HYDROGEN PRODUCTION FROM GLYCEROL USING COPPER AND NICKEL LOADED ZEOLITE BASED CATALYST

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To my beloved mother and father,

for their love and support

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ABSTRACT

The increasing of the growth rate for vehicles leads to the high production of biodiesel and gives a large amount of glycerol as the by-product via transesterification reaction. Moreover, the limited of the world demand for glycerol makes the glycerol as a waste and abundant substance. For that reason, glycerol conversion into valuable chemical such as hydrogen fuel production is essential since conventional source of hydrogen production is mainly from fossil. Commonly, the metal catalyst which been used for hydrogen production via steam reforming is costly that give worrisome to the industries. Therefore, in this study, copper (Cu) and nickel (Ni) metal loaded on HZSM-5 zeolite catalyst is used for hydrogen production from glycerol via steam reforming. The study is focusing in analyzed the performance of Cu and Ni metal loaded on HZSM-5 and investigates the optimum conditions for hydrogen production which include reaction temperature, glycerol feed concentration or water/glycerol molar ratio (WGMR) and feed flow rate. The hydrogen production through steam reforming was carried out using a fixed bed type reactor while the range of studied parameters for reaction temperature (350-750^{o}C), glycerol feed concentration (3:1-11:1 of WGMR) and feed flow rate (0.25-1.25mL/min) were performed. The catalyst performance for hydrogen production was observed by different weight percentage of Cu (0.5-10%) and Ni (0.5-10%) loaded on HZSM-5 catalyst. It was found that 5wt% of Cu with 10wt% of Ni to be the best catalyst to produce higher hydrogen yield. By using statistical design, the optimum of hydrogen yield (3.98 of mol H_2/mol $C_3H_8O_3$ converted) was achieved at temperature 639^{o}C, 8:1 of WGMR and flow rate of 0.65mL/min.

ABSTRAK

Peningkatan pengeluaran biodiesel secara mendadak telah memberi kesan kepada gliserol yang berlebihan. Tambahan pula, permintaan pasaran yang kurang terhadap gliserol menyebabkan gliserol dianggap sebagai bahan yang terbuang. Atas sebab itu, penukaran gliserol kepada bahan kimia yang lebih bernilai seperti bahan api hidrogen adalah penting kerana sebelum ini, bahan api hydrogen dihasilkan daripada fosil. Kebanyakan penggunaan pemangkin logam dalam pengeluaran hidrogen melalui kaedah stim reformasi adalah mahal dimana telah membebankan pihak industri. Oleh itu, di dalam kajian ini, penghasilan hidrogen daripada gliserol melalui kaedah stim reformasi menggunakan logam kuprum (Cu) dan nikel (Ni) dimuatkan pada pemangkin zeolit HZSM-5. Kajian ini akan memberi tumpuan dalam menganalisis prestasi logam Cu dan Ni yang dimuatkan pada HZSM-5 dan menentukan keadaan optimum dalam penghasilan hidrogen termasuklah suhu tindakbalas, kepekatan suapan gliserol atau nisbah molar terhadap air/gliserol (*WGMR*) dan kadar aliran suapan. Pengeluaran hidrogen melalui kaedah stim reformasi menggunakan reaktor jenis *fixed bed* manakala pelbagai parameter telah dikaji seperti suhu tindak balas (350-750^{o}C), kepekatan suapan gliserol (3:1-11:1 *WGMR*) dan kadar aliran suapan (0.25-1.25mL/min) telah dilakukan. Prestasi pemangkin dalam pengeluaran hidrogen telah diperhatikan dengan menggunakan perbezaan peratus bagi berat komposisi Cu (0.5-10%) dan Ni (0.5-10%) yang dimuatkan pada pemangkin HZSM-5 di mana peratus bagi berat komposisi gabungan 5%Cu dan 10%Ni telah ditemui sebagai pemangkin terbaik dalam penghasilan hidrogen yang lebih tinggi. Dengan menggunakan reka bentuk statistik, penghasilan hidrogen yang optimum (3.98 mol H_2/mol $C_3H_8O_3$) telah dicapai pada suhu 639^{o}C, 8:1 *WGMR* dan kadar aliran suapan pada 0.65mL/min.

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LIST OF ABBREVIATIONS

Al_2O_3	-	Aluminium oxide
AlO_4	-	Aluminate
ANOVA	-	Analysis of variance
CCD	-	Central composite design
Ce	-	Cerium
CeO_2	-	Cerium oxide
$C_3H_8O_3$	-	Glycerol
CH_4	-	Methane
C_2H_4	-	Ethylene
C_2H_6	-	Ethane
CO	-	Carbon monoxide
Co	-	Cobalt
CO_2	-	Carbon dioxide
Cu	-	Copper
$Cu(NO_3)_2.6H_2O$	-	Copper nitrate hydrate
DF	-	Degree of freedom
F	-	Feed flow rate
GC	-	Gas chromatography
GC-FID	-	Gas chromatography-flame ionization detector
GC-TCD	-	Gas chromatography-thermal conductivity detector
H_2	-	Hydrogen
He	-	Helium
H_2O	-	Water
HZSM-5	-	Zeolite catalyst
Ir	-	Iridium

L	-	Linear term
La	-	Lanthanum
La_2O_3	-	Lanthanum oxide
Mg	-	Magnesium
MgO	-	Magnesium oxide
MS	-	Mean squares
N_2	-	Nitrogen
NG	-	Natural gas
Ni	-	Nickel
$Ni(NO_3)_2.6H_2O$	-	Nickel nitrate hexahydrate
OH	-	Hydroxyl groups
Q	-	Quadratic term
Rh	-	Rhodium
RSM	-	Response surface methodology
S/C	-	Steam/carbon ratio
SCR	-	Selective catalytic reduction
SEM	-	Scanning electron microscope
SiO_2	-	Silicon dioxide
SiO_4	-	Silicon tetraoxide
SS	-	Sum of squares
T	-	Temperature
TiO_2	-	Titanium oxide
TNT	-	Trinitrotoluene
TPR	-	Temperature programmed reduction
WGMR	-	Water to glycerol molar ratio
XRD	-	X-Ray Diffraction
Zr	-	Zirconium
ZrO_2	-	Zirconium oxide
3-D	-	Three-dimensional

LIST OF SYMBOLS

$-\alpha$ and $+\alpha$	-	Level of independent variables
β_0	-	Intercept coefficient (offset)
β_1, β_2 and β_3	-	Linear terms
β_{11}, β_{22} and β_{33}	-	Quadratic terms
β_{12}, β_{13} and β_{23}	-	Interaction terms
cents/lb	-	Cents per pound
g	-	Gram
h^{-1}	-	Per hour
k	-	Number of independent variables
K	-	Kelvin
kg	-	Kilogram
mg	-	Milligram
mL/g-cat.h	-	Milliliter per gram catalyst per hour
mL/min	-	Milliliter per minute
n_o	-	Number of experiments repeated at the center point
R	-	Coefficient of correlation
R^2	-	Coefficient of determination
vol%	-	Volume percentage
wt%	-	Weight percentage
X_1, X_2 and X_3	-	Encoded independent variables
Y	-	Predicted responses
^oC	-	Degree celsius
%	-	Percentage
^{o}	-	Degree
Ɵ	-	Intensity of XRD

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nowadays, the increasing of the growth rate for vehicles leads to the high production of biodiesel. Unfortunately, a massive biodiesel production gives a large amount of glycerol as the by-product via transesterification reaction. Moreover, the limited of the world demand for glycerol makes the glycerol as a waste and abundant substance.

As the growth rate for vehicles increasing over the year, the public have highly demand of the fuel. However, fuels which been used is mainly from fossil which gives a bad impacts to the environment and soon in the future, the fossil fuels will be dried out. This situation leads for the hydrogen fuel production as it called the cleanest of all fuels because its combustion results essentially zero emissions (Wang *et al.*, 2010).

Currently, hydrogen production is mainly depends on the hydrogen extraction from fossil fuel feedstock. Since the fossil fuels will be dried out in the future, glycerol will be used as the raw material to produce hydrogen and at the same time reducing the dependency on fossil-based fuels. Thus, the hydrogen production from glycerol is further discussed throughout in this study.

Several methods to produce hydrogen using glycerol as a raw material are applicable but at the end, Pompeo *et al.* (2011) stated that the steam reforming is one of the most used reactions in the hydrogen production. In addition, Iriondo *et al.* (2009) has stated that the conversion of glycerol to hydrogen via steam reforming gives some advantages where the steam reforming of hydrocarbons is a process known, mature and efficient technology. In order to obtain high production of hydrogen, several reaction parameters is been investigated in this study including reaction temperature, glycerol feed concentration and glycerol feed flow rate.

In most of the studies, various catalysts are been used in glycerol steam reforming where a high selectivity of hydrogen can be obtained. Generally, metal catalyst with modified support or based are usually been investigated by researchers. The examples of metal catalysts which commonly been used are noble metal catalysts (such as platinum, palladium and ruthenium) but Iriondo *et al.* (2009) has mentioned that the cost of noble metal catalysts is quite high. Meanwhile, for the modified support or based catalyst, Al_2O_3 (Buffoni *et al.*, 2009), SiO_2 (Pompeo *et al.*, 2011) and La_2O_3 (Iriondo *et al.*, 2009) are several examples that usually been used in glycerol steam reforming.

Therefore, the non-noble metal catalysts such as copper and nickel are decided to be used in this study because it is cheaper and more available compared to the noble catalysts (Nichele *et al.*, 2012). Moreover, Nichele *et al.* (2012) has presented the suitability of nickel-based catalysts in glycerol steam reforming and a study reported that copper-based catalysts are effective for steam reforming of methanol to produce hydrogen (Maria *et al.*, 2007). On the other hand, HZSM-5 zeolite is to be used as based catalyst which has a great potential for hydrogen production from glycerol since Jia *et al.* (2010) work has proved the ability of HZSM-5 used in acrolein production from glycerol.

1.2 Problem Statement

Recently, most researchers investigate that glycerol steam reforming process is been used in a high temperature condition which is above 600^oC in order to obtain high hydrogen production. One of the additional costs in industrial is related to the operating conditional such as temperature. The cost is getting higher with the higher operating temperature. Thus, the capability of zeolite based catalyst in reducing the reaction temperature as well as to obtain higher hydrogen yield is been investigated throughout this study.

Although commercial metal catalysts which is noble metal catalysts (such as platinum, palladium and ruthenium) provide higher hydrogen production but the cost of those catalysts give a worrisome to the industrial. Therefore, copper and nickel non-noble metal catalysts are decided to be used in this study for its cheaper price and more available than platinum, palladium and ruthenium.

Nickel is one of the metal catalyst which commonly been used in the most studies related to hydrogen production but, there are no experimental and officially documents reported for using copper and nickel using HZSM-5 zeolite based catalyst to produce hydrogen from glycerol via steam reforming. Thus, the potential of copper and nickel using HZSM-5 zeolite based catalyst in hydrogen production is to be investigated in this study.

1.3 Objective of the Study

The objectives of the study are:

i. To investigate the performance of copper and nickel loaded on HZSM-5 zeolite catalyst for hydrogen production from glycerol
ii. To determine the optimum conditions in production of hydrogen

1.4 Scope of the Study

The scopes of the study are:

i. To observe the conversion of glycerol to hydrogen by using different percentage of loading amounts for copper (0-10%) and nickel (0-10%) on HZSM-5 zeolite catalyst
ii. To study the effect of reaction parameters including reaction temperature (350-750^{o}C), glycerol feed concentration (3:1-11:1 of water/glycerol molar ratio) and feed flow rate (0.25-1.25mL/min) towards hydrogen production
iii. To optimize and design the operating conditions (reaction temperature, glycerol feed concentration and feed flow rate) and research methodology using Response Surface Methodology (RSM)

1.5 Significant of the Study

As fuel demand is increasing, the biodiesel production gives the excessive of glycerol amount and makes it as abundant substance. Therefore, converting the glycerol into valuable substance such as hydrogen is been focused in this study. At the same time, the dependency of hydrogen production from fossil fuel feedstock is to be reduced by using glycerol as the raw material and concurrently, helps to save the environment.

Using nickel as the metal catalyst for hydrogen production in glycerol steam reforming, the cost could be reduced since nickel is cheaper compared to the platinum, palladium and ruthenium which commonly used in this process. Besides that, using copper and nickel with HZSM-5 zeolite based catalyst in hydrogen production is a new research that should be observed and studied.

General description with some studies from other researchers related to the hydrogen production from glycerol using zeolite based catalyst are been discussed in the next chapter.

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