SELECTIVE CONVERSION OF GLYCEROL TO LACTIC ACID BY $CaO/\gamma\text{-}Al_2O_3$ SUPPORTED CATALYST

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by

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LIST OF ABBREVIATIONS

Al	Aluminium
Al_2O_3	Aluminium oxide
Au	Gold
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
C	Carbon
CaO/γ- Al_2O_3	Calcium oxide supported on gamma aluminium oxide
CG	Crude glycerol
CO_2	Carbon dioxide
EDX	Energy dispersive X-ray
FTIR	Fourier transformed infrared
G	Glycerol
H	Hydrogen
H_2O	Water
HCl	Hydrochloric acid
HPLC	High performance liquid chromatography

MCM-41	Mobile composition of matter No.41
Mg	Magnesium
MgO	Magnesium oxide
N_2	Nitrogen gas
NaOH	Sodium Hydroxide
O_2	Oxygen gas
OH	Hydroxyl
PET	Polyethylene terepthalate
TEM	Transmission electron microscopy
Ti	Titanium
SEM	Scanning electron microscopy
STP	Standard temperature and pressure
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
γ- Al_2O_3	Gamma-aluminium oxide

LIST OF SYMBOLS

A	Pre-exponential	$L \cdot mol^{-1} \cdot g^{-1} \cdot h^{-1}$
C_G	Concentration of glycerol	mol/L
C_{LA}	Concentration of lactic acid	mol/L
E_a	Activation energy	kJ/mol
k	Specific rate constant	h^{-1}
M	Molar mass	Dimensionless
r	Rate of reaction	$mol.g^{-1} \cdot h^{-1} \cdot L^{-1}$
S_{LA}	Selectivity of lactic acid	Dimensionless
t	time	h
T	Temperature	K
W	Weight of catalyst	g
X_G	Conversion of glycerol	Dimensionless

PENUKARAN TERPILIH GLISEROL KEPADA ASID LAKTIK DENGAN MENGGUNAKAN PEMANGKIN CaO/γ-Al_2O_3

ABSTRAK

Pengeluaran biodiesel telah membangun dengan pesat di Malaysia dan ia menjana lebihan gliserol mentah sebagai produk utama bersama. Berdasarkan keadaan semasa, penukaran gliserol kepada bahan kimia nilai tambah yang lebih tinggi seperti asid laktik telah menarik ramai penyelidik untuk memastikan kemampanan ekonomi industri biodiesel. Dalam kajian ini, CaO disokong pada alumina, γ-Al_2O_3 telah disintesis dengan berbeza muatan CaO (20-50 % berat) dan pengkalsinan terakhir pada suhu optimum iaitu 700 ° C. Pemangkin yang disintesis telah dicirikan melalui analisis permukaan, SEM, TEM, XRD, EDX, FTIR, TGA dan N_2 penjerapan sesuhu. Ciri-ciri pemangkin dihubungkaitkan dengan aktiviti mangkin dalam eterifikasi gliserol kepada asid laktik dan prestasi yang ditunjuk berdasarkan penukaran gliserol dan hasil asid laktik. Hasil yang tinggi asid laktik telah dikenal pasti dengan menggunakan pemangkin 30CaO/γ-Al_2O_3 yang telah disediakan dengan menggunakan 30% berat muatan CaO memuatkan dan dikalsinasikan pada suhu 700 ° C dalam pengeluaran asid laktik daripada gliserol. Kesan keadaan tindak balas seperti muatan pemangkin (5-20 % berat), suhu tindak balas (270-330 °C), masa tindak balas (0.5 - 4 jam) juga dijelaskan dan dihubungkaitkan dengan ciri-ciri mangkin. Selain itu, keadaan tindak balas terbaik diperolehi pada muatan pemangkin 10% berat, suhu tindak balas 290 ° C dan masa tindak balas 2 jam di bawah keadaan, 95% daripada penukaran gliserol dan 49% hasil asid laktik telah dicapai. Dari segi penggunaan semula, pemangkin ini adalah boleh digunakan semula sehingga 3 kali dalam tindak balas dengan penurunan dari 95% kepada 73% dalam penukaran gliserol, manakala penurunan dalam hasil asid laktik dari 47% kepada 27% dalam aktiviti pemangkin. Kajian kinetik pembentukan

asid laktik berjaya dilaksanakan dan didapati menepati model kinetic tertib pertama terhadap glycerol dengan tenaga pengaktifan sebanyak 61.730 kJ/mol. Sebagai kesimpulan, 30CaO/γ-Al_2O_3 merupakan pemangkin yang menunjukkan aktiviti yang baik dan ia merupakan pemangkin aktif yang sesuai untuk digunakan dalam tindak balas yang melibatkan gliserol.

SELECTIVE CONVERSION OF GLYCEROL TO LACTIC ACID BY CaO/γ-Al_2O_3 SUPPORTED CATALYST

ABSTRACT

The biodiesel production has been developing rapidly in Malaysia and it generates a surplus of crude glycerol as the primary co-product. Based on the current situation, the conversion of glycerol to higher value-added chemicals like lactic acid has attracted many researchers to ensure the economic sustainability of the biodiesel industry. In the present work, CaO supported on alumina, γ-Al_2O_3 catalyst was synthesized with different CaO loadings (20-50 wt. %) and the final calcination at optimum temperature was 700 °C. The synthesized catalyst were then characterized by means of surface analysis, SEM, TEM, XRD, EDX, FTIR, TGA and N_2 adsorption-desorption isotherm. The characteristics of the catalysts were correlated with the catalytic activity in glycerol etherification and the performance demonstrated based on the glycerol conversion and lactic acid yield. It was found that high yield of lactic acid was identified by using 30CaO/γ-Al_2O_3 catalyst which was prepared using 30 wt.% of CaO loading and calcined at 700 °C in the production of lactic acid from glycerol. Effects of reaction condition such as catalyst loadings (5-20 wt. %), reaction temperature (270-330 °C), reaction time (0.5-4 h) were also explained and correlated with the characteristics of the catalysts. On top of that, the best reaction conditions were obtained at 10 wt. % of catalyst loading, a reaction temperature of 290 °C and a reaction time of 2 h. Under these conditions, using 30CaO/γ-Al_2O_3 catalyst, 95 % of glycerol conversion and 49 % of lactic acid yield were obtained. In terms of reusability, this catalyst was reusable for up to 3 times in this reaction with decrease from 95% to 73% for glycerol conversion, while decrease from 47% to 27% in lactic acid yield in the catalytic activity. The kinetic study of lactic acid formation was successfully

conducted with a first order kinetic model and the activation energy of reaction of 61.730 kJ/mol was determined. As a conclusion, 30CaO/γ-Al_2O_3 catalyst showed good activity and it is an active catalyst that is suitable to be used in the reaction involving glycerol.

CHAPTER ONE

INTRODUCTION

1.1 Background

1.1.1 Biodiesel industry and its co product- crude glycerol

Biodiesel is an alternative fuel to diesel and it is commonly derived from vegetable oil, algae, or animal fat. The biodiesel industry has developed rapidly over the past few decades and has attracted considerable attention as a renewable, biodegradable and non-toxic fuel. The biodiesel is one of the best choices of the alternative fuels to petroleum in view of the depleting reserve of worldwide nowadays.

Based on Figure 1.1, the production of biodiesel in the United State was 135 million gallon in September 2016. The total 9 months for 2016 was the highest compared to 2014 and 2015 which was 1,137 million gallon. The total 9 month production for 2014 and 2015 were 916 and 948 million gallon, respectively. It shows that the production of biodiesel rapidly increases year by year. Because of biodiesel production growth, large amount of glycerol is produced during transesterification process of triacylglycerol and it is abundantly available in marketplace currently.

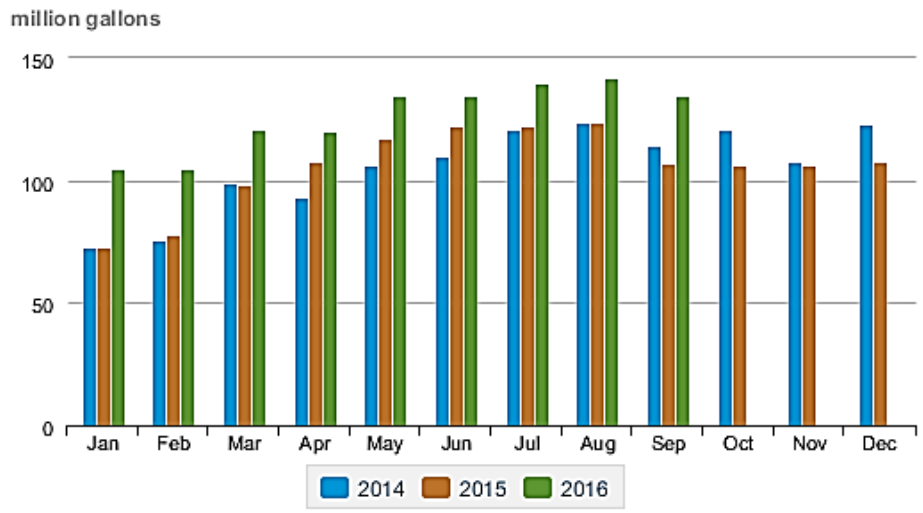

Figure 1.1 Monthly biodiesel production from 2014 until 2016.
(U.S Energy Information Administration, 2016)

Figure 1.2 shows the statistic of Malaysian biodiesel production from 2006 until 2014 (Johari et al., 2015). From year 2006 to 2008, there was an increase in biodiesel production. Unfortunately, by the year 2011, the production decreased drastically due to the increasing crude palm oil price as the feedstock for biodiesel production. However, the production of biodiesel elevated again in 2012 onwards due to expanded interest and global demand for biodiesel.

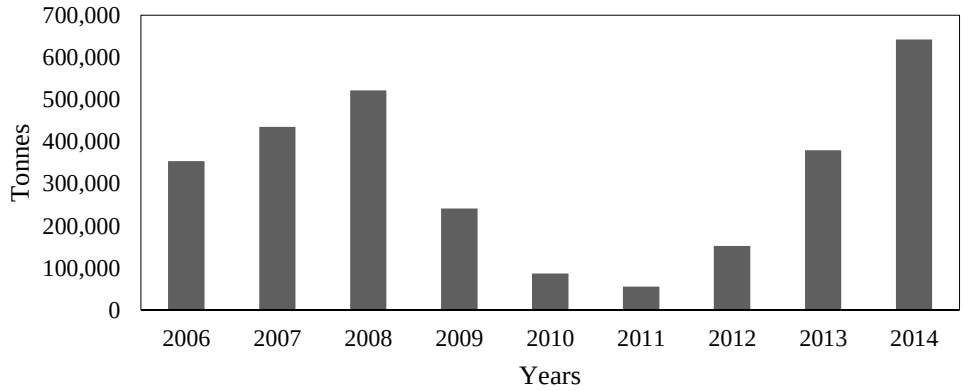

Figure 1.2 Statistic of Malaysian biodiesel production (Johari et al., 2015)

Figure 1.3 shows the summary on overall processing process of fats or oils to produce biodiesel (Shams et al., 2008). During the transesterification process of triglycerides (such as animal fats, waste cooking oil, vegetables oils and algae oil) with an alcohol (commonly methanol) to generate fatty acid methyl ester. Meanwhile, glycerol is produced as a co-product as presented in Figure 1.4. Base, acid or enzymes can be used to catalyze the reaction. In this process, biodiesel and crude glycerol form two different phases. For crude glycerol is in the lower phase and biodiesel forms at upper phase. This is due to differences in density and polarity.

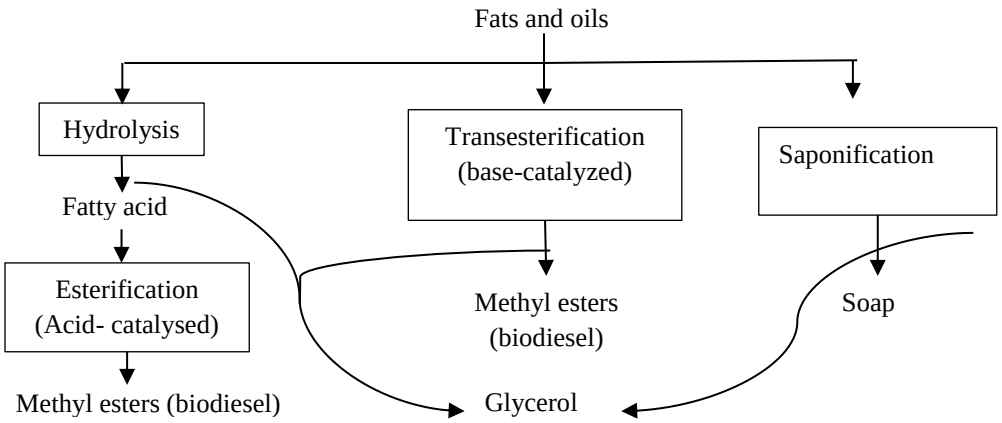

Figure 1.3 Biodiesel production from vegetable oils and animal fats and the relation with the co-product glycerol. (Shams et al., 2008)

Glycerol also known as glycerin forms during the transesterification process of triacylglycerol. As reported in Radiant Insight (2015), the market demand for glycerol was estimated to be USD 3 billion by 2022 and over 65 % of glycerol is generated as a product of biodiesel production. The huge amount of glycerol causes low prices of crude and refined glycerol generated each year and it has affected the glycerol market.

Some important applications of glycerol are seen in pharmaceutical, personal care, food industry and healthcare industries (Tan et al., 2013). As reported in Radiant

Insight (2015), The glycerol market demand was determined to be at 916.5 kilo tons in 2014 for Asia Pacific. For countries such as Malaysia, India, China, Indonesia and Japan strong demands are seen in food and beverage industries.

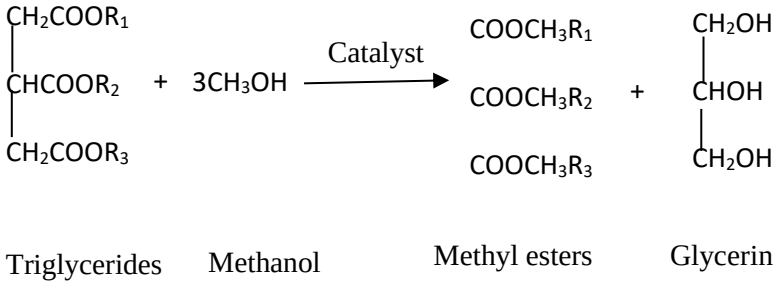

Figure 1.4 Transesterification reaction (Tan et al., 2013)

Thus, it is crucial to convert crude glycerol into value-added products or chemicals in order to ensure the economic sustainability of biodiesel industry. Besides that, it is also to reduce the environmental impacts of crude glycerol waste disposal. Hence, various conversions of glycerol to value-added chemicals have attract many researchers.

1.1.2 Conversion of crude glycerol

Glycerol (also called glycerine or glycerin) is an organic compound having chemical formula of $C_3H_8O_3$. It is a simple polyol compound that involves of three hydroxyl functional groups that are dependable for its solubility in water and its hygroscopic nature (Christoph et al., 2006).

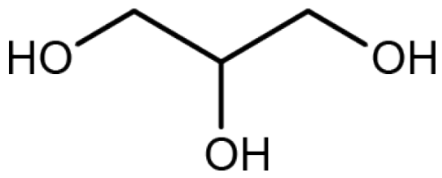

Figure 1.5 Chemical structure of glycerol

Glycerol can be converted using suitable catalysts to many chemicals such as solketal, acrolein, monoglycerides, propylene, polyol, lactic acid and etc. Table 1.1 shows some value-added products that can be produced from glycerol via many reactions such as dehydration, glycerolysis, thermochemical reaction etc.