HYDROTALCITE CATALYSTS PREPARED USING COMBUSTION METHOD FOR SELECTIVE ETHERIFICATION OF GLYCEROL TO DIGLYCEROL

by

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LIST OF SYMBOLS

Symbol	Description	Unit
μ	Micro	
A	Arrhenius factor (pre-exponential factor)	
Å	Angstrom	
C_A	Concentration of glycerol at time, t	mol/dm^3
C_{Ao}	Initial concentration of glycerol	mol/dm^3
C_G	Concentration of glycerol	mol/dm^3
E_a	Activation energy	kJ/mol
k	Reaction rate constant	$dm^3/mol.h$
n	Number of mol	mol
N_A	Initial amount of reactant	mol
P/P_o	Relative pressure	
R	Gas constant	J/mol.K
R^2	Correlation coefficient	
$-r_G$	Rate of reaction of glycerol	$mol/dm^3.h$
T	Temperature	$^oC/K$
t	Time	h
V	Volume	$dm^3/mol.h$
X	Conversion	
α	Alpha	
β	Beta	
θ	Theta	
λ	Gama	

LIST OF ABBREVIATIONS

a.u.	Arbitrary unit
Al	Aluminum
$Al(OH)_3$	Aluminum hydroxide
Al^{3+}	Aluminum ion
A^{n-}	Anion
BET	Brunauer Emmett Teller
C	Carbon
C-C	Carbon to carbon
CMTS	Chloromethylsilane
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
d	Basal spacing
EDX	Energy dispersive X-ray
FID	Flame ionization detector
FRU	Fructose
GC	Gas chromatography
GLU	Glucose
H	Hydrogen
H_2O	Water
HCl	Hydrochloric acid
HMDS	Hexamethyldisilazane
HT	Hydrotalcite
KNO_3	Potassium nitrate

LDH	Layered double hydroxide
M^{2+}	Divalent metal ion
M^{3+}	Trivalent metal ion
Mg	Magnesium
$Mg(OH)_2$	Magnesium hydroxide
Mg^{2+}	Magnesium ion
MgO	Magnesium oxide (periclase)
N_2	Nitrogen
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulfate
NaOH	Sodium hydroxide
NO_3^-	Nitrate ion
OH^-	Hydroxyl ion
rpm	Rotation per minute
S	Sulfur
SAC	Saccharose
SEM	Scanning electron microscope
SO_4^{2-}	Sulfate ion
XRD	X-ray diffraction

MANGKIN HIDROTALSIT DISEDIAKAN MENERUSI KAEDAH PEMBAKARAN UNTUK PENGETERAN SELEKTIF GLISEROL KEPADA DIGLISEROL

ABSTRAK

Kebimbangan terhadap masalah pengurangan petroleum diesel telah menggalakkan pelbagai usaha untuk menggantikannya secara alternatif dengan bahan api biodiesel. Malangnya, penghasilan biodisel secara besar-besaran telah menyebabkan penghasilan gliserol secara berlebihan. Penyelidikan terhadap penambahbaikan gliserol kepada produk tambah nilai harus dilaksanakan supaya pasaran gliserol dapat diperkukuhkan kembali. Dalam penyelidikan ini, gliserol telah ditambahbaikkan kepada digliserol tindakbalas pengeteran bermangkin bes. Tindakbalas ini telah dijalankan dengan kehadiran hidrotalsit sebagai pemangkin. Hidrotalsit telah disediakan melalui kaedah pembakaran. Penghasilan hidrotalsit telah dikaji dengan memfokus terhadap pembolehubah eksperimen yang berbeza-beza iaitu jenis bahan api yang digunakan, suhu pengkalsinan, sumber multi-anion dan amaun anion CO_3^{2-}. Bagi proses pengeteran, kajian terhadap akitiviti pemangkin hidrotalsit telah dijalankan pada tindakbalas bersuhu antara 200^{o}C hingga 240^{o}C dan masa tindakbalas sehingga 16 jam. Kajian terhadap tindakbalas kinetik telah dijalankan dengan memvariasikan suhu tindakbalas daripada 200^{o}C hingga 260^{o}C. Pencirian tekstur dan sifat kimia hidrotalsit telah ditentukan melalui belauan sinar-X untuk kehabluran, analisa permukaan untuk pencirian permukaan, penunjuk Hammett untuk kekuatan bes dan sifat kebesan, SEM untuk morfologi permukaan dan EDX untuk komposisi kimia. Glukosa, fruktosa dan sakarosa telah digunakan sebagai bahan api dan suhu pengkalsinan antara 450^{o}C hingga 850^{o}C. Glukosa telah dikenal pasti sebagai bahan api yang paling baik dimana pemangkin ini adalah yang paling aktif dengan penukaran gliserol sebanyak 12.34 % dan kememilihan digliserol sebanyak 97.73 % dalam masa 8 jam. Entalpi sesuai yang dibekalkan oleh glukosa semasa pengkalsinan telah membentukan struktur hidrtalsit yang baik untuk tindakbalas ini. Tambahan lagi, hidrotalsit yang dikalsin pada suhu 650^{o}C menunjukkan aktiviti yang tinggi dengan penukaran gliserol sebanyak 77.74 % dalam masa 16 jam. Ion-ion logam telah disebarkan dengan seragam ke dalam lapisan rangkaian hidrotalsit hidroksida berganda pada 650^{o}C. Kesan-kesan multi-anion telah dikaji dengan menggabungkan sumber anion tambahan (NO_3^- dan SO_4^{2-}) dengan sumber anion utama (CO_3^{2-}). Sampel tri-anion ($CO_3NO_3SO_4$) telah menunjukkan aktiviti pemangkin yang paling stabil dengan penukaran gliserol sebanyak 40.73 % dan kememilihan digliserol sebanyak 92.73 % selama 16 jam. Peningkatan populasi anion diantara lapisan hidrotalsit boleh meningkatkan sifat kebesan. Sampel dengan 50% amaun anion CO_3^{2-} merupakan sampel yang paling sesuai digunakan untuk pengeteran berbanding sampel dengan 30 % dan 70 % amaun anion CO_3^{2-}. Oleh itu, amaun sumber anion utama (CO_3^{2-}) yang sesuai boleh mempengaruhi kestabilan hidrotalsit semasa tindakbalas. Kesimpulannya, pengeteran gliserol telah berjaya dilaksanakan dengan menggunakan hidrotalsit sebagai pemangkin. Kajian ini telah mencadangkan bahawa pengubahsuaian hidrotalsit boleh menambahbaikkan aktiviti pemangkin hidrotalsit semasa tindakbalas. Justeru, penyelidikan ini berpotensi dalam mengatasi masalah lebihan gliserol dan memperluaskan kegunaan gliserol dalam pelbagai industri.

HYDROTALCITE CATALYSTS PREPARED USING COMBUSTION METHOD FOR SELECTIVE ETHERIFICATION OF GLYCEROL TO DIGLYCEROL

ABSTRACT

The concern on the depleting problem of petroleum diesel has encouraged many attempts to alternatively replace it with biodiesel fuel. Unfortunately, the enormous increase in the biodiesel production has mainly caused the surplus of glycerol production. Researches on utilizing and upgrading glycerol to value-added products should be promoted to stabilize the global market of glycerol. In the present study, glycerol was upgraded to diglycerol through a basic-catalyzed etherification reaction. The reaction was carried out in the presence of hydrotalcite as catalyst. Hydrotalcite was prepared using a combustion method. The hydrotalcite synthesis was studied by focusing on different experimental variables i.e. types of fuel used, calcinations temperatures, multi-anion source and amount of CO_3^{2-} anion. For the etherification process, the catalytic activity of hydrotalcite was performed at the reaction temperatures between 200^{o}C to 240^{o}C in 16 h. The reaction kinetics was studied by varying the reaction temperature from 200^{o}C to 260^{o}C. The textural and chemical characteristics of the hydrotalcite were elucidated by means of X-ray diffraction for crystallinity, surface analysis for surface characteristics, Hammett indicator for basicity and basic strength, SEM for surface morphology and EDX for chemical composition. Glucose, fructose and saccharose were used as fuel and the calcination temperature were 450^{o}C to 850^{o}C. Glucose was identified as the most favourable fuel where the resulting catalyst was the most active with a conversion of 12.34 % and diglycerol selectivity of 97.73 % in 8 h. An appropriate enthalpy provided by glucose during the calcination led to the formation of hydrotalcite that was favourable for etherification reaction. Furthermore, hydrotalcite calcined at 650^{o}C demonstrated the highest activities with a conversion of 77.74 % in 16 h. Metal ions were distributed uniformly into the layered double hydroxide network at 650^{o}C. The multi-anions effects were studied by combining the added anion sources (NO_3^- and SO_4^{2-}) with the main anion source (CO_3^{2-}). The tri-anion ($CO_3NO_3SO_4$) sample showed the most stable catalytic activity with the conversion of 40.73 % and diglycerol selectivity of 92.73 % in 16 h. The increase in anion population in the interlayer of hydrotalcite might increase the basicity thus increasing the catalytic behavior. The sample with 50% amount of CO_3^{2-} anion was the most appropriate one to be used for etherification compared to 30 % and 70 % sample. Thus, the appropriate amount of main anion source (CO_3^{2-}) could influence the stability of hydrotalcite during reaction. In a nut shell, the etherification of glycerol to polyglycerol was successfully accomplished using hydrotalcite as the catalyst. This study suggested that the modification of hydrotalcite might improve the catalytic activity of hydrotalcite during reaction. Thus, for future use, this study was very high potential in overcoming the glycerol surplus problem and broadens the utilization of glycerol in many industries.

CHAPTER 1

INTRODUCTION

1.1 The boom of biodiesel

The world fuel industry has witnessed an enormous burgeoning of renewable fuel courage by the awareness on the depletion of fossil fuels. The multi-usages and wide applicability to the transportation, industrial sector and human activities have led the petroleum-based fuels to be the most important fuels used worldwide. This might cause to the global depletion of fossil fuel and it is now a necessity to develop a renewable fuel alternative that fits its criteria. The environmentally friendly fuel technology of biodiesel in replacing the petroleum diesel has enticed the world with its efficacy. The recent production and commercialization of biodiesel has encouraged the world to switch from petroleum-based fuel to this brand new green technology energy source. In tandem with overcoming the imminent scarcity of petroleum diesel, the development of biodiesel also encourages many downstream industries to diversify their starting materials.

Recently, the world has made an endeavour to reduce the usage of fossil fuel and includes renewable fuels as the future main fuels. In 2005, the European Union Directive stated that the renewable fuel should constitute 2% of the traffic fuel and by the end of 2010, the figure was predicted to increase to 5.75%. In tandem with this effort, necessary renewable fuel policies have been developed that cover the mandates, tax incentives, and subsidies to ensure the viable expansion of biodiesel industry in the future (ABG Inc, 2010). This effort has widely opened the opportunities of biodiesel to be used globally thus replacing the role of petroleum based fuels as the world main energy source.

Basically, biodiesel is produced from the transesterification process of triglyceride in which 90 wt % of methyl ester (biodiesel) and 10 wt % of glycerol are produced. The process is enhanced by alkali-catalysts to produce better biodiesel yield. This has been reviewed by Leung et al. (2010) in which they mainly focused on the effect of some variables such as catalyst and reaction conditions. The optimized reaction condition might assist in overcoming the undesirable reactions that lead to the production of undesired products (soap and etc.) while at the same time directly increases the biodiesel yield.

1.2 Glycerol from biodiesel production

Conventionally, the market of glycerol has foreseeably developed on the basis of 3 major strides. Each of them may have a substantial effect on the long term glycerol production market. The strides begin with the development of glycerol production industry from the approval for the use of Olestra by the end of 1994 by the US Food and Drug Administration. Then, it followed by the investment of the large scale corn fermentation (bioethanol) in the United States (Walker and Korbitz, 1994). Currently, the development continues with the main focus given to glycerol that is produced as a by-product from the manufacture of biodiesel. By-production of glycerol from the transesterification process is achieved when the triglyceride (animal or plant fats) consisting of 3 long chains fatty acids is linked to 3 hydroxyl groups with an ester bond upon reaction with an alcohol causing the breakage of the ester bond. This reaction directly cleavages the ester bond thus producing crude solution of glycerol in water (Leung et al., 2010, Miller Klein Associates, 2006). Meanwhile, the fatty acid chains that are released will combine with carbonyl group from the alcohol to form biodiesel.

From 1992 to 2003, the glycerol production was dominated by fatty acids and soap industries where the amount of glycerol produced was quite stable and the price at that time was rather high with high market demand (Figure 1.1). After 2005, biodiesel industry emerged and dominated the production of glycerol amounting to nearly 60% compared to other industries (2006 to 2010). The production of glycerol from biodiesel sharply increased from about 400,000 MT in 2005 to the outstanding amount of 1,600,000 MT in 2010. This domination gave significant impact on the surplus of glycerol where the sudden increase made the glycerol market price unstable.

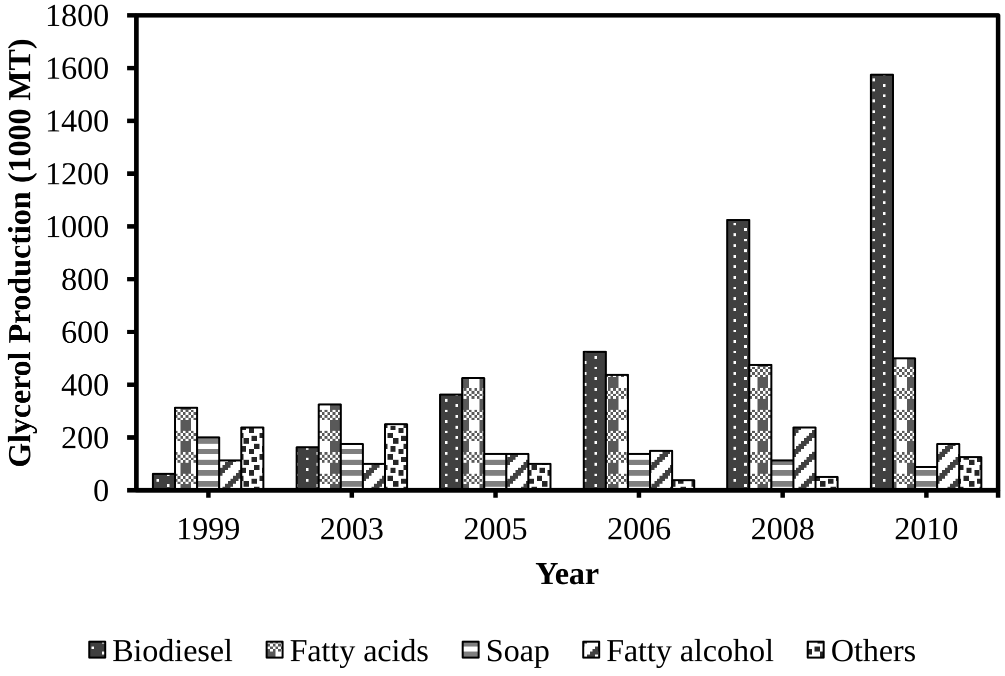

Figure 1.1: Glycerol production by source (ABG Inc, 2010)

1.3 Glycerol glut problem

Despite of the worldwide increasing pace of biodiesel production, there is an inevitable problem that arises which is the glycerol glut. The world market of glycerol is currently facing an oversupply problem which is purportedly caused by the intensification of biodiesel industry. The production of biodiesel through the transesterification process creates a massive amount of glycerol by-product. As shown in Figure 1.2, it was reported in 2010 that 64 % of glycerol market originated from biodiesel industry. Meanwhile, another 34 % was contributed by fatty acids, fatty alcohol, soap and other industries. The boom of biodiesel industry causes the domination of the global glycerol production. Besides, the development of biodiesel also has enticed many biomass sources to be used as raw material. This scenario has influenced the oleochemical industries to face the same implication as well. When the raw material used in the oleochemical industry is quite similar to that in biodiesel industry, there is a competition on the supply of raw materials and causes its price to increase. In line with this reasoning, the advent of biodiesel will directly cause an overabundance of glycerol and indirectly causes a decline of oleochemical industry.

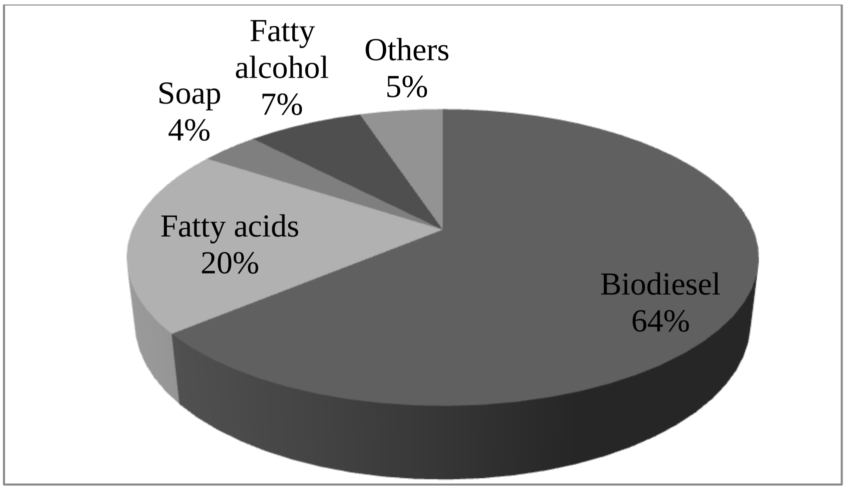

Figure 1.2: Market of glycerol in 2010 (ABG Inc, 2010)

From section 1.1, the renewable fuel policy can be correlated with the sharp increase in glycerol production from 2005 to 2010. The fraction of biofuel recommended by European Union Directive has clearly influenced the global production of glycerol. It is noted in Table 1.1 that the enforcement of the policy to constitute 5.75 % of traffic fuel with renewable source in 2010 was directly involved in the increase of glycerol production. The estimation has been made by Yazdani and Gonzalez (2007) in which up to 1.25 million tons of glycerol might be produced when the enforcement is fully implemented. The enormous increase in glycerol production (7.66 million tons) has been estimated to happen when the renewable energy content is further increased to 20 % in the future (2020). The implementation of the energy policy is such a good endeavour that should be done with respect to the promotion of renewable energy in the future. However, the holistically consideration on the glycerol surplus problem should also be given serious attention.

Table 1.1: Correlation of fraction and global production of glycerol

Year	Fraction of biofuel (by European Union Directive)	Global production of glycerol (tons)
2005	2 %	0.8 million
2010	5.75 %	1.25 million
2020	20 %	7.66 million (prediction)

1.4 Glycerol market price fluctuation

With the current rate of production, the global amount of glycerol is expected to increase every year and the surplus of glycerol might cause the plummeting of the global glycerol price and market demand. High purity natural glycerol has a fairly stable market price and the global market demand was also very promising of about $1200 to $1800 per ton from the 1970s until the last few years before the emergence of biodiesel industries (Miller Klein Associates, 2006). The production of biodiesel has affected the global glycerol market with the sudden increase to 800 000 tons of glycerol produced in 2005 (400 000 tons from biodiesel) compared to only 60 000 tons in 2001 (Yazdani and Gonzalez, 2007).

Figure 1.3 shows the fluctuation of glycerol price over the recent years. As suggested by the figure, the production and price of glycerol trend are interrelated. From 1996 to 2001, the glycerol price was reported to be stable with a stable production of glycerol. However, there were rather small ups and downs in the market price trend of glycerol. The price dropped from 1996 to 1998 in about 325 USD/Mg but it was poised back in 2000 (870 USD/Mg). Even when the fluctuation was significant, the price at that time was still acceptable. Unfortunately, from 2004 onwards, the market was facing a worst downturn when the price sharply decreases until reached < 100 USD/Mg. It is actually predicted to further decrease if the feasible technology for utilizing glycerol to be converted to value-added products cannot be developed in time.

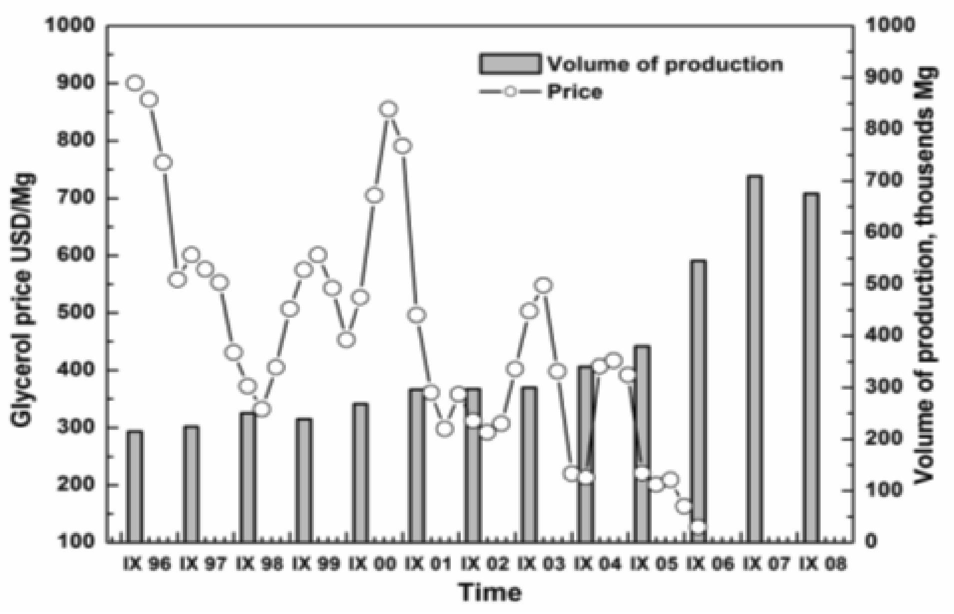

Figure 1.3: Price fluctuation of glycerol (Stelmachowski, 2011)

Therefore, instead of enforcing necessary policy for the promotion of renewable fuel, the consequent effects with respect to the vulnerability of glycerol should also be schemed out. Thus, efforts and technologies that lead to the development of the glycerol utilizing industry can be encouraged to poise back the glycerol market.

1.5 Problem faced by global supplier

The value of crude glycerol has miserably dropped until the current prices for pure glycerol and crude glycerol are quoted at \$0.50 to \$1.50/lb and \$0.04 to \$0.33/lb, respectively (Ayoub and Abdullah, 2012). Most biodiesel producers attach zero value to the crude glycerol, and at least some producers have to pay for its transport to a purification unit. Crude glycerol can be assumed to have a negative value in the future (Miller Klein Associates, 2006).

Malaysia and Germany are the two largest importers in the world as shown in Figure 1.4. Imports of crude glycerol from Germany decreased steadily over time and decreased to nearly zero by 2007. This is because the market price for crude glycerol did not meet the cost to ship crude glycerol from Europe to the United States (ABG Inc, 2010). The market price value of crude glycerol is grossly low compared to that of pure glycerol. The value of glycerol market price is some time does not meet the shipping cost which is very high from different countries to the United States. Thus, the imports from Germany will face a loss. Similar problem can also happen to Malaysia. Palm oil industry in Malaysia has historically put the country as the major player in the free fatty acids in the international arena. As the advent of biodiesel industry, free fatty acid has become the most crucial raw material. It means that, the country will produce even more glycerol as the biodiesel production is intensified. Thus, the import value of Malaysia's crude glycerol will experience further decline until it achieves nearly zero in the future.

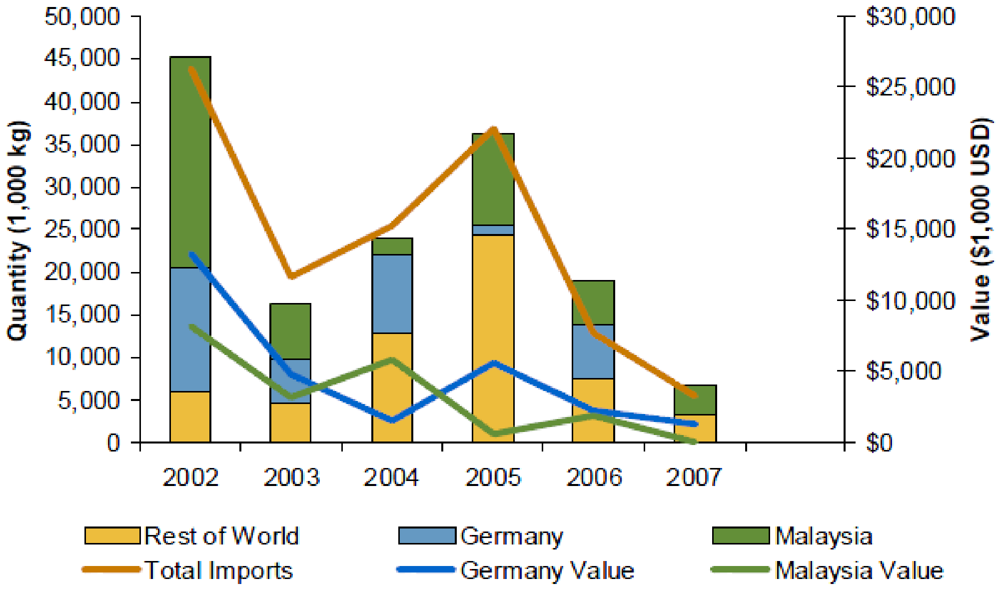

Figure 1.4: Crude glycerol imports by country (ABG Inc, 2010)

Technically, in 2011, it was expected that 2 million ton of the total 5.1 million ton of glycerol would be used which meant that only 40 % of the crude glycerol was utilized while the remaining 60 % was considered as oversupply (Frost and Sullivan, 2008b). In 2007, 490,000 tons of crude glycerol was sold in Europe and by 2013, the market is expected to reach 775,700 ton (Frost and Sullivan, 2008a). The 2008 consumption was estimated at 395000 ton with a 1.7 % growth per year (Arnold, 2008).

1.6 Glycerol purification and waste management problem

In 1990's, glycerol was traditionally produced as a by-product of fats hydrolysis in soaps production and this process was significantly one of the contributors to the global glycerol production volume of about 600,000 tons annually. However, soaps industry as a main producers for glycerol was getting lesser importance due to the replacement of soaps with detergent (Agarwal, 1990). Unfortunately, in 2000 onwards, the scenario has been becoming worst with the emergence of biodiesel industry that contributes about 65% to 85% (w/w) of crude glycerol (Gonzalez-Pajuelo et al., 2005, Mu et al., 2006). Crude glycerol from biodiesel contains a variety of other elements such as metals e.g. calcium, sodium, potassium, magnesium, phosphorous, or sulphur and 25 % carbon (Thompson and He, 2006). Hence, purification process is highly required. The refining processes depend on the availability of glycerol purification facility such as filtration, chemical addition and fractional vacuum distillation to yield a commercial grade and also economically depends on the production scale (Thompson and He, 2006).

There is a problem when the 80 % purity of glycerol is still not considered as an acceptable quality as it is usually contaminated with methanol. It has been a major focus for the glycerol refiner that they have to produce a pharmaceutical-grade glycerol with nearly 100% purity. The currently developed technology to remove impurities present in the biodiesel by-product glycerol is based on high temperature low-pressure distillation process. However, as glycerol is contacted with methanol, it is unsuitable for that type of process (Pagliaro et al., 2009). Consequently, majority of companies that produced glycerol have shut down their production due to the plunge in glycerol prices (Dharmadi et al., 2006, Deckwer, 1995).

The next problem that emerges from the surplus of low value crude glycerol is its disposal problem. Incineration is the current method of disposal for the surplus glycerol in which it is used to produce energy (Slinn et al., 2008, Atia et al., 2008). However, burning of glycerol as a fuel will cause the generation of toxic material as at high temperature as glycerol will polymerize and partially oxidize into acrolein which is a highly toxic material (Pérez et al., 2009). Thus, glycerol from biodiesel industry should be transformed into suitable value-added chemicals instead of being incinerated that may produce a highly polluting material. Besides, it is desirable to produce something new from the transformation of low value glycerol to that can provide benefits to the economy and society.

1.7 Upgrading glycerol using heterogeneous catalyst

Problems regarding the surplus of glycerol that are directly responsible for the market downturn of global glycerol market can be overcome by inventions towards utilization of glycerol itself. In order to upgrade the low graded glycerol, its molecular structure can be polymerized through etherification process. The process will upgrade glycerol to the other value-added products and might broaden the potential for utilization of glycerol to many industries. Therefore, the surplus problem can be effectively managed.

Catalytic etherification of glycerol can enhance its conversion to form useful products. It can be catalyzed by either homogenous or heterogeneous catalyst. Conventionally, homogenous catalyst is usually used. Whereas the conversion of the fuel is usually high, it gives some problems with respect to the difficulty to separate the product as both reaction product and catalyst are in the same phase. Homogenous catalyst is nowadays gradually being replaced with heterogeneous catalyst that is more beneficial in terms of catalyst separation and reusability. Furthermore, the design of the solid catalyst has made significant advancement in which both physical and chemical characteristics of the catalyst can be modified. This is a clear advantage compared to homogenous catalyst in which only chemical characteristics can be altered. As such heterogeneous catalyst is more flexible while the robustness of the catalyst can be improved by modifying the surface area, pore size, particle size and chemical composition.

Heterogeneous catalysts could be acidic or basic in nature. For etherification, it is preferred to use basic catalyst rather than acidic one as the product is more selective (avoid higher oligomer) while showing higher etherification activity (Ruppert et al., 2008). However, there is a problem when dealing with basic catalyst with respect to the leaching of active material. The active metal component in the catalyst could leach out from the structure to cause lower product purity. Many researchers are striving to come out with various catalytic systems in order to solve the leaching problem. Acid catalyzation has several disadvantages where the reaction products formed are cyclic polyglycerols. Deterioration of product quality will occur as it can lead to secondary reactions which are dehydration and oxidation of the intermediate product (Martin and Richter, 2011). Whereas, the conversion of reactant to product is relatively higher and faster, the selectivity is still low (Medeiros et al., 2009). Basic catalysis of glycerol is seems to be very effective as the product is more selective with higher degree of conversion.

1.8 Problem statement

Many previously reported works make use of various types of heterogeneous catalyst for etherification of glycerol and promising results have been reported. For basic catalyst, some mesoporous catalysts used are such as a series of metal (alkaline earth) oxides, modified zeolites, impregnated alkaline metal on mesoporous support and many others. The resulting product shows such a good quality with high reactant conversion. However, some problems arise particularly with respect to the leaching of metal into the product. The leached fraction becomes homogenous catalyst that leads to further increase in production cost as purification process is still needed.

Layered material catalysts are also effective heterogeneous catalysts that can be used for converting glycerol to value-added product. Hydrotalcite (HT) is one of the potential layered material catalysts. The use of HT catalyst has been reported by Garcia-Sancho et al. (2011) and it was synthesized using co-precipitation and urea hydrolysis methods. The resulted catalyst showed no leaching problem and the conversion was higher than 50 %. In this present work, HT has been used to enhance the etherification process. The preparation method involves the use of combustion step and the subsequent steps consist of the preparation of metal oxide and recrystallization. This method has clear advantages as no solvent is needed and shorter period is required for the synthesis. Basically, this method can potentially overcome the leaching of alkaline metal as the basicity of the catalyst is controlled by anions in the interlayer. Therefore, the desired product is expected to attain high purity. Fuels for the combustion step are studied using 3 different sugars (glucose, fructose and saccharose) and the effects on the layer structure have been investigated. Besides, the calcinations temperature has been varied. Carbonate, nitrate and sulphate anion have been used at different combinations and ratios.

1.9 Objectives

1. To synthesize suitable layered material catalyst (hydrotalcite) to be used for diglycerol production from glycerol etherification process
2. To characterize the microstructural, physical and chemical characteristics of the catalysts for correlation with the observed behaviors during the etherification process.
3. To study the catalytic reaction process during the etherification and optimize the reaction for better conversion yield and selectivity towards the desired product.
4. To conduct the kinetic studies of etherification process using selected catalyst.

1.10 Scope of the study

In this study, etherification reaction is used to convert the glycerol to diglycerol. The layered material catalyst considered is hydrotalcite (HT). HT is selected on the basis of its basic characteristics which are very favourable to enhance the process by providing basic condition during the reaction. The basicity of HT has been created by means of suitable anions that can directly influence the gallery height between the layers. This will affect the porosity of the catalyst and the population of anions between the brucite-like layers. HT will be synthesized by means of a combustion method with the aid of fuels (sugars). The synthesis time is short and no solvent is needed. The effects of calcination (450 to 850 ^{o}C), types of fuel used (glucose, fructose and saccharose) and types of anion (CO_3, NO_3, SO_4) have been investigated. HT catalysts will be subjected to several tests that have been carried out including surface characteristics, surface morphology analysis, elemental analysis, crystallinity analysis, basic strength and basicity analysis.

The etherification reaction run has been carried out at up to 16 hour at a temperature of 240^{o}C under nitrogen flow. In a typical run, 1 wt % catalyst has been used for every 50 g of glycerol. During the reaction, the anion from the HT will provide a basic condition by releasing the hydroxyl ions (OH^-) that facilitates the polymerization of glycerol. The conversion and selectivity have been analyzed by means of gas chromatograph equipped with a flame ionization detector FID and a micro-capillary HT 5 column. Modification of the catalyst has also been carried out in order to improve the conversion and selectivity of glycerol to diglycerol. HT has been synthesized using a combustion method and modification has been done step by step starting from the type of fuel used followed by calcinations temperature (450-

$850^{o}C$) and combination of multi-anions source through recrystallization (CO_3, NO_3, SO_4). The performance of the modified HT has been evaluated based on the conversion of glycerol to diglycerol with high selectivity towards diglycerol in the product.

1.11 Thesis organization

This thesis is organized into 5 chapters. Chapter One (Introduction) will introduce the general scenario on the energy crisis that are responsible for the boom of biodiesel industry that eventually have direct impact on the global glycerol market. Besides, this chapter also provides brief overview on glycerol glut issue and the major reasons to the glycerol market downturn. It also highlights the purification problems that lead to the glycerol waste. The importance of upgrading low grade glycerol to diglycerol is also highlighted. Besides, this chapter also covers the problem statement, objectives of research, scope of study and finally thesis organization.

Chapter Two (Literature Review) will review the background information about this present study background. This chapter provides the literature review in details on the properties, characteristics and production of glycerol (reactant) and diglycerol (product). In addition, this chapter also reviews the relevant reported studies on the etherification process including the acid and basic catalyzed of the reaction using homogeneous and heterogeneous catalysts. Besides it also reviews the operating conditions of the etherification reaction including reaction temperature, reaction time and amount of catalyst used. This chapter also focuses on hydrotalcite (HT) and the review on the structure, method of synthesizing HT catalyst, combustion method and the catalytic activity of HT is thoroughly made. Finally, literature review on the kinetics study of glycerol etherification reaction and the equations involved is also presented.

Chapter Three (Experimental Methods and Analysis) will describe the materials and chemicals used during the present study together with the specifications. This chapter also details out the experimental methodologies and the setup used during the synthesis of HT catalyst and etherification process. It also briefly describes the characterization methods of the catalysts and analysis of reaction products.

Chapter Four (Results and Discussions) will present the results made in the present and their discussion. First part of this chapter contains the results and discussion on the synthesis of HT catalyst differed by several parameters i.e. fuel types, calcinations temperature, multi-anion source and the amount of CO_3^{2-}anion. It is followed by the characterization of the HT catalyst synthesized. Subsequent topics on this chapter contain the performance of HT catalysts based on the catalytic activity of HT during the glycerol etherification to diglycerol. Finally, the kinetics study of glycerol etherification using single and tri-anion source HT catalyst is also presented.

Chapter Five (Conclusions and Recommendations) will conclude the overall research findings made in this study. It also gives some recommendations for future research work based on the understanding and knowledge generated from the glycerol etherification study using HT as catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Glycerol

In 1783, glycerol ($C_3H_8O_3$) or 1,2,3-propane triol, a very sweet flavour and multi usage chemical was discovered by Carl Wilhelm Sheele (Behr et al., 2008). Glycerol was a very important chemical introduced into the industry at that time because of its uniquely natural sweet flavour, odourless, colourless, viscous, low toxicity and water soluble characteristics. The world has witnessed a huge transition in glycerol production, from only by treatment of oils with alkali to production through saponification. The current major production is through alcoholysis of fatty acids (biodiesel) to produce low graded glycerol as the by-product. Purified glycerol (95 %) that is commercially used is usually referred as ‘glycerine’ while the anhydrous compound of 1,2.3-propanetriol was specifically called ‘glycerol’ (Ayoub and Abdullah, 2012).

Table 2.1 shows general physical and chemical properties of glycerol. Glycerol is a compound with three-carbon chains that is produced from the modification of triglycerides through a certain process to eliminate the ester bond. Every carbon chain is attached with a hydrophilic hydroxyl group in which it is responsible in modifying and upgrading of glycerol to a multipurpose substance. The viscous and crystal clear liquid that is soluble in water and sometimes reacts as an alcohol with the presence of trihydric alcohols (hydroxyl groups) making it applicable for pharmaceutical purposes. However, in order to meet the pharmaceutical grade, all these properties (viscous and crystal clear liquid) should be strictly followed. The problem arises when the production of glycerol as a side product also usually contains many contaminants and cannot be directly used as a pharmaceutical starting material. As the purity of glycerol is usually low and it has to undergo several highly costly purification processes that will eventually affect the current price of glycerol.

Table 2.1 : General physical and chemical properties of glycerol (Perry et al., 1997)

Properties	**Values**
Chemical formula	$CH_2OH–CHOH–CH_2OH$
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
Heat of fusion at 18.07°C	47.49 cal/g
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

Glycerol can be categorized into three main types which are crude glycerol, purified glycerol and refined or commercialized glycerol. Crude and purified glycerol show significant differences in several parameters where the purification processes on the crude glycerol are really needed to obtain a refined and commercialized glycerol to be used in many applications. The general differences are shown in Table 2.2. The effort of upgrading crude glycerol is to increase the glycerol content to decrease the contaminant content, to achieve pH neutralization and to remove the cloudy colour. The glycerol produced from any processes such as transesterification as by-product is regularly a glycerol mixture with about 60 % to 80 % of glycerol purity. Increasing the glycerol content to 99.8 % usually requires costly processing steps in order to meet the expected quality of the refined or commercial glycerol. Crude glycerol contains high amount of impurities and it differs from purified or refined glycerol in which the moisture, ash and soap contents should be reduced to almost at most 0.1 %.

Table 2.2: Quality parameters of crude, purified and refined/commercial glycerol (Hazimah et al., 2003)

Parameter	Crude glycerol	Purified glycerol	Refined/commercial glycerol
Glycerol content (%)	60–80	99.1–99.8	99.2–99.98
Moisture content (%)	1.5–6.5	0.11–0.8.	0.14–0.29
Ash (%)	1.5–2.5	0.054	<0.002
Soap (%)	3.0–5.0	0.56	N/A
Acidity (pH)	0.7–1.3	0.10–0.16	0.04–0.07
Chloride (ppm)	ND	1	0.6–9.5
Color (APHA)	Dark	34–45	1.8–10.3

The abundance of glycerol with the currently uncontrolled production has enticed many attempts especially among researchers to come out with new inventions that can utilize to cope with the glycerol surplus problem. The upgrading from low graded to high graded glycerol has been widely attempted with various methods of modification on the physico-chemical characteristics of glycerol. There are many research works towards regarding the upgrading of glycerol to other products through etherification, oligomerization, esterification of glycerol and many other processes to convert it to its derivatives. Figure 2.1 shows the possibility of glycerol to be upgraded to high value added chemicals through several processes. In this case, the glycerol is either directly converted to functional chemicals or glycerol derivatives like glycerol carbonate are being used as starting materials in many industries.

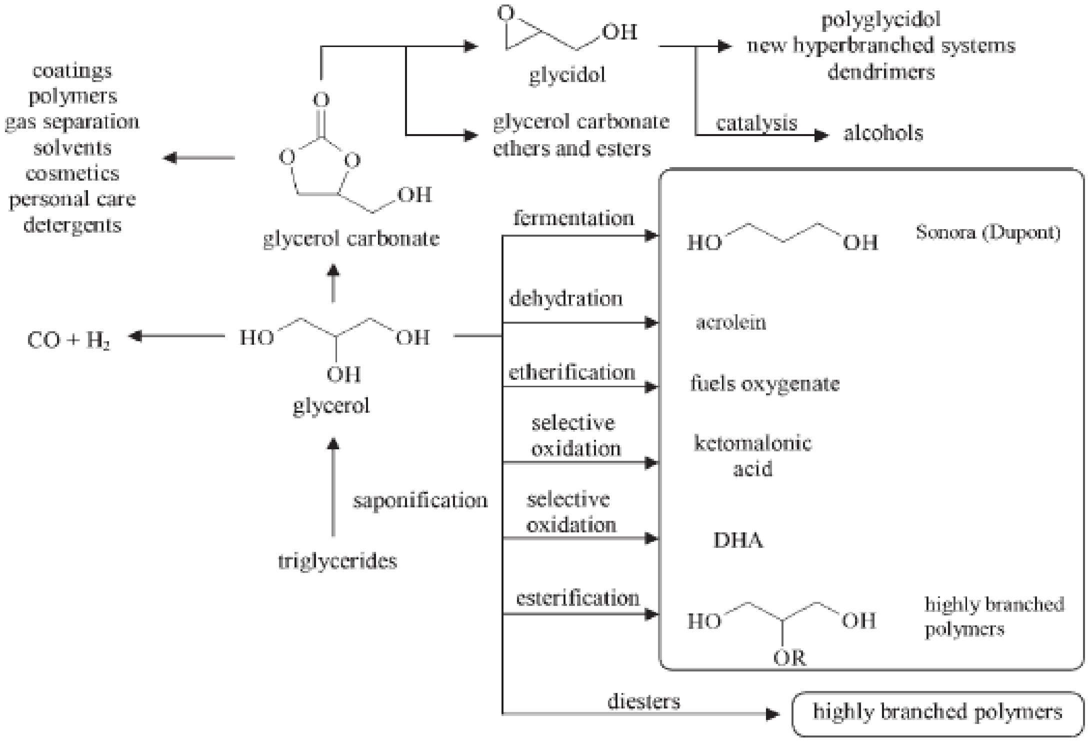

Figure 2.1: The platform of glycerol to its functional chemicals (Pagliaro et al., 2007)

Behr et al. (2008) has reviewed the glycerol derivatives produced by several processing including the formation of glycerol esters, glycerol ethers, glycerol acetals and ketals, glycerol to functional chemicals and also the formation syngas from glycerol. Esters of glycerol can be produced by reacting glycerol with carboxylic acid in a transesterification process under suitable reaction conditions. Carbonylation of glycerol in which the glycerol carbonates are produced by reacting carbon dioxide and glycerol is also possible. The directly reacting glycerol with certain of catalyst can enhance the production of glycerol oligomers (di-, tri-, tetra-glycerol and etc.)

under specific reaction conditions. Meanwhile, when glycerol is reacted with aliphatic alcohol, alkyl halide and addition of alkene, the alkyl ethers of glycerol are produced. Telomerisation of glycerol will produce unsaturated ethers of alcohol that can be utilized as surfactants due to their amphiphilic nature.

Besides, they also reviewed the formation of functional chemicals from glycerol (Behr et al., 2008). The acetalisation of glycerol will produced various aldehydes or ketones that are very useful as ignition accelerators and antiknocks additives, scent or flavour, basis of surfactant and disinfectant or solvent in cosmetics or medical purposes. The hydrogenolysis of glycerol will produce propanediols which are applicable as diols in the production of polyesters, polycarbonates and polyurethanes and as additives, solvents and other chemical agents. Epichlorohydrin from glycerol can be produced from the reverse of classic synthesis and it consumes less water. The oxidation of glycerol product is categorized based on the degree of oxidation of hydroxyl group. The oxidation of secondary, tertiary and further oxidation of hydroxyl will produce dihydroxyacetone, glyceraldehydes and a series of carboxylic acids, respectively. Meanwhile, the dehydration of glycerol will produce acrolein which is applicable as an intermediate in the production of acrylic acid, glutaraldehyde and methionine. Lastly, glycerol can be used to synthesize synthetic gases including carbon monoxide and hydrogen through specific reforming of steam and gasification process. The summary of glycerol derivatives and applicable processes are tabulated in Table 2.3.

Table 2.3 : The Summary of glycerol derivatives.

Glycerol derivatives	Process	Product	Reference
Glycerol esters	Esterification, Carbonylation	Glycerol esters with carboxylic acid e.g. : monoglycerides, diglycerides Glycerol carbonates	(Aresta et al., 2006, Chang and Chen, 2011, Jérôme et al., 2004, Yoo and Mouloungui, 2003)
Glycerol ethers	Etherification, Oligomerization,Telomerisation	Glycerol oligomers e.g. : diglycerol, triglycerol and etc. Glycerol alkyl ethers e.g. : glycerol 1-monoethers, glycerol tertiery-butyl ether (GTBE), sodium glycerolate. Glycerol alkenyl ether (telomers) e.g. : unsaturated ethers of glycerol	(Behr and Urschey, 2003, Klepáčová et al., 2005, Marquez-Alvarez et al., 2004, Queste et al., 2007)
Glycerol acetals and ketals	Acetalisation, Transacetalisation	Cyclic acetals e.g. : [1,3]dioxan-5-ols, [1,3]dioxolan-4-yl-methanols	(Climent et al., 2004b, Deutsch et al., 2007, Piantadosi et al., 1959, Showler and Darley, 1967)
Glycerol to propanediols	Hydrogenolysis	1,2-propanediols and 1,3-propanediols	(Braca et al., 1991, Chaminand et al., 2004, Lahr and Shanks, 2005, Miyazawa et al., 2006)
Glycerol to epoxides	Oligomerization	Epichlorohydrin	(Klumpe, 2007)
Glycerol oxidation and dehydration	Oxidation, Dehydration	Glycerol oxidation product e.g. : Dihydroxyacetone (DHA), glyceraldehyde, glyceric acid, tartonic acid, mesoxalic acid. Glycerol dehydration e.g. : Acrolein	(Carrettin et al., 2003, Kimura, 1998, Vollenweider and Lacroix, 2004)
Glycerol to synthesis gas	Steam reforming, Aqueous phase reforming (APR), Supercritical water gasification (SCWG)	Carbon monoxide, pure hydrogen	(Davda et al., 2005, Hirai et al., 2005, Kersten et al., 2006)

2.2 Diglycerol

The linking of a single monomer of glycerol to the other to give a so-called polyglycerol is one of the routes that are available for upgrading the physical structure of glycerol. Basically, polyglycerol consist of components (isomers) that differ in the condensation degree with different number of glycerol units in a linear of hyperbranced chain. The formation of linear and branched isomer depends on the reaction of primary and secondary hydroxyl (Barrault and Jerome, 2008). Oligomerization is applicable to the polymerization of glycerol to lower number of glycerol units (2-4 glycerol units). In this work, etherification of glycerol is preferred to be conducted leading to the formation of polyglycerol.

Table 2.4 shows the changes in physical properties of glycerol and its higher oligomers. Generally with the increase in the molecular weight of the oligomers, the density shows a corresponding increase with the addition of glycerol units in the chain. The capability to break the ethers bond is also becoming harder because of the effect of the chain structure so that the correlation between temperature and pressure must be taken into account. Hydroxyl number can be measured experimentally and it is defined as the mg of KOH equivalent to the hydroxyl content of 1 g of sample. It is generally known that the hydroxyl number decrease with the ascending number of glycerol units. It also influences the changes of polarity, solubility, viscosity and colour (from water clear to dark yellow) (Martin and Richter, 2011).

Table 2.4 : Some physical data of polyglycerols (Martin and Richter, 2011)

Name	Molecular formula	Molecular weight (g/mol)	Density (g/cm^3)	Boiling Point (^{o}C)/(Pa)	Hydroxyl number (mg KOH/g)
Glycerol	$C_3H_8O_3$	92	1.2560	290	1830
Diglycerol	$C_6H_{14}O_5$	166	1.2790	205/13.3	1352
Triglycerol	$C_9H_{20}O_7$	240	1.2646 (40^{o}C)	>250/13.3	1169
Tetraglycerol	$C_{12}H_{26}O_9$	314	1.2687 (40^{o}C)	69-73 (melting point)	1071
Polyglycerol-3			1.2840	-	-

In this work, the product of interest from the etherification process is diglycerol. Diglycerol (DG) is expected to be the most abundant product that is formed in a pool of isomers during the reaction. There are linear, branched and cyclic dimers and the formation of these various structures is dependent on the location of hydroxyl group that interacts with another hydroxyl group from the other monomer. The structures of all categories of isomeric diglycerol dimers are shown in Figure 2.2. Couplings of primary to primary location, primary to secondary location, secondary to secondary location and secondary etherification result in the prim-prim, prim-sec, sec-sec and cyclic dimers respectively (Cassel et al., 2001). The dimensions and basal spacing value (d) of each dimers are shown in Table 2.5 (Martin et al., 2012).