

**HYDROGEN PRODUCTION VIA GLYCEROL DRY
REFORMING OVER NICKEL CATALYST
SUPPORTED ON SiO₂ AND Al₂O₃ MODIFIED BY La**

FARAHANI BINTI SARAJUDDIN

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**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

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ABSTRACT

Currently, energy has become the most demand for human needed. The utilization of future energy that is clean and sustainable becomes increasingly urgent because of dwindling petroleum reserves and mounting environmental concerns that are associated with fossil fuel. Hydrogen has been considered as the most suitable alternative for future energy aiming to reduce the dependence on fossil fuel and carbon based emission. Previously, non-renewable resources mainly coal, fossil fuel, petroleum coke, and petroleum residues has been widely used as the main feedstock for syngas (H_2 and CO) production. However, due to the various factors such are global warming, the unstable price and availability of petroleum-based oil as well as the environmental pollution, the desirability towards biomass (glycerol) as the alternative energy feedstock has attract the world's attention. Glycerol which a by-product of biodiesel production is one of the most promising renewable sources associated environmental impacts from the usage of the fossil fuels in which it minimal carbon dioxide (CO_2) emission and more preferable in fuels production. In recent years, the production of hydrogen from glycerol via steam reforming widely investigated, only a few studies on dry reforming with CO_2 . Therefore, this project was attempted to study the production of hydrogen via glycerol dry reforming over nickel (Ni) catalyst supported on silica oxide (SiO_2) and alumina (Al_2O_3) modified with lanthanum (La). This works aims to synthesis, characterize, and screening Ni catalyst supported on SiO_2 and Al_2O_3 with promoted in La solution using various techniques such are Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) analysis , Mastersizer 2000 Ver.5.60 and elemental analysis. The catalyst characterization includes their porosity, structure, crystalline behaviour, and a physiochemical property is investigated. It shows that the promoted catalyst possessed smaller metal crystalline size, hence higher metal dispersion compared than both Ni/Al_2O_3 and Ni/SiO_2 catalyst. In addition, the particle size distribution measured by Mastersizer measurement for promoted alumina catalyst gave higher size distribution which about $0.452\ m^2/g$ compared than silica oxides support. The reaction studies for syngas production at $T=973\ K$ for 3 hour reaction time with the inlet flowrate and carbon to to glycerol ratio is 0.03 ml/min and 1 had successfully produced H_2 with glycerol conversion and H_2 yield that peaked at 5.8% and 28% respectively over 3% La content. The catalyst screening shows that the alumina support gave excellent catalytic performance compared than silica oxide due to the larger surface area and smaller crystallite size that ensured accessibility of active catalytic area.

ABSTRAK

Pada masa ini, kepentingan tenaga untuk keperluan manusia semakin meningkat. Tambahan pula, kekurangan rizab petroleum dan pencemaran alam sekitar akibat penggunaan bahan api fosil mendesak kepada penghasilan tenaga yang bersih dan kekal. Hidrogen merupakan tenaga yang boleh diperbaharui dan mengurangkan pergantungan kepada bahan api fosil dan pelepasan karbon. Sebelum ini, sumber-sumber yang tidak boleh diperbaharui terutamanya arang batu, bahan api fosil, kok petroleum, dan sisa petroleum telah digunakan secara meluas sebagai bahan mentah utama untuk syngas (H_2 dan CO). Walau bagaimanapun, disebabkan oleh pelbagai faktor seperti pemanasan global, harga yang tidak stabil dan ketersediaan minyak berasaskan petroleum dan juga pencemaran alam sekitar, kebaikan ke arah biomass (gliserol) sebagai bahan asas tenaga alternatif telah menarik perhatian dunia. Gliserol, hasil daripada penghasilan biodiesel merupakan salah satu bahan asas yang menjanjikan impak yang lebih baik berbanding bahan api fosil di mana ia dapat meminimumkan pelepasan gas CO_2 . Walau bagaimanapun, hanya sedikit kajian diberikan untuk pengeluaran hidrogen dari gliserol. Oleh itu, kajian ini bertujuan untuk mengkaji pengeluaran hidrogen menggunakan kaedah reformasi gliserol berasaskan mangkin nickel disokong oleh oksida yang berbeza iaitu SiO_2 dan Al_2O_3 dan diubahsuai dengan La. Kajian ini berfungsi untuk sintesis, mencirikan, dan saringan nickel pemangkin disokong pada oksida berbeza SiO_2 dan Al_2O_3 diubahsuai dengan Lantanum menggunakan pelbagai teknik analisis seperti Imbasan Elektron Mikroskop (SEM), X-Ray Belauan (XRD) analisis, Mastersizer 2000 Ver.5.60 dan analisis unsur. Pencirian pemangkin termasuk struktur, kelakuan kristal, dan harta physiochemical telah dikaji. Kajian menunjukkan bahawa pemangkin yang diubahsuai oleh lanthanum memiliki saiz kristal logam kecil, penyebaran logam itu lebih tinggi berbanding daripada kedua-dua Ni/Al_2O_3 dan Ni/SiO_2 pemangkin. Di samping itu, taburan saiz zarah diukur dengan ukuran Mastersizer untuk pemangkin alumina yang diubahsuai memberikan taburan saiz yang lebih tinggi iaitu $0.452 \text{ m}^2 / \text{g}$ berbanding daripada oksida silika magkin. Kajian tindak balas bagi pengeluaran syngas pada $T = 973 \text{ K}$ untuk tindak balas masa 3 jam dengan kadar alir masuk dan karbon untuk nisbah gliserol ialah $0.03 \text{ ml} / \text{min}$ dan 1 telah berjaya menghasilkan H_2 dengan penukaran gliserol dan hasil H_2 yang memuncak pada 5.8% dan 28 %. Pemeriksaan pemangkin menunjukkan bahawa sokongan alumina memberikan prestasi pemangkin cemerlang berbanding daripada oksida silika kerana kawasan permukaan yang lebih besar dan saiz kristal yang lebih kecil.

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1 INTRODUCTION

1.1 Motivation and statement of problem

Energy is known as the most important resources for people nowadays. After the energy crisis in 1970s, the need to find alternative energy resources that are clean and sustainable becomes increasingly urgent as the fossil fuel which is the main source of energy production has to be limited. This limitation is arises because of decreasing petroleum reserves and mounting environmental concerns that are associated with fossil fuel utilization.

The development of energy has focused on making available sufficient for both primary and secondary sources to meet the needs of society. It is widely used in many sectors such as transportation, agricultural, industrial and many more. Thus, energy demand is a key component of the sustainable energy question considering the demand in addition to supplies. Based on the Figure 1, as the population increases and people experience higher standard of living, the world energy demand will continue to increase.

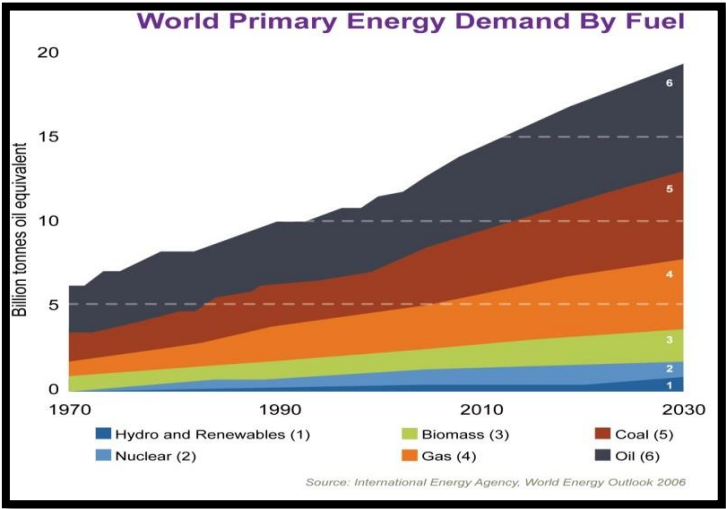


Figure 1.1 World Primary Energy Demand by Fuel

Currently, fossil fuels which also known as the primary energy that can be found in nature are the main supplier or raw materials to supply this energy are finite; however, it cannot sustain the current trends in use. These will required an increase in sustainable energy sources to balance the depleting fossil fuels. As raw fossil feeds are diminishing resources, chemical and energy related industries are examining alternative renewable energy sources, while conversion to commodity chemicals facilitates the replacement of petroleum by renewable

resources. For a long period, it has been proposed to use renewable resources for the production of transportation fuels, especially syngas.

Production of syngas from glycerol had received an attractive attention during the past few years and has been considered as the most viable alternative energy resources to replace the fossil fuels as feedstock. At the same time, glycerol is one of the most promising renewable sources associated environmental impacts from the usage of the fossil fuels in which it minimal CO₂ emission which is more preferable in fuels production. Moreover, with the advantages of glycerol such as it has higher biodegradability, can easily be obtained from inexpensive, readily available feedstock, renewability as well as higher combustion efficiency making it potentially to be discovered by researcher in their studies. Glycerol is produced as the main byproduct of biodiesel production by transesterification of vegetable oil and animal fats. It has been reported that the production of glycerol will exceed the demand as the production of biodiesel increased which yielded about 10% (wt/wt) and the prices of glycerol has dropped over the last few years due to the oversupply.

As a result, it is imperative to find alternative uses for excess glycerol and produce value added secondary products such as fuels or chemicals since the global market demand for biodiesel is expected to increase by 37 billion gallons on 2016 with an annual growth of 42% (Wang et al., 2006). The utilization of glycerol to produce value added products is a promising abundant source which could improve the biodiesel industry even more economically feasible. Recently, many researchers had shown strong interest in developing the conversion of glycerol into value-added chemical and fuels including hydrogen.

In recent years, the production of hydrogen or syngas from glycerol via various methods has been considered and widely investigated such as steam reforming, partial oxidation, auto thermal reforming, aqueous reforming and supercritical reforming. However, the production of hydrogen via dry reforming of glycerol is still less to be known. Thus, this project was attempted to review syngas production methods using glycerol in which focusing on CO₂ dry reforming process of glycerol. Dry reforming process has a lot of advantages such as this process does not require much energy compared than steam reforming as well has shown higher yield of syngas produces with the ratio of CO₂ to glycerol is 1. Therefore, this alternative has opened a new development of producing syngas from CO₂ dry reforming of glycerol over nickel catalyst supported on oxides.

Catalyst containing Ni has been widely used in reforming technologies due to their excellent capacity for carbon-carbon bond cleavage, as well as its availability and low cost compared to noble metals such as Rh, Pt, and Pd (Vivian et al., 2013). However, these catalysts are also

known to favor the deposition of carbon (coking), which may reduce the performance of the catalyst. Significantly, coking onto the catalyst can be reduced by supporting on oxides such as aluminum oxide (Al_2O_3), silicon oxide (SiO_2), cerium oxide (CeO_2), lanthanum oxide (La_2O_3), magnesium oxides (MgO), and zirconium oxide (ZrO_2).

Aluminum oxide (Al_2O_3) and silicon oxide (SiO_2), which is a common heterogeneous base catalyst has been consider as the best selection for this experiment as it shows higher activity, mild reaction conditions, reusable and low cost. Primarily, heterogeneous base catalyst have benefits of being reusable, noncorrosive, perform greater tolerance to water and free fatty acids in feedstock, have a simpler purification process for glycerol and easy to separate from biodiesel product. Thus, this paper reports a study on CO_2 dry reforming of glycerol over alumina (Al_2O_3) and silicon oxides (SiO_2) . supported Lanthanum-promoted Ni catalyst.

1.2 Objectives

- This work aims to synthesis, characterize, and screening Ni catalyst supported on Al_2O_3 and SiO_2 with promoted on lanthanum solution using SEM, XRD, BET surface area, and elemental analyzer.
- To conduct a catalytic activity test for catalyst screening on different types of oxides (Al_2O_3 and SiO_2) promoted with lanthanum solution.

1.3 Scope and Research Contribution

The overall thrust of this thesis is the development of a La-Ni/ SiO_2 and La-Ni/ Al_2O_3 system for glycerol dry reforming. The specific scopes of this research are to:

- Synthesis, characterize, and screening of Ni catalyst supported on various oxides such as Al_2O_3 and SiO_2 with promoted on lanthanum solution using SEM, XRD, BET surface area, and elemental analyzer.
- Optimization of syngas production by conducting a catalytic activity test for catalyst screening on different types of oxides (Al_2O_3 and SiO_2) promoted with lanthanum solution.

1.4 Organization of this thesis

The flow of the chapters is defined as follow:

Chapter 2 presents an overall literature review. The growth of energy utilization is explained in section 2.2. The studies of glycerol by-product and the usage of it in replacement of fossil fuel are presented in this chapter. In addition, the study of glycerol possible route for syngas production is clarified in section 2.4. Finally, section 2.5 is dedicated to the deactivation of catalyst with emphasis on carbon-induced deactivation. The different promoter and supports on oxides are also discussed in this section.

Chapter 3 explains the experimental details. This encompasses catalyst preparation, catalyst characterization techniques and glycerol dry reforming experimental set up.

Chapter 4 describes the detail description on how different support and promoted will affect the glycerol conversion and hydrogen yield as well as the deactivation of catalyst.

Chapter 7 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 General Overview

Development of new power generation technology and relevant alternative fuels increasingly important issues in the search for feasible ways to address the growth in global energy demand. As the most viable alternative fuel, biodiesel has received an attractive attention during past few years because of the decreasing petroleum reserves and the associated environmentally impacts from the usage of fossil fuels. Currently, glycerol as the main by-product during production of biodiesel has getting interest by many researcher to develop the conversion of glycerol into added value product since annual biodiesel production is expected to increase, and the production of glycerol may exceed demand. Therefore, the possible uses of excess glycerol should be investigated. Glycerol can be used to produce a variety of chemicals and fuels including syngas. Syngas is as gas mixture that comprises of carbon monoxide, carbon dioxide and hydrogen. It can be produced from glycerol via several process such are steam reforming, aqueous-phase reforming (APR), supercritical reforming, dry auto thermal reforming, and partial oxidation reforming. Previously, a lot of studies had investigated the production of hydrogen via this process, however still less work studies on CO₂ dry reforming of glycerol. Therefore, this project was aim to investigate the production of synthesis gas (syngas) via CO₂ dry reforming of glycerol process over noble metal based catalyst.

2.2 Energy

Nowadays, energy becomes the most demand for the mankind and its utilization is vital for human needed. The development of energy has focused on making available sufficient for both primary and secondary energy sources to meet the needs of society. Primary energy which includes electricity, biomass energy, geothermal energy, fossil fuels, nuclear energy, solar energy, and wind energy is the form of energy found in nature that has not been subjected to any conversion or transformation process. Primary energy can be non-renewable or renewable energy where non-renewable energy is the one that will run out or need thousand or million years to be filled again such as fossil fuel, whereas renewable energy is energy that obtained from natural resources which can be provided continuously.

Secondary energy refers to the more convenient forms of energy which are transformed from other, primary, energy sources through energy conversion processes. Energy is widely used in many sectors such as industrial, residential, agricultural and etc. Contemporary industrial societies use primary and secondary energy sources for transportation and the production of many value added products.

The world Energy Council (WEC) expects the demand in energy to have increased by between 50 to 70 per cent over 1992 figures by the year 2020 where 50 % of the countries in the world are in the transformation of industrialization with economic growing rapidly, some at 10% or more. This calls for an ever-increasing supply of coal, oil and now natural gas. The rise in the world population making the global situation more challenging where it is reported that today's population of nearly 6 billion will increase up to 10 billion by 2050 and 80% of that population will be in developing countries. Thus, their demand for the services provided by energy and an improved life-style is undeniable.

This increase demand is the exponential growth of the world's human population as shown in the Figure 2.1. As more of the developing world becomes more industrialized, the more energy humans will need.

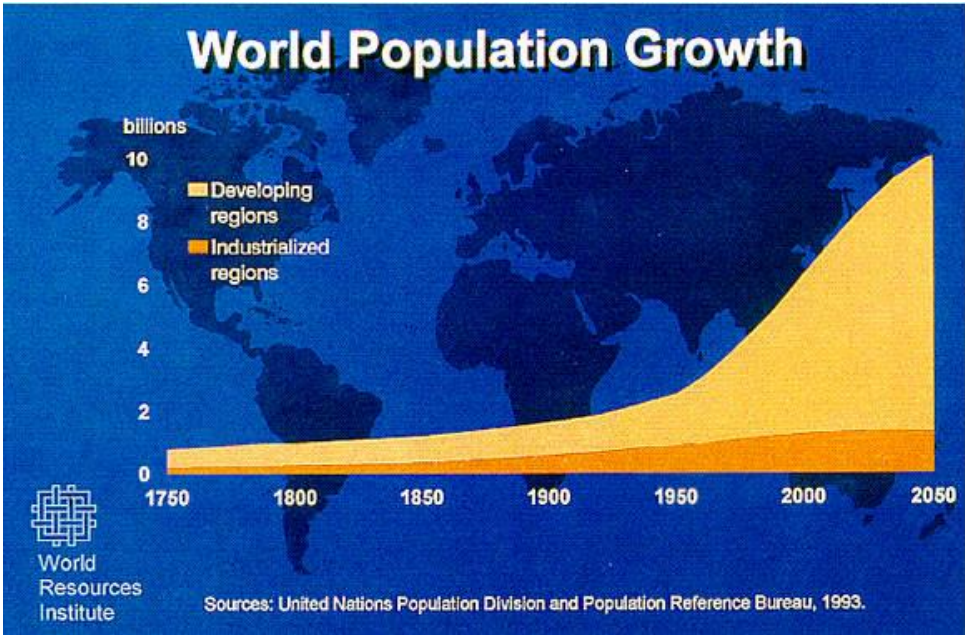


Figure 2.1 World Population Growth, 1750-2050

Worldwide energy use has been increasing and is projected to keep on increasing as shown in the Figure 2.2, especially the demand for oil.

World Energy Consumption by Fuel Type, 1970-2020

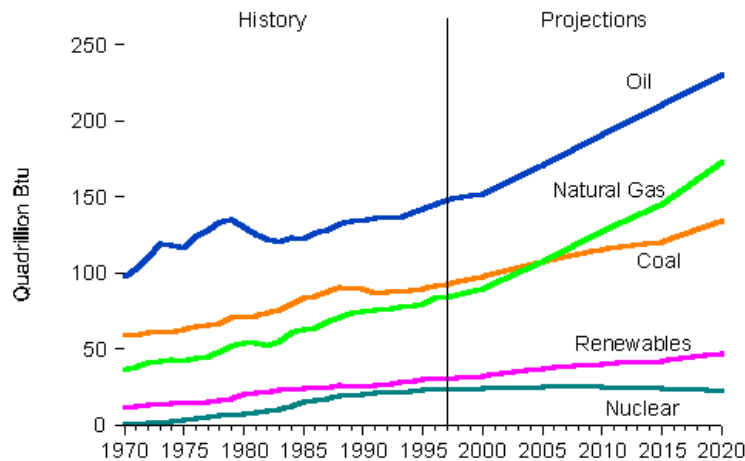


Figure 2.2 World Energy Consumption by Fuel Type, 1970-2020

Source: EIA (Energy Information Administration), official energy statistics from the US government
[International Energy Outlook 2000](#)

Obviously, renewable energy and nuclear energy have made important supplements to traditional fossil fuel sources during the second past century, with renewable energy (including non-commercial fuel such as wood) currently providing 18% and nuclear 6% of the world's energy, all the rest comes from the combustion of coal, oil, and gas.

Depletion of coal, natural gas, and fossil fuel has become serious issues. Coal will be quickly depleted if it is used to compensate for declining oil and gas. Coal cannot be strip mined or transported from the mines without oil to power mining machinery and trains. There is not sufficient time to make a useful transition from oil and gas to coal. Coal cannot make a significant contribution to energy need at the end of the century. Energy from renewable sources will increase, but without fossil fuels the energy available will be only ten to twenty percent of the need. A cleaner energy future depends on the development of the alternative energy technologies to meet the world's growing energy requirements but that also mitigate carbon dioxide emission.

2.2.1 Fossil Fuels-Coal, Oil and Natural Gas

Fossil fuels which consist of three major forms including coal, oil, and natural gas are formed by natural processes such as anaerobic decomposition of buried dead organisms over hundreds of millions of years ago. According to the Energy Information Administration (EIA, 2007) it was expected that the primary sources of energy in 2007 consisted of petroleum (36.0%), coal (27.4%), natural gas (23.0%), total to an 86.4% share for fossil fuels in primary energy consumption in the world. In 2006, non-fossil sources included hydroelectric (6.3%), nuclear (8.5%), and others (geothermal, solar, tidal, wind, wood, waste) total to 0.9%. The consumption of world energy was growing about 2.3% per year.

Fossil fuels are considered as non-renewable resources because it required a millions of years to form, and reserves are being depleted much faster than new one are being made. Other than that, the usage or productions of fossil fuels raise environmental concerns. Thus, a development of global movement towards the generation of renewable energy is under way to help meet increased energy needs.

2.2.2 Renewable Energy

Renewable energy refers to sources of energy that is always there which are continually replenished on human timescale such as sunlight, wind, rain, tides, waves, and geothermal heat. The supply is so large that there is no foreseeable end in future as it is finite due to entropy and the laws of thermodynamics. About 16% of global final energy consumption comes from renewable resources, with 10% of all energy from traditional biomass, primarily used for heating, and 3.4% from hydroelectricity. A development of renewables included small hydro, modern biomass, wind, solar, geothermal, and biofuel accounted for another 3% and are increasing rapidly.

Renewable energy resources and important opportunities for energy efficiency exist over wide geographical areas, compared to other energy sources, which are concentrated in a limited number of countries. Thus, resulting in significant energy security and economic benefits due to the rapid deployment of renewable energy and energy efficiency, and technological diversification of energy sources. Renewable energy replaces conventional fuels in four distinct areas such as electricity generation, hot water/space heating, motor fuels, and rural (off-grid) energy services. The other important advantage of renewable energy is that it produces much less pollution during combustion process which lead to a negative carbon

dioxide emission and net carbon dioxide removal from the atmosphere is lesser contrast with fossil fuels. The development of renewable energy has getting much interest for many researchers as it is very valuable and contributes huge benefits in human civilization. A number of renewable types of energy are discussed in this chapter which included solar energy, wind energy, biomass energy, and geothermal energy.

Following is a graph that shows the percentage of our total energy provided by renewable energy.

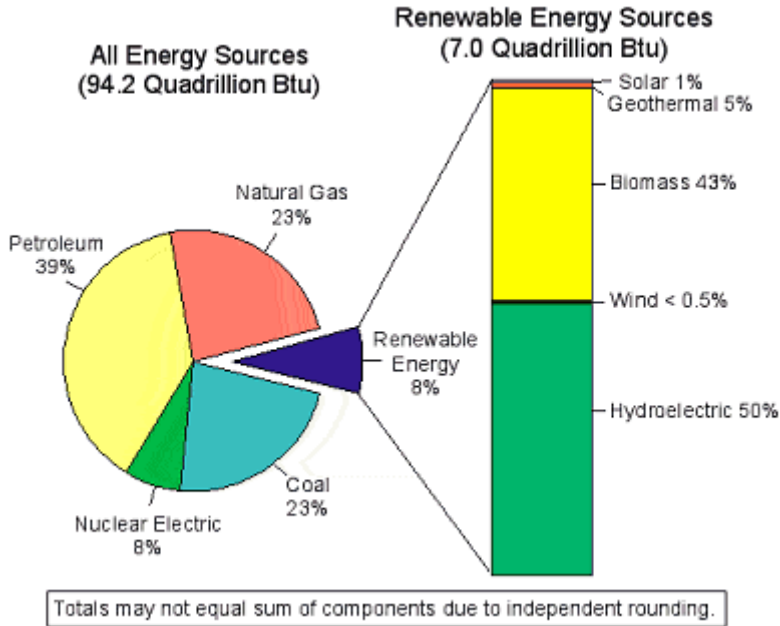


Figure 2.3 Graph of Total Energy Provided by Renewable Energy

Source : Courtesy of [Renewable Energy Annual](#) website

2.2.3 Energy for Transportation

Transport fuels or renewable biofuels have contributed an important consumption of oil in the United State since 2006. The worldwide production of biofuels in 2009 about 93 billion liters displaced the equivalent of an estimated 68 billion liters of gasoline, equal to about 5% of world gasoline production. The conversion of biofuels from biomass includes a wide range of fuels such as liquid biofuels (bioethanol, oils or biodiesel), gaseous biofuels i.e. biogas, landfill gas and synthetic gas. It has been considered as an alternative fuels to gasoline and

diesel. Nowadays, due to the concerns of air pollution and petroleum-dependence, new clean-burning fuels made from fuels other than oil have been investigated including methanol, ethanol, natural gas, propane, and even electricity.

2.2.4 Syngas

Syngas which is the mixture of fuel gas consisting primarily of hydrogen, carbon monoxide, and very often some carbon dioxide is the direct end-product of the gasification process. Though it can be used as a standalone fuel, the energy density of syngas is only about 50 percent that of natural gas and is therefore mostly suited for use in producing transportation fuels and other chemical products. As its unabbreviated name implies, synthesis gas is mainly used as an intermediary building block for the final production (synthesis) of various fuels such as synthetic natural gas, methanol and synthetic petroleum fuel. In a purified state, the hydrogen component of syngas can also be used to directly power hydrogen fuel cells for electricity generation and fuel cell electric vehicle (FCEV) propulsion.

Nowadays, a development technology that can efficiently exploit the potential of syngas energy has risen. Currently, most syngas is produced from natural gas. Apart from it, electrolysis also can be used to produce syngas by the separation of water components into oxygen and hydrogen. Algae and bacteria also used sunlight as their energy source, to produce syngas under certain conditions. Syngas is high in energy, yet an engine that burns pure hydrogen produces almost no pollution.

Syngas as an alternative fuel to replace fossil fuel can be used for transportation, particularly for road and air transportation as it is non-polluting fuel with high gravimetric energy density. It can also be used efficiently in jet engines, internal combustion engines and in fuel cells, and it has favorable safety characteristics. Almost the entire car manufacturers are heavily involved in development of the syngas powered vehicles, and some of them have gone far beyond just demonstrating this in prototype vehicles.

Currently, the excess of glycerol as the main by-product during biodiesel production has getting interest by many researchers to investigate the possible uses into added value product. Glycerol has been considered as renewable feedstock to produce functional chemicals including syngas. It has a high energy density (6.26 kWh L⁻¹) and is also non-toxic, non-flammable, and non-volatile, which are ideal properties for a wide variety of power applications.

2.3 Glycerol (Biodiesel by-product): Feedstock

The dramatic increase in demand for transportation fuels and the increase in environmental concerns, coupled with diminishing crude oil reserves, have increased the awareness on renewable energy. Biodiesel is one of the promising alternatives and renewable fuels have been received an attractive attention viewed during the past few years and its production capacity has been well developed by many researchers. Although world biodiesel production was expected to increased, in fact, it is less than the anticipated target and has increased at a slower rate due to its high production cost (Xiaohu et al., 2010). The utilization of glycerol as the main by-product of biodiesel production is a promising abundant source which could improve the economic viability of biodiesel industry.

Biodiesel production will generate about 10% (w/w) glycerol as the main byproduct. In other words, every gallon of biodiesel produced generates approximately 1.05 pounds of glycerol. This indicates a 30-million gallon per year plant will generate about 11,500 tons of 99.9% pure glycerin. It was estimated that the world biodiesel market would reach 37 billion gallons by 2016 which implied that approximately 4 billion gallons of crude glycerol would be produced (Wang et al., 2006). In the meantime, the increased production of biodiesel influenced remarkably the glycerol market due to the large surplus of excess crude glycerol during the process of biodiesel production. As example, in 2007, the refined glycerol's price was painfully low, approximately \$0.30 per pound compared to \$ 0.70 before the expansion of biodiesel production in the United States. Accordingly, the price of crude glycerol decreased from about \$ 0.25 per pound to \$ 0.05 per pound (Kerr et al., 2007). Therefore, it is imperative to find out the development of sustainable processes for utilizing this crude glycerol.

Since purified glycerol is a high-value and commercial chemical with thousands of uses, the crude glycerol shows great opportunities for new applications. For that reasons, more attention is being paid to the utilization of crude glycerol from biodiesel production into value-added chemicals in order to cover the biodiesel production cost and to promote biodiesel industrialization on a large scale (Fangxia et al., 2012). Although intensive investigations have focused on utilizing crude glycerol directly, review papers on crude glycerol utilization are limited. This review mainly addresses the current and potential value-added applications of crude glycerol from biodiesel production.

2.3.1 Value-added opportunities for crude glycerol

Worldwide, crude glycerol derived from biodiesel conversion has increased from 200,000 tonnes in 2004 (Pagliaro et al., 2008) to 1.224 million tonnes in 2008. Meanwhile, the global market for refined glycerol was estimated to be roughly 900,000 tonnes in 2005 (Nilles., 2006). Therefore, it is of great significance for researcher to find new applications for refined and crude glycerol. Recently, numerous papers have been published on direct utilization of crude glycerol from biodiesel production. In the following sections, detailed discussions on utilization of crude glycerol are presented.

2.3.1.1 Glycerol to Chemicals and Materials

a) Glycerol to Citric Acid

A few reports are available on the use of glycerol for citric acid biosynthesis. Citric acid has a variety of applications such as food additive which used as a flavoring and preservative in food and beverages, especially soft drinks. Other than that, it can be utilize as an additive in cosmetics, toiletries, and pharmaceuticals. The production of citric acid from crude glycerol by *Yarrowia lipolytica* ACA-DC 50109, including Strain K-1, Strain AWG-7, and Strain 1.31, under batch cultivation conditions (Rywinska et al., 2009) was investigated. The experimental results demonstrated that when *Y.lipolytica* Wratislavia K1 was used, a lower concentration of citric acid about 87-89 g/L and a high concentration of erythritol up to 47 g/L were obtained.

b) Glycerol to 1, 3-Propanediol

The anaerobic fermentative production 1, 3-propanediol is the most promising option for biological conversion of glycerol. It has been demonstrated that crude glycerol could be used directly for the production of 1, 3-propanediol in fed-batch cultures of *Klebsiella pneumoniae* (Mu et al., 2006). The differences between the final 1, 3-propanediol concentrations were small for crude glycerol from the methanolysis of soybean oil by alkali- (51.3 g/L) and lipase-catalysis (53 g/L). This implied that the composition of crude glycerol had little effect on the biological conversion and a low fermentation cost could be expected. More recently, the production of 1, 3-propanediol, from crude glycerol from *Jatropha* biodiesel by *K.pneumoniae* ATCC 15380, was optimized. The obtained 1, 3-propanediol yield, purity and recovery were 56 g/L, 99.7% and 34%, respectively (Hiremath et al., 2011). Apart from that, an incorporated

bioprocess that combined biodiesel production by lipase with microbial production of 1, 3-propanediol by *K.pneumoniae* was developed in a hollow fiber membrane. The bioprocess avoided glycerol inhibition on lipase and reduced the production cost (Mu et al., 2008).

c) *Glycerol to Lactic Acid*

Versatile applications of the salts and esters of lactic acid could be shown in the fields of the industrial, food, cosmetic, and pharmaceutical industries and agriculture (Datta et al., 2006). Hong et al, conducted the study of some fundamental problems of lactic acid production from glycerol which including the selection of suitable strain for producing high concentration and productivity of lactic acid from glycerol. It was found that, the strain AC-521, a member of *Escherichia coli*, is the most suitable one for lactic acid production from glycerol among the eight bacterial strains, based on its 16S rDNA sequences and physiological characteristic. The results shows that the maximum concentration of lactic acid and glycerol consumption could be achieved after 88 h of fed-batch fermentation, which yielding about 0.9 mol mol^{-1} glycerol and 85.8 g L^{-1} of lactic acid with the productivity of $0.9 \text{ g L}^{-1} \text{ h}^{-1}$.

2.3.1.2 *Glycerol to Fuels and Fuels Additive*

a) *Oxygenated Chemicals*

As fuel additive, oxygenate synthesized compound, (2, 2-dimethyl-1, 3-dioxolan-4-yl) methyl acetate, could be produced from crude glycerol and used as a biodiesel additive. It could improve biodiesel viscosity and could meet the requirements established for diesel and biodiesel fuels by the American and European Standards (ASTM D6751 and EN 14214, respectively) for flash point and oxidation stability. This new compound could compete with other biodiesel additives (Garcia et al., 2008). Further, acrolein is an important starting chemical for producing detergents, acrylic acid ester and super absorber polymers. Sereshki et al. (2010) reported a process involving adding liquid crude glycerol directly into a fluidized bed reactor, vaporizing it, and then reacting them to produce acrolein over a tungsten doped zirconia catalyst. In this process, glycerol evaporated in the fluidized bed reactor leaving behind salt crystals which were only loosely bound to the surface and could be separated from the catalyst using mechanical agitation. This process has the potential to reduce the accumulation of salt in the reactor.

b) Syngas

Crude glycerol was proven to be a viable alternative for producing hydrogen or syngas (Slinn et al., 2008). Gasification was the main employed technique. Thermo-gravimetric coupled with FTIR spectroscopy analysis proved that the thermal decomposition mechanism of crude glycerol mainly involved four phases and CO₂, H₂, CH₄, and CO were the main gas products (Dou et al., 2009). Gasification with in situ CO₂ removal was effective and had high energy efficiency. Supercritical water gasification of crude glycerol was performed under catalyzed and alkaline catalyzed conditions. The reaction temperature determined the decomposition degree. When NaOH was employed as catalyst nearly 90 vol.% of the product gas was H₂ and no char was produced (Onwudili et al., 2010). Additionally, co-gasification of crude glycerol and hardwood chips, in a downdraft gasified, was another promising option for utilizing crude glycerol. The loading amount of crude glycerol had significant influence on CO and CH₄ concentration, while having no effect on H₂ and CO₂ yield. The study suggested that the co-gasification could perform well in downdraft gasifiers with hardwood chips mixing with liquid crude glycerol up to 20 wt. % (Wei et al., 2010). The conversion of crude glycerol to syngas is importance since the demand of hydrogen is growing due to the technological advancements in fuel industry. Glycerol could be converted into syngas in each following processes: steam reforming, partial oxidation, auto thermal reforming, aqueous phase reforming, supercritical reforming, and dry reforming. A detailed discussion of these processes will be review in the next sections.

2.4 Conventional Processes of Glycerol to Syngas

2.4.1 Steam Reforming

The steam reforming is the most commonly used method for producing hydrogen in the chemical industry. It is a high temperature endothermic process which uses a catalyst to react the glycerol with water to produce hydrogen. The overall reaction of hydrogen production using steam reforming of glycerol is described as below:



Adhikari et al, (2009) had studied the thermodynamic analysis of hydrogen production by steam reforming of glycerol. They conclude that, the best condition for producing hydrogen were at >900 K temperature, atmospheric pressure, and 9/1 of water/glycerin molar ratio.

They also explained that, under this condition, methane production is minimized and the carbon formation is thermodynamically inhibited. The viability of using steam reforming to produce hydrogen from glycerol was also investigated by Slinn et al., (2008). A platinum alumina catalyst was chosen to optimize the operating conditions for glycerol steam reforming and the reformer gas yield was measured by using mass spectroscopy. Optimum reformer performance was reached at temperature of 880 ° C, flow rate 0.12 mol/min (glycerol) per kg, and the steam/carbon ratio of 0.25. However, the yield of by product glycerol was on average 30% less than pure glycerol under the same conditions. They found that the facts of long chain fatty acid impurities are harder to reform and more likely to form carbon.

Another studied by Hirai et al., (2005), on production of hydrogen by steam reforming of glycerin on ruthenium catalyst. They have reported that a Ru/Y₂O₃ catalyst afforded very high activity in a extended run. The catalyst loaded from group 8 were prepared via a conventional impregnation method, using various supported oxides and among the catalyst studied thus far, ruthenium on Y₂O₃ gave the best results. It was proved by the increasing of ruthenium loading (up to 3%) will increase the hydrogen selectivity up to 90% and complete conversion at 600°C. The key findings from their work and others are summarized in Table 2.1.

Table 2.1 Catalysis studies on the steam reforming of glycerol

Metal Catalyst	Support	Modifier	Reaction conditions	Reaction results	Researcher and years
Ru	Y ₂ O ₃ , ZrO ₃ , CeO ₂ , La ₂ O ₃ , SiO ₂ , MgO, Al ₂ O ₃	None	P=101.3kPa T=773 to 873K S/C ₁ = 3.3	Ru(3 wt %)/ Y ₂ O ₃ : Conversion=98% H ₂ yield= 85%	Hirai <i>et al.</i> (2005)
Ir, Co, Ni	CeO ₂	None	P= 101.3kPa T=673 to 723K WGVR= 9:1	Ir/CeO ₂ : Conversion = 100% H ₂ selectivity = 85%	Zhang <i>et al.</i> (2007)
Ni	γ-Al ₂ O ₃	Fe, Co, Na, Cu	P=101.3kPa T=873K WGR= 6:1	Ni/Al ₂ O ₃ -Co: H ₂ yield = 50% Ni/Al ₂ O ₃ -Fe: H ₂ yield = 25% Ni/Al ₂ O ₃ -Na: H ₂ yield = 38%	A.Ebshish <i>et al.</i> (2011)

				Ni/Al ₂ O ₃ -Cu: H ₂ yield = 35%	
Ir	La ₂ O ₃	Na, Mg, Ca	P= 101.3kPa T= 823 to 1023K	Ca modified Ir(3)/La ₂ O ₃ : Conversion = 87.1% H ₂ selectivity = 74.5%	Yang <i>et al.</i> (2012)
Ni	TiO ₂ , SiO ₂ , ZrO ₂	None	P=101.3kPa T=923K	NiZrF: Conversion= 87% CH ₄ selectivity = 0 and CO < 10% H ₂ yield = 84%	Rossetti <i>et al.</i> (2013)
Ni	La ₂ O ₃ -SiO ₂	None	P=101.3kPa T= 873 K WGR= 3:1	Ni ₃₀ LaSi: Conversion = 79% H ₂ yield = 28%	Thyssen <i>et al.</i> (2013)

WGMR: Water to glycerol ratio. WGVR: Water to glycerol volume ratio. S/C₁ = steam to carbon molar ratio.