SELECTIVE CONVERSION OF GLYCEROL TO LACTIC ACID USING NICKEL SUPPORTED ON CALCIUM OXIDE AND MAGNESIUM OXIDE

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Au	Gold
Al_2O_3	Aluminium oxide
BET	Brunauer-Emmett-Teller
C	Carbon
CO_2-TPD	Temperature programmed desorption of carbon dioxide
CuO	Copper oxide
CaO	Calcium oxide
Ce_2O	Cerium oxide
DHA	Dihydroxyacetone
EDX	Energy dispersive X-ray
HPLC	High performance liquid chromatography
Ir	Iridium
KOH	Potassium hydroxide
La_2O_3	Lanthanum oxide
MgO	Magnesium oxide
MoO_3	Molybdenum oxide
NiO	Nickel oxide
NaOH	Sodium hydroxide
OH^-	Hydroxide ions
Pd	Palladium
Pt	Platinum
Rh	Rhodium

SrO	Strontium oxide
SEM	Scanning electron microscopy
SiO_3	Silicate
TGA	Thermal gravimetric analysis
TiO_2	Titanium dioxide
XRD	X-ray diffraction
ZrO_2	Zirconia oxide
ZnO	Zinc oxide

LIST OF SYMBOLS

Symbols	Description	Unit
A	Pre-exponential factor	min^{-1}
C_{LA}	Concentration of lactic acid	$mol \cdot L^{-1}$
C_{GLY}	Concentration of glycerol	$mol \cdot L^{-1}$
C_{GLYO}	Initial concentration of glycerol	$mol \cdot L^{-1}$
E_a	Activation energy	$kJ \cdot mol^{-1}$
k	Reaction rate constant	min^{-1}
M	Molarity	Dimensionless
pH	Potential hydrogen	Dimensionless
R	Gas constant	$J \cdot K^{-1} \cdot mol^{-1}$
R^2	Correlation coefficient	Dimensionless
t	Time	min
T	Temperature	K
X_{GLY}	Conversion of glycerol	Dimensionless
Y_{LA}	Yield of lactic acid	Dimensionless

PENUKARAN TERPILIH GLISEROL KEPADA ASID LAKTIK DENGAN MENGGUNAKAN NIKEL YANG DISOKONG OLEH KALSIUM OKSIDA DAN MAGNESIUM OKSIDA

ABSTRAK

Peningkatan pesat dalam pengeluaran biodiesel di seluruh dunia menjana lebihan gliserol mentah sebagai produk utama yang memberi kesan yang buruk kepada harga pasaran gliserol. Untuk mengekalkan industri gliserol, pembangunan kepada produk bernilai tinggi daripada gliserol amat diperlukan. Asid laktik telah mendapat perhatian yang meluas disebabkan kepelbagaian aplikasinya di dalam industri makanan, kosmetik dan farmaseutikal. Dalam penyelidikan ini, gliserol telah ditukarkan kepada asid laktik melalui tindak balas pemangkin bes. Jenis mangkin yang berbeza (MgO, CaO, NiO, NiO/MgO dan NiO/CaO) telah digunakan pada tindak balas ini. Di antara pemangkin ini, NiO/CaO menunjukkan aktiviti yang tinggi dan telah dipilih untuk kajian yang seterusnya. Mangkin NiO/CaO telah disentesis dengan nisbah molar Ni/Ca (0.25, 0.43 dan 0.67) dan suhu pengkalsinan yang berbeza (800, 900 dan 1000°C). Di samping itu, sifat fizikokimia bagi mangkin ini telah dicirikan melalui penjerapan nitrogen, penyahjerapan karbon dioksida berprogramkan suhu (CO_2-TPD), mikroskop pengimbas elektron (SEM) dan analisis gravimetri termal (TGA). Kesan keadaan tindak balas seperti masa tindak balas (30–160 minit), suhu tindak balas (280-300°C) dan bebanan mangkin (10-20 % berat) dikaji bagi mengenalpasti keadaan tindak balas yang terbaik untuk dapatkan hasil asid laktik yang tinggi. Didapati bahawa mangkin NiO/CaO menunjukkan aktiviti yang tertinggi dengan nisbah Ni/Ca 0.43 dan dikalsin pada 900°C. Tambahan lagi,

didapati mangkin ini sesuai untuk digunakan pada tindak balas ini kerana ia memiliki kadar bes yang tinggi iaitu 11.28 mmol/g. Oleh itu, peningkatan jumlah bes pada mangkin mungkin menggalakkan pertukaran gliserol kepada asid laktik. 93.2% penukaran gliserol dan 41.3% hasil asid laktik telah berjaya diperolehi pada 290°C dalam 1.5 jam dengan bebanan mangkin 15% berat. Selain itu, mangkin ini boleh digunakan semula sehingga dua kali dengan sedikit penurunan dalam penukaran gliserol dari 89.3% ke 78.0%. Ini disebabkan oleh pengurasan kalsium daripada mangkin ke dalam gliserol. Walau bagaimanapun, sebanyak 28.7% hasil asid laktik boleh diperolehi setelah dua kitaran pemangkin. Model kinetik bagi kepekatan gliserol dalam penukaran gliserol dengan menggunakan 0.43NiO/CaO-900 sebagai mangkin telah juga dibangunkan. Model ini mampu untuk menerangkan reaksi sebenar di dalam reaktor pada kadar suhu 280-300°C. Oleh itu, ia kelihatan yang mangkin NiO/CaO mempunyai potensi pemangkin untuk penghasilan asid laktik dari gliserol.

SELECTIVE CONVERSION OF GLYCEROL TO LACTIC ACID USING NICKEL SUPPORTED ON CALCIUM OXIDE AND MAGNESIUM OXIDE

ABSTRACT

The rapid increase of biodiesel production worldwide generates an excess of crude glycerol as the primary co-product which negatively affect the price of glycerol in the market. In order to sustain the glycerol industry, the development of value-added chemicals from glycerol is necessary. Among them, lactic acid has received a considerable attention due to its numerous applications in the food, cosmetic and pharmaceutical industries. In this study, glycerol was upgraded to lactic acid through a base catalyzed reaction. Different types of catalyst (MgO, CaO, NiO, NiO/MgO and NiO/CaO) were used in this reaction. Among these catalysts, NiO/CaO showed high activity and was selected for the following study. NiO/CaO catalysts were synthesized with different molar ratios of Ni/Ca (0.25, 0.43 and 0.67) and calcination temperatures (800, 900 and 1000°C). In addition, the physicochemical properties of these catalysts were characterized by nitrogen adsorption, temperature programmed desorption of carbon dioxide (CO_2-TPD), scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). Effects of reaction conditions such as reaction time (30-160 min), reaction temperature (280-300°C) and catalyst loading (10-20 wt. %) were also studied to identify the best reaction conditions obtain high lactic acid yield. It was found that NiO/CaO catalyst demonstrated the highest activity at a Ni/Ca ratio of 0.43 and calcined at 900°C. Furthermore, this catalyst was found to be excellent to be used in this reaction as it possessed the high amount basicity of 11.28 mmol/g. Thus, the

increase in the total basicity of the catalyst might have favored its glycerol conversion to lactic acid. 93.2% of glycerol was converted to give 41.3% yield of lactic. Besides, this catalyst was reusable up to two cycles with a reduction in glycerol conversion from 89.3% to 78.0%. This could be due to leaching of calcium from the catalyst into glycerol. Nevertheless, high yield of lactic acid up to 28.7% could still be obtained after two catalytic cycles. A kinetic model for the glycerol concentration in glycerol conversion using 0.43NiO/CaO-900 as catalyst is also developed. This model could well describe the actual reaction occurring in the reactor in a temperature range of 280-300°C. Therefore, it appeared that CaO/NiO catalyst is a potential catalyst for lactic acid production from glycerol.

CHAPTER ONE

INTRODUCTION

1.1 Introduction to glycerol

Glycerol is known as a biodegradable, renewable and environmentally friendly product. With such properties, glycerol grabs the attention as alternative green fuel for organic reactions and applicable in many areas. Glycerol can be obtained as a by-product from the biodiesel production process when triglycerides (vegetable oils or animal fats) which consist of long chains of fatty acids are attached to three hydroxyl groups upon reaction with alcohol (methanol) in the presence of alkaline catalysts (Pagliaro et al., 2008). Generally, biodiesel that is produced through transesterification process of triglyceride will produce around 10 wt. % of crude glycerol or for every 100 kg of methyl ester (biodiesel) produced, approximately 10 kg of crude glycerol is generated (Yang et al., 2012).

From 2000 to 2005, glycerol production was dominated by fatty acid industry where the annual production of glycerol was remained relatively stable with the price of refined glycerol during that period ranged from USD 1,600 to USD 1,800 per ton (Quispe et al., 2013). However, by 2006 biodiesel industry started to dominate the production of glycerol from other industries causing a significant increase in the production of glycerol. The massive increase in glycerol production causes the price of glycerol to decline each year (Figure 1.1). This trend is expected to continue since there is high demand on biodiesel in the market as it is the most promising energy source to replace fossil fuel, especially when fossil fuel is estimated to be depleted by 2050 (Goyal et al., 2013).

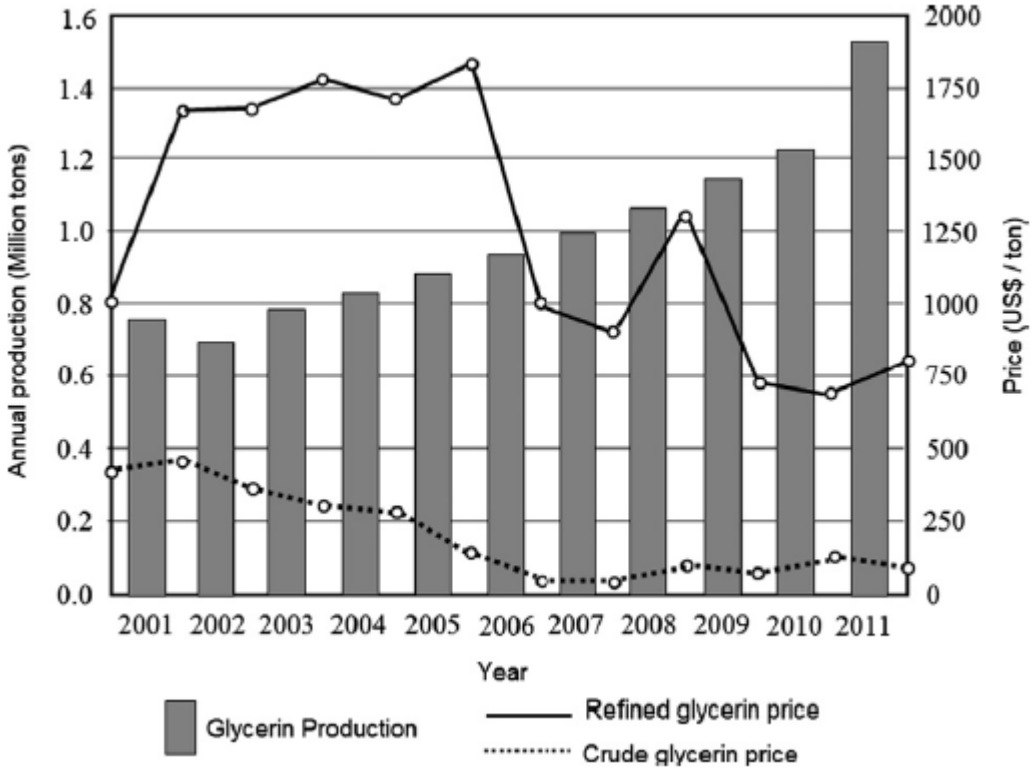

Figure 1.1: Glycerol production within 2001-2011 and prices (Quispe et al., 2013).

The global glycerol market nowadays facing an oversupply problem because of the remarkable increase in biodiesel production. The distribution of glycerol production in different industries is shown in Figure 1.2. Apparently, biodiesel industry is the highest contributor to the glycerol market at around 67% in comparison to other contributing industries such as fatty acid, fatty alcohol, soap and others (ABG Inc, 2010). Besides, it was reported that the residual glycerol produced from biodiesel industry has the potential to be the source of energy by using incineration method. Although this method seems to be plausible in order to solve the problem regarding the glut of glycerol in the market but burning of glycerol at high temperature will generate highly toxic materials such as acrolein (Guerrero-Pérez et al., 2009).

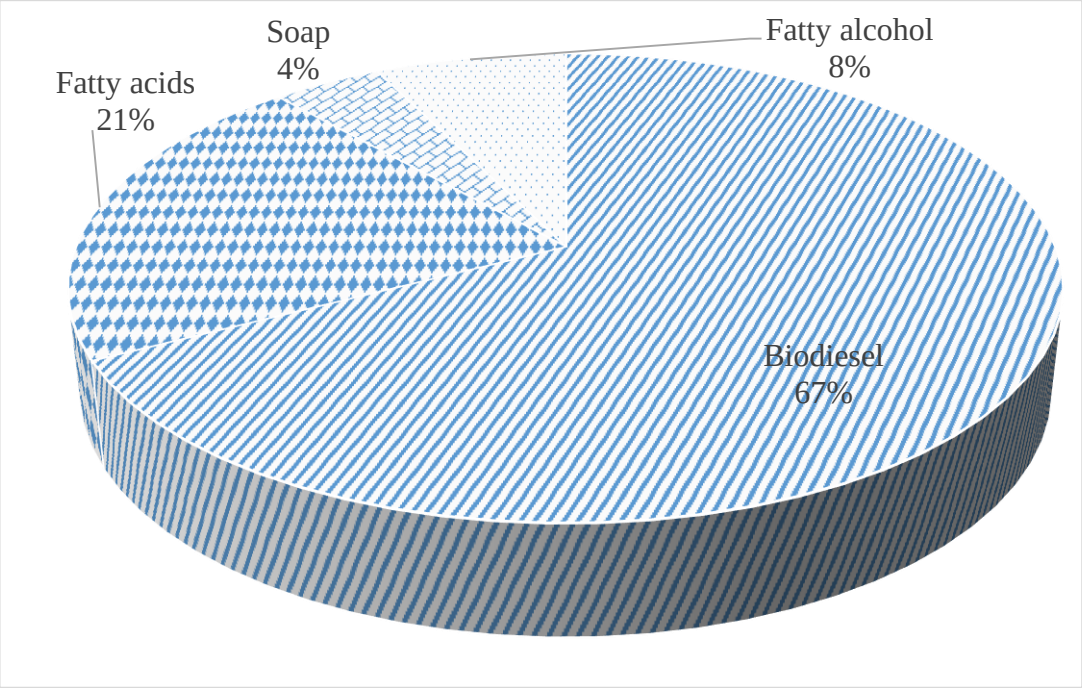

Figure 1.2: Source of glycerol in 2010 (ABG Inc, 2010).

To overcome the problem regarding the surplus of glycerol in the market, many researches are focusing their research on the utilization of glycerol to obtain value-added chemicals that could help to stabilize glycerol market price. The unique properties of glycerol offer a variety of versatile products to be produced in downstream industries. At present, large number of value-added products such as propionic acid, 1,3-propanediol, acrolein, alcohol (methanol and ethanol), monoglyceride and many more can be obtained from glycerol.

1.2 Lactic acid

Among a number of value-added chemicals that can be produced from glycerol, lactic acid has received a considerable attention in the past few years. Lactic acid or 2-hydroxypropanoic acid consist of a hydroxyl group adjacent to the carboxyl group as shown in Figure 1.3. These hydroxyl and carboxyl groups responsible in modifying lactic acid into other value-added chemicals such as lactic amide, lactide, pyruvic acid and acrylic acid that are very useful in many applications (Andres et al., 2013).

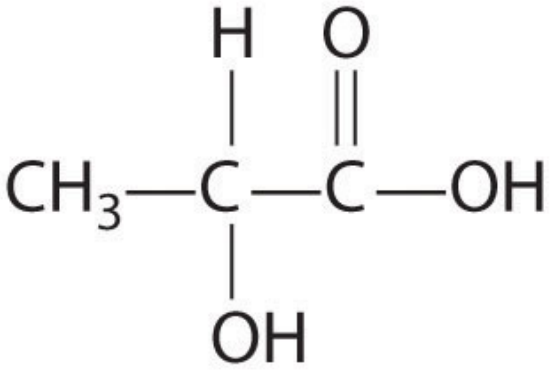

Figure 1.3: Chemical structure of lactic acid.

The annual production of lactic acid continued to increase steadily for the past 10 years with the price of lactic acid range of USD 2,075 to USD 2,300 per ton with the global lactic acid market was valued at about USD 1.28 billion in 2014 and is expected to reach USD 9.8 billion by 2025 (Grand View Research, 2017). The increase in lactic acid production each year is due to the high demand in food applications such as pH control agent, food additive and preservative agent. Moreover, lactic acid is also incorporated in cosmetic and personal care products for its humectant properties. Due to its ability to form another value-added chemicals,

lactic acid also is widely used in other industries such as packaging, textile and pharmaceutical. The applications and uses of lactic acid are summarized in Table 1.2.

Table 1.1: Physical and chemical properties of lactic acid.

Properties	**Values**
Chemical formula	$C_3H_6O_3$
Molecular weight	90.08
Physical appearance	Colourless to yellow liquid
Melting point (°C)	53
Boiling point (°C)	>200
Solubility in water (g/100g H_2O)	Miscible
pKa	3.86

Table 1.2: Applications of lactic acid in different fields.

Application	Uses	Purposes	Reference
Food industry	Food additives, preservative agent and pH regulator	Production of yogurt and cheese	(Razali and Abdullah, 2017)
Textile industry	Polymer additives, adhesives, coatings, printing toners, and surfactants	For use in tents, patio umbrellas, and awnings	(Kwan et al., 2018)
Cosmetic industry	Moisturizing, pH adjuster, exfoliant, antimicrobial and rejuvenating effects on the skin	Manufacture of hygiene such as toothpaste, mouthwashes and many others	(Andres et al., 2013)
Pharmaceutical industry	Prostheses, surgical sutures, dialysis solution mineral and drug delivery systems	Production of dermatologic drugs and prevention for osteoporosis	(Pagliaro et al., 2008)
Packaging industry	Production of biodegradable plastic	Food packaging	(Hu et al., 2017)

There are two alternative routes for producing lactic acid either by fermentation or chemical catalysis. Presently, lactic acid is commercially produced mostly through fermentation of carbohydrates (glucose or sucrose). Microbes like *L. delbrueckii, L. amylophilus and L. bulgaricus* are commonly used in the fermentation process for the production of lactic acid (Andres et al., 2013). The selection of microorganism for the fermentation processes is essential since each of the microorganism has its own characteristics which can determine the yield and selectivity of lactic acid.

Alternatively, commercial production of lactic acid can be achieved through chemical synthesis route by hydrolysis of lactonitrile by strong acid such as sulphuric acid. Lactonitrile could be obtained as a by-product from the manufacture of acrylonitrile (Chen et al., 2014). Lactonitrile can be achieved when acetaldehyde is reacted with hydrogen cyanide under high pressure in the presence of a base. The advantage of using lactonitrile route to manufacture lactic acid is that the procedure is simple in comparison to the fermentation route as described earlier. However, because of the limitations for the raw materials and expensive operational costs, this process is not very feasible for industrial application.

1.3 Problem statement

Although fermentation process is an excellent process in producing high yield of lactic acid, there are major drawbacks. Some problems faced by fermentation process are associated with the high maintenance costs of the process due to the fact that certain types of microorganism require specific conditions for producing lactic acid. Conditions such as pH level, temperature, time, aeration and agitation must be closely monitored. Moreover, purification process is needed in order to reduce impurities in the final product. Expensive purification method such as membrane