REMOVAL OF TAR IN BIOMASS GASIFICATION PROCESS: A COMPARISON OF CATALYTIC AND NON-CATALYTIC TAR CRACKING

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A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF ENGINEERING
IN ENERGY TECHNOLOGY AND MANAGEMENT

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ABSTRACT

One of the major issues in biomass gasification technology is how to deal with the biomass tar. Catalytic and non-catalytic tar thermal cracking and tar steam reforming were studied by using naphthalene as a model tar compound. The experiments were conducted in a lab-scaled fixed bed reactor. Fe/Al_2O_3 and Ni-Fe/Al_2O_3 catalysts were prepared and used as the catalyst for tar decomposition. Results indicate that carbon conversion into gas of tar thermal cracking and tar steam reforming was increased obviously with an increase of reaction temperature from 600 to 800°C. The presence of Fe/Al_2O_3 catalyst gave a higher in carbon conversion into gas with the increasing of H_2 production than that case of without catalyst. In addition, the catalytic performance of Fe/Al_2O_3 catalyst in term of tar reduction became more significant in tar steam reforming than that in tar thermal cracking. When comparing with that of the Fe/Al_2O_3 catalyst, the Ni-Fe/Al_2O_3 catalyst was superior. The performance in tar steam reforming resulting in the increase of carbon conversion into gas. This was probably due to the presence of Ni-Fe bimetallic particles.

Keywords: Tar, Biomass gasification, reforming

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CHAPTER 1

INTRODUCTION

1.1 Rationale and Problem Statement

Gasification is one of the most promising thermochemical conversion processes for energy production from biomass. A mixture of combustible gas is known as producer gas mainly comprised of carbon monoxides (CO), carbon dioxide (CO_2), hydrogen (H_2), and traces of methane. Besides the above mentioned components in gaseous products, biomass gasification also produces variable amount of ash particles, volatilized alkali metals and tar (Uddin et al., 2008). Tar is an undesirable product of biomass gasification because of the various problems associated with the condensation and formation of tar aerosols, which presents significant impediment to the application of biomass gasification systems. Considerable research concerning the decomposition of tar has been undertaken.

Over the past few decades, catalytic tar steam reforming has received much attention for reducing tar and has been more extensively studied with the decomposition of tar model compounds and/or real biomass tar. At present, the development of catalyst for tar removal has been considered with respect to the nature of catalytic metal species, type of catalyst support and also the method of catalyst preparation. The criteria of catalyst selection may be previously summarized as following: (i) the catalysts must be effective in the removal of tars, (ii) if the desired product is syngas, the catalysts must be capable of reforming methane, (iii) the catalysts should provide a suitable syngas ratio for the intended process, (iv) the catalysts should be resistant to deactivation as a result of carbon fouling and sintering, (v) The catalysts should be easily regenerated, (vi) the catalysts should be strong and (vii) the catalysts should be inexpensive (Sutton et al., 2001).

Previously, the catalytic decomposition/cracking of tar was generally carried out at 650–900°C using nickel-based catalysts or/and natural dolomites. Nickel-based catalysts are very active in the destruction of tars, but are easily deactivated due to carbon deposition and sintering. Due to the serious toxic problem of nickel-based catalyst disposal, an alternative metal catalyst, such as an iron-based catalyst, has been developed for tar destruction. Furthermore, the iron-based catalysts are cheaper and less toxic than the nickel-based catalysts (Uddin et al., 2008).

Therefore, in this study, tar thermal cracking and tar steam reforming with and without an iron-based catalyst were carried out in a lab-scaled fixed bed reactor. Naphthalene, which is a major problematic tar that forms during biomass gasification, was used as a model tar compound. The effects of temperature, steam addition and the presence of catalyst were investigated.

1.2 Literature Review

A number of research studies concerning the decomposition of tar have been undertaken mostly using thermal cracking and catalytic steam reforming. There are several types of catalysts that have potential for tar cracking of producer gas such as natural dolomites, nickel-based catalysts, etc. Most of the researchers have studied these decomposition reactions using tar model compounds.

1.2.1 Thermal cracking

High temperatures influence the stability of tar and convert it to other species. Higher temperatures have led to lower yield of tar and higher yields of gaseous products. Many studies show that thermal cracking temperature of tar range from 700 to 1250°C (Anis, S., and Zainal, Z. A., 2011). Jess reported that thermal decomposition of naphthalene starts at 1100-1200°C. The most conversion in this studied was 95% at 1200°C.

1.2.2 Catalytic steam reforming

One tar removal method, catalytic steam reforming, is a very attractive technique for tar removal. Several kinds of catalysts were developed and applied in this process, such as mineral, Ni-based and noble metal catalysts (Li et al., 2009). Natural minerals, such as dolomite and olivine, are inexpensive and can be used to catalyst the reforming of tar. Although dolomite shows good catalytic activity for tar reforming, it is fragile resulting in the need of frequent catalyst replacement. Olivine is another inexpensive catalyst for the reforming of tar with high attrition resistibility. However, the catalyst needs to be pre-treated to obtain high activity for tar reforming and is easily deactivated, e.g. due to the loss of Fe dispersion. Despite intensive studies using natural minerals as catalysts, the reaction pathways for tar reforming, including the roles of support, remain poorly understood (Min et al., 2011).

1.2.2.1 Olivine-based

Kuhn et al. (2008) studied four olivine catalysts (three untreated of different origins and one calcined) for lowering the amount of these compounds in biomass-derived syngas by reforming model compounds (naphthalene, toluene, and methane). Treatments prior to reaction were shown to largely impact the catalytic activity and physiochemical properties of the olivine catalysts depending on its origin. The formation of free Fe phases following decomposition of a Fe-bearing serpentine phase ($(Mg,Fe)_3Si_2O_5(OH)_4$) near the surface of untreated olivine catalysts proved most important for facilitating higher activity compared to olivine catalysts with little or no serpentine phase initially. The most active catalyst was efficient at naphthalene removal (90% conversion at 800°C°C, but more active catalysts are needed for applications where methane removal is required. Additionally, carbon deposition during naphthalene-steam reforming as well as Fe clustering during naphthalene-steam reforming and exposure to reducing conditions suggested stability may be a liability.

The origin of olivine catalysts and treatments prior to catalytic tests influenced the activity for $C_{10}H_8$ and CH_4-H_2O reforming. The phase in which Fe was present and its location played a strong role in understanding the differences in catalytic activity. Of the secondary phases, the Fe-bearing serpentine phase enriched at the surface was judged to be the most important for achieving high catalytic activity. When it decomposed, free Fe was deposited on or near the surface. The nature of the initial thermal treatment also had a vital influence over the catalytic activity and physiochemical properties. Results support that Fe is involved in the active site. Due to poor CH_4-H_2O reforming activity and potential deactivation due to both carbon deposition and loss of Fe dispersion, improvements in activity and stability of these materials are needed.

1.2.2.1 Dolomite catalyst

In a study by Sarıoglan (2012), the tar removal performance of dolomite and commercial precious metal-based steam reforming catalysts were investigated by using the surrogated compounds of tar, namely benzene, toluene and xylene, at changing tar loads and temperatures. Steam dealkylation of alkyl aromatic hydrocarbons has been observed on dolomite and precious metal-based catalyst. Gaseous products, such as H_2 and CO_2, started to be measured at 563°C, and the detection of benzene and toluene in the case of xylene reforming proved the presence of selective reforming reactions on alkyl groups. Total steam reforming of aromatic rings has not been observed as sub-stoichiometric formation of reforming products meaning that selective steam reforming was only applied onto the alkyl groups of aromatics. Steam dealkylation reaction favorably occurred at 500-600°C, whereas thermal degradation and/or polymerization of aromatic compounds became the prevailing reaction with increasing operation temperatures beyond 700°C. Tar conversion was found to be independent on inlet tar load unless excess steam was present. Co-existence of tar and methane seemed beneficial as proved by enhanced methane reforming activity and complete tar removal. This improvement has been explained by the polymerization reaction of tar compounds and formation of unmeasurable soot particles.

The reverse water gas shift reaction was seen to occur, possibly due to the presence of iron in the dolomite. The direction of the water gas shift reaction was dictated by the gas composition in such a way as to reach thermodynamic equilibrium. The Boudouard reaction was another concern to be taken into account on dolomite during tar removal. For a gasification atmosphere, which was taken from a coal gasification pilot plant, combined with reforming products such as CO, CO_2 and H_2 inhibited the occurrence of steam methane reforming reaction on dolomite. The observed increase in methane concentration during tar removal study on dolomite at 750°C has signed the hydrodealkylation of methyl groups of alkyl aromatics by giving benzene under the experimented conditions. Thermal decomposition of aromatic compounds seemed to be the prevailing reaction as proved by the observation of blackened inner reactor surface of the dolomite bed and a decrease in total tar load at the outlet stream.

The conversion of xylene to toluene and benzene, and the formation of gaseous products confirm steam dealkylation reactions on precious metal-based catalysts. Highest benzene and lowest xylene fractions in the outlet tar content at mild temperatures, namely at 563°C is the indicative of favorable operating point for steam dealkylation reaction. Increased amount of gaseous products with temperature and detection of benzene and toluene in the outlet stream can be taken as a measure of selective steam reforming reaction on alkyl groups and to some extent an indication of thermal degradation/ polymerization of aromatic compounds. Tar conversion was found to be independent on inlet tar load unless excess steam was present. The loss of activity with excess steam was attributed to a possible sintering phenomenon of active sites on the catalyst surface.

Coking and the fouling of aromatics on the catalyst’s surface seemed to be predominant at the reaction temperatures above 750°C. The co-existence of tar and methane seemed beneficial as proved by enhanced methane reforming activity and complete tar removal, since aromatic groups, such as benzene show high reactivity to the presence of methane. This improvement has been explained by the polymerization reaction of tar compounds, most likely via the interaction of benzyl radicals and acetylene (Coll et al. 2001).

Their study showed that tar compounds with alkyl groups, such as toluene, xylene, ethylbenzene, and trimethyl benzene can be dealkylated to benzene via noble-based catalysts. Thereby, a significant relief of the tar load could be achieved. In addition, if recovered, dealkylated tar compounds would have a commercial value.

Gusta et al. (2009) studied catalytic gasification of wood biomass using a double-bed microreactor in a two-stage process (see Figure 1.1).

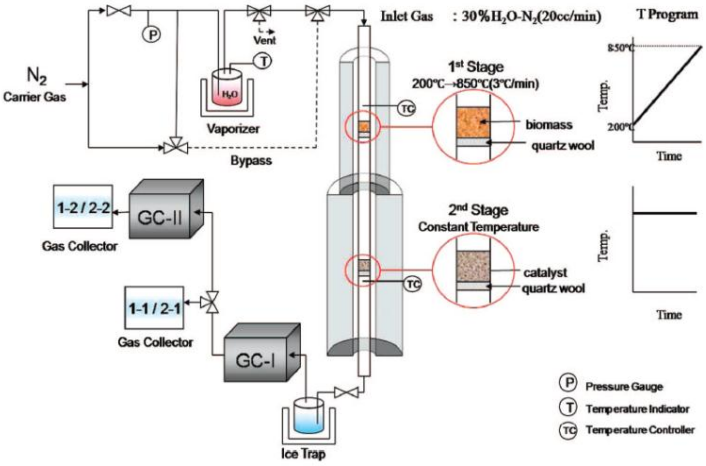


Figure 1.1 Dual-stage apparatus for semibatch packed-bed steam gasification (Gusta et al., 2009).

Temperature-programmed steam gasification of biomass was performed in the first bed at 200-850°C. Following in series was isothermal catalytic decomposition and gasification of volatile compounds (including tars) in the second bed containing various dolomites. Dolomites from Canada, Australia, and Japan were examined for their effects on tar conversion and the overall gaseous product. Tar conversion results are given in Figure1.2

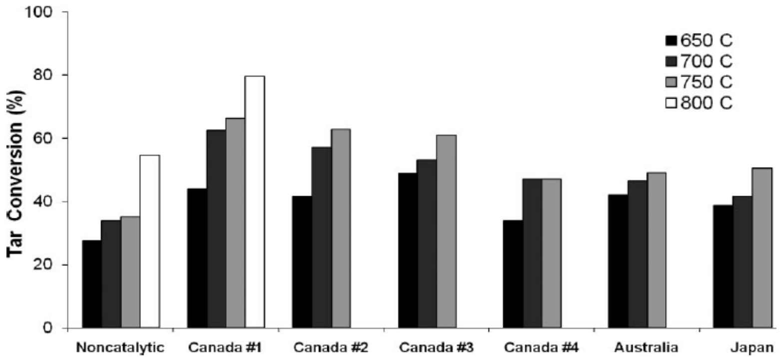


Figure 1.2 Tar conversion results for dolomites over several temperatures (0.065 cm^3 of catalyst, 0.040 g of biomass, 42 cm^3/min N_2, and 18 cm^3/h H_2O) (Gusta et al., 2009).

Significant improvements were achieved by the use of dolomites in a downstream packed bed for all temperatures examined. During catalyst screening at 650, 700, and 750° C, the average tar conversion was improved by 14, 17.5, and 21% over non-catalytic results, respectively. This research study found that the dolomites with higher iron content had higher activity for tar conversion. However, a plot of Fe wt.% versus tar conversion for all catalysts did not yield a clear trend, indicating that other catalyst properties are significant factors. When considering the measured properties of the dolomites, Australian and Japanese dolomites were observed to be somewhat different from the Canadian dolomites. Therefore, the relation between iron content and tar conversion was plotted using Canadian dolomites only, as seen in Figure 1.3.

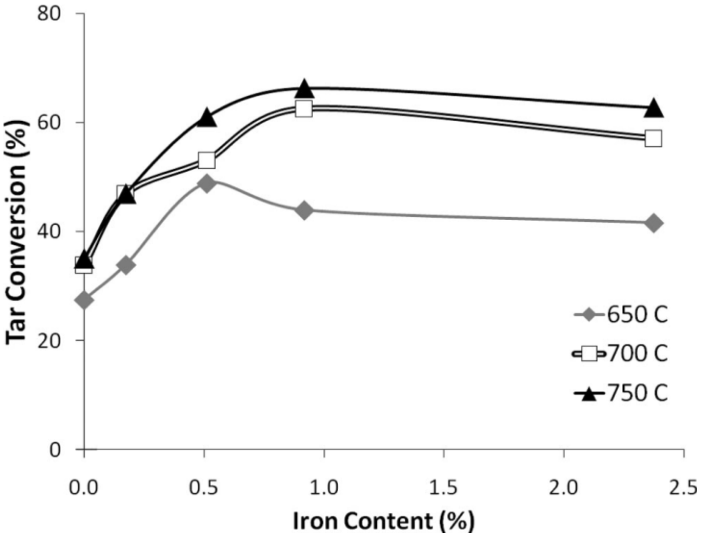


Figure 1.3 Percent tar conversion versus iron content for Canadian dolomites (0.065 cm^3 of catalyst, 0.040 g of biomass, 42 cm^3/min N_2, and 18 cm^3/h H_2O) (Gusta et al., 2009).

The iron content in dolomite was found to promote tar conversion and the water-gas shift reaction, but the effectiveness reached a plateau at 0.9 wt% Fe in Canadian dolomites. The maximum tar conversion of 66% was achieved at 750 °C using a Canadian dolomite with 0.9 wt % Fe (1.6 cm^3/g of biomass). Carbon conversion to gaseous products increased to 97% using 3.2 cm^3 dolomite/g of biomass at the same temperature. The dolomite seemed stable after 15 h of cyclic use at 800 °C.

1.2.2.2 Nickel-based catalyst

Coll et al. investigated the steam reforming reaction over two types of nickel-alumina catalysts with the following model compounds: benzene, toluene, naphthalene, anthracene and pyrene. The experiments show that the reactivity of the different model tar compounds over the ICI 46-1 catalyst decreases as follows: benzene > toluene >> anthracene >> pyrene > Naphthalene. It should be made clear that for these experiments, steam to carbon ratio and the catalyst loading used were different for each tar compound depending on the reactivity of the organic compound.

1.2.2.3 Iron-based catalyst

Noichi et al. used naphthalene as the tar model compound in the presence of an iron–alumina catalyst (Fe–Al) and iron–zirconia catalyst (Fe–Zr) at 850 °C in a fixed bed reactor. They reported that CO and H_2 were the main products with a very small amount of CO_2 of steam reforming of naphthalene. For Fe-Al catalysts, with the increase of Fe content, the activity for naphthalene conversion was enhanced except 100Fe-0Al (Figure 1.5). For Fe-Zr catalysts were also the activity of the catalyst enhanced with the increased of Fe content. In addition, the Fe-Zr catalysts were found to more stable than the Fe-Al catalysts. Figure 1.6 shows the results for steam reforming of naphthalene on Fe-Zr catalyst.

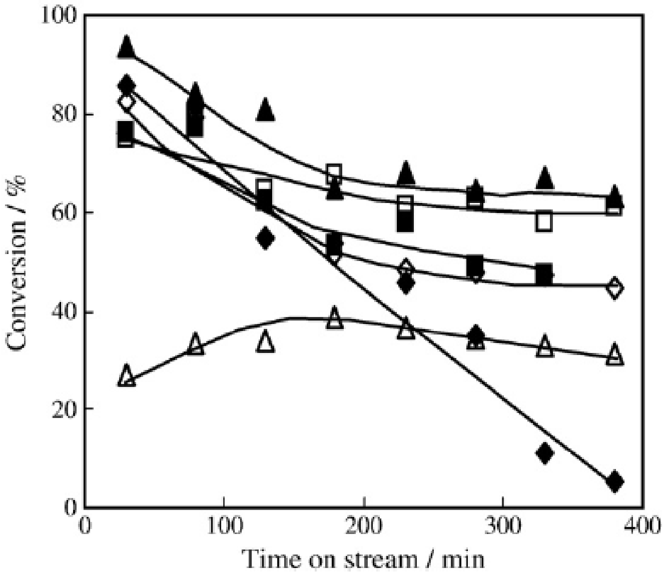


Figure 1.4 The catalytic activity of Fe–Al catalysts with different Fe contents for the steam reforming of naphthalene at 850 °C (♦30Fe–70Al, 40Fe–60Al, ■50Fe–50Al, □60Fe–40Al,▲70Fe–30Al, △100Fe) (Noichi et al., 2010)

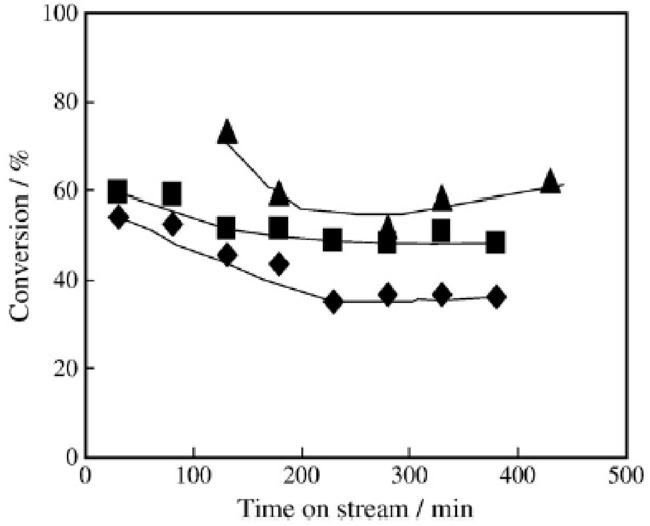


Figure 1.5 The catalytic activity of Fe–Zr catalysts with different Fe content for steam reforming of naphthalene at 850 °C (♦30Fe–70Zr, ■50Fe–50Zr, ▲70Fe–30Zr) (Noichi et al., 2010)

Table 1.1 Overview of literature on naphthalene decomposition

Model tar	Catalyst	Operating conditions	Inlet gas composition	Observations
Naphthalene (El-Rub et. al., 2002	Dolomite, Olivine, Ni-based	T=900°C, P=1atm, s=0.3 s	CO_2, H_2O, N_2	$X_{Dolomite,900°C}$=61%; $X_{Olivine,900°C}$=55%; $X_{Ni\text{-}based,900°C}$=100%;
Anthracene, Benzene, Naphthalene, Pyrene, Toluene (Coll et. al., 2001	UCI G90-C, ICI 46-1 (Ni-based)	T=700–875 °C, M=0.5–1 g, τ'=0.0083–0.55 $hg_{cat}\,g_{tar}^{-1}$, τ'=0.0004–0.0247 $hkg_{cat}\,m^{-3}{}_{gas}$	H_2O	$X_{Toluene,800°C}$=80%, $X_{Benzene,800°C}$=85%, $X_{Naphthalene,825°C}$=40%, $X_{Anthracene,825°C}$=70%, $X_{Pyrene,825°C}$=45%; The larger the aromatic ring, the stronger the coke formation
Naphthalene, Toluene, Benzene (Jess, 1996)	None	T=700–1400 °C, P=160 kPa, τ=0.3–2 s	H_2O, H_2, N_2	For 95% conversion at 1200°C

1.3 Objectives

1) To study the efficiency of tar cracking in the gasification process by comparing catalytic to non-catalytic steam reforming.

2) To test and compare the tar cracking performance of iron-based and nickel/iron-based catalysts.

CHAPTER 2

THEORIES

2.1 Introduction of Biomass Gasification

Biomass is defined as organic matter that is derived directly from living organisms and is available on a renewable basis (Devi et al., 2003). Biomass includes forest and mill residues, agricultural crops and waste, wood wastes, animal wastes, livestock operation residues, aquatic plants, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast, fast-growing trees and plants, and municipal and industrial wastes. The energy from biomass can be used to produce energy.

Biomass gasification is typically characterized as the incomplete combustion of biomass to produce a fuel gas of low to medium heating values. Gasification lies between the extremes of combustion and pyrolysis (anaerobic thermal decomposition) and occurs as the amount of oxygen supplied to the burning biomass is decreased. Combustible constituents in the fuel gas include mainly carbon monoxide (CO), hydrogen (H_2), trace methane (CH_4), and some higher hydrocarbons. Inert constituents are primarily nitrogen, carbon dioxide (CO_2), and water vapor (H_2O_{vap}). Depending on the gasification scheme used, the heating value of the fuel gas generally ranges between 3.7 and 7.5 MJ/Nm^3 for direct gasifiers, and between 11 and 17 MJ/Nm^3 (300-450 Btu/scf) for indirect gasifiers. By comparison, natural gas has a heating value of around 37 MJ/Nm^3 (Rezaivan et al., 2005).

Gasification involves the reaction of carbon with air, oxygen, steam, carbon dioxide, or a mixture of these gases at 500-1,400 °C or higher to produce a synthetic gas. Normally, the combustion process operates at stoichiometric conditions with excess air, but gasification processes operate by using a controlled amount of oxygen (generally 35 percent of the amount of O_2 theoretically required for complete combustion or less), such that both heat and new gaseous fuel are produced as the feed material is consumed.

The producer gas can be used to provide electrical power and heat, or used as a raw material for the synthesis of chemicals, liquid fuels, or other gaseous fuels, such as hydrogen. Producer gas can be used to run internal combustion engines, as substitutes for furnace oil in direct heat applications and to produce methanol in an economically viable way. Methanol is an extremely attractive chemical that is useful both as fuel for heat engines and as chemical feedstock for industries. Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas, where only selected biomass materials can produce the fuel. Figure 2.1 shows the principle gasification process for converting a carbonaceous material to combustible or synthetic gas and the application of gasification.

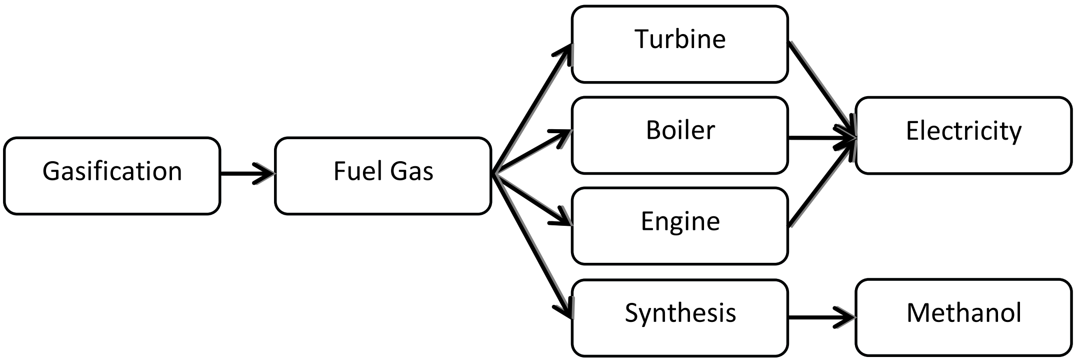


Figure 2.1: The principle gasification process

For heat applications, the gasification of biomass may be advantageous if direct heating by flue gases is considered. The advantage of using producer gas is that it can be easily burned with low NO_x emissions. When strict emission levels on flue gas contaminants are required, the producer gas can be cleaned before use. A gas flame can easily be directed to a certain heating zone. And each burner can be controlled easily (the process is similar to cooking on a gas stove).

The energy in the producer gas is to a large extent chemically-bound energy (about 80 percent). If the cleaning system requires cooling of the producer gas, only thermal energy, which represents approximately 20 percent of the contained energy, gets lost. By using an intensive gas cleaning system in combination with a well-designed burner, a clean flow of hot flue gases can be produced for direct heat applications.

If heat is applied in an indirect heating system using heat exchangers (e.g. boilers), both gasification and combustion systems can be used. In general, direct combustion systems may offer the highest overall efficiency, whereas gasification may offer the highest controllability.

The power generation from biomass gasification technology is far less mature and is still in the development stage. Advanced gasification cycles, which have not yet been realized on a commercial or even a demonstration scale, are promising, and much development work is going on to make these cycles commercially available.

Small-scale applications are required if biomass (as in most cases) is only available in limited quantities. This should also apply locally to avoid excessive transport costs. For steam cycles and gasification technology, work continues to develop reliable and affordable small-scale equipment.

2.1.1 Gasification process

Four distinct processes take place in a gasifier as the fuel makes its way to gasification. They are drying, pyrolysis, combustion, and reduction processes (Figure 2.2).

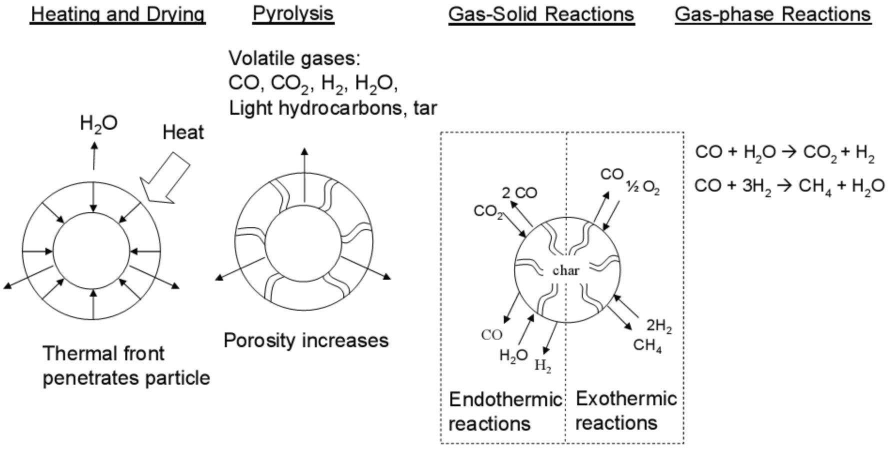


Figure 2.2: Fundamentals of gasification

Drying: The solid feedstock (biomass) is heated and dried at the top of the gasifier unit. Water is the first constituent to evolve.

$$\textit{Moist feedstock} + \textit{Heat} ==> \textit{Dry feedstock} + H_2O_{vap} \qquad (1)$$

Pyrolysis: The dried biomass enters the second process called “Pyrolysis” in which the gaseous products from devolatilization are partially burnt with the existing air.

$$\textit{Dry feedstock} + \textit{Heat} ==> \textit{Char} + \textit{Volatiles} \qquad (2)$$

Up to the temperature of 200°C, only water is driven off. Between 200 to 280°C, carbon dioxide, acetic acid and water are given off. The real pyrolysis, which takes place between 280 to 500°C, produces large quantities of tar and gases containing carbon dioxide. Besides light tars, some methyl alcohol is also formed. Between 500 to 700°C, the gas production is small and contains hydrogen.

Oxidation or Combustion: The combustible substance of a solid fuel is usually composed of carbon, hydrogen and oxygen. In complete combustion, carbon dioxide is obtained from carbon in fuel and water is obtained from the hydrogen, usually as steam. The combustion reaction is exothermic and yields a theoretical oxidation temperature of 1450 °C. The main reactions are given by:

$$C + O_2 = CO_2 \qquad (+402\ MJ/kg\ mole) \qquad (3)$$

$$2H_2 + O_2 = 2H_2O \qquad (-241MJ/kg\ mole) \qquad (4)$$

Reduction or gasification: The products of partial combustion (water, carbon dioxide and un-combusted partially cracked pyrolysis products) now pass through a red-hot charcoal bed where the following reduction reactions take place.

$$C + CO_2 = 2CO \qquad (-164.9\ MJ/kg\ mole) \qquad (5)$$

$$C + H_2O = CO + H_2 \qquad (-\ 122.6\ MJ/kg\ mole) \qquad (6)$$

$$CO + H_2O = CO_2 + H_2 \qquad (+42\ MJ/kg\ mole) \qquad (7)$$

$$C + 2H_2 = CH_4 \qquad (+75\ MJ/kg\ mole) \qquad (8)$$

$$CO_2 + H_2 = CO + H_2O \qquad (-\ 42.3\ MJ/kg\ mole) \qquad (9)$$

Reaction (5) is a Boudouard Reaction and (4) is a water gas reaction. Both reactions are main reduction reactions and being endothermic 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 (approximately 700-800°C), is the lower calorific value of gas.

2.1.2 Tar from Biomass Gasification

When biomass is burnt, many particulates such as dust, ash and tar are released in the flue gas. Tar contaminant is a serious problem for its use e.g. engines and turbines.

Many definitions of biomass tar have been given by many institutions working on biomass gasification. Some of these are: *"The mixture of chemical compounds which condense on metal surfaces at room temperature", "The sum of components with boiling point higher than 150°C", "All organic contaminants with a molecular weight larger than benzene".*

However, one general (uniform) definition does not exist. Apart from the general definition of tars, definitions have been given for heavy tars, gravimetric tars and light tars (Paasen et al., 2004).

Tar is one of the most unpleasant constituents of the gas, as it tends to deposit in the carburetor and intake valves, causing sticking and troublesome operations. It is a product of highly irreversible process taking place in the pyrolysis zone. The physical property of tar depends upon temperature and the heat rate. The appearance ranges from brown and watery (60% water) to black and highly viscous (7% water). There are approximately 200 chemical constituents that have been identified in tar so far. Very little research work has been done in the area of removing or burning tar in the gasifier so that relatively tar-free gas comes out. Thus, the major effort has been devoted to cleaning this tar by filters and coolers. A well-designed gasifier should put out less than 1 g/m^3 of tar.

2.1.3 Tar Formation

When biomass is heated, the molecular bonds of the biomass are broken. The smallest molecules are gaseous, and the larger molecules are called primary tars. These primary tars, which are always fragments of the original material, can react to secondary tars by further reactions at the same temperature and to tertiary tars at high temperatures. This tar formation pathway can be visualised as follows:

Mixed Oxygenates → *Phenolic Ethers* → *Alkyl Phenolics* → *PAH* → *Heterocyclic Ethers*

Figure 2.3: Tar maturation scheme (Li and Suzuki, 2009)

2.1.3.1 Chemical mechanisms of tar formation

Although an understanding of the mechanisms of tar transformation has not been yet elucidated, the mechanisms are an interesting topic, because they can be simplified for what might be otherwise an overwhelming body of knowledge by finding the most probable pathways of tar transformations. And these can also be provided possible routes for kinetic modeling of tar formation and destruction, based on organic reaction pathways.

During the tar transformation process, the oxygenated compounds (primary tar) react with secondary tar or tertiary tar, depending on the transformation pathway. However, if the reactions continuously occur, the final formation of tar will be turn into stable structures such as benzene formed. In practice, there are difficult to simplify because of the chain side reactions that depend on the size of the molecule, condition in a process and other effects. Figure 2.4 shows the conversions of tar formations from primary to tertiary tar.

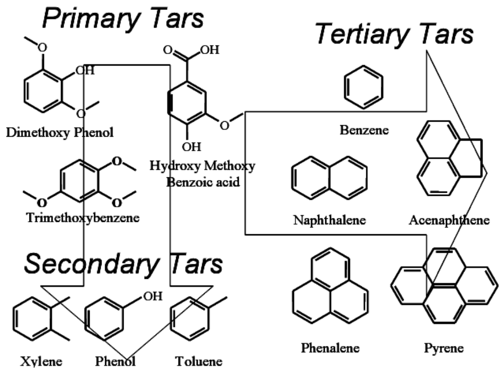


Figure 2.4: The conversion of tars (Hindiyarti et al., 2003)

Generally in organic mechanisms, molecular bonds are destroyed at weak composition, based on a bond dissociation energy calculation model, which is one method to simplify the mechanisms of a reaction. Figure 2.5 shows the bond dissociation energies for the model compounds of some molecules.

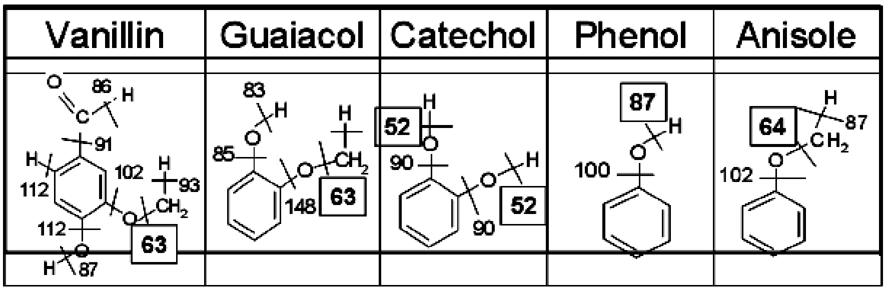


Figure 2.5: Bond dissociation energies for the model compounds (Hindiyarti et al., 2003)

Figure 2.5 shows at the weakest bond of a typical compound is the position of a bond breaking and reacting with some radicals, such as hydrogen abstraction from second weak bonds or/and cyclopentadienyl (a stable radical), leading to polyaromatic hydrocarbons (PAH). However, a reaction can be possible in any mechanisms pathway such as the mechanism of vanillin can be expressed both unimolecular and biomolecular reaction. Hence, the advantages of chemical models provide useful information about tar species transformations.

2.1.3.2 Composition of biomass tar

The product gas also contains variable amounts of ash particles, volatile alkali metals and tar, which is a complex mixture of aromatics that includes a significant fraction of polycyclic aromatic hydrocarbons. The typical composition of biomass tars are shown in Figure 2.6.

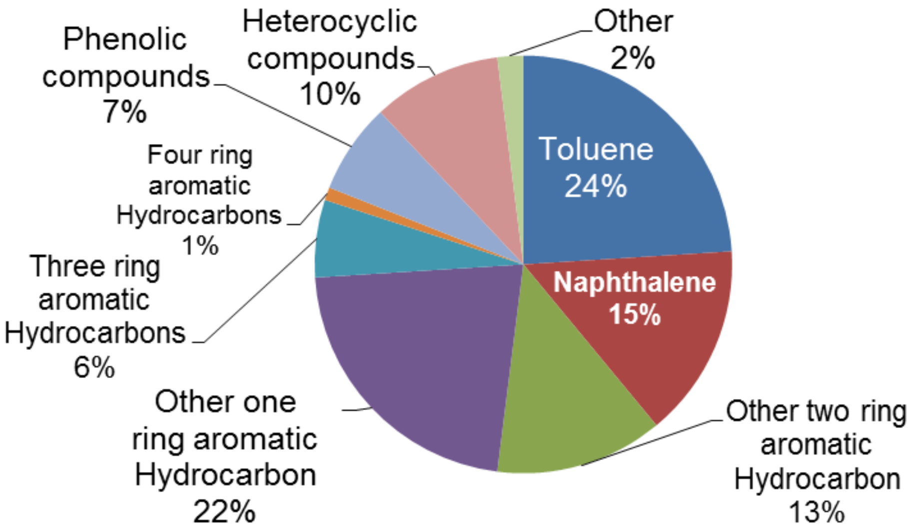


Figure 2.6: Typical composition of biomass tars (wt %) (Shen, Y., and Yoshikawa, K., 2013)

On the other hand, tar components can be classified into five classes based on condensation behavior and water solubility. Condensation behavior is important, e.g. with respect to fouling in gas cooling or gas cleaning equipment. On the one hand, oxygenated or heterocyclic tar compounds containing O and/or N atoms, such as phenol, are highly water soluble due to their high polarity. They may lead to hazardous wastewater, resulting in high disposal costs for low-temperature gas cleaning systems. In this condition, the main tar categories and their solubility/condensability can be separated into five different tar classes as follows (Evan et al., 1987).

Class 1: GC, GC-MS undetectable tars. This class consists probably of un-reacted fuel fragments, which can be problematic even at very high temperatures.

Class 2: Heterocyclic compounds (such as phenol, pyridine, and cresol). These are compounds that have generally high water solubility, and hence, will cause contamination of wastewater.

Class 3: Aromatic Compounds (such as benzene and toluene). Although these are found in high concentrations in the product gas, due to their low dew point, they will stay in the gas phase. Light aromatic hydrocarbons are not important in condensation and water solubility issues.

Class 4: Light polyaromatic hydrocarbons consisting of two and three rings. At low concentrations, these compounds are in the gas phase, but will cause plugging and deposition at high concentrations.

Class 5: Heavy polyaromatic hydrocarbons comprising more than 3 rings. Even at very low concentrations (ppm. level), condensation of these compounds will occur at the discussed gas cleaning temperatures.

This classification includes all tar components for which the data about solubility and condensability is available in the literature.

2.1.4 The Problems of Tar

A gas engine or a gas turbine requires an acceptably low level of contaminant, such as tar, acids, hydrogen chloride, sulfur gases, ammonia and nitrogen compounds, solid dust particles, alkali metals and heavy metals. Tar impose serious limitations in the use of producer gas due to the fouling of the downstream process equipment, engine wear and high maintenance costs. By far, tar removal is the most problematic. Thus, the successful implementation of gasification technology for gas engine/turbine based power projects depends much on the effective and efficient removal/conversion of tar from the producer gas.

Before the producer gas can be used in a gas engine or turbine, it must be cooled and cleaned of tars. Tars may condense on valve sand fittings, hampering the ability of valves to function properly. Tars cause corrosion and erosion of cylinder walls and pistons. When the gas is used in a heat application, requirements for gas quality are not strict, especially when the gas remains at high temperatures during transportation to the burner (this prevents tars from condensing).

Tar removal is one solution to decrease the problem of this particulate. The classical way to remove tars is to cool the gas, which causes the tars to condense. A condenser may be built from wide pipes and cooled on the outside by the surrounding air. When this is done, tars condense on the walls of the pipes and can be drained off at the bottom. This type of tar condenser is quite large for the amount treated, and is therefore, not suitable for treating large volumes of gas.

Cooling the gas by spraying water into the gas stream with a venturi scrubber causes the tars to condense onto the water droplets. The effectiveness of the tar removal can be controlled by adjusting the pressure drop over the spray nozzle, which influences droplet sizes of the water spray. Humidified packed beds are also applied to increase the cooling surface in a tar condensing device. The bed material may consist of specially designed rings or other shapes, but it could also consist of such things as simple coconut fibers or even ping-pong balls. In the direct water cooled tar removal systems, some of the dust, HCI, sulfur oxides, and depending on the temperature in the condenser alkali metals are also removed by the water. A major drawback of direct water cooled systems is the tar-contaminated waste-water stream, which needs treatment before disposal. If this waste-water stream is disposed of without cleaning, it will cause severe environmental damage.

Tar cracking in a bed of char or a catalyst, such as nickel or dolomite, at high temperatures (600-1,000°C) may be an alternative to the wet-gas cleaning systems. In such devices, heavy tars in the producer gas are cracked into light, combustible gases that will not condense at the normal operating temperatures of a gas engine. However, such tar cracking systems are still in development, and hence, not yet commercially available.

However, there are still many questions related to tar, and the problems they may cause. Tar itself is a complex mixture of condensable hydrocarbons, and still requires a satisfactory definition. It is also necessary to understand its composition and formation in order to design systems for its optimum removal or conversion and for minimizing its formation in the gasifier and interactions downstream to the end use device.

2.1.5 Tar removal methods

Tar removal methods can be categorized in two types, depending on the location where tar is removed: either in the gasifier itself (known as the primary method) or outside the gasifier (known as the secondary method). Secondary methods are suitable for tar treatment from a producer gas. Two approaches usually used in this method are wet gas and hot gas treatment. Figure 2.7 shows tar removal efficiency (%). The figure shows that catalytic cracking has high tar removal efficiency.

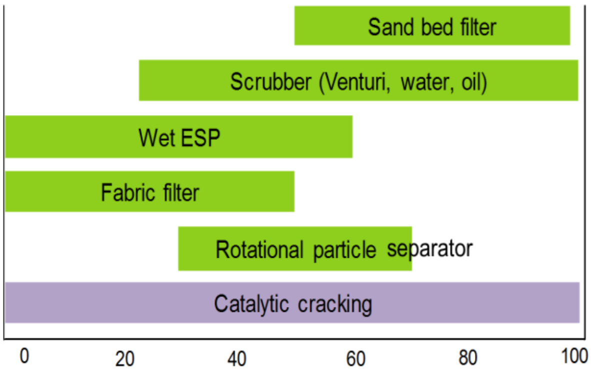


Figure 2.7: Tar removal efficiency (%)

2.2 Catalysts for Tar Removal

Remarkable progress has been achieved in recent years in the design of gasifiers. However, gas cleaning is still the bottleneck in advanced gas utilisation that limits the deployment of the use of biomass for electricity generation. The continual build-up of condensible organic compounds (often referred to as tars) present in the product gas can cause blockages and corrosion, and also reduce overall efficiency. In addition, the presence of impurities (such as methane) can affect the end usage of the syngas and the techniques involved in the removal of the impurities in such processes are costly. Nitrogen and sulphur are present in many of the by-products, and the corresponding oxides are produced during the combustion of the fuel gas. These oxides (NO_x and SO_x) can have a negative environmental impact.

Since the mid-1980s, interest has grown in the subject of catalysis for biomass gasification. The advances in this area have been driven by the need to produce a tar-free product gas from the gasification of biomass, since the removal of tars and the reduction of the methane content increases the economic viability of the biomass gasification process. The literature in this area ranges from papers on bench-scale reactors to those on the use of plant-scale gasifiers. Research on catalysts for use in the process is often carried out specifically in relation to gasifier design or biomass feed type.

The catalytic decomposition of the unwanted hydrocarbons is also known as hot gas cleaning. The catalysts employed in this process are responsible both for purification and bringing about compositional adjustment of the product gas. Hot gas conditioning is achieved by passing the raw gasifier product gas over a solid catalyst in a fluidised-bed (or a fixed-bed) under temperature and pressure conditions that essentially match those of the gasifier. As the raw gas passes over the catalyst, the hydrocarbons may be reformed on a catalyst surface with either steam (Eq. (10)) or carbon dioxide or both (Eq. (11)) to produce additional carbon monoxide and hydrogen:

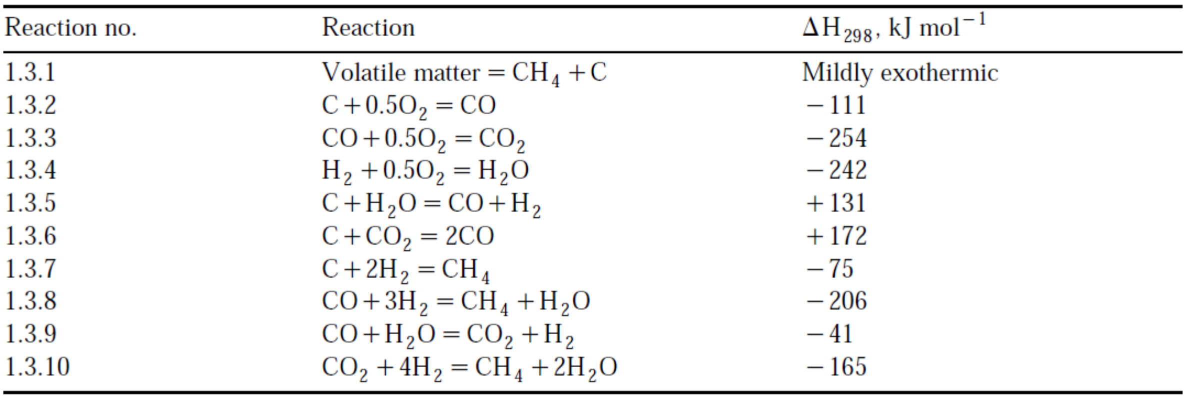
$$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \qquad (10)$$

$$C_nH_m + nCO_2 \leftrightarrow 2CO + \left(\frac{m}{2}\right)H_2 \qquad (11)$$

Additional steam or carbon dioxide may be added for the reforming processes.

The use of a catalyst to reform condensible organic compounds and methane can increase the overall efficiency of the biomass conversion process by 10%. Lindman (1981) investigating air gasification, reported higher efficiency being achieved by lower oxygen consumption, better heat recovery and higher carbon conversion as compared to a process based on non-catalytic techniques. Thermal cracking of the hydrocarbons is also possible; however, this method is not considered a feasible option as it requires high temperatures (>1100°C) to achieve high cleaning efficiency, and it also produces soot.

Table 2.1 Main chemical reactions of biomass gasification (Sutton et al., 2001)



Reaction no.	Reaction	ΔH_{298}, kJ mol^{-1}
1.3.1	Volatile matter $= CH_4 + C$	Mildly exothermic
1.3.2	$C + 0.5O_2 = CO$	-111
1.3.3	$CO + 0.5O_2 = CO_2$	-254
1.3.4	$H_2 + 0.5O_2 = H_2O$	-242
1.3.5	$C + H_2O = CO + H_2$	$+131$
1.3.6	$C + CO_2 = 2CO$	$+172$
1.3.7	$C + 2H_2 = CH_4$	-75
1.3.8	$CO + 3H_2 = CH_4 + H_2O$	-206
1.3.9	$CO + H_2O = CO_2 + H_2$	-41
1.3.10	$CO_2 + 4H_2 = CH_4 + 2H_2O$	-165

Catalysts for use in biomass conversion may be divided into two distinct groups, which are dependent on the position of the catalytic reactor relative to that of the gasifier in the gasification process. The first group of catalyst (primary catalysts) is added directly to the biomass prior to gasification, which catalyses the reactions in Table 1. The addition is either by wet impregnation of the biomass material or by dry mixing of the catalyst with it. These catalysts primarily have the purpose of reducing the tar content and have little effect on the conversion of methane and C hydrocarbons in the product gas. The second group of catalysts is placed in a secondary reactor downstream from the gasifier. Independent of the type of gasifier, they can be operated under different conditions than those of the gasification unit. The catalysts are active in reforming hydrocarbons and methane, according to Eqs. (10) and (11).

CHAPTER 3

METHODOLOGY

3.1 The model compound of tar

In this research, naphthalene was used as the tar model compound, because it is a polyaromatic hydrocarbon (PAH) with high thermal stability and decomposes very slowly (El-Rub et al., 2002).

3.2 Catalyst preparation

3.2.1 Preparation of Fe/Al_2O_3 catalyst

The Fe/Al_2O_3 catalyst was prepared by an impregnation method using an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. After the impregnation, the samples were dried at 110℃ for 12 h followed by the calcination at 500℃ for 3 h under air atmosphere.

3.2.2 Preparation of Ni-Fe/Al_2O_3 catalyst

The Ni-Fe/Al_2O_3 catalysts were prepared by a co-impregnation method using a mixed aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$. Content of Ni and Fe loading were varied, i.e. 3 wt.% Ni and 12 wt.% Fe of catalyst weight (represented 3%Ni-12%Fe/Al_2O_3) and another was 12 wt.% Ni and 3 wt.% Fe of catalyst weight (represented 12%Ni-3%Fe/Al_2O_3). After the co-impregnation, the samples were dried at 110℃ for 12 h followed by the calcination at 500℃ for 3 h under air atmosphere.

3.3 Catalyst characterization

The crystalline structures of the prepared catalysts were analyzed by an X-ray diffractometer (XRD, Rigaku, Ultimate Japan). The intensity data were collected over a 2θ range of 20 – 90° with a scan speed of 5° (2θ) min^{-1} and a scan step of 0.02° (2θ).

3.4 Experimental Apparatus and procedure

The experiment using naphthalene as the tar model compound was carried out in a fixed-bed quartz reactor with an externally heated furnace. The reactor has the height of 400 mm (of which the heated zone is 300 mm) and the diameter of 10 mm is shown in Figure 3.1. The schematic diagram of experimental setup is shown in Figure 3.2. The flow of gases was controlled by a mass flow controller.

In a typical run, the catalyst was loaded onto the quartz wool in the reactor at 1 cm high. Then the temperature of the reactor was increased to 500°C in 5% H_2/N_2 using 30 ml/min for 2.30 hours for catalyst reduction. The reaction was commenced by flowing the gas mixture containing naphthalene and steam.

Naphthalene was stored in a reservoir, placed before the reactor, which was externally warmed up by means of a heater at 130-140°C. The N_2 stream was passed through the reservoir and saturated with naphthalene. The flow rate of N_2 was 70 ml/min. The concentration of naphthalene can be adjusted by changing the temperature inside the reservoir. To prevent the blockage of the piping and the reactor by naphthalene condensation, the line after the reactor was always maintained at 200°C using a heating coil.

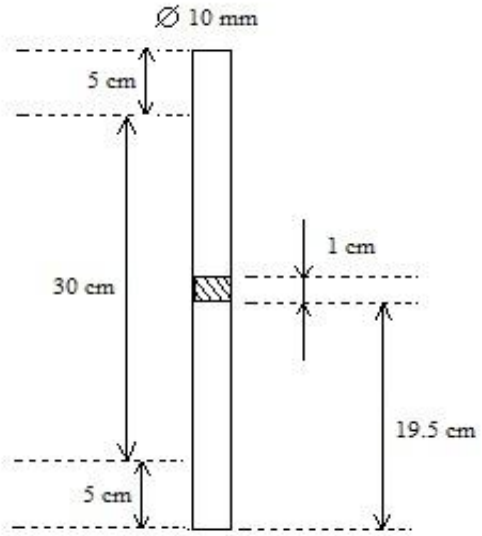


Figure 3.1 Fixed-bed quartz reactor

For steam reforming experiments, the steam produced by a steam generator at 300°C injected deionized water into the reactor with the N_2 flow rate of 30 ml/min. The total gas flow rate was 100 ml/min and the steam-to-carbon ratio was about 0.083. The gas product was collected every 20 minutes by 2L-gas bag throughout the experiment and was further analyzed by gas chromatograph (GC Shimadzu-14B and Shimadzu-2014). Tar product was trapped from the gaseous stream by iced-cold traps for further analysis by GC/MS technique. The standard deviation of carbon conversion into gas in each experiment was in the range of 1-3%.

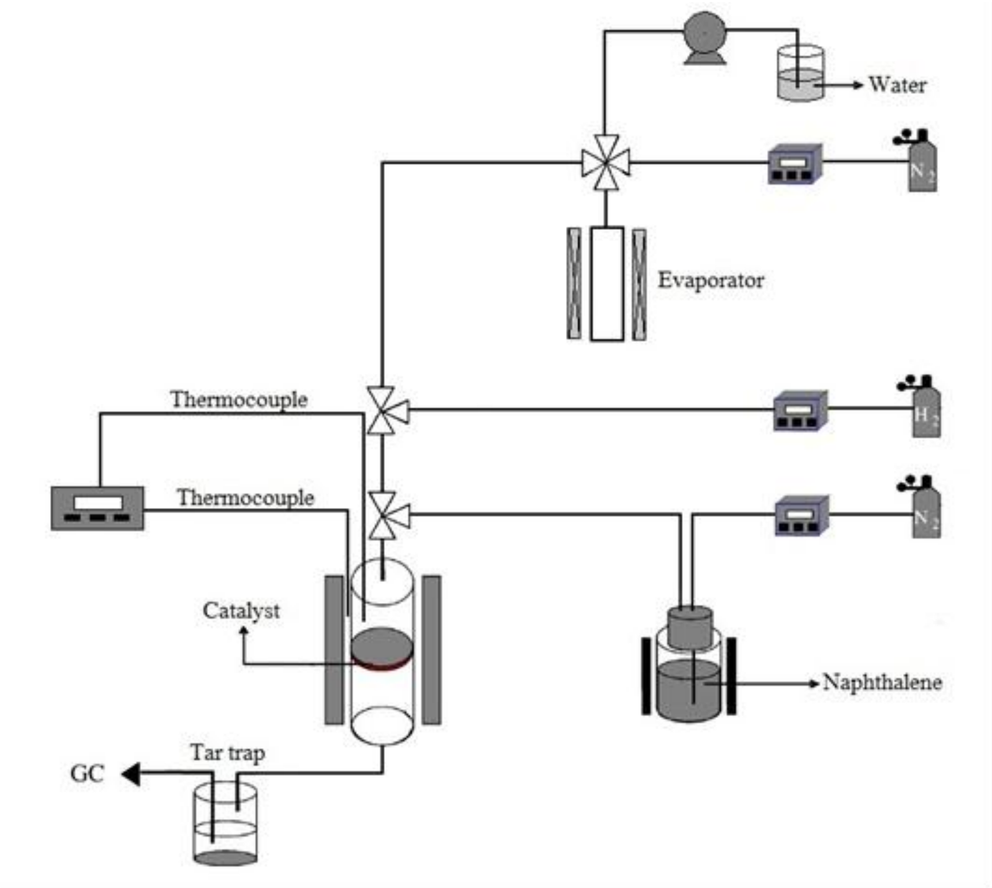


Figure 3.2 Experimental setup for catalytic steam reforming

3.5 Product gas analysis

The gas product, which was collected from the experiment processes, were analyzed by using two models of the gas chromatograph: GC-14B (Shimadzu), shown as in Figure 3.3(a), and GC-2014 (Shimadzu), as shown in Figure 3.3(b). Four major gas products were analyzed including CO, CO_2, H_2 and CH_4. The CO and CO_2 were analyzed using GC-14B with TCD detector through a molecular sieve (MS-5A) and porapak Q column, respectively. The H_2 and CH_4 were analyzed using GC-2014 through TCD and FID detectors, respectively.

(a) (b)

Figure 3.3 (a) Gas chromatography with thermal conductivity detector (GC-14B)
(b) Gas chromatography (GC-2014)

Carbon conversion into gas (%) calculation

The carbon conversion into gas (%) in this work was calculated as follows:

$$\text{Carbon conversion into gas (\%)} = \frac{[CO]_{out}+[CO_2]_{out}+[CH_4]_{out}}{10\,[C_{10}H_8]} \times 100$$

Where: $[C_{10}H_8]$ = The concentration of naphthalene entering the reactor
$[CO]_{out}$ = The concentration of carbon monoxide leaving the reactor
$[CO_2]_{out}$ = The concentration of carbon dioxide leaving the reactor
$[CH_4]_{out}$ = The concentration of methane leaving the reactor

CHAPTER 4
RESULTS AND DISCUSSION

Thermal decomposition and steam reforming of naphthalene with and without the presence of catalyst in a fixed bed reactor were investigated. The influences of temperature in range of 600 to 800°C and catalyst types were investigated in term of carbon conversion into gas and the composition of gas. The iron-based and nickel/iron-based catalysts were used in this experiment.

For this research, the results can be separated in three sections: catalyst characterization, thermal decomposition of naphthalene and steam reforming of naphthalene.

4.1 Catalyst Characterization

The crystalline structures of the catalysts were investigated by X-ray diffraction (XRD). Figure 4.1 shows the XRD patterns of Fe/Al_2O_3 and $Ni\text{-}Fe/Al_2O_3$ catalyst. The peaks of Al_2O_3 at $2\theta = 43.4°$ was taken as reference. With Fe metal addition on Al_2O_3 support, the peak intensity of Fe_2O_3 was observed at $2\theta = 33.1°$ and 35.6°. For $Ni\text{-}Fe/Al_2O_3$ catalyst, NiO peaks were found at 2θ between 37.2° and 43.2° as well as the peaks Fe_2O_3.

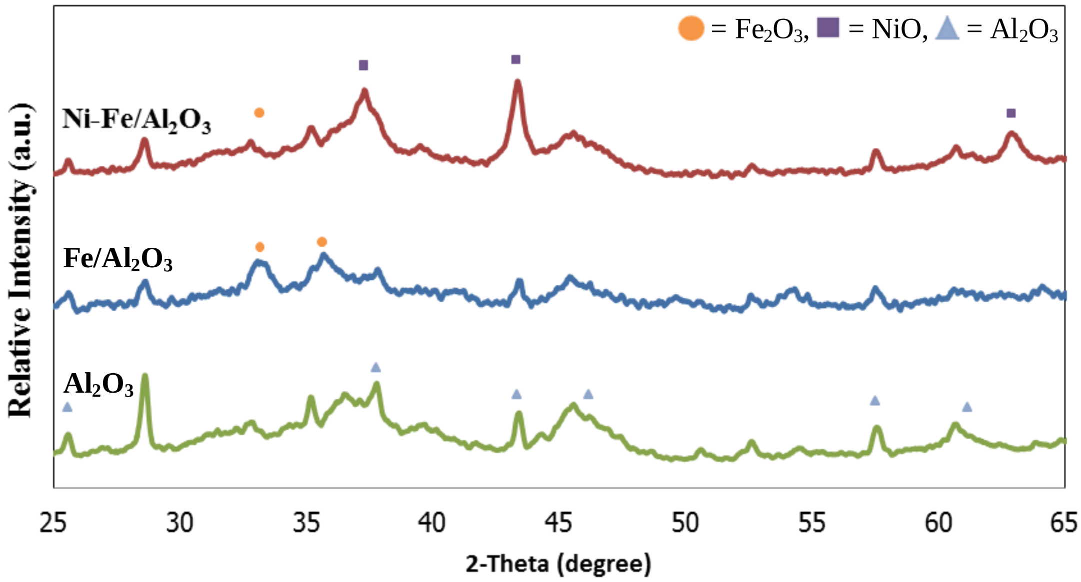


Figure 4.1 XRD patterns of Fe/Al_2O_3 and $Ni\text{-}Fe/Al_2O_3$ catalysts.

4.2 Thermal Decomposition of Naphthalene (without steam addition)

The effects of reaction temperature and the presence of catalysts on the thermal decomposition of naphthalene were investigated. Figure 4.2 presents the effects of temperature and the catalysts on carbon-conversion into gas (%) from naphthalene thermal decomposition. Without catalyst, the carbon conversion into gas increased from 0.68 to 4.39% when increasing temperature from 600 to 800°C. These results were consistent with the study of Ates and Isikdag (2009), which also observed that temperature is the importance factor to promote the rate of thermal cracking reaction. From the thermal cracking of tar reaction, the long-chained compounds will break down into comparatively smaller compounds. The thermal cracking reaction can be described with reactions (1) (Devi et al., 2005).

Thermal cracking: $pC_nH_x \rightarrow qC_mH_y + rH_2$ (1)

C_nH_x represents tar and

C_mH_y represents hydrocarbon with smaller carbon number than C_nH_x

With the presence of the Fe/Al_3O_2 catalyst, the carbon conversion into gas was higher at both temperatures. The effect of reaction temperature was more pronounced as compared to the case without a catalyst. The carbon conversion into gas was increased from 4.59 to 11.36 % when temperature was increased from 600°C to 800°C. As tar elimination reactions are known to be kinetically limited, the reaction rates can be increased by increasing the temperature and/or using a catalyst (El-Rub et al., 2004). It is likely that the Fe/Al_3O_2 catalyst promoted the thermal decomposition reaction and the tar molecules are broken down to lighter gases and soot (Fjellerup et al., 2005).

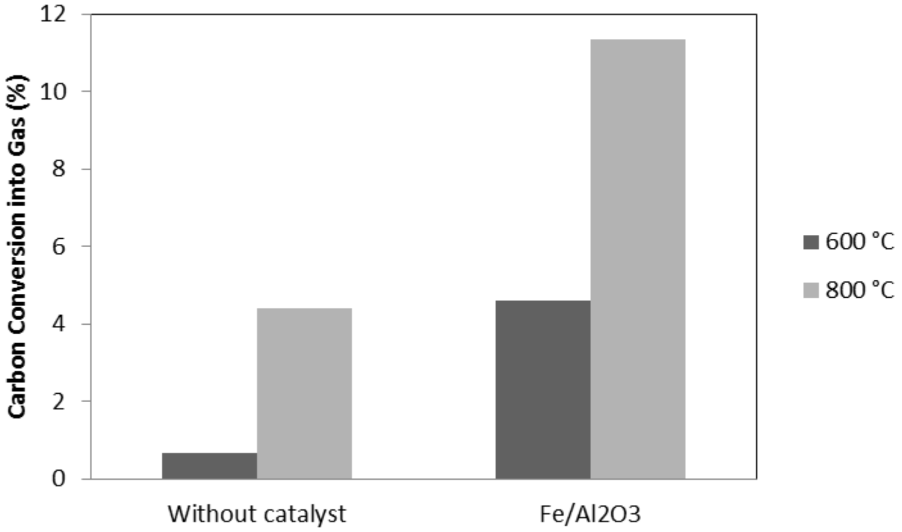
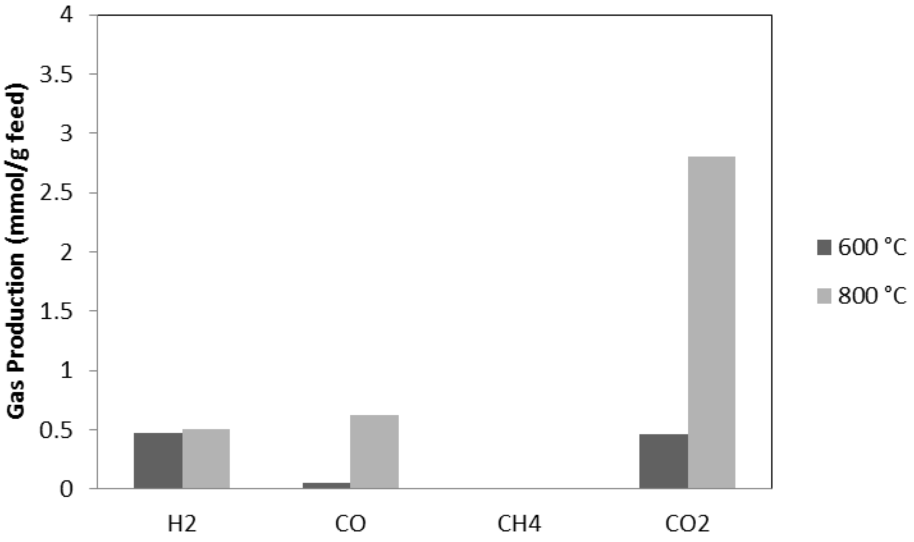


Figure 4.2 Effects of temperature and catalyst on carbon conversion into gas (%) from naphthalene thermal decomposition.

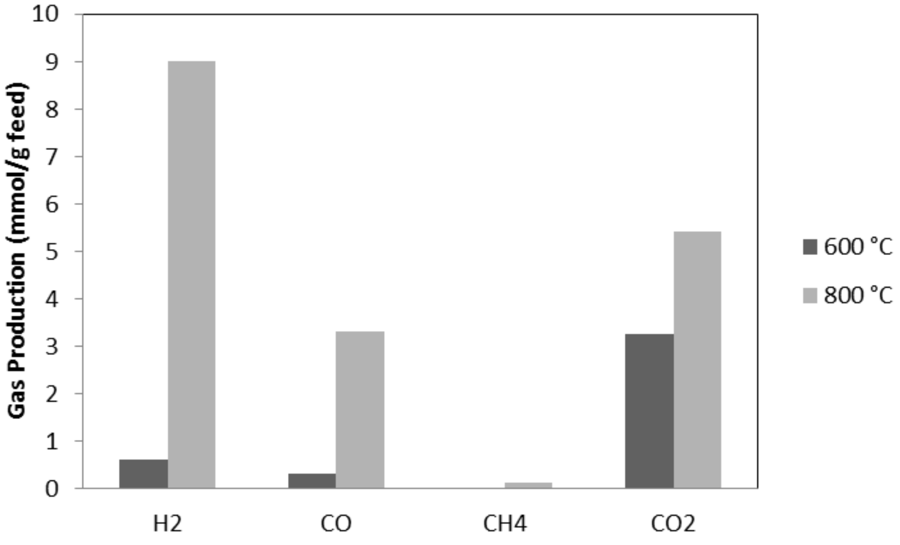
The effect of temperature on the product gas composition for naphthalene decomposition with and without Fe_2O_3 is presented in Figure 4.3. Without a catalyst, increasing temperatures resulted in increased CO and CO_2 production from the initial value of 0.05 to 0.62 mmol/g feed and 0.06 to 0.82 mmol/g feed, respectively. A different tendency was observed in case of H_2 and CH_4. With increasing temperature, H_2 and CH_4 remained stable at approximately 0.5 and 0.01 mmol/g feed, respectively.

The effect of temperature on the product gas species for naphthalene decomposition in the presence of Fe_2O_3 was also examined and the results were presented in Figure 4.3(b). With increasing temperature, the yields of H_2, CO, CH_4 and CO_2 were increased. In this experiment, H_2 was increased from 0.62 to 9.02 mmol/g feed, CO was increased from 0.32 to 3.32 mmol/g feed, CH_4 was slightly increased from 0.01 to 0.13 mmol/g feed and CO_2 was increased from 3.25 to 5.42 mmol/g feed.

Comparing the gas production in the case of without a catalyst and with Fe/Al_2O_3 catalyst at 800°C, the total gas production was increased when the Fe/Al_2O_3 catalyst was applied. In this experiment, H_2 was increased from 0.51 to 9.02 mmol/g feed, CO was increased from 0.62 to 3.32 mmol/g feed, CH_4 was increased from 0.01 to 0.13 mmol/g feed and CO_2 was increased from 2.80 to 5.42 mmol/g feed when use catalytic thermal decomposition. These results are in good agreement with the study by Uddin et al. (2008), which reported that iron oxide catalyst has a positive effect on the composition of the gaseous products of biomass decomposition. It was similarly found that the production of H_2 and CO_2 increased in the presence of iron oxide catalyst when compared to the non-catalytic gasification, which is explained by the mechanism as shown in Figure 4.4. The surface iron (-Fe) connected to bulk iron oxide Fe_3O_4 reacts with tar to produce CH_4, C_2H_4, H_2O, CO and H_2 over the iron oxide catalyst.



(a)



(b)

Figure 4.3 Effect of temperature on gas production (mmol/g feed) (a) without catalyst and (b) Fe/Al_2O_3 catalyst in naphthalene thermal decomposition.

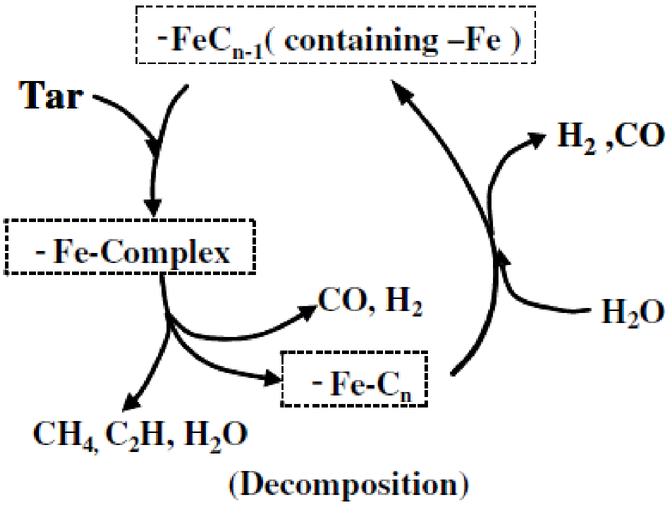


Figure 4.4 Schematic diagram of mechanism of a catalytic decomposition of biomass tar over iron-based catalyst (Uddin et al., 2008)

4. 3 Steam reforming of Naphthalene

4.3.1 Effect of Reaction Temperature

The effect of reaction temperatures at 600°C, 700°C and 800°C on carbon conversion with the Fe/Al_2O_3 catalyst are shown in Figure 4.5. It was observed that there was an increase in the carbon conversion with increasing temperature. At 800°C, the carbon conversion was 16%.

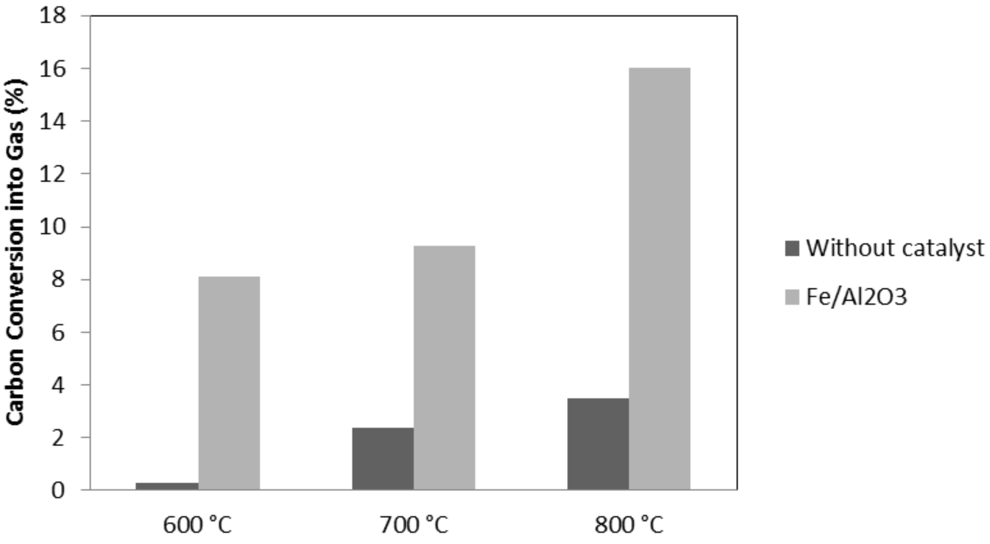
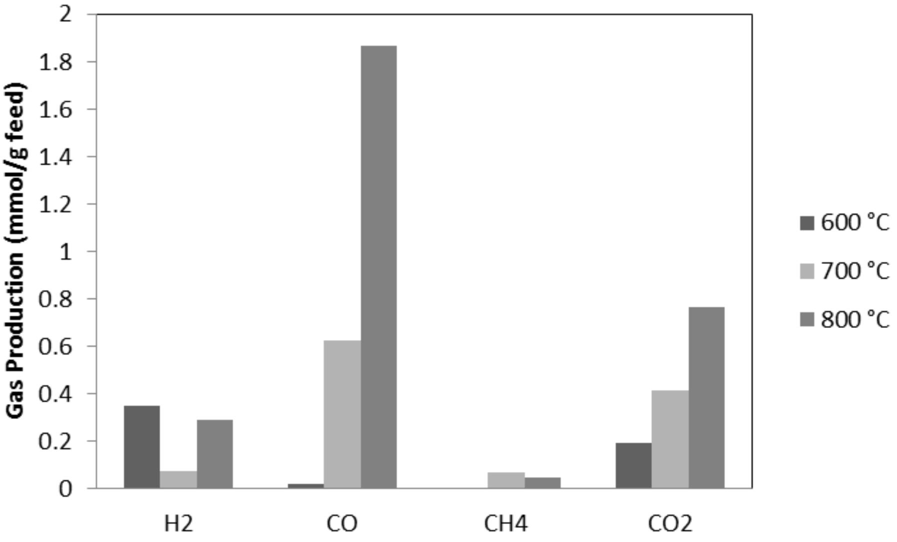
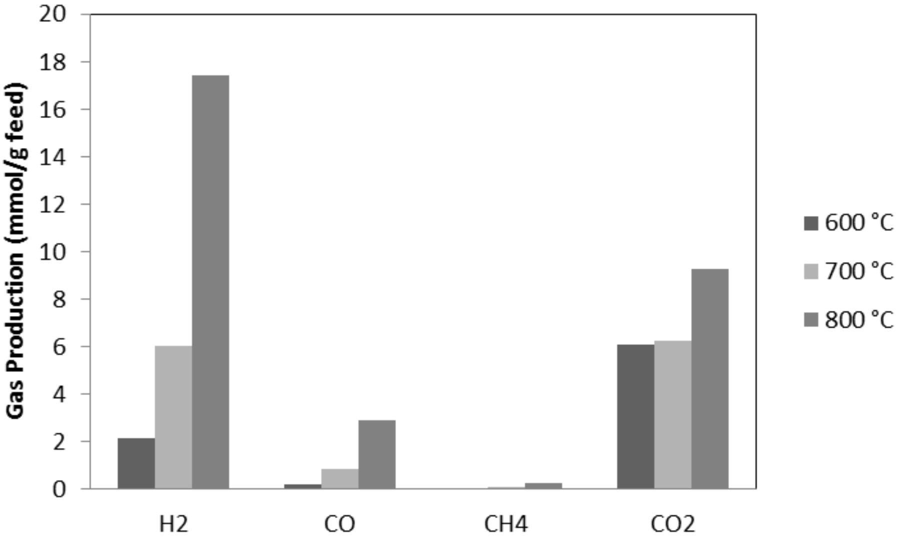


Figure 4.5 Effect of reaction temperature on carbon-conversion (%) with Fe/Al_2O_3 catalyst in naphthalene steam-reforming

Figure 4.6 shows the effect of reaction temperature on gas production (mmol/g feed) with Fe/Al_2O_3 catalyst in naphthalene steam reforming. The trends of all gas production were increased when the temperature was increased.



(a)



(b)

Figure 4.6 Effects of reaction temperature on gas production (mmol/g feed) (a) without catalyst and (b) with Fe/Al_2O_3 catalyst in naphthalene steam-reforming

4.3.2 Effect of Steam Addition

As described in the previous section, the carbon conversion of catalytic steam reforming at 800°C showed the highest value when compared to the other temperatures. Therefore, the temperature at 800°C was investigated in catalytic steam reforming.

The result of the effect of steam addition at 800°C on carbon conversion (%) with and without steam is shown in Figure 4.7. The carbon conversion was increased from 11.36 to 16% when steam was added. The increased carbon conversion was resulted from steam reforming reaction.

Catalytic steam reforming is the best way to destroy tar components by converting them into gases. This process involves the partial oxidation of the tar components using steam to produce hydrogen. The reaction pathway can be described by Reactions (2) and (3) (Coll et al., 2001).

Steam reforming: $C_xH_y + H_2O \rightarrow xCO + (x + y/2)H_2$ (2)

Water-gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$ (3)

Figure 4.8 shows the effects of steam addition of the catalyst at 800°C on gas production with and without steam. The trends of all gas production was increased when steam was added. In contrast, the trend of CO gas was decreased. The results show that H_2 was increased from 9.02 to 17.41 mmol/g feed, CO_2 was increased from 5.43 to 9.28 mmol/g feed, CH_4 was increased from 0.12 to 0.28 mmol/g feed and CO was decreased from 3.32 to 2.92 mmol/g feed. According to water-gas shift reaction, which is shown in equation (3), CO reacts with water to form CO_2. In additions, these results are consistent with a diagram of mechanism of a catalytic water-gas shift reaction over iron-based catalyst (See in Figure 4.9). The produced CO is converted to CO_2 and H_2 by water gas shift reaction. The reaction occurred over the iron oxide active site that is different from that occurred during tar decomposition reaction (Uddin et al., 2008). Therefore, CO in catalytic steam reforming process was reduced when compared with catalytic thermal decomposition.

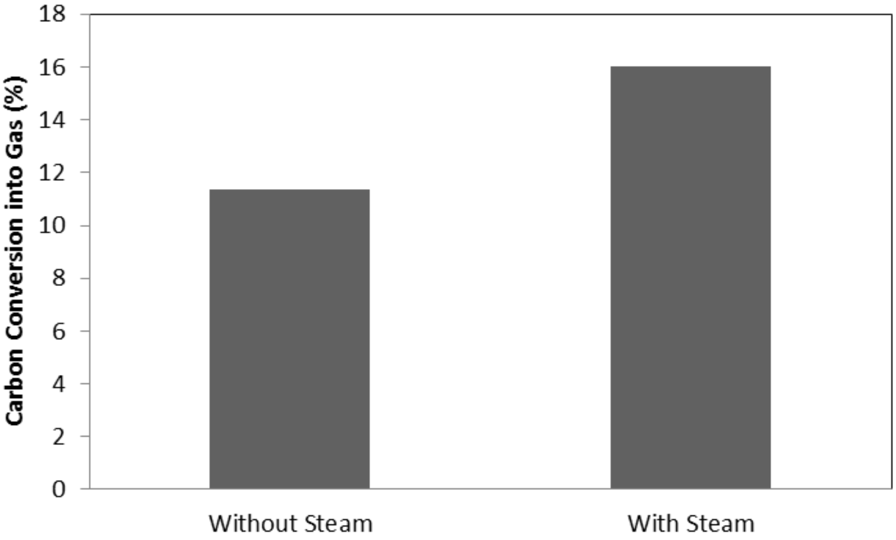


Figure 4.7 Effect of steam addition of Fe/Al_2O_3 catalyst at 800°C on carbon-conversion (%) with and without steam.

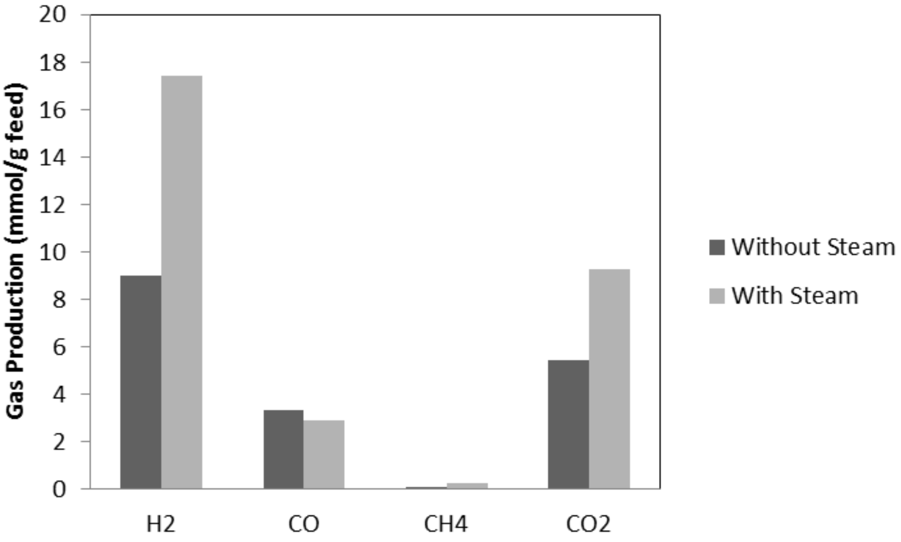


Figure 4.8 Effect of steam addition of Fe/Al_2O_3 catalyst at 800°C on gas production (mmol/g feed) with and without steam

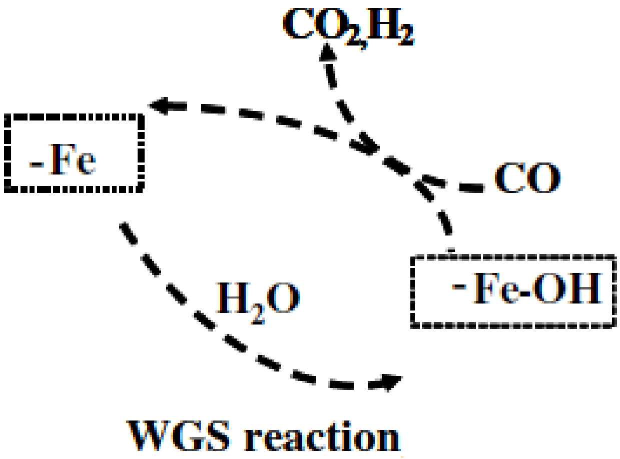


Figure 4.9 Schematic diagram of mechanism of a catalytic water-gas shift reaction over iron-based catalyst (Uddin et al., 2008)

4.2.3 Effect of Catalyst type

All prepared catalysts, including Fe/Al_2O_3 and Ni-Fe/Al_2O_3, were tested with the decomposition of naphthalene at 800 °C. It is noted that the reaction without catalyst was also carried out for comparison. The effect of catalyst with steam at 800°C on carbon conversion into gas is shown in Figure 3. It was found that the carbon conversion into gas of naphthalene with the presence of catalysts were 16–30%, which was significantly higher than those from without catalyst case. A comparison of carbon conversion into gas between Fe/Al_2O_3 and Ni-Fe/Al_2O_3 catalyst found that the Ni-Fe/Al_2O_3 catalyst gave the higher in carbon conversion than Fe/Al_2O_3 catalyst about 14%. This can be explained that the addition of Ni might promote the reforming reaction of naphthalene as can be seen the higher in H_2 and CO yields in Figure 4. In addition, the higher activity of Ni-Fe/Al_2O_3 could be explained by the synergy effect between Ni and Fe bimetallic species (Wang et al., 2011).

In contrast, the higher amount of Ni loading with in cases of the presence of 12%Ni-3% Fe/Al2O3 catalyst gave the lower in catalytic activity on naphthalene reforming as can be evidenced in the lower of carbon conversion into gas. With regards of product gas composition, H_2, CH_4, CO, and CO_2 were the main gaseous species from naphthalene reforming. The effect of catalyst type on gas production is shown in Figure 4. It was found that the 3%Ni-12%Fe/Al_2O_3 catalyst gave the highest H_2 and CO in steam reforming of naphthalene at 800°C. It indicates that the catalytic performance of Fe/Al_2O_3 catalyst was increased by a little amount of Ni loading. This result was consistent with the previous study (Oemar et al., 2013) which reported that the presence of Ni-Fe bimetallic particles in $LaNi_{0.8}Fe_{0.2}O_3$ catalyst had displayed higher performance than the $LaNiO_3$ catalyst for H_2 production due to the presence of Ni-Fe bimetallic particles. Moreover, Ni species has been known as the catalyst for tar cracking and steam reforming of hydrocarbon following the reaction as shown in Equations (4) and (5) (Yamazaki et al., 1996).

$$CH_4 + Ni \rightarrow CH_x - Ni + \left(\frac{4-x}{2}\right) H_2 \quad (4)$$

$$CH_x - Ni + H_2O \rightarrow \left(\frac{x}{2}+1\right)H_2 + CO \quad (0 \le x < 4) \quad (5)$$

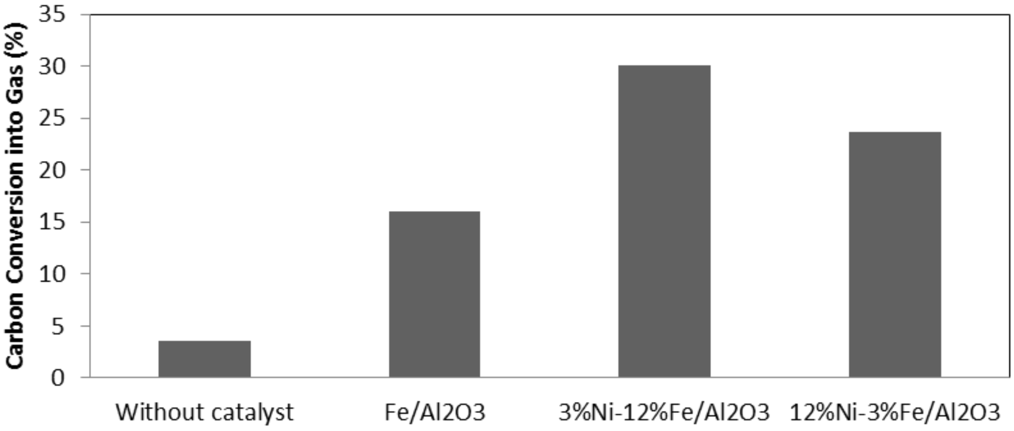


Figure 4.10 Effect of catalyst with steam at 800°C on carbon-conversion (%) in naphthalene steam reforming

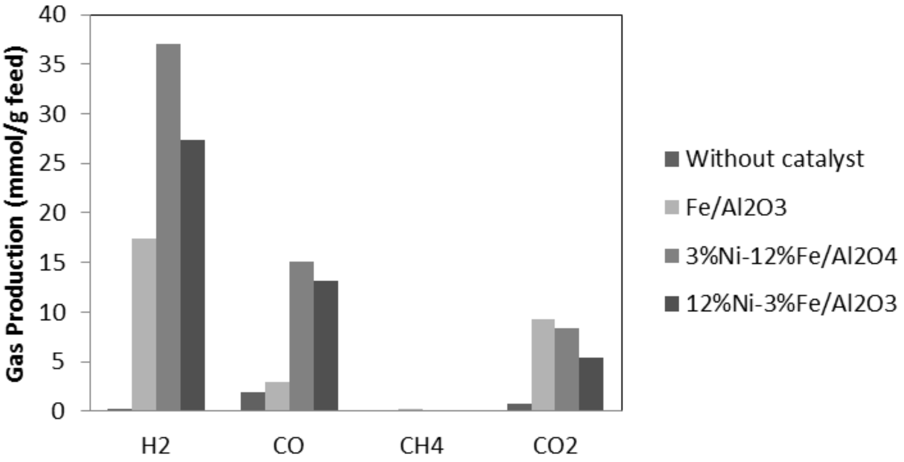


Figure 4.11 Effect of catalyst with steam at 800°C on gas production (mmol/g feed) in naphthalene steam reforming

CHAPTER 5
CONCLUSION

5.1 Conclusion

This work focused on the effect of tar cracking in the gasification process by comparing catalytic and non-catalytic steam reforming. Naphthalene was selected as the tar model compound for this study. The catalytic cracking was test by using Fe/Al_2O_3 and Ni-Fe/Al_2O_3 catalysts. The tar cracking tests were carried out in a fixed bed reactor at 600, 700, and 800°C. The catalysts were analyzed using XRD. From the results of the study, the major conclusions can be made as follow:

(1) The reaction temperature (600-800°C) of naphthalene thermal cracking on carbon conversion into gas – the carbon conversion into gas without and with a Fe/Al_2O_3 catalyst were increased 6.45 and 2.47 times respectively when the temperature was increased. Comparison of the carbon conversion between non-catalyst and Fe/Al_2O_3 catalyst at 600 and 800°C, the results showed that the catalytic thermal decomposition gave carbon conversion into gas higher than the thermal degradation without catalyst 6.75 and 2.59 times, respectively. In addition, the gas production was also increased with increasing temperature.

(2) The results from the experiments of steam addition at 0.083 ratios (S/C) were observed such that the carbon conversion into gas increased 1.41 times. The trends of all gas production were also increased with adding steam. In addition, the reaction temperature (600-800°C) also has an effect with carbon conversion into gas and gas product. It was observed that there was an increase in the carbon conversion into gas with increasing temperature. And, the trends of total gas production were also increased when temperature increased.

(3) The type of catalyst on steam reforming has the effect to carbon conversion into gas and gaseous products. From this experimental, it was found that 3%Ni-12%Fe/Al_2O_3 catalyst gave the highest carbon conversion around 30.05% as well as the highest H_2 production.

5.2 Future works

It is recommended for future works to investigate a wider range of operating conditions, such as steam-to-carbon ratio, naphthalene concentration, catalyst loading, type of catalysts, etc. The findings should also be extended to real biomass tars.

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APPENDIX A: CALCULATION

Naphthalene feed rate calculation

Naphthalene feed rate resulted from the difference in weight between before and after naphthalene was put into the system. The weight of naphthalene in term of gram unit was converted to mmol/min.

Example of calculation

Weight of naphthalene into the system for 60 minutes = 0.406 g

If the weight of naphthalene into the system for a minute = 0.406÷60 = 0.0068 g/min

Molecular weight of naphthalene = 128 g/mol

Therefore, the naphthalene feed rate $= \frac{0.0068\ g/min}{128\ g/mol} \times 1000$

= 0.05 mmol/min

Steam to carbon ratio calculation

Water feed rate at 25°C = 0.09 ml/min = 0.09 g/min

Specific volume of superheated steam at 300°C = 21.67 ml/g

Steam inlet flow rate = 0.09 g/min × 21.67 ml/g = 1.95 ml/min

Naphthalene inlet flow rate = 0.05 mmol/min

Carbon in naphthalene $= \frac{0.05\ mmol/min}{10}$ = 0.005 mmol/min

Change steam inlet into mmol/min by assuming that steam is ideal gas at 300°C

$$PV = nRT$$

$$n = \frac{(1atm)\cdot(1.95ml/min)}{82.05736\frac{cm^3\cdot atm}{K\cdot mol}\cdot 573\ K}$$

$$n = 0.415\times10^{-4}\ mol/min$$

So that steam to carbon ratio at inlet $= \frac{4.15\times10^{-4}\times10^{3} mmol/min}{0.005\ mmol/min}$

= 0.083

Gas product calculation

Table A1 shows peak areas of the concentration of gas standards analyzed by gas chromatography. These areas of peaks were used in calculation a gas product which received from experiment. The gas product was collected every 20 minutes into gas bag for 60 minutes are analyzed by gas chromatograph. The volume of gas in each gas bag has 2000 ml. The peak areas of product gas, which result from thermal decomposition experiment at 600°C, are shown in Table A2. Table A3 shows the example of calculate concentration of gas product in gas bag 1. The concentration of gas product, which results from the calculation, is shown in Table A4.

Table A1 Concentration of gas standards

Type of gas	**Concentration (%)**	**Area**
H_2	1.12	117418.8
CO	1	26897.2
CH_4	0.98	68234762.75
CO_2	1	31100.9

Table A2 The peak areas of product gas

No. of gas bag	**Peak area of gas product**			
	H_2	**CO**	**CH_4**	**CO_2**
1	14451.3	517.8	304363.55	4507.95
2	2000.4	-	20743.95	3069.15
3	2544.1	-	40797.6	757.5

Table A3 Examples of calculations

Type of gas	**Area**	**Concentration (%)**	**Volume of gas (mL)**	**Mole of gas (mmol)**
H_2	14451.3	(1.12×14451.3)/ 117418.8	(0.1378×2000)/100	2.7569/(0.08206×298)
CO	517.8	(1×517.8)/ 26897.2	(0.0193×2000)/100	0.3850/(0.08206×298)
CH_4	304363.55	(0.98×304363.55)/ 68234762.75	(0.0044×2000)/100	0.0874/(0.08206×298)
CO_2	4507.95	(1×4507.95)/ 31100.9	(0.1449×2000)/100	2.8989/(0.08206×298)

Table A4 Concentration of gas production

Gas bag 1: (0-20 minutes)

Type of gas	**Area**	**Concentration (%)**	**Volume of gas (mL)**	**Mole of gas (mmol)**
H_2	14451.3	0.1378	2.7569	0.1127
CO	517.8	0.0191	0.3850	0.0157
CH_4	304363.55	0.0041	0.0874	0.0036
CO_2	4507.95	0.1449	2.8989	0.1185

Gas bag 2: (20-40 minutes)

Type of gas	**Area**	**Concentration (%)**	**Volume of gas (mL)**	**Mole of gas (mmol)**
H_2	2000.4	0.0191	0.3816	0.0156
CO	-	-	-	-
CH_4	20743.95	0.0003	0.0059	0.0002
CO_2	0.0261	0.0261	0.5228	0.0213

Gas bag 3: (40-60 minutes)

Type of gas	**Area**	**Concentration (%)**	**Volume of gas (mL)**	**Mole of gas (mmol)**
H_2	2544.1	0.0243	0.4853	0.0198
CO	-	-	-	-
CH_4	40797.6	0.0006	0.0117	0.0005
CO_2	757.5	0.0065	0.1290	0.0053

Overall gas production

Type of gas	**Mole of gas (mmol)**	**mmol/g feed**
H_2	0.1482	0.4765
CO	0.0157	0.0506
CH_4	0.0043	0.0138
CO_2	0.1452	0.4669