CONVERSION OF GLYCEROL TO METHANOL OVER COPPER AND NICKEL SUPPORTED ON HZSM-5 ZEOLITE BY HYDROTHERMAL PROCESS

NURUL SYUHADA BT SPALIE

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Dedicated specially to my beloved mother, father, and family
for their love and encouragement

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ABSTRACT

The use of biodiesel nowadays is in highly demand and forecasted to increase steadily in the future. Due to the surplus of glycerol as the major by-product from biodiesel processing, it gain attention to convert glycerol to methanol such a renewable and biodegradable fuel. This study discussed on conversion of glycerol to methanol in a benign environment. The reaction was conducted using hydrothermal process with reaction temperature within 250-380°C, 60-90 min reaction time and various feed concentration. The hydrothermal stability has also been evaluated using modified catalyst. The catalyst used was HZSM-5 zeolites modified by impregnation of Cu and Ni metal. The catalysts were characterized by X-ray diffraction (XRD), Infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The catalysts performances have been investigated for glycerol conversion and methanol yield. Under the reaction condition, higher Ni metal loaded was found to show higher methanol yield from glycerol conversion. This study was carried out on the effect of reaction temperature, reaction time and feed concentration where 16 experimental runs were conducted. CuNi-HZSM-5 catalyst was chosen for further tested to determine optimum condition on methanol yield. Optimization of methanol yield from glycerol via Response Surface Methodology (RSM) showed 0.0697 mole of methanol/mole of glycerol reacted was obtained at the optimum reaction temperature 302°C, 59.2 min reaction time and 41.7 wt. % of feed concentration.

ABSTRAK

Penggunaan biodiesel diramalkan akan meningkat secara berterusan pada masa akan datang. Oleh kerana gliserol sebagai lebihan produk utama daripada pemprosesan biodiesel, penukaran gliserol kepada metanol mendapat perhatian untuk dijadikan sabagai tenaga yang boleh dipebaharui dan boleh dapat diuraikan melalui tindakan biologi oleh mikroorganisma. Oleh itu, kajian ini membincangkan tentang penukaran gliserol kepada metanol dengan menggunakan proses hidroterma. Tindak balas dijalankan dengan menggunakan reaktor berukuran 1 liter pada suhu tindak balas 250-380 ° C, 60-90 minit untuk masa tindak balas dan kepekatan suapan yang pelbagai. Pemangkin yang digunakan adalah HZSM-5 zeolite dan diubahsuai oleh logam Cu dan Ni. Pemangkin dianalisa dengan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah (FTIR), dan mikroskop imbasan electron (SEM). Pemangkin yang mengandungi komposisi Ni yang tinggi menunjukkan penghasilan metanol yang tinggi daripada gliserol. Interaksi antara suhu tindak balas, masa tindak balas dan kepekatan suapan dengan hasil metanol telah disiasat menggunakan kaedah gerak balas permukaan (RSM). Kajian pengoptimuman yang dijalankan menggunakan pemangkin CuNiHZSM-5 menunjukkan bahawa 0.0715 mol metanol / mol gliserol bertindak balas telah diperolehi pada suhu tindak balas optimum 302 °C, 59.2 minit masa tindak balas dan 41.7 wt. % untuk kepekatan suapan.

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LIST OF ABBREVIATIONS

Cu	-	Copper
Ni-HSZM-5	-	Nickel zeolite based catalyst
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
SO_2	-	Sulfur dioxide
GC-FID	-	Gas Chromatograph- Flame Ionization Detector
HPLC	-	High Performance Liquid Chromatography
XRD	-	X-ray Diffraction
GLYAC	-	Glyceric Acid
DHA	-	dihydroacetone
MESAC	-	Mexolic acid
HYPAC	-	Hyroxy-pyruvic acid
C-C	-	Carbon-carbon bond
EG	-	Ethylene Glycol
PEG	-	Polyglycerol Esters
MG	-	Monoglycerides
TAG	-	Triacatylglycerol
MTBE	-	*tert*-butyl ether
ETBA	-	ethyl *tert*-butyl ether
$(Cu.(NO_3)_2.6H_2O)$	-	Copper Nitrate Hydrate
$(Ni.(NO_3)_{2.}6H_2O)$	-	Nickel Nitrate Hexahyrate

LIST OF SYMBOLS

Θ	-	Angel
RFs	-	Response factor
x	-	Mass in gram

CHAPTER 1

INTRODUCTION

1.1 Background

Today, worldwide energy is supplied by petrochemical sources like fossil fuel and natural gas. The increasing consumption of these resources, which originated from fossil fuel, increased the emission of CO_2, SO_2 and NO_x from their combustion, hence contributed to environmental pollution. Previous study demonstrated that CO_2 level climbed up from year to year as a result of fuel burnt and causes the greenhouse gas effect (GHG), sea level increased, loss of biodiversity, formation of smog and acid rains, and changed of climate over the world (Gullison *et al.*, 2007). Nowadays, the number of motor vehicles on the road is approximately ten times higher than in 1950s, as a result of global population growth. While the number of vehicles used is predicted to increase 3 folds in near future, fossil fuel is consequently facing a serious problem due to high demand, as mentioned by Agarwal (2001). Hence, it is necessary to look for alternative fuel in an effort to reduce global warming by utilizing available sources such as biofuels, vegetable oils, biodiesel and etc.

Basically, the term biodiesel is referring to gaseous or liquid fuel used in transportation sector, and also as renewable replacement to petroleum-based diesel. The prefix “bio” indicates that the fuel either use biotechnologies or originated from the biological origin sources during manufacturing process (Pankin *et al.*, 2011). They found that biodiesel can either be methyl or ethyl ester of fatty acids made from biological origin, such as virgin or used vegetable oils (both edible and non-edible) and animal fat. Non-edible oils are from plant species such as *Hevca brasiliensis* (rubber), *Calophyllum inophyllum* (Nagchampa), *Jatropha curcas* (Ratanjyot), and *Pongamia pinnata* (Karanja), (Agarwal and Avinash, 2007).

Biodiesel itself is predominantly produced from biomass source, which is less polluting, has renewable nature and can be employed in any diesel engine without any adjustment since the properties is similar to mineral diesel (Demirbas, 2007). This alternative energy resource is the most selective one because of simple and rapid formation process compared to ethanol and methane production. During biodiesel production, glycerol is the major by-product, which represents approximately 10 wt% of the total production along with other impurities (Gullison *et al.*, 2007)

Because of that, glycerol production has been growing up recently and it is reported that many researchers showed interest in this area. Besides, for the last few years, biodiesel production was in high demand and it was expected that the price of glycerol would fall significantly, which represents a decreased of 50% from the real cost (Mccoy, 2005). This issue had received attention among researchers because large amount of glycerol has been produced and there are possibilities to use glycerol for producing new products. The properties of glycerol highlighted in Table 1.1 shows the capability to convert glycerol into various compounds (Thanh *et al.*, 2012). In addition, glycerol has many uses in different industries, for example in pharmaceutical, food, cosmetics industry, alternative fuels such as hydrogen, and many chemical intermediates can be produced (Demirbas, 2007). The purpose of creating new applications from glycerol is to produce new and valuable product that is economically practical. Therefore, this study focused on generating biofuel (i.e. methanol) from glycerol.

Table 1.1 Chemical and physical properties of glycerol (Perry *et al.*, 1997)

Properties	**Values**
Chemical formula	$CH_2OH\text{-}CHOH\text{-}CH_2OH$
Formula weight	92.09
Form and color	Colorless and liquid
Specific gravity	$1.260^{50/4}$
Melting point	17.9°C
Boiling point	290°C
Solubility in 100 parts	
Water	Infinity
Alcohol	Infinity
Ether	Insoluble
Specific heat in aqueous solution (mol%)	30°C (cal/g°C)
Viscosity of liquid glycerol	
At 100% purity	10cP
At 50% purity	25cP

1.2 Problem Statement

Nowadays, new approaches in generating renewable energy are still being investigated since there is finite amount of conventional source (i.e. fossil fuel). Methanol (biofuel) is one of the renewable energy that is biodegradable, environmentally friendly and suitable as petroleum replacement too. Few researchers have shown that there is a great potential to produce biofuels from glycerol by using hydrothermal process, as shown in their previous works. This process has been widely applied in several applications, such as catalytic dehydration in sub and supercritical region (Ott *et al.*, 2006), hydrothermal electrolysis (Yuksel *et al.*, 2010), gasification of glycerol in supercritical water (May *et al.*, 2010) and many more. Moreover, hydrothermal process is preferred because it can operate at lower temperature in the presence of catalyst, it is a straightforward process and also pollution-free since the reaction is carried out in a closed system. However, there are some constraints involved in generating this kind of fuel, regarding the use of catalyst in the process.

The challenge is to find ways for glycerol conversion that favors high selectivity of methanol production. Several studies reported that metal based catalyst such as platinum, nickel and copper can be employed in converting glycerol to other compounds. According to Brian *et al.*, (2010), commercial catalyst (Pt/C) has been tested to produce methanol and ethanol from glycerol at 330°C using batch system. However, platinum is very expensive to use even though high percentage of methanol yield that had been produced. Meanwhile, Cu-ZnO-Al_2O_3 has been found to favor in glycerol hydrogenolysis to propylene glycol at 340°C at 50 bar (Zhou *et al.*, 2010). In the study, the process operated at low temperature but using two steps hydrogenolysis mechanisms and it was hypothesized that the method was complex over catalyst used. Ni-HZSM-5 has been utilized in previous work, where Ana *et al*. (2011) mentioned that Ni-HZSM-5 has good balance between activities and attenuation of coke deposition to transform bioethanol into hydrocarbons.

This study aims to investigate the performance of catalysts that is expected to produce higher yield of methanol at lower temperature and shorter reaction time for conversion process. Thus, Cu and Ni were selected since they have been used in breaking C-O and C-C bond in hydrocarbons compound. Hence, by conducting this research, there are potentials to overcome those situations, where production of biofuels resulted in higher yield, low operational cost and also feasible to conduct.

1.3 Objectives of Study

The objectives of the study are:

1) To prepare and characterize HZSM-5 zeolite modify with Cu and Ni.

2) To test the performance and obtain the best catalyst for conversion of glycerol to methanol.

3) To optimize the reaction conditions for methanol yield using response surface methodology (RSM).

1.4 Scope of Study

In order to achieve the aforementioned objectives, three scopes of study have been identified as follows:

1) Catalysts were prepared with different composition of Cu and Ni supported on HZSM-5 zeolite ranging from 0-10 wt%.

2) The catalysts were characterized using XRD, FTIR, and SEM.

3) Screening test to evaluate the performance of the catalysts with different composition of Cu and Ni by hydrothermal process using 1 liter batch reactor.

4) Optimize the corresponding reaction conditions of the methanol yield using response surface methodology (RSM). Reaction conditions were: reaction temperature (215.9-384.1°C), reaction time (9.6-110.5 min) and feed concentration (16.4-83.6 wt %).

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