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โดยการรีฟอร์มมิ่งด้วยไอน้ำบนตัวเร่งปฏิกิริยานิกเกิล

นางสาวดารณี รู้ฤกษ์

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REMOVAL OF TAR FROM BIOMASS GASIFICATION PROCESS BY STEAM REFORMING OVER NICKLE CATALYSTS

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ดารณี รู้ฤกษ์ : การกำจัดน้ำมันดินจากกระบวนการผลิตแก๊สซิฟิเคชันจากชีวมวลโดยการรีฟอร์มมิงด้วยไอน้ำบนตัวเร่งปฏิกิริยานิกเกิล. (REMOVAL OF TAR FROM BIOMASS GASIFICATION PROCESS BY STEAM REFORMING OVER NICKEL CATALYSTS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ศ.ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. สุภวัฒน์ วิวรรธ์ภัทรกิจ, 103 หน้า.

น้ำมันดินเป็นผลิตภัณฑ์ข้างเคียงที่เป็นปัญหาสำคัญในกระบวนการแก๊สซิฟิเคชันของชีวมวลที่จะก่อให้เกิดการเปรอะเปื้อน การกัดกร่อนและการอุดตันของอุปกรณ์ต่างๆในกระบวนการ การรีฟอร์มมิงน้ำมันดินด้วยไอน้ำถือว่าเป็นอีกเทคนิคหนึ่งที่น่าสนใจมากสำหรับการกำจัดน้ำมันดินที่จะทำการเปลี่ยนน้ำมันดินที่เป็นไฮโดรคาร์บอนที่มีน้ำหนักโมเลกุลสูงให้เป็นผลิตภัณฑ์แก๊สที่ประกอบไปด้วย ไฮโดรเจน มีเทน คาร์บอนมอนอกไซด์ และคาร์บอนไดออกไซด์ ในงานวิจัยนี้จะทำการศึกษาการทำงานเบื้องต้นด้วยการจำลองระบบของปฏิกิริยารีฟอร์มมิงน้ำมันดินด้วยไอน้ำโดยการสมมติฐานที่สภาวะสมดุลทางอุณหพลศาสตร์และคำนวณด้วยโปรแกรมแอสเพนพลัสเพื่อหาสภาวะที่เหมาะสม (อุณหภูมิและอัตราส่วนระหว่างไอน้ำกับคาร์บอน) ทราบแนวโน้มและเป็นแนวทางในการทดลองปฏิกิริยารีฟอร์มมิงน้ำมันดินด้วยไอน้ำ ในการศึกษานี้น้ำมันดินที่ใช้ประกอบไปด้วย โทลูอีน แนฟทาลีน ฟีนอล และไพรีน ที่มีองค์ประกอบที่ได้แตกต่างกันในการผลิตแก๊สซิฟิเคชันจากชีวมวลที่อุณหภูมิต่างๆ (700-900 องศาเซลเซียส) โดยการทดลองจะศึกษาถึงปัจจัยต่างๆ ที่มีผลต่อปฏิกิริยารีฟอร์มมิงน้ำมันดินด้วยไอน้ำ เช่น อุณหภูมิ (450-650 องศาเซลเซียส) อัตราส่วนโดยโมลระหว่างไอน้ำกับคาร์บอน (1-5) ชนิดตัวรองรับตัวเร่งปฏิกิริยา (อะลูมินา แคลเซียมออกไซด์ และแมกนีเซียมออกไซด์) รวมไปถึงปริมาณโลหะที่ทำการโหลดลงไปบนตัวรองรับโดยใช้นิกเกิลเป็นตัวเร่งปฏิกิริยา จากศึกษาพบว่าผลที่ได้จากการจำลองระบบและการทดลองมีความสอดคล้องกันซึ่งอธิบายได้ว่าในการทำปฏิกิริยาที่อุณหภูมิสูงและอัตราส่วนระหว่างไอน้ำกับคาร์บอนที่สูงจะส่งผลให้ได้ปริมาณของผลิตภัณฑ์ไฮโดรเจนตามที่ต้องการมากขึ้น และพบว่าตัวเร่งปฏิกิริยา 20%Ni/Al_2O_3 เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพ และเสถียรภาพสำหรับปฏิกิริยารีฟอร์มมิงน้ำมันดินด้วยไอน้ำ

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก...................
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##5270754621 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : BIOMASS GASIFICATION / TAR / STEAM REFORMING HYDROGEN PRODUCTION

DARANEE RULERK: REMOVAL OF TAR FROM BIOMASS GASIFICATION PROCESS BY STEAM REFORMING OVER NICKEL CATALYSTS. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: SUPAWAT VIVANPATARAKIJ, D.Eng., 103 pp.

Tar is a major problem in a biomass gasification process, causing blocking, fouling, corrosion, erosion and abrasion of process equipments. Tar steam reforming is a very attractive technique for tar removal. It converts high molecular weight hydrocarbons of tar into smaller gas products including H_2, CH_4, CO and CO_2. Preliminary research focuses on simulation of tar steam reforming. It was assumed to be at thermodynamic equilibrium and the calculations were performed using Aspen plus. The simulation results help understand the effect of operating condition and identify suitable operating conditions (reaction temperature, S/C ratio) for the experimental tar steam reforming. Representative tar consisted of toluene, naphthalene, phenol and pyrene whose compositions varied with temperatures of biomass gasification (700-900 °C). The experimental study of the tar steam reforming reaction were carried out at different temperatures (450-650 °C), S/C ratios (1-5), type of supports (Al_2O_3, CaO, MgO) and %metal loading of a nickel catalyst. The experimental results follow the trends observed from the simulations that the reaction at high temperature and S/C ratio produce more hydrogen content. 20%Ni/Al_2O_3 was reported as a suitable catalyst which offered stable and efficiency activity for tar steam reforming.

Department: Chemical Engineering	Student's Signature ....
Field of Study: Chemical Engineering	Advisor's Signature ....
Academic Year: 2011	Co-advisor's Signature ....

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CHAPTER I

INTRODUCTION

1.1 Inspiration of the thesis

Nowadays, depletion of fossil fuel sources and environmental problems such as global warming are the world's major issues. However, due to the growth of the world's population, the energy demand is still continuously increasing. Therefore, a number of current researches have been focusing on renewable energy in order to replace the conventional fossil fuel-based energy. Biofuels, renewable energy, have been widely investigated, such as bio-methane, biomass to liquid (BTL), biomass to gas (BTG) and bio-hydrogen. Hydrogen is an attractive fuel due to its high energy density and clean energy (combustion of hydrogen does not cause any pollution, and no carbon dioxide, a major cause of global warming, is emitted). Many researches over the past decades have focused on hydrogen production technology as well as its applications with fuel cells for power generation. The hydrogen fuel can be produced from various feedstocks such as biomass, biogas, natural gas and coal, etc.

There are many potential hydrogen production processes. In this study the focus is on biomass gasification which is expected to be a real commercial process. Biomass gasification has attracted huge interest by producing a gas rich in H_2 and CO (Saxena *et al.*, 2008; Devi *et al.*, 2003) which can be used as a gaseous fuel for electricity generation or fuel cell. The major problem of biomass gasification is that the producer gas from this process usually contains unacceptable levels of tar causing environmental hazards and process-related problems from flue gas condensation at low temperatures, thus blocking, fouling corrosion, erosion and abrasion of process equipments such as engines and turbines.

Several methods for tar removal are possible (Stassen *et al.*, 2002): tar removal by physical processes e.g. filters, scrubbers, adsorption, cooling tower and wet electrostatic precipitators (Milne *et al.*, 1998) and chemical processes e.g. thermal methods, catalytic methods and steam reforming methods. Tar steam reforming is a very attractive technique for tar removal. Tar is converted into useful gas containing

H_2, CH_4, CO and CO_2. Tar is a complex mixture of aromatics which type composition of biomass gasification tars as reported by Milne *et al.*, (1998) include benzene, toluene represent one-ring aromatic hydrocarbons, naphthalene represent two-ring aromatic hydrocarbons, etc. There are 6 classes of tar based on the tar classification system developed by Bergman *et al.*, (2002). Each class is also divided into different types of tar according to its different nature.

To comprehensive of significant compounds in tars, it has been grouped as a mixture of four compounds with each compound representing a specific class of compounds and the composition equal to group in actual tars is used. The species and their amounts that were chosen to represent tars are toluene representing all the one-ring compounds, naphthalene representing two-ring compounds, phenol representing phenolic and other heterocyclic compounds, pyrene representing three-rings and higher compounds (Singha *et al.*, 2005). Several kinds of catalysts have been studied, researched, developed and used in removal of tar, such as mineral resource: calcined dolomites, magnesites, zeolites, olivine, mayenite mineral; alkali metal catalysts, Ni-based catalysts and novel metal catalysts (Han *et al.*, 2008).

However, it was reported that these catalysts have a various of problems, although they showed good activity in removal of tar. Without a pretreatment, natural mineral catalysts suffer from low activity and stability. Nickel-based catalysts have shown high activities for reforming of biomass gasification tar. When being used as the secondary catalysts, the supported nickel catalysts could attain nearly complete decomposition of both tar and ammonia decomposition (Han *et al.*, 2008 and Dou *et al.*, 2003). However, Ni catalyst suffers from coke deposition, leading to deactivation of the catalysts (Dayton *et al.*, 2002). Ni/CeO_2(75%)–ZrO_2(25%) showed the most pronounced catalytic performance in the steam reforming of benzene and showed strong resistance to coke deposition. Its activity is superior to a commercial Ni catalyst (Park *et al.*, (2010)). Steam reforming of toluene as a tar model compound using Ni/olivine catalyst was reported to have much higher activity and selectivity towards syngas than olivine alone (Swierczynski *et al.*, 2007). Three Ni-based catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (Zhang *et al.*, 2004). Dou *et al.*, (2003) studied tar cracking catalysts in a fixed-bed reactor. The Y-zeolite and NiMo catalysts were found to be the most effective, such that 100% tar removal can be achieved at 550 °C.

Apart from Ni-based catalysts, there have been other catalysts developed for tar removal. Hao *et al.*, (2005) investigated catalytic tar cracking and demonstrated that the catalyst activities followed the order: Ru/C > Pd/C > nano-$(CeZr)_xO_2$ > nano-CeO_2 > CeO_2. The conversion rate of tar catalyzed by dolomite was difficult to reach or exceed 90–95%, although dolomite could reduce the tar in syngas (Xiaodong *et al.*, 2003).

Nowadays tar reformer with biomass gasification has attracted considerable attention. This would affect the increased yield of syngas and lower pollution. In this work, improvement of hydrogen production from tar steam reforming was investigated. This study focused on finding suitable condition for tar reformer with biomass gasification which can provide the highest amount of H_2 yield and tar conversion by preliminary simulations using Aspen Plus program. It is also aimed at finding a suitable catalyst to be used in the steam reforming of tar for different mixtures of phenol, naphthalene, toluene, and pyrene as model compounds of tar at different temperatures of biomass gasification. The effect of operating parameters on the hydrogen production as well as the deactivation of catalysts is also investigated.

1.2 Objective

To develop a suitable catalyst for use in the removal of tars from biomass gasification at different temperatures and to investigate the effect of operating parameters on hydrogen production from tar steam reforming.

1.3 Scope of work

1. Simulate tar steam reforming using Aspen Plus program to determine suitable operating condition for tar steam reforming.
2. Survey information on tar compositions derived from biomass gasification at various temperatures – this information is used to prepare model compositions of tar for the experiments.
3. Prepare suitable catalysts for hydrogen production from tar steam reforming

based on available information of suitable catalysts.

4. Characterize the physical properties of synthesized tar steam reforming catalysts using various techniques; for examples, Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and BET surface area measurement.
5. Perform experiments at various support catalyst, %Ni loading, temperature reaction, steam/carbon molar ratio, and tar model compound from biomass gasification at various temperature to determine performances of the tar steam reforming over the synthesized catalysts.
6. Study coke formation on the catalysts after tar steam reforming by Thermo Gravimetric Analysis (TGA).

CHAPTER II

THEORY

2.1 Biomass gasification

2.1.1 Definition

Biomass gasification is an important process of change the energy stored in biomass by thermal conversion. Arising from not complete combustion of biomass resulting in gases produced which main compound of producer gases contains carbon monoxide (CO), hydrogen (H_2) and methane (CH_4). Energy technologies are in direct thermal or transformed to electrical energy by Direct fired. Also know as biomass such as straw, rice husk, coconut shell, wood and many agricultural residues used as fuel in the burning heat to bolier. It will change thermal energy to mechanical energy via steam turbine then, turn generator that produces power electicity. This process can be produce a potential energy source and can be used as energy source to replace the fuel is lost as well.

2.1.2 Principle of gasification

Gasification process of bringing fragment plants or biomass are burned in a confined area which not complete combustion formed product gases such as CO, H_2 and CH_4. The product gases are flammable as well and burned to provide heat directly and used to fuel of generator for electrical. The gasification efficiency is base on technology used in the gasifier or flammable gas. The products of combustion are (Figure 2.1) combustible gases like carbon monoxide (CO), hydrogen (H_2) and traces of methane and non useful products like tar and dust.

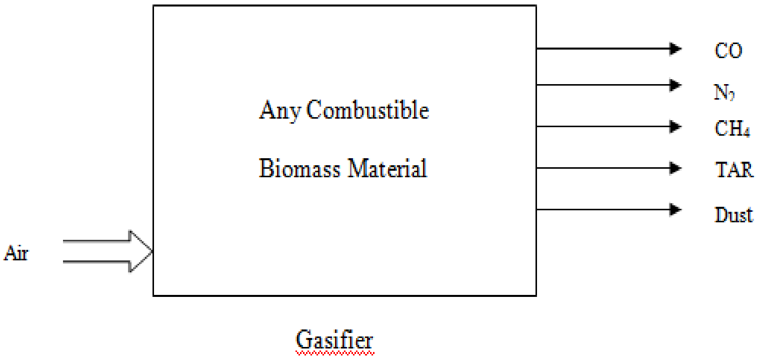


Figure 2.1 Products of gasification (Rajvanshi *et al.*, 1986).

2.1.3 Types of Gasifiers

There are a number of different types of gasifier (Figure 2.2). Each type of gasifier already has different advantages and disadvantages as summarized in Table. 2.1.

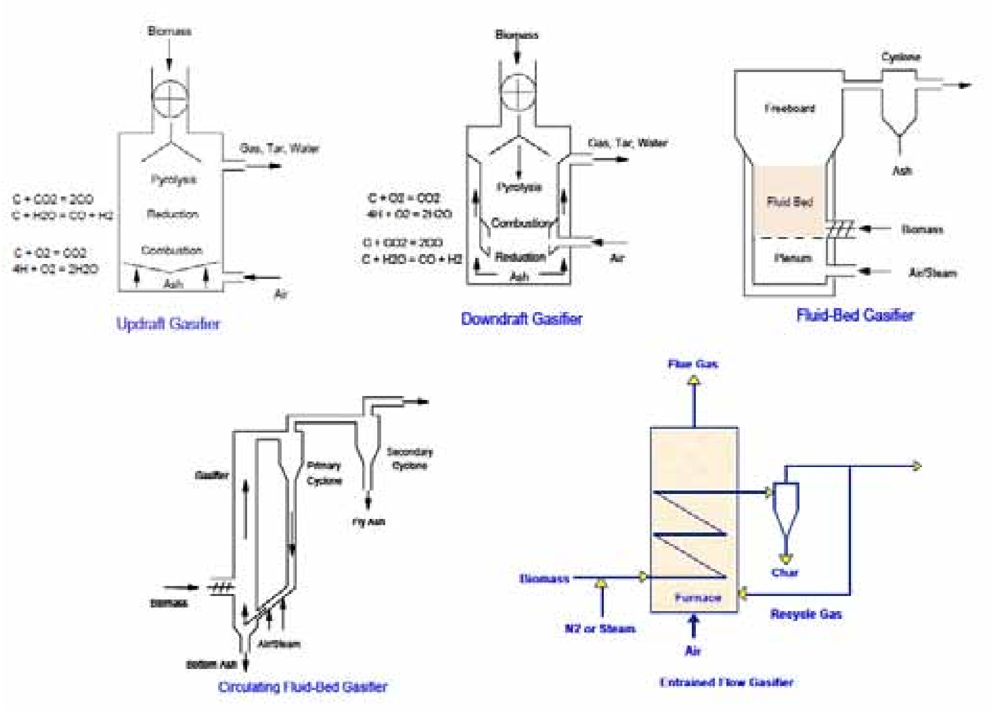


Figure 2.2 Various types of gasifier (Rajvanshi *et al.*, 1986).

Table 2.1 Features, advantages and disadvantages of various gasifiers (Rajvanshi *et al.*, 1986).

Gasifier Type	Features	Advantages	Disadvantages
Updraft	Air intake is at the bottom and the gas leaves at the top.	-No carbon in ash - Small pressure drop - Little tendency towards slag formation	- High tar yield - Scale limitations - Slagging potential
Downdraft	The producer gas is removed at the bottom of the apparatus, so that fuel and gas move in the same direction.	- Flexible adaptation of gas production to load - Low sensitivity to charcoal dust and tar content of fuel -Small scale applications	-Not feasible for very small particle size of fuel - Scale limitations - Producer Gas -Moisture sensitive
Fluidized Bed	Air is blown through a bed of solid particles at a sufficient velocity to keep these in a state of suspension.	-Large scale application - Feed characteristics -Direct/indirect heating	- Medium tar yield -Higher particle loading
Circulating Fluidized Bed	A sorbent and jets of air to suspend the mixture of sorbent and burning coal during combustion.	- Large scale application - Feed characteristics - Can produce syngas	- Medium tar yield -Higher particle loading
Entrained Flow	Dry pulverize solid, an atomized liquid fuel is gasified with oxygen in co-current flow.	- Can be scale - Potential for low tar - Can produce syngas	-Higher particle loading -Potentially high S/C - Particle size limit

2.1.4 Process Zones

Four processes are occurring in the gasifier as the fuel to gas-fuel gas. They are:

a) Drying
b) Pyrolysis
c) Combustion
d) Reduction

Although there is much overlap of the processes, each can be assumed to occupy a separate zone that is fundamentally different chemical and thermal reactions take place. Figure 2.3 shows schematically an updraft gasifier with different zones and their respective temperatures.

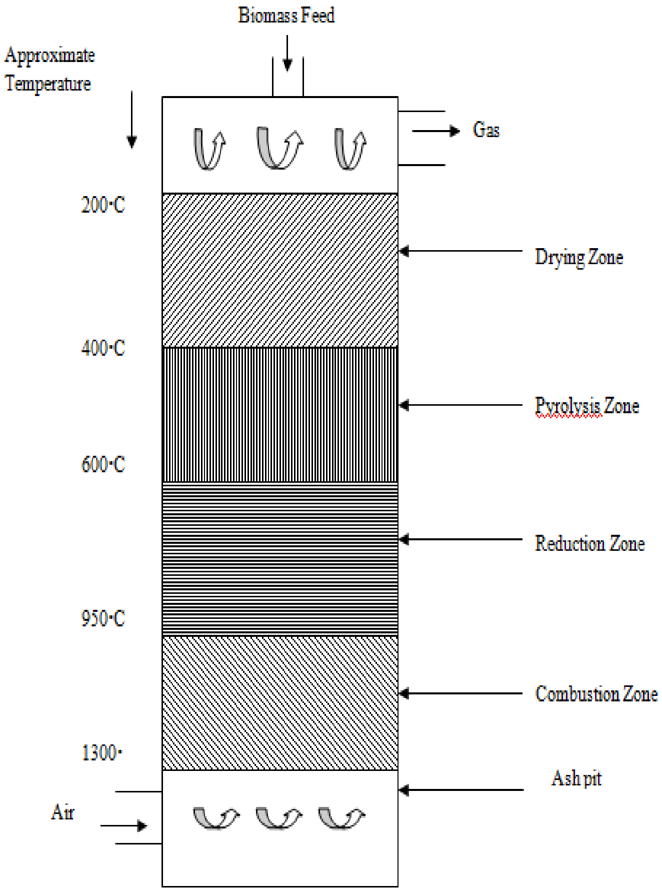


Figure 2.3 Various zones in updraft gasifier (Rajvanshi *et al.*, 1986).

2.1.5 Reaction Chemistry

The following major reactions take place in combustion and reduction zone**.**

a) Combustion zone or oxidation zone

The introduction of air into this zone to combustion with biomass fuel to the reaction between carbon, hydrogen and oxygen in the air. The effect of reaction is carbon oxide, water and heat energy around 1000 – 1500 °C which will emit heat to the next zone. The combustion reaction is exothermic and yields a theoretical oxidation temperature of 1450°C by Schapfer *et al.*, (1937). The main reactions, therefore, are:

$$C + O_2 \rightarrow CO_2 \qquad (+\ 393\ MJ/k\ mole) \qquad (2.1)$$

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (-\ 242\ MJ/k\ mole) \qquad (2.2)$$

An important point is keep the heat transfer to the next zone.

b) Reaction zone

When the products gas from first zone flowing to this zone and the temperature is reduced around 500 – 900 °C will be combustion again. Carbon dioxide is pass through the heat in this zone then it converted in to carbon monoxide which can be flammable where the following reduction reactions take place.

$$C + CO_2 \rightarrow 2CO \qquad (-\ 164.9\ MJ/k\ mole) \qquad (2.3)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (-\ 122.6\ MJ/k\ mole) \qquad (2.4)$$

$$CO + H_2O \rightarrow CO + H_2 \qquad (+\ 42\ MJ/k\ mole) \qquad (2.5)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (+\ 75\ MJ/k\ mole) \qquad (2.6)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (-\ 42.3\ MJ/k\ mole) \qquad (2.7)$$

Reactions (2.3) and (2.4) are main reduction reactions which are endothermic and have the capability of reducing gas temperature. Consequently the temperatures in the reduction zone are normally 800-1000°C. The lower the reduction zone temperature (~700-800°C), the lower calorific value of gas is.

c) Pyrolysis zone

Pylolysis of wood is a complex process that is still not completely understood (Schapfer *et al.*, 1937). At higher temperature than 200°C water is driven out and between 200 -280°C found that carbon dioxide, acetic acid and water to get off. Pyrolysis temperature is between 280 - 500°C, producing large amounts of tar and gases include carbon dioxide. Between 500 - 700°C the gas production is small and hydrogen. Various experiments on different gasifiers in different conditions have shown that on an average the condensate formed is 6-10% of the weight of gasified wood by Schapfer *et al.*, (1937). Some organic acids also come out during the drying process. These acids give rise to corrosion of gasifiers.

2.2 Steam reforming

Steam reforming is the efficient process to produce hydrogen and synthesis gas but the cost is less then, commonly used in commercial The implication of this process is enter the water capor (steam) into the system to react with hydrocarbons in biomass or gaseous such as natural gas, biogas and ethanol. Hydrogen gas is pulled out of steam and hydrocarbons then, the oxygen remaining from water and carbon rested from hydrocarbons will gather for the carbon monoxide. Process heat as well as fuel gas are used for the steam generation. The gas mixture flows from top to bottom through tubes arranged in vertical rows. While flowing through the tubes heated from the outside, the hydrocarbon/steam mixture reacts, forming hydrogen and carbon monoxide in accordance with the following reactions:

$$C_nH_m + n\ H_2O \Rightarrow n\ CO + ((n+m)/2)\ H_2 \tag{2.8}$$

$$CH_4 + H_2O \Leftrightarrow CO + 3\ H_2 \tag{2.9}$$

$$CO + H_2O \Leftrightarrow CO2 + H_2 \tag{2.10}$$

To reduce amount of methane in the synthesis gas while simultaneously improving the H_2 yield, prevent the formation of carbon element cause and it to accumulate on the catalyst, the reformer is operated with a higher steam/carbon than theoretically necessary.

As the overall heat of the main reactions (2.9) - (2.10) is endothermic, the required heat must be supplied by external firing. The residual gas from the pressure swing adsorption unit as well as heating gas from battery limits is used as fuel gas.

2.3 Tar reformer

2.3.1 Definition and composition of tar

As the formula (2.11) shows, the product gas obtained from biomass gasification include the main components of CO, H_2, CO_2, CH_4, H_2O, and N_2, in addition to organic (tars) and inorganic (H_2S, HCl, NH_3, and alkali metals) impurities and particulates. The organic impurities range from low molecular weight hydrocarbons to high molecular weight aromatic hydrocarbons. The lower molecular weight hydrocarbons can be used as fuel in gas turbine or engine applications, but are undesirable products in fuel cell applications and methanol synthesis.

$$\begin{aligned} \text{biomass} + O_2(\text{or}H_2O) &\longrightarrow CO,\ CO_2,\ H_2O,\ H_2,\ CH_4\text{, other hydrocarbons} \\ &\longrightarrow \text{tar, char, ash} \\ &\longrightarrow HCN,\ NH_3,\ HCl,\ H_2S,\ \text{other sulfur gas} \end{aligned} \qquad (2.11)$$

Tar is considered to be the condensable of the organic gasification products and large aromatic hydrocarbons. Tars are formed during gasification in a series of complex reactions. The formation of tar is highly dependent on the reaction conditions.

Table 2.2 Typical composition of biomass gasification tars (Milne *et al*., 1998).

Compound	Composition (wt.%)
Benzene	37.9
Toluene	14.3
Other one-ring aromatic hydrocarbons	13.9
Naphthalene	9.6
Other two-ring aromatic hydrocarbons	7.8
Three ring aromatic hydrocarbons	3.6
Four ring aromatic hydrocarbons	0.8
Phenolic compounds	4.6
Heterocyclic compounds	6.5
Others	1.0

Table 2.3 Chemical component in biomass tars.

Conventional flash pyrolysis (450 – 500 °C)	Acids, aldehydes, ketones, furans, phenols
High–temperature flash pyrolysis (600-650°C)	Benzene, phenols, carechols, napthalenes, biphenyls, phenanthrenes, benzaldehydes
Coventional steam gasification (700-800°C)	Napthalene, acenaphthylen, phenathrene benzaldehydes, napthofurans, bezanthracenes
High-temperature steam gasification (900-1000°C)	Napthalene, acenapthnylene, phenanthrene, fluoranthene, pyrene, acenanthylene

2.3.2 Tar chemical and physic

Some researchers by Anna *et al.*, (2006) divided tar components into five groups, as shown in Table 2.4. Tar leads to fouling when the gas becomes (over) saturated with it. This leads to aerosol formation and depositions inside the installation. These fouling phenomena are not of concern as long as all the tar is present in the gas phase. It is therefore believed that the tar problem is fundamentally not concerned with the tar quantity, but with the properties and the composition of the tar.

Thunman *et al.*, (2001) proposed the another formula of heating value of tar. A general assumption for the heating value of tar is that the composition of tar is close to that of wood between 400 and 700 °C, so the heating value of tar is between 22 and 26 MJ/kg (combustible substance), and between 700 and 1000 °C, the composition is close to that of lumped hydrocarbons. So, initially, it was thought that the heating value of tar could be determined from the heating value of its components, but the different substances present in tar and their amount were too difficult to find. Finally, a general correlation of Mason and Gandhi (Mason *et al.*, 1983) was adopted:

$$\text{HHV} = 146.58\ X_{C,tar} + 568.78\ X_{H,tar} - 51.53\ X_{O,tar} \quad (2.12)$$

where HHV is the high heating value, is expressed in Btu/lb. As 1 Btu/lb = 2.326 kJ/kg, it becomes in kJ/kg: HHV = 340.95 $X_{C,tar}$ + 1322.98 $X_{H,tar}$ -119.86 $X_{O,tar}$.

Table 2.4 List of tar compounds that are considered for different tar classes**.**

Tar class	Class name	Property	Representative compounds
1	GC-undertectable	Very heavy tars, cannot be detected by GC	Determine by subtracting the GC-detectable tar fraction from the total gravimetric tar.
2	Heterocyclic aromatics	Tars containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinolone, isoquinoline, dibenzophenol
3	Light aromatics (1 ring)	Usually high hydrocarbons with single ring; do not pose a problem regarding condensability	Toluene, ethyl benzene, xylenes, styrene
4	Light PAH compounds (2-3 ring)	2 and 3 rings aromatic compounds condense at low temperature	Indene, naphthalene, methylnaphthalene, biphenyl, ace naphthalene, fluorine, phenanthrene
5	Heavy PAH compounds (4-7 ring)	Larger than 3-ring aromatic compounds condense at high-temperature	Fluoranthene, pyrene, chrysene, perylene, coronene

2.3.3 Reaction mechanism and kinetics

Tar decomposition mainly occurs due to cracking, steam and dry reforming reactions as shown below by Devi *et al.*, (2005)

Cracking: $pC_nH_x \longrightarrow qC_mH_y + rH_2$. (2.13)

Stream reforming: $C_nH_x + nH_2O \longrightarrow (n + x/2)H_2 + nCO$ (2.14)

Dry reforming: $C_nH_x + nCO_2 \longrightarrow (x/2)H_2 + 2nCO$ (2.15)

Carbon formation: $C_nH_x \longrightarrow nC+(x/2)H_2$ (2.16)

C_nH_x represents tar, and C_mH_y represents hydrocarbon with smaller carbon number than C_nHx

Decomposition mechanism

The experimental results after analyzed, Jess *et al.* (1996) proposed the reaction scheme of converting of tar in the presence of H_2 and H_2O and shown in Fig. 2.4. It can be concluded that benzene is the key component of thermal decomposition of tar. He also pointed out that the converting of aromatic hydrocarbons in product gases from pyrolysis and gasification of solid fuels at temperatures of around 1200 °C. To convert the soot and organic cracking products primarily formed mainly to CO and H_2, even high temperature.

Nair *et al.*, (2004) proposed naphthalene decomposition by Pulsed Corona method, and shown in Fig. 2.5, which was proposed according to the product distribution observed during experiments. Byproducts were mainly formed by an oxidation mechanism. Intermediate compounds seen in Fig. 2.5 lead to byproduct formation of naphthalene-dione and phthalicanhydride. The main path for ring opening is via naphthoxy formation and its decomposition to indenyl via a thermal mechanism, which largely governs the decomposition scheme. After analysis and discussion, he proposed for the corona processing in a fuel gas mixture as shown in Fig. 2.6.

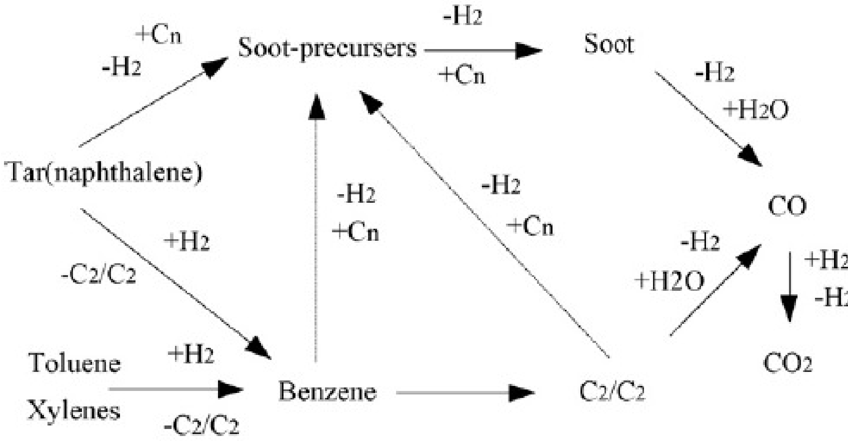


Figure 2.4 Simplified reaction scheme of thermal conversion of aromatic hydrocarbons the presence of hydrogen and steam (Chunshan *et al.*, 2009).

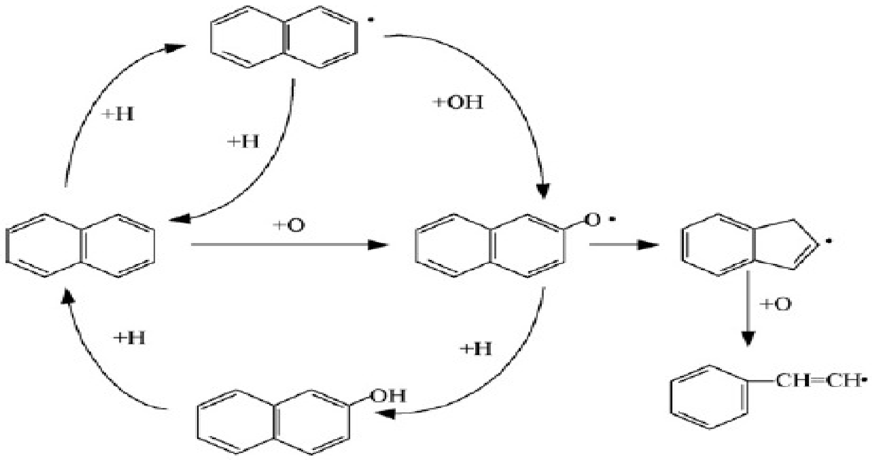


Figure 2.5 Naphthalene decomposition scheme (Chunshan *et al.*, (2009)).

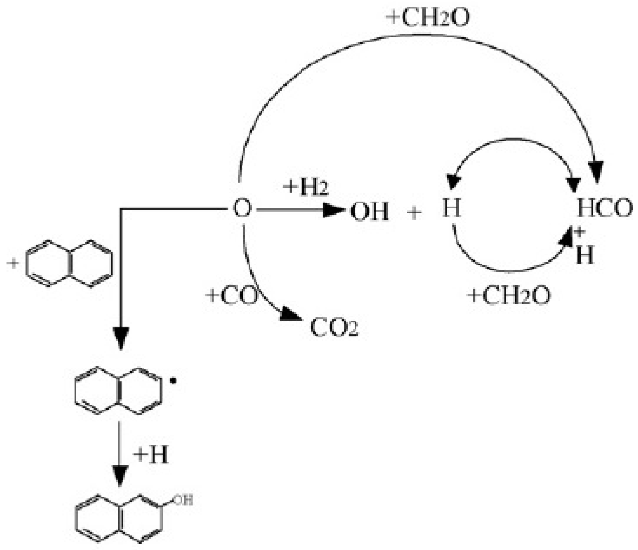


Figure 2.6 Main reaction pathways for reactive radicals in corona processing of fuel gas for naphthalene removal at 200 °C (Chunshan *et al.*, 2009).

2.3.4 Tar removal methods

The method must be efficient in terms of tar removal is economically feasible. But more importantly, it should not affect the formation of useful gaseous products. All the existing methods can be classified in two types base on the location where the tar is removed; either in the gasifier itself (known as primary method) or outside the gasifier (known as secondary method). The following sections describe both methods.

a) Primary methods

Primary methods can be defined as all the measures used in the processstep itself to prevent or convert tar formed in the gasifier. The primary method concept eliminates the use of secondary treatments as shown in Fig. 2.7. Primary methods are commercially. The primary issues include the suitable selection of the operating conditions using additives or a catalyst during gasification and suitable gasifier design.

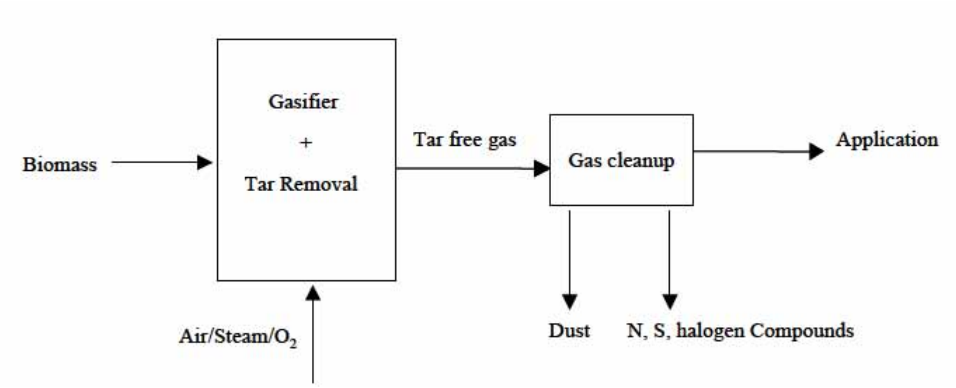


Figure 2.7 Tar reduction concept by primary method (Lopamudra *et al.*, 2003).

(b) Secondary methods

Secondary methods are conventionally used as treatments to the hot product gas from the gasifier. The concept of secondary methods is given in Fig.2.8. These methods can be chemical or physical treatment as follows

- Tar downstream the gasifier either thermally or catalytically,
- Mechanical methods such as using cyclone, baffle filter, ceramic filter, fabric filter, rotating particle separator, electrostatic filter and scrubber

Although, downstream gas cleaning methods are reported to be very effective in tar reduction but some cases they are not economically viable.

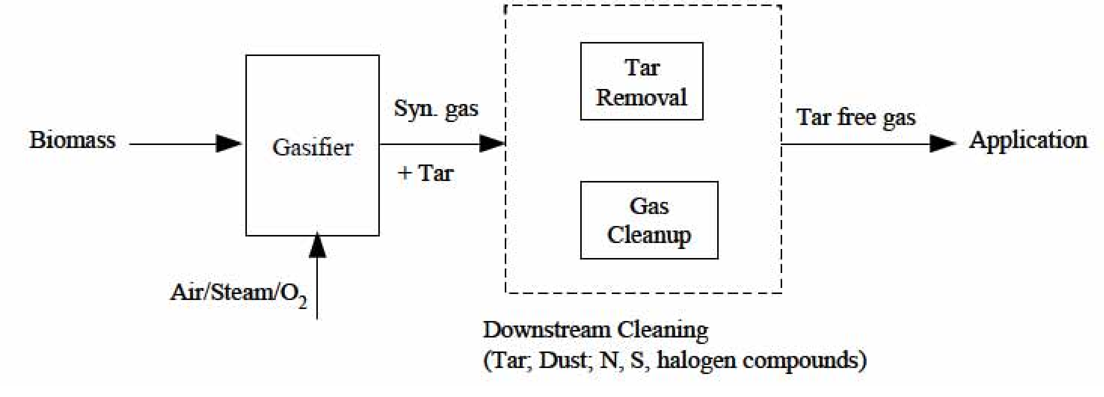


Figure 2.8 Tar reduction concept by secondary methods (Lopamudra *et al.*, 2003).

2.3.5 Catalysts for tar removal

The extensive research on catalysts that have the potential for decomposing tars generated in biomass gasification. Alkali metal catalysts have been studied due to increase in gasification reactions within the gasifier. In the case of materials such as dolomite, calcium–magnesium carbonates and Ni-based catalysts have been used widely for the secondary catalysts to reduce tar in product gas of gasification.

a. Dolomite catalysts

Dolomite is a mineral consisting main compound of calcium oxide and magnesium oxide with general chemical formula $CaMg(CO_3)_2$. In recent years, the calcined dolomite is a highly efficient catalyst for removal tar from the product gases. Several research will use the calcined dolomites (MgO–CaO) derived from the decomposition of dolomite at high temperatures around 800 - 900 °C, as the secondary catalysts which shown great success for minimizing tar in the product gas (Dayton et al., 2002).

Simell et al., (1996) studied the tar removal indicating that the presence of CaO in dolomite will help activity reaction in the tar conversion. Using calcined dolomites catalysts could increase the amount of H_2 and the H_2/CO ratio in the product gas as a result reform of the tars (Rapagna et al., 1998). The developement of a newly catalyst (Ni supported on dolomite) to maintain high activity and stability for the reaction a long time. In addition, carbon deposition on the surface of Ni/dolomite catalysts was negligible (Srinakruang et al., 2005). Although the dolomite catalyst can effective for remove tar, but there are many problems in the biomass gasification.

b. Nickel and other metal supported catalysts

Nickel-based catalysts are commercially catalyst because they are widely used in the petrochemical industry for reforming (Dayton et al., 2002). Ni-based catalyst shown high activity for tar reforming in biomass gasification. When used as the secondary catalysts, the supported nickel catalysts could achieve decomposition of both tar and ammonia by Han et al., (2008) and Dou et al., (2003). However, Ni catalysts were less effective for tar conversion due to the severe coke formation, causing deactivation of catalysts (Dayton et al., 2002). In some of the studies using Ni catalyst, a dolomite guard bed was used to reduce the initial tar level from the gasifier. The Ni catalyst was operating at 750-850°C and tar conversion was greater than 99% in tar steam reforming.

Ni catalyst can be poisoned by sulfur, chlorine and alkali metals from the product gas. Coke from the tar cracking can also poison the catalyst, especially when the tar level in gasification is high content. The coke on surface area catalyst can be removed by regenerated using combustion at high temperature. Moreover, high temperature processing of Ni catalyst can lead to sintering, phase transformation and volatilization of the Ni (Dayton et al., 2002).

c. Novel metal catalysts

In the past, some researchers found that the novel metal catalysts can provide better performance in the reaction of other catalysts and keep high efficiency on converted tar. Tomishige et al., (2004) compared the tar conversion rates over $M/CeO_2/SiO_2$ (M>Rh, Pd, Pt, Ru, Ni) catalyst during cellulose gasification. The order of catalyst activity in the cedar wood gasification at 600 °C was the following: Rh>Pd>Pt>Ni>Ru. The tar conversion rate was about 88% in the case of $Rh/CeO_2/SiO_2$

2.4 Tar steam reforming

Biomass gasification process can be produce hydrogen gas which is a clean fuel for present and future applications. However, tar is also on unwanted by-products. In addition to occurs by product without the need aeries that is tar. Tar consists of many compounds but this work selected toluene, naphthalene, phenol and pyrene as tar model compound. Toluene is one of the main compound tar representing one ring aromatic hydrocarbon, naphthalene representing two-three ring aromatic hydrocarbon, pyrene representing larger than 3 rings aromatic hydrocarbon . Finally, phenol is selected as tar model compound representing heterocyclic and phenolic aromatics. Fig.2.9 shown all tar model compounds selected for study as mixed tar to simulate with tar obtained from biomass gasification.

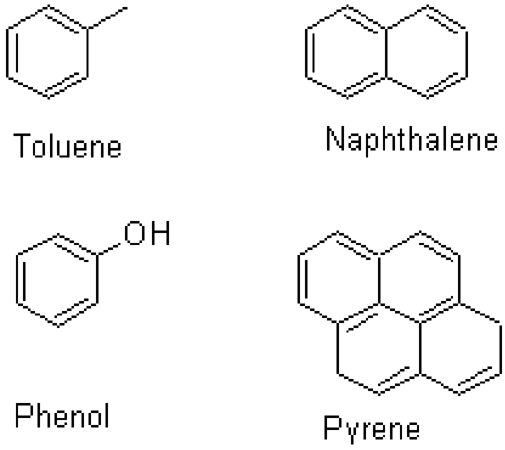


Figure 2.9 Tar model compound

The steam reforming of tar representative compounds (toluene, naphthalene, pyrene, and phenol) are given in Eqs.2.17-2.18. The methane steam reforming (Eq.2.21) and water gas-shift reaction (Eq.2.22) were also considered.

$$C_7H_8 + 7H_2O \longleftrightarrow 7CO + 11H_2 \qquad \Delta H_{393K} = +881.74 \text{ kJ/mol} \qquad (2.17)$$

$$C_{10}H_8 + 10H_2O \longleftrightarrow 10CO + 14H_2 \qquad \Delta H_{393K} = +1{,}177.8 \text{ kJ/mol} \qquad (2.18)$$

$$C_{16}H_{10} + 16H_2O \longleftrightarrow 16CO + 21H_2 \qquad \Delta H_{393K} = +651.7 \text{ kJ/mol} \qquad (2.19)$$

$$C_6H_6O + 5H_2O \longleftrightarrow 6CO + 8H_2 \qquad \Delta H_{393K} = +1{,}834.7 \text{ kJ/mol} \qquad (2.20)$$

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H_{393K} = +209.44 \text{ kJ/mol} \qquad (2.21)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H_{393K} = -40.01 \text{ kJ/mol} \qquad (2.22)$$

CHAPTER III

LITERATURE REVIEWS

The researches on tar reformer with biomass gasification have been carried out extensively. The literature reviews in this chapter are divided into three main parts. The first part is about the researches on tar steam reforming catalyst. The second part provides reviews on the operating conditions of tar reformer with biomass gasification. The last part is about tar model compound studied in tar steam reforming.

3.1 Tar steam reforming catalyst

The catalysts in this reaction are dictated by several operating conditions and preparation method. The past and the present has been extensive research on catalysts that have the potential for decompose tars in biomass gasification. Mostly alkali metal catalysts mainly studied as catalysts to enhance the reactions. Materials such as dolomite, calcium–magnesium oxide and Ni-based catalysts have been used widely as the catalysts to reduce tar in gasification to product gas. Some typical catalysts and their performance for decomposition/reforming of biomass tar and model compounds are summarized in Tables 3.1 and 3.2.

Nickel-based catalysts, used applied in the petrochemical industry for steam reforming, shown high activities for tar reforming and decomposition in biomass gasification. The supported nickel catalysts could nearly complete decomposition of tar but, Ni catalysts were less effective for tar conversion due to the severe coke formation, causing a deactivation of the catalysts. Jianfen *et al.*, (2008) developed supported nano-NiO/γ-Al_2O_3 catalyst for tar removal in biomass gasification/pyrolysis and enhance the quality of gases produced. In experimental pyrolysis without catalyst at 800°C, and studied the catalytic reaction temperature at 600, 700, and 800 °C, respectively. The result has been found gas product from pyrolysis at 800 °C in the no catalyst was 62.9 wt% but catalytic pyrolysis with NiO/γ-Al_2O_3 catalyst was 77.8-85.2 wt% which a higher than when compared with commercial catalyst. This shows that demonstrated an excellent catalytic activity for tar removal and improved the quality of the gas products.

Hyun *et al*., (2010) demonstrated the steam reforming of biomass gasification using benzene as a tar model compound over various Ni/metal oxide catalysts. From the results, the activity in terms of benzene conversion was in order of Ni/ZrO_2 < Ni/CeO_2 < Ni/γ-Al_2O_3 < Ni/CeO_2 (75%)–ZrO_2 (25%). Interestingly, Ni/CeO_2 (75%)–ZrO_2 (25%) showed the highest activity, although its surface area was much lower than that of Ni/γ-Al_2O_3 which can explained by the mechanism of steam reforming reaction (Takanabe *et al*., 2006; Iojoiu *et al*., 2007). It was also recommended that the Ni-precursor plays an important role in the catalytic activity.

Many studies using calcined dolomites (MgO–CaO) have shown great success for removal tar. Wang *et al*., (2005) studied catalytic cracking of tar using naphthalene as a tar model compound over Ni–dolomite. They concluded that in order to make the catalyst is stable for long time at high reaction temperature (700 °C). Coke formation was mainly cause to decrease of the catalytic activity and increase of the reaction bed resistance. In addition, Ni on dolomite catalysts prepared by precipitation method can accomplish high activity and stability for the toluene steam reforming and inhibited carbon formation even though operated at low temperature but could not prohibit carbon deposition during the reaction (Srinakruang *et al*., 2005).

As MgO and CaO are main component of dolomite then, researchers studied the this main component to develop much more by Chunshan *et al*., (2010) have prepared series of nickel catalysts Ni/MgO_x/CaO_{1-x} ($x = 0.3, 0.5, 0.7$, Ni: 5 wt%) for toluene steam reforming using different preparation methods. Above temperature 650 °C, toluene was nearly totally decomposed to H_2, CO and CO_2, no benzene or other poly-aromatic compounds were detected. This study suggested that the same preparation method, the concentration of MgO and CaO has nearly no influence on the H_2 yield. Similarly, Baohua *et al*., (2010) studied the catalytic conversion of toluene and naphthalene as a tar model compounds from hot coke oven gas to performence Ni/MgO–Al_2O_3 catalysts. They found that catalysts showed excellent catalytic activity, and stability to the direct catalytic conversion.

Some researchers found that the novel metal catalysts have high efficiency on tar reforming. Domna *et al*., (2009) focused on the study of phenol steam reforming to hydrogen production using a natural calcite material catalyst at 650– 800 °C. In the present work provides substantial and important fundamental focus on the effects of reaction temperature, increase of reaction temperature in the 650–800 °C resulting increases of both phenol activity and H_2selectivity. Moreover, increasing water feed concentration in the 40–50 vol% influence increases the hydrogen yield in the 650–800 °C.

And in later years Domna *et al*., (2010) investigated the steam reforming of phenol in the 350–550° C, a low-temperature range, in a fixed-bed micro-reactor using Ce–Zr–Mg–O mixed metal–oxide supported-Rh catalysts to provide a very clean product gas derived from biomass gasification. The support chemical composition (Ce–Zr–Mg–O) was found to significantly improve the catalytic activity in the 400–500 °C range compared to the Ce–Zr–O support composition used to deposit the same amount of Rh metal.

The desired properties of catalyst for tar steam reforming is high reaction rate and more resistant to degradation so, that it can operate for a long time. In this case, it is called in to study the accumulation of carbon on catalyst for tar steam reforming by Wang *et al.,* (2010). Catalytic reforming have been a problem due to catalyst deactivation by carbon deposition via boudouard reaction ($2CO = CO_2+C$) and methane decomposition ($CH_4 = C+2H_2$). Deactivation of catalyst by coke formation is very serious in fuel gas from biomass reforming process because raw fuel gas including some light hydrocarbons, tar, sulfur and particulates. In addition, coke formation arises from thermal catalytic cracking, reforming of hydrocarbon and tar. Results show that steam reforming can prevent the carbon deposition on the catalyst as by Garcia *et al*., (2000). This may be caused by several reasons such as, the water into feed could be react with methane ($CH_4+H_2O = CO+3H_2$) and carbon monoxide ($CO+H_2O = H_2+CO_2$) in reforming process which reduces the effectiveness of Boudouard reaction and methane decomposition. The reaction between water and tar can reduce amount of tar and prevent the tar adsorb on the catalyst surface to cause the accumulation of carbon. The added water also help stimulate oxidation on surface and improve the CO oxidation activity.

Table. 3.1 Summary of some typical catalysts used for decomposition/reforming tar model compounds.

Catalyst	Chemical composition of the catalyst	GHSV (h^{-1})	Temperature (°C)	Feed gas composition	Tar conversion (%)	Reference
Various dolomites	(18–21) wt.% MgO–(30–32) wt.%CaO–(0–3) wt.% SiO2–(0–0.8) wt.%Fe_2O_3– (0–1) wt.% Al_2O_3	10,600–12,000 11,000–12,000 13,000–16,000	794–850 814–923 805–810	Gas from air-blown biomass gasifier	84–91 94–97 71–92	Narvaez et al., (1996)
Chinese dolomite	20 wt.% MgO–31 wt.% CaO–0.7 wt.%SiO_2–0.5 wt.% Al_2O_3	12,000	650–850	N_2 bubbled through Melted biomass tar	43–95	Wang et al., (2005)
Chinese dolomite modified with Fe_2O_3	Dolomite with 5% Fe_2O_3				44–97	Wang et al., (2005)
ICI-46–1a	24 wt.% NiO–13 wt.% MgO–13 wt.%CaO–14 wt.% SiO_2–29 wt.% Al_2O_3				87–99	Wang et al., (2005)
Z4091a	5 wt.% Fe2O3–22 wt.% NiO–11 wt.%MgO–13 wt.% CaO–11 wt.% SiO_2–23 wt.%Al_2O_3				82–98	Wang et al., (2005)
Metallic iron Fe	n.a.	n.a.	600–800	Gas from fluidized-bed gasification Swedish birch	10–90 6–22	Tamhankar et al., (1985)

Table. 3.2 Summary of some typical catalysts used for decomposition/reforming tar model compounds.

Catalyst	Chemical composition of the catalyst	GHSV (h^{-1})	Temperature (°C)	Feed gas composition	Tar conversion (%)	Reference
$Fe_2O_3/SiO2_2$	55 wt.% SiO_2–45 wt.% Fe_2O_3	90,000	650	300 ppm C_6H_6, 10%H_2,N_2balance	100	Nordgreen et al., (2006)
North Carolina Olivine	6 wt.% Fe_2O_3–31 wt.% MgO–19 wt.% SiO_2	1166	800–900	16% H_2, 8% CO, 12.0% CO_2, 16% H_2O, 4% CH_4, balance N_2, 400 ppm $C_{10}H_8$	75–98	Kuhn et al., (2008)
Calcined Austrian Olivine	7 wt.% Fe_2O_3–28 wt.% MgO–21 wt.% SiO_2				32–92	Kuhn et al., (2008)
Austrian Olivine	7 wt.% Fe_2O_3–28 wt.% MgO–21 wt.% SiO_2				90–100	Kuhn et al., (2008)
Washington Olivine	6 wt.% Fe_2O_3–29 wt.% MgO–18 wt.% SiO_2				60–97	Kuhn et al., (2008)
Australian limonite	57 wt.% Fe_2O_3–2 wt.% SiO2–1 wt.% Al_2O_3	0.5 LHSV	440–460	80 wt.% –vacuum residue–20 wt.% decant oil	54–83	Matsumura et al., (2005)

3.2 Operating conditions of tar reformer

Fuel gas from biomass gasification contains amounts of tars depending on the type of gasifier used. Tars lead to the accumulation of carbon on the anode side of SOFCs and affect the performance of fuel cells. Singh et al., (2005) found that the thermodynamic of carbon deposition on a solid oxide fuel cell (SOFC). They studied the risk of carbon deposition due to the tars in the feed and the effect of various parameters like current density, steam, and temperature on carbon deposition. The amount of carbon was reduced to the steam content of the fuel stream was increased.

Most producer gas applications need to removal of dust and tar before the gas can be used. Ruiqin et al., (2006) synthesis NiO/olivine and doped with CeO_2. To evaluate the catalytic activity and resistance to carbon deposition on during steam reforming. Steam reforming was carried out the operate at temperatures between 700 and 830 °C using a molar ratio of steam/carbon ratio 5. The gas products are 60–64 vol% H_2, 17–33 vol% CO, 4–18 vol% CO_2 particularly effective compared to the other two NiO/olivine formulations in terms of both catalytic activity and coking resistance.

Gilbert et al., (2009) exmined from the cracking of tar and improve the efficient tar cracking feature during the pyrolysis–gasification process. The experimental temperature range of 500–800°C in the tar cracking zone was investigated. From the study on the effect of temperature, it was found that at 800°C in the tar cracking could produce a minimal amount of light condensable and gases. The longer residence times further decreased the amount of tar, but the heavy phase was very resistant to cracking.

Kazuhiro et al., (2007) studied tar reforming characteristics of the newly-developed Ni/MgO–CaO (based on dolomite) catalyst which was doped with WO_3. The results at the reaction temperature of 825°C confirmed exhibited higher activity at low temperature, and a better resistance to sulfur and coking, compared to commercially available catalysts. The developed catalyst successfully provided constant tar reforming better than 90% in the presence of H_2S at 800–850 °C. High temperature favors high yield H_2 because of endothermic of the reforming reactions. The S/C ratio has significant effect on reaction in the range from 1.2 to 4.7. At 800 °

C, it was demonstrated that H_2 and CO_2 yields increased when the S/C ratio increased. Moreover, for all temperatures studied, an increase in space-time led to an increase in CO_2 selectivity and H_2 yield, formed from CO because of the water gas shift reaction by Chunshan et al., (2009)

Wang et al., (2005) studied the reforming of naphthalene using Ni–dolomite catalysts which were cheap. At 700 °C, the results showed higher conversion and high H_2 yield but its cracking activity decreased rapidly within 10 h and then decreased slowly from 10 to 35 h.

3.3 Tar model compound studied in tar steam reforming

Tar is a complex mixture of condensable hydrocarbons which can be split into different classes based on the structure. In the study, tar has been selected to various tar model compound in tar steam reforming. Virginie et al., (2010) studied toluene as tar model compound because it is a key element obtained wood gasification at high temperature. Toluene steam reforming requires large quantities of water by stoichiometric reaction. The experiments with iron/olive catalyst revealed that water affects the generation of hydrogen and improve performance catalyst. At a suitable condition at 850 °C and H_2:H_2O=1.5:1, toluene conversion was about 95% and H_2 yield was 60%. There was also a study on efficiency and stability of Ni/olive catalyst by considering resistance to catalyst deactivation from accumulation of carbon by Swierczynski et al., (2008). Adverse reaction of toluene steam reforming is the carbon deposition reaction resulting from the decomposition toluene or methane and CO disproportion (Boudouard reaction). According to thermodynamics steam reforming reaction is favorable at a reaction temperature above 435 °C and carbon formation ($2CO \longleftrightarrow CO+C$) commonly occur at temperature less than 650 °C. Then, toluene steam reforming should react at higher than 650 °C. It was found that a good activity for decomposition of toluene as tar model compound similar to tar obtained from gasification.

Roberto et al., (2001) investigated the purification of syngas obtain from biomass gasification via catalytic steam reforming of naphthalene, benzene, anthracene, toluene, and pyrene as tar model compound. They have studied reaction using commercial nickel-based catalysts at 700-800°C. The conversion was calculated as the fraction of the carbon contained in the organic feed that converted to gas products (CO, CO_2 and CH_4). In addition to found that the reactivity of five model compounds of biomass gasification tars and their tendency to coke formation during steam reforming have been investigated in this work. The order of reactivity was benzene > toluene >> anthracene > pyrene >> naphthalene.

Takeshi et al., (2005) performed studied aim to prepared the Co/MgO catalysts and examined the catalytic performances for the naphthalene steam reforming which is a most difficult tar model compound to decompose. A 12 wt.% Co/MgO (600 °C) catalyst showed the best catalytic performance (conversion ~ 23%, 3 h). These catalysts showed low amount of coke deposition and high and stable activity under low steam/carbon mole ratio.

Polychronopoulou et al., (2004) studied the steam reforming of phenol on MgO-based supported Rh catalysts. The experimental results of wood gasification, phenol and toluene were selected as a main tar model compound from gasification. It was found to significantly influence the catalytic activity and H_2 selectivity in the 575–730 ◦C. increasing in the H_2 production is obtained by increased the water concentration in the 20–40 mol% range. The effect of phenol concentration in the feed also appears to be most positive, while the effect of temperature appears to be less important.

Domna et al., (2009) studied the reaction, cycle stability and coke deposition of natural calcite catalyst. Beside the main reaction of phenol steam reforming, it was also found that side reaction caused the formation of $CaCO_3$ as natural calcite catalyst consists of CaO. The characteristic features of the transient evolution of H_2 product suggests that adsorbed CO_2 formed on the CaO surface influence the kinetics of phenol steam reforming.

1-Methylnaphthalene was chosen as a model of the tar components for catalytic tests of five catalysts, including CaO, SiO_2, Al_2O_3, CuMn and NiMo. The NiMo catalyst having the highest surface area exhibited the highest activity of tar removal. The effects of reaction temperature and space velocity on tar removal were studied in the range of 250–650 °C and 3000–9000 h^{-1} (Binlin et al., 2008).

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental procedure used in this research. It can be divided into four sections. The first part describes the simulation of tar steam reforming. Section 4.2 explains catalyst preparation methods. The catalyst characterization techniques such as XRD, BET, SEM and TGA are described in Section 4.3. Finally, the details of the reaction setup for studying tar steam reforming is provided in Section 4.4.

4.1 Simulation of tar steam reforming

We simulated the tar steam reforming using Aspen Plus Program to understand the effect of operating parameters and to find a suitable range of operating condition. All 10 components were taken into account: naphthalene ($C_{10}H_8$), toluene (C_7H_8), phenol (C_6H_6O), pyrene ($C_{16}H_{10}$), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2)and water (H_2O). In the calculations, the inputs are molar quantities of the reactant naphthalene ($C_{10}H_8$), toluene (C_7H_8), phenol (C_6H_6O), pyrene ($C_{16}H_{10}$), nitrogen (N_2) and water (H_2O), and the outputs are 4 components of products and 6 components of reactants. The detail of tar steam reforming system used to Block type: RGibbs representing tar steam reforming reactor (TSR) is used to simulate the reaction based on multiphase equilibrium using Gibbs free energy minimization. The TSR reactor operates at temperature 350 -750 °C and a pressure of 1 atm. Thermodynamic properties are based on PENG-ROB and calculation options are phase equilibrium and chemical equilibrium. The tar steam reforming test using tar model compounds, and the test condition is listed in Table 4.1.

Table 4.1 Experimental condition for system modeling

Tar	1%mol
N_2 balance	99%mol
S/C ratio	1-7
Tar obtain biomass gasification	700 – 900 °C
Temperature	400 – 700 °C
Inlet tar	150 °C
Inlet water	110 °C
Pressure	1 atm

4.2 Catalysts preparations

4.2.1 Materials

The chemicals used in this study are specified as follows in **Table 4.2.**

Table 4.2 The chemicals used for catalyst synthesis in this study.

Chemical	Supplier
Nickel nitrate hexahydrate solution	-
Calcium oxide (CaO)	Riedel-de Haen
Magnesium oxide (MgO)	-
Aluminum oxide (Al_2O_3)	Aldrich chemistry

4.2.2 Preparation of catalyst

The Ni-based catalysts were prepared by impregnation method using CaO, MgO and Al_2O_3 supports with aqueous solution of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$). After solvent evaporation, the sample was dried overnight in an oven at 120 °C and then calcined with air at 800 °C for 4 h. The amount of Ni loading on the catalyst were controlled to be 10, 15, 20 wt%.

4.3 The reaction study in tar steam reforming

4.3.1 Chemicals

The reactants used for the reaction study are shown in Table 4.3.

Table 4.3 The chemicals used for the reaction study.

Chemical	Grade
Toluene	Analytical
Naphthalene	Analytical
Phenol	Analytical
Pyrene	Analytical

4.3.2 Apparatus

The catalytic tests were performed in a flow system shown diagrammatically in Figure 4.1. The setup consists of three sections. The first section is for preparing a tar model compounds with a controlled composition and flow rate. The second section is the reactor system including the fixed bed reactor and temperature control device. The third section is the analysis system where the gases from the reactor are analyzed by gas chromatography (GC). The instruments used in this system are listed and explained as follows:

The experiments were carried out at atmospheric pressure in a fixed-bed quartz reactor (9 mm diameter and 500 mm length) placed in a furnace with a temperature controller. The catalyst bed (0.3 g) was diluted with silicon carbide (1.0 g) by quartz wool in the uniform temperature zone. The temperature was monitored by a thermocouple placed outside of the reactor. Two motorised syringe pumps were used to introduce the liquids: water and mixture tar model compounds including toluene, naphthalene, pyrene and phenol which are then evaporated and carried to the reactor by a nitrogen flow controlled by a mass flow controller. The composition of tar model compounds feed is listed in Table 1. At the start of test, the catalyst was reduced in a flow of H_2, balanced with N_2 (50%) at 650°C for 1.5 h. The nitrogen flow rate was 20 mL/min. The different operating parameters were studied as summarized in Table 4.4.

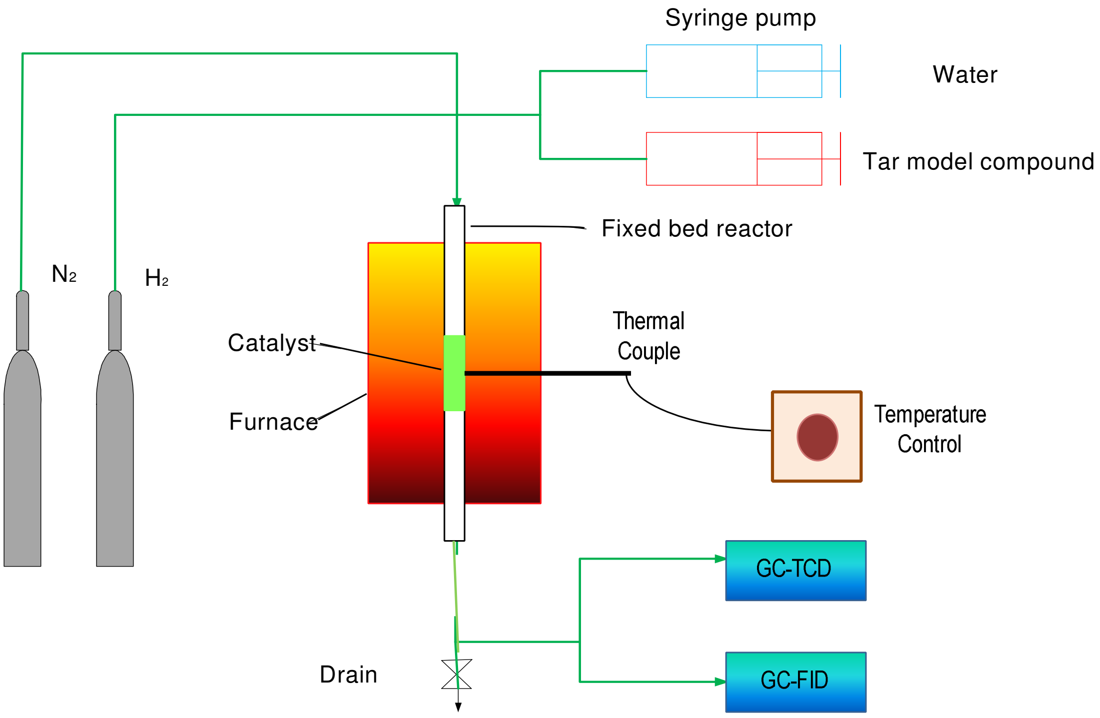


Figure 4.1 Schematic of the experimental system.

Table 4.4 Operation condition for tar steam reforming

Gas composition	N_2 balance
Tar	Toluene/Naphthalene/Phenol/Pyrene
Nitrogen flow rate	99% mol (20 mL/min)
Tar flow rate	1%mol (0.06 mL/min)
Temperature	450-650 °C at catalyst bed
Steam to carbon molar ratio	1 – 5
Pressure	Atmosphere

4.3.3. Product analysis

The product gases (H_2, CO, CO_2, and CH_4) were analyzed by a gas chromatography (GC-8A) equipped with a thermal conductivity detector (TCD). The molecular sieve 5A column and Porapak Q column were used with Ar as a carrier gas. Toluene, naphthalene, phenol and pyrene were analyzed by a gas chromatography (GC-14B) equipped with a flame ionization detector (FID) with a ZB-5HT Inferno column.

Table 4.5 Operating condition for gas chromatograph

Gas chromatograph	Shimadzu GC-8A	Shimadzu GC
Detector	TCD	FID
Packed column	Molecular sieve 5A , Porapak	ZB-5HT
Carrier gas	He (99.99 vol. %)	N_2 (99.99 vol. %)
Make-up gas	N_2 (99.99 vol. %)	H_2 (99.99 vol. %)
Column temperature	70 °C	325 °C
Injector temperature	70°C	250 °C
Detector temperature	100 °C	260 °C

The reactant and product gases are analyzed simultaneously by GC. Toluene, naphthalene, phenol, and pyrene conversion, the productivity of gas and H_2 yield were calculated. Toluene, napthalene, phenol, and pyrene conversions can be defined as Eq. (4.1):

$$\text{Conversion (\%)} = \frac{[\text{Ci}]_{,\text{in}} - [\text{Ci}]_{,\text{out}}}{[\text{Ci}]_{,\text{in}}} \times 100 \tag{4.1}$$

where $[C_i]$; molar flow rate i = toluene, naphthalene, phenol and pyrene.

The productivity of gas defined as the ratio of the amount of carbon in the product to the amount of carbon reacted was calculated by Eq. (4.2).

$$\text{Productivity of hydrogen} = \frac{[\text{Cj}]_{,\text{out}}}{\text{Overall mole of product}} \times 100 \tag{4.2}$$

$[C_j]$: molar flow rate j = H_2, CO, CO_2, CH_4, C_7H_8, C_6H_6O, $C_{10}H_8$ and $C_{16}H_{10}$.

Hydrogen yield, noted Y_{H2} (Eq.(4.3)), is expressed as the percentage of the stoichiometric potential corresponding to the total conversion of tar into H_2 according to the tar steam reforming.

$$\%\,\text{hydrogen yield} = \frac{[H_2]_{,\text{out}}}{[\sum_{k=1} H_2\,]_{\text{theory}}})\times 100 \quad ; k = \text{Eq } 2.17 - 2.22 \tag{4.3}$$

4.4 Catalyst characterization

The properties of the prepared catalysts were characterized by various techniques are discussed below.

4.4.1 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of powder were obtained using an X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for ful control of the XRD analyzer. The experiments were carried out using Ni-filtered CuKα radiation. Scans were performed over the 2θ ranges from 10° to 80°.

4.4.2 BET surface area measurement

The total surface area, pore volume and pore size are determined by using BET Micromeritrics ASAP 2020. The sample cell containing 0.3 g of sample is placed into the BET Micromeritrics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured.

4.4.3 Scanning Electron Microscope (SEM)

The catalyst granule morphology and elemental distribution were obtained using a Hitachi s-3400N scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 20 kV. The catalysts were prepared with platinum coating prior to analysis.

4.4.4 Thermo gravimetric analysis (TGA)

Coke formation on the catalysts after reaction was measured by thermo gravimetric analysis using Mettler–Toledo TGA/SDTA 815e apparatus to determine weight loss (%) of catalyst due to coke combustion.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Thermodynamic calculations of tar steam reforming

The study on modeling of tar steam reforming is divided into two parts. The first part deals with the tar steam reforming of mixed tar obtained from biomass gasification while the second part considers the reaction of each tar model compound. The study focuses on the effects of reaction temperature and S/C ratio on the performance of tar steam reforming reaction.

5.1.1 Simulations of tar steam reforming of mixture of tar model compound

In this section, the steam reforming of tar derived from biomass gasification was investigated. The tar compounds from wood pyrolysis were investigated at atmospheric pressure and temperature range of 700 – 900 °C and the compositions were found to be temperature-dependent (Brage *et al.*, 1996). Tar is usually represented by a mixture of four compounds with each compound representing a specific class of compounds and the composition equal to the composition of that group in actual tar. The compositions of tar model consist of toluene, naphthalene, phenol and pyrene. Figure 5.1 shows the tar compositions at different temperatures which was used in this study. In the simulations, temperature range of 400-700°C and S/C molar ratio varied from 1 to 7 were considered to study the effects of these operating parameters.

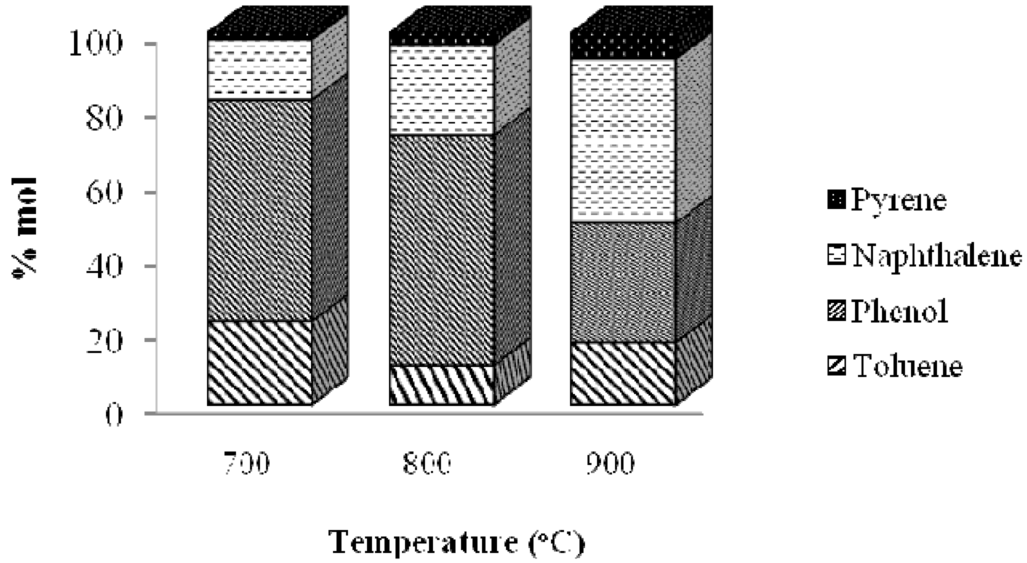


Figure 5.1 Major compounds chosen to represent tar model compound (Brage *et al.*,1996).

5.1.1.1 Effect of reaction temperature

Simulations of tar steam reforming using representative tar obtained from biomass gasification at 700 – 900 °C. Figures 5.2-5.4 show the compositions of gas product (mol%) (water and nitrogen are not included) at different reaction temperatures and S/C molar ratios. From the results, we noticed that the steam reforming of different tar compositions obtained from biomass gasification at different temperatures yield the gas product compositions with the same trend. It was found that the composition of H_2 always increases with increasing temperature and levels off at reaction temperatures above 650 °C. It converts high molecular weight hydrocarbons of all tars into synthesis gas. In addition, when increasing the reaction temperature, the composition of CO increases but the compositions of CH_4 and CO_2 in the gas product decrease especially at low temperature (350 – 450 °C). At temperatures higher than 550 °C, the CH_4 composition drops to near zero.

5.1.1.2 Effect of S/C ratio

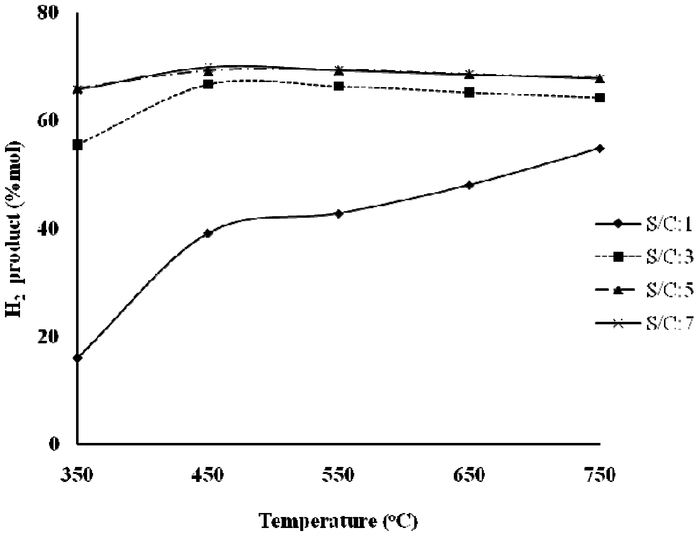
The effect of S/C ratio on tar steam reforming at various temperatures for tar compounds obtained from biomass gasification at different temperatures was considered. The results are shown in Figures 5.2-5.4. The compositions of H_2 and CO_2 are rapidly increased with increasing S/C ratios before they leveled off at S/C ratio above 5. The compositions of CO and CH_4 decrease rapidly until the S/C ratio of 5. The tar composition from the gasification at 800 °C offers the highest H_2 production when compared with those from the gasification at 700 and 900 °C.

The influences of S/C ratio and temperature on gas composition can be explained by the reactions involved in the tar steam reforming as reported for the cases of each tar model compound and mixture of tar compounds. The main reactions are provided in Eqs.2.17-2.20. A large S/C molar ratio induces the equilibrium reactions (Eq.2.21) and (Eq.2.22) to be shifted towards H_2 production. With the increase of temperature, H_2 content slightly increases when increasing S/C molar ratio. Almost all tar is converted to gas products.

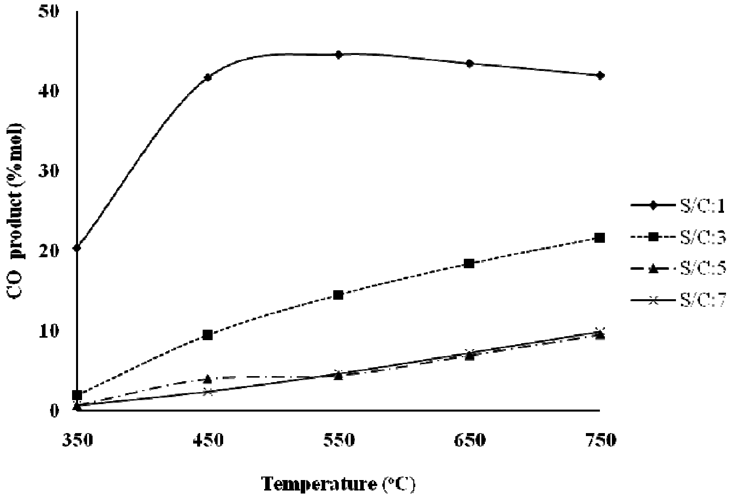
The thermodynamic simulation is considered as a good approach to bring understanding on the tar steam reforming especially when using the tar compositions reported from the real biomass gasification. Similarly, according to Wang *et al.*, (2006) who studied reforming of raw fuel gas from biomass gasification to syngas using NiO–MgO catalyst, raw fuel gas from biomass gasification contained H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, N_2 and tar which is a by-product from gasification. The raw fuel gas contained about 13 identifiable tar species. It was also reported that the amount of tar species obtained from biomass gasification can be converted into gas species almost completely. At high reforming temperature, a very high H_2 content and low tar content were reported. It is clear that the use of tar steam reforming can eliminate tar while increasing the production of synthesis gas.

5.1.2 Simulations of tar steam reforming with each tar model compound

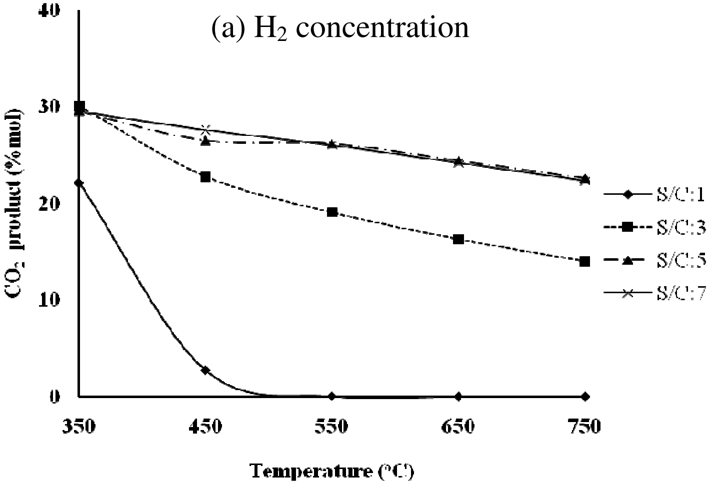
From the previous study, the effect of operating parameters (temperature, S/C ratio) on steam reforming reaction of mixed tar compounds obtained from biomass gasification was investigated. It was found that the operation at T = 550 °C and S/C ratio = 7 is the best condition for production of hydrogen. The tar composition obtained from the biomass gasification at 800°C gives the best hydrogen content probably because the tar contains compounds which are more easily to decomposed. This section focuses on the tar steam reforming of each tar model component (toluene, naphthalene, phenol and pyrene) to determine their reforming characteristics. In order to make comparison, the compositions investigated were based on the tar obtained from biomass gasification at 800°C and the steam reforming are operated at reaction temperature of 550°C and S/C ratio of 7. The simulations of tar steam reforming of each tar model compound indicate that the reforming ability of the tar model follows the order:



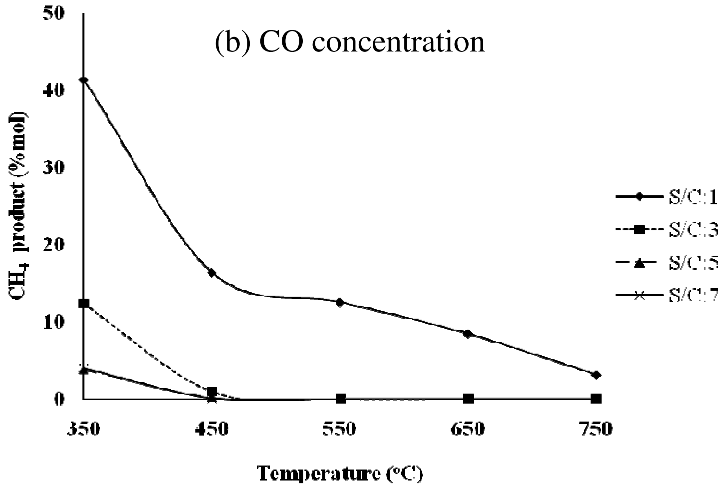
(a) H_2 concentration



(b) CO concentration

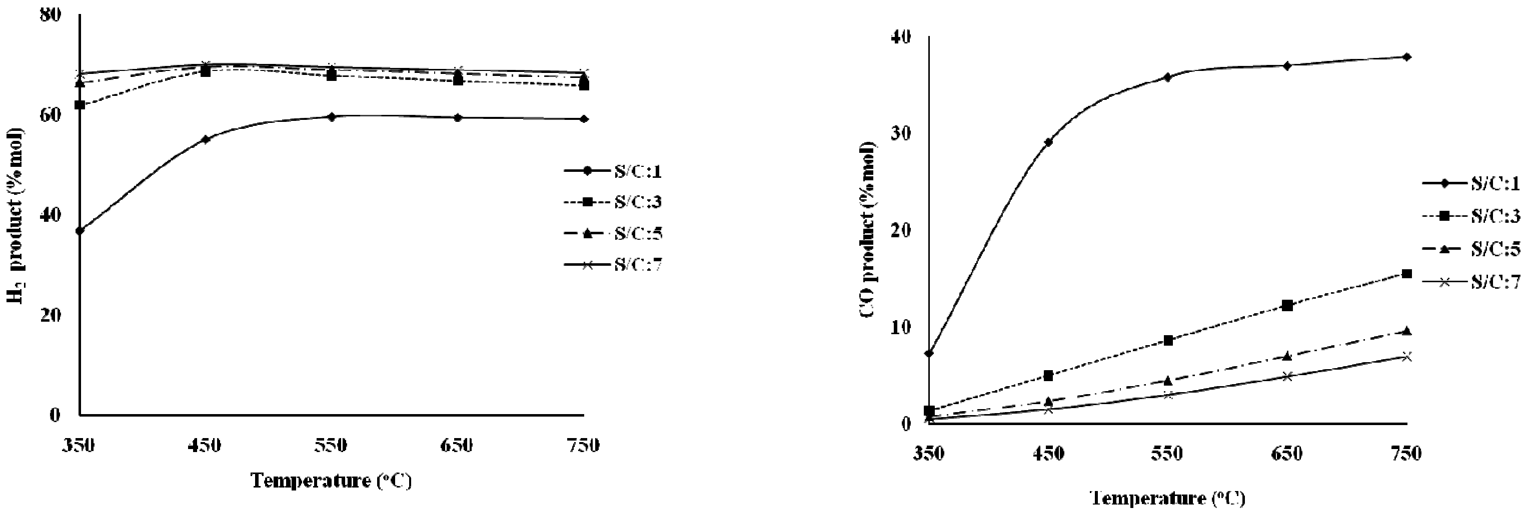


(c) CO_2 concentration

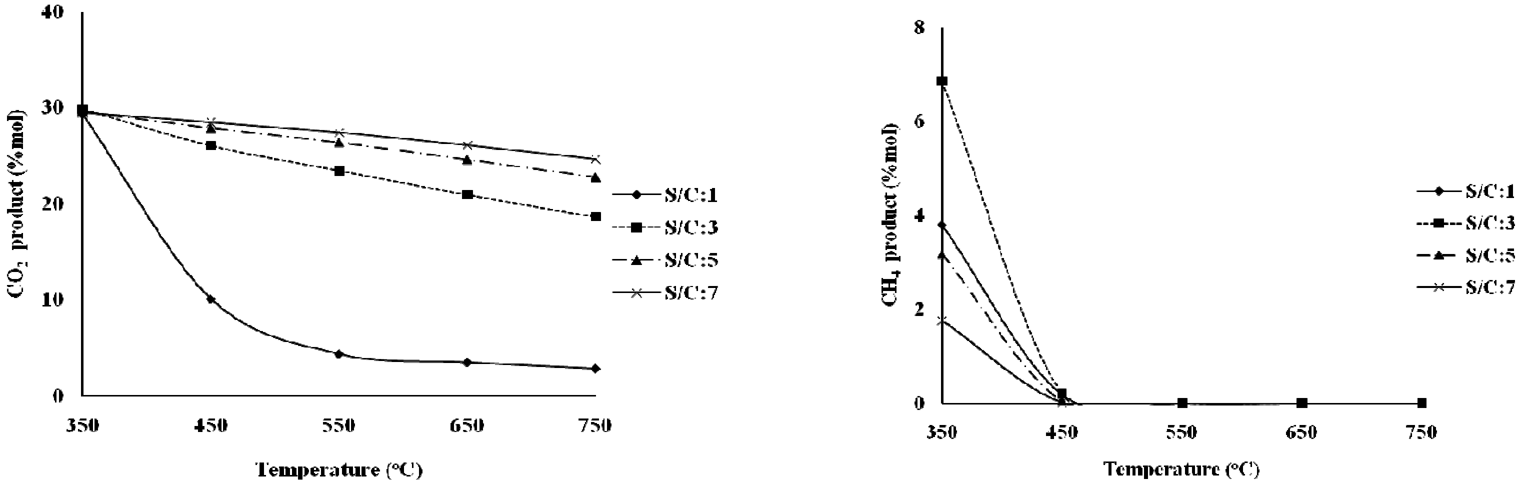


(d) CH_4 concentration

Figure 5.2 Effects of temperature and S/C ratio on theoretical equilibrium values of gas composition (Tar from biomass gasification at 700 °C).

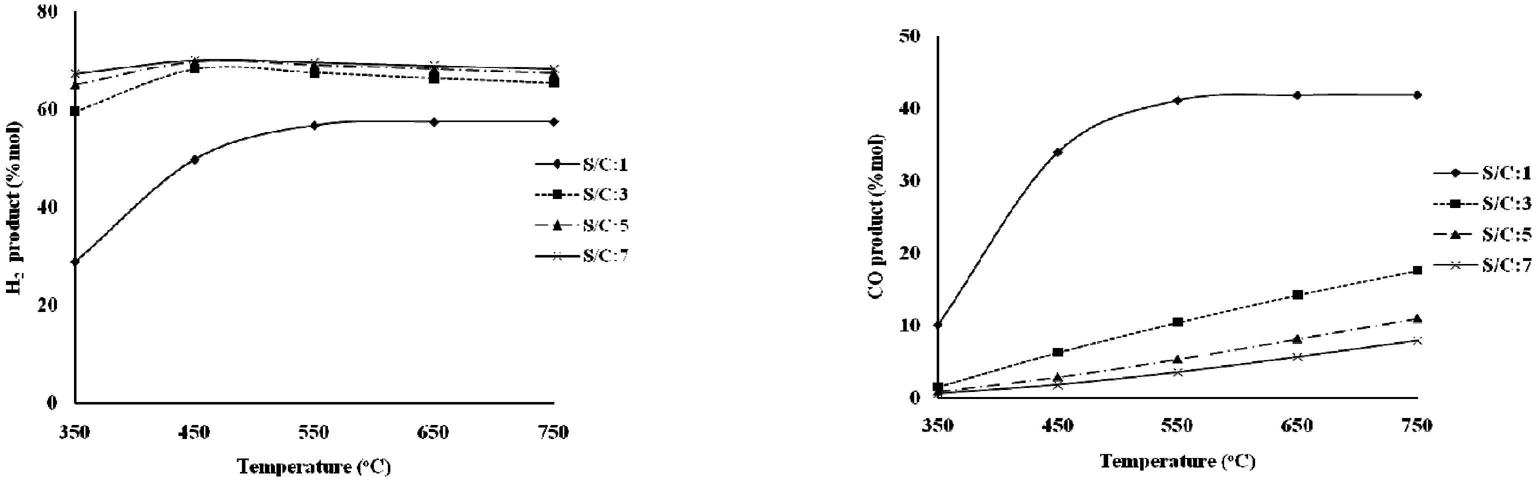


(a) H_2 concentration (b) CO concentration

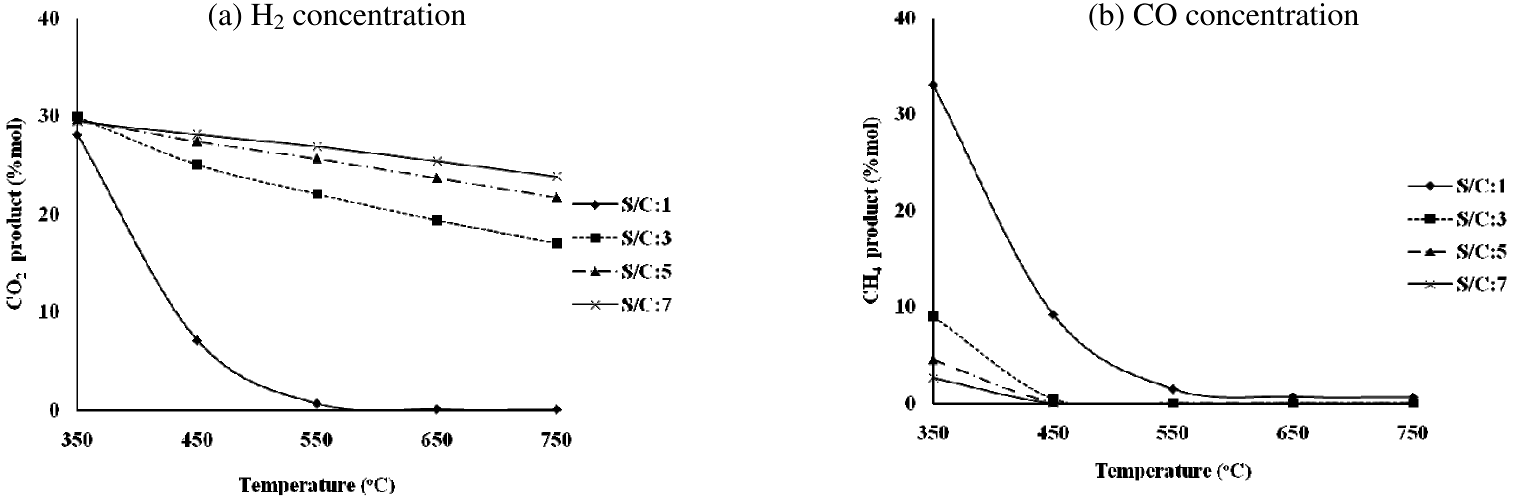


c) CO_2 concentration (d) CH_4 concentration

Figure 5.3 Effects of temperature and S/C ratio on theoretical equilibrium values of gas composition (Tar from biomass gasification at 800 °C).



(a) H_2 concentration (b) CO concentration



(c) CO_2 concentration (d) CH_4 concentration

Figure 5.4 Effects of temperature and S/C ratio on theoretical equilibrium values of gas composition (Tar from biomass gasification at 900 °C).

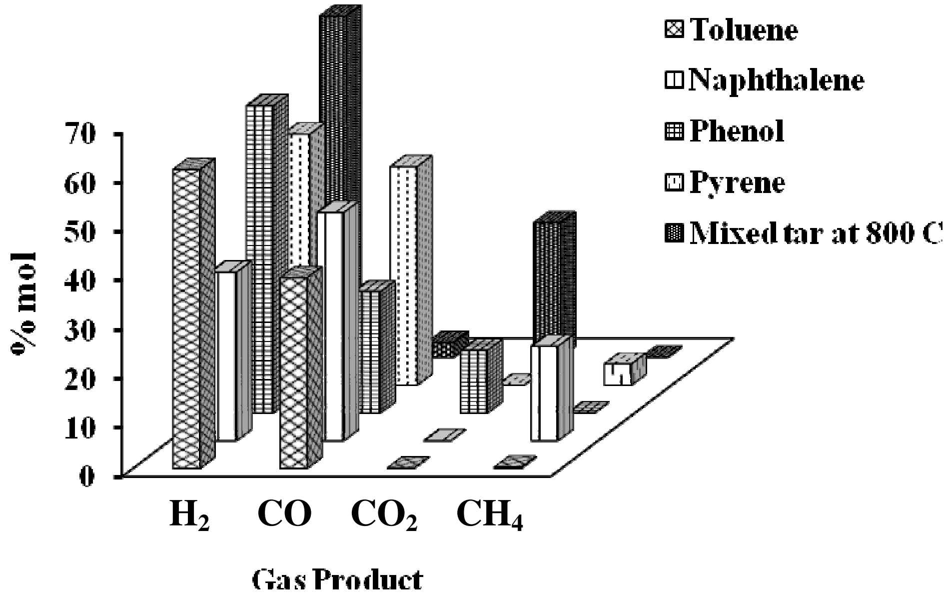


Figure 5.5 Effect on gas composition of each tar model in tar steam reforming (T = 550 °C and S/C = 7).

phenol > toluene > pyrene > naphthalene as shown in Figure 5.5. Phenol as a liquid compound at room temperature has a ring aromatic hydrocarbon structure which is relatively easy to decompose in the tar steam reforming reaction, thus providing high hydrogen content. Naphthalene and pyrene are solid at room temperature and has multi-aromatic hydrocarbon structures which are difficult to decompose, Based on the thermodynamics, each tar model compound could be completely decomposed and converted to gas product.

5.2 Characterization of fresh catalysts

Catalyst characterization before reaction test was carried out using X-Ray Diffraction (XRD), BET surface area measurement and Scanning Electron Microscopy (SEM).

5.2.1 X-Ray Diffraction (XRD)

The XRD profiles of fresh 15% Nickel on various supports are shown in Figure 5.6. The diffraction peaks of Ni^0 or NiO were not observed in 15%Ni/MgO. It may be due to the adhesion of nickel on support or the extent may be too small for the detection of Ni^0 or NiO, as reported by (Furusawa *et al.*, (2005). For 15%Ni/Al_2O_3 and 15%Ni/CaO catalysts, the distribution of nickel in the form Ni^0 or NiO was observed whose diffraction peaks of NiO located at 37.2, 43.2, 62.7, 75.2, 79.4 and Ni^0 located at 44.2, 51.7, 76.1 (Srisiriwat *et al.*, 2009).

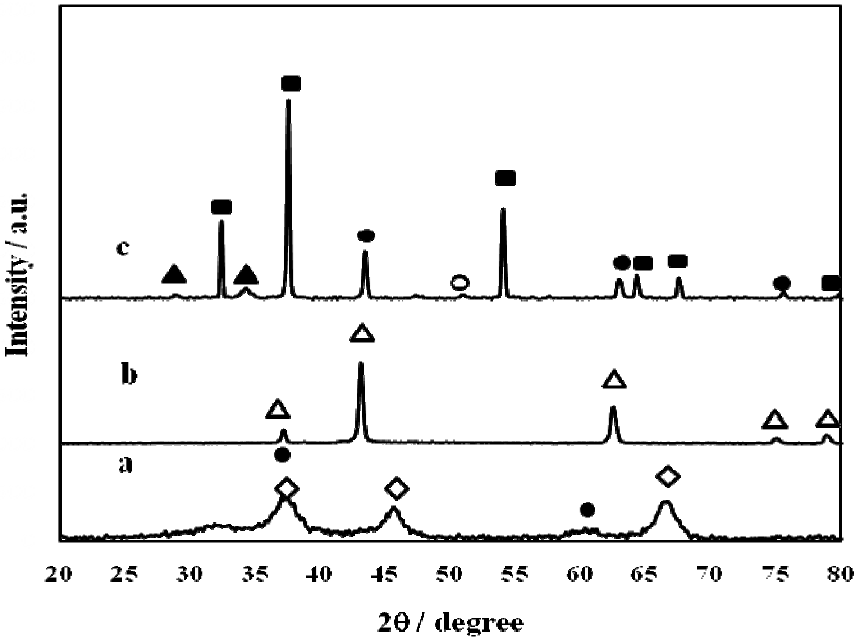


Figure 5.6 XRD patterns of Ni catalysts on different supports. (a) 15%Ni/Al_2O_3 (b) 15%Ni/MgO (c)15%Ni/CaO, (◇) Al_2O_3; (△) MgO; (■) CaO; (▲) $CaCO_3$; (●) NiO; (○)Ni

Figure 5.7 shows XRD profiles of various %Ni loading on Al_2O_3 support contained (10-20 %Ni). It shows that the increase of nickel loading results in the increase of the ratio of NiO intensity to Al_2O_3 intensity. This NiO phase in the fresh catalyst was completely converted to Ni metal after reduction.

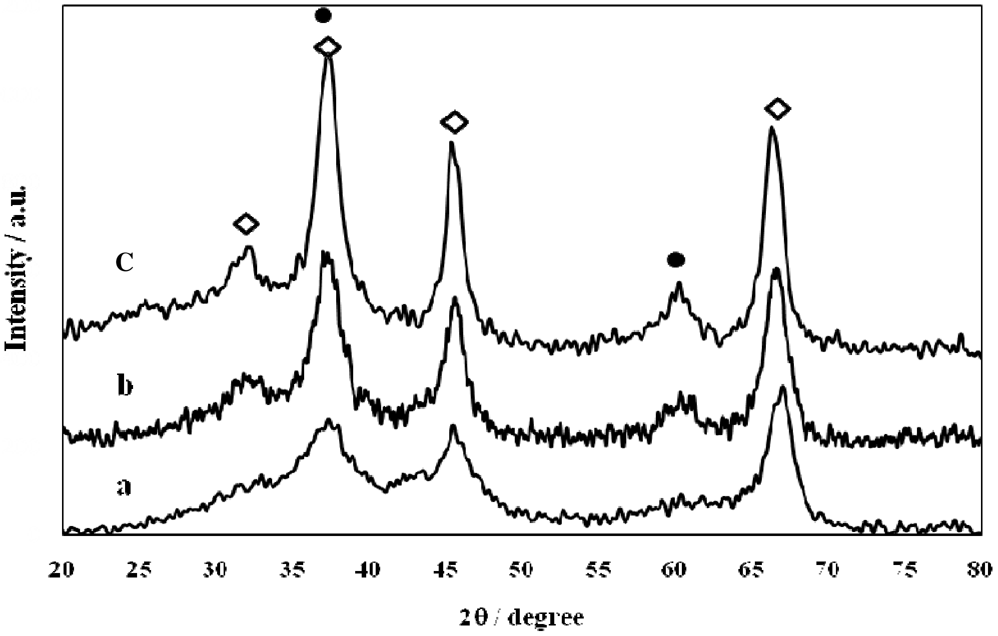


Figure 5.7 XRD patterns of fresh Ni catalysts (a) $10\%Ni/Al_2O_3$ (b) $15\%Ni/Al_2O_3$ (c) $20\%Ni/Al_2O_3$, (◇) Al_2O_3; (●) NiO

5.2.2 BET surface area measurement

The results of surface area and pore volume of catalysts are shown in Table 5.1. It can be seen that the surface area of supported Ni catalysts depends on the types of support. Considering only supports, it was found that the alumina support has higher surface area and pore volume than calcium oxide and magnesium oxide. For 15wt%Ni loading, the surface area is in the following order: 15wt% Ni/Al_2O_3 > 15wt% Ni/CaO > 5wt%Ni/MgO. For alumina supported catalyst, increasing of Ni content leads to the reduction of surface area and pore volume. The surface area is in the following order: $20wt\%Ni/Al_2O_3 < 15wt\%Ni/Al_2O_3 < 10wt\%Ni/Al_2O_3$, because the added Ni metal and/or NiO placed on surface and pore of Al_2O_3

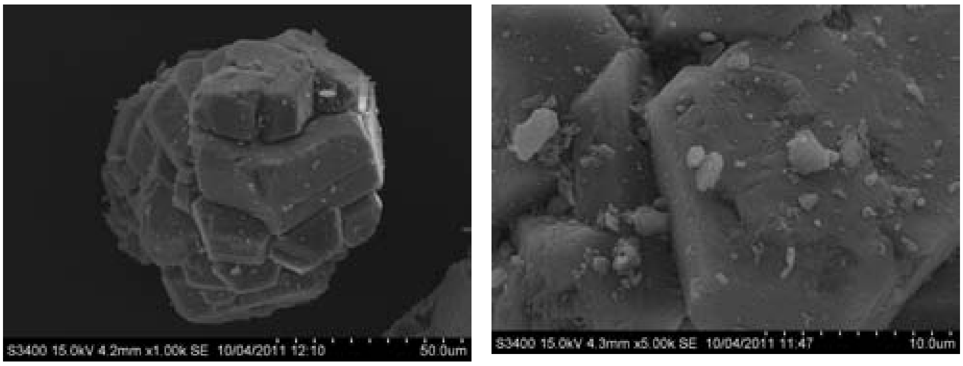
Table 5.1 Physical properties of various materials.

Material	BET surface (m^2/g)	Pore volume (cm^2/g)
CaO	8.0	0.0235
MgO	2.3	0.0065
Al_2O_3	144.7	0.2202
15 %wt. Ni/Al_2O_3	60.2	0.1694
15 %wt. Ni/CaO	3.8	0.0173
15 %wt. Ni/MgO	1.9	0.0035
10 %wt. Ni/Al_2O_3	81.3	0.1898
15 %wt. Ni/Al_2O_3	60.2	0.1694
20 %wt. Ni/Al_2O_3	40.1	0.1324

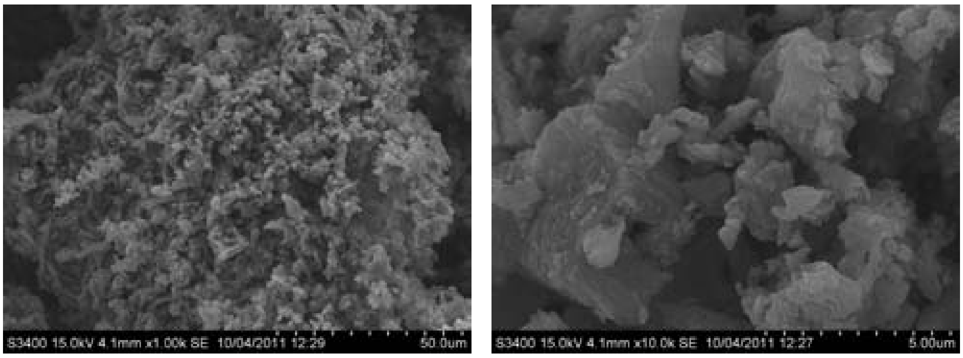
5.2.3 Scanning Electron Microscopy (SEM)

Figures 5.8 and 5.9 show the SEM images of the catalysts on different supports, respectively, while Figures 5.10 show the SEM/EDX images of the aluminum supported catalysts with different % Ni loading. The different textural characteristics of the 15% Ni catalysts on different supports are shown in Figures 5.8 (a-c). Distribution of Ni loading on alumina supports (Figure 5.8(a)) is not clear when compared with calcium oxide (Figure 5.8(b)) and magnesium oxide support (Figure 5.8(c)). Due to the small pore volume of calcium oxide and magnesium oxide supports as shown in Table 5.1, we can see nickel content on the surface area of supports clearly. For alumina support having the highest pore volume among the supports studied (Table 5.1), the obtained SEM images for Ni distribution on surface area is not clear probably because the high pore volume can allow more nickel to deposit into pores rather than on the surface. Then, Ni distribution on surface area of different supports could be better observed by using SEM/EDX whose results are given in Figure 5.9. The different textural characteristics of Ni/Al_2O_3 at different % Ni loading are shown in Figure 5.10 indicating better distribution of metal (nickel) on the support surface as the % loading increases. Figure 5.10 shows clearly, when the

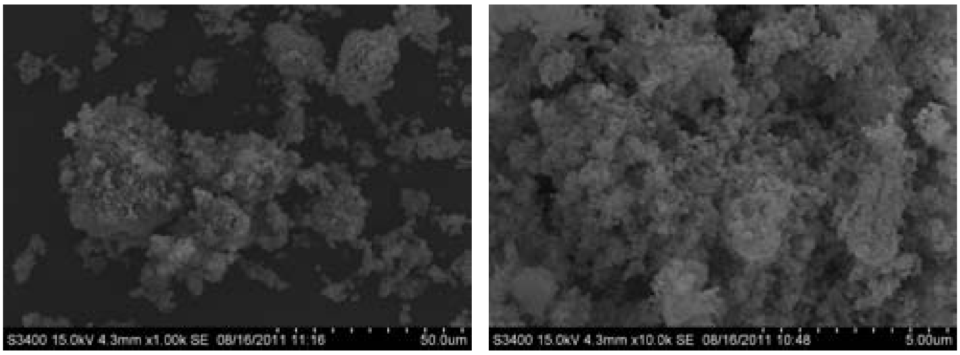
%Ni loading was increased, the Ni distribution on surface of alumina support becomes better.



(a) 15%Ni/Al_2O_3

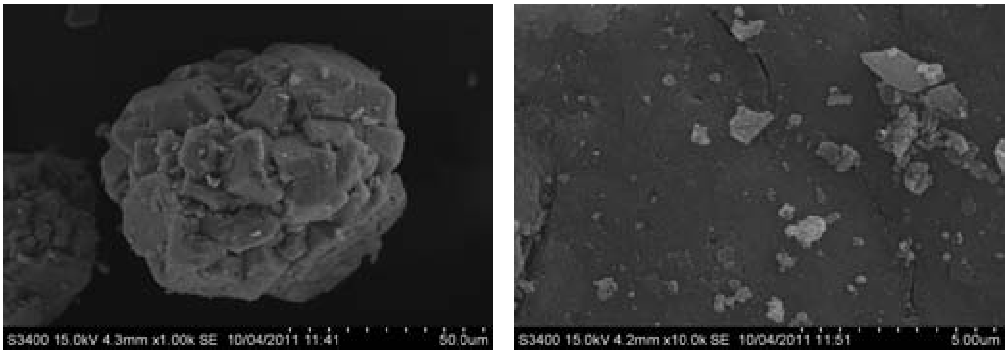


(b) 15%Ni/CaO

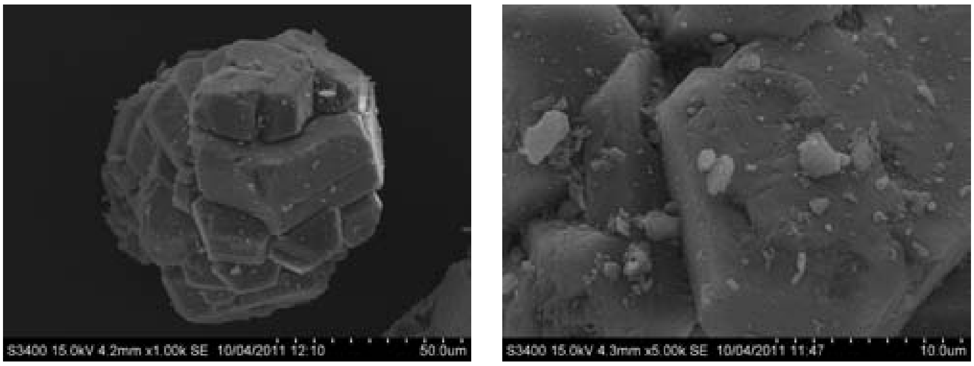


(c) 15%Ni/MgO

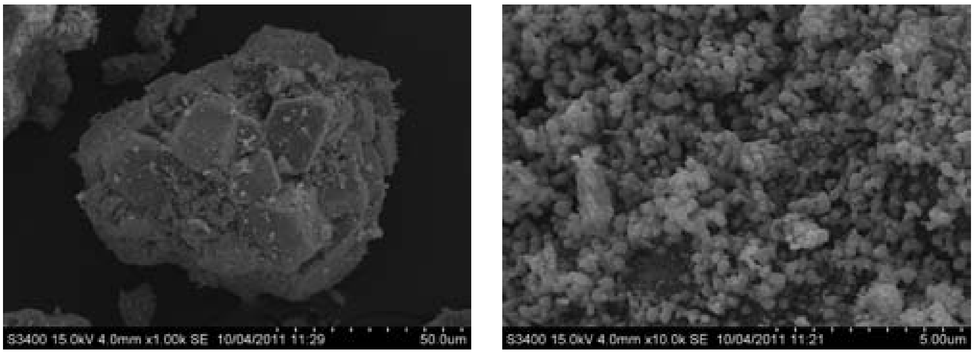
Figure 5.8 SEM images of fresh catalysts before running tar steam reforming on different supports(a) 15%Ni/Al_2O_3, (b) 15%Ni/CaO, (c) 15%Ni/MgO



(a) $10\%Ni/Al_2O_3$

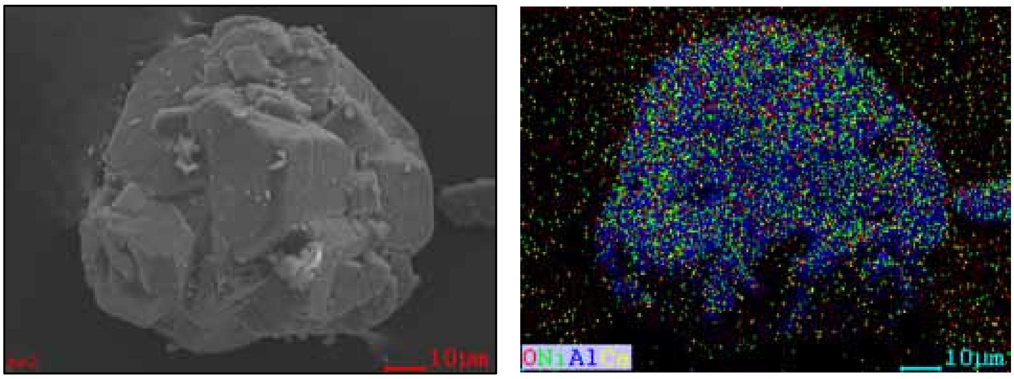


(b) $15\%Ni/Al_2O_3$

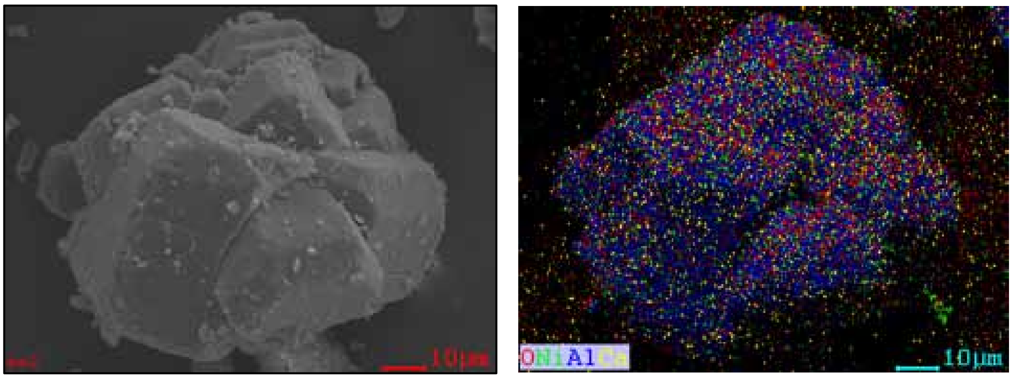


(c) $20\%Ni/Al_2O_3$

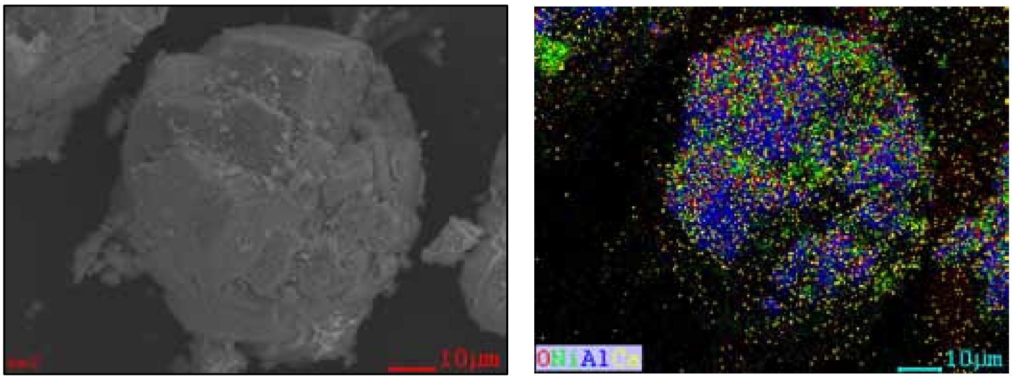
Figure 5.9 SEM images of fresh catalysts before running tar steam reforming at different %Ni loading. (a) $10\%Ni/Al_2O_3$,(b) $15\%Ni/Al_2O_3$,(c) $20\%Ni/Al_2O_3$



(a) 10%Ni/Al_2O_3



(b) 15%Ni/Al_2O_3



(c) 20%Ni/Al_2O_3

Figure 5.10 SEM /EDX images show Ni distribution of fresh catalysts before running tar steam reforming at different %Ni loading. (a) 10%Ni/Al_2O_3 ,(b) 15%Ni/Al_2O_3 , (c) 20%Ni/Al_2O_3

5.3 Catalytic performance on tar steam reforming

The catalytic performance of catalysts was investigated in the tar steam reforming. The reaction was carried out in a fixed-bed quartz reactor (9 mm diameter and 500 mm length) placed in a furnace equipped with a temperature controller. The catalyst of 0.3 g was diluted with silicon carbide (1.0g) and placed between quartz wool in the uniform temperature zone. The product gases (H_2, CO, CO_2 and CH_4) are analyzed by a gas chromatography (GC-8A) equipped with a thermal conductivity detector (TCD). Toluene, naphthalene, phenol and pyrene were analyzed by a gas chromatography (GC-14B) equipped with flame ionization detector (FID).

The study provides substantial and important fundamental information on the effects of (a) type of support (b) % metal loading (c) reaction temperature (d) S/C ratio and (e) tar compositions from various biomass gasification temperatures.

5.3.1 Effect of support

The study of type of supports on tar steam reforming reaction was carried out using Al_2O_3, CaO and MgO were selected as they have been widely used in tar steam reforming reaction. Table 5.2 summarizes the gas compositions from the tar steam reforming after 200 min reaction time for the tar compounds from biomass gasification at 700 °C. The experiments were performed at 450 °C and S/C ratio of 5 using 15%Ni loaded on different supports. Here we will evaluate the results obtained from the experiments in terms of H_2 yield (%), H_2 concentration (%mol) and H_2 production (mol/min) whose data are summarized in Appendix D. The hydrogen concentration (mol%) was defined as the mole of hydrogen divided by the total mole of all products. The hydrogen concentration results indicate that the supports of Al_2O_3 and CaO show higher reaction activity than MgO which offered the low hydrogen product in range of 60 mol %. Figure 5.11 shows the H_2 yields. Hydrogen concentration and H_2 yield decrease with increasing reaction time likely due to catalyst deactivation by carbon formation. The support of Al_2O_3 offers the highest % H_2 yield of 13% , From the result, it was clear that Al_2O_3 offers superior reactivity to the CaO and MgO supports. The tar conversions of toluene, phenol, naphthalene and pyrene are shown in Figure 5.12. It was found that 15%Ni/MgO gives the lowest tar conversion. Among different tar components, naphthalene conversion is the lowest probably because naphthalene has the most complex structure and therefore it is the most difficult to be decomposed.

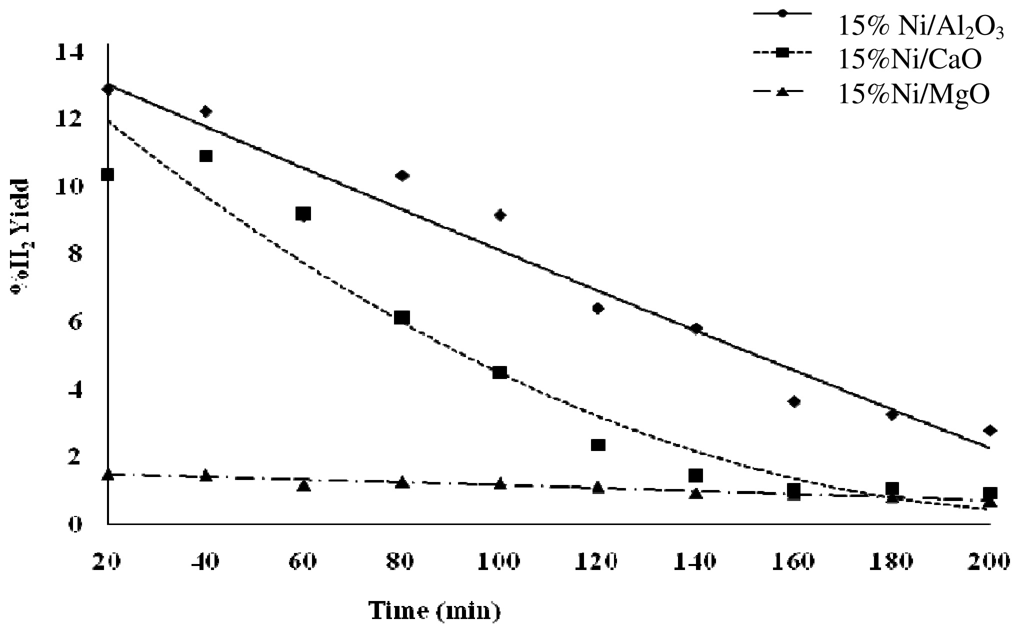
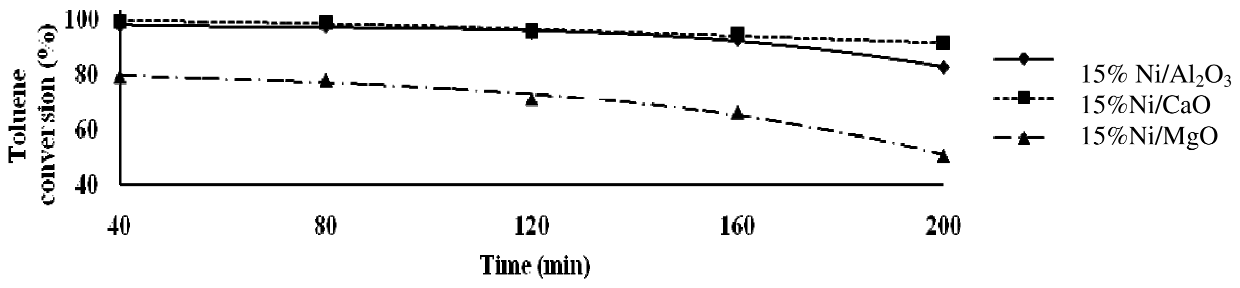
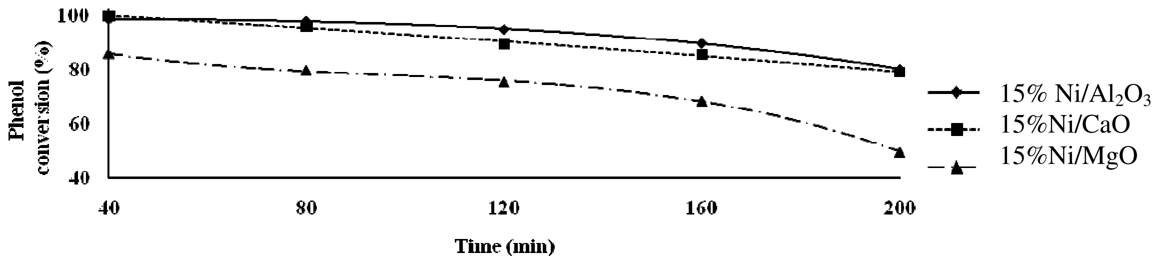


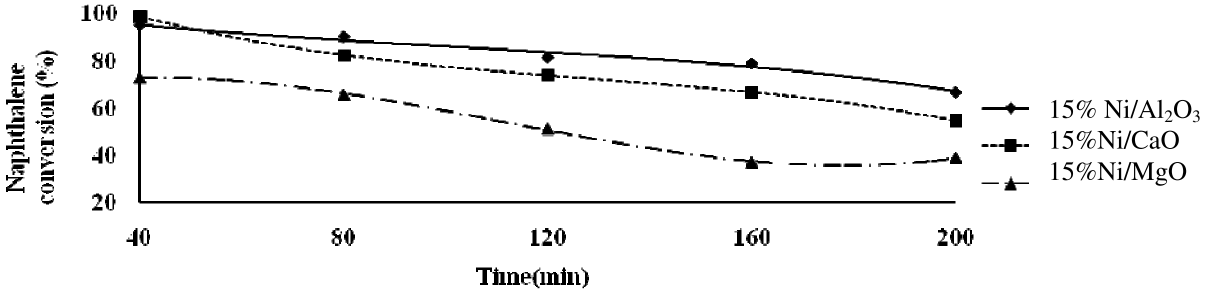
Figure 5.11 Effect of catalyst support on the H_2 yield from tar steam reforming (T = 450 °C, S/C ratio:5).



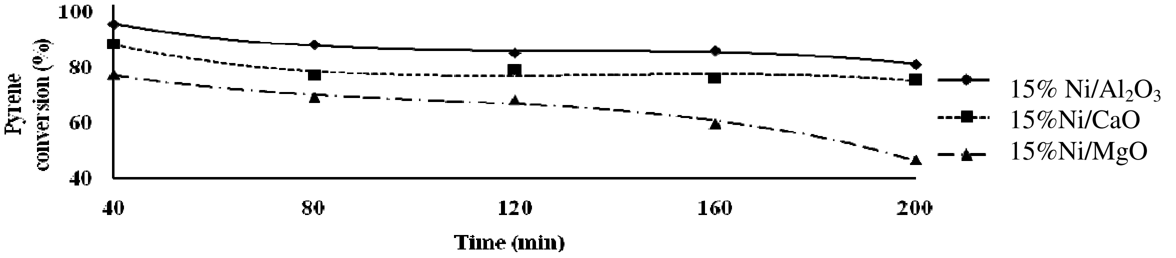
(a) Toluene



(b) Phenol



(c) Naphthalene



(d) Pyrene

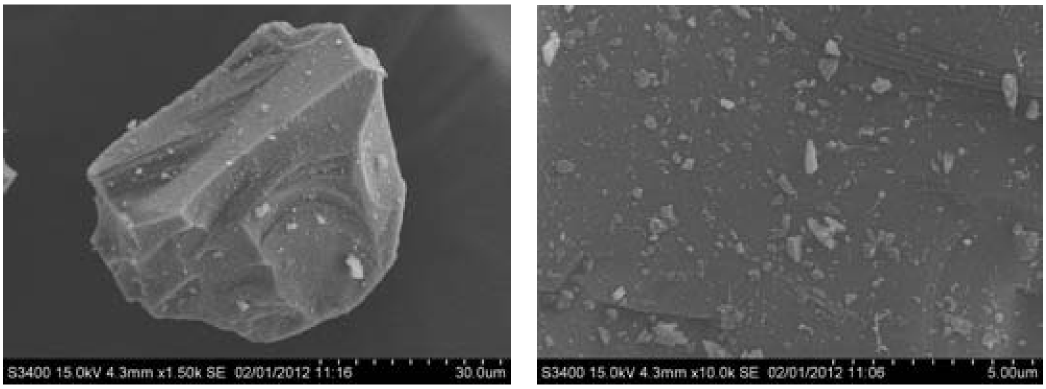
Figure 5.12 Tar conversion of supported catalysts on the tar steam reforming (a) Toluene (b) Phenol (c) Naphthalene (d) Pyrene (T =450°C, S/C ratio = 5).

Table 5.2 Effect of type of support gas composition of tar steam reforming (neglecting water and nitrogen).

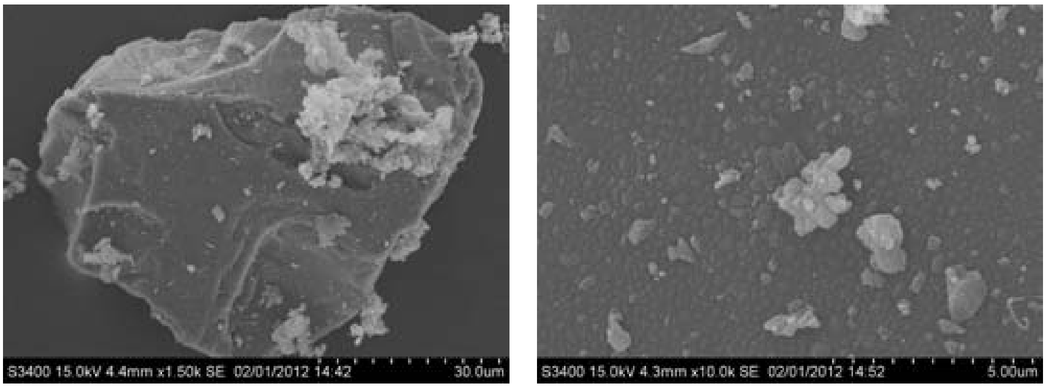
Catalyst	Reaction Temperature (°C)	S/C ratio	Time (min)	Gas Composition (%mol)							
				H_2	CH_4	CO	CO_2	C_7H_8	C_6H_6O	$C_{10}H_8$	$C_{16}H_{10}$
15%Ni/Al_2O_3	450	5	40	74.13	7.04	n.a.	18.07	0.15	0.29	0.01	0.03
			80	86.01	3.07	n.a.	9.17	0.24	0.63	0.79	0.10
			120	88.08	5.92	n.a.	-	0.81	2.53	2.45	0.21
			160	82.26	2.38	n.a.	-	2.05	8.40	4.95	0.32
			200	68.41	0.54	n.a.	-	5.28	17.46	7.84	0.47
15%Ni/CaO	450	5	40	78.27	8.10	n.a.	13.36	0.04	0.07	0.07	0.09
			80	86.89	2.13	n.a.	6.03	0.18	2.11	2.33	0.34
			120	77.14	-	n.a.	-	1.68	12.48	7.99	0.71
			160	52.10	-	n.a.	-	3.46	27.09	16.06	1.28
			200	41.37	-	n.a.	-	4.68	33.95	18.87	1.13
15%Ni/MgO	450	5	40	58.42	n.a.	n.a.	n.a.	10.07	21.29	9.33	0.89
			80	48.42	n.a.	n.a.	n.a.	10.15	28.99	11.28	1.16
			120	38.97	n.a.	n.a.	n.a.	12.25	32.58	14.83	1.10
			160	29.35	n.a.	n.a.	n.a.	13.50	38.26	17.62	1.28
			200	18.43	n.a.	n.a.	n.a.	16.15	50.08	13.95	1.39

The used catalysts after reaction time of 200 min were characterized to determine their changes in structural and surface using Scanning Electron Microscopy (SEM).

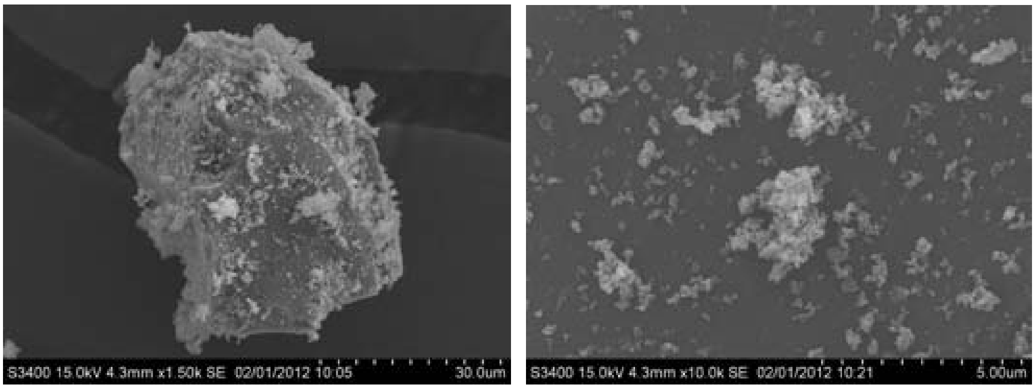
Figure 5.13 shows the SEM images of different supports at 15%Ni loading after reaction test at 450 °C, S/C ratio of 5 and tar steam reforming reaction time of 200 min. For 15%Ni/Al_2O_3 shown in Figure 5.13(a), the distribution of Ni loading on surface area decreased after the reaction. However, it was not quite clear as Ni was mostly dispersed in catalyst pores. For 15%Ni/CaO (Figure 5.13 (b)) and 15%Ni/MgO (Figure 5.13(c)), it was found that the Ni became agglomerated as seen by their large size and less fragmented. The order of the catalytic performance of the catalysts is in good agreement with the surface area values of the catalysts (Table 5.1). It is possible that the sintering of the catalyst resulted in reduction of its catalytic activity. Based on the experimental results, the alumina support is likely to be the most suitable one for loading Ni for catalyzing the tar steam reforming reaction.



(a) 15%Ni/Al_2O_3



(b) 15%Ni/CaO



(c) 15%Ni/MgO

Figure 5.13 SEM images of catalysts after run tar steam reforming at T 450 °C, S/C:5 (a) 15%Ni/Al_2O3, (b) 15%Ni/CaO, (c) 15%Ni/MgO

5.3.2 Effect of %Ni loading

According to the previous study on the effect of type of support, Al_2O_3 was selected as the catalyst support for further investigation on the effect of %Ni loading. In the study, the %Ni loading was varied at 10, 15, 20 wt.% and the reaction condition was 450 °C and S/C ratio of 5 using tar components from biomass gasification at 700 °C. The gas product compositions from the tar steam reforming after 200 min are given in Table 5.3.

The results indicates that at 15 %Ni/Al_2O_3 offers the highest H_2 concentration (mol%) compared to 10 %Ni/Al_2O_3 and 20 %Ni/Al_2O_3. It should be noted that after 2 h reaction, for 10 %Ni/Al_2O_3 H_2 concentration decreased rapidly. Considering H_2 product (mol/min) and % H_2 yield (Figure 5.14), it was found that 20 %Ni/Al_2O_3 showed the largest value of about 27% H_2 yield. The results of tar conversions shown in Figure 5.15 indicate that the 20%Ni/Al_2O_3 has almost the highest tar conversion of most tar components except the naphthalene conversion which is the most difficult to be decomposed.

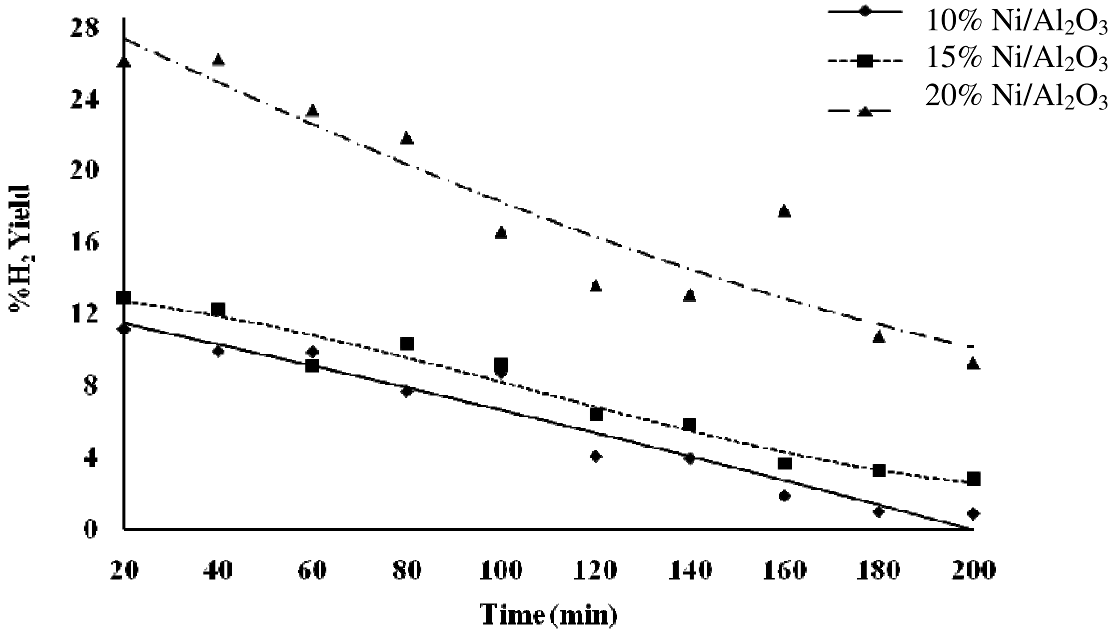
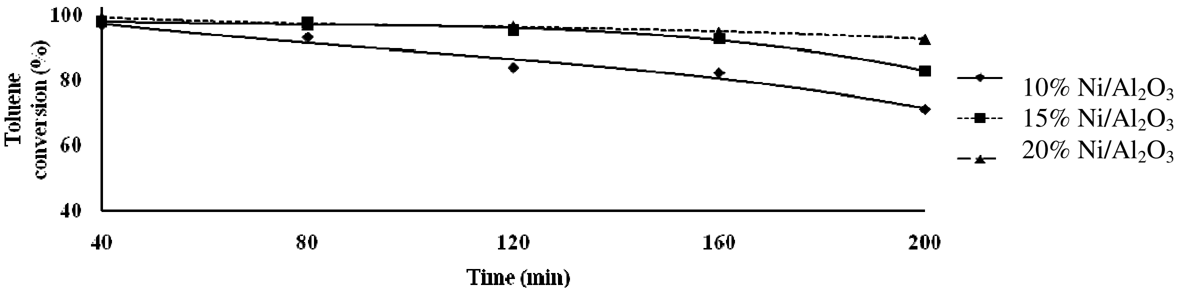
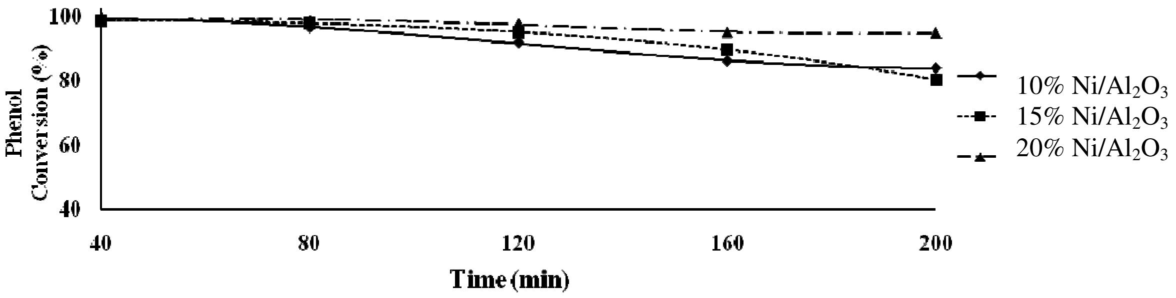


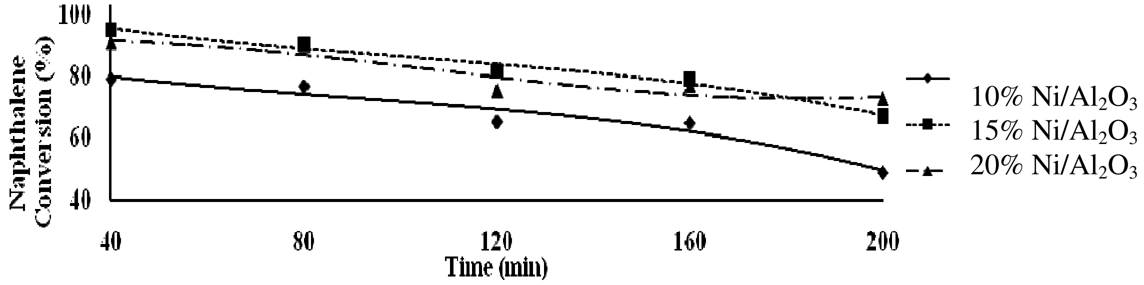
Figure 5.14 Effect of %Ni loading of Ni/Al$_2$O$_3$ on % H$_2$ yield of tar steam reforming (T = 450 °C, S/C ratio = 5).



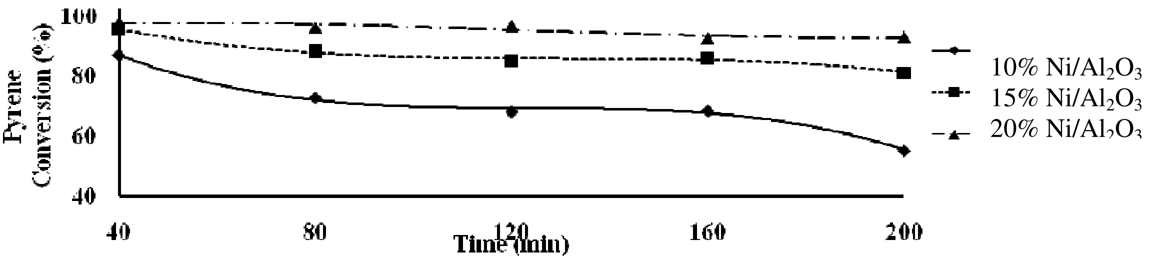
(a) Toluene



(b) Phenol



(c) Naphthalene



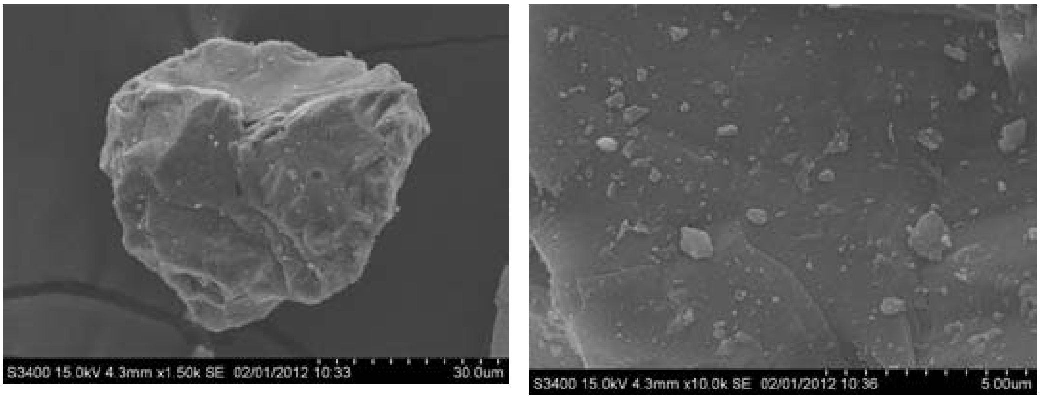
(d) Pyrene

Figure 5.15 Tar conversions of Ni/Al_2O_3 at different %Ni loadings (a) Toluene, (b) Phenol, (c)Naphthalene, (d) Pyrene (T = 450 °C, S/C ratio = 5).

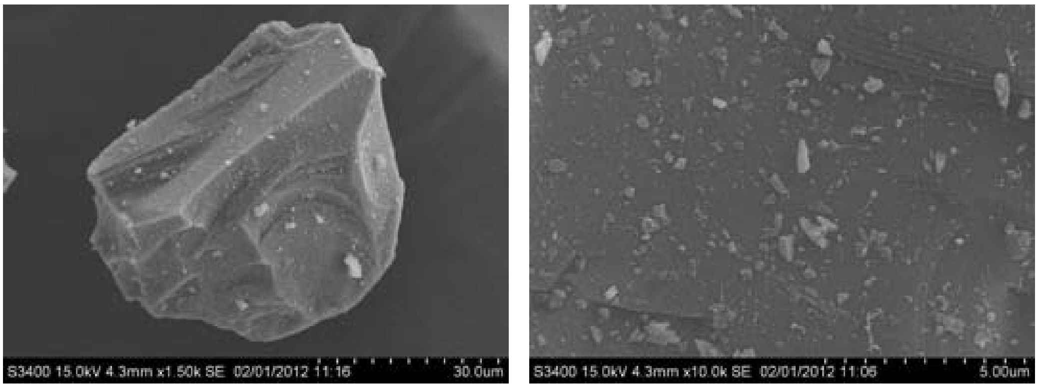
According to the results mentioned earlier, the SEM images of the fresh catalysts indicate that increasing nickel loading results in the better distribution of nickel on surface area of the support and higher reactivity. The SEM image of 20%Ni/Al_2O_3 after reaction at 450 °C and S/C ratio of 5 (Figure 5.16) showed that for all % loading, the observed of nickel on surface area become fewer and the nickel crystals become larger. However, for 20%Ni/Al_2O_3 catalyst (Figure 5.16(c)) the sintering of catalyst caused by a combination of nickel into larger grains is less obvious compared to 10%Ni/Al_2O_3 and 15%Ni/Al_2O_3. In addition, the XRD profiles of fresh Ni catalysts on alumina support in Figure 5.7 confirm that the increase of the Ni loading increased the ratio of NiO intensity. Thus, 20%Ni/Al_2O_3 catalyst is a potential catalyst with good activity and stability for the tar steam reforming reaction. It was therefore selected as a catalyst for further study to determine suitable operating condition.

Table 5.3 Effect of %Ni loading on gas composition of tar steam reforming (neglecting S/C ratio : 5, water and nitrogen).

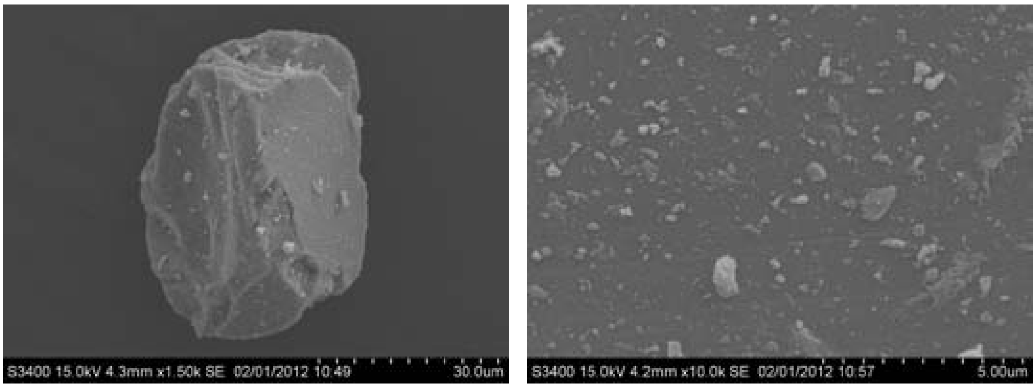
Catalyst	Reaction Temperature (°C)	Time (min)	Gas Composition (%mol)							
			H_2	CH_4	CO	CO_2	C_7H_8	C_6H_6O	$C_{10}H_8$	$C_{16}H_{10}$
10%Ni/Al_2O_3	450	40	97.26	15.85	n.a.	-	0.42	0.25	1.94	0.14
		80	94.29	11.33	n.a.	-	1.15	1.52	2.69	0.36
		120	82.23	13.67	n.a.	-	4.54	5.85	6.69	0.69
		160	62.56	1.45	n.a.	-	8.36	16.57	11.37	1.15
		200	36.19	-	n.a.	-	17.05	24.03	20.07	2.03
15%Ni/Al_2O_3	450	40	74.13	7.04	n.a.	18.07	0.15	0.29	0.01	0.03
		80	86.01	3.07	n.a.	9.17	0.24	0.63	0.79	0.10
		120	88.08	5.92	n.a.	-	0.81	2.53	2.45	0.21
		160	82.26	2.38	n.a.	-	2.05	8.40	4.95	0.32
		200	68.41	0.54	n.a.	-	5.28	17.46	7.84	0.47
20%Ni/Al_2O_3	450	40	68.67	2.46	n.a.	28.63	0.03	0.17	0.03	0.01
		80	53.44	1.79	n.a.	44.48	0.12	0.13	0.03	0.01
		120	53.39	1.35	n.a.	44.50	0.23	0.39	0.13	0.02
		160	51.08	1.34	n.a.	46.58	0.27	0.62	0.09	0.03
		200	52.20	1.16	n.a.	44.37	0.73	1.28	0.20	0.05



(a) 10%Ni/Al_2O_3



(b) 15%Ni/Al_2O_3



(c) 20%Ni/Al_2O_3

Figure 5.16 SEM images of catalysts after running tar steam reforming at T = 450°C, S/C ratio = 5 (a) 10% Ni/Al_2O_3, (b) 15% Ni/Al_2O_3, (c) 20%Ni/ Ni/Al_2O_3

5.3.3 Effect of reaction temperature

Table 5.4 shows the product compositions of the tar steam reforming of 20 %Ni/Al_2O_3 at 450, 550 and 650 °C and S/C ratio of 5. The results indicated that higher H_2 concentration (mol%) and H_2 product (mol/min) was achieved with increasing reaction temperature. At T = 650 °C, the value of the H_2 concentration was 83.85 mol%. Similarly, Figure 5.17 shows that %H_2 yield at 650 °C is the largest (about 61%). This is because the tar steam reforming is an endothermic reaction and, therefore, the reaction is favorable at high operating temperature due to both the thermodynamics and the improved kinetics at elevated temperature. Considering the CO_2 composition in the product, less CO_2 was present when increasing the operating temperature. The possible explanation is that the water gas shift reaction (Eq.2.22) is exothermic. At higher temperature, the reverse reaction consuming CO_2 becomes predominant.

The results on tar conversions are shown in Figure 5.18. All tar components could be better decomposed at higher temperatures. The conversions slightly decreased with increasing temperature except naphthalene which is the most difficult component with most difficult to be decomposed.

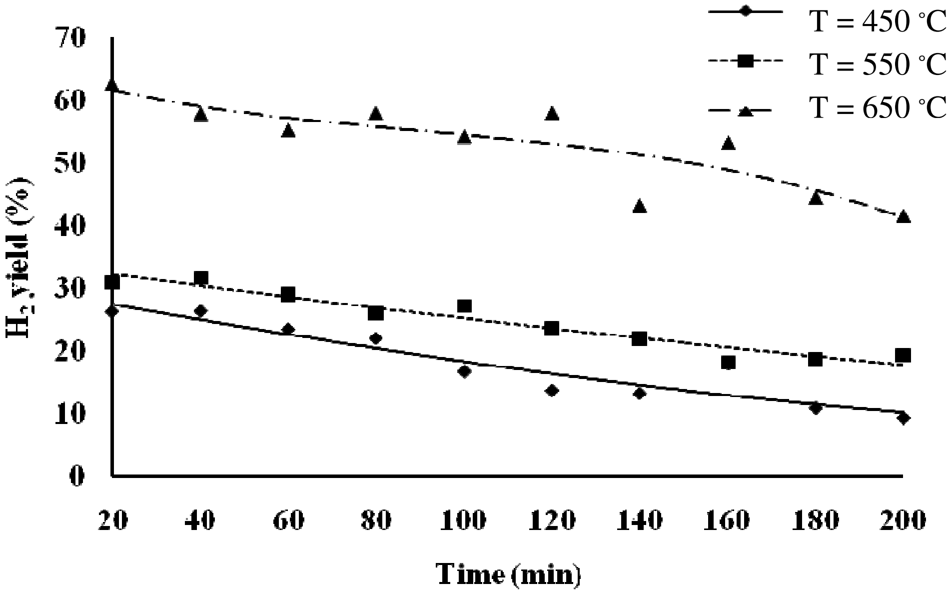
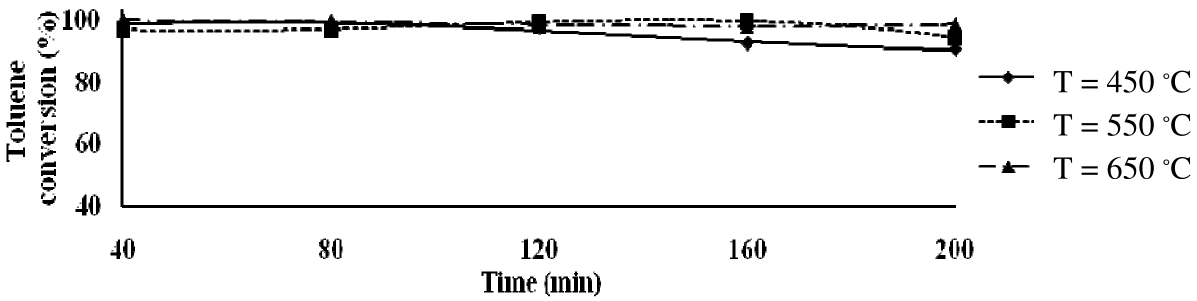
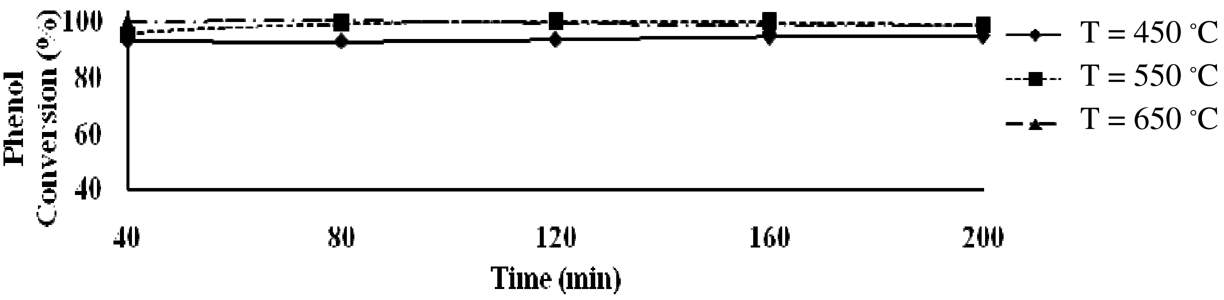


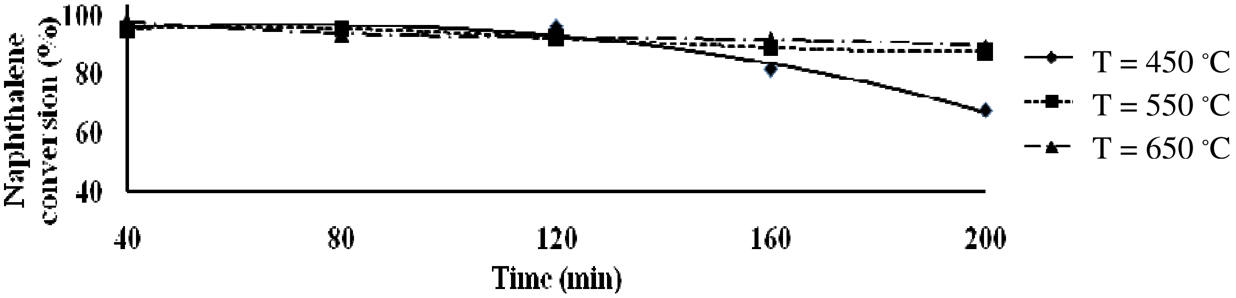
Figure 5.17 Effect of reaction temperature on the H_2 yield of 20%Ni/Al_2O_3 in tar steam reforming , (S/C ratio:5).



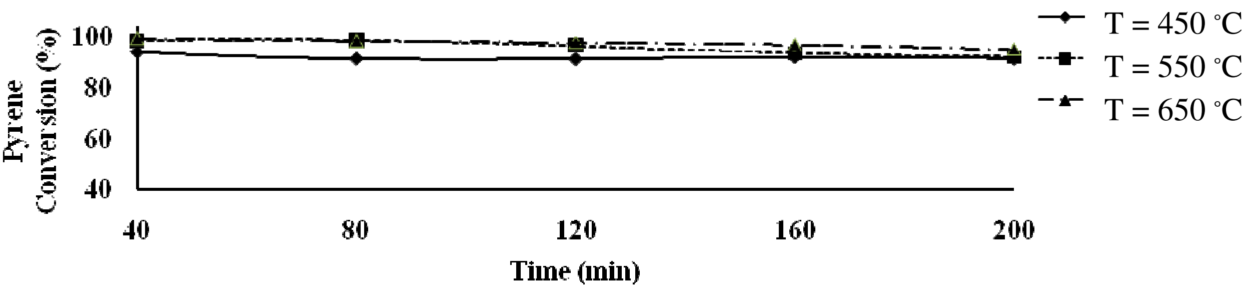
(a) Toluene



(b) Phenol



(c) Naphthalene



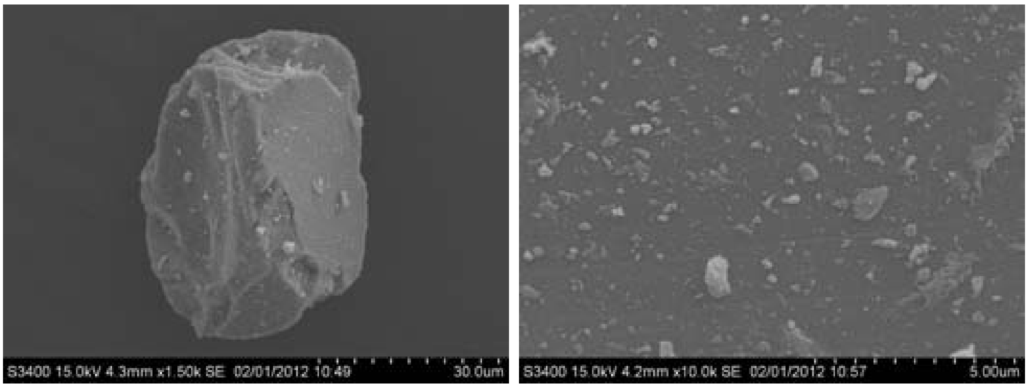
(d) Pyrene

Figure 5.18 Tar conversions of 20%Ni/Al_2O_3 catalyst on the tar steam reforming at various reaction temperatures, (a) Toluene, (b) Phenol, (c) Naphthalene, (d) Pyrene , (S/C ratio =5).

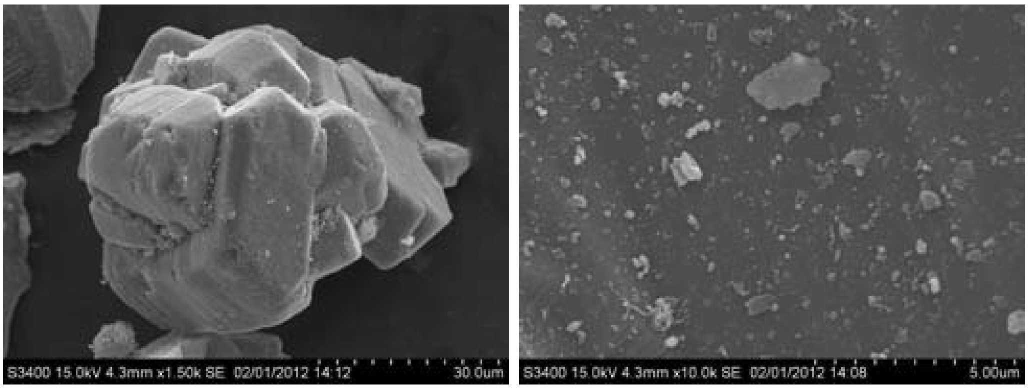
Table 5.4 Temperature effect on gas composition of tar steam reforming (S/C ratio = 5, neglecting water and nitrogen).

Catalyst	Reaction Temperature (˚C)	Time (min)	Gas Composition (%mol)							
			H_2	CH_4	CO	CO_2	C_7H_8	C_6H_6O	$C_{10}H_8$	$C_{16}H_{10}$
20%Ni/Al_2O_3	450	40	68.67	2.46	n.a.	28.63	0.03	0.17	0.03	0.01
		80	53.44	1.79	n.a.	44.48	0.12	0.13	0.03	0.01
		120	53.39	1.35	n.a.	44.50	0.23	0.39	0.13	0.02
		160	51.08	1.34	n.a.	46.58	0.27	0.62	0.09	0.03
		200	52.20	1.16	n.a.	44.37	0.73	1.28	0.20	0.05
	550	40	82.65	0.25	n.a.	17.06	0.01	0.07	-	-
		80	71.06	0.18	n.a.	28.14	0.01	0.01	0.07	-
		120	72.25	0.22	n.a.	27.14	0.14	0.17	0.09	0.01
		160	69.17	0.52	n.a.	29.80	0.21	0.18	0.35	0.01
		200	69.84	0.46	n.a.	28.70	0.25	0.30	0.44	0.02
	650	40	86.42	0.43	n.a.	13.15	-	-	-	-
		80	82.48	0.64	n.a.	16.76	-	-	0.12	-
		120	76.21	0.36	n.a.	23.32	-	-	0.11	-
		160	83.21	0.13	n.a.	16.37	0.05	0.08	0.15	0.01
		200	82.35	0.60	n.a.	16.61	0.09	0.14	0.20	0.01

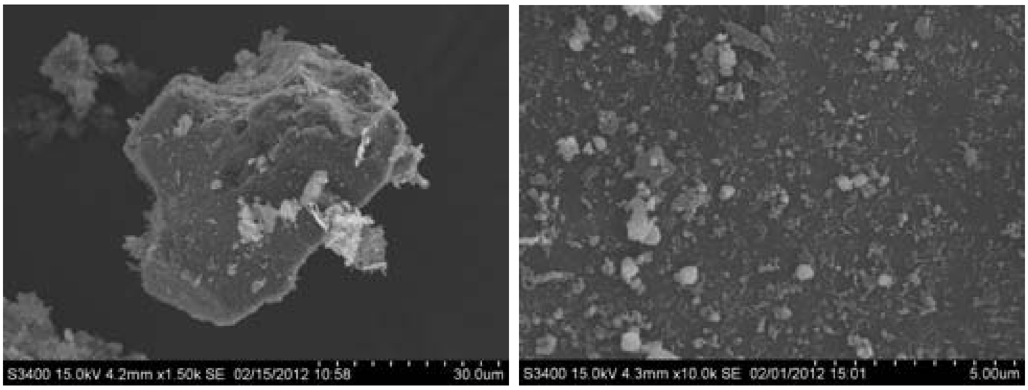
Figure 5.19 presents SEM images of the 20%Ni/Al_2O_3 catalyst after 200 min of tar steam reforming reaction at different temperatures (450, 550 and 650 °C, respectively). It was found that the Ni distribution on support decreased by increasing the reaction temperature. This is due to the more severe sintering problem of catalyst at higher temperature.



(a) T = 450 °C



(b) T = 550 °C



(c) T = 650 °C

Figure 5.19 SEM images of 20%Ni/Al_2O_3 catalysts after running tar steam reforming at different temperatures, (a) T = 450 °C, (b) T = 550 °C, (c) T = 650 °C, (S/C = 5).

5.3.4 Effect of S/C ratio

The effect S/C ratio at a range of 1-5 on tar steam reforming was performed using 20%Ni/Al_2O_3 at 650°C. The gas composition results of tar steam reforming after 200 min are given in Table 5.5. Increasing S/C ratio resulted in increasing H_2 product as well as %H_2 yield. The observed H_2 concentration and H_2 yield (Figure 5.20) varied in ranges of 74-85 mol% and 25-62 %, respectively. The highest H_2 product was observed at the S/C ratio of 5. Additional steam in the feed could help to improve the conversions of all tar components (Figure 5.21). The increased S/C ratio did not only promote the steam reforming but also the water gas shift reaction, resulting in higher H_2 concentration and yield.

The surface morphology of 20%Ni/Al_2O_3 catalysts after running reaction for 200 min is shown in Figure 5.22. Less metal agglomeration was observed for the catalysts tested at a higher S/C ratio. This should be another reason for the higher catalyst activity when operated at high S/C ratio.

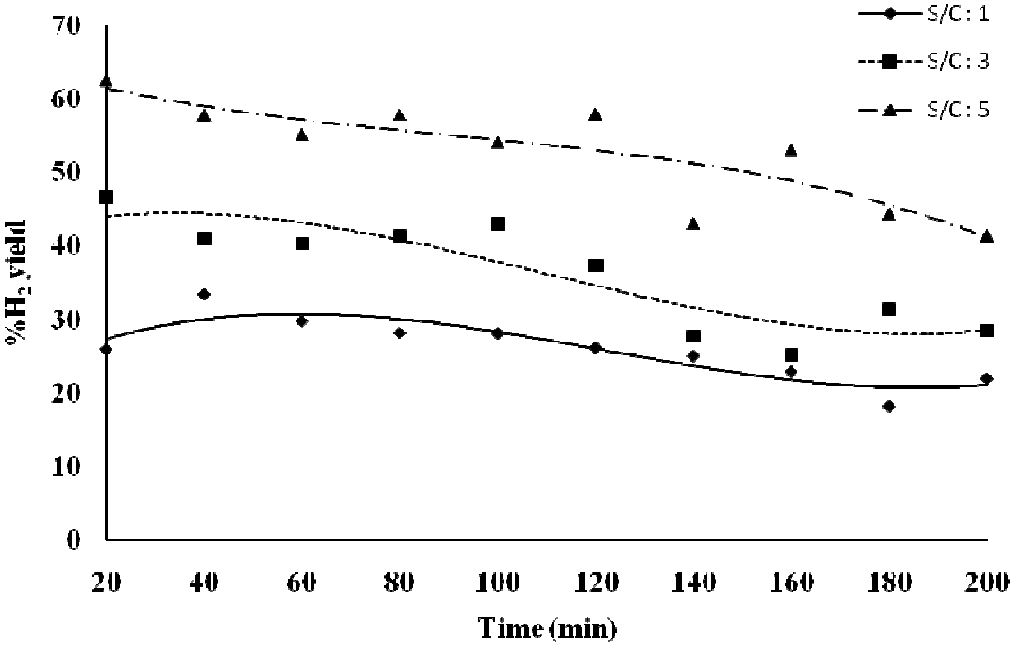
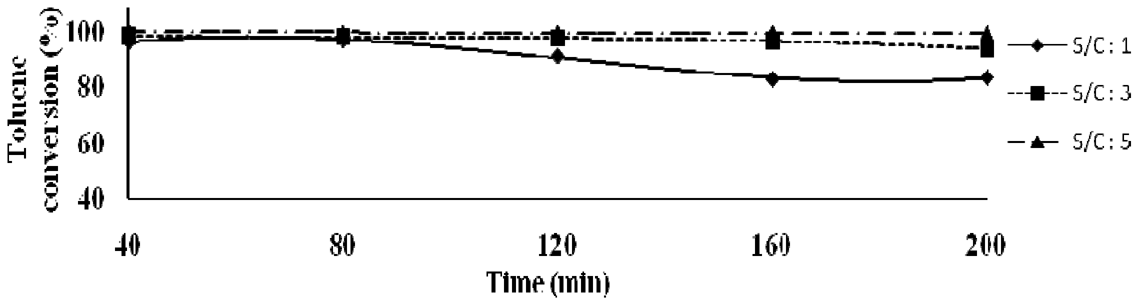
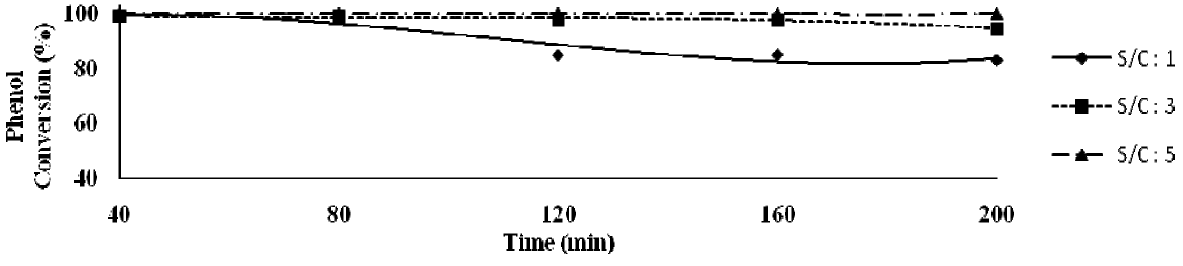


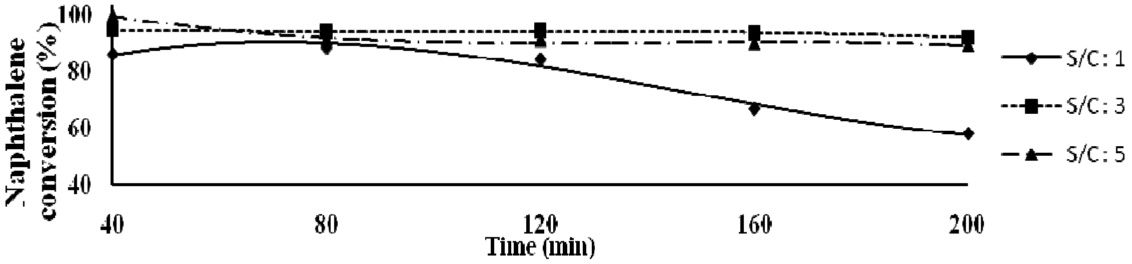
Figure 5.20 Effect of S/C ratio on % H_2 yield of tar steam reforming of 20%Ni/Al_2O_3 at T = 650 °C.



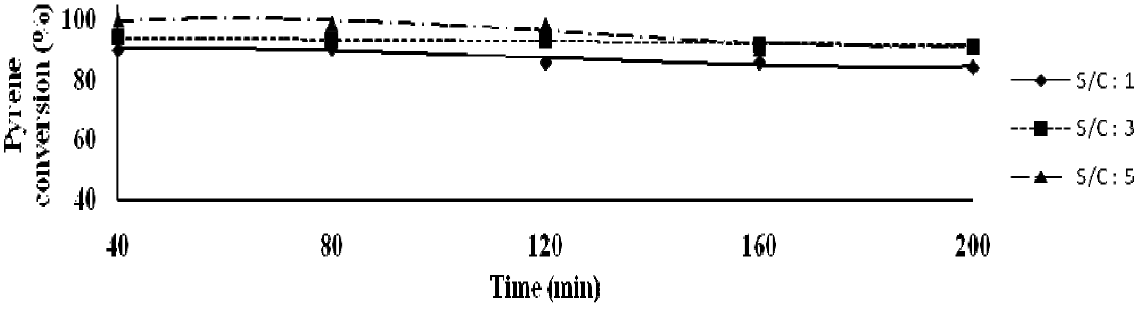
(a) Toluene



(b) Phenol



(c)Naphthalene

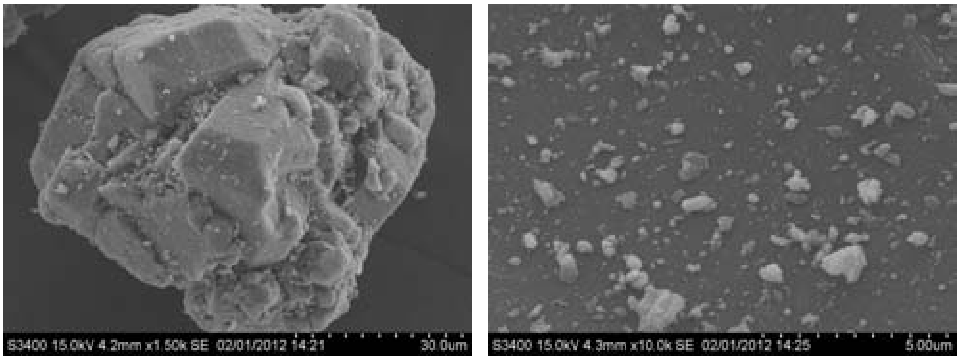


(d) Pyrene

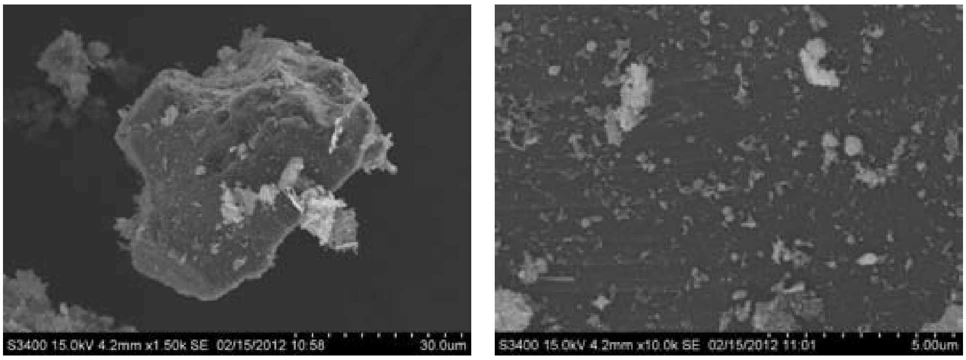
Figure 5.21 Tar conversions of 20%Ni/Al_2O_3 catalyst at various S/C ratios and T = 650 °C: (a) Toluene, (b) Phenol,(c) Naphthalene, (d) Pyrene.

Table 5.5 Effect of S/C ratio on gas composition of tar steam reforming (T = 650 °C, neglecting water and nitrogen).

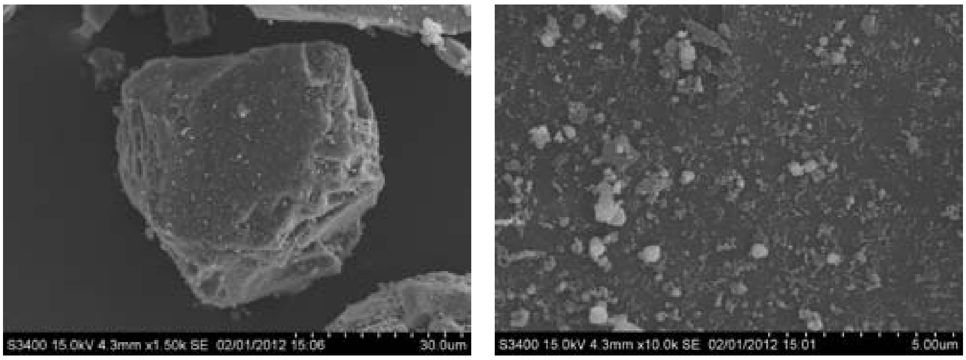
Catalyst	S/C ratio	Time (min)	Gas Composition (%mol)							
			H_2	CH_4	CO	CO_2	C_7H_8	C_6H_6O	$C_{10}H_8$	$C_{16}H_{10}$
$20\%Ni/Al_2O_3$	1	40	74.04	5.10	n.a.	20.36	0.10	0.10	0.28	0.02
		80	71.31	6.93	n.a.	21.25	0.10	0.12	0.27	0.02
		120	68.72	3.53	n.a.	25.60	0.30	1.44	0.37	0.03
		160	65.37	1.88	n.a.	29.66	0.63	1.56	0.86	0.04
		200	59.76	1.62	n.a.	35.23	0.60	1.72	1.06	0.01
	3	40	76.04	1.65	n.a.	22.11	0.04	0.07	0.09	0.01
		80	67.26	4.45	n.a.	28.08	0.04	0.07	0.09	0.01
		120	64.45	6.46	n.a.	28.80	0.05	0.14	0.09	0.01
		160	68.34	1.67	n.a.	29.48	0.11	0.21	0.16	0.02
		200	59.46	12.02	n.a.	37.77	0.16	0.41	0.15	0.02
	5	40	86.42	0.43	n.a.	13.15	-	-	-	-
		80	81.87	0.66	n.a.	17.35	-	-	0.12	-
		120	76.21	0.36	n.a.	23.32	-	-	0.11	-
		160	82.91	0.48	n.a.	16.31	0.05	0.08	0.15	0.01
		200	82.35	0.60	n.a.	16.61	0.09	0.14	0.20	0.01



(a) S/C :1



(b) S/C :3



(c) S/C :5

Figure 5.22 SEM images of 20%Ni/Al_2O_3 catalysts after running tar steam reforming at different S/C ratios at T = 650 °C: (a) S/C = 1, (b) S/C = 3, (c) S/C = 5.

5.3.5 Effect of tar compounds obtained from biomass gasification at various temperatures

Tar compositions from biomass gasification are dependent on type of biomass and operating condition. Figure 5.1 shows tar compositions from gasification of biomass (wood) at different temperatures (700–900°C) (Brage *et al.*,1996).

In this study the synthetic tar compounds were prepared by mixing each tar component at its corresponding composition to represent the real tar from biomass gasification. For tar from biomass gasification at 700 °C, the tar mixture was in liquid phase and could be fed directly to the reaction system using a syringe pump. However, the tar from the gasification at 800 and 900 °C mainly consisted of components in solid phase. Therefore, heating coils were needed to wrap around the syringe and feeding tubes to keep the feed solution at a high temperature and to preheat the feed. Based on this setup, experiments could be operated for the tar composition from the gasification at 800 °C; however, it was still unable to handle with the tar from the gasification at 900 °C unless the feeding system was further modified to withstand a higher temperature. In this study, only the tars from the gasification at 700 and 800 °C were considered

The effect of the tar compounds obtained from biomass gasification at different temperatures on tar steam reforming was performed using 20%Ni/Al_2O_3 at 650 °C and S/C ratio of 5. It was found that tar compound from biomass gasification at 800 °C gave the higher H_2 product and H_2 yield (Figure 5.23) than the compound at 700 °C. Figure 5.24 shows the undivided tar conversions of toluene, phenol, naphthalene and pyrene. The conversions of the tar from gasification at 800 °C were higher for all components except naphthalene. These results can be explained by considering the tar compositions. The content of naphthalene in the tar significantly increased with increasing gasification temperature. As naphthalene is a component which is more difficult to be decomposed, the conversion of naphthalene in the reforming reaction became lower for the tar from the gasification at 800 °C than the one from the gasification at 700 °C while the lower extents of other components allow their more complete conversions.

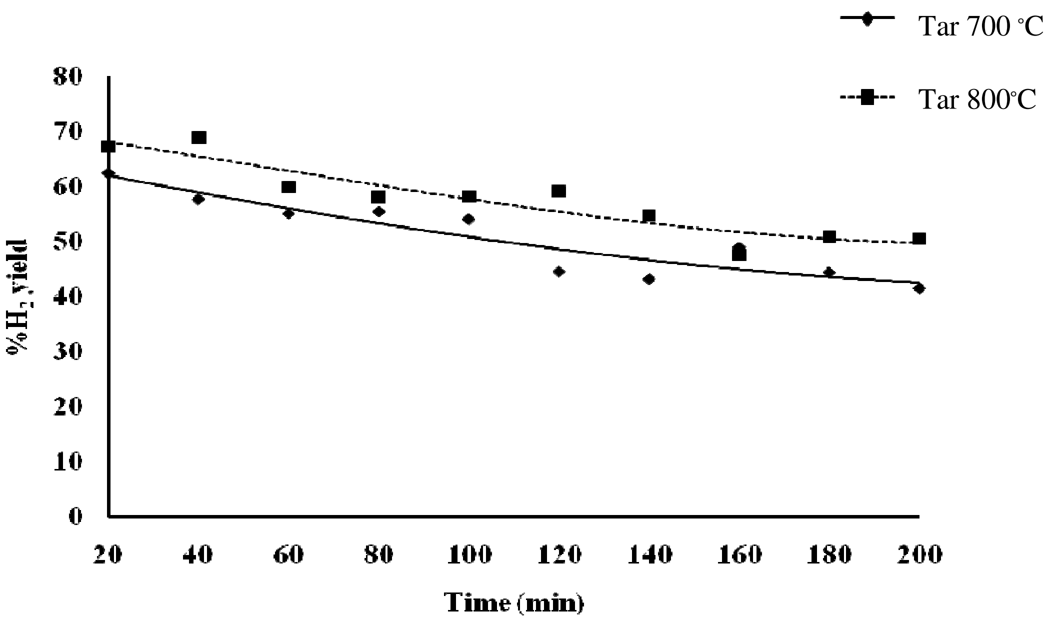
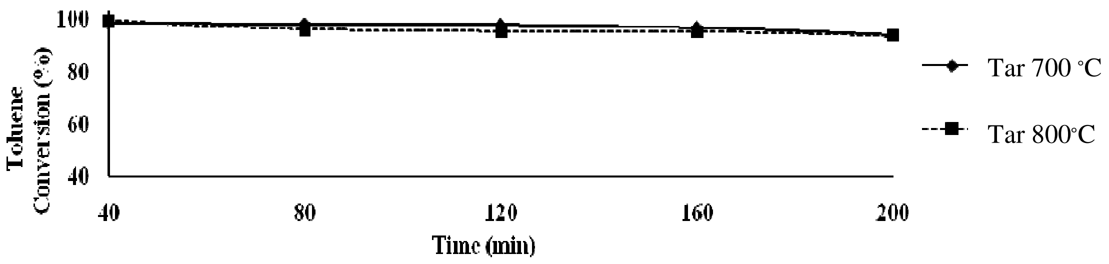
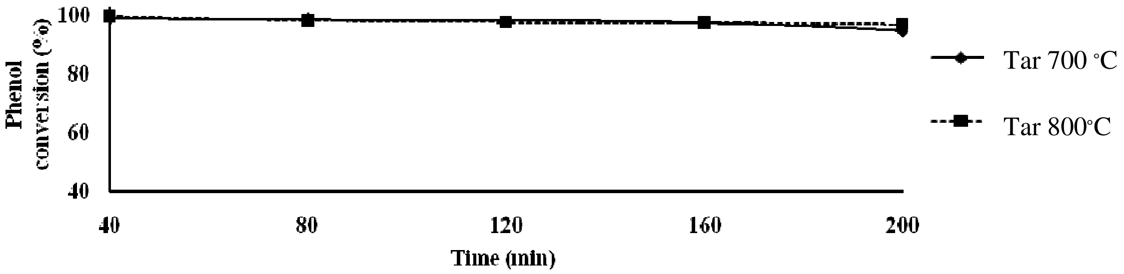


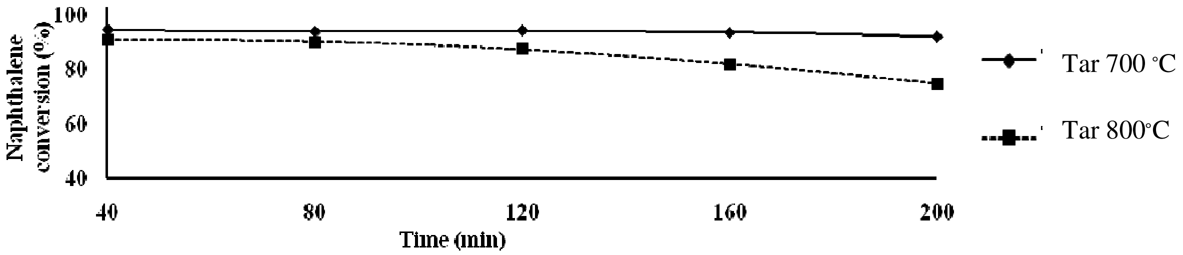
Figure 5.23 Effect of tar compositions from biomass gasification at different temperatures on % H_2 yield (20%Ni/Al_2O_3, T = 650°C and S/C = 5).



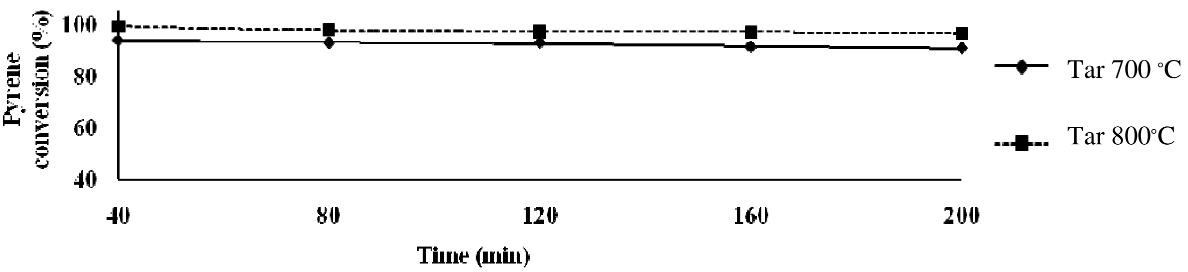
(a) Toluene



(b) Phenol



(c) Naphthalene



(d) Pyrene

Figure 5.24 Effect of tar obtained from biomass gasification at different temperatures on tar conversions (20%Ni/Al_2O_3, T = 650 °C and S/C = 5): (a) Toluene, (b) Phenol, (c) Naphthalene, (d) Pyrene

5.4 Catalyst characterization after running reaction

Catalyst characterization to analyze carbon deposition on the catalysts after operating the tar steam reforming reaction for 200 min was carried out using Thermo gravimetric analysis (TGA).

The reactivity of the catalysts becomes less when carbon deposition is formed on catalyst. There are many reaction routes that cause the formation of carbon or coke on the catalyst, for examples, thermal or catalytic cracking of tar compounds or their intermediate products.

Table 5.6 shows the weight changes of the used catalysts after 200 min of reaction time. The measurement was carried out up to 900 °C. It was found that the weight loss was more significant when the reforming took place at higher temperatures which promote cracking reactions. The carbon deposition could be reduced by operating the system at a higher S/C ratio as it is well known that the extra water could reduce the formation of various coke precursors. The previous results of 20%Ni/Al_2O_3 catalyst indicated that increasing S/C ratio has resulted in the increased production of hydrogen. Movever, the carbon deposition on surface area of the catalyst is reduced. Wang *et al.*, (2010) reported that increasing steam reaction could reduce the tar content and prevent the tar molecular adsorption on the catalyst surface, Thus preventing the carbon deposition on the catalyst. Increasing the reaction temperature promotes the thermal cracking of tar thus, it increases the amount of coke. The results showed that with increasing temperature, the hydrogen content increased reaction especially at high S/C ratio, this could be due to the faster kinetics The change in %Ni loading did not significantly affect the carbon deposition on the catalyst.

Table 5.6 The result of carbon deposition with TGA.

Catalyst	Condition reaction		Carbon deposition (%wt. loss)
	Temperature (°C)	S/C ratio	
10%Ni/Al_2O_3	450	5	1.57
15%Ni/Al_2O_3	450	5	1.15
20%Ni/Al_2O_3	450	5	1.39
20%Ni/Al_2O_3	550	5	2.41
20%Ni/Al_2O_3	650	5	5.40
20%Ni/Al_2O_3	650	1	6.81
20%Ni/Al_2O_3	650	3	5.95
20%Ni/Al_2O_3	650	5	5.34

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

In this research, the removal of tar from biomass gasification by steam reforming over nickel catalysts was investigated. The effects of type of support, %Ni loading, tar composition from biomass gasification and conditions (reaction temperature, S/C ratio) on the tar steam reforming reaction were considered. Sections 6.1 and 6.2 provide the conclusion and suggestion for future works, respectively.

6.1 Conclusions

1. The results of thermodynamic simulations in tar steam reforming reaction indicate that tar was favorably converted to synthesis gas (H_2,CO_2,CH_4 and CO) at high temperatures and S/C molar ratio. The composition of tar derived from biomass gasification at 800 °C offers the highest H_2 content. So, it is a great opportunity to bring the results of simultaneous tar steam reforming to study in the experimental system.
2. The experimental results in tar steam reforming were in good agreement with the trends observed in the thermodynamic simulation that high temperature operation and S/C ratio are favorable to hydrogen production. The high reaction temperature results in more carbon deposition on the catalyst due to catalytic cracking of tar (aromatic hydrocarbons) but high S/C ratio can retard the carbon deposition. 20%Ni/Al_2O_3 as a suitable catalyst showed stable activity for tar steam reforming at 650 °C and S/C ratio of 7.
3. Characterization of fresh catalysts by XRD, BET and SEM methods indicated that the Al_2O_3 support has BET surface and pore volume greater than CaO and MgO supports. The support Al_2O_3 allows the nickel loading into pore volume and surface area. When the %Ni loading was increased, the Ni distribution on surface area of alumina support becomes better. Then, 20%Ni/Al_2O_3 catalyst has good stability and suitability in tar steam reforming reaction.

4. Tar compositions are dependent on biomass gasification temperature. The steam reforming of tar from biomass gasification at 800 °C shows the highest hydrogen production as its compositions are hydrocarbon compounds that are easy to be decomposed.

5. Naphthalene and pyrene are the tar components that are stable and difficult to decompose in the tar steam reforming but toluene and phenol are easily eliminated, resulting in increased hydrogen content.

6.2 Recommendation

From the results mentioned above**,** the suggestions for further research are as follows:

1. The durability of catalyst in the tar steam reforming reaction for a long reaction time should be carried out to understand the deactivation and to design a novel catalyst.

2. Catalyst regeneration to remove the carbon deposition and to prolong the reaction time should also be considered.

3. The results of the study on the effect of tar steam reforming indicated that Al_2O_3 support is the high hydrogen content but, CaO support also gives high hydrogen content at early reaction time but, the CaO performance decreases rather quickly. It is known that CaO is a good adsorbent for CO_2 adsorption. The high performance of CaO at initial stage may be due to the reaction enhancement by the CO_2 adsorption. Further study on periodic concept on this CaO supported catalyst for this reaction should be interesting.

4. In the study reaction, should be to temperature programmed is ideal temperature for reaction.

5. Each of tar used in the study had the ability and features of different tar steam reforming reaction. Therefore, it should de study in the kinetic reaction of tar.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

In this case, the catalysts were prepared by incipient wetness impregnation method for different Ni contents (10, 15 and 20 wt%). The calculations were as follows:

For example, to prepare 15%Ni preparation by incipient wetness impregnation method using ($Ni(NO_3)_2.6H_2O$) for nickel source.

Molecular weight of Ni	=	58.6934
Molecular weight of $Ni(NO_3)_2.6H_2O$	=	290.79

Calculation of Ni content by 15 wt%.

For 100 g of the catalyst, the support weight is 85 g while the metal is 15 g. In the study, 3 g of support was used in the catalyst preparation.

If the support is 3 g so, the amount of metal is (15 / 85) × 3 = 0.5294 g We will configure the above value X g.

The metal content used to scale of precursor which calculated from formula

$= (FW \times X) / (B \times C)$

FW = Molecular weight of the precursor

B = Number of nickel atoms in the precursor

C = Weight

So, the Ni content $= (270.79 \times 0.5294) / (1 \times 58.6934)$

$= 2.6229$ g

APPENDIX B

CALIBRATION CURVE

Appendix B shows the calibration curve used to calculate amount of product from tar steam reforming reaction at various conditions. The desired product of the reaction is H_2 and the side products are CO, CO_2, CH_4. Moreover, it might be a reactant remaining in the gas outlet consisting of toluene, phenol, naphthalene and pyrene.

The gas chromatography (GC-8A) equipped with a thermal conductivity detector (TCD) with a molecular sieve 5A column and a porapak Q column operated with Ar as a carrier gas are employed to analyze the product gases (H_2, CO, CO_2, CH_4). Toluene, naphthalene, phenol and pyrene are analyzed by a gas chromatography (GC-14B) equipped with flame ionization detector (FID) with a ZB-5HT Inferno column.

Figure B.1-B.8 show the calibration curves whose Y-axis shows the mole of standard compound (hydrogen, carbon monoxide, carbon dioxide, methane, toluene, phenol, naphthalene and pyrene) and X-axis shows areas peak obtained from analysis of gas chromatography. The calibration curves of hydrogen, carbon monoxide, carbon dioxide, methane, toluene, phenol, naphthalene and pyrene are shown in **Figures B1-B8**, respectively.

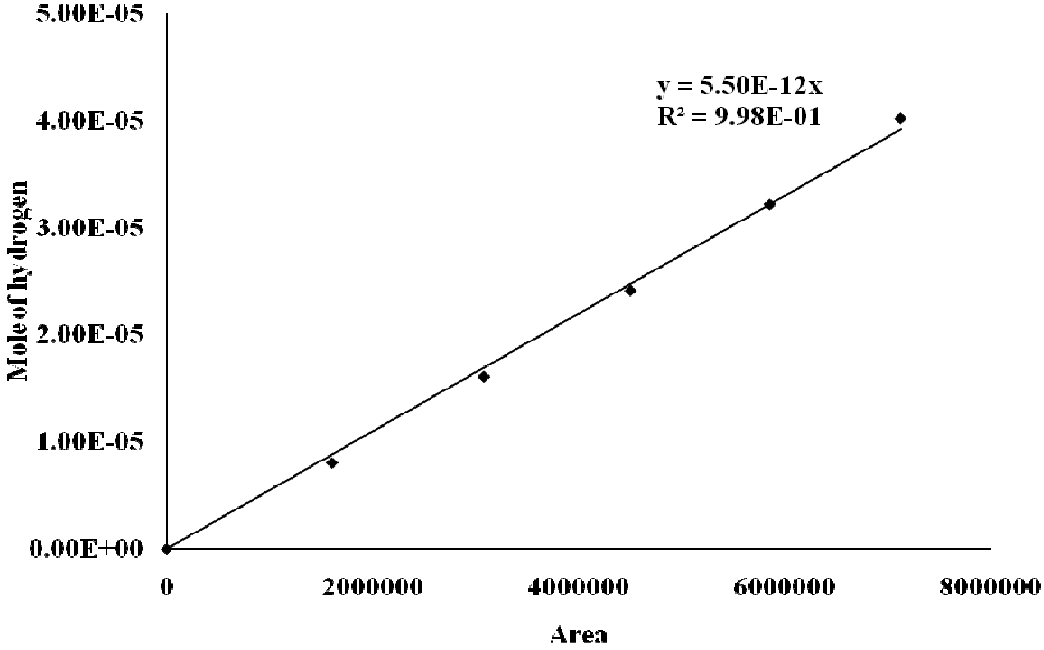

Figure B1 The calibration curve of hydrogen

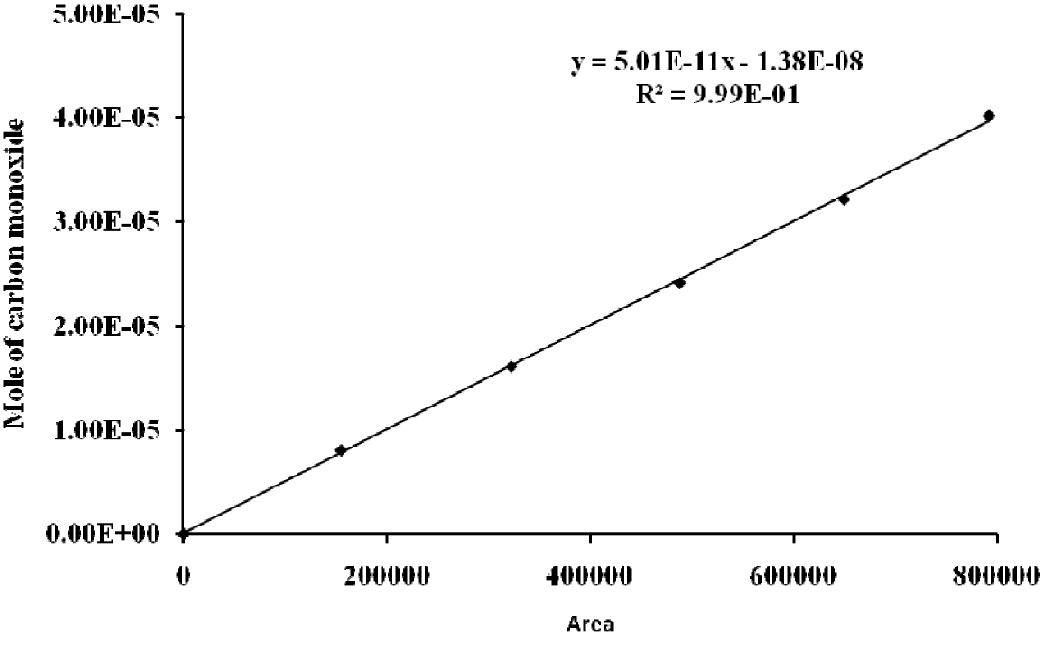

Figure B2 The calibration curve of carbon monoxide

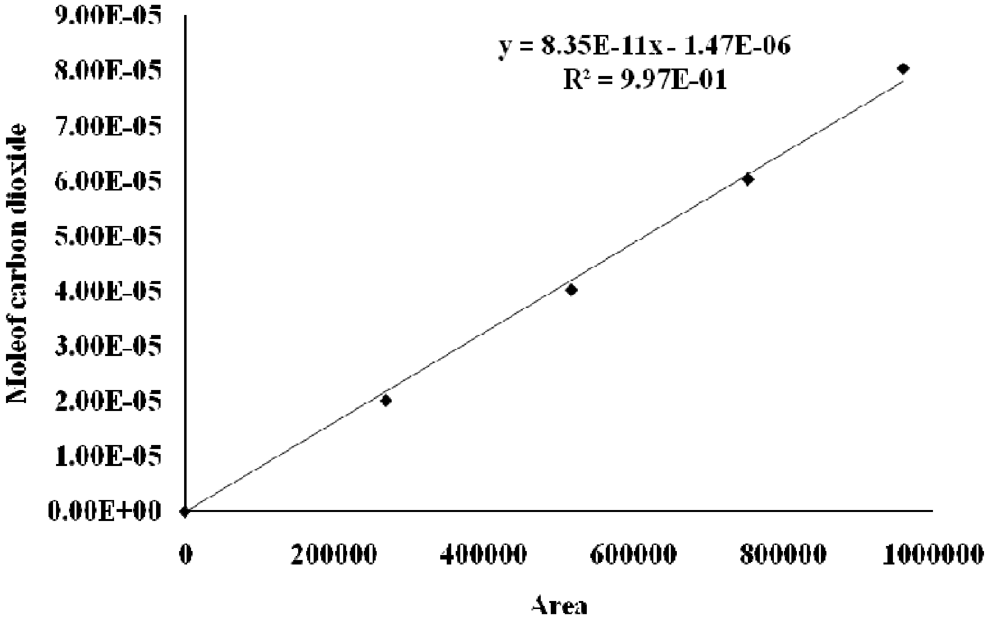

Figure B3 The calibration curve of carbon dioxide

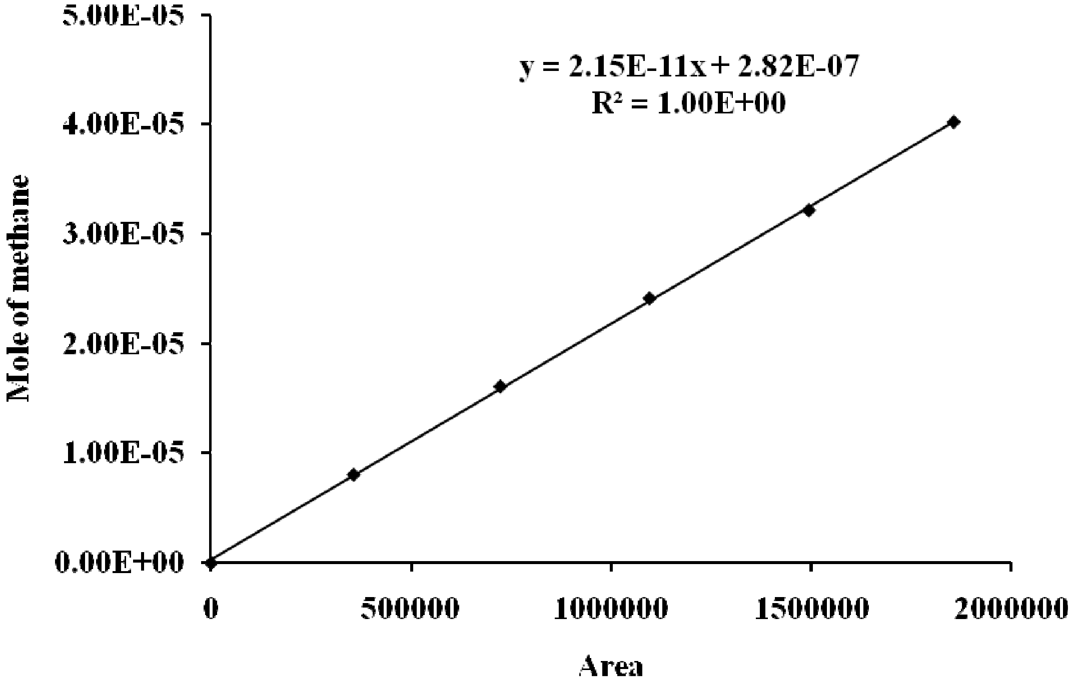

Figure B4 The calibration curve of methane

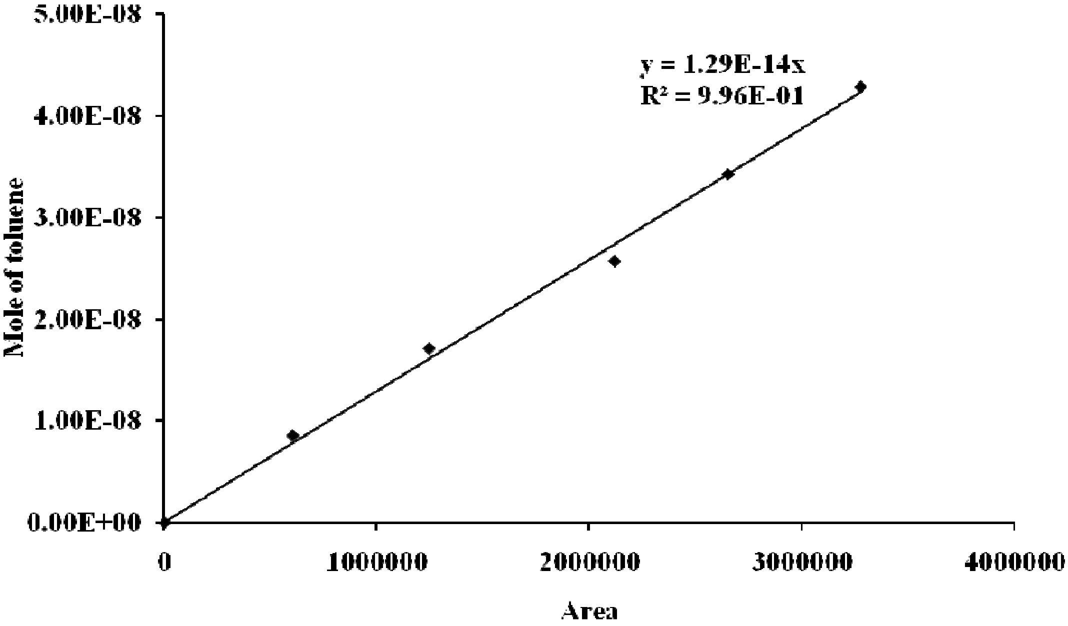

Figure B5 The calibration curve of toluene

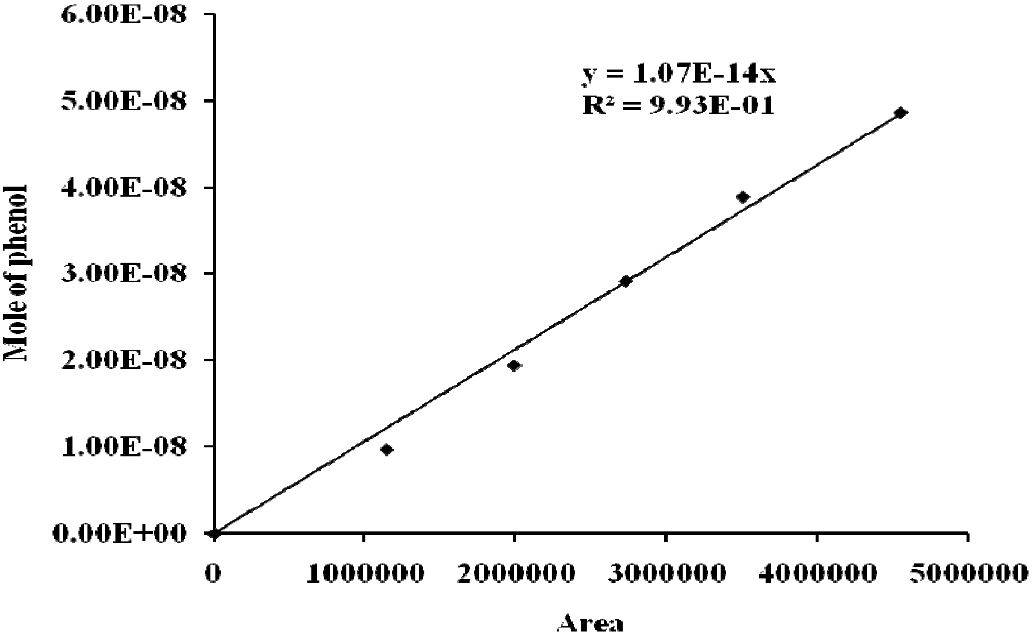

Figure B6 The calibration curve of phenol

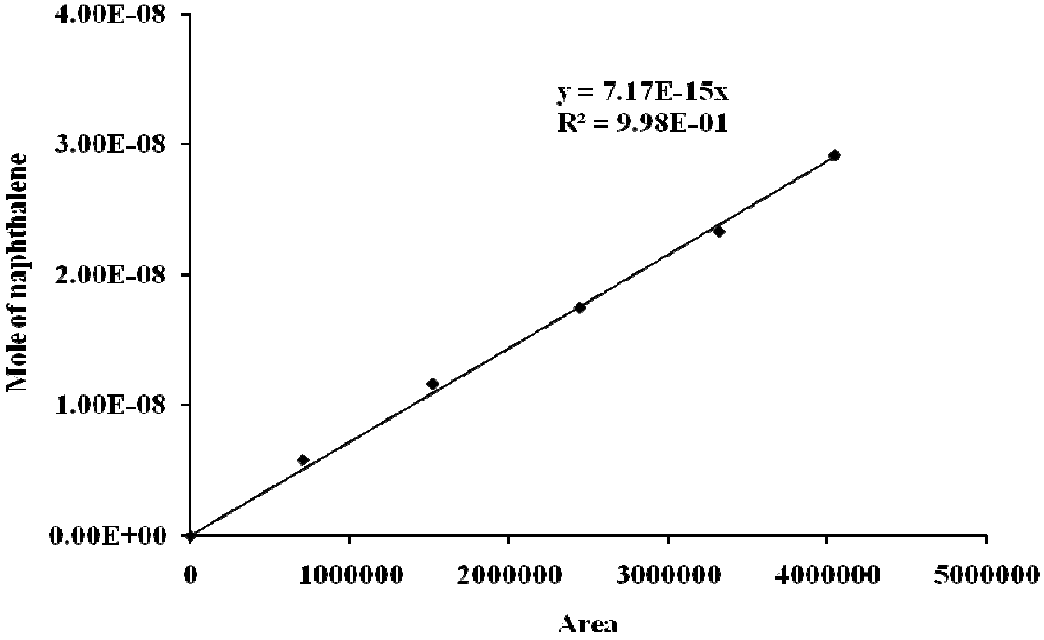

Figure B7 The calibration curve of naphthalene

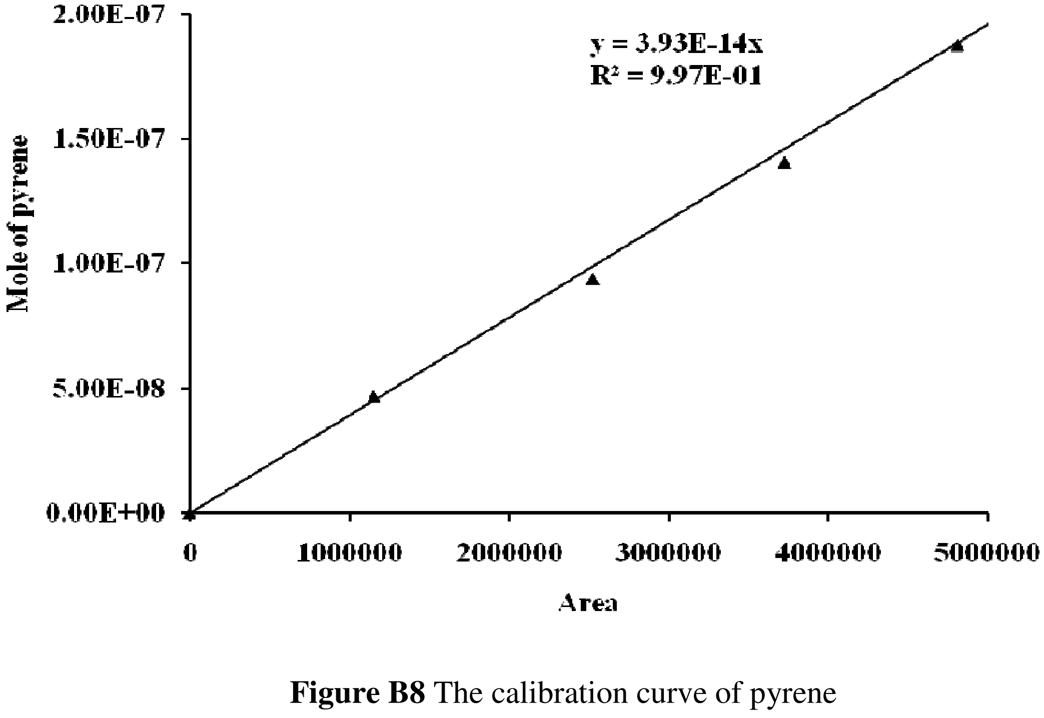

Figure B8 The calibration curve of pyrene

APPENDIX C

CALCULATION OF CONVERSION, PRODUCTIVITY AND HYDROGEN YIELD

The catalytic performance for the reaction between tar (toluene, phenol, naphthalene and pyrene) and steam (water) in tar steam reforming reaction was evaluated in term of conversion to represent the catalytic activity of the catalysts.

1. The percentage of gas productivity

$$\text{Productivity of hydrogen} = \frac{\text{(Mole of hydrogen, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C1)}$$

$$\text{Productivity of methane} = \frac{\text{(Mole of methane, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 2)}$$

$$\text{Productivity of carbon monoxide} = \frac{\text{(Mole of carbon monoxide, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 3)}$$

$$\text{Productivity of carbon dioxide} = \frac{\text{(Mole of carbon dioxide, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 4)}$$

$$\text{Productivity of toluene} = \frac{\text{(Mole of hydrogen, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 5)}$$

$$\text{Productivity of naphthalene} = \frac{\text{(Mole of naphthalene, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 6)}$$

$$\text{Productivity of phenol} = \frac{\text{(Mole of phenol, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 7)}$$

$$\text{Productivity of pyrene} = \frac{\text{(Mole of pyrene, out)}}{\text{Overall mole of product}} \times 100 \qquad \text{(C 8)}$$

Where moles of hydrogen, methane, carbon monoxide, carbon dioxide, toluene, naphthalene, phenol and pyrene can be measured by employing the calibration curve in **Figures B1-B8** respectively, **Appendix B**.

Mole of hydrogen
= ((Area of hydrogen peak from integrator plot on GC-9A) $\times 5.5\times10^{-12}$) (C9)

Mole of methane
= ((Area of methane hydrogen peak from integrator plot on GC-9A)
$\times 2.15\times10^{-11}$-$1.49\times10^{-6}$) (C10)

Mole of carbon monoxide
= ((Area of carbon monoxide peak from integrator plot on GC-9A)
$\times 5.0\times10^{-11}$-1.38×10^{-8}) (C11)

Mole of carbon dioxide
= ((Area of carbon dioxide peak from integrator plot on GC-9A)
$\times 8.3\times10^{-11}$-1.49×10^{-6}) (C12)

Mole of toluene
= ((Area of toluene peak from integrator plot on GC-14B) $\times 1.29\times10^{-14}$) (C13)

Mole of naphthalene
= ((Area of naphthalene peak from integrator plot on GC-14B) $\times 7.17\times10^{-15}$) (C14)

Mole of phenol
= ((Area of phenol peak from integrator plot on GC-14B) $\times 1.07\times10^{-14}$) (C15)

Mole of pyrene

= ((Area of pyrene peak from integrator plot on GC-14B) $\times 3.93\times 10^{-14}$) (C16)

Therefore,

Moles of all products

= (mole of hydrogen + mole of methane + mole of carbon monoxide + mole of carbon dinoxide + mole of toluene + mole of naphthalene + mole of phenol + mole of pyrene) (C17)

2. The percentage of tar conversion

$$\%\ \text{toluene conversion} = \frac{(\text{Mole of toluene, in - Mole of toluene, out})}{\text{Mole of toluene, in}} \times 100 \qquad \text{(C18)}$$

$$\%\ \text{naphthalene conversion} = \frac{(\text{Mole of naphthalene, in - Mole of naphthalene, out})}{\text{Mole of naphthalene, in}} \times 100 \qquad \text{(C19)}$$

$$\%\ \text{phenol conversion} = \frac{(\text{Mole of phenol, in - Mole of phenol, out})}{\text{Mole of phenol, in}} \times 100 \qquad \text{(C20)}$$

$$\%\ \text{pyrene conversion} = \frac{(\text{Mole of pyrene, in - Mole of pyrene, out})}{\text{Mole of pyrene, in}} \times 100 \qquad \text{(C21)}$$

3. The percentage of hydrogen yield

$$\%\ \text{hydrogen yield} = \left(\frac{\text{Mole of hydrogen, out}}{\text{Overall mole of hydrongen present in tar}}\right) \times 100 \qquad \text{(C22)}$$

Therefore, overall mole of hydrogen present in tar

= (11 × Mole of toluene, in) + (14 × Mole of naphthalene, in) + (8× Mole of phenol, in) + (21 × Mole of pyrene, in) +(7 × Mole of toluene, in)+ (10 × Mole of naphthalene, in) +(6× Mole of phenol, in)+ (16 × Mole of pyrene, in) (C23)

APPENDIX D

DATA EXPERIMENTAL

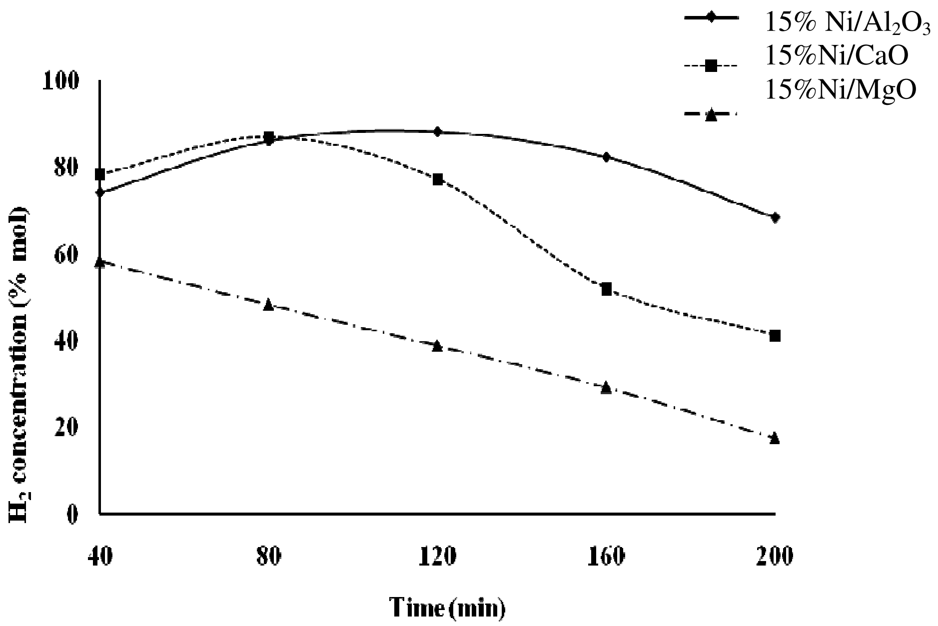

Figure D1 Effect of catalyst support on the tar steamreforming at T=450 °C, S/C ratio: 5 and the estimated curve of H_2 concentration (%mol).

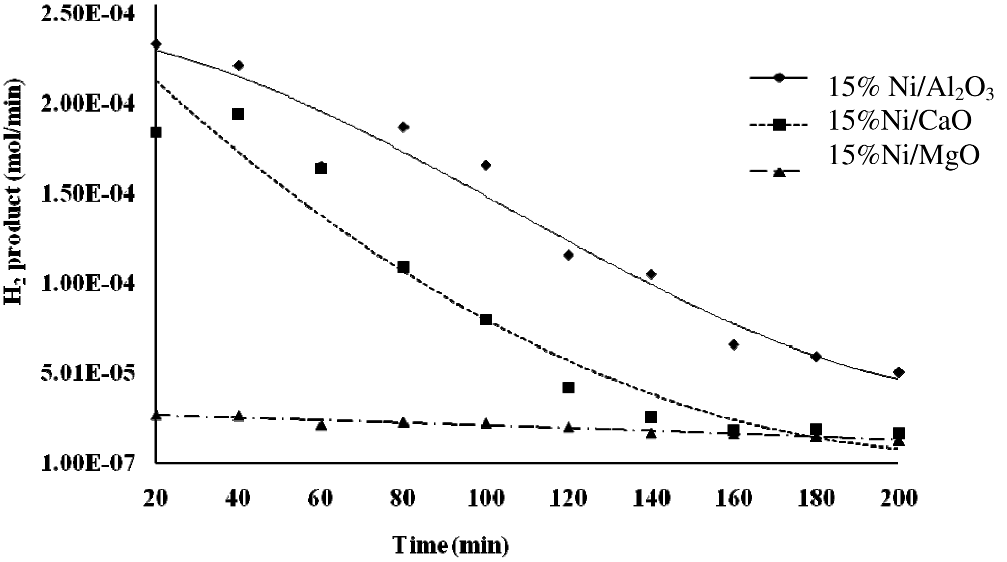

Figure D2 Effect of catalyst support on the tar steam reforming at T=450 °C, S/C ratio:5 and the estimated curve of H_2 product (mol/min).

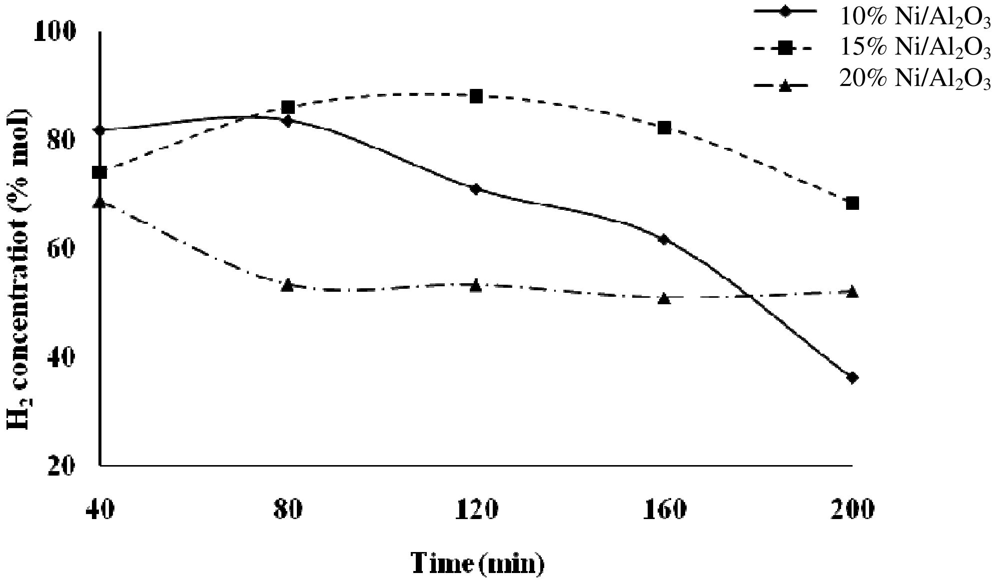

Figure D3 Effect of %Ni loading of Ni/Al_2O_3 on H_2 concentration (%mol) of tar steam reforming (T = 450 °C and S/C ratio = 5).

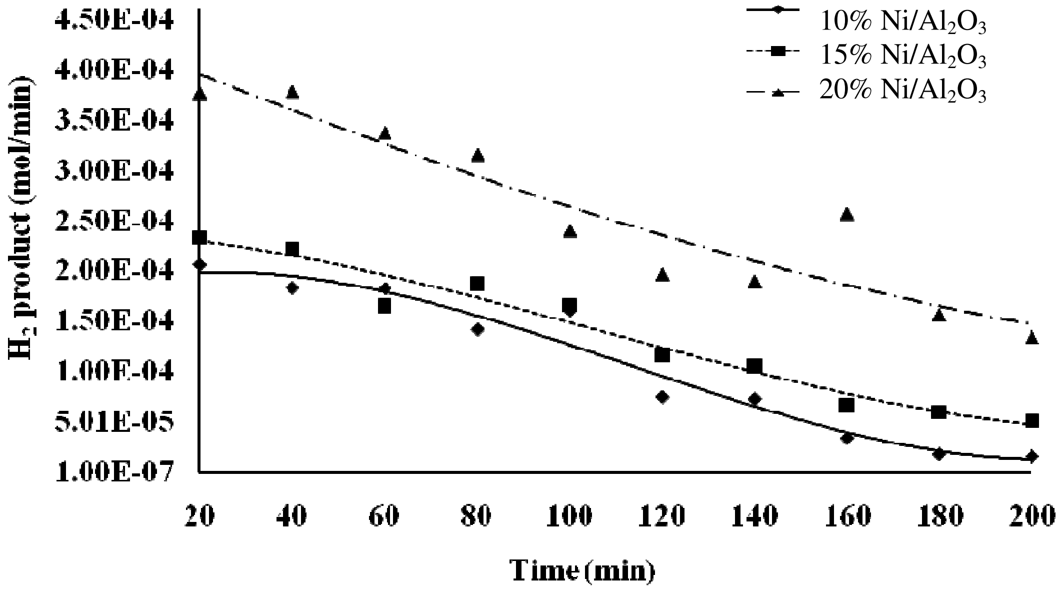

Figure D4 Effect of %Ni loading of Ni/Al_2O_3 on H_2 product (mol/min)of tar steam reforming (T = 450 °C and S/C ratio = 5).

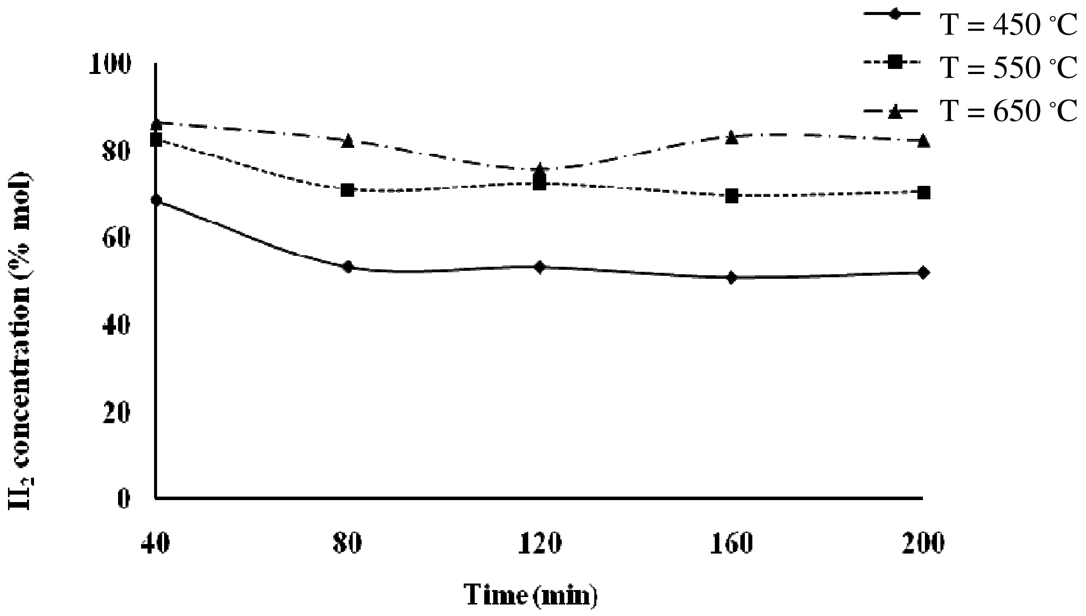

Figure D5 Effect of reaction temperature on H_2 concentration (mol%) of tar steam reforming (20%Ni/Al_2O_3, S/C ratio = 5).

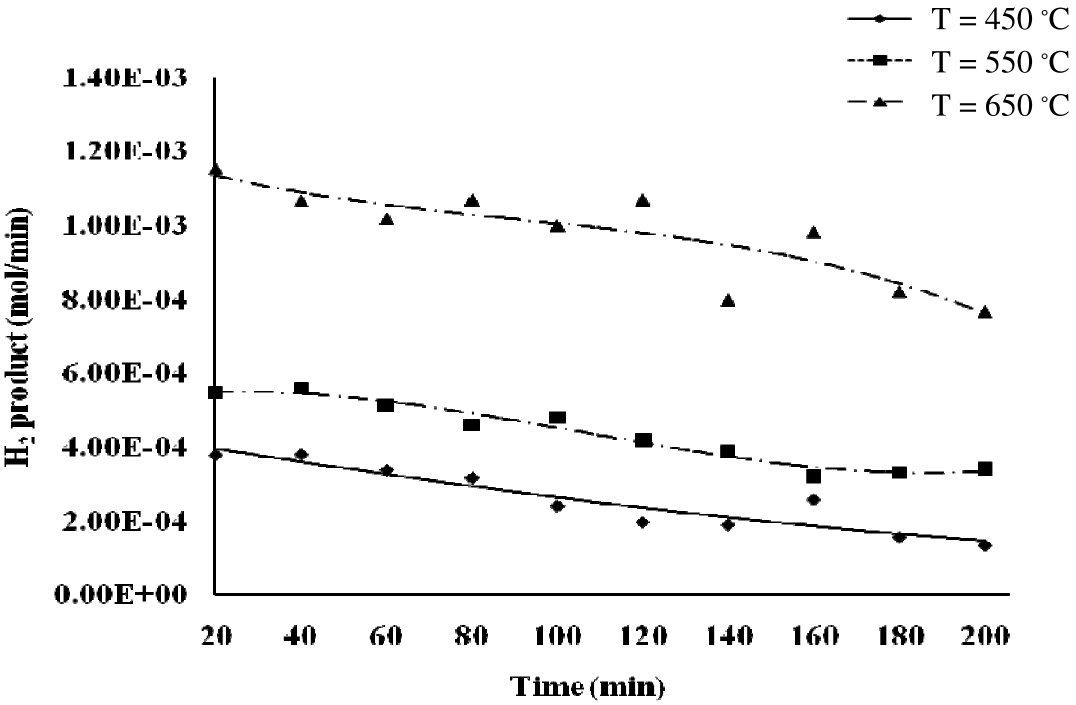

Figure D6 Effect of reaction temperature on H_2 product (mol/min) of tar steam reforming (20%Ni/Al_2O_3, S/C ratio = 5).

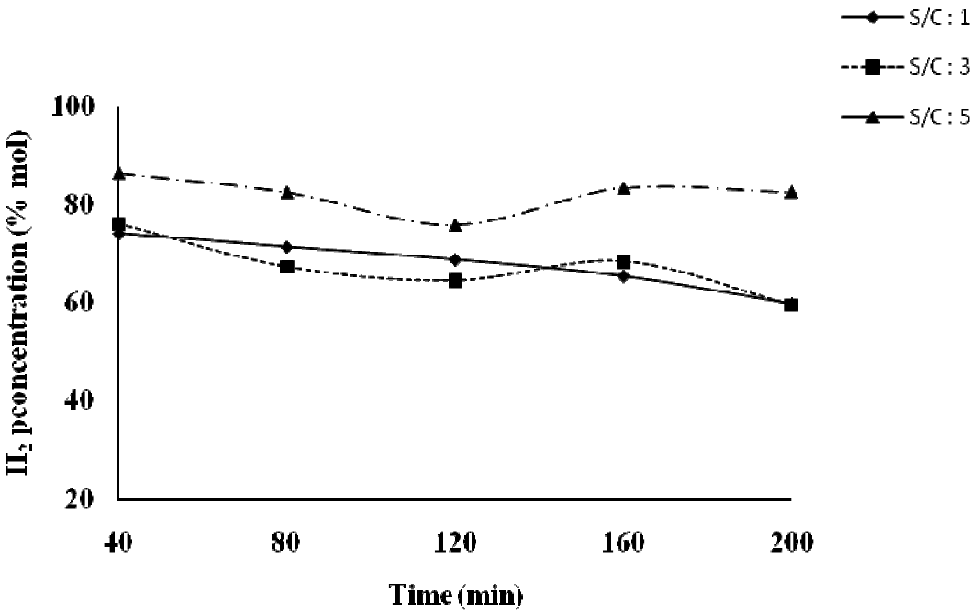

Figure D7 Effect of S/C ratio on H_2 concentration (mol%) of tar steam reforming of 20%Ni/Al_2O_3 at T = 650 °C.

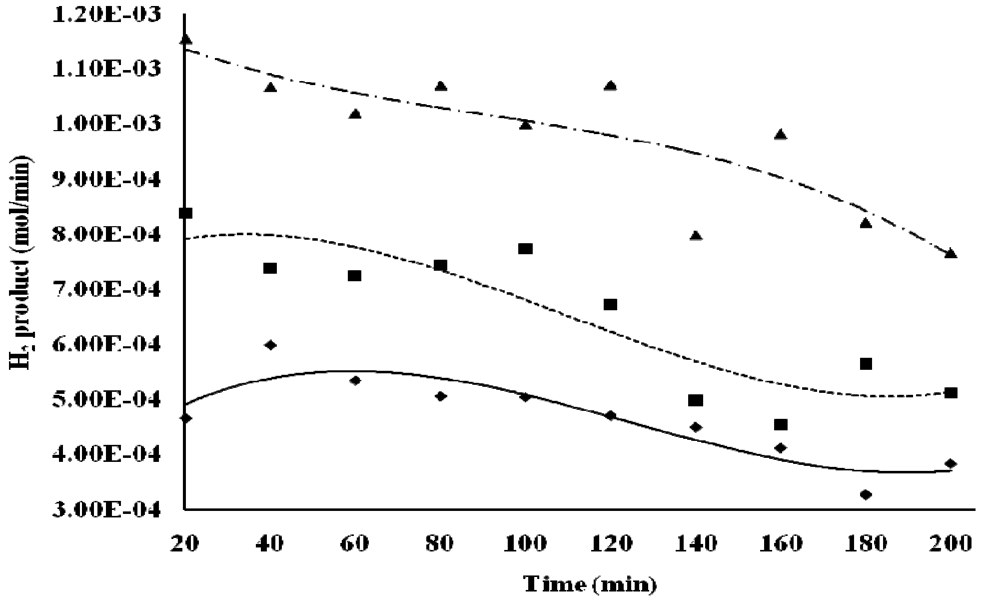

Figure D8 Effect of S/C ratio on H_2 product (mol/min) of tar steam reforming of 20%Ni/Al_2O_3 at T = 650 °C.

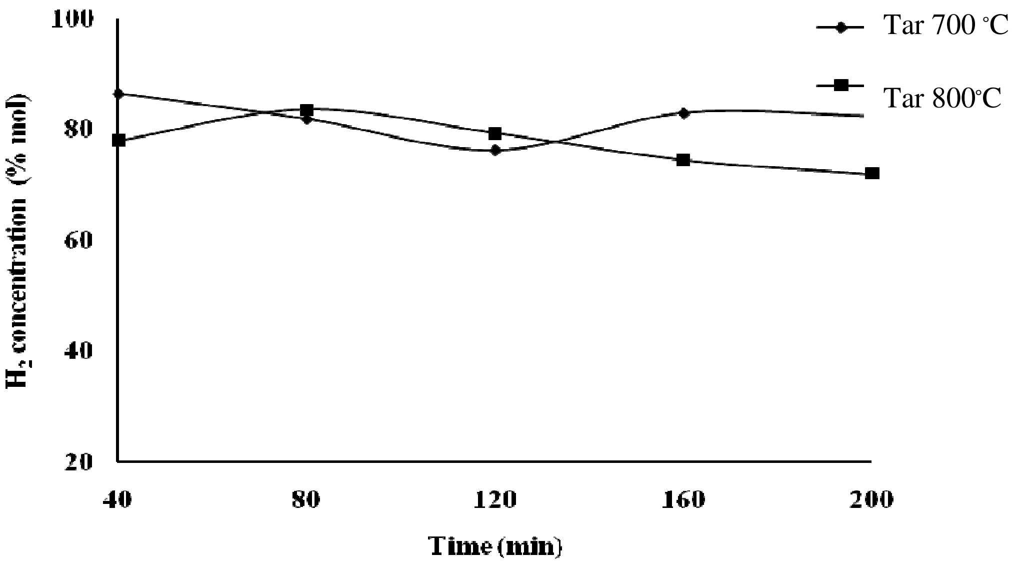

Figure D9 Effect of tar compositions obtained from biomass gasificationat different temperatures on H_2 concentration (mol%) (20%Ni/Al_2O_3, T = 650°C and S/C = 5).

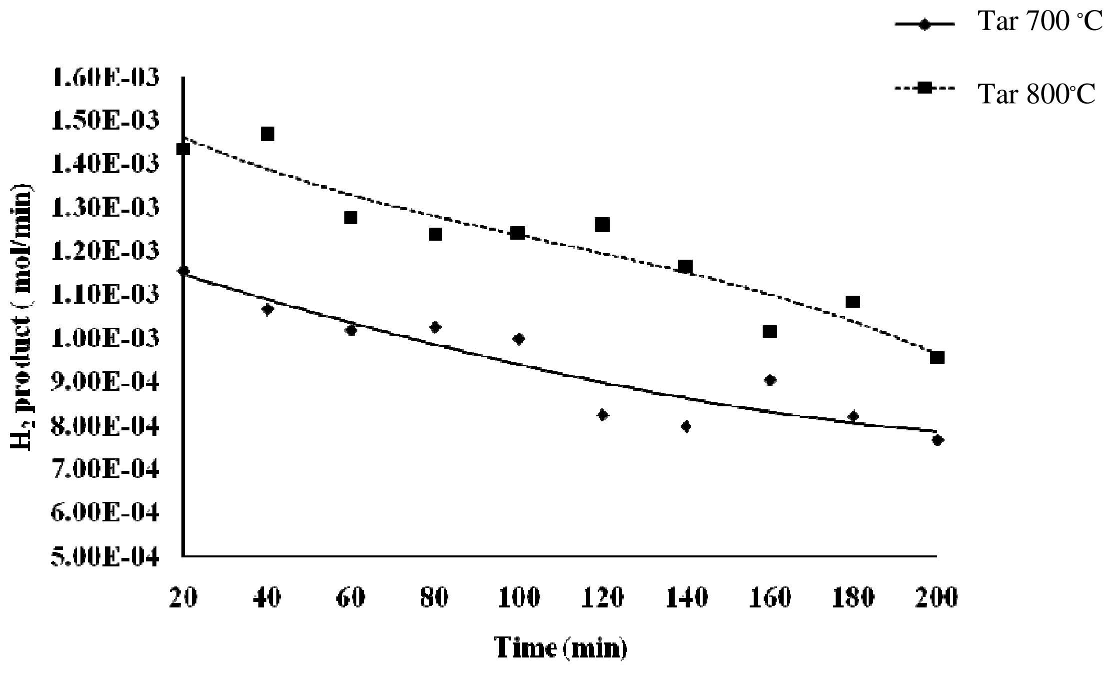

Figure D10 Effect of tar compositions obtained from biomass gasification at different temperatures on H_2 product (mol/min) (20%Ni/Al_2O_3,T = 650°C and S/C = 5).

APPENDIX E

MATERIAL SAFETY DATA SHEET

Toluene

Safety data for toluene

General

Synonyms: methylbenzene, phenylmethane, toluol, antisal 1A, CP 25, methacide, methylbenzol, NCI-C07272, RCRA waste number U220, tolu-sol
Molecular formula: C_7H_8

Physical data

Appearance: Colourless liquid with a benzene-like odor
Melting point: -93 ºC
Boiling point: 110.6 ºC
Specific gravity: 0.865
Vapor pressure: 22 mm Hg at 20 ºC (vapor density 3.2)
Flash point: 4 ºC
Autoignition temperature: 536 ºC

Stability

Stable. Substances to be avoided: oxidizing agents, oxygen and moisture. Highly flammable. Hygroscopic.

Toxicology

Harmful if inhaled, especially if breathed in over long periods. May cause drowsiness. Possible risk of harm to the unborn child.

Personal protection

Safety glasses, Good ventilation

Naphthalene

Safety data for naphthalene

General

Synonyms: Coal tar camphor, Naphthalin, Napthalinium, Naphthene; Albocarbon; Moth Ball

Molecular formula: $C_{10}H_8$, Molecular Weight: 128.17

Physical data

Appearance: white crystals solid, moth ball odor

Melting point: 80 ºC

Boiling point: 218 ºC

Specific gravity: 1.2

Vapor pressure: 1 (vapor density 4.4)

Flash point: 80 ºC

Autoignition temperature: 526 ºC

Odor Threshold: 0.038 ppm

Water/Oil Dist. Coeff.: Not available

Stability

Stable at room temperature in closed containers under normal storage and handling conditions

Toxicology

Absorbed through skin. Dermal contact. Eye contact. Inhalation. Ingestion.

Personal protection

Eyes: Wear chemical goggles.

Skin: Wear appropriate protective gloves to prevent skin exposure.

Clothing**:** Wear appropriate protective clothing to prevent skin exposure.

Phenol

Safety data for phenol

General

Synonyms: Monohydroxybenzene; Benzenol; Phenyl hyroxide; Phenylic acid

Chemical Name: Carbolic Acid

Chemical Formula: C_6H_5OH

Physical data

Appearance and Odor:colorlesssolution; mild, pleasant odor

Boiling Pt:=181.8°C, 359.2 F

Vapor Pres:76 mm @ 100°C

Vapor Density:3.24, Air = 1

Spec Gravity:1.06 (H_2O=1)

pH:6

Evaporation Rate & Reference:less than 0.01

Solubility in Water: approximately 5.0g/100mL

Percent Volatiles by Volume:N/Available

Solubility:Easily soluble in methanol, diethyl ether. Soluble in cold water, acetone. Solubility in water: 1g/15 ml water. Soluble in benzene. Very soluble in alcohol, chloroform, glycerol, petroleum, carbon disulfide, volatile and fixed oils, aqueous alkalihydroxides, carbon tetrachloride, acetic acid, liquid sulfur dioxide. Almost insoluble in petroleum ether. Miscible in acetone. Sparingly soluble in mineral oil.

Stability and Reactivity data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Heat, ignition sources (flames, sparks), light, incompatible materialsIncompatibility with various substances: Reactive with oxidizing agents, metals, acids, alkalis.

Corrosivity: Extremely corrosive in presence of copper. Slightly corrosive in presence of stainless steel(304), of stainless steel(316). Noncorrosive in presence of glass, of aluminum.

Special Remarks on Reactivity: Air and light sensitive. Prone to redden on exposure to light and air. Incompatible with aluminum chloride, peroxydisulfuirc acid, acetaldehyde, sodium nitrite, boron trifluoride diethyl ether + 1,3-butadiene, isocyanates, nitrides, mineral oxidizing acids,calcium hypochlorite, halogens, formaldehyde, metals and alloys, lead, zinc, magnesium and their alloys, plastics, rubber,coatings, sodium nitrate + trifluoroacetic acid. Phenol + isocyanates results in heat generation, and violent polymerization. Phenol + 1,3-butadiene and boron trifluoride diethyl ether complex results in intense exothermic reaction. Phenol +acetaldehyde resultes in violent condensation.

Special Remarks on Corrosivity: Minor corrosive effect on bronze. Severe corrosive effect on brass.

Polymerization: Will not occur.

Toxicology

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Inhalation. Ingestion.

Other Toxic Effects on Humans: Very hazardous in case of skin contact (corrosive, irritant), of ingestion, . Hazardous in case of skin contact (sensitizer, permeator), of eye contact (corrosive), of inhalation (lung corrosive).

First Aid Measures

Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact: Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Personal protection

Protective Equipment: Gloves. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Pyrene

Safety data for pyrene

General

Synonyms: Benzo[def]phenanthrene; Pyrenepract; Pyrene (purity)

Molecular Formula: $C_{16}H_{10}$

Physical data

Physical state and appearance: Solid. (Crystalline solid. Powdered solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 202.26 g/mole

Color: Yellow.

pH (1% soln/water): Not applicable.

Boiling Point: 404°C (759.2°F)

Melting Point: 151.2°C (304.2°F)

Specific Gravity: 1.271 @ 23 C (Water = 1)

Water/Oil Dist. Coeff.: The product is more soluble in oil; log(oil/water) = 4.9

Ionicity (in Water): Not available.

Dispersion Properties: Is not dispersed in cold water, hot water. See solubility in diethyl ether.

Solubility: Soluble in diethyl ether. Insoluble in cold water, hot water. Pyrene is fairly soluble in organic solvents.

Stability and Reactivity data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents.

Toxicology

Routes of Entry: Inhalation. Ingestion.

Special Remarks on other Toxic Effects on Humans: Acute Potential Health

Effects: Skin: May cause skin irritation. May be absorbed through skin. Eyes: May cause eye irritation. Conjunctival irritation may be noted. Inhalation: May cause respiratory tract irritaiton. Ingestion: May cause gastrointestinal tract irritation.

First Aid Measures

Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15
minutes. Get medical attention.

Skin Contact: In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse.

Personal protection

Protective Equipment: Gloves (impervious). Synthetic apron. Not applicable. Safety glasses.

VITA

Ms. Daranee Rulerk was born in January 27th, 1988 in Pattani, Thailand. She finished high school from Dechapattanayanukul School, Pattani in 2005. After that, she studied at Prince of Songkla University, Songkla, Thailand for 4 years and received Bachelor's Degree from the Department of Chemical Engineering in March 2010. Then, she required to study in the Master's Degree at the Department of Chemical Engineering, Chulalongkorn University in 2010.

In July 2011, she participated in the 1th International Conference on Sciences and Social Sciences Regional (ICSSS 2010), Mahasarakham Thailand for oral presentation on the topic of "Thermodynamic study of tar removal from fuel gas from biomass gasification using tar steam reforming".