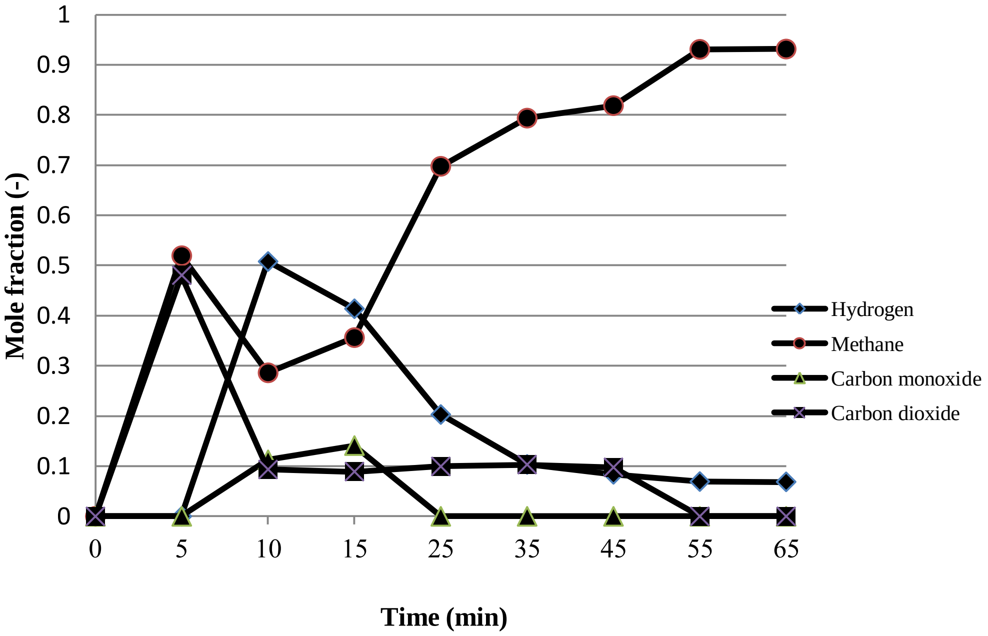

Figure 5.37 Mole fraction of Reduction reaction in chemical looping combustion on NiO/CeO_2 with CaO

Figure 5.38 shows the results of oxidation of Ni/CeO_2 physically mixed with CaO that was similar to the results of oxidation of Ni/Al_2O_3 physically mixed with CaO, as shown in Figure 5.30.

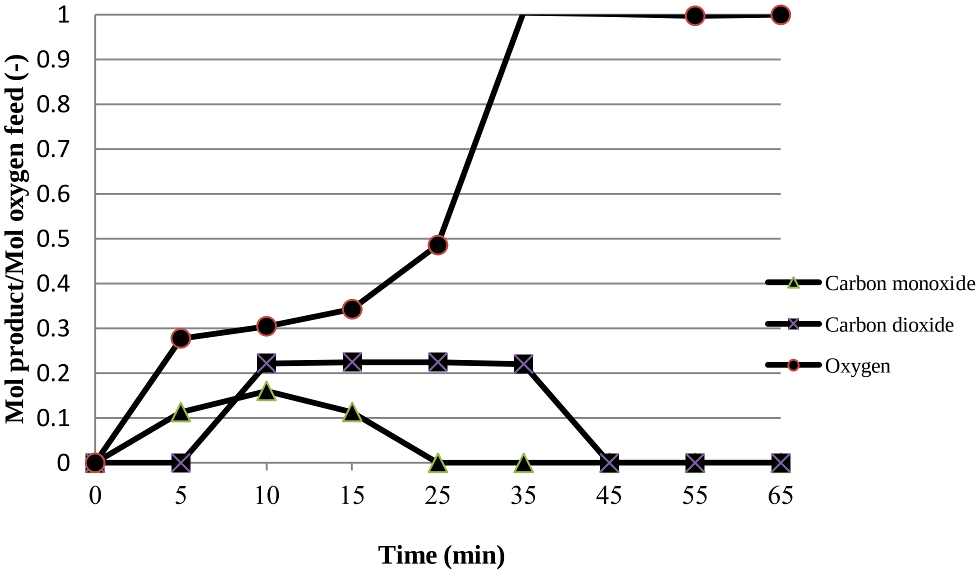

Figure 5.38 Oxidation reaction in chemical looping combustion on NiO/CeO_2 with CaO

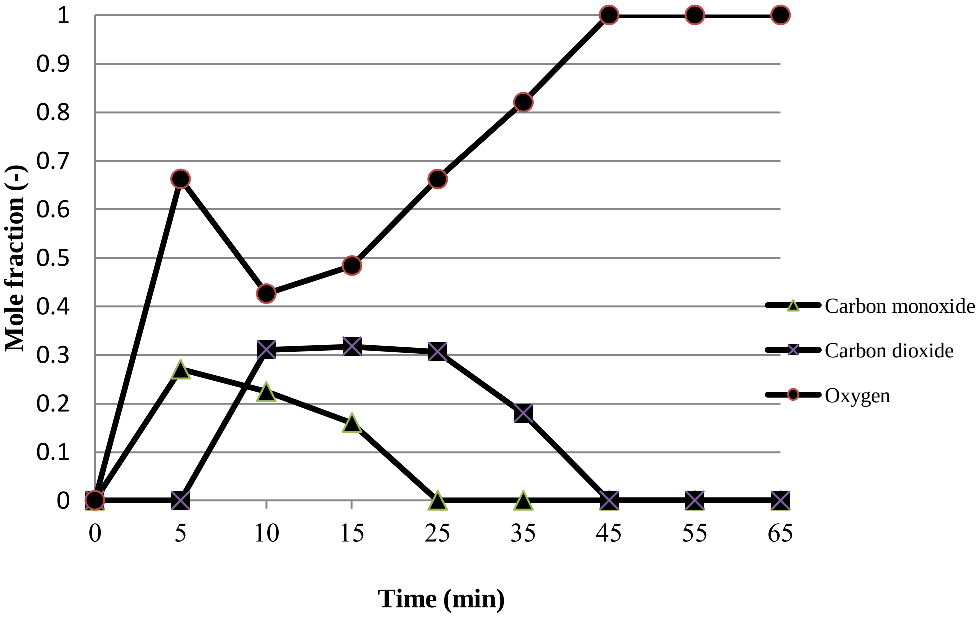

Figure 5.39 Mole fraction of Oxidation reaction in chemical looping combustion on NiO/CeO_2 with CaO

5.2.4 Chemical looping reforming

At the beginning of chemical looping reforming process, complete combustion occurred because there are plenty amount of oxygen existing in NiO, after that, the oxygen on metal oxide are less, incomplete combustion is occurred and some fraction of methane reacts with steam via catalytic steam reforming which is metal that occurred after some oxygen atoms on metal oxide are reacted. Finally, when metal oxide is depleted of oxygen, there is only metal or catalyst (Ni metal) which favors hydrogen production via catalytic steam reforming.

In these experiments, $2x10^{-6}$ mol/s (3 ml/min) of methane and $4x10^{-6}$ mol/s (6 ml/min) of steam were fed along with nitrogen gas which was carrier gas. Total flow of gas transporting through the bed reactor was 50 ml/min. All of the experiments were operated at the same condition as chemical looping combustion experiments.

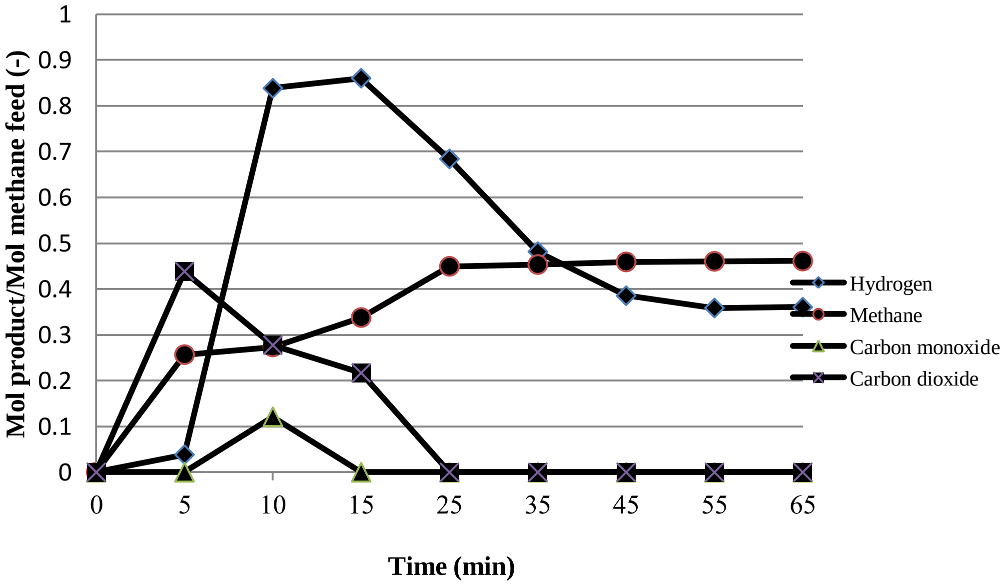

Figure 5.40 Reduction reaction in chemical looping reforming on NiO/Al_2O_3 with SiC

Figure 5.41 shows experimental results for the case of NiO/Al_2O_3 was physically mixed with SiC (without any CO_2 sorbent). The maximum hydrogen purity produced was 60.8%.

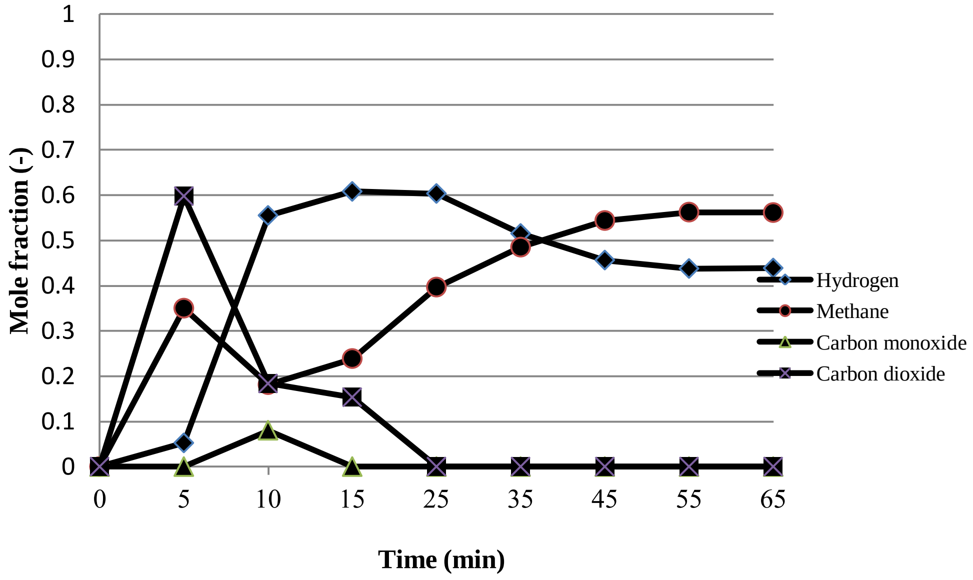

Figure 5.41 Mole fraction of reduction reaction in chemical looping reforming on NiO/Al_2O_3 with SiC

From Figure 5.42 and Figure 5.43, oxidation of Ni/Al_2O_3 physically mixed with SiC shows similar results to those of the oxidation of Ni/Al_2O_3 physically mixed with SiC of the chemical looping combustion case.

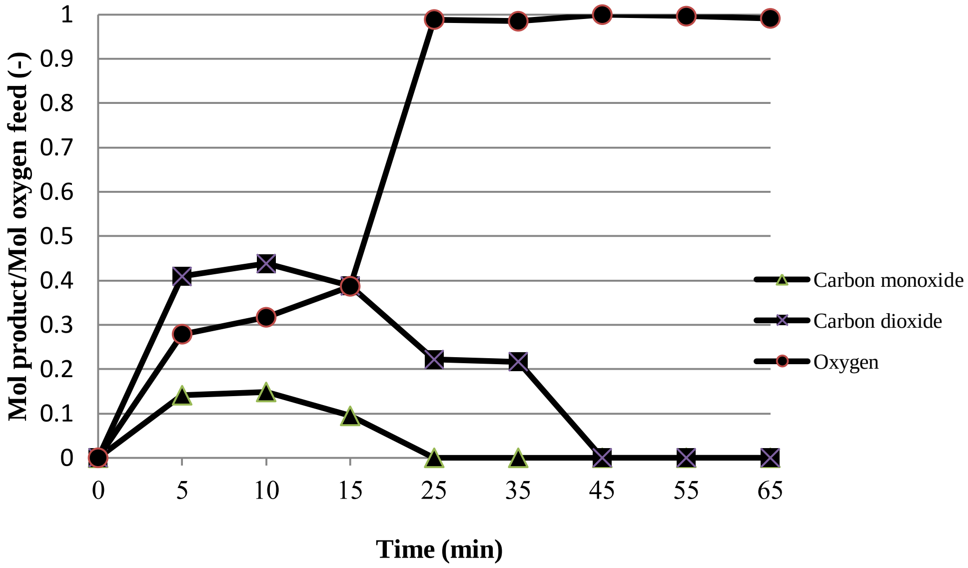

Figure 5.42 Oxidation reaction in chemical looping reforming on NiO/Al_2O_3 with SiC

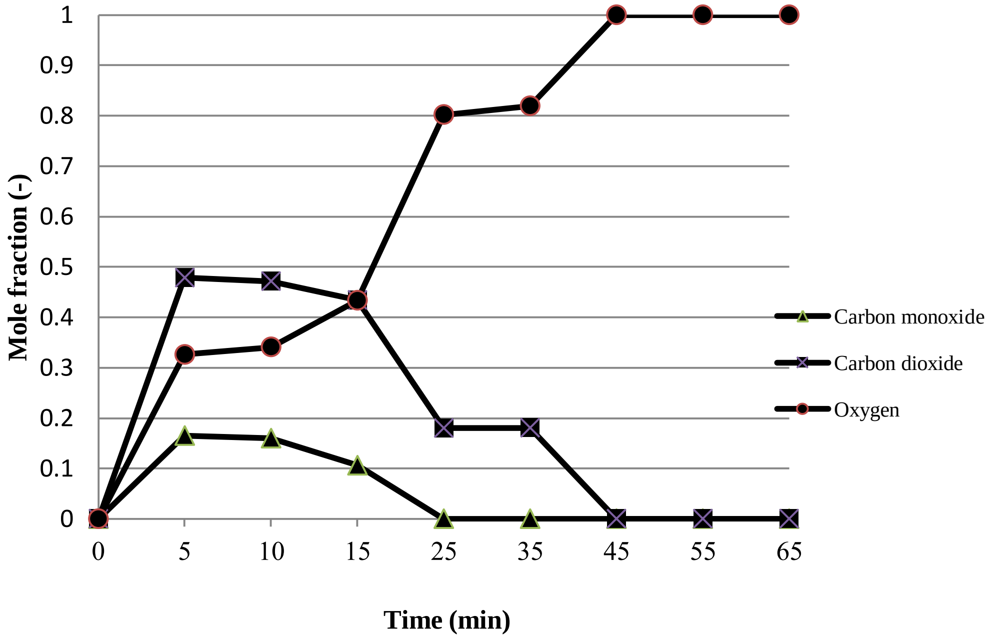

Figure 5.43 Mole fraction of oxidation reaction in chemical looping reforming on NiO/Al_2O_3 with SiC

When CaO was physically mixed with NiO/Al_2O_3, the hydrogen purity and methane conversion were increased compared with the case of NiO/Al_2O_3 physically mixed with SiC (no sorbent) as shown in Figure5.44 because CaO adsorbed CO_2 from the gas product. In this case was different from the chemical looping combustion because steam was fed with methane, so there were steam reforming and water-gas shift reactions occurred. Therefore, CaO would adsorb CO_2 from the product stream, thus shifting the reaction so that the methane conversion was increased.

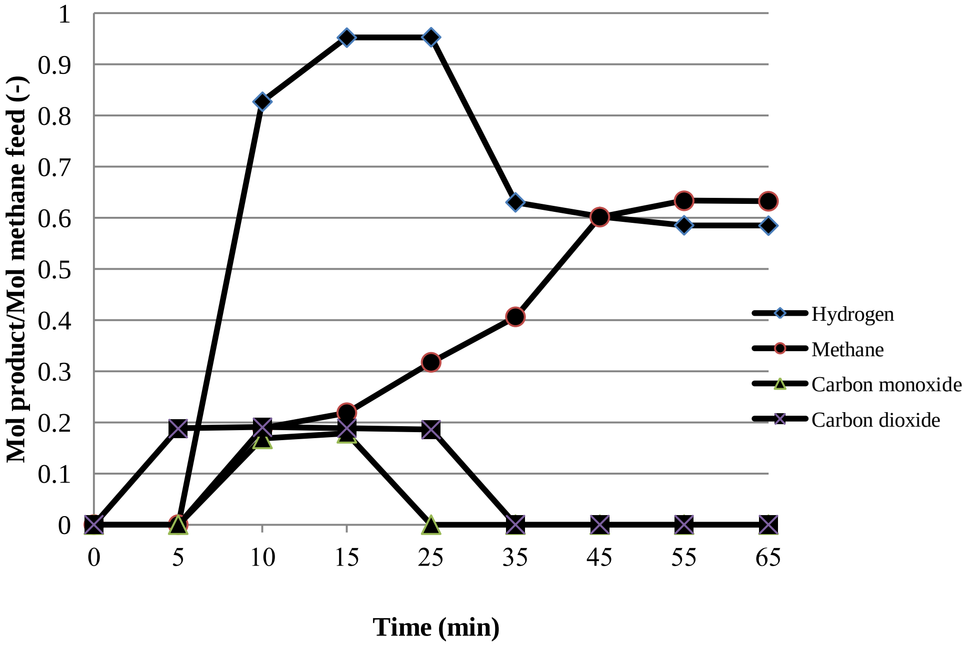

Figure 5.44 Reduction reaction in chemical looping reforming on NiO/Al_2O_3 with CaO

The highest hydrogen purity produced was increased to 65.45%, as shown in Figure 5.45.

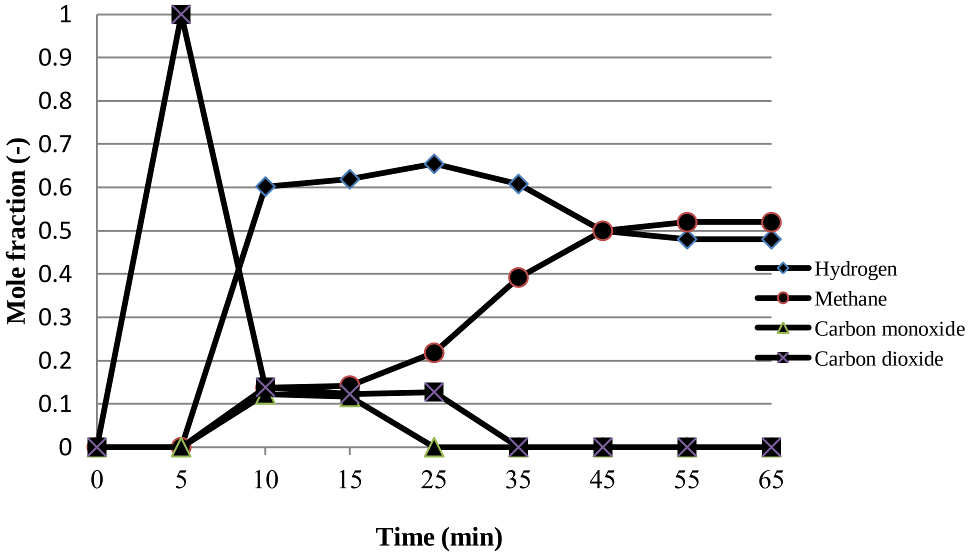

Figure 5.45 Mole fraction of reduction reaction in chemical looping reforming on NiO/Al_2O_3 with CaO

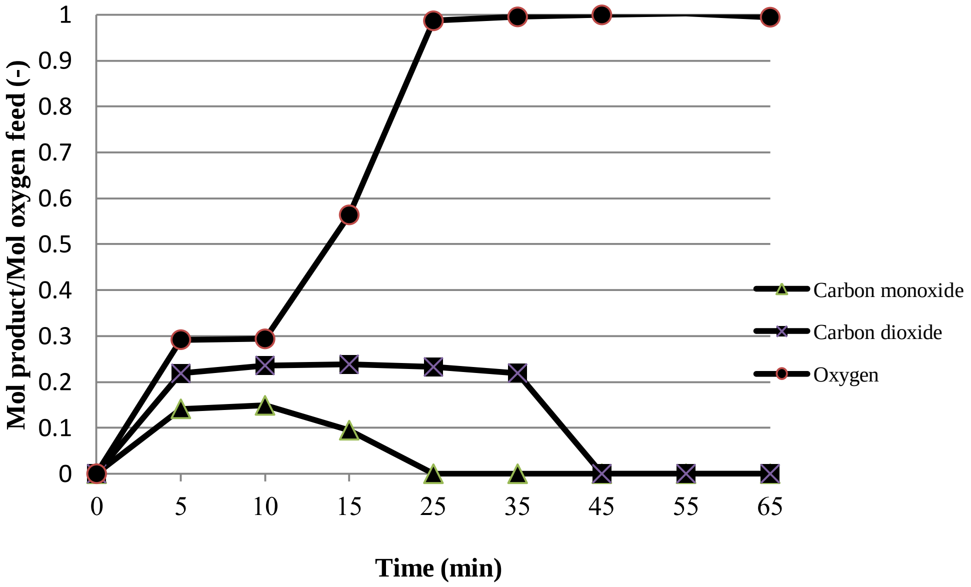

Figure 5.46 Oxidation reaction in chemical looping reforming on NiO/Al_2O_3 with CaO

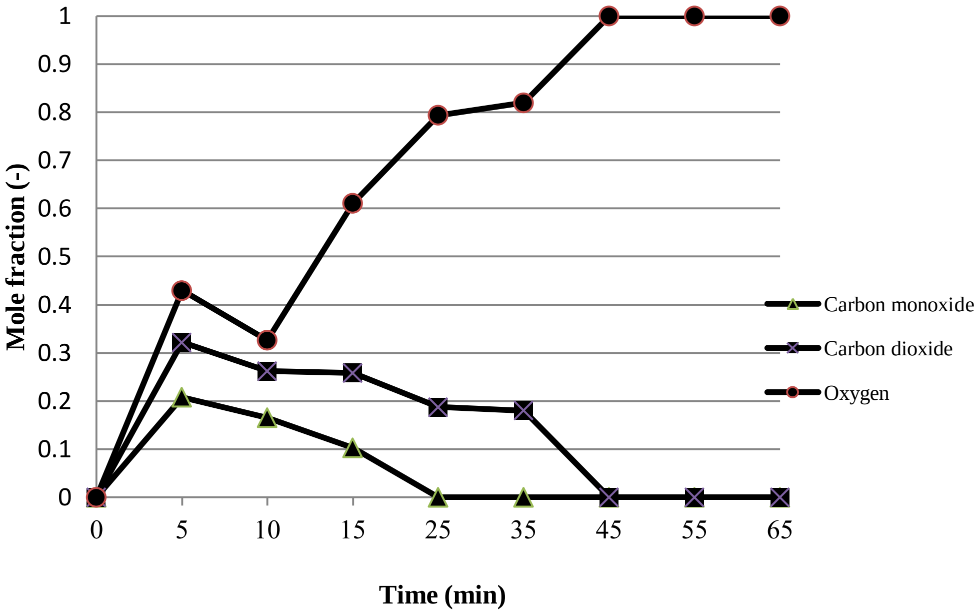

Figure 5.47 Mole fraction of oxidation reaction in chemical looping reforming on NiO/Al_2O_3 with CaO

A comparison between NiO/Al_2O_3 and NiO/CeO_2, showed that NiO with ceria support produced greater amount of hydrogen than that from alumina support. Ceria support is famous for its high oxygen storage capacity which can be released to react with methane in addition to oxygen from NiO.

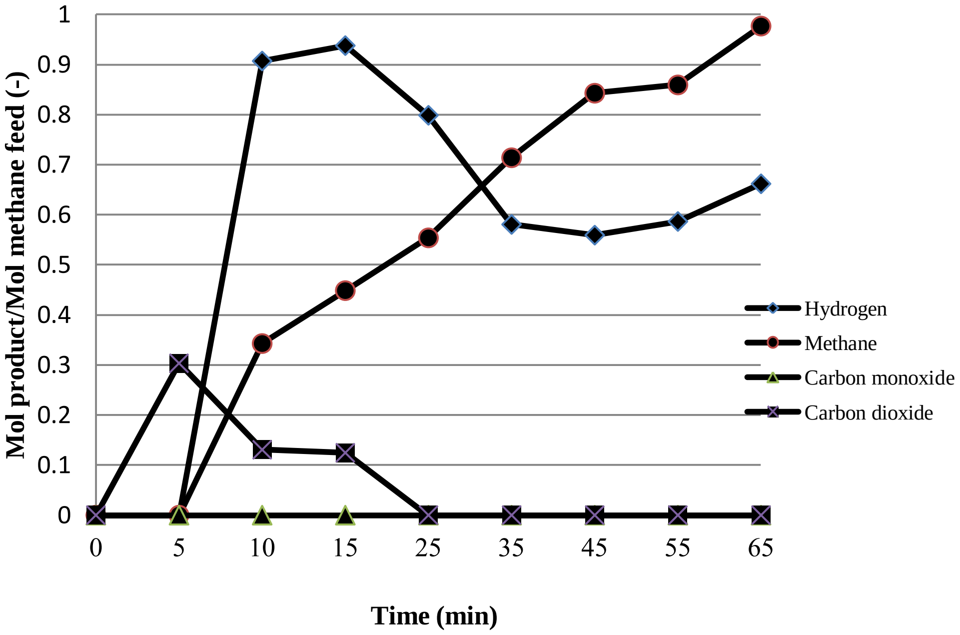

Figure 5.48 Reduction reaction in chemical looping reforming on NiO/CeO_2 with SiC

According to Figure 5.49, the chemical looping reforming using NiO/CeO_2 as an oxygen carrier without the use of CaO produced hydrogen at the highest purity of 65.7%, which is even higher than that achieved from the case of NiO/Al_2O_3 physically mixed with CaO.

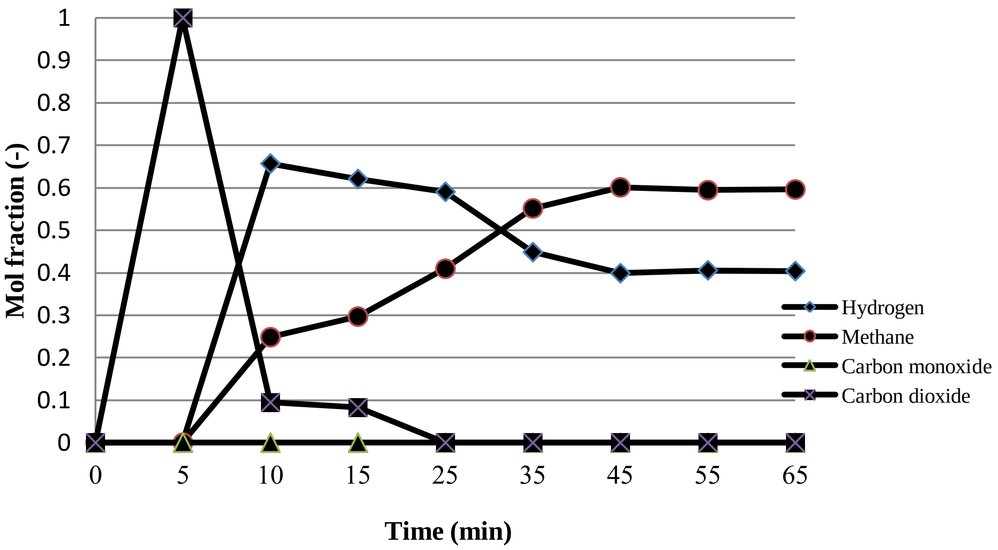

Figure 5.49 Mole fraction of reduction reaction in chemical looping reforming on NiO/CeO$_2$ with SiC

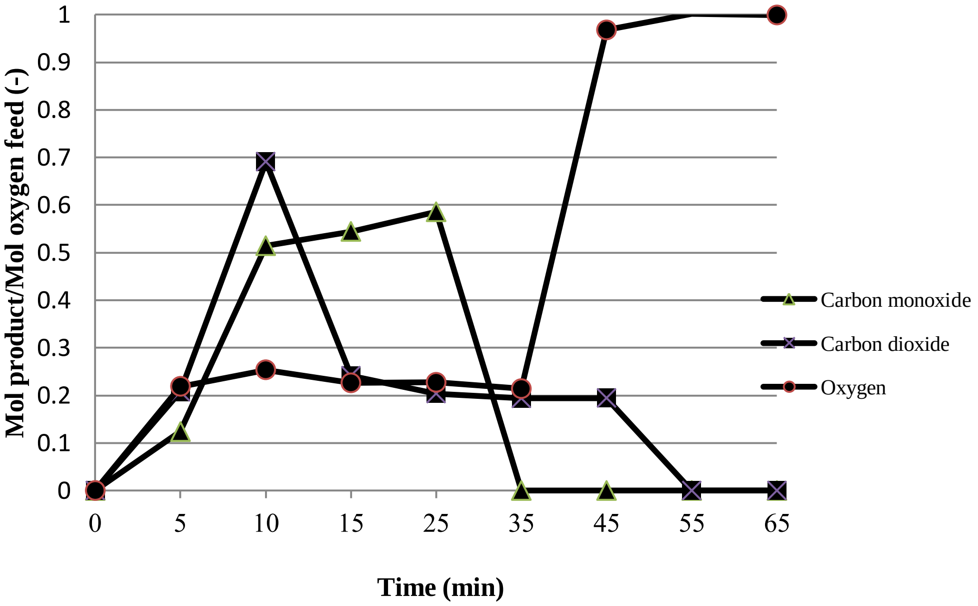

Figure 5.50 Oxidation reaction in chemical looping reforming on NiO/CeO$_2$ with SiC

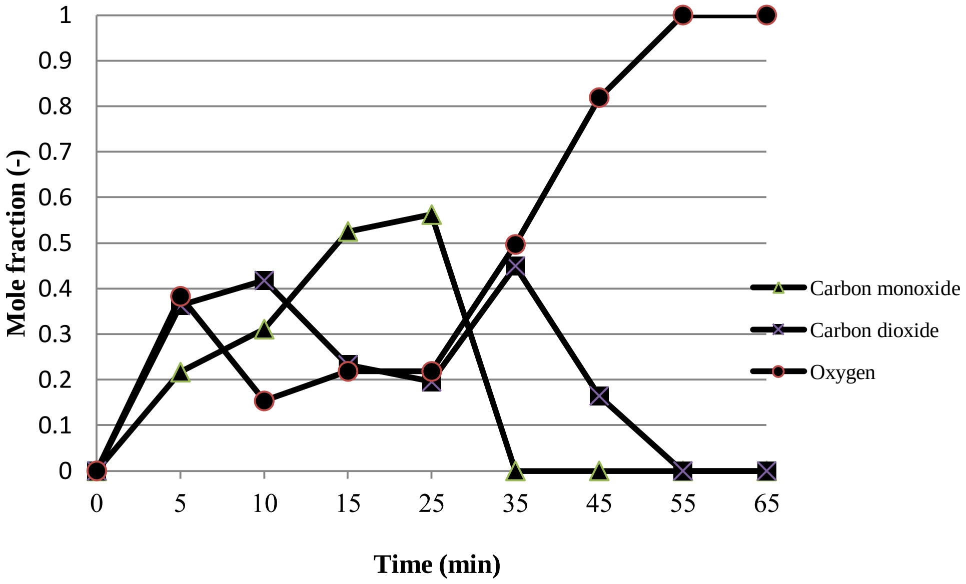

Figure 5.51 Mole fraction of oxidation reaction in chemical looping reforming on NiO/CeO_2 with SiC

When CaO was physically mixed in NiO/CeO_2, the results were shown in Figure 5.52 indicating similarity with the results of the alumina support. However, in this case, the maximum hydrogen purity was 72.36%, as shown in Figure 5.53. Therefore, addition of CaO as a CO_2 sorbent is beneficial to hydrogen production in chemical looping reforming.

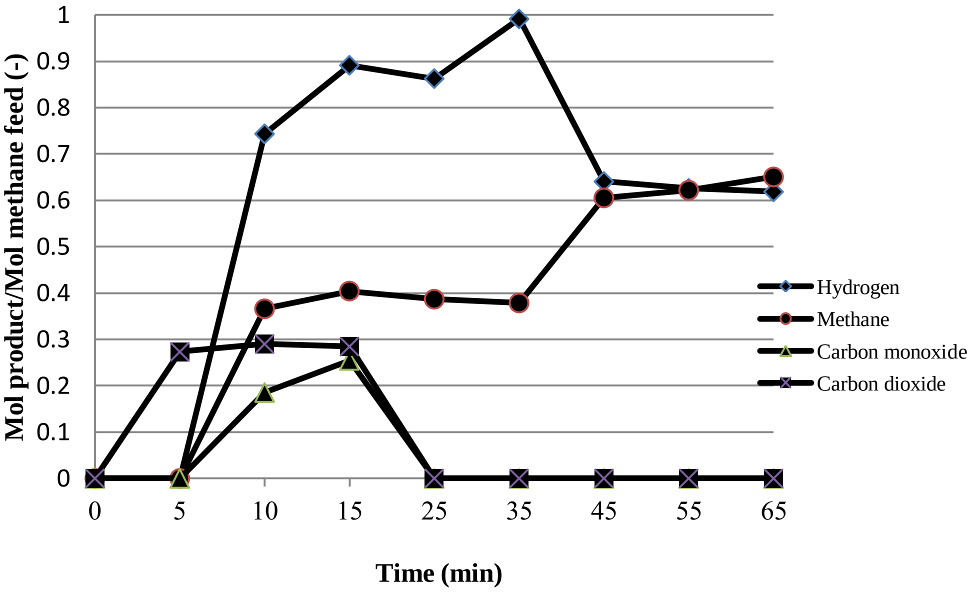

Figure 5.52 Reduction reaction in chemical looping reforming on NiO/CeO$_2$ with CaO

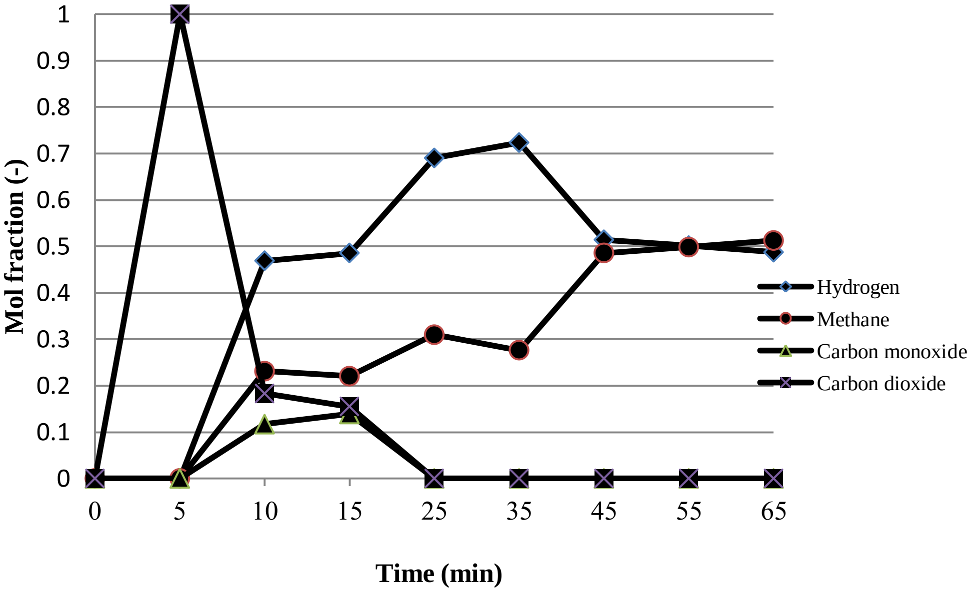

Figure 5.53 Mole fraction of reduction reaction in chemical looping reforming on NiO/CeO$_2$ with CaO

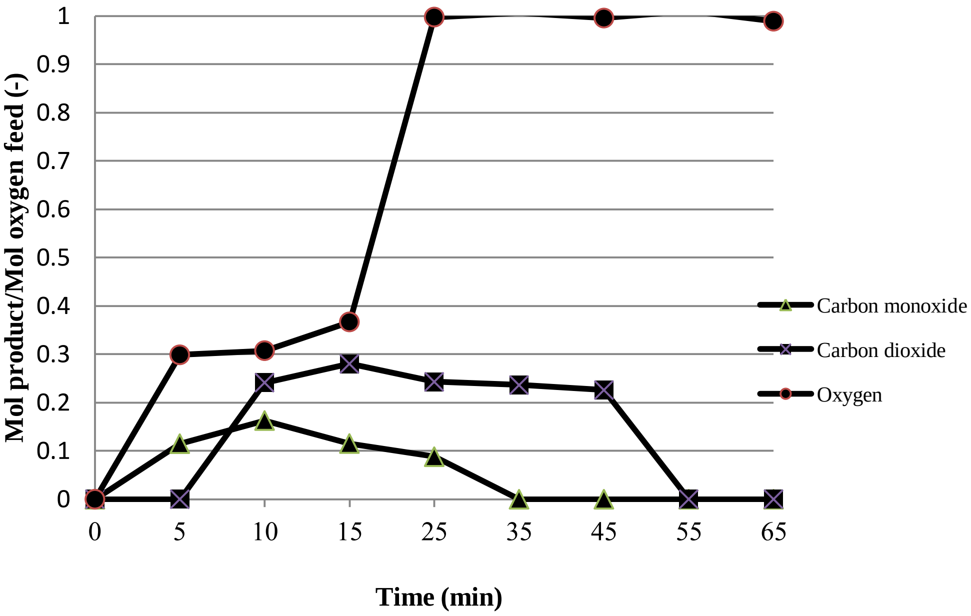

Figure 5.54 Oxidation reaction in chemical looping reforming on NiO/CeO_2 with CaO

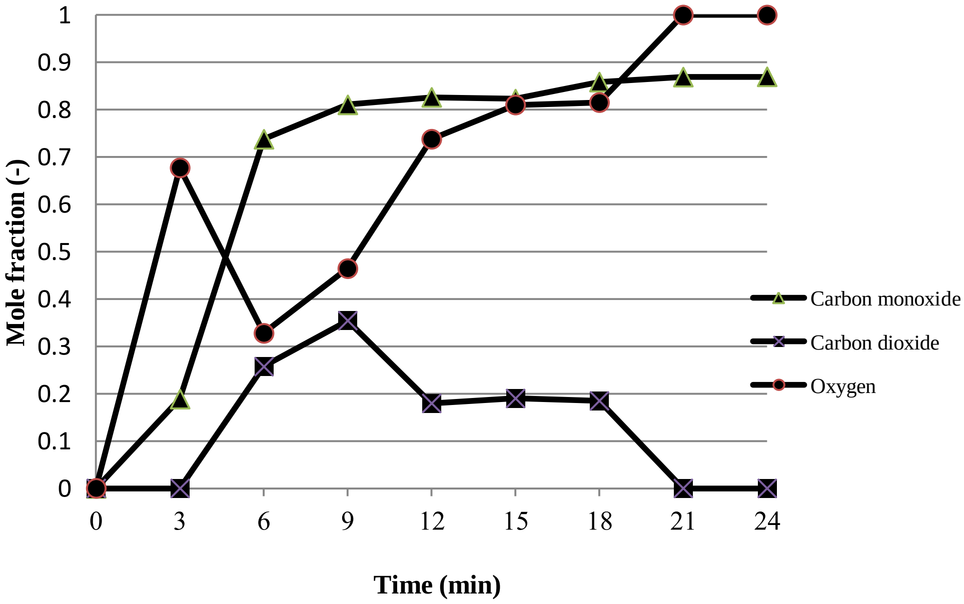

Figure 5.55 Mole fraction of oxidation reaction in chemical looping reforming on NiO/CeO_2 with CaO

From chemical looping reforming experiments, they were found that ceria support would help nickel oxide produce higher hydrogen purity more than alumina support, and when CaO was added, hydrogen product at higher purity was obtained. From all chemical looping experiments, chemical looping reforming on NiO/CeO_2 with CaO produced highest hydrogen purity.

The chemical looping reforming results were similar to the chemical looping combustion results but had higher hydrogen purity, as shown in table 5.8, because steam that fed in chemical looping reforming reacting with methane via steam reforming reaction to produce more hydrogen. Moreover, using CaO as CO_2 sorbent helped to purify hydrogen product and shift the reaction to produce more hydrogen, which was contrast with the chemical looping combustion case that CaO would prevent hydrogen production because carbon dioxide was a reactant of dry reforming reaction.

Table 5.10 Maximum hydrogen purity produced from each chemical looping process

Process	Samples	%Maximum hydrogen purity
Chemical looping combustion	NiO/Al_2O_3+SiC	47.39
	NiO/Al_2O_3+CaO	41.51
	NiO/CeO_2+SiC	61.49
	NiO/CeO_2+CaO	50.79
Chemical looping reforming	NiO/Al_2O_3+SiC	60.80
	NiO/Al_2O_3+CaO	65.45
	NiO/CeO_2+SiC	65.70
	NiO/CeO_2+CaO	72.36

After oxidation, not all of carbon formed on solid was oxidized. Energy-dispersive X-ray spectroscopy (EDX) was used for analyzing the solid after experiments. The results were shown in Table 5.11, NiO/CeO_2 after oxidation had less carbon than NiO/Al_2O_3 after oxidation, so, NiO/Al_2O_3 would be deactivated from carbon formation faster than NiO/CeO_2.

Table 5.11 Carbon on oxygen carrier after experiments

Oxygen carrier	% Weight carbon
NiO/Al_2O_3	2.83
NiO/CeO_2	1.79

According to the results, the advantage of ceria support is not only for its high oxygen storage which helps produce more hydrogen but also suppresses carbon formation on the oxygen carriers.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The conclusion of experimental and simulation results of conventional chemical looping reforming and sorption enhanced chemical looping reforming (with CO_2 sorbent) are summarized. Technical comparisons of all processes at different values of ratio of steam per methane, ratio of NiO per methane, and operating condition) for hydrogen production via chemical looping reforming with and without CO_2 sorbent are provided. Finally, the recommendations of future works are suggested.

1. From the simulation study, the following conclusions can be drawn:
    1) From the simulation results of conventional chemical looping reforming via Aspen plus program, more steam helps to convert methane to more hydrogen. Regarding high hydrogen purity and low energy requirement, steam : methane ratio of 2:1 and NiO : methane ratio of 1:1, and high temperature is favorable to produce more hydrogen.
    2) From the simulation results of chemical looping reforming with CO_2 sorbent via Aspen plus program, although a temperature is favorable to high hydrogen production, too high temperature (>700^{o}C) offers low carbon dioxide adsorption on CaO and, therefore, the beneficial effect of sorption-enhanced reaction is not obvious. Regarding of high hydrogen purity and low energy requirement, in case of using CO_2 sorbent, operation at temperature of 600^{o}C is the appropriate operating condition.
2. From the experimental study, on conventional chemical looping combustion, chemical looping combustion with CO_2 sorbent, conventional chemical looping reforming, and chemical looping reforming with CO_2 sorbent, the

comparison of supports (alumina support and ceria support) in each system was investigated. The following conclusions can be drawn:

1) From the results of the conventional chemical looping combustion, silicon carbide was used to physically mix with metal oxide on support to increase bed height as high as the chemical looping reforming with CO_2 sorbent case to have the same residence time. Methane was fed through the packed bed reactor packed with nickel oxide which is subsequently converted to nickel. NiO/CeO_2 showed higher reactivity than NiO/Al_2O_3.
2) From the results of the chemical looping combustion with CO_2 sorbent, CaO was used to physically mix with metal oxide on support. It showed similarity with conventional chemical looping combustion but with lower hydrogen purity because CaO as CO_2 sorbent adsorbed carbon dioxide that prevents dry reforming reaction (methane reacts with carbon dioxide and the products are hydrogen and carbon monoxide).
3) From the results of the conventional chemical looping reforming, silicon carbide was used to be physically mixed with metal oxide on support. Methane and steam in methane: steam ratio of 1: 2 were fed through the packed bed reactor, packed with nickel oxide. The product stream showed higher hydrogen purity than the conventional chemical looping combustion and the chemical looping combustion with CO_2 sorbent because some fraction of methane that did not react with nickel oxide would react with steam to form carbon monoxide and hydrogen, moreover, carbon monoxide would react with steam to form carbon dioxide and hydrogen. NiO/CeO_2 showed higher reactivity than NiO/Al_2O_3, similar to that observed in the chemical looping combustion.
4) From the simulation results of chemical looping reforming with CO_2 sorbent, CaO was used to physically mixed with metal oxide on support. It showed similar results as those of the conventional chemical

looping reforming but with higher hydrogen purity because CaO as CO_2 sorbent adsorbed carbon dioxide that would shift reaction to produce more hydrogen as follows.

RXN.4 $H_2O + CO \leftrightarrow \underline{CO_2} + H_2$ $\Delta H_{298K} = -41.2$ kJ/mol

RXN.10 $CH_4 + 2NiO \leftrightarrow \underline{CO_2} + 2H_2 + 2Ni$ $\Delta H_{298K} = 169.9$ kJ/mol

5) From the results mentioned before, chemical looping using nickel oxide on ceria support can produce greater amount of hydrogen than those on alumina support because the ceria support can release oxygen by itself to react with methane together with oxygen on the metal oxide. Moreover, after a regeneration of Ni by oxidation, NiO/CeO_2 has less carbon than NiO/Al_2O_3.

6.2 Recommendation

1. Pressure drop is a main problem in a fixed bed reactor process because of micron size of particles; it can be solved by making catalyst pellets formed by other methods instead of impregnation of nickel oxide on micron-sized support such as spray drying, extrusion process, etc.
2. Mass flow is a manual metering valve that cannot be directly fixed; it can be solved by using digital mass flow meter instead.

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APPENDIX

APPENDIX

Base case of conventional chemical looping reforming:

1) Calculation of hydrogen purity

Hydrogen purity was calculated by mol of hydrogen product divided by total mol product (subtracted mol of water)

Example Chemical looping reforming, 1 mol of methane and 2 mol of steam, 1 mol of NiO at 500^{o}C

The product stream was

Hydrogen	1.26937	mol
Methane	0.41587	mol
Carbon dioxide	0.51698	mol
Carbon monoxide	0.06715	mol
Water	1.89888	mol
Total	4.16825	mol

Hydrogen purity (after condensing water) = mol of hydrogen/(total mol-mol of water)

= 1.26937/(4.16825-1.89888)

= 0.559349 = 55.93%

2) Calculation of energy required

For chemical looping reforming case, the energy can be got from the result of fuel reactor (RGibbs)

Example Chemical looping reforming, 1 mol of methane and 2 mol of steam, 1 mol of NiO at 500^{o}C

Fuel reactor : Net heat duty = -112.61 kJ

3) Calculation for carbon activity

Calculation of carbon activity of reaction I

$$\alpha_{C,CO} = K_I \frac{P_{CO}^2}{P_{CO_2}} \qquad \text{equation 1}$$

Calculation of carbon activity of reaction II

$$\alpha_{C,CH_4} = K_{II} \frac{P_{CH_4}}{P_{H_2}^2} \qquad \text{equation 2}$$

Calculation of carbon activity of reaction III

$$\alpha_{C,CO-H_2} = K_{III} \frac{P_{CO}P_{H_2}}{P_{H_2O}} \qquad \text{equation 3}$$

Calculation of carbon activity of reaction IV

$$\alpha_{C,CO_2-2H_2} = K_{IV} \frac{P_{CO_2}P_{H_2}^2}{P_{H_2O}^2} \qquad \text{equation 4}$$

Example Chemical looping reforming, 1 mol of methane and 2 mol of steam, 1 mol of NiO at 500°C

The product stream was	Hydrogen	1.26937	mol
	Methane	0.41587	mol
	Carbon dioxide	0.51698	mol

Carbon monoxide	0.06715	mol
Water	1.89888	mol
Total	4.16825	mol

$$P_{H_2} = \frac{\text{mol of hydrgen}}{\text{Total mol of product}} = \frac{1.26937}{4.16825} = 0.3045$$

$$P_{CH_4} = \frac{\text{mol of methane}}{\text{Total mol of product}} = \frac{0.41587}{4.16825} = 0.0998$$

$$P_{CO_2} = \frac{\text{mol of carbon dioxide}}{\text{Total mol of product}} = \frac{0.51698}{4.16825} = 01240$$

$$P_{CO} = \frac{\text{mol of carbon monoxide}}{\text{Total mol of product}} = \frac{0.06715}{4.16825} = 0.0161$$

$$P_{H_2O} = \frac{\text{mol of water}}{\text{Total mol of product}} = \frac{1.89888}{4.16825} = 0.2772$$

At 500^{o}C ; K_I = 244.692, K_{II} = 0.38674, K_{III} = 44.7012, K_{IV}= 7.389

Calculation of carbon activity of reaction I

$$\alpha_{C,CO} = K_I \frac{P_{CO}^2}{P_{CO_2}} = 244.692\ \frac{0.0161^2}{0.1240} = 0.512$$

Calculation of carbon activity of reaction II

$$\alpha_{C,CH_4} = K_{II} \frac{P_{CH_4}}{P_{H_2}^2} = \ 0.38674 \frac{0.0998}{0.3045^2} = 0.416$$

Calculation of carbon activity of reaction III

$$\alpha_{C,CO-H_2} = K_{III} \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \ 44.7012 \frac{(0.0161)\text{x}(0.3045)}{0.4556} = 0.481$$

Calculation of carbon activity of reaction IV

$$\alpha_{C,CO_2-2H_2} = K_{IV}\frac{P_{CO_2}P_{H_2}^2}{P_{H_2O}^2} = 7.389\frac{(0.1240)x(0.3045)^2}{0.4556^2} = 0.409$$

Base case of chemical looping reforming with CO_2 sorbent:

1) Calculation of hydrogen purity

Hydrogen purity was calculated by mol of hydrogen product divided by total mol product (subtracted mol of water)

Example Chemical looping reforming, 1 mol of methane and 2 mol of steam, 1 mol of NiO and 1 mol CaO at 500°C

The product stream was			
	Hydrogen	2.80852	mol
	Methane	0.04778	mol
	Carbon dioxide	0.00075	mol
	Carbon monoxide	0.00037	mol
	Water	1.09592	mol
	Total	3.95333	mol

Hydrogen purity (after condensing water) = mol of hydrogen/(total mol-mol of water)

= 2.80852/(3.95333-1.09592)

= 0.98289 = 98.29%

2) Calculation of energy required

For chemical looping reforming with CO_2 sorbent case, the energy can be calculated from the summary of result of fuel reactor (RGibbs) and result of calcination reactor (RGibbs)

Example Chemical looping reforming with CO_2 sorbent, 1 mol of methane and 2 mol of steam, 1 mol of NiO and 1 mol CaO at 500°C

Fuel reactor : Net heat duty = -281.23412 kJ

Calcination reactor : Net heat duty = 228.814362 kJ

Summary : -259.24347+152.227596 = -52.42 kJ

3) Calculation for carbon activity

Calculation of carbon activity of reaction I

$$\alpha_{C,CO} = K_I \frac{P^2_{CO}}{P_{CO_2}} \qquad \text{equation 1}$$

Calculation of carbon activity of reaction II

$$\alpha_{C,CH_4} = K_{II} \frac{P_{CH_4}}{P^2_{H_2}} \qquad \text{equation 2}$$

Calculation of carbon activity of reaction III

$$\alpha_{C,CO-H_2} = K_{III} \frac{P_{CO}P_{H_2}}{P_{H_2O}} \qquad \text{equation 3}$$

Calculation of carbon activity of reaction IV

$$\alpha_{C,CO_2-2H_2} = K_{IV}\frac{P_{CO_2}P_{H_2}^2}{P_{H_2O}^2} \qquad \text{equation 4}$$

<u>Example</u> Chemical looping reforming, 1 mol of methane and 2 mol of steam, 1 mol of NiO at 500°C

The product stream was			
	Hydrogen	2.80852	mol
	Methane	0.04778	mol
	Carbon dioxide	0.00075	mol
	Carbon monoxide	0.00037	mol
	Water	1.09592	mol
	Total	3.95333	mol

$$P_{H_2} = \frac{\text{mol of hydrgen}}{\text{Total mol of product}} = \frac{2.80852}{3.95333} = 0.7104$$

$$P_{CH_4} = \frac{\text{mol of methane}}{\text{Total mol of product}} = \frac{0.04778}{3.95333} = 0.0121$$

$$P_{CO_2} = \frac{\text{mol of carbon dioxide}}{\text{Total mol of product}} = \frac{0.00075}{3.95333} = 0.0002$$

$$P_{CO} = \frac{\text{mol of carbon monoxide}}{\text{Total mol of product}} = \frac{0.00037}{3.95333} = 0.0001$$

$$P_{H_2O} = \frac{\text{mol of water}}{\text{Total mol of product}} = \frac{1.09592}{3.95333} = 0.2772$$

At 500°C ; $K_I = 244.692$, $K_{II} = 0.38674$, $K_{III} = 44.7012$, $K_{IV} = 7.389$

Calculation of carbon activity of reaction I

$$\alpha_{C,CO} = K_I \frac{P_{CO}^2}{P_{CO_2}} = 244.692\ \frac{0.0001^2}{0.0002} = 0.012$$

Calculation of carbon activity of reaction II

$$\alpha_{C,CH_4} = K_{II} \frac{P_{CH_4}}{P_{H_2}^2} = \ 0.38674 \frac{0.0121}{0.7104^{\,2}} = 0.009$$

Calculation of carbon activity of reaction III

$$\alpha_{C,CO-H_2} = K_{III} \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \ 44.7012 \frac{(0.0001)x(0.7104\,)}{0.2772} = 0.011$$

Calculation of carbon activity of reaction IV

$$\alpha_{C,CO_2-2H_2} = K_{IV} \frac{P_{CO_2}P_{H_2}^2}{P_{H_2O}^2} = \ 7.389 \frac{(0.0002)x(0.7104\,)^2}{0.2772^2} = 0.009$$

VITAE

Miss Apichaya Yahom was born in Bangkok, on June 15, 1989. She finished high school from Rajinibon School, Bangkok in 2007. She received her Bachelor's Degree in Chemical Engineering from Chulalongkorn University in 2011. She subsequently continued studying Master degree of Chemical Engineering, Chulalongkorn University since May 2011. She has been studying Master's Degree of Chemical Engineering, Chulalongkorn University, Thailand, 2013.