# Li-Mg/SBA-15 CATALYST FOR SELECTIVE ETHERIFICATION OF GLYCEROL TO DIGLYCEROL

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# Li-Mg/SBA-15 CATALYST FOR SELECTIVE ETHERIFICATION OF GLYCEROL TO DIGLYCEROL

by

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# LIST OF SYMBOLS

| | | |
|---|---|---|
| a.u. | Arbitrary unit | Dimensionless |
| A | Arrhenius factor (pre-exponential factor) | Dimensionless |
| $C_G/C_{Go}$ | Glycerol converted at time, t | Dimensionless |
| dX/dt | Differential of conversion of glycerol with respect to time | (mol/h) |
| H_ | Hammett basicity | Dimensionless |
| k | Reaction rate constant | ($dm^3$/mol.h) |
| $N_A$ | Initial numbers of mol | (mol) |
| R | Gas constant | (J/mol.k) |
| $-r_A$ | Rate of reaction | (mol.$dm^3$/h) |
| S | Selectivity to higher other oligomers | (%) |
| $S_2$ | Selectivity to diglycerol | (%) |
| $S_3$ | Selectivity to triglycerol | (%) |
| $S_N1,2$ | Nucleophilic substitution | Dimensionless |
| T | Reaction temperature | ($^oC$) |
| t | Reaction time | (h) |
| V | Total volume | ($dm^3$) |
| X | Conversion of glycerol | (%) |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| αα’-DG | αα’-diglycerol isomer |
| αß-DG | αß-diglycerol isomer |
| ßß’-DG | ßß’-diglycerol isomer |
| APHA | American Public Health Association |
| BASF | Badische Anilin Soda Fabrik |
| BJH | Barrett-Joyner-Halenda |
| BET | Brunauer-Emmett-Teller |
| $C_3H_8O_3$ | Glycerol |
| $C_6H_{14}O_5$ | Diglycerol |
| $C_9H_{20}O_7$ | Triglycerol |
| DG | Diglycerol |
| DFT | Density functional theory |
| EOy-POx-EOy | Poly(ethylene oxide) - poly(propylene oxide) – poly(ethylene oxide) |
| FAU | Faujasite |
| G | Glycerol |
| GCMS | Gas chromatography mass spectroscopy |
| HLB | Hydrophilic-lipophilic balance |
| HMDS | Hexamethyldisilazane |
| $H_2SO_4$ | Sulfuric acid |
| IUPAC | International Union of Pure and Applied Chemistry |
| P123 | Pluronic 123 |
| PEO | Poly(ethylene oxide) |
| MCM | Mobil composition of matter |
| SBA | Santa-Barbara amorphous |
| SEM | Scanning electron microscope |
| TEM | Transmission electron microscope |
| TEOS | Tetraethylorthosilicate |
| TG | Triglycerol |
| TMCS | Trimethylchlorosilane |
| XRD | X-ray diffraction |

# MANGKIN Li-Mg/SBA-15 UNTUK TINDAKBALAS PENGETERAN TERPILIH GLISEROL KEPADA DIGLISEROL

## ABSTRAK

Peningkatan mendadak pengeluaran gliserol mentah menjanjikan peluang besar bagi penyelidik untuk menggunakan ia sebagai bahan mentah yang boleh diperbaharui untuk menghasilkan produk yang berfaedah. Pengeteran gliserol kepada poligliserol menggunakan mangkin bes heterogen telah dikaji secara intensif sejak beberapa tahun kebelakangan ini tetapi pemahaman yang mendalam masih belum dicapai. Silika berliang meso adalah salah satu bahan sokongan mangkin yang memberangsangkan kerana ciri yang unik seperti kestabilan haba yang tinggi, luas permukaan yang besar dan membenarkan peresapan molekul besar di dalam liang mangkin. Tujuan utama kajian ini adalah untuk menyediakan mangkin bes heterogen untuk pengeteran gliserol kepada poligliserol. SBA-15 telah disintesis dengan baik dan mempamerkan jumlah liang yang banyak, luas permukaan yang tinggi dengan taburan liang bersaiz kecil. Mangkin disediakan dengan kaedah impregnasi logam aktif (Li, Mg dan Cs) ke dalam SBA-15. Bahan-bahan mangkin telah dianalisis dengan analisis permukaan, analisis pembelauan sinar-X, mikroskop elektron transmisi (TEM), mikroskop imbasan elektron (SEM) dan ujian kekuatan bes Hammett. 5 wt. % litium dan cesium boleh mengakibatkan kerosakkan sebahagian struktur SBA-15. Impregnasi binari SBA-15 dengan magnesium diikuti oleh logam yang tidak stabil iaitu litium boleh mengekalkan struktur liang meso. Magnesium bertindak sebagai lapisan untuk memelihara struktur sekaligus meningkatkan penyebaran litium di permukaan SBA-15. 5Li5Mg/SBA-15 adalah nisbah logam terbaik untuk kestabilan mangkin dan 10Li10Mg/SBA-15 boleh memberikan kebesan yang tinggi untuk pengeteran gliserol. Kesan penyediaan mangkin dan proses pembolehubah yang berbeza (suhu tindak balas, peratusan mangkin dan masa tindak balas) telah ditunjukkan dalam proses pengeteran gliserol. Mangkin 5Li10Mg/SBA-15 dan 10Li10Mg/SBA-15 mempamerkan aktiviti dan kememilihan untuk digliserol yang tinggi. Mangkin 5Li5Mg/SBA-15 hanya menunjukkan penukaran gliserol yang rendah walaupun ia adalah mangkin yang paling stabil berbanding yang lain. Mangkin 10Li10Mg/SBA-15 menunjukkan hasil digliserol tertinggi sebanyak 63 % dengan penukaran gliserol sebanyak 72 % dan kememilihan untuk digliserol kira-kira 82 %. Kondisi yang terbaik telah diperolehi pada 240 $^{o}$C untuk suhu tindak balas, 2 wt. % peratusan mangkin dan 18 jam untuk masa tindak balas. Satu kajian kinetik tindak balas untuk mangkin 5Li10Mg/SBA-15 dan 10Li10Mg/SBA-15 telah dikaji dengan julat suhu antara 220-280 $^{o}$C menggunakan model persamaan Arrhenius. Nilai tenaga pengaktifan masing-masing ialah 116.09 kJ/mol dan 117.46 kJ/mol. Nilai tenaga pengaktifan yang diperolehi bersesuaian dengan keadaan tindak balas yang digunakan. Selain itu, mangkin 10Li10Mg/SBA-15 menunjukkan keupayaan kememilihan bentuk untuk mempengaruhi taburan isomer digliserol di dalam liang. Mangkin ini menghasilkan banyak isomer αβ-digliserol berbanding dengan tindakbalas mangkin homogen. Hubungkait antara taburan isomer digliserol dengan suhu dan masa tindak balas juga ditunjukkan.

# Li-Mg/SBA-15 CATALYST FOR SELECTIVE ETHERIFICATION OF GLYCEROL TO DIGLYCEROL

## ABSTRACT

Drastic increase in crude glycerol production promises a great opportunity for researchers to use it as a renewable feedstock to produce beneficial products. Etherification of glycerol to polyglycerols using heterogeneous base catalysts has been studied intensively over the past few years but in-depth understanding on the process is yet to be achieved. Mesoporous silicas are the most promising ones among all catalyst supports due to their unique characteristics of high thermal stability, large surface area and present no limitation when dealing with large molecules. The primary aim of this study was to prepare heterogeneous base catalysts for the etherification of glycerol to polyglycerols. SBA-15 was successfully synthesized and it exhibited large pore volume, high surface area and good structural ordering with narrow pore size distribution. The catalysts were prepared by impregnating active metals (Li, Mg and Cs) into the SBA-15. The catalyst materials were subjected to the surface analysis, X-ray diffraction analysis, transmission electron microscope (TEM), scanning electron microscope (SEM) and Hammett basic strength test. 5 wt. % of lithium and cesium could result in partial structural collapse of SBA-15. Binary impregnation of SBA-15 with magnesium followed by the most active metal i.e. lithium could preserve the mesoporous structure. Magnesium acted as a coating layer to preserve SBA-15 framework as well to enhance dispersion of lithium. 5Li5Mg/SBA-15 was the best loading for catalyst stability and 10Li10Mg/SBA-15 could provide high basicity for glycerol etherification. Effects of catalyst preparation and different process variables (reaction temperature, catalyst loading and reaction time) were successfully demonstrated in the glycerol etherification process. 5Li10Mg/SBA-15 and 10Li10Mg/SBA-15 catalysts exhibited high activity and selectivity in the reaction. 5Li5Mg/SBA-15 catalyst favored low glycerol conversion even though it was most stable catalyst. 10Li10Mg/SBA-15 presented the highest diglycerol yield of 63 % with corresponding glycerol conversion of 72 % and a selectivity to diglycerol of about 82 %. The best conditions were obtained at 240 $^{o}$C for the reaction temperature, 2 wt. % of catalyst loading and 18 h of the reaction. A reaction kinetic study for 5Li10Mg/SBA-15 and 10Li10Mg/SBA-15 catalyst was successfully studied in the temperature range of 220-280 $^{o}$C using Arrhenius equation model and the values of activation energy were found to be at 116.09 kJ/mol and 117.46 kJ/mol, respectively. The values were considered just satisfactory and appropriate with the reaction conditions. Besides, 10Li10Mg/SBA-15 catalyst showed shape selective effect to affect the distribution of diglycerol isomers inside the pore. The catalyst predominantly yielded αβ-diglycerol isomer in contrast to homogeneously catalyzed reaction. The dependence of diglycerol isomers distribution on the temperature and reaction time were also successful demonstrated.

# CHAPTER ONE

# INTRODUCTION

## 1.1 General introduction

Glycerol has recently attracted much attention due to increasing rate of its production especially in biodiesel production. The US production of biodiesel is expected to grow at a rate of 50–80 % per year in which it resulted in 400 million gallons expected to be produced by the year 2012 (Pagliaro et al., 2008). The global market for glycerol is forecast to reach 4.4 billion Pounds by the year 2015 (Vocus, 2010). Figure 1.1 and Figure 1.2 represent the projection of global glycerol production over the years that led to market price reduction. Major producers of glycerol like Malaysia and Indonesia, mostly derived from palm oils, seem to be the important contributors for glycerol decreasing price to US$ 0.33 kg or below (Pagliaro et al., 2008; Nilles, 2006).

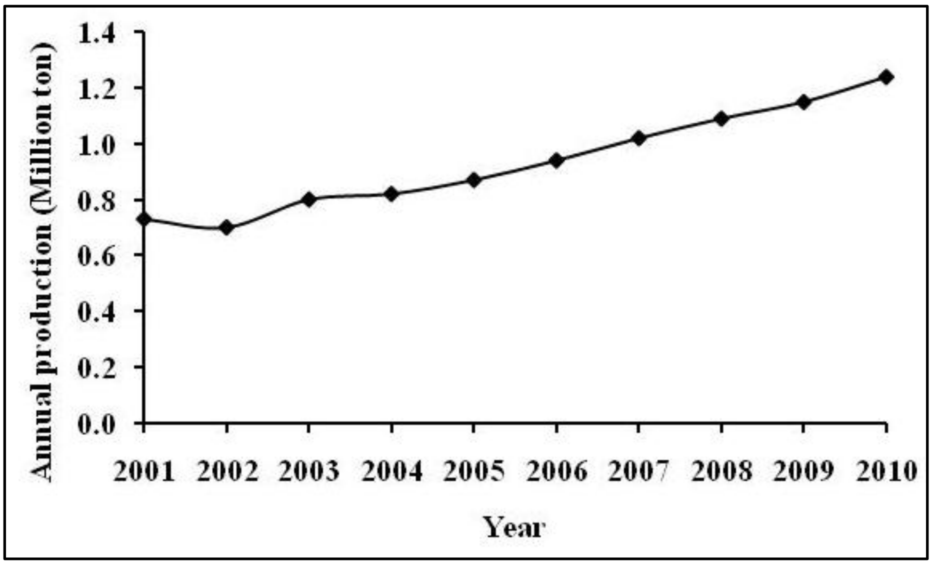


Figure 1.1: Global production of glycerol during 2001-2010 (Yazdani and Gonzalez, 2007).

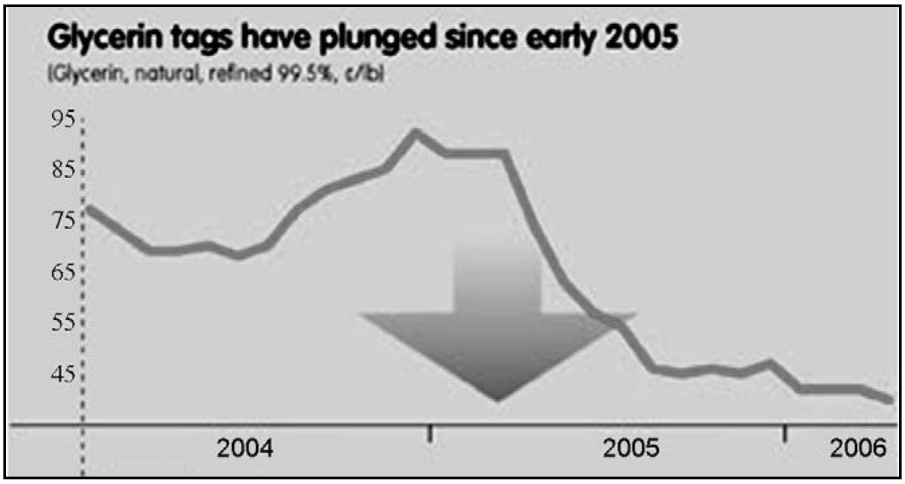


Figure 1.2: Glycerol price trend within 3 years from 2004 to 2006 (Woo, 2007).

The price of crude glycerol continues to decline and directly affects biodiesel production. By taking into consideration the value of glycerol, the biodiesel cost of production could be reduced from US$ 0.63 per liter to US$ 0.38 per liter as reported by Tyson (Tyson, 2003). However, the price of pure glycerol varied from US$ 0.50 to US$ 1.50/lb and that of crude glycerol was as low as US$ 0.04/kg to US$ 0.33/kg over the past few years (Omni Tech International, 2008). The price of glycerol in the market is expected to continue to drop in such an over saturated market.

Crude glycerol is the main by-product of the conversion of oils and fats through transesterification process in biodiesel production. For every gallon of biodiesel, 10 wt. % of crude glycerol will be produced (Johnson and Taconi, 2007). Crude glycerol is thick and too viscous. The purity and characteristics of crude glycerol in the transesterification process is determined by catalyst type used, alcohol excess and reaction conversion (Bournay et al., 2005). The crude glycerol derived from biodiesel production is generally not suitable for industrial use because of the impurities such as alcohol, heavy metals, salts and water. Hence, it is important to develop the glycerol conversion technologies which not only spurs biodiesel industry but can also switch the crude glycerol to value-added products for commercial uses.

The potential for bacteriological transformation of glycerol has been introduced for production of cosmetic, food and pharmaceutical applications (Gätgens et al., 2007; Song and Lee, 2006; Imandi et al., 2007; Solaiman et al., 2006). However, biochemical process often subject to low reaction rate and the final product must go through long purification processes.

In general, the conversion of glycerol to more valuable products can be classified into two ways which are oxidation or reduction of the glycerol into other three carbon compounds and reaction of glycerol with other molecules to form new species. There are many other processes to selectively oxidize and/or reduce glycerol such as dehydration, esterification, etherification, hydrogenolysis and many more. The various applications of glycerol are summarized in Table 1.1. These processes will lead to different products such as acrolein, glycidol, various types of acid and polyglycerols. Polyglycerols with low condensation degree such as di- and/or triglycerol are very important products that are being used as feedstock for production of emulsifiers in the food industry, humectants for cosmetic, as an antistatic agent for plastics, as a surface controller for fibers, as a sizing agent, etc (Corma et al., 2007; Jakobson, 1986). Therefore, there is a huge market for polyglycerols and the challenge is to find a selective conversion process of glycerol to polyglycerols. Moreover, producing value-added chemicals from glycerol instead of incineration is desirable in the consideration of both environmental protection and economic benefit.

Table 1.1: Commodity chemicals from glycerol.

| Process | Product | Uses | References |
|---|---|---|---|
| Etherification | Mono-, di- and tri-tert-butyl ethers | Used as oxygenase fuels | (Frusteri et al., 2009) |
| | Polyglycerols | Starting material for production of emulsifiers in the food and cosmetics industry, or of additives in polyvinyl chloride manufacturing | (Clacens et al., 2002)<br>(Ruppert et al., 2008)<br>(Richter et al., 2008b) |
| Esterification | Monoglyceride | Used as emulsifiers in food and cosmetics industries | (Kapoor and Gupta, 2012) |
| | Glycerol carbonate | High value-added product with many potential applications | (Rokicki et al., 2005)<br>(Aresta et al., 2009)<br>(Climent et al., 2010) |
| Reduction | 1,2-Propanediol | Used as a moisturizer to maintain moisture in medicines, cosmetics, food, and tobacco products. | (Pagliaro et al., 2007)<br>(Yuan et al., 2010) |
| | 1,3-Propanediol | Used as a monomer in the synthesis of polyesters and polyurethanes | (Biebl and Marten, 1995)<br>(Abbad-Andaloussi et al., 1998) |
| Oxidation | Dihydroxyacetone | Used as an ingredient in sunless tanning products. | (Navrátil et al., 2001)<br>(Li et al., 2010) |
| | Glyceraldehyde | Starting material for production of glyceric acid, hydroxypyruvic acid, tartaric acid, monoxalic acid and oxalic acid. | (Pinter et al., 1967) |
| Dehydration | Acrolein | Primarily used as an intermediate in the synthesis of acrylic acid and as a biocide. | (Tsukuda et al., 2007)<br>(Watanabe et al., 2007) |
| Chlorination | Dichloropropanol | Used extensively in many industrial processes (e.g. production of epichlorohydrin). | (Lee et al., 2008) |

Etherification of glycerol to polyglycerols becomes an interesting topic to discuss. Currently, active research works are directed towards finding good catalyst that has high stability, higher catalytic activity and more selective to targeted products. Based on previous research work, homogenous acid catalyst are very active in etherification of glycerol but not selective to the targeted product (Seiden and Martin, 1976; Medeiros et al., 2009; Koter and Ceglowska, 1986; Clacens et al., 2002). However, the use of heterogeneous acid catalyst would produce more cyclic polyglycerol compounds (Eshuis et al., 1997). Some researchers work on basic catalysts as they could provide the higher activity and very selective to the desired products. The use of zeolites (Hees et al., 1993) and MCM-41 (Clacens et al., 2002) as catalysts slightly increase the selectivity of the reaction due to some shape-selective effect. It has also been reported that basic alkali metals are good promoters to the activity and selectivity in the reaction.

SBA-15 impregnated with reactive metals such as alkali metals and alkaline earth metals have been studied in the basic heterogeneous low reaction temperature of etherification of glycerol to polyglycerol (i.e diglycerol and triglycerol). The potential of this material which is polymer-templated silicas with hexagonally ordered mesopores have been investigated for their stability, reactivity and selectivity in the etherification of glycerol. SBA-15 has larger pore size and has better hydrothermal stability than MCM-41 due to its thicker wall (Yun and Ihm, 2008). Other than that, the existence of micropores interconnecting hexagonally ordered mesopores would facilitate diffusion inside the entire porous structure and makes SBA-15 more suitable for many catalytic applications (Klimova et al., 2006; Fulvio et al., 2005).

## 1.2 Problem statement

In recent years, there has been a dramatic increase in the price of crude oil due to depletion of its resources. As a consequence, the price of transportation fuels shows a steady increase. This trend has resulted in rapid growth of biodiesel production. Increases in environmental concerns make biodiesel the best option as the alternative fuel. However, a sharp increase in biodiesel production results in an uncontrolled crude glycerol surplus. Without proper management, crude glycerol that is generated during biodiesel production can create a potential financial implication to the biodiesel producers and gives adverse effect to the environment. Crude glycerol contains impurities such as alcohol, salts, heavy metals and water and must be purified first before it can be used. Tight supply and demand market of glycerol makes it not a feasible option to sell the crude glycerol to the refiners. It is also not very economical since the biodiesel producer should bear the freight cost which can exceed the cost of crude glycerol.

Hence, the need for advanced development of glycerol conversion technologies is an upmost importance and the best option to solve this problem. Conversion of crude glycerol into more valuable and high demand products such as polyglycerols presents a profitable opportunity for the biodiesel industry. Homogeneously catalyzed glycerol etherification usually needs extra steps for product purification. Therefore, heterogeneous catalytic process is expected to be an effective glycerol etherification process with minimal environmental impact and management cost. There are two modes available for glycerol etherification reaction to take place whether in basic or acidic condition. Acidic condition provides fast reaction but yields predominantly cyclic polyglycerols. Hence, heterogeneous basic catalysis system is the best option that could avoid the remaining problem.

Research works nowadays are focused on mesoporous materials as potential catalysts. Mesoporous silica could provide high surface area, uniformity in pore size and high thermal stability which promise great opportunity in glycerol etherification reaction. However, the frameworks of mesoporous silica materials are neutral so that the applicability is limited. Therefore, in the present study, alkali metals have been used as active metal components to improve the basicity of mesoporous catalyst for the reaction. Effects of basic components introduction into the mesoporous frameworks should be thoroughly investigated. Many researchers report the reduction in surface area of mesoporous structure after being impregnated with alkali metals.

In view of these pros and cons as well as limited research reports available on heterogeneous base catalyzed glycerol etherification, the main goals of this study are therefore directed towards the synthesis of the high surface area mesoporous catalysts and the identification of the potential active metals which meet specific needs for effectively glycerol etherification. Other than that, the kinetic study must be considered in this reaction for deep understanding on the catalyst activity and selectivity to the desired product. The problems remaining in the past research works on etherification of glycerol are good motivation to study and investigate the most suitable reaction conditions for the production of a good quality polyglycerol.

## 1.3 Objectives of the research

This study embarks on the following objectives:

1. To synthesize mesoporous SBA-15 support to be subsequently functionalized with reactive metals (Li, Mg, Cs) for selective etherification of glycerol to diglycerol.

2. To characterize the surface, structural, physical and chemical properties of the mesoporous catalysts for correlation with the observed behaviors during the glycerol etherification process.
3. To optimize the operating conditions of the glycerol etherification reaction for better yield and selectivity of the desired products.
4. To study kinetic of the reaction and shape selectivity of the catalyst.

## 1.4 Scope of the research

The first part of present study concentrates on catalyst preparation which includes the preparation of SBA-15 as catalyst solid support and impregnation of support with lithium, magnesium and cesium. The prepared materials were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), surface analysis, and Hammett indicators.

The second stage of this study consists of catalytic activity, the investigation of catalyst performance. The etherification of glycerol to polyglycerol has been carried out with the presence of catalyst at certain operating reaction conditions. Operating parameters investigated include reaction temperature (220-280 $^{o}$C), reaction time (2-18 h) and catalyst loading (1-4 wt. %).

The last part of this research work is the analysis of product mixture by using a gas chromatograph. Product mixture analyses indirectly determine the catalyst activity, selectivity and yield of the desired product. Besides, a kinetic study for the reaction has been conducted using Arrhenius equation to obtain the activation energy ($E_a$) and reaction rate ($-r_A$). Shape selectivity of the catalyst also has been discussed.

## 1.5 Organization of the thesis

The thesis comprises five chapters. Chapter 1 briefs the current scenario on biodiesel industry that lead to dramatic increase in glycerol production. The problem statement lists out some of the problems faced with respect to environmental impacts of crude glycerol discharges and also discusses the consequent development due to this surplus. The objectives of this research work are given in this chapter as well.

Chapter 2 summarizes the related information published in the literature including the catalytic reaction of glycerol etherification, reaction mechanism and catalyst development. The factors affecting etherification process is also discussed.

Chapter 3 lists the chemicals and materials that have been used in catalyst preparation and the setup of etherification batch reactor. This chapter also discusses the experimental procedures in detail includes preparation of catalyst, product analysis, reaction kinetic and shape selectivity study of the catalyst.

Chapter 4 represents the experimental results and discussion of the findings in the study. It consists of four main experimental studies which are; (1) characterization of SBA-15 support and catalysts (2) effects of operating variables on the catalytic activity (3) reaction kinetic study and corresponding parameter evaluation and (4) shape selectivity of the catalyst.

The overall outcome obtained in the present study are summarized and concluded in Chapter 5. Suggestions and recommendations on further improvement of the research work that can be considered in the future works are also highlighted in this chapter.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Glycerol

Glycerol (or glycerin, IUPAC name: propane-1,2,3-triol) is a colorless, odorless and viscous liquid which has three hydroxyl groups attached to its molecular structure. It has sweet taste and low toxicity. The good features of glycerol such innocuous nature, biodegradable and non-toxic liquid to human health and also to environment enable it to be used in the cosmetics, drugs, food and toiletries (Ash, 2004). This simple poly-ol compound is very soluble in water and highly hygroscopic. The chemical properties of glycerol are listed in Table 2.1 below.

Table 2.1: Chemical properties of glycerol (Perry et al., 1997).

| Properties | Values |
|---|---|
| Molecular formula | $C_3H_8O_3$ |
| Molar mass | 92.09 g/mol |
| Density | 1.261 g/cm$^3$ |
| Melting point | 291.0 K |
| Boiling point | 563.0 K |
| Refractive index | 1.4746 |
| Solubility in 100 parts | |
| Water | Infinity |
| Alcohol | Infinity |
| Ether | Insoluble |
| Viscosity of liquid glycerol | |
| At 100% purity | 10 cP |
| At 50% purity | 25 cP |
| Diffusivity in | (DL x 10$^5$ sq cm/s) |
| i-Amyl alcohol | 0.12 |
| Ethanol | 0.56 |
| Water | 0.94 |

Crude glycerol is traditionally produced in oleochemical industry. However with the emergence of biodiesel industry in the recent years created glycerol glut in the market. Crude glycerol produced from biodiesel industry is often dark in appearance with the presence various impurities such as ash and chloride. These properties make it not suitable for use in food, pharmaceuticals or cosmetics industries that usually need high purity of glycerol content of up to 99 %. Crude glycerol normally has 60-80 % of glycerol content. Table 2.2 presents the quality parameters of different categories of glycerol. Moisture, ash and soap contents are commonly present at higher quantity in biodiesel-derived crude glycerol as compared to purified glycerol. Crude glycerol derived from biodiesel waste stream is expensive to be purified to above 99 % purity. It must be refined well for the formation of consumer products like food or drug. Therefore, the present work is mostly focused on the application of crude glycerol to evaluate its potential for upgrading into value added chemicals, hence allowing the biodiesel industry to become more cost-effective and environmental friendly in the long term.

Table 2.2: Quality parameter between crude and purified glycerol (Hamizah, 2003).

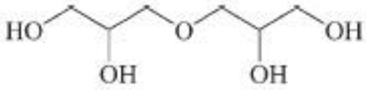
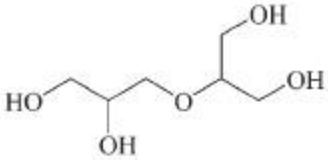
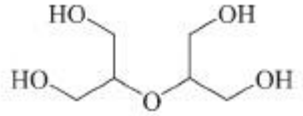
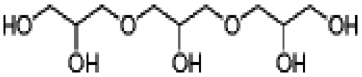
| Parameter | Crude glycerol | Purified glycerol |
|---|---|---|
| Glycerol content (%) | 60-80 | 99.1-99.8 |
| Moisture contents (%) | 1.5-6.5 | 0.11-0.8 |
| Ash (%) | 1.5-2.5 | 0.054 |
| Soap (%) | 3.0-5.0 | 0.56 |
| Acidity (pH) | 0.7-1.3 | 0.10-0.16 |
| Chloride (ppm) | ND | 1.0 |
| Color (APHA) | Dark | 34-45 |

## 2.2 Polyglycerols

Polyglycerols consists of glycerol units linked by an ether linkage. It comprises diglycerol, triglycerol, tetraglycerol and higher oligomers. Table 2.3 shows the basic data properties of polymerized products of glycerol. Polyglycerol are glycerol derivatives, that are mainly polyglycerol esters and they have been used in many applications since the beginning of 20th century. The possibility to control their hydrophilic-lipophilic balance (HLB) enables polyglycerols to be used in the manufacture of new products for cosmetics (Sun et al., 2003), food additives (Stewart and Hughes, 1972), surfactants (Hoefer and Krampitz, 1991), lubricants (Kojima and Sakaya, 2011), etc. Polyglycerols may widely differ in composition, depending upon their production process. Polyglycerols esters are often obtained in two-step procedure which is the preparation of a polyglycerol fraction followed by the esterification or transesterification of the polyglycerol with different acids or ester by using homogenous catalysts (Corma et al., 2007).

The quality of polyglycerol produce in etherification process is a great concern. Polyglycerol with higher viscosity provides greater body to personal care formulations and at the same time reduces the amount of thickening agent needed. Its thermal stability should be higher in order to accommodate high reaction temperatures. Other than that, higher refractive index is important in determining for transparent emulsion formulations. In order to obtain the transparent emulsions, the refractive index of the aqueous and oily phases needs to be similar (Sun et al., 2003). Biodegradability is also very important in an environmental point of view. High biodegradability of polyglycerols is caused by low content of cyclic products. In addition, cyclic polyglycerols will affect the taste, performance, and odor of the products by degrading the products into which they are incorporated. The cyclic formations of polyglycerols need to be minimized as much as possible.

Table 2.3: Properties of diglycerol and triglycerol (Behrens and Mieth, 1984; Jakobson, 1986).

| Molecule | Molecular formula (weight, g/mol) | Molecular structure | Density (g/cm$^3$) | Boiling point ($^o$C)/(Pa) |
|---|---|---|---|---|
| Diglycerol | $C_6H_{14}O_5$<br>(166) | <br>α,α’-Diglycerol<br><br>α,β-Diglycerol<br><br>β,β’-Diglycerol | 1.2790 | 205/133 |
| Triglycerol | $C_9H_{20}O_7$<br>(240) |  | 1.2646 | >250/13.3 |

In order to obtain linear polyglycerol, basic catalyst is often used in the glycerol etherification process while acid catalyst will produce more cyclic polyglycerol. A method for preparing polyglycerols with low cyclic polyglycerol content by condensing glycerol in the presence of an alkali catalyst and an aluminium oxide absorbent was disclosed by Koma (1986). Jakobson and Siemanowski (1990) disclosed a process for preparing polyglycerols which are low in cyclic components. Sometimes, further purification process needs to be used in order to remove the unnecessary product. Distillation process is commonly applied to remove unreacted glycerol and cyclic diglycerol on the heating glycerol under reduced pressure (Seiden and Martin, 1976; Aoi, 1995). Cyclic polyglycerol actually give adverse effect to the product and needs to be avoided by choosing the suitable synthesis method.

## 2.3 Etherification of glycerol to polyglycerol

Finding the most suitable and stable catalyst for glycerol etherification is a challenging task. The continuous improvement and extension of previous study is still underway to find the most selective and active catalyst with high thermal stability. Basically, the etherification reaction will take place either in acidic or basic catalysis condition. The selection of the catalyst among these two different conditions will surely affect the final product of the reaction.

### 2.3.1 Acid catalysis in glycerol etherification

In acidic catalysis system, compound such as sulfuric acid ($H_2SO_4$) can be used as a proton source. The glycerol etherification reaction starts when one of $OH^-$ groups from the glycerol molecule is protonated by $H^+$. Water as a leaving group will be splitted off during the formation of a carbocation. This nucleophile will attack the hydroxyl group of another glycerol molecule to form ether. Deprotonation of ether will result in diglycerol formation. The acid catalyzed reaction mechanism is shown in Figure 2.1 and it is of $S_N1$ type of organic reaction.

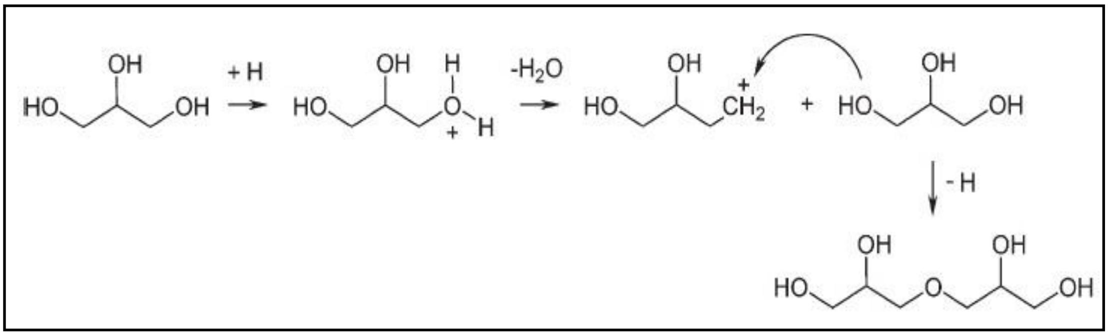


Figure 2.1: Etherification of glycerol based on $S_N1$ type mechanism (Richter et al., 2008a).

Generally, the nature of catalyst that is commonly used comes in two types; whether they will act as homogeneous or heterogeneous catalyst, each of which has pros and cons. Homogeneous catalyst means the catalyst and reactant are in the same phase. At the end of the reaction, the final product must undergo a purification step. It can be usually separated by distilling under vacuum. The adverse and inevitable part is the occurrence of secondary reactions such dehydration and oxidation that can deteriorates the product quality by coloration (Martin and Richter, 2011). Past research works on homogeneous acid catalyst showed that the activity of the catalyst was good and fast but not selective enough to the targeted product (Medeiros et al., 2009; Koter and Ceglowska, 1986). At high temperature, $H_2SO_4$ is very active for glycerol etherification since it takes only 2 h to convert more than 90 % of glycerol as shown in Table 2.4. However, the final product contains 80 % of non-identified substances of which diglycerol is the desired product.

Table 2.4: Acidic catalysis for glycerol etherification.

| Type of catalyst | T($^{o}$C) | X (%) | $S_2$ (%) | $S_3$ (%) | S (%) | Ref |
|---|---|---|---|---|---|---|
| Acidic homogeneous | | | | | | |
| 0.3 wt. % $H_2SO_4$ | Under reduced P=7mbar | 54.8 | 31.6 | 13.6 | 9.6 | (Jakobson and Siemanowski, 1990) |
| Dodecyl benzenesulphonic acid | 150 | 50 | 33 | 11 | 4 | (Medeiros et al., 2009) |
| $H_2SO_4$ | 280 | >90 (2h) | | 20 | | (Martin and Richter, 2011) |
| Acidic heterogeneous | | | | | | |
| Zeolite beta (Si/Al=50) | 200 | 100 | 60 | 30 | 10 | (Eshuis et al., 1996) |
| 4 wt. % Zeolite beta (Si/Al=12) | 260 | 70 (7h) | 40 | 30 | - | (Krisnandi et al., 2008b) |
| MCM-41 (Si/Al=40) | 220 | 50 | 10 | | | (Krisnandi et al., 2008b) |
| 2.5 % Mg saponite clay | 250 | 24 (24h) | 17(lin) | 7 | | (Kraft, 2003) |
| | 250 | 70 (78h) | 40(lin) | | | |

(X=glycerol conversion, $S_2$=selectivity to diglycerol, $S_3$=selectivity to triglycerol, S=selectivity to higher other oligomers)

The introduction of heterogeneous catalyst to support the reaction allows simple separation process. Unfortunately, the reaction can yield more cyclic compounds rather than linear polyglycerol. Table 2.4 lists the previous studies on glycerol etherification over acidic catalysts by many researchers. Direct comparison between the performances of the catalysts could not be done as the operating conditions for all reaction are different. Glycerol etherification was carried out at 200 $^{o}$C in the presence of an acid zeolite having an average pore size of at least 0.6 nm (Eshuis et al., 1996). The result showed that at least 50 wt. % of cyclic polymers was obtained. Therefore, it could be concluded that etherification of glycerol in the presence of an acid zeolite catalyst would result in high percentage of cyclic polymeric products. Additionally, the zeolites with higher Si/Al ratio showed the high catalyst activity. In another approach, Kraft (2003) disclosed a method for polymerizing glycerol using magnesium saponite in the H form as catalyst. From the study, they revealed an advantage in terms of catalyst life and the process yielded predominantly more linear oligomers and branched at lower conversions than expected. Hence, the use of acid catalyst still did not provide a solution to control the selectivity to diglycerol and triglycerol.

### 2.3.2 Basic catalysis in glycerol etherification

In basic system, etherification of glycerol occurs when hydroxide from base interacts with one glycerol molecule. This interaction renders the nucleophilic character of the hydroxyl oxygen to attack the second glycerol molecule to produce diglycerol by splitting off water molecule as shown in Figure 2.2.

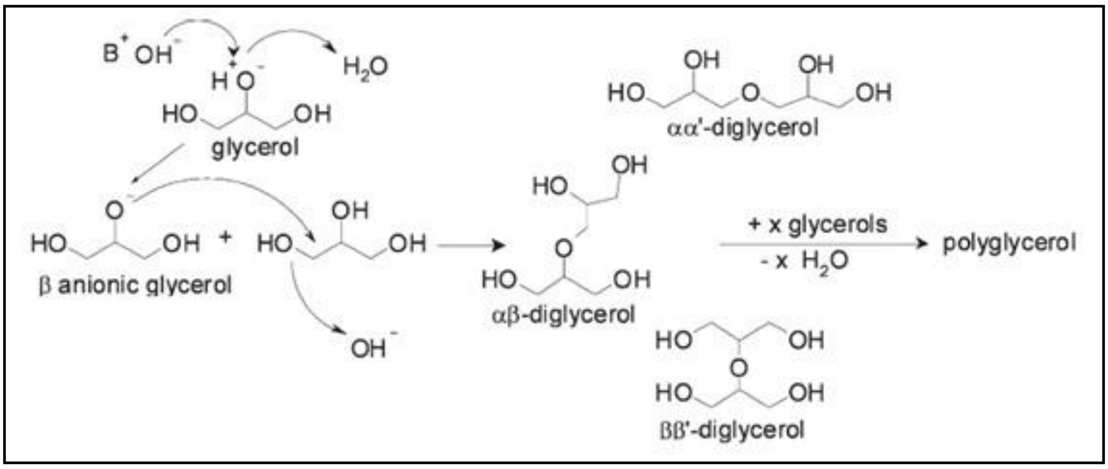


Figure 2.2: Etherification of glycerol based on $S_N2$ type mechanism (Richter et al., 2008a).

The use of a base as a catalyst in glycerol etherification was developed as early as the 80's. It was reported that carbonates were better and more active than hydroxides and oxides in basic homogeneous catalysis system because of better solubility in glycerol (Garti et al., 1981). However, as the reaction was catalyzed by dissolved alkali, purification steps were necessary to obtain polyglycerol. Table 2.5 lists previous research works about glycerol etherification using both phases of catalyst. Jeromin and co-workers studied the etherification of glycerol over sodium hydroxides at 230 $^{o}$C. Results showed that only about 12.5 % weight of diglycerol was obtained and two distillation steps under vacuum in order to obtain 98 % purity of diglycerol were needed. Hence, the search for novel solid catalyst is very indispensable to reduce the overall processing cost of the process.

Porous solid catalyst for this reaction was introduced since 1993 (Hees et al., 1993). The use of zeolites as catalysts slightly increased the selectivity to diglycerol due to some shape-selectivity effect. NaX and CsHY zeolites showed higher selectivity of higher than 90 % even though they were less active at the beginning of the reaction. It was also reported that basic alkali metal was the best catalyst to the activity and selectivity of diglycerol in the reaction. In 2002, Clacens and co-workers investigated the selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. It was found that cesium impregnated material was the best active component for this catalyst that provided excellent catalyst activity of up to 80 % of glycerol conversion and the reaction was very selective to di- and triglycerol of about >90 %. It was suggested that cesium impregnation using grafting method was the best way to prepare the catalyst with high stability to prevent catalyst leaching during reaction. Compared to zeolites, mesoporous silica based catalyst showed improved selectivity to lower polyglycerols.

Table 2.5: Basic catalysis for glycerol etherification.

| Catalyst | T ($^oC$) | X (%) | $S_2$ (%) | $S_3$ (%) | S (%) | Ref |
|---|---|---|---|---|---|---|
| Basic homogeneous | | | | | | |
| 0.5 wt. % NaOH | 230 | 13.6 (8h) | 91.9 | 7.4 | 0.7 | (Jeromin et al., 1998) |
| 2 wt. % $Na_2CO_3$ | 240 | 76 (9h) | 46 | 34 | 13 | (Krisnandi et al., 2008b) |
| | 260 | 96 (8h) | 24 | 35 | 22 | (Clacens et al., 1998; Charles et al., 2003) |
| 2 wt. % NaOH | 240 | 63 (9h) | 60 | 32 | 7 | (Krisnandi et al., 2008b) |
| 0.7 wt. % $Cs_2CO_3$ | | 71 (8h) | 39 | 19 | 6 | (Richter et al., 2008b) |
| 0.3 wt. % CsOH | 260 | 74 (8h) | 32 | 21 | 5 | (Richter et al., 2008b) |
| Basic heterogeneous | | | | | | |
| BaO | 220 | 80 (20h) | 40 | | | (Ruppert et al., 2008) |
| 2 wt. % NaX | 260 | 100 (24h) | 25 | 26 | 29 | (Krisnandi et al., 2008b) |
| 2 wt. % NaY | 260 | 79 (24h) | 47.5 | 18.5 | 8 | (Krisnandi et al., 2008b) |
| 2 wt. % NaBeta | 260 | 52.5 (24h) | 44.5 | 7.2 | 0 | (Krisnandi et al., 2008b) |
| 2 wt. % Cs/MCM-41 | 260 | 85 (16h) | 63 | 30 | n.a | (Clacens et al., 2002) |

(X=glycerol conversion, $S_2$=selectivity to diglycerol, $S_3$=selectivity to triglycerol, S=selectivity to higher other oligomers)

### 2.3.3 Effect of operating variables

#### 2.3.3 (a) Effect of reaction temperature

It has been well established that chemical reaction rate is strongly influenced by the reaction temperature. This justifies a thorough review in this work to understand and elucidate the effects towards glycerol conversion and product selectivity. The distinction effect of temperature towards reaction rate, conversion and selectivity has been discussed in some reports. The investigation on influence of reaction temperature in the range of 180–260 $^oC$ on solventless glycerol etherification with the presence of homogeneous alkali catalysts has been reported (Ayoub et al., 2012). The authors observed that the highest conversion on 100 % was achieved at a temperature of 240 $^oC$ after 6 h in the presence of 2 wt. % LiOH. However, the selectivity to diglycerol was very low (<20 %) and the value decreased with increases in temperature and reaction time. However, 220 $^oC$ was not sufficiently high for the etherification reaction as the glycerol conversion was only 23 % at 8 h.

The effect of the reaction temperature on glycerol etherification in the presence of the 2 wt. % of $Ca_{1.6}Al_{0.4}La_{0.6}O_3$ catalyst has been also demonstrated (Gholami et al., 2013). The reaction temperature ranged from 150-260 $^oC$. The authors found that maximum glycerol conversion of 91 % was achieved after 8 h at 250 $^oC$. The selectivities to diglycerol and triglycerol under these conditions were 53.2 % and 37.8 %, respectively. The selectivity of diglycerol was found to be decreased as the temperature and reaction time were increased. On the other hand, the glycerol conversion was very low at reaction temperatures below 200 $^oC$. It was also observed that high temperature could promote to discoloration and polygycerol odor generation. It was clearly shown that temperature strongly affected the reaction activity and yield of the desired product. Therefore, reaction temperatures in the range of 220-280 $^{o}$C have been studied in the present study.

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### 2.2.3 (b) Effect of catalyst loading

Catalyst loading will also affect the reaction rate. In homogeneous catalysis system, Ayoub et al. (2012) studied the effect of catalyst loading in solventless etherification of glycerol at 260 $^{o}$C in the presence of LiOH catalyst varied from 10.4 to 83.5 mmole while the other reaction variables were kept constant. The authors observed that the glycerol totally converted after 6 h when the amount of LiOH was increased from 2 to 4 wt. %. The conversion of glycerol and selectivity to diglycerol were found to gradually increase as the LiOH amount was increased from 0.5 to 2 wt. %. The reaction system attained its maximum selectivity of about 30 % with 2 wt. % loading of catalyst after 4 h. However, further increase in catalyst loading exceeding 2 wt. % will decrease the glycerol conversion and diglycerol selectivity. As 2 wt. % of LiOH catalyst showed the best diglycerol yield during the reactions, this loading was decided as the best catalyst loading for glycerol etherification reaction.

In the case of heterogeneous catalyst, effect of catalyst loading on the etherification glycerol at 250 $^{o}$C was also investigated by Gholami et al. (2012). The $Ca_{1.6}Al_{0.4}La_{0.6}O_3$ catalyst concentration was varied between 0.5 and 5 wt. % while the other reaction variables were kept constant. The authors observed that the conversion of glycerol achieved its maximum level of 91 % with corresponding diglycerol selectivity of approximately 53.2 % after 8 h with the present of 2 wt. % catalyst. The similar trends were observed whereby both glycerol conversion and diglycerol selectivity with increasing catalyst amount from 2 to 4 wt. %. Hence, it might be concluded that the optimum catalyst loading to give high conversion of glycerol and selectivity to diglycerol was 2 wt. %. However, in the present study, the catalyst loading for this reaction has been further investigated.

### 2.2.3 (c) Effect of reaction time

Reaction time is the strong factor that will affect the glycerol conversion and selectivity to the desired product of diglycerol. Clacens et al. (2002) investigated Cs impregnated MCM-41 heterogeneous catalyst (25 x $10^{-4}$ mol/g Cs, Si/Al=20) in glycerol etherification and it was found that the highest glycerol conversion of 80 % was achieved at 24 h of reaction. The conversion seemed to be increased gradually as time reaction was increased. However, the selectivity to diglycerol decreased to 75 % at 24 h of reaction time. Ruppert et al. (2008) also proved time the dependence of glycerol etherification at low temperature of 220 $^{o}$C over alkaline earth metal oxides (BaO, SrO, CaO and MgO) as potential heterogeneous catalysts. The authors found that MgO showed almost no conversion in the etherification of glycerol and a conversion level well below 10 % was achieved after 20 h. In the case of BaO and SrO, the conversion was initially low but gradually increased to 80 % after 20 h. For CaO, glycerol conversion was slightly lower in comparison with BaO and SrO but the value could reach 60 % after 20 h of reaction time. MgAl mixed oxides for glycerol etherification at a low temperature of 220 $^{o}$C has been developed in the recent years (García-Sancho et al., 2011). As expected, long time reaction was needed to achieve high glycerol conversion. Low conversion of glycerol (2.2 %) was obtained within the first 3 h and after an induction period, the glycerol conversion rapidly increased up to 47 % after 24 h. However, the presence of triglycerol was found to be 10 % at 24 h.

In the case of homogeneous catalytic system, reaction time to achieve high conversion could be decreased to as low as below 8 h. Ayoub et al. (2012) reported that the maximum glycerol conversion achieved was 100 % after 6 h in the presence of 2 wt. % LiOH at 240 $^{o}$C in a batch mode reaction. However, the selectivity to diglycerol was still low. The authors observed that after 2 h of reaction, diglycerol selectivity was only 30 % and the value decreased as the reaction was further prolonged to 8 h. Hence, it could be concluded that reaction time has real influence to the reaction activity and yield of diglycerol. The contribution of this operating condition in the etherification process has been studied intensively.

## 2.4 Catalyst

### 2.4.1 Catalyst support

Catalyst support is the solid material usually with a high surface area that can promote a reaction to occur by spreading out active species on its surface. Good support material usually has large surface area with high porosity to ease molecular diffusion, high thermal stability under reaction conditions, high resistance to metal sintering and inertness to undesired reactions (Fogler, 1999). Hence, typical supports in accordance with these characteristics include various kinds of carbon, alumina and silica. The porosity of catalyst support will define the surface area of that support. High volume of porosity usually will provide large surface area of the support. The use of porous materials as catalyst supports have been extensively studied in the past. Porous materials can be divided into three classes according to IUPAC notation. The materials that have pores size less than 2 nm will be classified as microporous materials, 2 to 50 nm as mesoporous materials and more than 50 nm as macroporous materials (Sing et al., 1985). All these porous materials may also be useful as adsorbents (Branton et al., 1993) and supports (Corma et al., 1995).

Many kinds of porous materials for catalytic reaction purposes have been extensively described in literature (Taguchi and Schüth, 2005). For etherification reaction catalysis, microporous materials such zeolites (Hees et al., 1993) and mesoporous materials such clays (Kraft, 2003), silicas and aluminas (Clacens et al., 2002) are widely used and have been demonstrated by many researchers lately. Zeolites have a narrow and uniform micropore size distribution. It is postulated that the reaction takes place exclusively inside the pores so that formation of bulky products such as cyclic dimmers or higher oligomers will be suppressed due to its shape selectivity effect. However, this assumption is not fulfilled as sites on the external zeolite surface and sites located at the pore entrances would act in a geometrically unrestricted way. Diglycerol and triglycerol will be averaged outside the pores by further reaction and did not form in the interior zeolite micropores (Krisnandi et al., 2008b).

Zoelites can be differentiated based on its pore size. Zeolite A has pore entrance of 0.38 nm. Medium pore size zeolite ZSM-5 has pore openings of 0.51-0.55 nm while zeolite β and zeolite X or Y have large pore size about 0.66 and 0.7 nm, respectively. Considering the sizes of glycerol and diglycerol (refer the Table 2.6), good support materials should have pore entrance larger than 0.515 nm to allow access of the neutral glycerol to the interior of the zeolite structure. In addition, pore size should be even larger than 0.753 nm to enable diglycerol formation. Therefore, zeolite β and zeolite X and Y would be more suitable for glycerol etherification to occur. Meanwhile, FAU structure zeolites X and Y would allow the formation of bulkier cyclic isomers or linear higher oligomers with the presence of large pore size