CATALYTIC ESTERIFICATION OF PALM-BASED LAURIC ACID AND DIETHYLENE GLYCOL VIA MICROWAVE HEATING

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**FACULTY OF ENGINEERING
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ABSTRACT

Diethylene glycol esters of fatty acids are mixtures of diethylene glycol mono- and di-esters of saturated and unsaturated fatty acids derived from edible oils and fats. The products are produced either by direct esterification of diethylene glycol with fatty acids or by transesterification of diethylene glycol with oils or fats. This study involved in maximizing the conversion of lauric acid to glycol ester via esterification with diethylene glycol, aided by calcined Zn-Mg-Al catalyst in a 250-ml reactor using both conventional and microwave heating. Preliminary catalytic screening involving tin (II) oxalate, Amberlyst-15 and calcined Zn-Mg-Al catalysts in esterification of lauric acid and diethylene glycol via microwave heating resulted 65.4%, 31.6% and 95.4% of lauric acid being converted, respectively. In addition, conversions obtained from the solid acid catalysts appeared to be higher than autocatalytic esterification of only 15.8%. The optimum operating condition for esterification via microwave heating was established at 190 ^{o}C, 2:1.3 mole ratio of lauric acid to diethylene glycol with 5% of catalyst dosage for 90 min. Calcined Zn-Mg-Al catalyst under optimised condition gives 98.2% of lauric acid conversion. The recyclability of the catalysts in the esterification of lauric acid with diethylene glycol were also carried out. It shows that calcined Zn-Mg-Al and tin (II) oxalate both can be used up to six cycles as compared to Amberlyst-15 catalyst that has lost part of its activity after the third cycle. The microwave heating remains attractive for heating catalytic esterification as it accelerates the reaction speed at shorten period of time from 8 hours to 1.5 hours as compared to conventional heating.

ABSTRAK

Ester glikol adalah hasil produk daripada campuran dietilin glikol mono- dan di-ester asid lemak tepu dan tidak tepu yang diperolehi daripada minyak makan dan lemak. Produk dihasilkan sama ada dengan esterifikasi secara langsung di antara dietilin glikol dengan asid lemak atau melalui transesterifikasi dari glikol dengan minyak atau lemak. Kajian ini melibatkan proses memaksimumkan penukaran asid laurik kepada ester glikol melalui esterifikasi, dibantu oleh mangkin teraktif Zn-Mg-Al menggunakan reactor bersaiz 250-ml melalui pemanasan gelombang mikro. Saringan awal esterifikasi bermangkin adalah melibatkan tiga jenis pemangkin (tin (II) oxalate, Amberlyst-15 dan Zn-Mg-Al teraktif), memberi penukaran asid laurik adalah sebanyak 65.4%, 31.6% dan 95.4% menggunakan tin (II) oxalate, Amberlyst-15 dan Zn-Mg-Al teraktif. Di samping itu, penukaran yang diperolehi daripada pemangkin asid pepejal kelihatan lebih tinggi daripada esterifikasi tanpa mangkin iaitu hanya 15.8%. Keadaan operasi yang optimum untuk esterifikasi melalui pemanasan gelombang mikro adalah pada suhu 190 ºC, nisbah asid laurik kepada dietilin glikol adalah 2: 1.3, dos pemangkin 5% pada masa tindakbalas selama 90 min. Mangkin Zn-Mg-Al teraktif di bawah keadaan yang optimum memberikan 98.2% penukaran asid laurik. Proses kitar semula mangkin dalam esterifikasi asid laurik dengan dietilin glikol juga dijalankan. Ia menunjukkan bahawa Zn-Mg-Al teraktif dan tin (II) oxalate boleh digunakan untuk enam kitaran berbanding dengan Amberlyst-15 pemangkin yang telah kehilangan sebahagian daripada aktivitinya selepas kitaran ketiga. Pemanasan gelombang mikro adalah sesuai digunakan dalam pemanasan pemangkin esterifikasi kerana ia mempercepatkan kelajuan tindak balas dengan memendekkan tempoh proses tindakbalas dari 8 jam kepada 1.5 jam berbanding dengan pemanasan konvensional.

ACKNOWLEDGEMENT

TABLE OF CONTENT

LIST OF TABLES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

CAGR	Compound Annual Growth Rate
H_2SO_4	Sulphuric Acid
p-TSA	Para-Toluene Sulphonic Acid
HTLC	Hydrotalcite Like Compound
NMR	Nuclear Magnetic Resonance
GC	Gas Chromatography
AV	Acid Value
OFAT	One Factor at Time
PO	Palm Oil
PKO	Palm Kernel Oil
CNO	Coconut Oil
MPOB	Malaysian Palm Oil Board
USDA	United States Department of Agriculture
PGMEs	Propylene Glycol Mono Esters
FDA	US Food and Drug Administration
HLB	Hydrophilic- Lipophilic Balance
UNDESA	Union Derivan SA
FFA	Free Fatty Acid
LDH	Layered Double Hydroxide
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
OHV	Hydroxyl Value
HNO_3	Nitric Acid
AOCS	American Oil Chemists' Society
KOH	Kalium Hydroxide

EGDS	Ethylene Glycol Di-Stearate
FTIR	Fourier Transform Infra-Red
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis
DTG	Differential Thermal Gravimetric
FID	Flame Ionization Detector
HPA	Hypophosphorous Acid
Zn	Zinc
Mg	Magnesium
Al	Aluminium
XRD	X-ray Diffraction
BET	Brunauer-Emmett- Teller Method
BJH	Barrett- Joyner-Halenda Method
TPD	Temperature Programmed Desorption
CO_2	Carbon Dioxide Gas
NH^3	Ammonia Gas
LA	Lauric Acid
DEG	Diethylene Glycol
DEG-ML	Diethylene Glycol Mono-Laurate
DEG-DL	Diethylene Glycol Di-Laurate
^{1}H-NMR	Proton –Nuclear Magnetic Resonance
^{13}C-NMR	Carbon- Nuclear Magnetic Resonance

CHAPTER 1: INTRODUCTION

1.1   Research Background

There is an increasing trend of chemical industries toward new processes that should meet stringent environmental or energy requirement such as generation of nearly zero waste chemicals, less energy and potentially to be used in various industrial application. Glycol esters are new chemical compound derived from fatty acid esterified with diol under optimum condition that have wide potential functions. Glycol esters as emulsifier can be applied in household and personal care products (Elwira *et al.*, 2013), as coalescent aid in paint formulations (Jiratumnukul *et al.*, 2000), engine oil additives (Gao *et al.*, 2007), biolubricants (Vanitah *et al.*, 2015, Zulina *et al.*, 2018) and also as phase change material in energy storage (Cemil *et al.,* 2008). In 2017, Technavio's analyst forecast the global emulsifier market to grow at a CAGR of 7.16% during the period 2017-2021 (Market Report World, 2017).

Esters can be produced either by direct esterification of diol/ alcohol reacted with fatty acids in the presence of catalyst or even conducted in autocatalytic mode. Self-esterification process can be proceeded successfully by considering significant factors such as reactants properties, operating conditions and materials stability (Hans *et al.*, 2004). For example, the autocatalytic esterification between lauric acid and glycerol was well performed at 130 ºC with smaller dosing of methyl lactate in the reaction for miscibility purposes (Ayyagari *et al.*, 2002). Typically in chemical industry, esterification was conducted in the presence of homogeneous acid catalyst such as sulphuric acid (H_2SO_4) or para-toluenesulphonic acid (*p*-TSA). The optimized process could produce maximum content of esters yield, but this homogeneous catalysed reaction may generate enviromental and corrosion problems.

At higher temperature of homogeneous catalytic esterification using *p*-TSA, may lead to the formation of catalyst ester in the product mixture with high toxicity and harmful to others. Furthermore, since homogeneous catalyst is in the same phase with the product mixture, the purification process later requires additional steps such as neutralization and tedious separation. This will increase the production cost.

1.2   Problem Statement

Conventionally, homogeneous acid catalyst was employed in the esterification process. The advantages of these catalyst are short reaction time and produced higher yields. However, there are many disadvantages such as corrosiveness and impossibility of recycling the catalyst (Kaluram *et al.*, 2015). The environmental concerns related to the disposal salt formed during final neutralization of acids and technical problems associated with their use, such as corrosion and separation operations, constitute a strong driving force to search for alternative processes.

The employment of heterogeneous catalyst as a substitute of these homogeneous catalysts for the production of glycol ester was explored, as it will provide better separation as well as lowering the generation of waste, environmental impact and cost. Lee *et al.*, (2010) reported countless studies have been published to develop new heterogeneous catalysts. The use of heterogeneous catalyst offers improved process efficiency by eliminating the need for quenching steps and reducing the purification steps (Semwal *et al.*, 2011). Moreover, this catalyst can be recycle as it is easy to separate with the product mixture.

Furthermore, there is no investigation has been reported to produce glycol ester via heterogeneous esterification of fatty acid and diethylene glycol. Therefore, this present study will focus on the use of heterogeneous catalysts, specifically hydrotalcite-like compounds (HTLC) for the esterification of palm-based lauric acid and diethylene glycol for fatty glycol ester production using microwave heating. In addition, conventional esterification will be carried out for the purpose of comparison. For the conventional methods, two types of esterification will be carried out, i.e autocatalytic esterification and catalytic esterification. The findings obtained from the optimization study to optimize to process parameters is essential for feasible process development.

1.3 Research Objective

This research has the following objectives:

1) To produce diethylene glycol ester from autocatalytic esterification of lauric acid and diethylene glycol using conventional heating

2) To determine the best catalyst for the production of diethylene glycol ester using catalytic conventional esterification and microwave method

3) To investigate the effect of various process parameters on esterification and then to use the optimized parameters in maximizing the formation of glycol di-ester yield

4) To evaluate the recyclability and leaching of the heterogeneous catalyst

1.4 Scope of Study

This work is divided into four phases. The first phase focuses on the conventional esterification of lauric acid and diethylene glycol conducted in the absence of catalyst as a benchmark. The reaction was performed in a stirred reactor under various operating conditions.

Several important parameters were investigated such as reaction temperature, stirring speed rate and reactant mole ratio. The minimum acid value (AV< 4) was monitored by acid value titration. Conversion of lauric acid and composition of glycol ester comprised of mono- and di-glycol ester were analysed using Gas Chromatography (GC). Confirmation of the glycol ester produced was detected using Nuclear Magnetic Resonance (NMR) spectrometer.

Second phase of this work involves the production of glycol ester via catalytic esterification process. Various types of heterogeneous catalyst were screened to obtain the suitable catalyst that able to give better yield of di-ester content. The conversion of lauric acid and fatty glycol ester compositions obtained using the heterogeneous catalysts were also compared with the conventional homogeneous para toluene sulfonic acid catalyst (*p*-TSA) catalyst. The reaction was conducted according to the optimum parameters obtained from autocatalytic process carried out previously in phase 1.

The optimization of the operating conditions of the heterogeneous esterification process using microwave heating with the aim to obtain maximum yield of di-ester content was performed in the third phase. The effects of reaction temperature, catalyst particle size, catalyst dosage, reactant mole ratio and reaction time towards lauric acid conversion were investigated and these process parameters were manually optimized using the one factor at a time (OFAT) method.

The fourth phase of the study emphases on the recyclability evaluation of the heterogeneous catalysts by recycling the catalysts from the one cycle to the subsequent cycle. Leaching tests of the potential heterogeneous catalyst in products (glycol ester) were also investigated throughout the recycle process.

1.5   Thesis Outline

This thesis includes five chapters. **Chapter 1** highlights the readers on brief background, objectives, and research problem identification. It also describes the scope of the research work. **Chapter 2** compiles the findings of previous studies related to this research. The process to prepare fatty glycol ester involving conventional esterification of fatty acid via heterogeneous catalysis were discussed in detailed, emphasizing on the heterogeneous catalysts structure, advantages as well as their catalytic activities in various chemical processes. The overview of palm oil and oleochemical industry as well as the ester market were also discussed in this chapter. **Chapter 3** describes the materials and methods used in this work which include the reaction process, the characterization procedures and the optimization of the reaction conditions. The results and findings were presented and discussed comprehensively in **Chapter 4**. Conclusion and recommendations for future works of this study were listed in **Chapter 5.**

CHAPTER 2: LITERATURE REVIEW

2.1 Overview of Palm Oil

Palm oil and palm kernel oils are extracted from *elaeis guineensis* tree. They both come from palm trees, but palm oil comes from the palm fruit, while kernel oil is extracted from the palm seed. A typical picture of palm fruit and palm kernel as well as crude palm oil is shown in Figure 2.1 (Lai *et al.*, 2012). They are different in chemical compositions and physical characteristics. Palm oil is often used for edible purposes while palm kernel oil is mainly used for non-edible purposes such as making soaps, cosmetics and detergents. Palm kernel is extracted from the fruit's seed. It has more saturated fat than palm oil making it more solid and ideal to be used in soaps, detergents and cosmetics. Palm kernel oil is similar to coconut oil in terms of chemical composition, physical characteristics and usage (Palm Oil Health, 2015). These two commodity oils both have high levels of lauric acid. Typical fatty acid composition is given in Table 2.1.

Figure 2.1: Typical image of palm fruit and palm oil (Lai *et al.*, 2012)

Table 2.1: Fatty acid composition (wt. %) of the two commodity
(Palm Oil Health, 2015)

	Fatty Acid Carbon Chain Length							
	8:0	**10:0**	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**
Palm Kernel	3	4	45	18	9	3	15	2
Coconut	8	7	48	16	9	2	7	2

2.1.1 Palm Oil Industry

Palm oil and palm kernel oil were jointly emerged as the largest commodity among the oils and fats in the world market with 38.7% of the total oils and fats production. According to Global Edible Oil Production, (2017) the world production of major oils and fats was 184.08 million tonnes. Soybean oil production followed at the second place accounting its part at 53.15 million tonnes (28.9%) as shown in Figure 2.2. It was recorded close to one-third (71.32 million tonnes) of world total oils and fats production from a planted area of 19.04 million hectares, mainly from Indonesia and Malaysia. Malaysian palm oil alone fetched RM 46.12 billion export revenue from its India and European Union markets (Kushairi *et al.*, 2018). Malaysia and Indonesia are the major exporters of palm oil globally with both having 36.5% and 53.2% of the market share respectively. Currently, Malaysia is the second largest producers of palm oil, after Indonesia as the world leader producer.
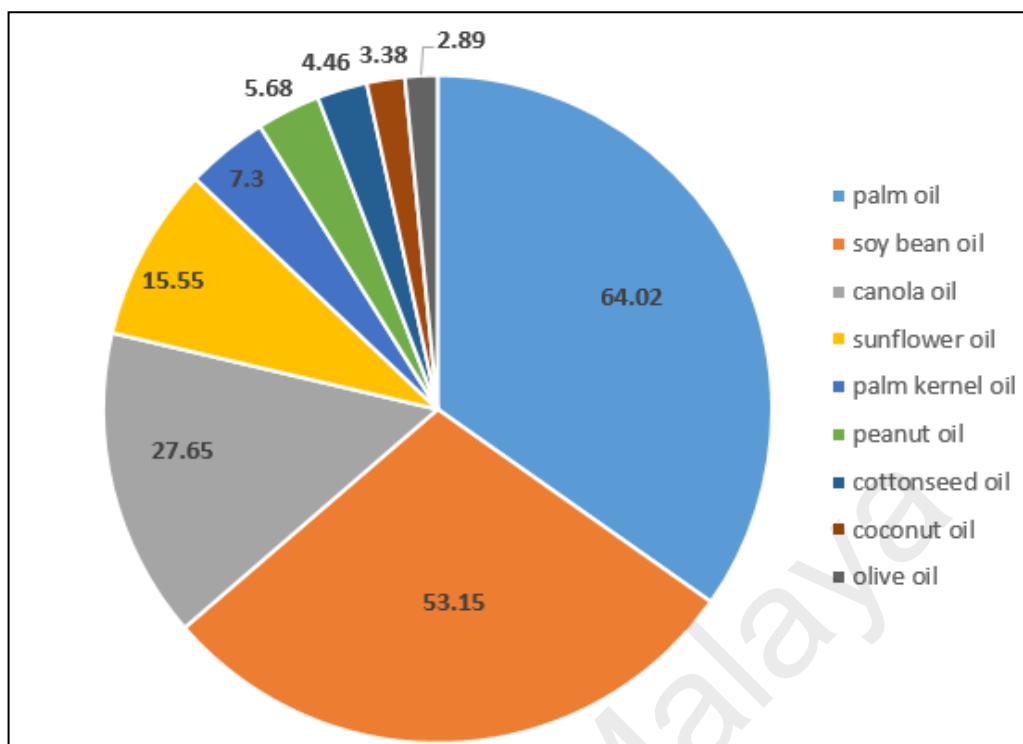
Figure 2.2: World production of major oils and fats (million tonnes)
(Global Edible Oil Production, 2017)

2.1.2 Oleochemical Industry

The palm-based oleochemical manufacturing industry has contributed significantly to the economic growth of Malaysia. Two important palm products such as PO and PKO, are converted into five basic oleochemical intermediates: fatty acids, methyl ester, fatty alcohol, fatty amine and glycerol. According to MPOB Statistics, (2017) the major oleochemical products exported were fatty acids with 0.92 million tonnes or 36% of the total oleochemical exports, followed by fatty alcohol (0.56 million tonnes or 21%) as indicated in Figure 2.3.
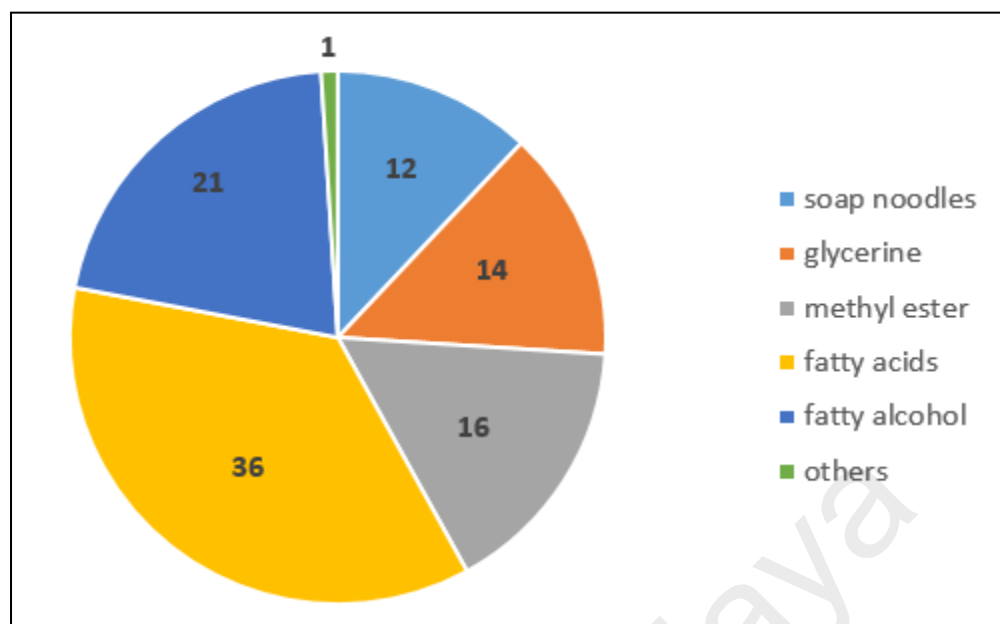
Figure 2.3: World major exports of oleochemical products (million tonnes) (MPOB Statistics, 2017)

These basic oleochemicals are produced in different grades of quality depending on the desired applications. Oleochemicals are used in the manufacturing of variety of end-products, ranging from soaps and detergents to electronic components, as described by Ting (2001) shown in Table 2.2.

Table 2.2: Applications of oleochemicals (Ting, 2001)

Industry/Product	Uses
Soaps and Detergents	Industrial and domestic products, specialty surfactants
Lubricants and Hydraulic Fluids	General and specialty industrial lubricants and biodegradable base oils, hydraulic fluids
Paints and Coatings	Alkyd and other resins, drying oils, varnishes and other protective coatings
Plastics	Stabilizers, plasticizer, mould-release agents, lubricants, anti-static agents, anti-fogging aids, polymerization emulsifiers
Biofuels	Methyl esters and alcohols
Waxes	Ingredients in waxes and polishes
Personal Care	Soaps, shampoos, lotions

2.1.3 Palm-based Fatty Acid

Lauric acid is also known as dodecanoic acid, a 12-carbon, straight-chain carboxylate surfactant and a saturated fat. The combined production of these two oils has risen from 14 to 15.3 million tonnes in the last six years and coming almost entirely from palm kernel oil (PKO) as tabulated in Table 2.3. According to USDA Rabobank, (2018) PKO is now the major lauric oil. This is linked to the increasing area under oil palm cultivation leading to more palm oil and more palm kernel oil. The main producers of palm kernel oil are from Malaysia and Indonesia, whereas Philippines, Indonesia and India are the main producers of coconut oil. There has been considerable development of the oleochemical industry in South East Asia, particularly in Malaysia, resulting in increasing quantities of the lauric oils used in the country of origin.

Table 2.3: The world production and consumption of palm kernel oil (PKO) and coconut oil (CNO) from 2012/13 to 2017/18 (USDA Rabobank, 2018)

Year Production (P) and Consumption (C) of PKO and CNO (in million tonnes)												
	2012/13		2013/14		2014/15		2015/16		2016/17		2017/18	
	P	C	P	C	P	C	P	C	P	C	P	C
PKO	10.2	10.0	10.4	9.9	10.6	10.4	10.2	10.0	11.0	10.2	11.6	10.4
CNO	3.8	3.9	3.7	3.7	3.7	3.6	3.6	3.6	3.7	3.6	3.7	3.6

Lauric oils are mainly used in the oleochemical industry, due to their high lauric acid content. Table 2.4 shows data of industrial usage accounts for about 75% and 49% of global 2017/18 PKO and CNO application, respectively (USDA Rabobank, 2018). Sclarini *et al.*, (2013) reported the uses of lauric acid as a vegetable shortening in food industry.

In manufacturing of household and personal care product, lauric acid is used for the production of soap. For these purposes, lauric acid is reacted with sodium hydroxide to give sodium laurate which is soap. Research by Oghome *et al.*, (2012) has shown that lauric acid on skin can help control acne-causing bacteria. It is often used at higher levels to impart a pleasant natural fragrance. Typically, lauric acid is used in cosmetic formulations as solubiliser in emulsions.

Table 2.4: Proportion of lauric oils used for industrial application, 2017/18 (USDA Rabobank, 2018)

Type of Oil	Field of Industrial Applications (%)		
	Industrial	**Food**	**Feed**
Palm Kernel Oil	74.6	25.1	0.3
Coconut Oil	48.8	50.2	1.0

2.2 Oleochemical Processes

Oleochemicals can be divided into two groups of products, i.e. basic oleochemicals and oleochemical derivatives. Some chemical substances formed from basic oleochemical substances also include fatty acid esters (Zhou *et al.*, 2016), alcohol ethoxylates (Cox *et al.,* 1999), alcohol sulphates (Nur Syazani *et al.*, 2013), alcohol ether sulphates (Nur Syazani *et al.*, 2013), sugar esters (Arniza *et al.*, 2019), glycerol derivatives (Ismail *et al.*, 2010; Nik Siti *et al.*, 2013; Noor *et al.*, 2016), quaternary ammonium salts (Haliza *et al.*, 2016), fatty amides (Hoong *et al.*, 2004; Masyithah *et al.*, 2016) and other oleochemical products.

There are few different chemical reaction processes available to produce new fine chemicals. In oleochemical manufacturing, the important processes include esterification, ethoxylation, hydrogenation and transesterification, among others. Figure 2.4 indicates some of the major processes by which various oleochemicals and their derivatives can be obtained from fats and oils as reported by Ricthler *et al.*, (1984).

2.2.1 Esterification Process

Esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid with an alcohol while removing the water that is formed. The reaction is expressed by the general equation 2.1:

$$\text{RCOOH} \quad + \quad \text{R'OH} \quad \rightleftharpoons \quad \text{RCOOR'} \quad + \quad \text{H}_2\text{O} \qquad (2.1)$$

$$\text{acid} \qquad\qquad \text{alcohol} \qquad\qquad \text{ester} \qquad\qquad \text{water}$$
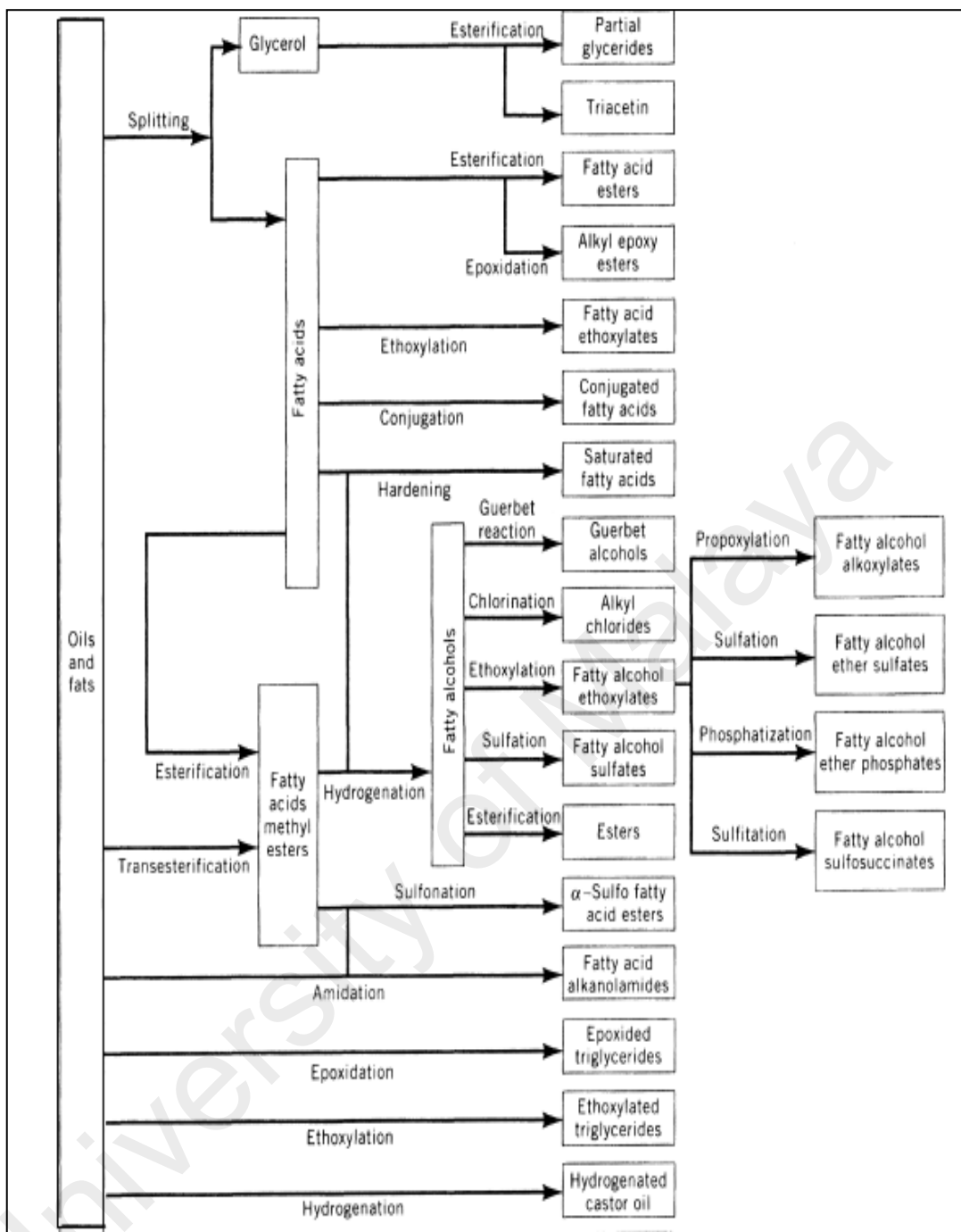
**Figure 2.4: Oleochemical raw materials and their derivatives
(Richtler *et al.*, 1984)**

A mineral acid catalyst is usually needed to ensure the reaction occur at a required rate. Esters can also be formed by various other reactions. These include the reaction of alcohol with acid chloride or anhydride. The chemical structure of the alcohol, the acid, and the acid catalyst used in the esterification reaction all effect its rate. Simple alcohols such as methanol and ethanol react very fast because they are relatively small and contain no carbon atom side chains that would hinder their reaction as discussed by Kuldeep *et al.*, (2012). These solid catalysts work well with acid sensitive esters because they can be separated from the product by filtration and therefore, the catalyst does not spend very much time in contact with the acid unstable product. Patai *et al.*, (1991) reported on the continuous process for making esters was first patented in 1921 and has been used extensively in the manufacture of large quantities of esters.

2.2.2 Palm-based Glycol Ester

Esters of glycol with palm-based fatty acids occur naturally in fats and oils, and they are widely used for edible and industrial purposes. The preparation of palm-based glycol esters to obtain higher yield by direct esterification is very difficult because of the tendency to get complete esterification even though a large excess of the glycol is used. The glycols are poor solvents for the fatty acids and consequently the reaction proceeds slowly. Goldsmith, (1943) mentioned that monoesters, once formed, are more readily miscible with the acid and therefore react more rapidly than glycol resulting in the formation of di-esters before all of the glycol is consumed. High reaction temperature tends to increase the mutual solubility of fatty acids, and if the reagents are stable enough, direct reaction may lead to produce high conversion of ester.

A study on synthesis of propylene glycol monoesters (PGMEs) was carried out by chemical method involving esterification of propylene glycol with fatty acids in the presence of acid or alkaline catalysts at high temperature (over 220 ºC) and high pressure was reported by Seino and Uchiobori, (1984). The product obtained had a complexed mixture, dark in colored, off-flavors and toxic as well as low in purity. Stutz *et al.*, (1973) described PGMEs are good water-in-oil emulsifiers because of its lower hydrophilic- lipophilic balance (HLB) values than many glycerol monoesters. PGMEs are surface-active compounds that have been proven to be effective emulsifiers. PGMEs form a film around entrapped air bubbles which then stabilize food emulsion system. The US Food and Drug Administration (FDA) approved PGMEs for use in foods and pharmaceuticals (Artman, 1975). PGMEs are often used in cakes and non-dairy whipped products, such as imitation creams, whipped toppings, and spray-dried topping products. Nash and Brinkman, (1972) revealed PGMEs can be used in combination with mono- and diglycerides to obtain excellent cake batter behavior, resulting in increased volume and uniform structure of cake.

Liu and Shaw, (1995) produced esters by synthesized enzymatically between propylene glycol with different acyl donors in organic solvents. Lipase from *Pseudomonas Cepacia* was added in the mixtures and shaken at 30 ºC. Based on the result obtained, the yield of the esters was affected by the acyl donors, organic solvents, temperature, water content, pH memory and reaction time. The yields of propylene glycol mono-laurate, mono-myristate, mono-palmitate, mono-stearate and mono-oleate with acid anhydrides as acyl donors were 97.2, 79.6, 83.7, 89.7 and 93.4 mM, respectively.

The production of glycol ester by direct esterification of propylene glycol with lauric acid aided by immobilized lipase (Lipozyme IM-77) was studied by Shaw *et al.*, (2003). It was found that 96% lauric acid was converted using optimum conditions (37.6 ºC of reaction temperature, 7.6 hours of reaction time, 37.1% of enzyme amount and 26:1 of substrate molar ratio).

2.2.3 Possible Application of Fatty Acid Glycol Ester

Based on current market, organic esters are valuable intermediates in several branch of chemical industry. They have wide applications in plasticizers, solvents, perfumery also used as flavouring agents and preservative in the food industry chemicals and as precursors to a gamut of pharmaceuticals, agrochemicals, and other fine chemicals. Glycol mono and di-laurate are major product of esterification of glycol with acid donor and they have widely used as self-dispersing surface active agent. Elwira *et al.*, (2012) suggested esters compound w/o or o/w emulsifier with an auxiliary agent as emulsifying agent in cosmetics, paints and coatings (Jiratumnukul *et al.*, 2000), engine oil (Gao *et al.*, 2011), lubricants (Vanitah *et al.*, 2015) and polymers (Kim *et al.*, 2016). Union Derivan SA, (2002) claimed glycol esters are potentially to be used as emulsifier, opacifier, thickener and dispersing agent. As for personal care product, glycol ester are used as pearlizing agent in opalescent shampoos, hair cream and fatty body (thickener) for lipsticks.

2.3 Technologies for Esterification Process

Fatemeh *et al.*, (2017) reported that heating method is one of the key factor for the process improvement. Usually, conventional esterification was performed at high temperature through several hours of conductive heating (reflux or distillation set up using hot plates or heating mantles). However, it took a longer reaction hours to give higher yield of esters at optimum process conditions. As an alternate energy source, the use of microwaves as heating source is an efficient technology to promote chemical reactions at shorter time with less energy consumption but higher conversions (Mazzocchia *et al.*, 2004).

Microwave heating is a new tool in chemistry, which widens the scope of conventional thermal heating and gives chemists novel and exciting possibilities. Microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules of solvents, reagents or catalysts. Mazo *et al.*, (2012) reported autocatalytic esterification of maleated castor oil proceeded more quickly when using microwaves and described the non-thermal effects of microwave heating. The literature reported some advantages of this technology, such as the ease of operation, low energy consumption, short processing times and fast heating as compared to the conventional heating (Leadbeater *et al.*, 2006). For instance, reductions in reaction times have been observed using microwave heating in the esterifications of lauric acid with 1,2-propanediol using commercial lipases (Yadav *et al.*, 2006), propionic acid with ethanol using Amberlyst-15 (Toukoniitty *et al.*, 2005), free fatty acids from palm oil with methanol using H_2SO_4 and cationic resins (Mazo *et al.*, 2010). A glance through the literature on microwave heating has been used to facilitate acid, base, and enzyme catalyzed esterification reactions (Donati *et al.*, 2005; Kerep *et al.*, 2006; Rejasse, 2004; Huang *et al.*, 2005; Yadav *et al.*, 2004).

2.4   Fatty Acid Glycol Ester Production

Catalysts can be divided into two main types which is homogeneous and heterogeneous. In a homogeneous reaction, the catalyst is in the same phase as the reactants. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. It is appropriate to begin the discussion on homogeneously catalyzed esterification with a comparison of factors in relation to the corresponding heterogeneously catalyzed reaction and the comparison is tabulated in Table 2.5.

Table 2.5: Comparison of homogeneous and heterogeneous catalyzed esterification (Hattori, 2010)

Factors	Homogeneous catalysis	Heterogeneous catalysis
Reaction rate	Fast and high conversion	Moderate conversion
After treatment	Catalyst cannot be recovered, must be neutralized leading to waste chemical production	Can be recovered
Processing methodology	Limited use of continuous methodology	Continuous fix bed operation possible
Presence of water / free fatty acids	Sensitive	Not sensitive
Catalyst reuse	Not possible	Possible
Cost	Comparatively costly	Potentially cheaper

2.4.1 Homogeneous Catalyzed Esterification

Study reported by Hernando *et al.*, (2007) on the reaction of oleic acid with methanol using homogeneous sulfuric acid (H_2SO_4) catalyst investigate the effects of temperature and amount of reactants (alcohol and initial fatty acid) over the fatty acid conversion. Results showed that the amount of catalyst used only affect the conversion time. However, the final conversion was still the same regardless of different catalyst amount used. When molar ratio was varied, the amount of alcohol affects the reaction rate. When the amount of alcohol is higher, the rate of reaction became slower but resulting in higher conversion of FFA. By using homogeneous catalyst, it is hard to separate the catalyst from the product since it is miscible in the product. Thus, the yield and the purity of the product were lower (Marchetti *et al.*, 2008). Homogeneous acid catalyzed reactions may generate many environmental and corrosion problems. Hence, esterification reactions catalyzed by heterogeneous catalysts are attracting increasing attention as discussed by Kamath *et al.*, (2011), Shu *et al.*, (2010) and Charoenchaitrakool *et al.*, (2011).

2.4.2 Heterogeneous Catalyzed Esterification

The use of heterogeneous catalysts in the esterification reactions avoids the existing problems: instrument corrosion, waste generation from acid neutralization process, and product separation difficulty associated with the use of homogeneous liquid acid such as sulphuric acid, and it is extremely important in developing more environmentally friendly and economical process. Liu *et al.*, (2013) reported the utilization of the heterogeneous catalyst aminophosphonic acid resin D418 in the energy-efficiency microwave-assisted esterification reaction between stearic acid and ethanol. More than 90% conversion of esterification was achieved under optimum conditions. D418 with 9 wt% catalyst dosage exhibited remarkable catalytic performance for ethyl stearate formation at temperature of 80 ^{o}C and atmospheric pressure. It is proven that ester can be produced in 7 hours by microwave heating, while it took 12 hours by conventional heating.

Chemat *et al.*, (1997) studied on the esterification of stearic acid ($C_{18:0}$) and butanol in a microwave oven aided by heterogeneous reaction. The heterogeneous catalysts were such as $Fe_{2.}(SO_4)_3$, $TiBu_4$ and montmorillonite KSF. Results showed that the rate of esterification are influenced by the presence of a catalyst. The yields are improved by application of dielectric heating (95%) compared with conventional heating (82%) for heterogeneous esterification conducted at 140 ^{o}C for 120 min.

Some works on the esterification of low-chain fatty acids with solid acid catalysts were also reported in literature. For example, the esterification of fatty acids with 2-ethylhexanol (Raner *et al.*, 1992). Other types of acids used such as with 2,4,6-trimethylbenzoic acid (Carlos *et al.*, 2009), acetic acid (Cemil *et al.*, 2008), and propionic acid (Liu *et al.*, 1998). In these studies, solid acid catalysts were employed, enabling the esterification reactions under relatively mild conditions (temperature and time) as compared to those usually applied in autocatalytic systems.

Esterification via Hydrotalcite – like Compounds Catalyst

The employment of heterogeneous acid catalyst in esterification of fatty acid and diethylene glycol for the production of glycol ester has been explored as shown in Figure 2.5. There is not much research has been reported on esterification from fatty acid and diol aided by heterogeneous catalyst, specifically hydrotalcite-like compounds (HTLCs) and as such, this current work can be considered as the first experimental investigation to produce glycol ester via heterogeneous catalysis. HTLCs which are known as layered double hydroxide (LDH) or anionic clays, represent a group of important inorganic materials used as adsorbents, anion exchangers and catalysts or catalysts precursors for different types of chemical reactions.

According to Cavani *et al.* (1991), in order to understand the structure of these compounds, it is necessary to start from the structure of brucite, $Mg(OH)_2$ as the hydrotalcite-type anionic clays have similar structure to that of brucite, $Mg(OH)_2$, whereby each of the Mg^{2+} ion is octahedrally surrounded by six OH^- ions as shown in Figure 2.6a.

The hydrotalcite structure is obtained when some of the Mg^{2+} ions in the hydroxyl layer are replaced by trivalent cations with a similar radius as illustrated in Figure 2.6b. When Mg^{2+} ions are substituted by a trivalent ion having almost similar radius (such as Al^{3+} for hydrotalcite), a positive charge is generated in the hydroxyl layer. This net positive charge is compensated by $(CO_3)^{2-}$ anions, which lie in the interlayer region between the two brucite-like layers and in the free space of this inter-layer, water molecules are also present as can be seen in Figure 2.6c.
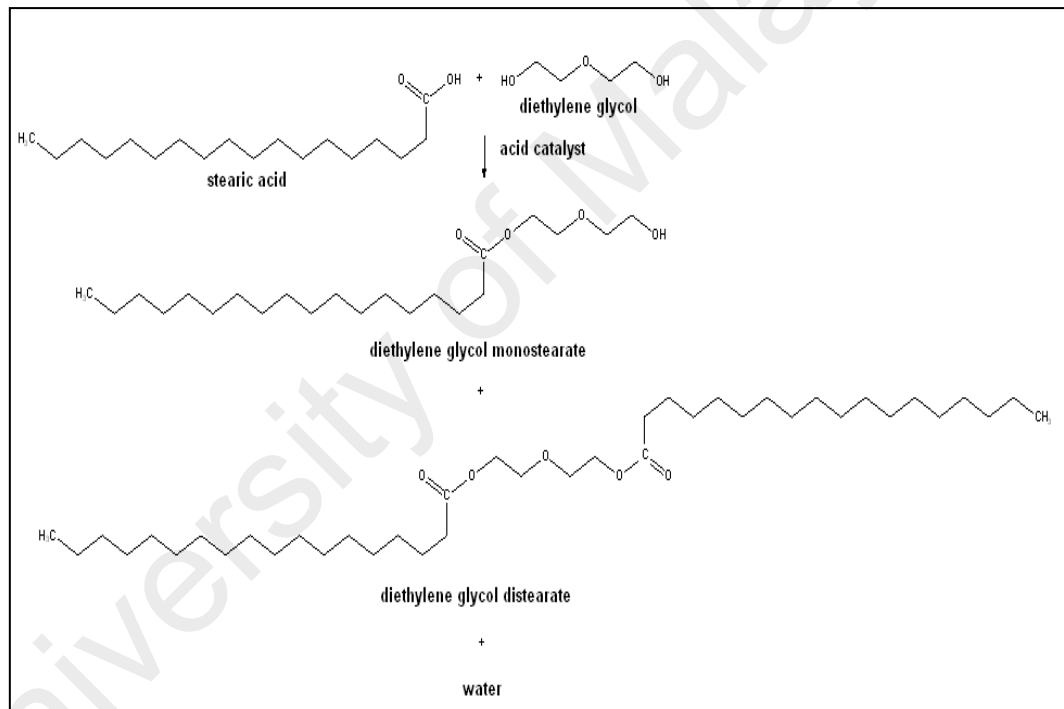
Figure 2.5: Catalytic esterification of diethylene glycol and stearic acid (MPOB Report No 824, 2017)

Cavani *et al.* (1991) reported that upon calcination, HTLCs forms mixed oxides which have several advantages over other heterogeneous base catalysts such as high dispersion of active sites, high thermal stability and large surface area. The basic properties of the mixed oxides depend on the Mg-Al ratio in the hydrotalcites compounds. Moreover, the mixed oxides give rise to well- dispersed and thermally stable metal particles by reduction treatments when reducible cations are present. HTLC also have "memory effect", which allows the reconstruction under mild conditions of the original hydrotalcite structure when contacting the product of the thermal treatment with water solutions containing various anions.
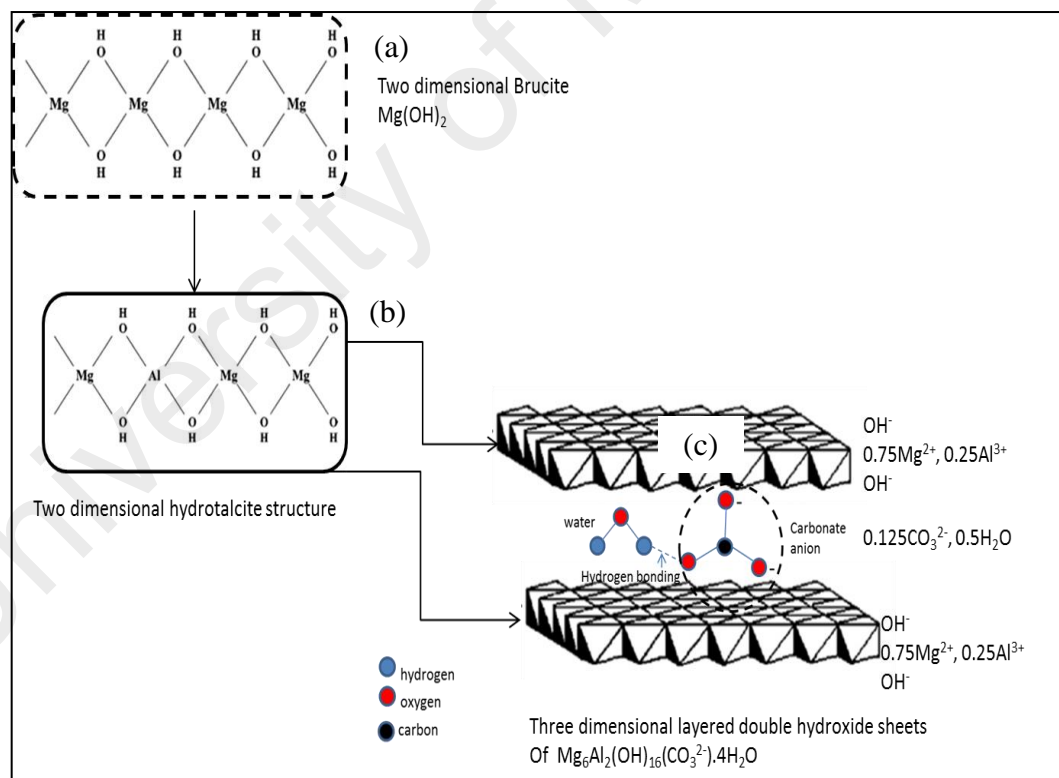
Figure 2.6: Structure of hydroxide layers in: (a) Brucite-Mg (OH)$_2$; (b) Hydrotalcite-Mg$_6$Al$_2$(OH)$_{16}$(CO$_3^{2-}$).4H$_2$O; (c) Atom positions (Cavani *et al.*, 1991)

2.5   Analysis and Characterization of Fatty Acid Glycol Ester

According to Cemil *et al.*, (2008) ethylene glycol di-stearate (EGDS) as glycol ester was produced by direct esterification of stearic acid and ethylene glycol. It is potentially to be used as a novel phase change material. Spectroscopic and thermal behavior analyses were employed to characterize the compound. Fourier Transform Infra-Red (FT-IR) spectroscopy was used for completion of reaction confirmation. Density of EGDS was determined by using a pycnometer. For thermal properties, Differential Scanning Calorimetry (DSC) analysis was used to determine melting point, crystallization points and latent heats. Thermal Gravimetric Analysis (TGA) and Differential Thermal Gravimetric (DTG) were used to determine weight loss (Mustafa *et al.*, 2017).

Jiratumnukul *et al.,* (2000) analysed glycol esters produced from soybean oil fatty acids using Gas Chromatography (GC). The composition of obtained soy oil glycol ester was determined using GC (Hewlett-Packard 5890 Series II GC, Palo Alto, CA) equipped with a flame-ionization detector (FID). The GC column was a methyl silicon gum high-performance capillary column, 5 m in length. The operating conditions for this column were 40 and 20 psi nitrogen and hydrogen carrier gas, respectively, with a column temperature gradient between 100 °C and 275 °C at 10°C.min^{-1} ramping. The retention times and compositions of reaction products are shown in Table 2.6.

Table 2.6: Retention time of standards and reaction products by Gas Chromatography (Jiratumnukul *et al.*, 2000)

Standards	Retention time (min)
Palmitic acid	8.3
Ethylene glycol palmitate	10.4
Oleic acid	10.0
Ethylene glycol oleate	12.2
Linoleic acid	9.6
Ethylene glycol linoleate	11.9

Infra-Red (IR) spectroscopy analysis was conducted to determine the functional group of the compound produced (Jiratumnukul *et al*., 2000). Results showed a peak of OH stretching at wavelength 3500 cm^{-1} in the spectra of the glycol derivative products but it did not appear in the soybean oil spectra. There were peaks of C–O stretching of alcohol at wavelength 1350 and 1450 cm^{-1} in the spectra of the glycol derivative soybean oil esters, but those peaks were not seen in the soybean oil spectra.

Determination of Hydrophilic-Lipophilic Balance (HLB) values are according to the basic equation based on the hydrophilic moiety in the molecule. Jiratumnukul *et al.*, (2000) reported the greater the HLB value, the more miscible the material would be with water. Table 2.7 shows the properties of glycol ester derivatives, glycol ether and ester alcohol.

Table 2.7: Physical properties of glycol derivatives soy oil esters^a
(Jiratumnukul *et al.*, 2000)

Properties	Units	Soy Oil Derivatives Esters[a]						
		EG	DEG	PG	DPG	ME	EB	TEXANOL®
Density	g.cm^{-3}	0.94	0.93	0.91	0.91	0.87	0.9	0.95
HLB[b]		2.7	4.8	3.4	5.9	n.a	14.9	n.a
Interfacial tension	dyne.cm^{-1}	36.2	36.1	33.3	35.7	30.1	27.4	28.9
Solubility parameters								
δtotal	J.cm^{-3}	18.6	18.2	18.0	17.6	17.9	20.7	19.3
Δ*d*	J.cm^{-3}	16.2	15.8	15.7	15.4	17.2	15.9	15.6
Δ*p*	J.cm^{-3}	2.03	2.04	1.88	1.85	1.50	4.9	3.07
Δ*h*	J.cm^{-3}	8.8	8.7	8.5	8.3	4.6	12.3	10.9

a Abbreviations: EG, ethylene glycol soybean oil derivative; DEG, diethylene glycol derivative; PG, propylene glycol derivative; DPG, dipropylene glycol derivative; ME, methyl ester; EB, ethylene glycol monobutyl ether; TEXANOL® (ester alcohol), trademark of Eastman Chemical Company; n/a not applicable;

b HLB, hydrophilic lipophilic balance.

2.6   Summary

Glycol esters of fatty acids are potentially used as emulsifiers in the cosmetics and textile sectors. They are normally produced by chemically homogeneous catalysed esterification or enzymatic route. There were some drawbacks when using homogeneous acid catalyst which may form toxic and carcinogen esters if the reactions were carried out at high temperature. Enzymatic reactions are quite difficult to handle as they are highly sensitive, easily denatured even by changes in pH and high cost of isolation and purification that discourages their use. Due to various issues related to environmental impact, handling and complex separation process, the employment of heterogeneous catalyst has been replaced in the production of glycol ester.

Exploration on the use of hydrotalcite-like compounds (HTLC) as heterogeneous catalysts in esterification of fatty acids have received considerable attention in different organic syntheses. HTLCs are thermally stable at high temperature, good mass transfer, high selectivity, environmental compatibility and reusable for many organics syntheses under conventional heating. No research has been reported on the use of HTLC catalyst via microwave heating, hence the present research intents to investigate thoroughly on this new route.

CHAPTER 3: METHODOLOGY

The methodology of this study is simplifies into flowchart as illustrated in Figure 3.1

```
                        Production of Glycol Ester
                 ┌──────────────────┴──────────────────┐
          Conventional                            Microwave
            Heating                                 Heating
      ┌─────────┴─────────┐              ┌─────────────┴─────────────┐
 Autocatalytic      Catalytic      Autocatalytic              Catalytic
 Esterification   Esterification   Esterification           Esterification
```

Phase 1: Benchmark Process Optimization
- No catalyst
- Atmospheric

Variable Parameters
- Temperature
- Reactants mole ratio
- Stirring speed rate

Product confirmation
- NMR
- FTIR

To meet objective #1

Phase 2: Preliminary Catalysts Screening
- 4 types of catalysts
  ❖ *p*-TSA
  ❖ calcined Zn-Mg-Al
  ❖ tin (II) oxalate
  ❖ Amberlyst-15

Process conditions used based on optimization data from Phase 1
Observation of the potential catalyst that able to obtain higher conversion using conventional system

To meet objective #2

Phase 3: Optimization study of process conditions using heterogeneous catalysts
- Screening of 3 types of catalysts
  ❖ calcined Zn-Mg-Al
  ❖ tin (II) oxalate
  ❖ Amberlyst-15

Selection of the best catalyst that able to obtain higher conversion using microwave system
Variable Parameters
- Temperature
- Reactants mole ratio
- Catalyst dosage
- Catalyst particle size
- Reaction time

To meet objective #3

Phase 4: Recyclability evaluation and leaching test
- ❖ Eight reaction cycles were carried out for three types of catalysts according to optimize process conditions
- ❖ Leaching test of calcined Zn-Mg-Al in products

To meet objective #4

Figure 3.1: Process flowchart of glycol ester production

3.1 Materials for the Production of Fatty Acid Glycol Ester

Palm-based lauric acid (98% purity) was obtained from Emery Oleochemical (M) Sdn. Bhd, Malaysia. The commercial-grade of diethylene glycol (Sigma Aldrich, 99.9% purity) was purchased from Bumi Pharma Sdn Bhd, Malaysia. The chemicals were used as received. The hydrotalcite-like compound (HTLC) comprised of Zn-Mg-Al was developed in-house by the Malaysian Palm Oil Board (MPOB). The commercial catalysts such as p-toluene sulphonic acid (p-TSA) and tin (II) oxalate were purchased from Sigma Aldrich whereas Amberlyst-15 was obtained from Dow Chemical Company. These catalysts were used without any treatment. The properties of lauric acid and diethylene glycol are tabulated in Table 3.1.

Table 3.1: Properties of palm-based lauric acid and diethylene glycol (DEG) (Material Safety Data Sheet, MSDS)

Test parameter	Specifications	
	Lauric acid, C_{12}	Diethylene Glycol, DEG
Purity, %	≥98	≥ 98%
Molar mass, $gmol^{-1}$	200.32	106.12
Appearance	White powder	Colourless liquid
Melting point, ^{o}C	43.8	-10.45
Boiling point, ^{o}C	297.9	220-230
Relative density, gcm^{-3}	1.01	1.118
Solubility	In alcohol, phenyls, acetates	Miscible in water

The palm-based glycol esters produced were compared with the commercial sample, PEGOSPERSE 100-L from Lonza Company, USA. PEGOSPERSE 100-L is diethylene glycol di-laurate from soy-bean oil with self-dispersing surface active agent. The properties of PEGOSPERSE 100-L is as tabulated in Table 3.2.

Table 3.2: Properties of PEGOSPERSE-100L
(MSDS by Lonza, USA)

Test parameter	Specifications
Acid value, mgKOH.g^{-1} sample	4 max
Moisture, % KF	0.5 max
Appearance @ 25 $^{\circ}$C	Clear liquid
HLB	7

3.2 Catalyst Preparation

The Zn-Mg-Al is a layered double hydroxide (LDH) type catalyst known as hydrotalcite-like compound (HTLC) as shown in Figure 3.2. It was developed in-house by the Malaysian Palm Oil Board and used as the heterogeneous catalyst for the esterification process in this present study. The HTLC could be a good catalyst for this study as it offers several advantages over other heterogeneous acid or base catalysts, such as high dispersion of active sites, high thermal stability and large surface area as described by Cavani *et al.,* (1991). Furthermore, limitations on the use of solid acid catalysts was also reported in terms of their low thermal stability (Amberlyst-15 withstand temperature only <140 $^{\circ}$C), resistance to mass transfer (zeolites), and loss of active sites in the presence of a polar support (HPA/silica) (Barros *et al*, 2013).
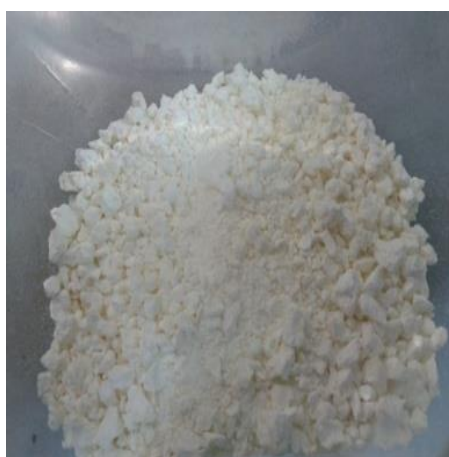
Figure 3.2: Calcined Zn-Mg-Al as heterogeneous catalyst

Zn-Mg-Al catalyst was synthesized by co-precipitation technique under pH controlled as reported by Reichle, (1985). Figure 3.3 shows the flow diagram of the catalyst preparation. The preparation starts with the dilution of metal salt solution and precipitating agent in a single container. The metal salt solution comprised of divalent cation salt (212.85 g) and trivalent cation salt (93.75 g) were dissolved in 1 L of deionized water. The precipitating agent solution was prepared by dissolving the carbonate anion (42.4 g) and hydroxide anion (16 g) in 0.5 L of deionized water. Both solution were then mixed at 60 ºC under vigorous stirring for 18 hours. In the next step, the obtained precipitate was filtered, washed with hot deionized water until neutral pH was reached. The precipitate was then dried overnight at 120 ºC. Later, the dried catalyst was undergone calcination process at 600 ºC for 5 hours before further characterization analysis.
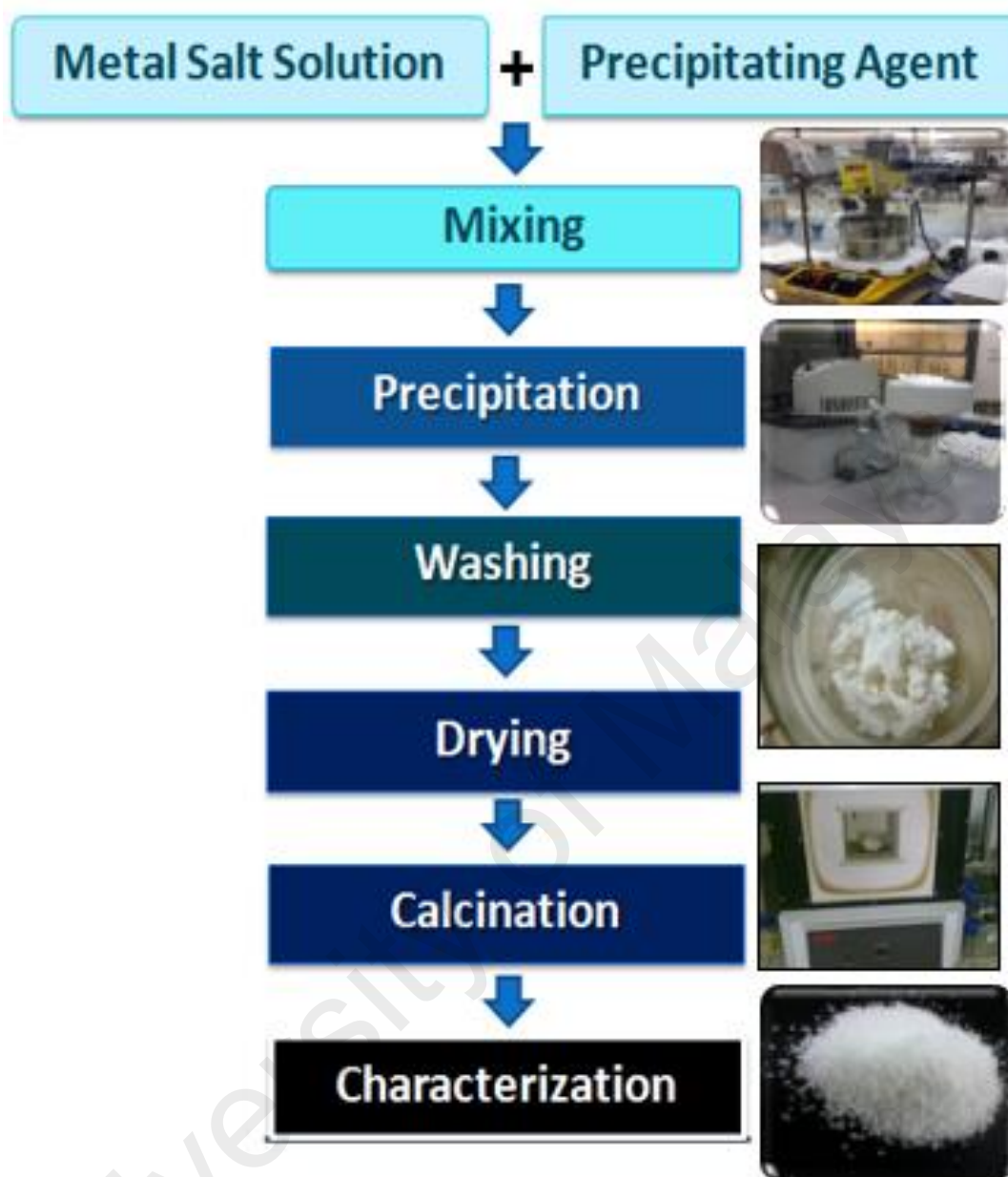
Figure 3.3: Flow diagram of calcined Zn-Mg-Al catalyst preparation.

3.3 Catalyst Characterization

Characterization of the heterogeneous catalyst was performed using X-ray diffraction (XRD), specific surface area, pore sizes and pore volume determination as well as thermal behavior analysis.

3.3.1 X-ray Diffraction (XRD)

The synthesized in-house Zn-Mg-Al catalyst was analysed by X-ray Diffraction (XRD) using a diffractometer equipped with secondary monochrometer (Bruker D8 ADVANCE, Germany), CuKα1 radiation and interface to a DACO-MP data acquisition microprocessor provided with Diffract / AT software. The purpose of the analysis is to confirm the synthesized in-house catalyst revealed the hydrotalcite-like compound pattern from XRD library.

3.3.2 Nitrogen Adsorption using Brunauer- Emmett- Teller (BET) Technique

Textural properties of the catalyst such as specific surface area, pore sizes and pore volume was measured by using Brunauer- Emmett- Teller (BET) technique (BELCAT; MicrotracBEL Corporation, Japan) under relative pressure range from 0.05 to 0.98. The average distribution of pore sizes was calculated using the BJH method. The adsorption and desorption isotherms were obtained at -196 ^{o}C. Prior to each measurement, all samples were degassed at 120 ^{o}C for 5 hours under vacuum. The pore volume and pore size distributions were obtained according to the Barret-Joyner-Halenda (BJH) method from the adsorption branch data. For this analysis, both fresh and calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15 were analysed their surface area.

3.3.3 Temperature-Programmed Desorption (TPD)

The acidic and basic active sites of the catalysts (calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15) were determined using a Temperature-Programmed Desorption (TPD) method (BELCAT; MicrotracBEL Corporation, Japan) under the following conditions: Pre-treatment at 500 °C for 2 hours. Probe: NH_3 (acidic active site) and CO_2 (basic active site). The temperature programmed was set from 50 °C to 800 °C at ramping rate 5 °C.min^{-1} according to Padmasri *et al.*, (2002).

3.4 Production of Glycol Ester

Esterification can be carried out either autocatalytic or aided by catalyst. The heating system used are such as conventional method or energy saving system (microwave heating). The purpose of this study was to investigate autocatalytic and catalytic esterification of lauric acid with diethylene glycol.

3.4.1 Conventional Autocatalytic Esterification as Benchmark

The autocatalytic esterification was carried out for the purpose of benchmark since there was no study on glycol ester previously. Lauric acid (LA) was reacted with diethylene glycol (DEG) conventionally in a 250 ml three-neck spherical flask fitted with a magnetic stirrer, thermometer and a distillation condenser as shown in Figure 3.4a. The glass reactor allowed visual inspection of the reactor content during reaction. The process produces two major products, diethylene glycol mono-laurate (DEG-ML) and diethylene glycol di-laurate (DEG-DL). Water was generated as a by-product. The reactants were mixed and heated to the desired reaction temperature and no vacuum was applied.

The reaction was completed when acid value (AV) of fatty acid is achieved to the required application needs (AV < 4 mg KOH. g^{-1} sample). Removal of water is important, as its removal will favor the forward reaction. The unreacted starting material (DEG) and moisture in the product mixture were then further removed by vacuum distillation. After distillation, the palm-based fatty acid glycol ester was obtained. The reaction conditions of the esterification were optimized by varying parameters such as reactants mole ratio, reaction temperature and stirring rate. The effect of parameters were evaluated over lauric acid conversion. The reaction temperature was varied between 150 ^{o}C-230 ^{o}C. The reactants mole ratio (LA: DEG) was also varied (1:1, 1:1.5 and 2:1). The experiments were carried out at atmospheric pressure and the stirring rate was varied from 300 rpm to 1200 rpm.

3.4.2 Conventional Preliminary Screening of Catalytic Esterification

The optimum operating conditions obtained from Section 3.4.1 was used for the preliminary screening of the catalyst in esterification reaction. Comparison of the catalytic performance between the homogeneous and heterogeneous catalysts were evaluated. The homogeneous *p*-toluene sulphonic acid (*p*-TSA) catalyst and three types of heterogeneous catalysts (in-house calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15) were used in esterification of lauric acid (0.5 mole, 100 g) with diethylene glycol (0.25 mole, 26.5 g) using conventional heating as illustrated in Figure 3.4a. It is important to note that, at higher temperature of homogeneous catalytic esterification using *p*-TSA, may lead to the formation of catalyst ester in the product mixture with high toxicity and harmful to others (MPOB Report No. 824, 2017).

3.4.3 Esterification of Lauric Acid and Diethylene Glycol via Microwave Heating

The esterification of lauric acid (LA) and diethylene glycol (DEG) was carried out using microwave heating (MARS SYNTHESIS, CEM Corporation USA) focusing on the heterogeneous catalytic obtained from preliminary screening. Three types of heterogeneous catalysts (in-house calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15) were used in the screening as mentioned in previous section 3.4.2. Esterification performed in the absence of catalyst was also carried out for control purposes and denoted as blank reaction.

Figure 3.4b shows the schematic diagram of the experimental set-up of microwave system equipped with two magnetrons, a 250-ml three-neck round bottom glass reactor, magnetic stirrer, distillation condenser and fibre optic temperature sensor. 5% w/w catalyst dosage was charged in reactant mixture containing LA (0.5 mole, 100 g) and DEG (0.25 mole, 26.5 g). The operating conditions was set at temperature of 210 ºC with reactants mole ratio of 2:1 (LA: DEG) and 180 min of reaction time. The best catalyst performed on the catalytic activity were then will be used for further optimization of other parameters to maximize the di-ester content. Optimization of other parameters was performed with continuous magnetic stirring at 300 rpm, the reaction temperature was varied from 120 ºC to 210 ºC. Other investigated parameters were catalyst dosage, reactant mole ratio, reaction time and catalyst reusability as tabulated in Table 3.3. The reactor vessel was removed after allowing the reaction mixture to cool to 50 ºC. The heterogeneous catalyst was separated by vacuum filtration after the reaction completed.

Product mixture was then analysed using gas chromatography. The percentage conversion of lauric acid was represented as equivalent to the glycol esters formed. Data reported were the average value ± standard errors of the measurement. Each experiments were performed in triplicate.

Table 3.3: Range of process conditions investigated for the reaction

Reaction Parameter	Range	Unit
Mole ratio (lauric acid : diethylene glycol)	2:1- 2: 2.5	-
Temperature	120- 210	$^{\circ}C$
Catalyst Dosage	1-9	%
Catalyst Particle Size	100 – 1000	µm
Reaction Time	20- 180	min
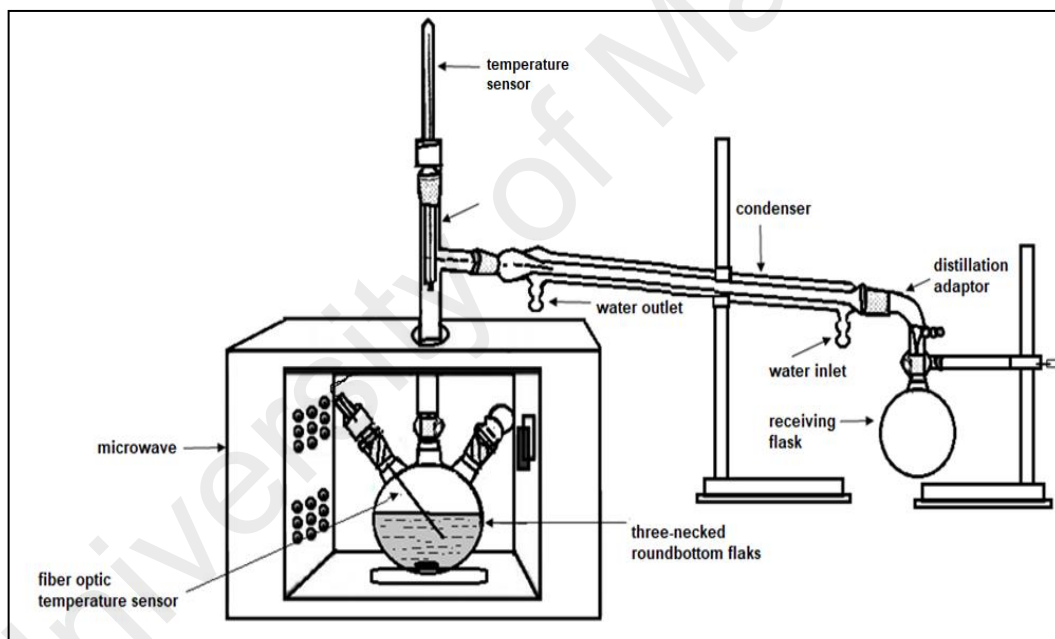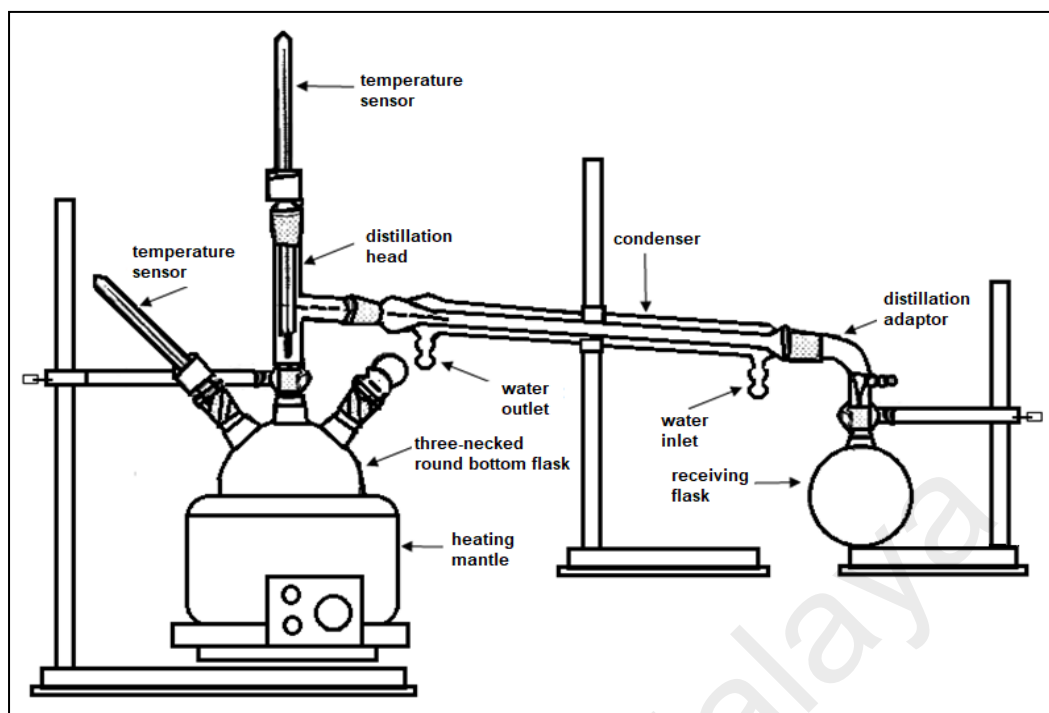
Figure 3.4: Catalytic esterification set-up via; a) conventional heating, b) microwave heating.

3.5 Effect of Process Parameters on Catalytic Esterification of Lauric Acid via Microwave Heating

The effect of process parameters in esterification of lauric acid and diethylene glycol such as reaction temperature, reactant mole ratio, catalyst particle size, catalyst dosage and reaction time on the lauric acid conversion was investigated. The influence of reactant mole ratio parameter was also observed on the composition of mono- and di-glycol ester.

The percentage of conversion was calculated using the equation (3.1).

$$\text{Conversion of lauric acid (\%)} = \left\{ \frac{\text{Weight of lauric acid reacted}}{\text{Initial weight of lauric acid}} \right\} \times 100$$

(3.1)

Where the amount of lauric acid reacted was calculated based on the peak area (%) of lauric acid analyzed by gas chromatography analysis and the initial weight of lauric acid is the initial amount of the raw material used in the reaction.

A few preliminary experimental works were conducted to observe the influence of process parameters on the lauric acid conversion and the yield of mono- and di-ester content. The parameters range was based on the previous studies reported that similarly related to this esterification process in the presence of heterogeneous catalyst. The evaluation approach of this study was based on one-factor-at-a-time method.

3.5.1 Effect of Reactants Mole Ratio

The catalytic activity of calcined Zn-Mg-Al on esterification of palm-based lauric acid to glycol ester via microwave heating was further inspected by varying reactant mole ratio. Five mole ratios were evaluated at 2:1, 2:1.3, 2: 1.5, 2:1.7 and 2:2.5 to investigate the influence of reactant mole ratio on the formation of diethylene glycol (DEG) mono- and di-ester content. Other reaction conditions were held constant at reaction temperature of 190 $^\circ$C, 5% w/w catalyst dosage, 300 rpm and reaction time of 90 min.

3.5.2 Effect of Reaction Temperature

Effect of temperature on lauric acid conversion was investigated by varying the temperature at 120, 150, 170, 190 and 210 $^\circ$C while keeping all the other reaction conditions at constant values. Reaction was conducted at atmospheric pressure, agitator speed of 300 rpm and mole ratio of 2:1 (LA: DEG). The lowest temperature was chosen at 120 $^\circ$C as lower than that, the reaction rate was too slow. The maximum temperature studied was at 210 $^\circ$C as the boiling point of diethylene glycol is at 220-230 $^\circ$C.

3.5.3 Effect of Catalyst Dosage

Effect of catalyst dosage on lauric acid conversion was studied by varying the dosage at 1, 3, 5, 7 and 9% w/w of lauric acid. Other process parameters were held constant at reaction temperature of 190 $^\circ$C, agitator speed of 300 rpm and mole ratio of 2:1.3 (LA: DEG).

3.5.4 Effect of Catalyst Particle Size

The particle size distribution of the catalyst was measured using stack of sievers varied from 100 to 1000 µm mesh size. The sieve shaker (Automatic Sieve Shaker D403, Milano Italy) which will separate the catalyst into various size range. Effect of catalyst particle size on lauric acid conversion was studied using different particle sizes (100 µm, 212 µm, 500 µm, 710 µm and 1000 µm). Other process parameters were held constant at reaction temperature of 190 °C, 5% w/w of calcined Zn-Mg-Al catalyst, agitator speed of 300 rpm and mole ratio of 2:1.3 (LA: DEG).

3.5.5 Effect of Reaction Time

Effect of reaction time on conversion of lauric acid was studied by varying the duration from 20 min to 180 min. Other process parameters were held constant at reaction temperature of 190 °C, 5% w/w calcined Zn-Mg-Al catalyst dosage sieved at 212 µm, agitator speed of 300 rpm and 2:1.3 mole ratio of LA to DEG.

3.6 Recyclability and Leaching Tests of Catalyst

The evaluation of the Zn-Mg-Al catalyst recyclability was performed for eight cycles in esterification of lauric acid using optimized reaction parameters. For the purpose of comparison, the reusability of tin (II) oxalate and Amberlyst-15 were also conducted. After the first cycle, the catalysts are recovered from product mixture by vacuum filtration and centrifugation. The next step was overnight drying to remove moisture from catalyst cake and the subsequent cycle was resumed without any further pre-treatment.

Leaching of the catalyst into the product would implicate a time-consuming and costly cleaning step, which would make the whole process more expensive. According to Gruber-Woelfler *et al.*, (2013), leaching of the active species of the catalyst into the reaction medium was determined by measuring the metal content in glycol ester sample using the Inductively-Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The analysis was conducted using Perkin Elmer Emission Spectrometer Model Plasma 1000. For sample preparation, 1 g of glycol ester sample was added into 10 ml nitric acid (50% concentration) and the sample mixture was heated for 10 min at 95 $^{\circ}$C. Then, 5 ml of concentrated nitric acid (HNO_3) was added to the mixture and heated for another 30 min at 95 $^{\circ}$C. After the mixture was cooled down, 2 mL of deionized water and 3 mL of hydrogen peroxide (30% concentration) were added into the mixture and heated again for 2 hours at 95 $^{\circ}$C. Subsequently, 7 mL of hydrogen peroxide (30% concentration) and 10 mL of concentrated hydrochloric acid were added into the mixture and heated again for 15 min at 95 $^{\circ}$C. Finally, the sample mixture was cooled down, filtered and marked up to 100 mL with deionized water.

3.7 Analyses and Property Evaluation of Fatty Acid Glycol Esters

The progress of the reactions was monitored by acid value (AV) determination for samples withdrawn at selected reaction intervals. The percentage (%) of unreacted diethylene glycol was measured by the hydroxyl value (OHV) analysis. Gas chromatography analysis (GC) was used to detect the number of compounds present in the product mixture as percentage under the GC peak area appointed for each ester (DEG mono-ester and DEG di-ester) together with the unreacted fatty acid as starting material.

3.7.1 Acid Value Analysis

Titration method was used to estimate the acid value (AOCS Official Method Te 1a-64) which determine the amount of fatty acids consumed during the esterification process.

3.7.2 Moisture Content Analysis

Water content in the sample was analyzed using Mettler Toledo C30 Karl Fischer Compact Titrator. About 0.5 mL of sample was weighted using syringe. A few drops was injected into the sample chamber and the syringe was weighed again using back-weighing technique. Once the titration was completed, the percentage of moisture will be calculated automatically.

3.7.3 Hydroxyl Value Analysis

Hydroxyl value was defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram sample, mg KOH. g^{-1} sample. The analysis was applicable to fatty acids and their derivatives, such as fatty alcohols, mono- and diglycerides and hydroxystearic acids according to AOCS Official Method Cd 13-60. The analysis was divided into two parts, which are determination of acidity and determination of acetylation. Table 3.4 shows the amount of sample needed for the acetylation according to the hydroxyl value. A pyridine-acetic anhydride reagent was prepared by mixing 3 volumes of pyridine with 1 volume of acetic anhydride. 5 mL of pyridine-acetic anhydride reagent was pipetted and added to the flask containing the sample. Another 5 mL reagent was pipetted and poured into an empty flask for the reagent blank.

Table 3.4: Amount of sample for acetylation according to the hydroxyl value (AOCS Method Cd 13-60)

Hydroxyl value	Sample weight
0 to 20	10 g ± 0.1 g
20 to 50	5 g
50 to 100	3 g
100 to 200	2 g
Fatty alcohol	1 g

3.7.4 Hydrophilic-Lipophilic Balance (HLB) Index

The Hydrophilic-Lipophilic Balance (HLB) method is based on the premise that all surfactants combine both hydrophilic and lipophilic groups in one molecule and that the proportion between the weight percentages of these two groups for non-ionic surfactants is an indication of the behavior that may be expected from that product as indicated in Table 3.5.

Table 3.5: Hydrophilic-Lipophilic Balance (HLB) scale with classification of surfactant function (Griffin, 1954)

Region	Functions	HLB Index
Hydrophobic (oil soluble)	antifoaming agents	2-3
	w/o emulsifying agents	3-6
Water dispersible	wetting and spreading agents	7-9
Hydrophilic (water soluble)	o/w emulsifying agents	8-16
	Detergents	13-15
	solubilizing agents	15-18

The HLB index is useful because it allows a prediction of the action that may be expected from a surfactant; for example a low value, about 4, will be a water-in-oil emulsifier; a high value, about 16, will be a solubilizer. What is referred to here is the type of behavior that can be expected, rather than the efficiency that will be accomplished. When two non-ionic emulsifiers, one hydrophilic and the other lipophilic, were mixed in varying ratios the efficiency of the blend as an emulsifier for a particular oil would reach a maximum. By using pairs of different surfactants to emulsify the same oil, it is apparent that this maximum occurred at the same weight percentage of hydrophilic substance in the surfactant blend. Thus, the HLB value is a function of the weight percentage of the hydrophilic portion of the molecule of a non-ionic surfactant and may be calculated for non-ionic surfactant using Griffin's Method (Griffin, 1954).

3.7.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

Proton (^{1}H) and Carbon (^{13}C) NMR spectra was determined using a 400 MHz JEOL NMR spectrometer (USA). NMR is an analytical chemistry technique to determine the content and purity of a sample as well as its molecular structure. NMR can quantitatively analyse mixtures containing known compounds. For unknown compounds, NMR can either be used to match against spectral libraries or to infer the basic structure directly. Once the basic structure is known, NMR can be used to determine molecular conformation in solution as well as studying physical properties at the molecular level such as conformational exchange, phase changes, solubility and diffusion.

3.7.6 Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR)

Products obtained were then further characterised using Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR Spectrum 100, Perkin Elmer, USA) spectroscopy to determine functional group. Approximately 22 mg of the ester samples were placed in the sampling accessory obtaining the best contact with the crystal. The empty accessory was used to obtain the background spectrum. The approximate total time required for spectral collection was 5 min. All spectra were recorded within a range of 4000-600 cm^{-1} with a 4 cm^{-1} resolution. Each spectrum was calculated as the average of 20 scans and subjected to background subtraction. The tests were carried out in triplicates and the average of the three were used to construct the models.

3.7.7 Gas Chromatography (GC)

The reaction products were separated by gas chromatography (HP5890, Agilent Technologies, USA) equipped with SGE-HT5 capillary column (30 m x 250 µm x 0.1 µm) and detected by flame ionization detector (FID) at 360 $^{\circ}$C. The oven was set initially at 100 $^{\circ}$C, held for 5 min and increased at ramping rate of 6 $^{\circ}$C min^{-1} to 350 $^{\circ}$C. The flowrate of helium gas (as a carrier) was set at 20 mL. min^{-1} and the injector temperature with split ratio of 10:1 was set at 350 $^{\circ}$C.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of Catalyst

The synthesized in-house catalyst (Zn-Mg-Al) was characterized its pattern identification, surface area measurement and acidic basic active sites determination. For commercial catalysts (Amberlyst-15 and tin (II) oxalate), only surface area and acidic basic active sites were measured, in order to observe the effect on the catalytic performance towards spectroscopy behaviour.

4.1.1 X-ray diffraction (XRD) of Calcined Zn-Mg-Al

In order to produce a selective and active solid catalyst, an X-ray diffraction (XRD) analysis was employed. X-ray diffractogram in Figure 4.1 indicates calcined Zn–Mg–Al catalyst revealed the hydrotalcite-like compound pattern. According to the '*search and match*' technique and phase identification database, the pattern peaks of calcined Zn-Mg-Al corresponding to (100), (002), (101), (110), (103) and (112) planes matched with zinc magnesium aluminium hydroxide carbonate hydrate pattern ($Zn_{0.33}$ $Mg_{0.67}$ $Al_{0.33}$ $(OH)_2$ $(CO_3)_{0.167}$ $(H_2O)_{0.5}$) (Vaccari, 1998).
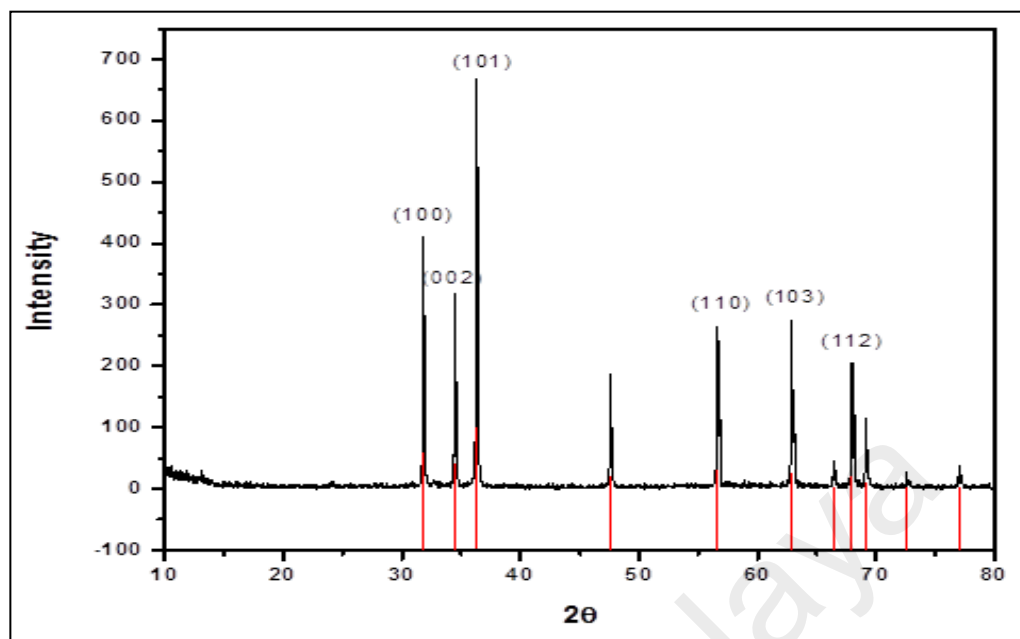
Figure 4.1: X-Ray Diffraction (XRD) pattern of calcined Zn-Mg-Al catalyst

4.1.2 Specific Surface Area, Pore Sizes and Pore Volume of Calcined Zn-Mg-Al

Physisorption studies were carried out for both fresh and calcined Zn-Mg-Al catalyst to determine the textural properties, the isotherm adsorption/desorption and pore size distribution. Fresh Zn-Mg-Al catalyst as precursor was prepared up to drying step and this precursor was compared with calcined Zn-Mg-Al catalyst in terms of properties changes. As can be observed in Figure 4.2, both fresh and calcined Zn-Mg-Al catalysts have the characteristic of mesoporous materials as they show type IV isotherm with pronounced N_2 hysteresis loop (Zou *et al.*, 2006). These catalysts attributed to the capillary condensation in the mesoporous medium at relative pressure of 0.65-0.98. Both catalysts exhibit the narrow pore size distribution at the range of 12-120 Å (1.2- 12 nm) as demonstrated in the BJH pore-size distribution.
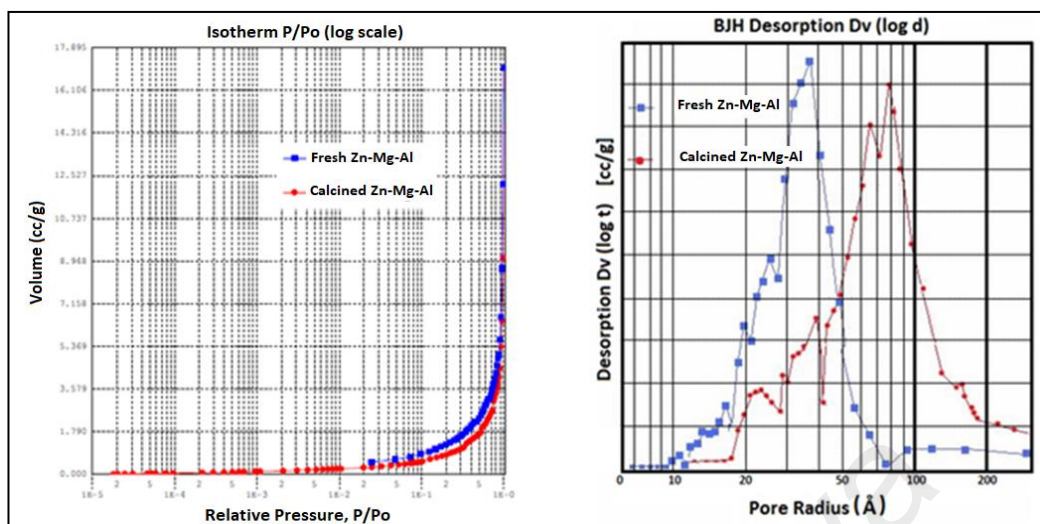
Figure 4.2: N$_2$ sorption curves and pore size distribution of Zn-Mg-Al catalyst

Table 4.1 summarizes the textural properties of Zn-Mg-Al catalysts. The specific surface area measured for fresh Zn-Mg-Al catalyst was 81 m^{2}g^{-1}. The surface area was increased to 117 m^{2}g^{-1} when the catalyst sample was calcined at 600 °C. The result agreed with the principle of calcination that larger surface area can provide larger active site (Witoon *et al.*, 2018). Hence, lauric acid and diethylene glycol molecules could effectively and selectively react due to ample active sites provided by calcined Zn-Mg-Al. This catalyst is potentially able to promote the esterification of lauric acid with diethylene glycol at ambient pressure, attributed to its mesoporous pore volume range from 2 to 50 nm.

Table 4.1: Textural properties of Zn-Mg-Al catalysts

Catalyst	S_{BET} (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Diameter (nm)	Atomic Ratio [M(II) : M(III)]
Fresh	81	0.19	3.81	3.04: 1.00
Calcined	117	0.59	7.74	3.09: 1.10

4.1.3 Temperature Programmed Desorption of Calcined Zn-Mg-Al

The acidic-basic active sites of the calcined Zn-Mg-Al catalyst were determined by TPD of NH_3 and CO_2. For the purpose of comparison, the acidic-basic properties were also obtained for the two other commercial catalysts (tin (II) oxalate and Amberlyst-15). Figure 4.3 presented the NH_3-TPD and CO_2-TPD profiles of the calcined Zn-Mg-Al catalyst.

The ammonia desorption curves (NH_3-TPD) in Figure 4.3a indicates desorption of ammonia reached a first maximum at 130 ^oC due to the existence of hydroxyl group in materials, attributed to the presence of Bronsted acid sites on catalyst surface (Di Cosimo *et al*., 2000; Shen *et al.*, 1998). High concentration of acidic active sites was measured in calcined Zn-Mg-Al catalyst with 0.65 mmol.g^{-1}. The difference in the electronegativity of magnesium (Mg) and zinc (Zn) leads to the production of more acidic hydrotalcite-like compound structure (Sanchez *et al.*, 2014; Bezen *et al.*, 2011; Rossi *et al.*, 2016).

The peaks obtained in the CO_2-TPD profiles as shown in Figure 4.3b can be consigned based on the analysis at the temperature range of 100 °C – 500 °C. At this condition, literature reported that the Mg-Al mixed oxides are characterized by the presence of CO_2 desorption peaks (Debek *et al.*, 2015; Pavel *et al.*, 2012). The behavior of this CO_2 desorption peaks can be defined as a shoulder at 100 °C – 500 °C, attributed to CO_2 desorption from weak Bronsted hydroxyl group (weak-strength basic sites) as discussed by Di Cosimo *et al.,* (1998). It is mentioning that calcined Zn-Mg-Al exhibits both acidic-basic active sites due to its bifunctional catalyst type. However, in the case of esterification, only acidic active site is being used.
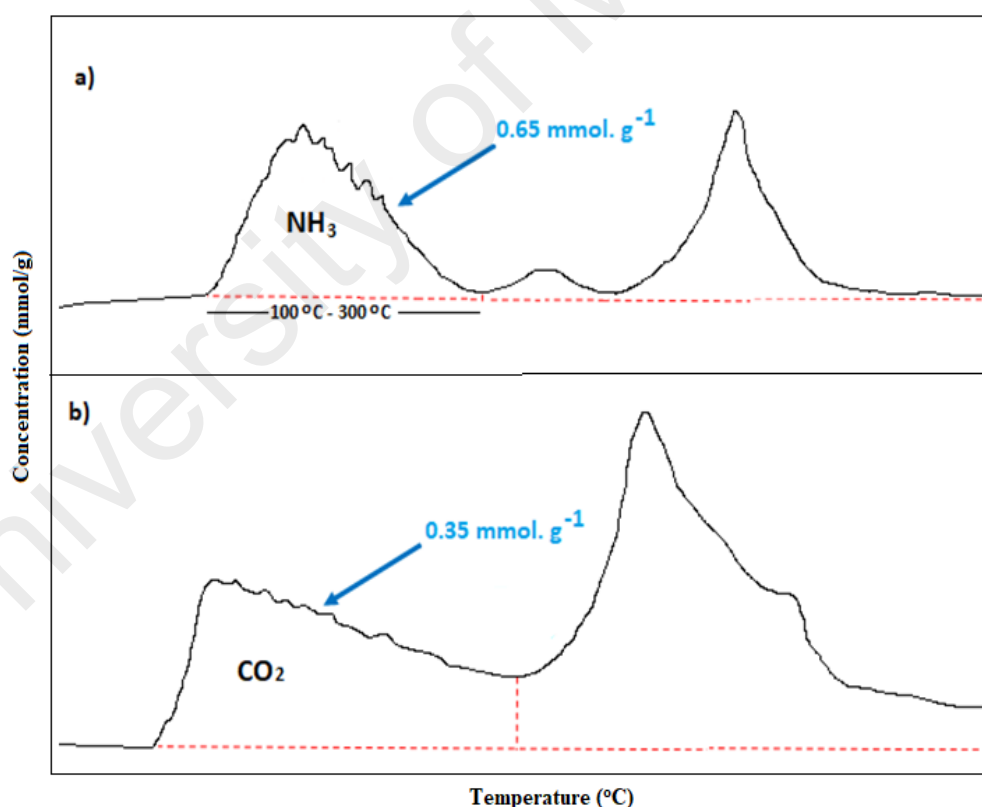
Figure 4.3: Temperature-Programmed Desorption (TPD) spectra of calcined Zn-Mg-Al catalyst a) NH₃-TPD (acidic active sites); b) CO₂-TPD (basic active sites);

A summary of surface area, acidic and basic active sites of the catalysts used in the esterification of diethylene glycol and lauric acid are listed in Table 4.4. The characteristics were analysed using Brunaeur-Emmett-Teller (BET) method and temperature program desorption (TPD), respectively. Amberlyst-15 exhibits the highest acidity with 1.7 mmol.g^{-1} although smaller surface area was measured (43 m^2.g^{-1}). As for tin (II) oxalate, the surface area and acidic active sites were determined to be 52 m^2.g^{-1} and 0.30 mmol.g^{-1}, respectively. In theory, the reactant is adsorbed on the surface of the catalyst and the effective concentration of the reactant is generally increased on the surface, the reactants are brought closer and the reaction speed is increased. The synergistic effect of textural properties could lead to the improvement of the catalytic performance (Emam, 2013; Fatimah *et al.*, 2014)

Table 4.2: Surface area, acidic and basic active sites of catalysts

Catalyst	Surface area (m^{2}g^{-1})	Acidic Active Site (mmol.g^{-1})	Basic Active Site (mmol.g^{-1})
Calcined Zn-Mg-Al	117	0.65	0.35
Tin (II) oxalate	52	0.30	n.a
Amberlyst-15	43	1.7	n.a

4.2 Conventional Autocatalytic Esterification of Lauric Acid

To the best of knowledge since there is no study has been reported on the production of glycol ester, the autocatalytic esterification reaction was carried out between lauric acid and diethylene glycol as a benchmark. The proposed possible products from the reaction are shown in Figure 4.4 which are such as diethylene glycol mono-laurate (DEG-ML), diethylene glycol di-laurate (DEG-DL) and water.
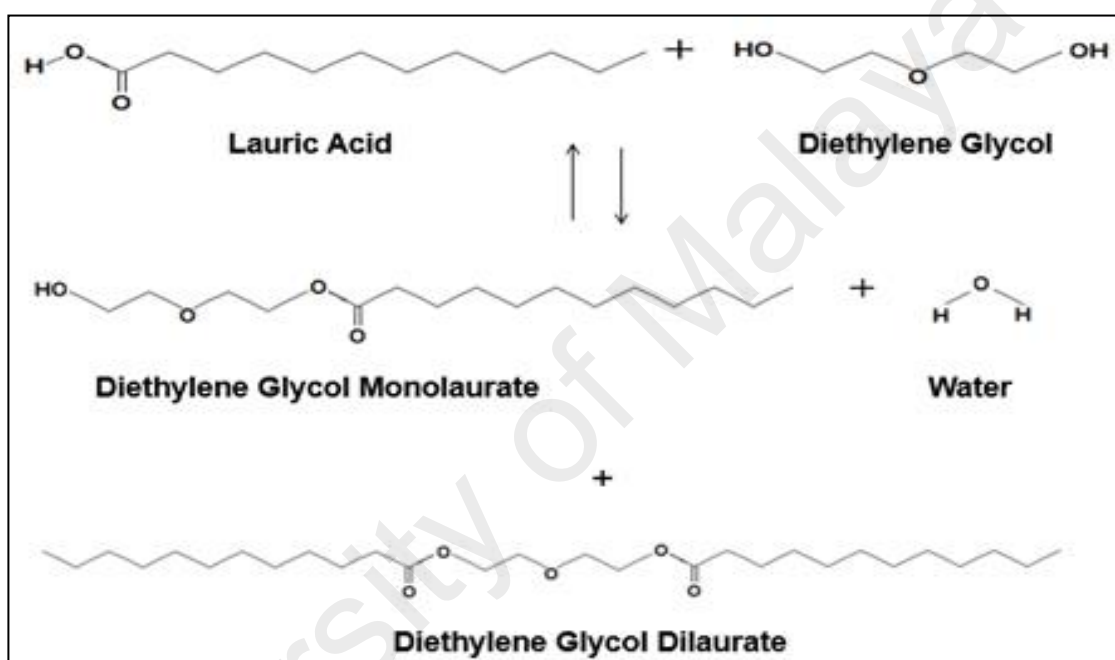
Figure 4.4: Stoichiometric scheme of esterification between lauric acid and diethylene glycol

4.2.1 Effect of Stirring Speed Rate

Figure 4.5 shows the effect of stirring speed rate on lauric acid (LA) conversion. Based on the conversion trend, stirring speed rate have no influence on the reaction rate. At the reaction temperature of 150 ºC, the conversion of LA increased slightly from 88.5% up to 89% with the increase of stirring speed rate from 300 rpm to 1200 rpm.

Similar trend was observed when the reaction was performed at reaction temperature of 210 ºC with LA conversion of 93.4% at 300 rpm. This indicates that the effect of stirring speed rate on LA conversion was negligible. Hence, the optimum stirring speed rate chosen was 300 rpm to ensure complete mixing.
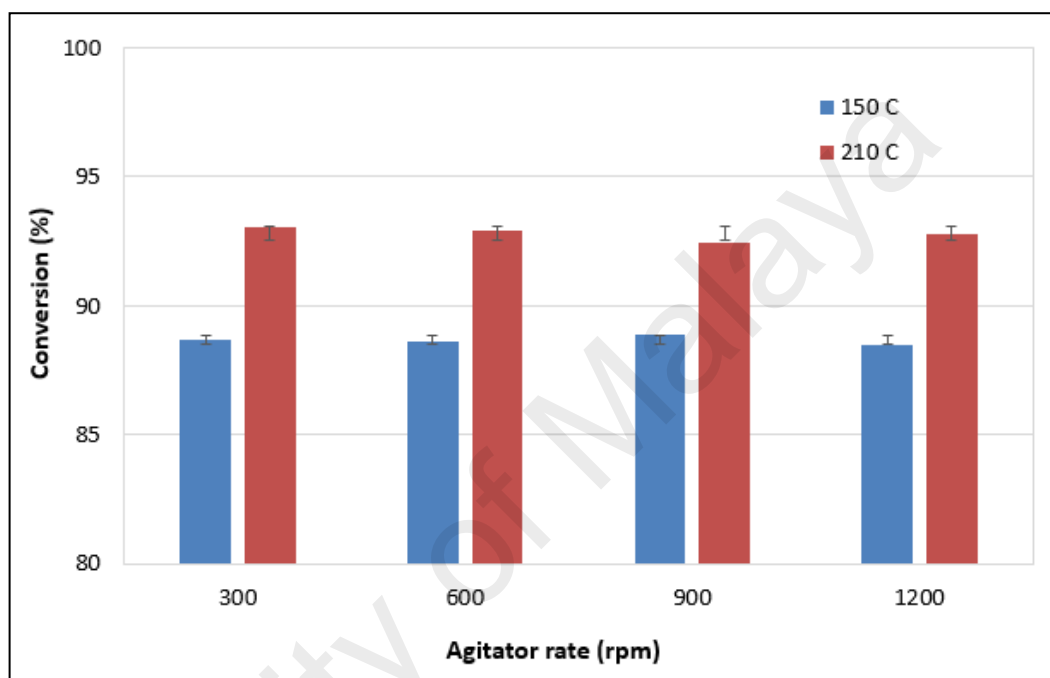
Figure 4.5: Effect of stirring speed rate on lauric acid conversion. reaction conditions: 150 ºC and 210 ºC, mole ratio of 1:1 (LA: DEG), at atmospheric pressure

4.2.2 Effect of Reaction Temperature

The effect of reaction temperature on the esterification was studied at 150 ºC, 170 ºC, 190 ºC, 210 ºC and 230 ºC. Other process parameters were fixed at mole ratio of LA: DEG of 2:1 and 300 rpm. Figure 4.6 shows the plot of LA conversion increased with the increase in temperature. At lower temperature of 150 ºC, a minimal conversion was obtained with 72% LA conversion throughout 20 hours reaction time.

71

After 22 hours, the reaction reached equilibrium with a maximum LA conversion of approximately 74%. A slightly higher conversion was observed when the reaction was conducted at 170 ºC with maximum conversion of 82%. At temperature of 190 ºC, the conversion of LA increased rapidly to more than 80% within 10 hours of reaction time and started to reach plateau after 12 hours of reaction time. By increasing the temperature to 230 ºC resulted in an apparent increased conversion with maximum LA conversion of more than 90% and it approached a plateau after 4 hours of reaction time. Hence, 230 ºC was found to be the best temperature to perform the esterification as there is the limitation of DEG which starts to boil at 245 ºC (MSDS of Diethylene Glycol).
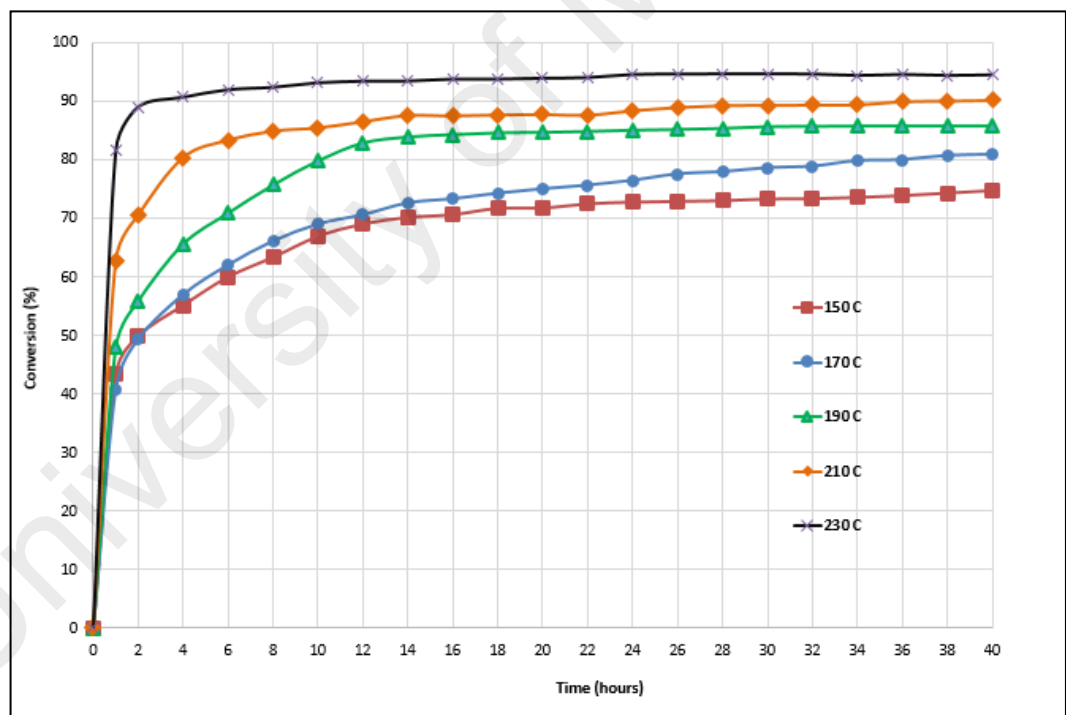

Figure 4.6: Effect of reaction temperature on lauric acid conversion reaction conditions: molar ratio of LA: DEG = 1:1, 300 rpm and 40 hours at atmospheric pressure

4.2.3 Effect of Reactants Mole Ratio

To study the effect of mole ratio of LA: DEG on product composition, three mole ratios were investigated, i.e 1:1, 1:1.5 and 2:1. Figure 4.7 shows that as the molar ratio of LA to DEG was increased from 1:1 to 2:1, DEG-DL content increased whereas DEG-ML content decreased. At mole ratio of 1:1, a maximum percentage composition of DEG-ML obtained was 42.9% with DEG-DL content of 49.5%. After 20 hours reaction time, the compositions of DEG-ML and DEG-DL content were at constant due to no excess of DEG to speed up the reaction. Acid value (AV) was determined to be 8.5 mg KOH.g^{-1} sample with LA conversion 93.4%. By using excess amount of DEG in the reaction while setting the mole ratio of LA: DEG at 1:1.5 resulted in the increase of DEG-DL content of 54.9% with traces amount of unreacted LA detected. It is also note advisable to use excess DEG as this require extra step of DEG separation from the product.

The autocatalytic esterification was then performed between 2 mole of LA reacted with a mole of DEG with the aim to increase the production DEG-DL at lowest acid value. The other parameters were fixed at constant value. Based on plot of the trend composition of the DEG-ML and DEG-DL as shown in Figure 4.8, LA was reacted further with DEG-ML to form the DEG-DL. The DEG-ML composition was reduced with the increment of DEG-DL content in the reaction mixture. The observation was also in accordance with only traces amount of DEG are detected in the product. The lowest AV and hydroxyl value (OHV) obtained measured was 3.75 mg KOH.g^{-1} sample and 15.3 mg KOH.g^{-1} sample, respectively. The maximum composition of DEG-ML and DEG-DL obtained were 0.79% and 96.2%, respectively. Therefore, the mole ratio of 2:1 was chosen as the optimum ratio.
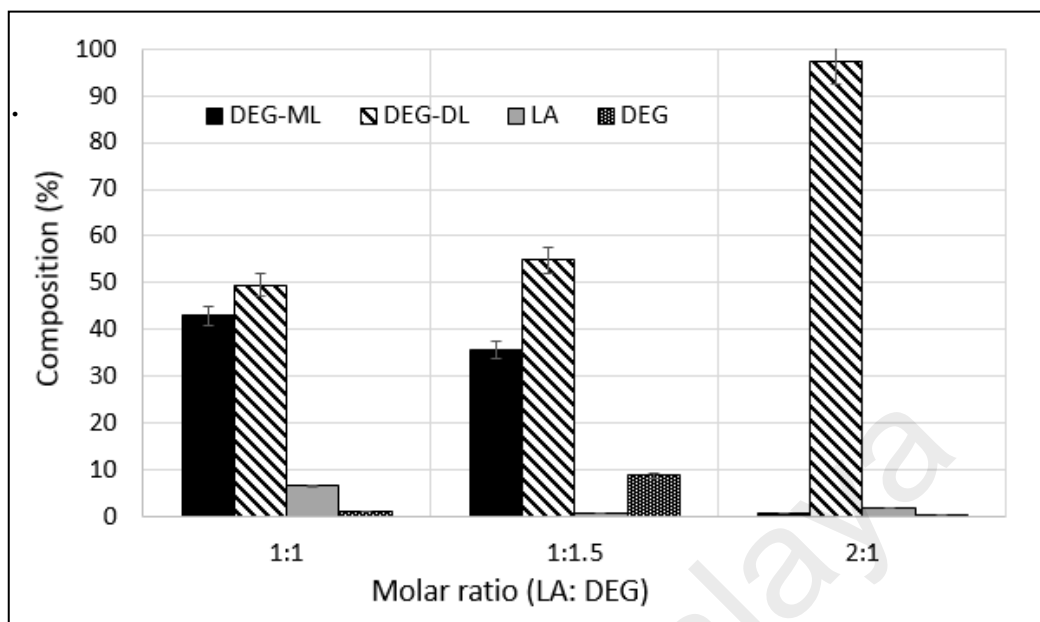
Figure 4.7: Effect of reactants mole ratio (LA: DEG) on DEG mono-laurate (DEG-ML) and DEG di-laurate (DEG-DL) compositions. reaction conditions: 230 ^{O}C, 1 atm., 300 rpm and 20 hours
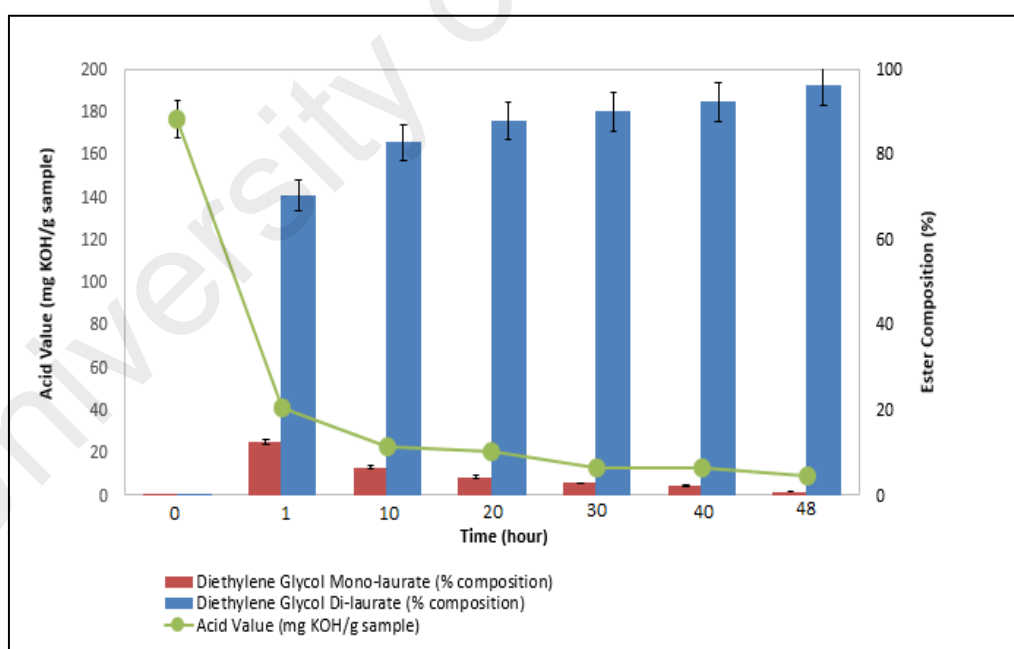
Figure 4.8: Acid value profile and products composition for autocatalytic esterification via conventional heating. Reaction conditions: 230 ºc, 1 atm., 300 rpm, 1:1 mole ratio of LA: DEG and 48 hours

74

4.2.4 Effect of Vacuum Distillation on Moisture Content

Table 4.3 tabulate the properties and percentage compositions of autocatalytic of lauric acid (LA) and diethylene glycol (DEG). Based on this table, it appeared that by using 2 moles of LA in the reaction, the composition of di-ester (DEG-DL) increased to 94% as compared with mole ratio of 1: 1 (LA: DEG). The moisture content obtained for DEG-DL was higher than the allowable limit (max 0.2%). Hence, further purification on the product was carried out using vacuum distillation. The aim of this additional step is to remove the water content lower than 0.2%. Besides, this post-treatment could also distilled-off the unreacted DEG to ensure higher purity of glycol ester. The condition for vacuum distillation was set at 14 mbar and temperature of 120 $^{\circ}$C. The moisture content and OHV after drying was reduced to 0.12% and 11.8 mg KOH.g^{-1} sample, respectively. The composition of DEG-DL also increased up to 1%, whereas AV reduced to 18% after the procedure.

Table 4.3: The properties and percentage composition (based on GC chromatogram) of autocatalytic of lauric acid and diethylene glycol

Vacuum Distillation	Properties **			Compound Composition (Based on GC Chromatogram)			
	AV [a]	OHV [b]	H$_2$O [c]	LA unreacted (%)	DEG unreacted (%)	DEG-ML (%)	DEG-DL (%)
Before	3.75	15.3	0.38	3.01	0.01	0.79	96.21
After	3.09	11.8	0.12	2.05	0.00	0.78	97.17

[a] AV =acid value; [b] OHV = hydroxyl value; [c] H$_2$O = moisture content;
** Reaction conditions: mole ratio LA: DEG= 2:1, 230 ºC, 1 atm, 300 rpm, 48 h
   Vacuum distillation conditions: 120ºC, 14 mbar, 4 h

4.2.5 Product Characterization

Nuclear Magnetic Resonance (NMR) Analysis

The product from esterification reaction was characterized by Nuclear Magnetic Resonance (NMR). Figure 4.9 shows the ^{1}H-NMR spectra of DEG-DL. DEG-DL with 97.17% purity was analyzed with the proton (^{1}H) NMR. –CH$_3$ in the lauric acid portion was referred to the peak at 0.875 ppm (t, 3H). –CH$_2$- in the lauric acid part was corresponded to the peak at 1.24 ppm (s, 16H). Other peaks at 1.61 ppm (s, 2H) and 2.31 ppm (t, 2H) belonged to R-CH$_2$-CH$_2$-COO- group. Another group recognized as HO-CH$_2$-CH$_2$-OOC-R was also identified at the peaks at 3.68 ppm (t, 2H) and 4.22 ppm (q, 2H).
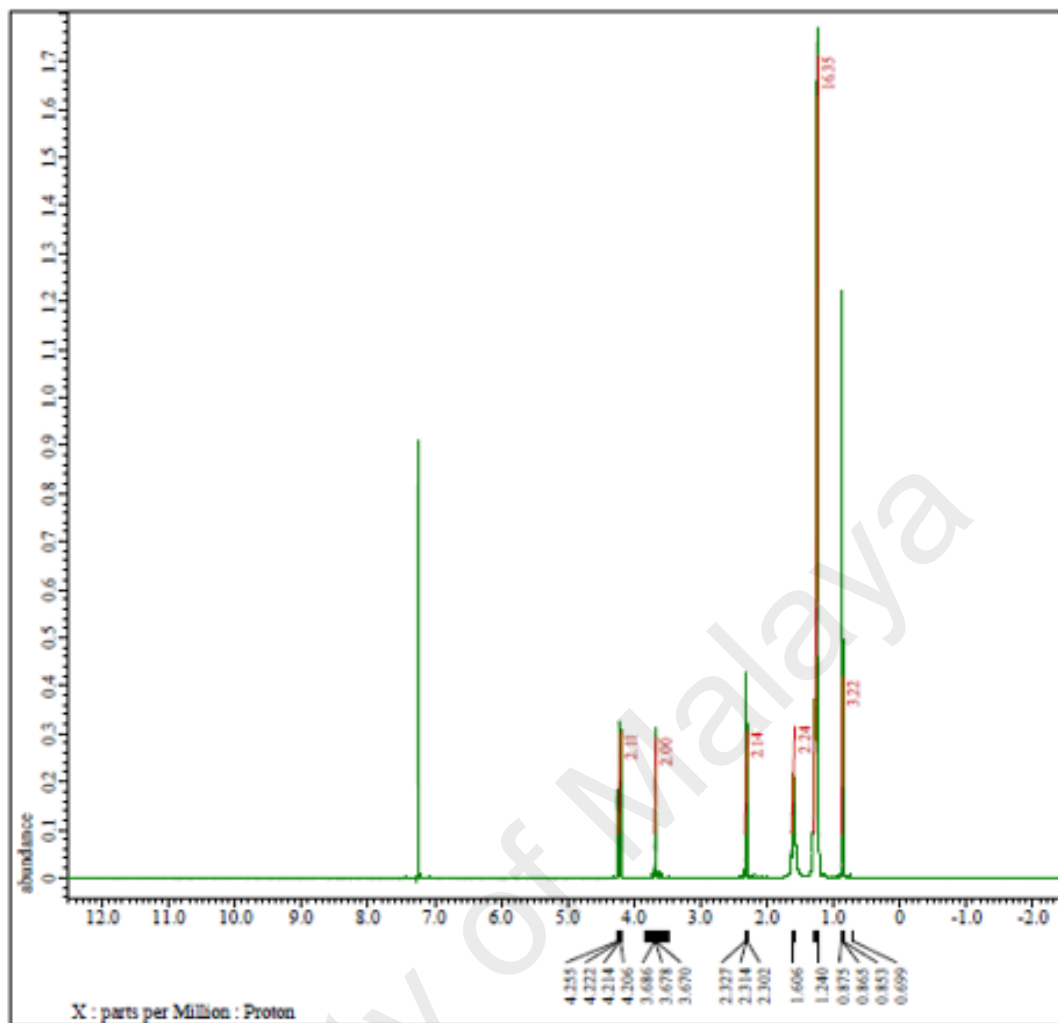
Figure 4.9: ^{1}H Nuclear Magnetic Resonance (NMR) spectra of palm-based diethylene glycol di-laurate (97.17% purity)

Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR)

The functional group analysis of starting materials and DEG-DL produced at different reaction time were investigated using ATR-FTIR. FTIR spectra shown in Figure 4.10 illustrates DEG compound obtained at wavenumber 3346 cm^{-1} corresponding to a peak of hydroxyl (OH-) stretching. However, this peak vanished in the DEG-DL spectra. At wavenumber of 1696 cm^{-1} in the LA spectra revealed carboxylic group stretched and ester group was produced at wavenumber 1737 cm^{-1}. The C-O stretching peaks were obtained at wavenumber 1352 and 1429 cm^{-1}.
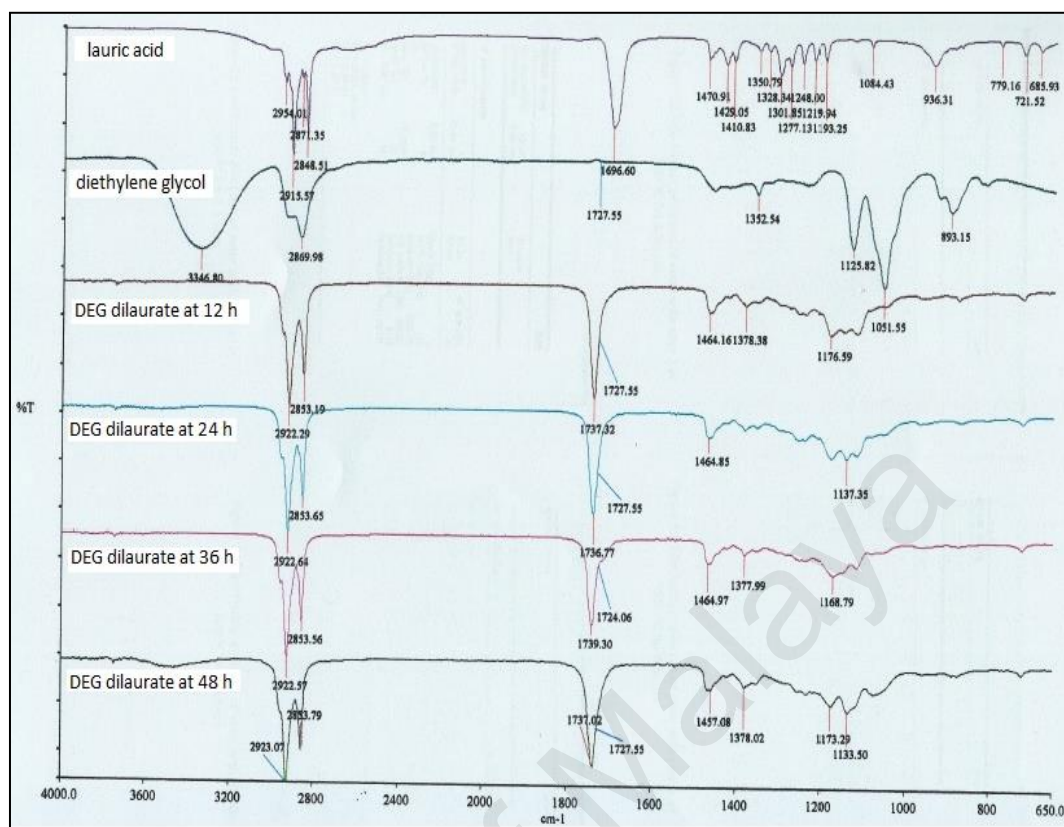
**Figure 4.10: Fourier Transform Infra-Red (FTIR) spectra of starting
materials and diethylene glycol di-laurate produced**

Hydrophilic Lipophilic Balance (HLB) Index

HLB index for DEG-DL produced was calculated to be 7.5. The DEG-DL is
potentially function as a self-dispersing nonionic compatible with surface active
agents. It is suggested as a water-in-oil or oil-in-water emulsifier with an auxiliary
agent. The DEG-DL produced is potentially to be used in textiles, as ingredients
in cosmetic formulations, coating and paper defoamer formulations according to
the physico-chemical properties tailor-made to applications.

4.3 Catalytic Esterification of Lauric Acid via Conventional Heating

Three types of heterogeneous catalysts (calcined Zn-Mg-Al, Amberlyst 15 and tin (II) oxalate) were screened to find the suitable catalyst for the esterification of lauric acid (LA) and diethylene glycol (DEG) using conventional method. The reaction parameters used are according to the optimum operating conditions obtained from the autocatalytic in Section 4.2.

4.3.1 Preliminary Catalytic Screening using Homogeneous and Heterogeneous Catalysts

Figure 4.11 shows the acid value profile determined over the reaction time for the heterogeneous catalysts and the results were also compared with the conventional homogeneous acid catalyst (p-TSA). Preliminary evaluation shows that the heterogeneous catalysts are able to be used for the esterification of LA with DEG based on acid value (AV). As can be seen in Figure 4.11, when the reaction was performed using p-TSA catalyst, AV reduced to 1.4 mg KOH. g^{-1} sample from initial acid value at 8 hours reaction time. This strong mineral acid tend to produce higher yield of ester product at shorter period. However, earlier study reported on the drawbacks of cooperating homogeneous catalyst in the reaction since it may form toxic catalyst ester while conducting the reaction at high temperature (Haliza *et al*., 2016). This is confirmed by the GC chromatogram obtained in Figure 4.12. Since homogeneous catalyst is in the same phase with the product mixture, the process requires additional steps such as neutralization and tedious separation. This will increase the production cost and uneconomical process.
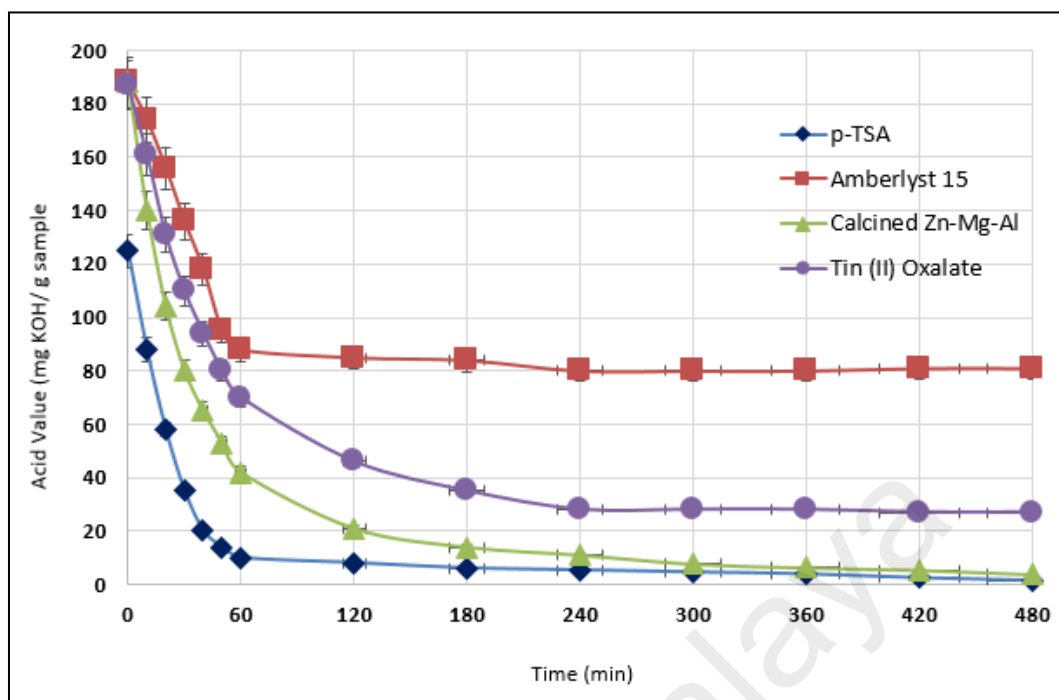
Figure 4.11: Catalytic screening of various types of catalyst in esterification of lauric acid using conventional heating at optimum conditions. Reaction conditions: 230 ºc, 1 atm., 300 rpm, 2:1 mole ratio of LA: DEG, 5% w/w catalyst dosage at 8 hours

As for the reactions aided by other three heterogeneous catalysts, the trend follows the following order: calcined Zn-Mg-Al > tin (II) oxalate > Amberlyst 15. Lauric acid conversions of more than 90% was observed when the reaction was aided by both calcined Zn-Mg–Al and tin (II) oxalate. It appears that calcined Zn-Mg-Al catalyst gave highest rate of reaction in the esterification process. Reactions employing calcined Zn-Mg–Al demonstrated similar lauric acid conversion with the conventional approach using *p*-TSA. Besides, Zn-Mg–Al is preferred as it derived from a cheap source of nitrate–based salt. Esterification using calcined Zn-Mg–Al can be a potential green process over the conventional approach using *p*-TSA. Hence, calcined Zn-Mg–Al catalyst was selected as the best catalyst for this study.

Figure 4.12: GC chromatogram analysis for esterification of lauric acid and diethylene glycol at different process (a) autocatalytic reaction; (b) catalytic reaction with *p*-TSA catalyst; (c) standard *p*-toluene sulphonate ester

4.4 Esterification of Lauric Acid via Microwave Heating

The heterogeneous catalysts (in-house calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15) were again has been preliminary screened their catalytic performance towards lauric acid (LA) conversion using microwave system to ensure the ability to produce di-ester content.

4.4.1 Screening of Catalysts

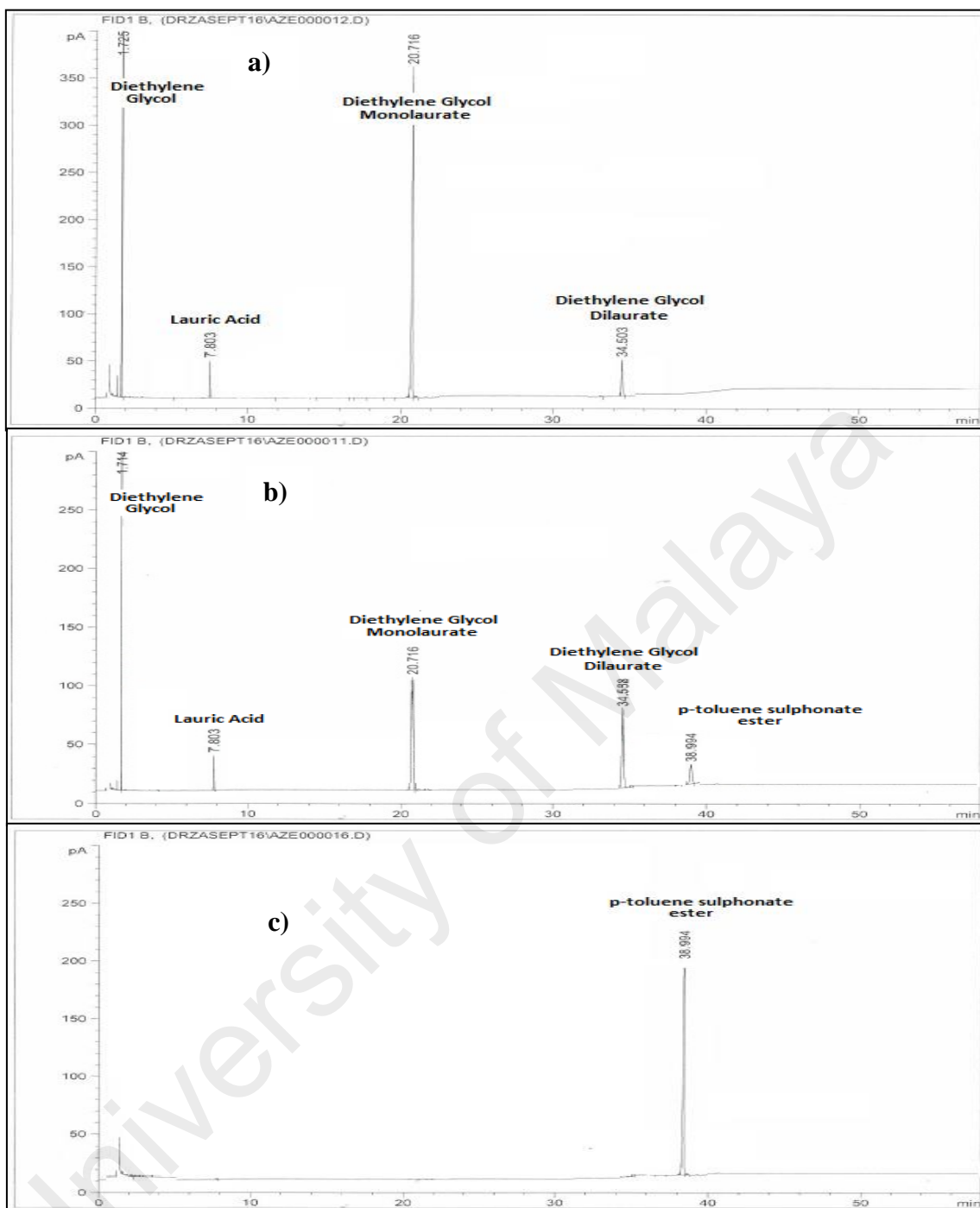The results of preliminary catalytic screening of various types of catalysts are shown in Table 4.4. From this table, autocatalytic esterification (blank reaction) gives the lowest LA conversion (15.8%). With the incorporation of heterogeneous catalyst in this reaction, exhibit increasing in activity towards production of diethylene glycol di-laurate (DEG-DL). The conversion follows the order of calcined Zn-Mg-Al > tin (II) oxalate > Amberlyst-15 > autocatalytic. The activity of Amberlyst-15 gives the lowest conversion as compared to tin (II) oxalate and calcined Zn-Mg-Al. Although the acidic active site concentration of Amberlyst-15 is high and theoretically may result in high yield, this catalyst have poor thermal stability with maximum temperature only up to 120 ºC (Siril, 2008). Thus, the low conversion rate of this catalyst is mainly due to the decomposition of the catalyst at the operating temperature of the reaction, 210 ºC. Calcined Zn-Mg-Al catalyst gives the highest conversion with > 95% conversion of lauric acid. This catalyst is a hydrotalcite -like compound comprises of the formation of layered structure containing three metals in one phase. Based on physicochemical properties of this bifunctional catalyst, it is thermally stable at high temperature up to 500 ºC and exhibit both acidic and basic active site.

For this study, it can be said that the most important factor for the reaction that influence the yield of ester are the temperature and the catalyst. High temperature and the presence of the catalyst that is thermally stable will result in high yield. Other factors that contribute to higher yield are high acidity, large surface area and pore space (Edwin *et al.*, 2016). Based on the result of the preliminary screening, it is confirmed that the best catalyst was calcined Zn-Mg-Al. Hence, this catalyst would be used for further optimization of the esterification via microwave heating.

Table 4.4: Preliminary catalytic screening of various types of catalysts in esterification of lauric acid (LA) and diethylene glycol (DEG) via microwave heating

Catalyst Type	Lauric Acid Conversion (%)
Blank (autocatalytic)	15.8
Amberlyst-15	31.6
Tin (II) Oxalate	65.4
Calcined Zn-Mg-Al	95.4

Operating conditions: T = 210 ºC, t = 180 min, mole ratio LA: DEG = 2:1, catalyst dosage = 5% w/w catalyst, catalyst particle size = 212 µm

4.4.2 Effect of Reaction Temperature

In this work, the temperature was varied at 120 ºC, 150 ºC, 170 ºC, 190 ºC and 210 ºC with other parameters remained constant (5% w/w calcined Zn-Mg-Al catalyst dosage, 2:1 mole ratio of LA: DEG, 300 rpm and 180 min reaction time). The profile trend for lauric acid conversion over time was plotted and shown in Figure 4.13. It can be seen from the figure, esterification conducted at 120 ºC only managed to convert less than 45% of lauric acid.

As the reaction temperature increased to 150 °C, 170 °C, 190 °C and 210 °C, the conversion are 83.5%, 94.6%, 96.7% and 95.4%, respectively. The latter condition (210 °C) shows approximately 1.3% decreased in lauric acid conversion as compared to the reaction conducted at 190 °C. This probably because of the diethylene glycol may evaporate at 210 °C which is close to the boiling point of diethylene glycol (220-240 °C). Similar conversion trend was plotted when the reaction was performed at temperature over 170 °C. In the first 90 min, the conversion was increased proportionally to the temperature. Later, the conversion is slowing as the esterification reached a plateau and equilibrium. Therefore, 190 °C was chosen to be the best temperature to perform the esterification process.

Figure 4.13: Effect of reaction temperature on conversion of lauric acid. Reaction conditions: 5% calcined Zn-Mg-Al, 300 rpm, 2:1 mole ratio (LA: DEG) and 180 min

4.4.3 Effect of Reaction Time

Investigation of the effect of the reaction time on the lauric acid conversion was conducted for the catalytic esterification of lauric acid. From the result plotted in Figure 4.14, it can be seen that the lauric acid conversion improved rapidly from 20 min (65.4%) to 90 mins (96.7%). The increased in conversion might be due to the collisions between the solid catalyst (calcined Zn-Mg-Al) and reactant molecules as the reaction time proceed. However, the conversion profile remains stagnant as the time was prolonged from 90 to 180 min. This might be due to the reversible reaction occurred where hydrolysis took place. In hydrolysis, water molecules may break the ester linkage as the surface saturated with water formation. Thus, prolonged reaction time was not feasible to the reaction and the reaction duration for esterification aided by calcined Zn-Mg-Al catalyst can be established for 90 min and would be used for further experiments.
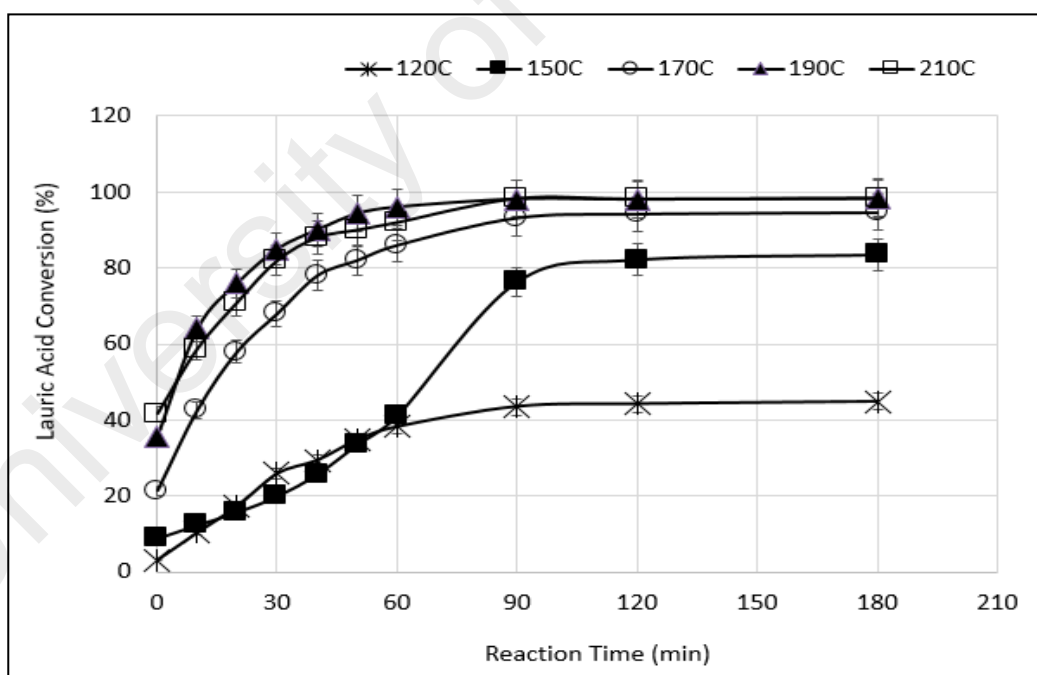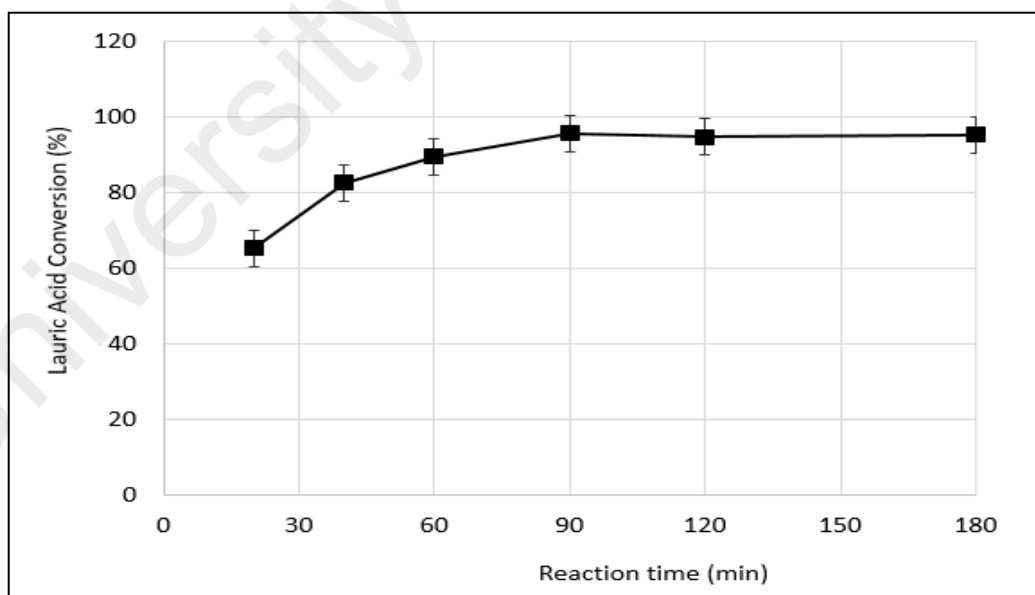

Figure 4.14: Effect of reaction time on conversion of lauric acid
Reaction conditions: 190 ºC, 5% calcined Zn-Mg-Al, 300 rpm, 2:1 mole ratio (LA: DEG)

4.4.4. Effect of Reactants Mole Ratio

The catalytic activity of calcined Zn-Mg-Al was further inspected by varying reactants mole ratio with other parameters be fixed. Five mole ratios were chosen, from 2:1 to 2:2.5 to investigate the effect of reactants mole ratio of LA to DEG on the formation of DEG-ML and DEG-DL content as can be seen in Figure 4.15. Excess of DEG in the reaction is an alternative way to increase conversion rate of lauric acid. This also to speed up the forward reaction in order to eliminate water completely as by-product. It can be observed from the plot that as the mole ratio of LA to DEG increased from 2:1 to 2:1.3, the yield of DEG-DL content is increased from 91.9% to 96.2% corresponding to 98.2% LA conversion and acid value of 3.34 mg $KOH.g^{-1}$ sample. The yield of DEG-DL content decreased drastically to 56.8% with the increasing reactant mole ratio up to 2: 2.5. The results obtained might be due to the surplus of diethylene glycol employed in the reaction lead to lower lauric acid concentration as more diol diluted in the mixture. Hence, the optimum reactant mole ratio of LA to DEG selected for this esterification reaction was 2:1.3.
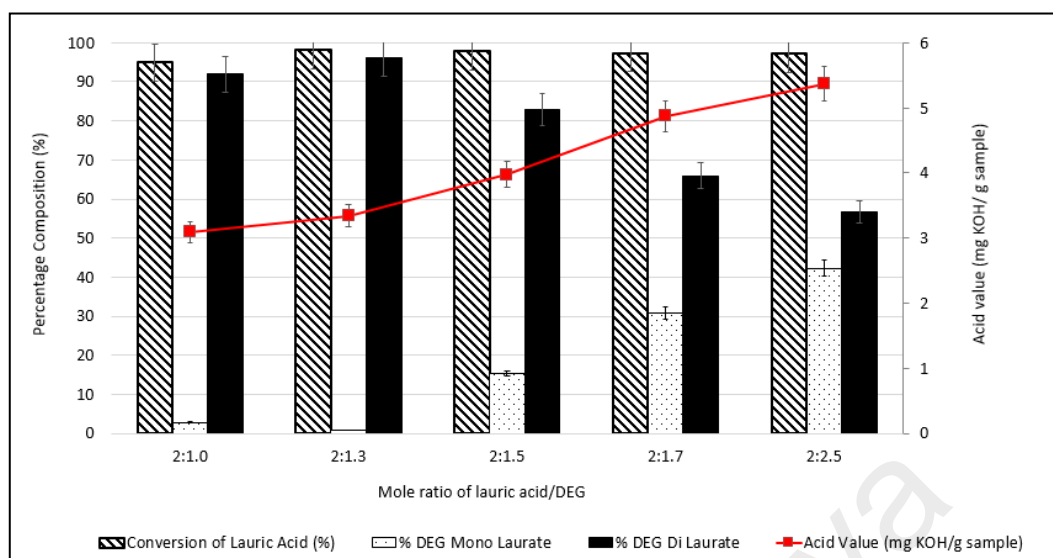
Figure 4.15: Effect of reactant mole ratio (MR) lauric acid to diethylene glycol at final acid value (AV) obtained on lauric acid conversion, mono- and di-laurate compositions. Reaction conditions: 190 °C, 5% calcined Zn-Mg-Al, 300 rpm and 90 min

4.4.5 Effect of Catalyst Dosage

The heterogeneous catalyst was employed in the esterification of LA with DEG, to obtain maximum content of DEG-DL under optimum conditions. The catalyst dosage of calcined Zn-Mg-Al was varied at 1%, 3%, 5%, 7% and 9% for 90 min reaction time. The trend of LA conversion towards different calcined Zn-Mg-Al dosage was plotted as can be seen in Figure 4.16. The conversion percentage increased from 90.8% to 98.2% with the increasing of catalyst dosage from 1% to 5%, respectively. Nevertheless, as the calcined Zn-Mg-Al catalyst dosage further increased to 7% and 9%, there is no significant difference on the lauric acid conversion can be observed. This is due to mass transfer rate limitation factor that delayed the catalytic activity and reached plateau thereafter. Thus, a calcined Zn-Mg-Al catalyst dosage of 5% is sufficient to give maximum conversion at a high reaction rate.
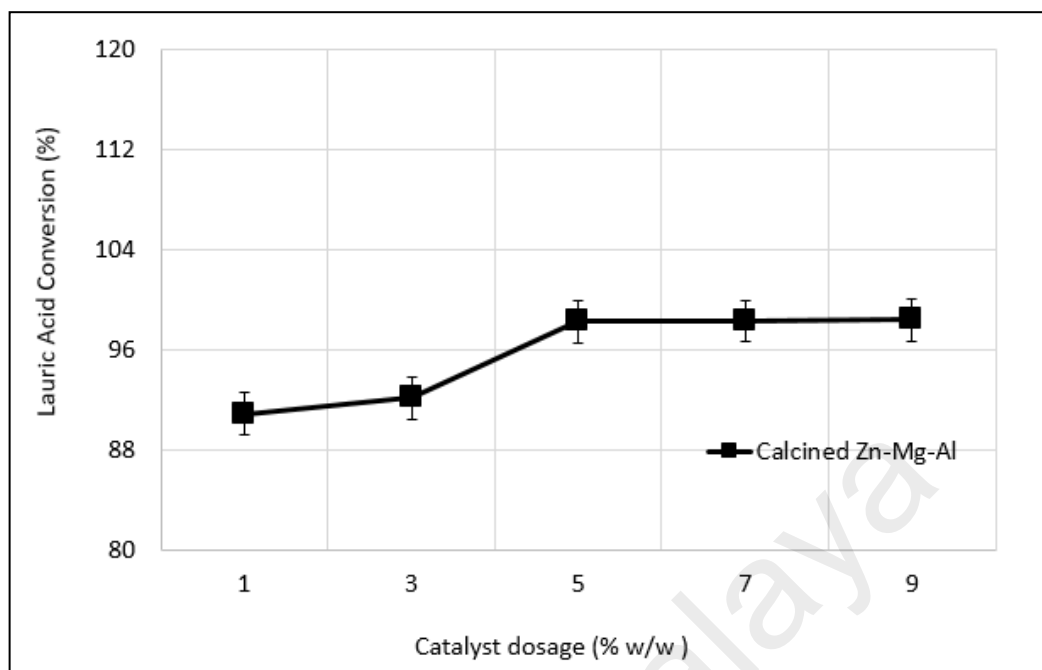
Figure 4.16: Effect of calcined Zn-Mg-Al catalyst dosage on lauric acid conversion. Reaction conditions: 190 ºC, 300 rpm, 212 µm, 2:1.3 mole ratio of LA: DEG and 90 min

4.4.6 Effect of Catalyst Particle Size

Calcined Zn-Mg-Al catalyst was sieved with different sizes (100 µm, 212 µm, 500 µm, 710 µm and 1000 µm) to investigate the effect of catalyst particle size on the esterification of lauric acid. The plotted bar chart in Figure 4.17 shows the reduction trend of lauric acid conversion with increasing of the catalyst particle size with 90 min reaction time. The lauric acid conversion decreased about 15% from 98.2% after the catalyst particle size was increased from 212 µm to 1000 µm. The latter particle size exhibited the lowest conversion due to the external diffusion restriction that occurred when the reactant molecules diffuse through the fluid layer surrounding the catalyst particles. As the particle size used is bigger, a longer time required for the reactant to go through into catalyst particle. Hence, catalyst with particle size of 212 µm was used for this optimization study.
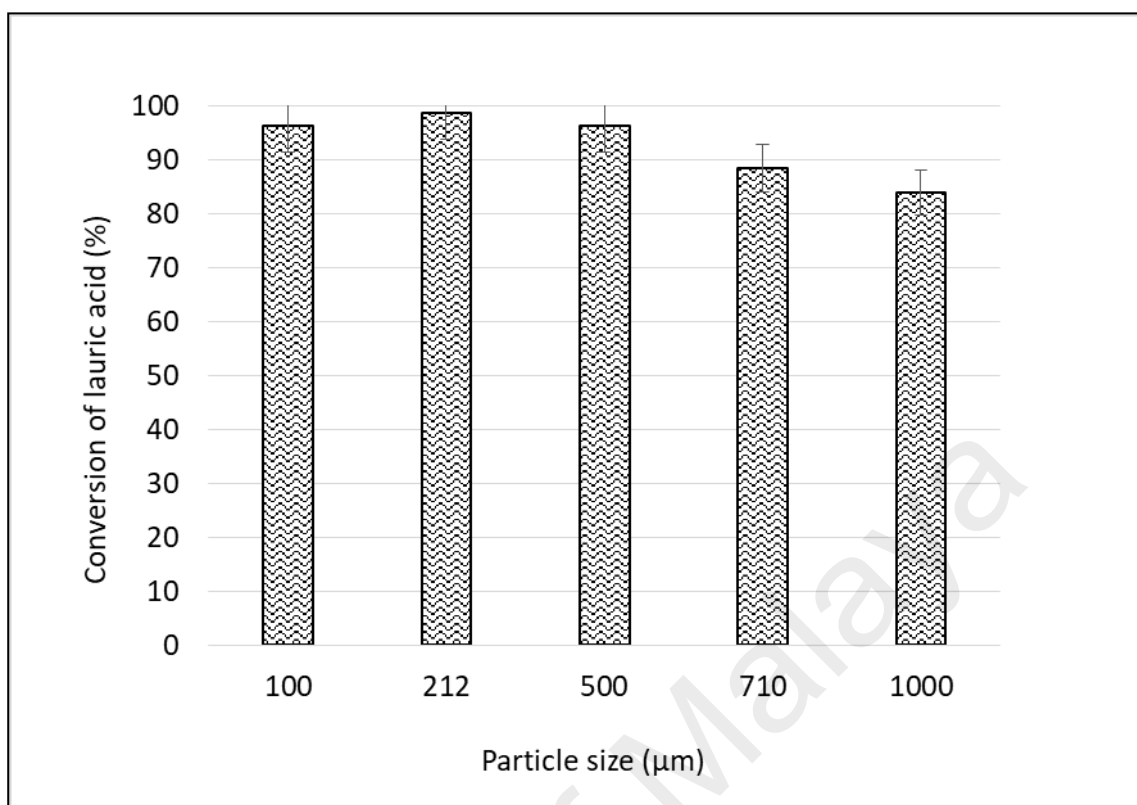
Figure 4.17: Effect of calcined Zn-Mg-Al catalyst particle size on lauric acid conversion. Reaction conditions: 190 ºC, 5% w/w calcined Zn-Mg-Al, 300 rpm, 2:1.3 mole ratio of LA: DEG and 90 min

4.5   Recyclability of Catalyst

Figure 4.18 shows the results of the recyclability study for the three heterogeneous catalysts in successive cycles of esterification batches. The result highlighted that both calcined Zn-Mg-Al and tin (II) oxalate both can be used for six cycles as compared to Amberlyst-15 that lost part of its activity in the third cycle. Low activity performance of Amberlyst-15 is mainly due to its low thermal stability, <120 ºC. The results show that strong evidence of the calcined Zn-Mg-Al stability with less than 2% decrease in conversion (six cycles).
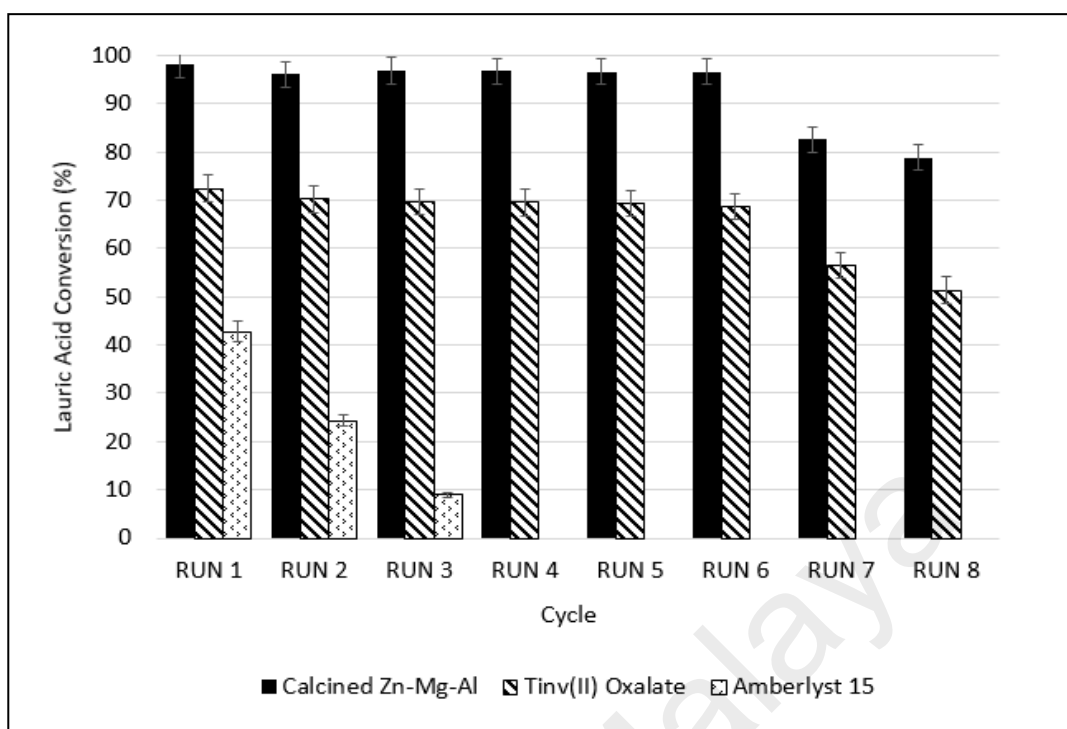
Figure 4.18: Recyclability of the solid catalysts (calcined Zn-Mg-Al, tin (II) oxalate and Amberlyst-15) on lauric acid conversion. Reaction conditions: 190 ^{O}C, 300 rpm, 5% w/w of catalyst, 2:1.3 mole ratio of LA: DEG and 90 min

4.6 Leaching of Calcined Zn-Mg-Al Catalyst Active Species into Reaction System

Leaching test was performed for Zn, Mg and Al metals in the product samples started after the first cycle up to eight cycles according to the reusability test described previously in section 4.5. Figure 4.19, Figure 4.20 and Figure 4.21 show the plots of leaching test of Zn, Mg and Al metal, respectively. As can be seen from these figures, Zn, Mg and Al metal in glycol ester product were detected in traces amount throughout the six cycles with only 0.5% metal concentration after seven cycles. The trace amount of Zn, Mg and Al metal detected are ≤ 8 mg. L^{-1}, ≤ 6 mg. L^{-1} and ≤ 3 mg. L^{-1}, respectively. Based on these findings, the catalytic activity of calcined Zn-Mg-Al is capable in maintaining its activity for six subsequent cycles without any metal active species leaching to the product mixtures.
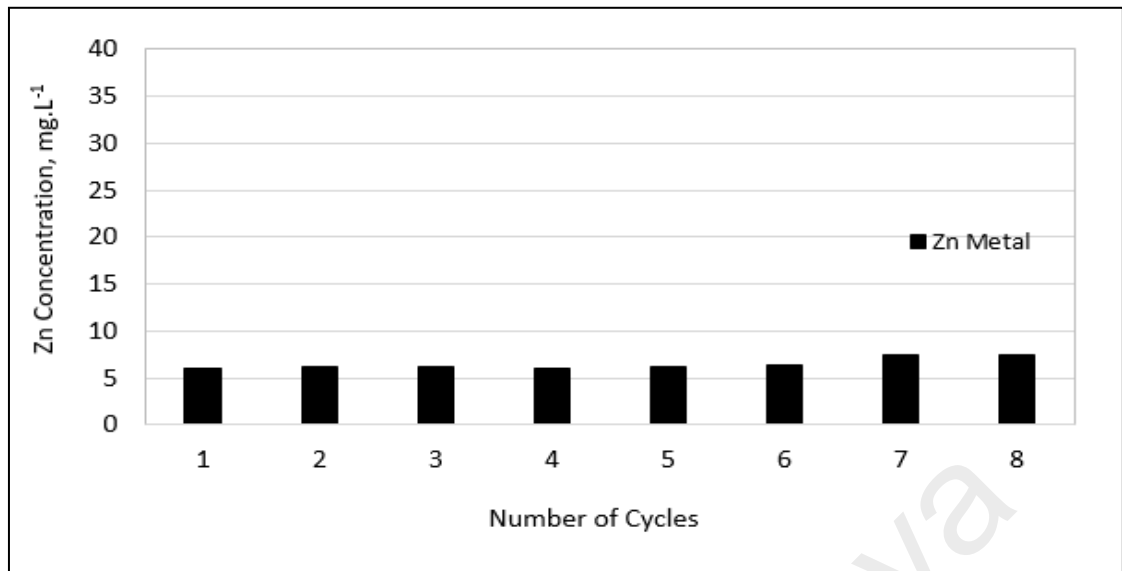
Figure 4.19: Leaching test profile for Zn metal in glycol ester
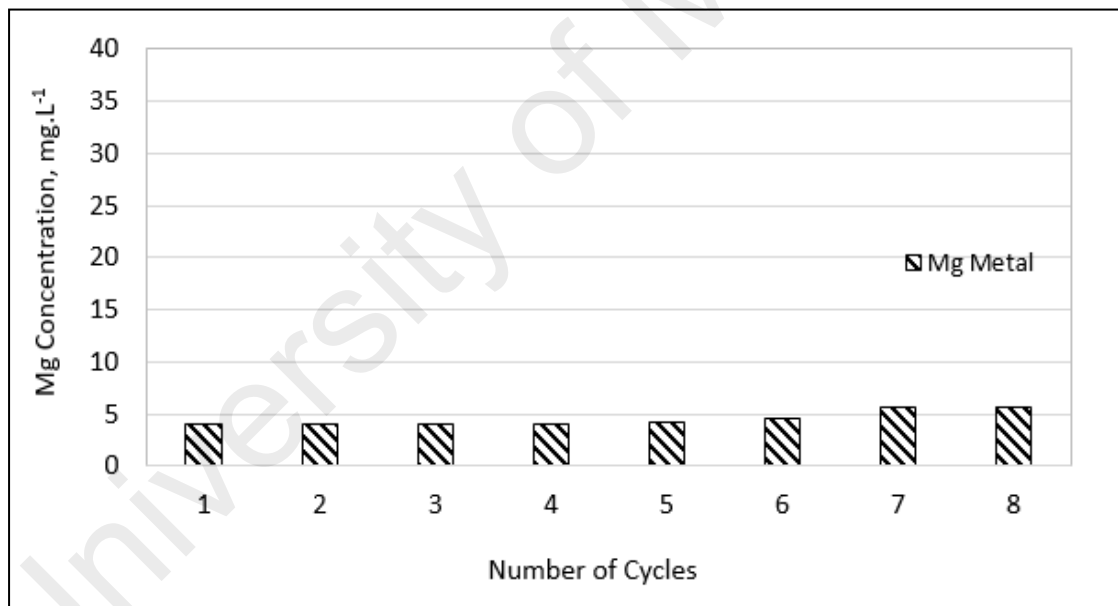
Figure 4.20: Leaching test profile for Mg metal in glycol ester
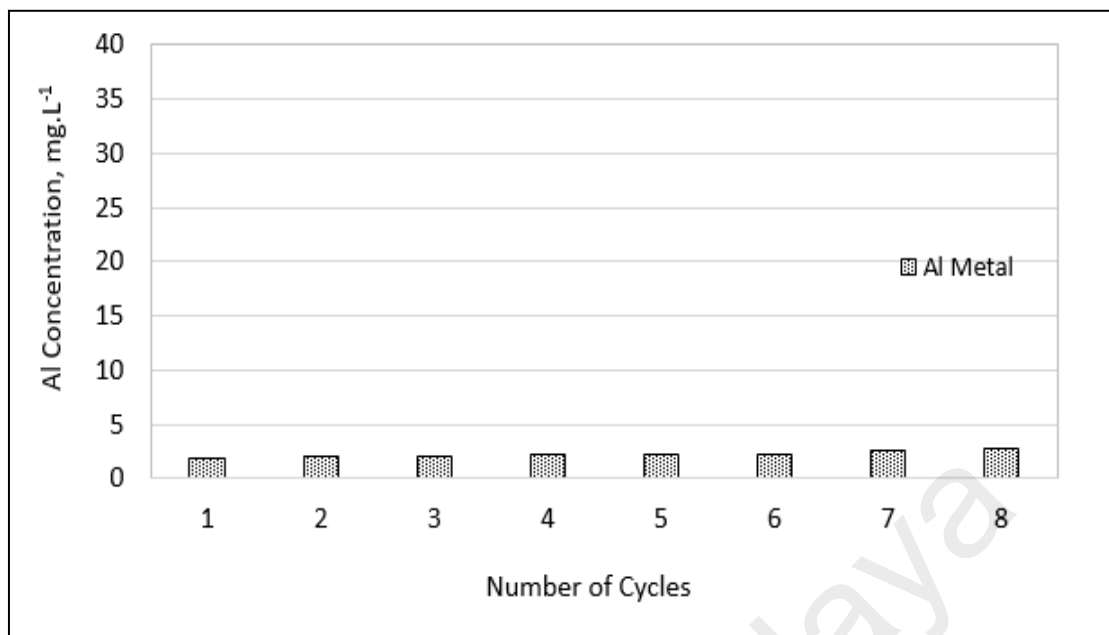
Figure 4.21: Leaching test profile for Al metal in glycol ester

4.7 Comparison between Conventional Heating vs Microwave Heating over Reaction Time

Figure 4.22 shows the profile of lauric acid conversion over time of both autocatalytic and catalytic esterification at optimum condition obtained from esterification reaction via microwave heating and conventional heating. The longest duration time took for conventional autocatalytic esterification to achieve highest lauric acid conversion was at 48 hours whereas the time was reduced to 6 hours when the autocatalytic reaction was conducted using microwave heating. From the plot, it can be observed, under the same parameters, it took about 8 hours to achieve the similar conversion (98.05%) via conventional catalytic esterification. Unlike conventional heating, which only heats the material at the surface, microwave energy penetrates deeper into the material and supplies energy. As a result, heat can be generated throughout the whole volume of the materials.

Therefore, rapid and uniform distribution of heat in the material can be achieved through microwave heating (Yu *et al.*, 2007). The effect of microwave irradiation in chemical reactions is a combination of the thermal effect and non-thermal effects, i.e., overheating, hot spots and selective heating, and non-thermal effects of the highly polarizing field, in addition to effects on the mobility and diffusion that may increase the probabilities of effective contacts. In addition, the catalytic esterification of lauric acid via microwave heating experienced a shorter time (1.5 hours) as compared to conventional heating (8 hours). The energy transfer from microwave radiation directly passes through the vessel wall into the molecules mixture during reaction and using dipole rotation mechanism so called dielectric heating for interaction between molecules and chargers in electric field (Mazo *et al.*, 2012).
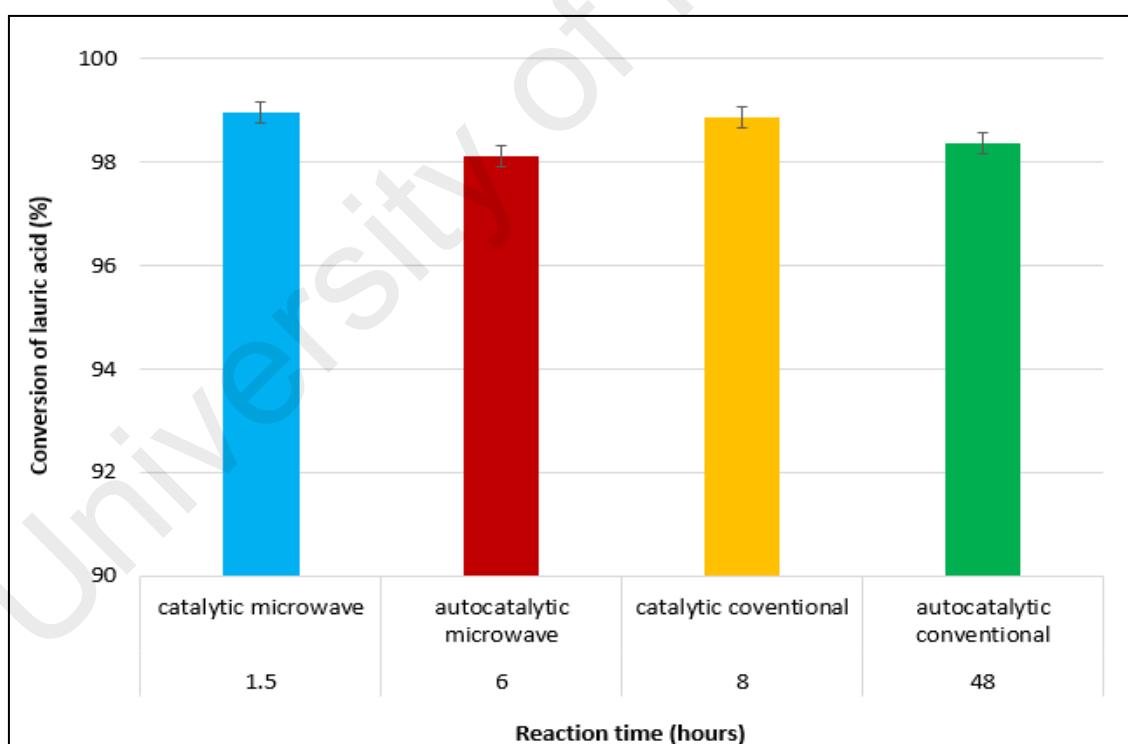
Figure 4.22: Profile of lauric acid conversion over time course using different heating system for production of diethylene glycol di-laurate. Reaction conditions: 190 ^{O}C, 300 rpm, 5% calcined Zn-Mg-Al catalyst dosage and mole ratio of 2: 1.3 (LA: DEG)

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

This chapter summarizes all the research findings obtained according to the research objectives. Recommendations for improvement in future works on the application of palm-based DEG-DL produced by heterogeneous catalysed esterification of fatty acid via microwave heating also has been mentioned .

5.1   Conclusion

The autocatalytic esterification of palm-based lauric acid and diethylene glycol for the production of diethylene glycol di-laurate was carried out for the purpose of benchmark. The optimized operating condition was established at temperature 230 $^{\circ}$C, stirring speed rate of 300 rpm and mole ratio lauric acid to diethylene glycol of 2, using this optimized condition, lauric acid conversion of more than 98% was obtained with 48 hours reaction time. High purity of diethylene glycol di-laurate was achieved via further step of vacuum distillation. The structure of desired compound was confirmed via proton Nuclear Magentic Resonance (^{1}H- NMR) characterization, whereby the corresponding peaks produced matched the di-ester compound structure. The HLB index calculated was 7.5, referred this non-ionic type surfactant funtioned as wetting and spreading agents could be recommended for cosmetic applications. Four types of catalyst including homogeneous and heterogeneous catalysis were screened under optimized condition by conventional heating to find the best catalyst for the esterification of lauric acid and diethylene glycol. The order of the catalytic activity of these catalysts is as follows: ρ-TSA (homogeneous) > calcined Zn-Mg-Al (hydrotalcite-like compound) > tin (II) oxalate > Amberlyst-15 (ion-exchange resin).

Among all the catalysts investigated, ρ-TSA exhibited the highest conversion of lauric acid and high reaction rate. However, due to some drawbacks of this homogeneous catalyst as the catalyst ester detected in the product mixture, the use of the ρ-TSA catalyst is not advisable. Hence, calcined Zn-Mg-Al catalyst was selected as the best catalyst for the esterification of lauric acid and diethylene glycol as it gave about 98% lauric acid conversion and maximum di-ester content with 8 hours reaction time. More over the use of calcined Zn-Mg-Al is preferred as it is less hazardous than the homogeneous catalyst and can be recycled which simplifies the downstream separation process.

A maximum content of diethylene glycol di-laurate (DEG-DL) was successfully produced from esterification of lauric acid and diethylene glycol aided by calcined Zn-Mg-Al catalyst using microwave heating with much shorter period of time as compared to conventional heating. The calcined Zn-Mg-Al catalyst managed to produce bigger surface area with high acidity active sites exhibited maximum lauric acid conversion (98.2%) as compared to other heterogeneous catalysts. The effect of reaction temperature, reaction time, catalyst dosage, and reactants mole ratio and catalyst particle size were evaluated. At optimized operating conditions of 190 $^{\circ}$C, 5% w/w of calcined Zn-Mg-Al catalyst dosage with particle size of 212 μm, stirring speed rate of 300 rpm, a mole ratio 2:1.3 (lauric acid: diethylene glycol) and a reaction duration of 90 min gave 96.2% of DEG-DL. This microwave heating method was at least five times faster than the conventional method, affording a significant saving of time and energy. This study discovered the potentiality of calcined Zn-Mg-Al catalyst to be aided in catalytic esterification of lauric acid for production of DEG-DL.

The evaluation of the catalyst recyclability was performed for eight times in esterification of lauric acid via microwave heating under optimized reaction parameters. The result highlighted that calcined Zn-Mg-Al and tin (II) oxalate both can be used for six cycles as compared to ion exchange resin type (Amberlyst-15) that lost part of its activity after the third cycle. The latter catalyst showed low activity performance due to its low thermal stability, <140 $^\circ$C.

Leaching test was performed for Zn, Mg and Al metals in the product samples started after the first cycle up to eight cycles according to the reusability test. It shows that Zn, Mg and Al metal in glycol ester product detected are only traceable amount throughout the six cycles and increment of 0.5% metal concentration after seven and eight cycles. The similar trend produced by the three metal active species leading to be negligible and insignificant. The trace amount of Zn, Mg and Al metal detected in the product mixture are ≤ 8 mg. L^{-1}, ≤ 6 mg. L^{-1} and ≤ 3 mg. L^{-1}, respectively. Based on the finding for metal active species leaching test, the catalytic activity of calcined Zn-Mg-Al capable of maintaining its activity for six subsequent cycles.

5.2 Recommendations for Future Studies

The maximum content of di-ester is potentially function as wetting and spreading agent for various industrial applications. As such, it is suggested to perform specific physicochemical properties of the di-ester compound tailored to the specific application requirement.

The optimum parameters for catalytic esterification of lauric acid and diethylene glycol was established via microwave heating. Hence, it is recommended to further expand the research scope to kinetic investigation on the esterification reactions of palm-based fatty acid, as no kinetic data of the reaction is available.

It is also recommended to investigate on the possible mechanism of the esterification of lauric acid into mono and di-ester and deactivation of the calcined Zn-Mg-Al catalyst upon recycling process.

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List of Publications and Paper Presented

1   NOOR AZEERAH ABAS, Rozita Yusoff, Mohamed Kheireddine Aroua, Haliza

     Abdul Aziz, and Zainab Idris. (2020). Production of palm-based glycol ester

     over solid acid catalysed esterification of lauric acid via microwave heating.

     Chemical Engineering Journal, 382, 122975.

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2   NOOR AZEERAH ABAS, Rozita Yusof, Haliza Abdul Aziz and Zainab Idris.

     (2020). Production of Palm-based Diethylene Glycol Di-laurate via

     Autocatalytic Esterification. *Journal of Oil Palm Research,* 0003.

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3   NOOR AZEERAH ABAS, Rozita Yusof, Haliza Abdul Aziz, and Zainab Idris.

     (2018). Solid acid catalysed esterification of lauric acid assisted by microwave

     heating. *Conference paper for 5th International Conference of Oil and Fats*, 14-

     15 August 2018,UKM Bangi Malaysia