PRODUCTION OF HYDROGEN BY STEAM REFORMING OF GLYCEROL OVER NICKEL SUPPORTED CATALYST

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To my supportive husband and family

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ABSTRACT

The production and utilization of biodiesel are forecasted to increase steadily in the future. The increasing biodiesel production will also accumulate glycerol in the global market. Glycerol is a potential feedstock for generating hydrogen because one mole of glycerol can produce up to four moles of hydrogen. However, little attention has been given for the hydrogen production from glycerol. The purpose of this research is to develop a Ni supported catalyst for the production of hydrogen by steam reforming of glycerol. Five catalysts were prepared in the study by wet impregnation technique. The catalysts were characterized by X-ray diffraction (XRD), Brunauer Emmett Teller (BET) surface area analysis and scanning electron microscopy (SEM) methods. This research also studied the effect of catalysts support on selectivity of hydrogen and glycerol conversion in preselected reaction condition. Under the reaction conditions, Ni supported on Al_2O_3 was found to show high production of hydrogen selectivity and glycerol conversion. Ni/Al_2O_3 was then further tested to investigate the effects of temperatures, feed flow rates (FFR) and water glycerol molar ratios (WGMR) on selectivity of hydrogen and glycerol conversion in order to determine the optimum condition for steam reforming of glycerol. The experiments were designed by applying 2^3 full factorial central composite designs with two centre points. Optimization of steam reforming of glycerol via response surface methodology (RSM) revealed that 80.2 % maximum hydrogen selectivity was obtained at the optimum reaction temperature of 884.9 °C, 0.97 mL/min FFR and 12.1:1 WGMR.

ABSTRAK

Pengeluaran dan penggunaan biodiesel dijangka akan meningkat secara berterusan pada masa akan datang. Peningkatan biodiesel ini secara tidak langsung juga akan menambahkan kuantiti gliserol dalam pasaran. Gliserol adalah bahan mentah yang berpotensi untuk menjana gas hidrogen kerana satu mol gliserol boleh menghasilkan sehingga empat mol hidrogen. Walau bagaimanapun, hanya sedikit kajian diberikan untuk pengeluaran hidrogen dari gliserol. Kajian ini bertujuan untuk membangunkan mangkin berasaskan nikel untuk penghasilan hidrogen menggunakan kaedah stim reformasi gliserol. Lima mangkin telah disediakan dalam kajian ini melalui teknik penghamilan basahan. Kesemua mangkin dianalisis menggunakan kaedah X-ray pembelauan (XRD), analisis permukaan Brunauer Emmett Teller (BET) dan imbasan mikroskop elektron (SEM). Di samping itu, kajian ini turut menyelidik kesan mangkin pada pengeluaran hidrogen dan penukaran gliserol dalam keadaan tindak balas yang telah dipilih. Di bawah keadaan tindak balas tersebut, mangkin Ni pada struktur sokongan Al_2O_3 menunjukkan penghasilan yang tinggi terhadap pengeluaran hidrogen dan penukaran gliserol. Ni/Al_2O_3 kemudian diuji untuk menyiasat kesan suhu, kadar aliran suapan (FFR) dan nisbah molar stim gliserol (WGMR) untuk mendapatkan keadaan optimum bagi stim reformasi gliserol. Kajian ini telah direka dengan menggunakan 2^3 faktorial dengan dua titik pusat. Optimisasi stim reformasi gliserol melalui kaedah tindak balas permukaan (RSM) memberikan 80.2 % hidrogen maksimum pada suhu tindak balas yang optimum iaitu 884.9 °C, 0.97 mL/min suapan kadar aliran dan 12.1:1 WGMR.

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LIST OF ABBREVIATIONS

Al_2O_3	-	Aluminium oxide
atm	-	Pressure symbol
BET	-	Brunauer Emmett Teller surface area
C	-	Carbon
C_2H_4	-	Ethylene
C_2H_5OH	-	Ethanol
C_2H_6	-	Ethane
$C_3H_8O_3$	-	Glycerol
CCD	-	Centre composite design
Ce	-	Cerium
CH_4	-	Methane
CO	-	Carbon monoxide
Co	-	Cobalt
CO_2	-	Carbon dioxide
Cu	-	Copper
EDX	-	Energy Dispersive X-Ray
et al.	-	Indicates more than one people
f	-	Forward reaction
FFR	-	Feed flow rate
g	-	Gram
GC	-	Gas chromatography
GHSV	-	Gas hourly space velocity
h	-	Hour
H/H_2	-	Hydrogen
H_2O	-	Water
kg	-	Kilogramme

kJ - Kilo Joule
La_2O_3 - Lanthanum oxide
lb - Pound
m^2 - Square metre
m^3 - Cubic metre
MgO - Magnesium oxide
min - Minute
mL - Millilitre
mm - Milimetre
N/N_2 - Nitrogen
Ni - Nickel
NiO - Nickel oxide
nm - Nanometre
O/O_2 - Oxygen
P - Pressure
Pd - Paladium
ppm - Part per million
Pt - Platinum
r - Reverse reaction
Rh - Rhenium
RR - Reforming ratio
RSM - Response surface methodology
Ru - Ruthenium
S - Steam
S - Sulphur
sec - Second
SEM - Scanning Electron Microscopy
SiC - Silica carbide
SiO_2 - Silica oxide
SR - Steam reforming
T - Temperature
US - United States
vs. - Versus
WGMR - Water glycerol molar ratio

WGS	-	Water gas shift
WHSV	-	Weight hourly space velocity
wt	-	Weight
XRD	-	X-Ray Diffraction
ZrO_2	-	Zirconium oxide

LIST OF SYMBOLS

$ - United States currency
% - Percentage
°C - Degree Celsius
β - Beta
α - Alpha
γ - Gamma
λ - Lambda (wavelength)
τ - Tau (time)
θ - Theta (temperature)
Δ - Delta (increment)
μ - Micro
Å - Angstrom
n - Integer Number
~ - Approximately
= - Equals
< - Less than
> - Greater than
≤ - Less than or equals to
® - Registered

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CHAPTER I

INTRODUCTION

1.1 Background of Research

Global energy consumption is expected to increase dramatically in the next decades, driven by rising standards of living and a growing population worldwide. At present, world energy needs are largely met by use of fossil fuels, chiefly oil, natural gas and coal. There is a rising consciousness that we may not be able to depend on petroleum as the principal source of fuels and chemicals in the coming decades. The limited amounts of fossil fuels, especially petroleum and concurrent environmental problems such as greenhouse gases have prompted the world to look for clean sustainable resources as alternatives to meet the increasing energy demands (Gonçalves *et al.*, 2008). Among the new energy sources, the biodiesel appears as one of the most promising and feasible new renewable energy source and have lower impact on the CO_2 emissions. Its production and use has been stimulated in many countries, especially in Europe (Miyazawa *et al.*, 2007).

Biodiesel is produced from vegetable sources such as soybean, sunflower, canola, cotton seed, rapeseed and palm oil as well as animal fats using the processes such as micro emulsions, thermal cracking (pyrolysis) and transesterification (Corma *et al.*, 2008). Under base or acid catalyst conditions, in the existence of methanol, there occurs formation of three methyl esters of fatty acid molecules, which are the biodiesel themselves, releasing glycerol as by-product (Chai *et al.*, 2007). Furthermore, it is obtained as a by-product in hydrolysis of fat and soap-manufacturing process apart from production of biodiesel (Tsukuda *et al.*, 2007). Biodiesel has high potential as alternative liquid transportation fuel because it is renewable, CO_2 neutral and also has similar properties as diesel fuel (Valliyappan *et al.*, 2008a). Hydrogen is an energy carrier which can replace oil and reduce pollution and greenhouse gas emissions when it is generated from renewable sources. At present, hydrogen is derived from fossil fuels such as natural gas, naphtha or coal (Liu, 2008).

Steam reforming is a potential method for obtaining hydrogen from hydrocarbons. A two step global reaction mechanism is presented below in which the carbohydrate (glycerol) undergoes thermal decomposition in the first reaction to form CO and H_2. The CO is then reacting with steam (oxidizer) in the second reaction to form CO_2 and additional H_2.

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2 \qquad (1)$$

$$CO + H_2O \leftrightarrow 3CO_2 + H_2 \qquad (2)$$

Reactions (1) and (2) can be added to yield:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (3)$$

Equilibrium must be reached between those two reactions and will depend on the amount of steam and oxygen added to the reactor, as well as the temperature and pressure of the reaction. Oxygen may be added to steam reforming reaction, but glycerol oxygen content is sufficient in reaction (1) to balance the reaction.

The steam reforming of glycerol has been investigated over a wide variety of supported metal catalysts and several reviews on the subject have been published (Buffoni *et al.*, 2009; Cheng *et al.*, 2010a; Chiodo *et al.*, 2010). The activity, product distribution and catalyst stability have been found to be dependent upon the catalyst composition, support material, catalyst preparation and pre-treatment technique and reaction conditions. Steam reforming catalyst will be explained thoroughly in the next chapter.

1.2 Statement of Problems

Fossil fuel is one of the major energy resources being widely used to meet our energy requirements (Kelly-Yong *et al.*, 2007). This is the major source of global warming as the resources are depleting fast. A full environmental benefit of generating power from hydrogen can be achieved only when it is produced from renewable sources such as solar power or biomass. Biodiesel has high potential as liquid transportation fuel because of its environmental benefits such as minimal emission of CO_2 when compared to regular diesel fuel (Valliyappan *et al.*, 2008a).

It is estimated that approximately 80 % of the biofuel in Europe are biodiesel (Corma *et al.*, 2008). Canadian government has planned to produce 500 million litres of biodiesel by 2010 and it is forecasted that biodiesel could make up as much as 20 % of all transportation fuels by 2020 (Luo *et al.*, 2008). Glycerol is a by-product obtained during the production of biodiesel. For each 90 m^3 of biodiesel produced from transesterification of vegetable oils, approximately 10 m^3 of glycerol are generated (Gonçalves *et al.*, 2008). These scenarios indicate that the commercial feasibility of the biodiesel program is directly linked with the commercial use of the glycerol. In Europe, with the increasing use of biodiesel, the glycerol prices are lowering (Zhang *et al.*, 2007). Thus, Corma *et al*. (2008) stated that the cost of unrefined glycerol could decrease to 0.44 $/kg. Such possible cheap glycerol prices ahead make the development of processes for the conversion of glycerol into alternative fuels desirable thus; it might be an elegant green alternative to the petrochemical route.

Hydrogen is the most abundant element in the universe but, free hydrogen does not exist naturally on earth in its gaseous form. Hydrogen is not an energy source but an energy carrier since it must be produced from a primary source such as water, natural gas, coal, petroleum or biomass. The development of clean, sustainable and cost-competitive hydrogen production processes is a key to a viable future hydrogen economy. Glycerol is a potential feedstock to produce H_2 because one mol of glycerol can theoretically produce up to four moles of hydrogen. When glycerol is gasified at high temperature to produce hydrogen, it is possible to get CO as one of the gaseous products. Formation of syngas (H_2 + CO) in the ratio H_2/CO equal to 2:1 could be used as a feedstock in Fischer-Tropsch synthesis to produce green diesel (long chain hydrocarbon). Alternatively, gases which are produced from glycerol would have medium heating value and can be used as a fuel gas to produce electricity (Valliyappan *et al.*, 2008a).

The development of alternative sources of energy is becoming important in this era of diminishing petroleum reserves and to increase environmental awareness. Glycerol is an intriguing candidate in this respect because it is renewable and its consumption is neutral with respect to greenhouse gas emissions (Simonetti *et al.*, 2007a). Obviously, the effective utilization of glycerol as a hydrogen source depends critically on the discovery of new catalysts with high selectivity toward hydrogen and sufficient reaction rate under mild conditions. With this background, Wen *et al.* (2008) studied the activities and stabilities of Pt, Ni, Co and Cu catalysts for H_2 production by aqueous phase reforming of glycerol, as well as the effect of support on activity and catalyst stability. The effects of active metal, reaction temperature and reaction pathways were investigated extensively.

1.3 Research Objective

The overall objective of this thesis was the identification of a supported nickel catalyst that delivered stable performance for the steam reforming of glycerol. In an attempt to achieve high hydrogen selectivity, the effects of operating condition and catalyst properties are studied. An experimental system was built to study the catalytic activity of various supported nickel catalysts. Therefore, the research embarks on the following objectives:

i. To study the supported nickel catalysts physical properties for glycerol steam reforming process to hydrogen
ii. To investigate the catalysts performance for steam reforming process from glycerol to hydrogen
iii. To present the optimized condition operation for the catalytic reforming system

1.4 Scope of Study

In order to achieve the objective, four scopes have been identified in this research as follows:

i. To set up the system in fixed-bed reactor
ii. To study the conversion of glycerol to hydrogen over various supports on Ni catalyst
iii. To study the effect of operation condition and various supported Ni catalyst on the hydrogen selectivity

iv. To optimize and design the operation condition and research methodology using Response Surface Methodology (RSM)

1.5 Significance of Study

Over the last decade, biodiesel has been successfully used as an alternative fuel and as a fossil fuel additive. The increasing production of biodiesel is predicted to spread and increase, as biodiesel provides sufficient advantages to fossil fuels (Centi and Santen, 2007). Glycerol, the main by-product in the production of biodiesel, is regarded by Pagliaro and Rossi (2008) as a promising source for future biorefinery, as it can be converted to various derivatives used in fuels, chemicals, automotive, pharmaceutical and detergent. In addition, the production costs of biodiesel can be lowered by selling waste glycerol (Zhang *et al.*, 2007). Therefore, the application of glycerol is an important subject thus; further studies on the steam reforming process of glycerol are necessary.

This study is important to the environmental and economic concerns such that a continuous process that uses renewable sources is much desirable. In this work, hydrogen production from glycerol solution by steam reforming process over various supported Ni catalysts, the effect of operation condition and optimization study will be examined. This research will lead towards advancement of knowledge and aid in the design of more active catalysts, certainly impacting in the positive way of steam reforming technologies.

1.6 Thesis Outline

The research set off further in depth at the design of experimental rig for steam reforming process of glycerol, the relation between catalyst properties and the products obtained from series of experiments. Chapter 1 already discuss the introduction of the research, problem statement, objectives and scopes of this particular research.

Chapter 2 discusses the literatures related to the steam reforming of glycerol process and thermodynamic considerations. This chapter also reviews the glycerol properties as well as the characteristics of Ni, Al_2O_3, ZrO_2, MgO, SiO_2 and La_2O_3. Furthermore, it will explain the factors controlling selectivity for steam reforming process.

Chapter 3 contains an explanation of the methodology used in the experiments and characterization of catalysts. In this chapter, the experimental rig for steam reforming of glycerol is described. Furthermore, this chapter illustrate the catalyst preparation and catalytic testing procedure as well as the method to analyze the liquid and gaseous products. Finally, the catalyst characterization techniques are explained.

Chapter 4 discusses the catalyst characterization results such as XRD, BET, and SEM. Moreover, the result of catalyst testing also is presented in this chapter. This chapter also will discuss the effect of reaction parameters for the best catalyst employed in the process. The optimized results are presented by using STATISTICA software. Chapter 5 summarize the results, examines the research limitations and offers suggestions for further studies.

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