FATTY ESTERAMINE PRODUCTION VIA HETEROGENEOUS TRANSESTERIFICATION OF PALM-BASED METHYL PALMITATE AND TRIETHANOLAMINE

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FATTY ESTERAMINE PRODUCTION VIA HETEROGENEOUS TRANSESTERIFICATION OF PALM-BASED METHYL PALMITATE AND TRIETHANOLAMINE

ABSTRACT

Fatty esteramine is most significantly used as a precursor in the production of esterquats, a biodegradable cationic surfactant. Preliminary evaluation on fatty esteramine production via heterogeneous transesterification of palm-based methyl palmitate as an alternative to the conventional process using homogeneous catalyst was performed in early part of this study followed by screening of various types of hydrotalcite-like compound (HLTC) used as the heterogeneous catalyst. Prior to the optimization process, preliminary study on the effects of process parameters such as mole ratio of reactants, temperature, vacuum, catalyst dosage, agitator speed and reaction time on conversion of methyl palmitate was performed. Optimization of the operating conditions was conducted via Response Surface Methodology approach. Stability of the HTLC catalyst was evaluated in terms of its reusability and leaching of the active species. This novel heterogeneous transesterification process appeared as a viable route for the production of fatty esteramine as the desired product of mono, di and tri-esteramine were successfully produced. Among the various HTLC investigated, Ca-Al catalyst showed the best catalytic activity towards the transesterification process as it gave the highest conversion of methyl palmitate and yielded fatty esteramine compositions similar to the conventional homogeneous catalyst. Temperature, vacuum and catalyst dosage are among the most significant variables affecting the conversion of methyl palmitate and di-esteramine formation. The optimum reaction conditions obtained from RSM optimization were temperature of 169 ^{o}C, catalyst dosage of 0.74%, vacuum of 278.6 mbar and agitation speed of 200 rpm. Ca-Al catalyst was reusable and the conversions as well as fatty esteramine compositions were sustained for three subsequent cycles. Ca-Al exhibited insignificant leaching of the calcium and aluminium active species into the fatty esteramine throughout the recycling process.

Keywords: fatty esteramine, hydrotalcite-like compound, transesterification, methyl palmitate.

PENGHASILAN ESTERAMINA LEMAK MELALUI PROSES TRANSESTERIFIKASI METIL PALMITAT BERASASKAN SAWIT DAN TRIETANOLAMINA DENGAN MENGGUNAKAN MANGKIN PEPEJAL

ABSTRAK

Esteramina lemak kebanyakannya digunakan sebagai bahan mentah bagi penghasilan esterkuat, surfaktan kationik yang mudah terbiodegradasi. Penghasilan esteramina lemak melalui proses transesterifikasi metil palmitat berasaskan sawit dengan menggunakan mangkin pepejal sebagai alternatif kepada proses konvensional yang menggunakan mangkin cecair, telah dijalankan di peringkat awal kajian ini diikuti dengan penyaringan pelbagai jenis *hydrotalcite-like compound* (HTLC) yang digunakan sebagai mangkin pepejal bagi proses transesterifikasi ini. Kajian awal mengenai kesan-kesan parameter proses seperti nisbah bahan tindak balas, suhu, vakum, dos mangkin pepejal, kelajuan pengacauan dan masa tindak balas ke atas penukaran metil palmitat telah dijalankan sebelum mendapatkan proses parameter yang optimum dengan menggunakan kaedah *Response Surface Methodology* (RSM). Kestabilan mangkin HTLC telah dinilai dari segi penggunaan semula mangkin dan larut resap aktif spesis mangkin tersebut ke dalam produk esteramina lemak. Proses transesterifikasi menggunakan mangkin HTLC yang novel ini telah berjaya menghasilkan produk mono, di dan tri-esteramina. Di antara beberapa jenis mangkin HTLC yang disaring, mangkin Ca-Al telah dipilih sebagai mangkin pepejal dalam kajian ini kerana ia menunjukkan penukaran metil palmitat yang tertinggi dan menghasilkan komposisi esteramina lemak yang setanding dengan mangkin cecair konvensional. Hasil kajian menunjukkan bahawa suhu, vakum dan dos mangkin pepejal adalah di antara parameter proses yang memberi impak yang ketara terhadap penukaran metil palmitat dan penghasilan di-esteramina. Tindak balas optimum yang diperolehi menggunakan kaedah RSM adalah pada suhu 169 ^{o}C, dos mangkin pepejal sebanyak 0.74%, takat vakum pada 278.6 mbar dan kelajuan pengacauan sebanyak 200 rpm. Hasil kajian menunjukkan bahawa mangkin Ca-Al boleh diguna semula sebanyak tiga kitaran, di mana telah didapati bahawa penukaran metil palmitat serta komposisi esteramina lemak adalah sama bagi tiga kitaran tersebut. Ujian larut resap ke atas mangkin Ca-Al telah menunjukkan bahawa hanya sedikit kandungan aktif spesis kalsium dan aluminium telah melarut resap ke dalam sampel esteramina lemak bagi ketiga-tiga kitaran tersebut.

Kata kunci: esteramina lemak, *hydrotalcite-like compound*, transesterifikasi, metil palmitat.

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CHAPTER 1: INTRODUCTION

1.1 Research Background

Commercially available cationic surfactants are nitrogen derivatives, where most of the alkyl group of this surfactant is derived from natural oils and fats. Historically, tallow has been widely used as feedstock by surfactant producers due to its availability, versatility and low cost. Nowadays, vegetable-based feedstocks are gaining acceptance in surfactant manufacturing over the animal-based raw materials. The vegetable-based feedstocks can be obtained from various seeds such as soybean, sunflower, oil palm fruits, coconut and rapeseed. Quaternary ammonium compounds are the largest class of nitrogen-based cationic surfactants. They contain at least one nitrogen atom that is covalently bonded to four alkyl or aryl substituents.

Another interesting class of quaternaries is esterquats, which are characterized by the presence of hydrophobic alkyl chains that link to the positively charged nitrogen molecule via ester bonds. This ester linkage provides site for easy hydrolysis to fatty acids and short chain quats, where subsequently microorganisms will be able to digest the fatty acid to give carbon dioxide and water when drained into sewage system (Tyagi *et al.*, 2006). Excellent environmental profile and good softening effect of the esterquats have made them a better replacement for the conventional dihydrogenated tallow dimethyl ammonium chloride (DHTDMAC) as an active ingredient in fabric softeners. Besides, esterquats are also used in hair conditioner formulation. Other applications include their use in the manufacture of organoclays for drilling mud, as an antistatic in polymer products as well as ingredients in bactericidal and sanitiser products (Idris *et al*, 2005).

Generally, esterquats are produced via a two-stage process in which, fatty acid or ester is first esterified or transesterified with triethanolamine to produce mixture of mono, di and tri-esteramine. Subsequently, quaternization with a methylating agent of the esteramine, intermediate for esterquat is involved in the latter stage to introduce a positive charge onto the molecule. Typically, the esterification or transesterification is catalyzed by a homogeneous acid or base catalyst. Synthesis of the esteramine is the key step in the production of esterquats and performing the esterification or transesterification process at optimum conditions will lead to maximum conversion to esteramine.

Preparation of esteramine for the production of esterquats from fatty acid having chainlength of C_6 – C_{22} and triethanolamine in the presence of hypophosphorous acid catalyst was patented by Trius *et al*. (1991). According to his patent, the esterifications aided by the homogeneous catalyst were performed at 160 ^oC, vacuum of 1.33 mbar and catalyst dosage of 0.15%. Research and development works on the preparation of fatty esteramine from esterification of triethanolamine with palm-based fatty acid or ester using chemical catalysts have been initiated by the Malaysian Palm Oil Board in 1995. The works developed by Idris *et al*. (1995) involved esterification of triethanolamine and myristic acid in the presence of phosphinic acid (50% concentration) with mole ratio myristic acid to triethanolamine of 2:1, 140 ^oC with xylene as solvent and reaction time of 4 hours. In the same year, transesterification of triethanolamine with methyl myristate employing 1% sodium methoxide homogeneous catalyst was also developed by Idris *et al*. (1995). Unlike the esterification process, transesterification of methyl myristate could be accomplished at milder temperature between 80 to 100 ^oC within 2 hours reaction without the presence of solvent.

In 2003, a process to produce esterquats via esterification of distilled palm-stearin fatty acid in the presence of homogeneous acid catalysts was patented by Idris *et al*. (2003). According to the patent, acid catalysts such as phospinic acid, sulfuric acid and para toluene sulfonic acid were employed in the esterification process performed at 160 ^{o}C and vacuum between 1 – 40 mbar to form esteramine. Palm-stearin fatty acid used as the raw material described in this patent does not require any prior hydrogenation as compared to other vegetable oils because it has sufficient ratio of saturated to unsaturated fatty acid compositions, suitable for fabric softener application. A milder process for esterquats production through transesterification between triethanolamine and palm stearin methyl ester was patented by Haliza and co-workers in 2006. Sodium methoxide of 1% solution was used as the homogeneous catalyst in the transesterification process performed at 100 ^{o}C, 200 mbar, 5% catalyst dosage, 540 rpm and mole ratio (methyl ester:triethanolamine) of 2:1.

1.2 Problem Statement

Conventionally, both homogeneous acid and base catalysts can be used for the production of fatty esteramine. Homogeneous acid catalysts such as hypophosphorous acid, phosphinic acid or sulphuric acid are employed in the esterification of fatty acids and triethanolamine, whereas base catalysts such as sodium or potassium alkoxides (e.g. sodium methoxide) are used in the transesterification of methyl ester and triethanolamine. However, separation of these homogeneous catalysts from the product are difficult (Chen *et al.*, 2007) and neutralization of these catalysts generate large amount of wastewater (Climent *et al.*, 2006). Homogeneous acid catalysts are highly toxic and corrosive, whereas base catalyst such as sodium methoxide can cause serious human health hazards upon contact.

The employment of heterogeneous catalyst as a substitute of these homogeneous catalysts for the production of esteramine was explored, as it will provide better separation as well as lowering the generation of waste, environmental impact and cost. There are a few studies reported on the employment of heterogeneous catalysts via direct esterification from fatty acids to produce esteramine (Jiang *et al.* 2007, Geng *et al.*, 2011, Jiang *et al.*, 2012). However, production of esteramine via direct esterification of fatty acids and triethanolamine in the presence of solid acid catalyst is not preferred as it requires costly corrosion resistant equipment. In addition, the starting raw material from fatty acid gives a dark colored product, causing additional downstream processes such as bleaching and distillation (Narula, 1995).

There is no investigation has been reported to produce esteramine via heterogeneous transesterification of methyl ester and triethanolamine. Therefore, this present study will focus on the use of heterogeneous catalysts, specifically hydrotalcite-like compounds (HTLC) for the transesterification of palm-based methyl palmitate and triethanolamine for fatty esteramine production.

1.3 Research Objectives

This research has the following objectives:

1) To screen various types of HTLC for transesterification of palm-based methyl palmitate and triethanolamine.
2) To investigate the effect of various process parameters on transesterification and to maximize the formation of di-esteramine yield by optimizing the process parameters using Response Surface Methodology (RSM).
3) To evaluate the reusability and leaching of the HTLC as the heterogeneous catalyst

1.4 Research Scope

This research consists of two main aspects. The first aspect focuses on the production of fatty esteramine via novel heterogeneous transesterification process. The reaction was carried out in a stirred reactor under various reaction conditions. The conversion of methyl palmitate and compositions of fatty esteramine which consist of mono,di and tri-esteramine were then analysed using gas chromatography. In order to evaluate the formation of fatty esteramine via this new route, the structures of mono,di and tri-esteramine from transesterification of palm-based methyl palmitate and triethanolamine aided by HTLC catalyst were confirmed via gas chromatography – mass spectrometer analysis. Various types of HTLC catalysts were screened to find the suitable catalyst that give maximum conversion of palm-based methyl palmitate and di-esteramine content. The conversion of methyl ester and fatty esteramine compositions obtained using the HTLC catalysts were also compared with the conventional homogeneous sodium methoxide catalyst.

The second aspect is the optimization of the operating conditions of the heterogeneous transesterification process with the aim to obtain maximum di-esteramine yield. Response Surface Methodology (RSM) approach was adopted for the optimization of the process parameters, whereby face-centered cube experimental design and analysis of variance (ANOVA) were done sequentially. The predicted optimized operating conditions were then validated by conducting a manual experiment based on the optimum process parameters provided by the RSM method. Optimization by RSM method was done on four process parameters, i.e. temperature, vacuum, catalyst dosage and agitator speed. Prior to optimization using RSM, preliminary study was carried out to determine the experimental regions in order to investigate the levels of each process parameters (variables) required in RSM. The effects of reaction temperature, vacuum, catalyst dosage, agitator speed and reaction time on the conversion of methyl palmitate were investigated and these process parameters were manually optimized by using the one factor at a time (OFAT) method. Reusability tests on the HTLC catalyst were performed under the optimum operating conditions by recycling the heterogeneous catalyst from one cycle to the subsequent cycle without neither washing nor drying after it was separated from the reaction mixture via vacuum filtration. Leaching of the HTLC catalyst active sites in the fatty esteramine samples were investigated throughout the recycling process.

1.5 Thesis Outline

This thesis comprises of five chapters. **Chapter 1** highlights the readers on brief background of the research and identifies the research problem. It also describes the objectives and the scope of the research. **Chapter 2** reviews on the palm oil and oleochemical industry as well as the surfactant market. Fatty esteramine as an intermediate for esterquats, a cationic surfactant, is discussed extensively in terms of its characteristics, applications in fabric care products and process involves in the fatty esteramine production. Processes to prepare fatty esteramine involving esterification of fatty acid as well as transesterification of triglycerides and methyl ester via homogeneous catalysis were made comprehended by reviewing and analyzing previous literatures. In-depth analysis of the previous heterogeneous catalysis for the production of fatty esteramine via fatty acid route and the potential heterogeneous catalysis via methyl ester route to be employed in this present study were discussed in detailed, emphasizing on the heterogeneous catalysts structure, advantages as well as their catalytic activities in various chemical processes. **Chapter 3** presents the detailed methodologies on the reaction process and characterization procedures of catalyst and product and also the computerized methods of the optimization of the reaction conditions. The results and findings were interpreted and discussed comprehensively in **Chapter 4**. Conclusion and recommendations for future works of this study were stated in **Chapter 5.**

CHAPTER 2: LITERATURE REVIEW

2.1 Overview of Palm Oil

Palm oil and palm kernel oil are two types of oils and fats that can be extracted from the oil palm *(elaeis guineenis*) fruits. Semi solid at room temperature, these oils and fats can be fractionated into solid and liquid fractions to yield stearin and olein respectively. Palm oil is semi-solid at room temperature (28 ^{o}C) and the melting point range between 32^{o}C – 40 ^{o}C. Palm oil has a balanced fatty acid composition in which the level of saturated fatty acids is almost equal to that of the unsaturated fatty acids. Palmitic acid (41- 47%) and oleic acid (36–41%) are the major component acids along with linoleic acid (9-12%) and only a trace amount of linolenic acid. The low level of linoleic acid and virtual absence of linolenic acid make the oil relatively stable to oxidative deterioration. Palm oil consists of a mixture of mono, di and triglycerides. Physical and chemical properties of palm oil and palm oil products depend very much on the composition of the triglycerides.

2.1.1 Palm Oil Industry

According to MPOB Statistics 2016, the world production of major oils and fats was 203.9 million tonnes in 2016. Among the oils and fats in the world market, palm oil and palm kernel oil were jointly emerged as the largest commodity produced, accounting for 64.7 million tonnes or 31.7% of the total oils and fats production. Following closely behind is the soybean oil, sharing its part at 51.5 million tonnes (25.3%) as shown in Figure 2.1 (MPOB Statistics, 2016). In 2016, 79.8 million tonnes of major oils and fats were exported worldwide and palm oil and palm kernel oil were accounted for 58.5% of the total export as indicated in Figure 2.2.

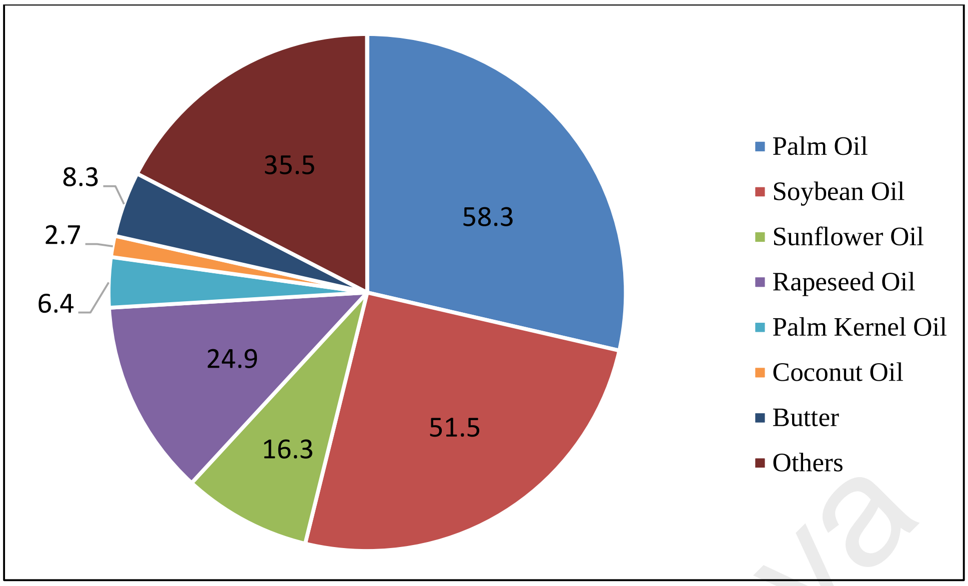


Figure 2.1: World Production of Major Oils and Fats (million tonnes) (MPOB Statistics, 2016)

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.

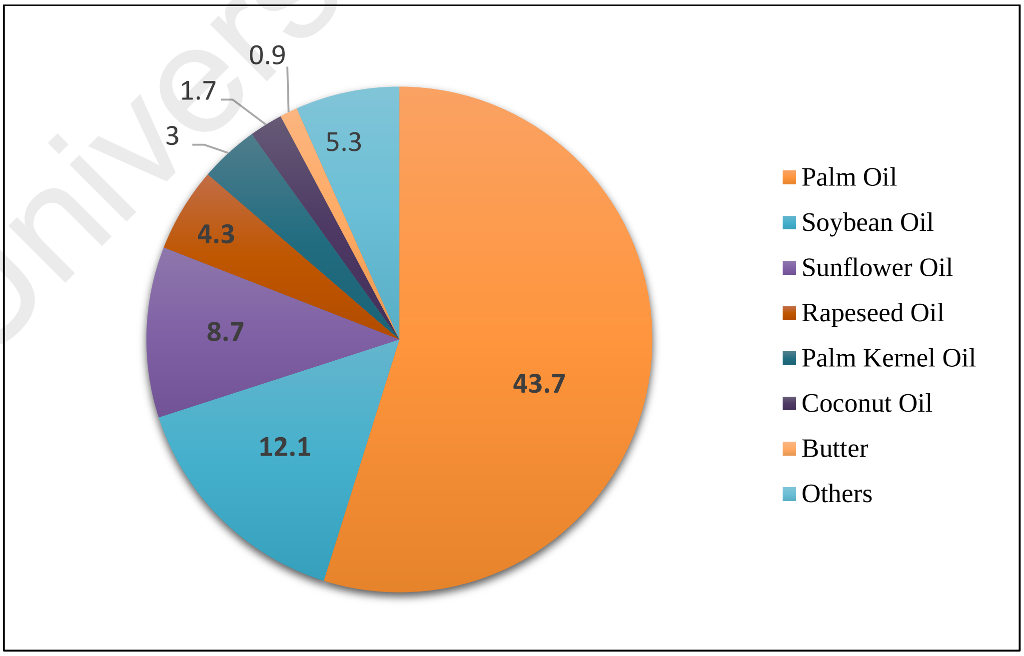


Figure 2.2: World Exports of Major Oils and Fats (million tonnes) (MPOB Statistics, 2016)

2.1.2 Oleochemical Industry

Most of the palm oil produced is used for food purposes and less than 20% goes into the non-food applications particularly in oleochemical sectors. Although smaller in volume, this is an important area of application since most of the palm oil products are further processed to higher value added products. A consistent and predictable supply of palm oil has led to the development of oleochemical industry in Malaysia. In 2016, Malaysia's production capacity of oleochemicals is about 3 million tonnes where about 2.76 million tonnes of Malaysian's oleochemicals are exported.

The major oleochemical products exported were fatty acids (0.92 million tonnes or 33.4% of total oleochemical exports), followed by fatty alcohol (0.56 million tonnes or 20.2%), methyl ester (0.48 million tonnes or 17.3%), soap noodles (0.41 million tonnes or 14.9%) and glycerine (0.39 million tonnes or 14.2 %). The five basic oleochemicals are fatty acids, fatty esters, fatty alcohols, fatty amine and glycerol. 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 detergent to electronic components, as described by Ting (2001) shown in Table 2.1.

2.1.3 Palm-based Methyl Ester

Fatty acid methyl ester is the most important derivative of fatty acid. The most common fatty ester is fatty acid methyl ester but its direct application is limited. Fatty acid methyl ester is usually converted into fatty alcohol, fatty alcohol sulphates (FAS), fatty alcohol ether sulphates (FAES), fatty esteramine and

Table 2.1: 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

methyl ester sulphonate (MES). With recent concern on the environment, fatty acid methyl esteris used as biofuel or biodiesel. There are two commercial processes for the production of fatty esters i.e. via transesterification of oils and fats and esterification of fatty acids. Transesterification of fats and oils is the most commonly used process for the manufacture of methyl esters, except in cases where methyl ester of specific fatty acids are needed. Transesterification of triglycerides produces methyl esters and glycerol. The reaction mechanism of transesterification can be described as in Figure 2.3. Another route of producing methyl ester is via esterification of fatty acids with methanol and water will be formed as the by-product. The reaction is expressed by the following equation 2.1.

$$\mathrm{RCOOH} \quad + \quad \mathrm{CH_3OH} \longleftrightarrow \mathrm{RCOOCH_3 + H_2O} \qquad (2.1)$$

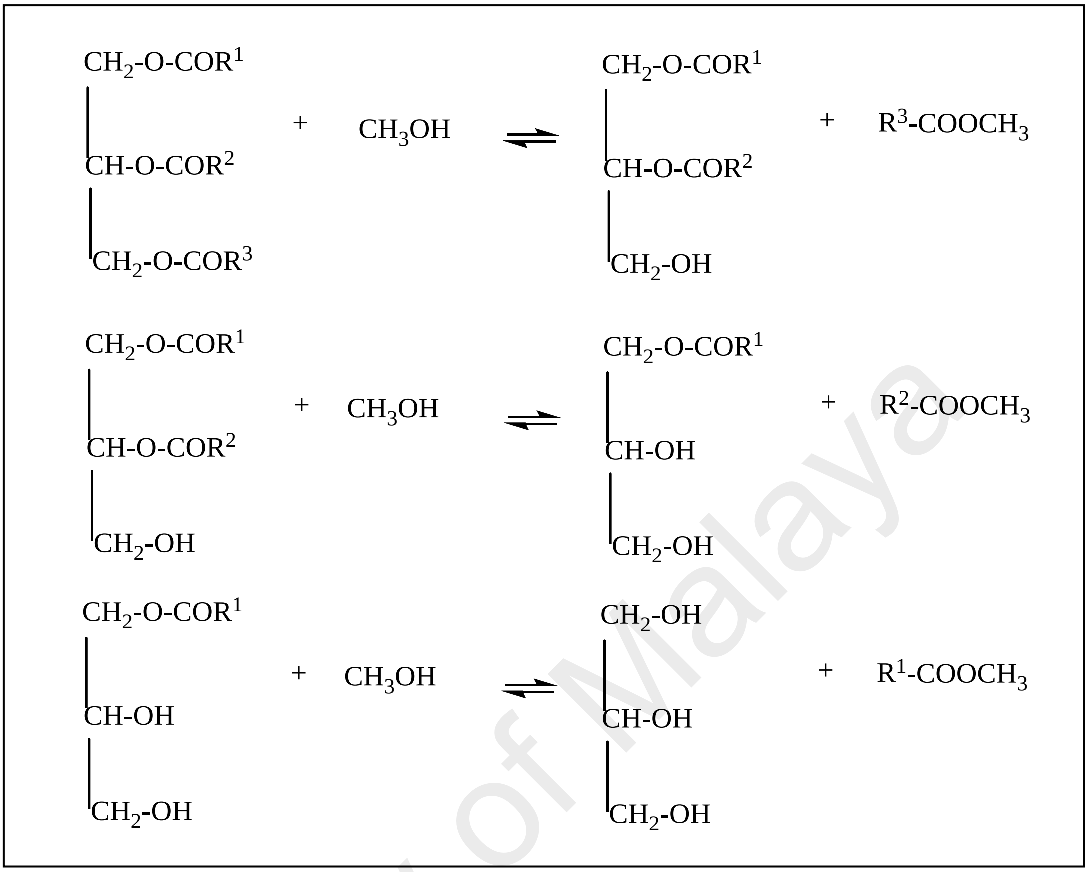


Figure 2.3:Transesterification of Triglycerides with Methanol

(Suyenty *et al.*, 2007)

2.2 Fatty Esteramine

2.2.1 Characteristic of Fatty Esteramine

Fatty amines can be classified into primary, secondary and tertiary amines depending on the number of alkyl groups attached to the nitrogen atom. Primary and secondary amines are used as starting material for the production of tertiary amine, which can be classified into mono, di and tri fatty alkyl tertiary amines. When the alkyl group contain ester bond, fatty mono, di or tri-esteramine are obtained as described by Idris *et al.,* 1998 (Figure 2.4). Fatty esteramine compound derived from tertiary amino alcohol consists of amine and ester functional groups depending on its starting feedstock.

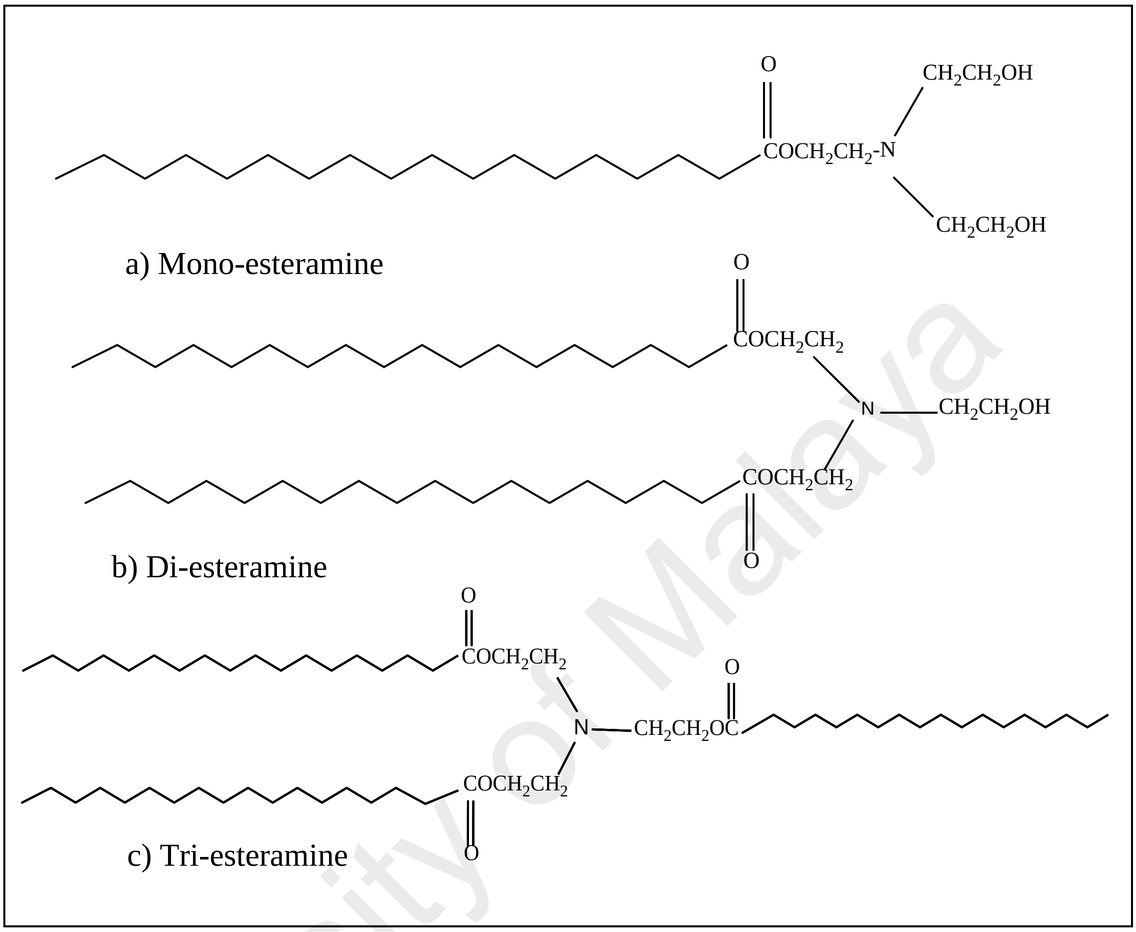


Figure 2.4: Expected Products from Esterification of Oleic Acid and Triethanolamine (Idris *et al.*, 1998)

The presence of ester functionality in between the long hydrocarbon chain and the parent tertiary amine molecule has helped in providing substantial biodegradability properties of the compound upon contact with water at certain pH when discharged into the sewerage drain. Fatty esteramines are characterized as non-ionic surfactant, thus, do not have a charged group. The hydrophilic function of the compound is provided by a water-soluble ester group that does not ionise to any great degree (Porter, 1994).The most significant application of fatty esteramine is as an intermediate for esterquats production, a biodegradable cationic surfactant.

2.2.2 Possible Application of Fatty Esteramine and Its Derivatives

The importance of fatty esteramine compound as well as its derivatives depends largely on its hydrocarbon feedstock, which play an important role in exhibiting respective physico-chemical performances. Its established functional performance has made it possible to incorporate this compound in various products to function as bactericide and surface conditioners in cosmetics, personal care and fabric care products (Shanklin *et al.*, 2006), as adjuvants for pesticides and fertilizers (Gustavsson *et al*., 2004), as adhesive promoter in plastisol (Van de Berg *et al*., 2000), as detergent in fuel composition (Farmer *et al*., 1999), as oil and gas well stimulation materials (Stains *et al*., 1991) and metalworking fluids (Kodali, 2001).

Surface Conditioners in Fabric Care and Personal Care Products

Good biodegradability as well as softening, antistatic and bactericidal properties of fatty esteramine-based esterquats has rendered them important compounds for meeting increasingly stringent environmental regulations and consumer demands for better performance products. The main application of quaternaries is in the textile industry. In particular, bis (hydrogenated tallow alkyl) dimethyl ammonium chloride is fast being replaced by fatty esteramine-based esterquats as the main ingredient in fabric softeners due to uncertainties surrounding the former's environmental acceptability. Esterquats are also used as an antistatic finish for synthetic fibre and as dye retardants by competing for positive dye sites on the fibre. In hair products, fatty esteramine-based esterquats are used as a rinse after shampooing to impart softeners and antistatic properties to the hair (Porter, 1994).

Oilfield Chemicals

The rising demand for crude oil and natural gas from the industrializing nations has created high prices in energy sources. In the effort to overcome the problem in the current oil and natural gas production, a continuous high level of oilfield activities is then expected. The increase in utilization of well stimulation and enhanced oil recovery methods followed by continuous push into deepwater drilling has created a wide range of opportunities for the supplier of oilfield chemicals to explore in the utilization of fatty esteramine from a reneawable feedstock (Stains *et al*., 1991).

Gasoline and Other Fuel Additives

Automobile engines tend to form deposits within combustion chamber and on the surface of engines components due to evaporation, oxidation and polymerization of hydrocarbon fuels. This deposit caused significant increase in fuel consumption and emission of pollutants. Increasing concern over fuel quality by automobile industries has led to the development of voluntary gasoline detergent standard, which will increase demand for deposits control agents. Fatty esteramines with the right hydrocarbon chain and hydrophilic-lipophilic balance (HLB) index has been reported to perform as fuel detergent (Farmer *et al*., 1999).

Consumer Pesticides and Fertilizers

The driving factor that will boost demand in this specialized product category is introduction of new products featuring convenient packaging, safety aspect and unique formulations such as ready-to-use, super concentrated versions or control release system which requires adjuvants to boost performance and stability of the emulsion system. The fatty esteramines in the form of ethoxylated version has been identified to be suitable as adjuvant for pesticides besides being biodegradable and improved uptake and efficacy of pesticides (Gustavsson *et al*., 2004).

Nanomaterials in Construction

Polyesteramines incorporated into nanomaterials for construction may offer improved performance properties for adhesive, concrete, coatings, flooring, glass, lighting equipment, plumbing fixtures and other construction products. The overall outlook for these materials is very promising with coating materials expected to constitute the largest application for nanomaterials in construction occupying 73% of the overall demand by application followed by composites (12%) and other applications (15%) (Industry Study No. 2185, 2007).

2.3 Cationic Surfactant

Generally, the basic chemical nature of surface active agent molecules or surfactant is illustrated in Figure 2.5. The hydrophobic tail is generally a long-chain hydrocarbon radical and it also can be a halogenated or an oxygenated hydrocarbon or a siloxane chain. The hydrophilic head group is an ionic or highly polar group that contributes some water solubility to the molecule. The nature of the hydrophile is the primary key for the classification of surfactants, with the subgroups categorised by the nature of the hydrophobe (Myers, 1988). Based on the nature of the hydrophile, four general groups of surfactants are defined: anionic, cationic, nonionic and amphoteric surfactants.

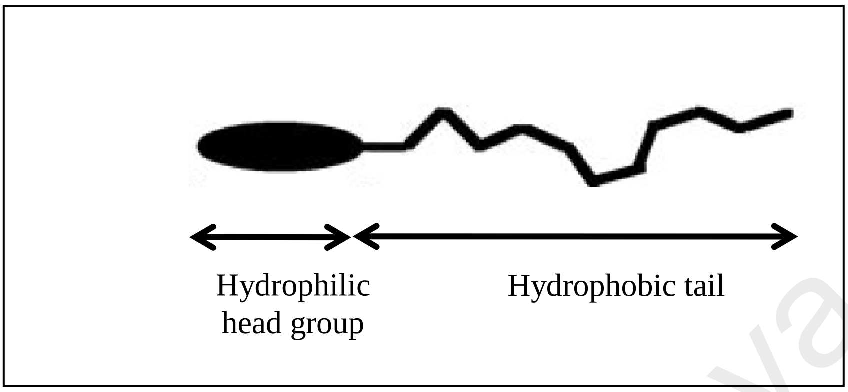


Figure 2.5: The Basic Chemical Nature of a Surface Active Molecule (Myers, 1988).

Cationic surfactant is characterizedby the present of the hydrophobic alkyl chain linked to the positively charged nitrogen atom. This class of surfactant accounts for only 4-5 % of the total surfactant production as shown in Figure 2.6 (Colin *et al.*, 2011). Cationic surfactant exhibit two very important features, whereby their positive charge allows them to adsorb on negatively charged substrates, as most solid surfaces are at neutral pH. This capacity confer to them an antistatic behavior and a softening action for fabric and hair rinsing. The positive charge enable them to operate as corrosion inhibitors as well as solid particle dispersion.They are used as emulsifiers in asphaltic emulsions and coatings in general, in inks, wood pulp dispersion and magnetic slurry. Another feature of cationic surfactant is that they are bactericides. They are used to clean and sterilize the surgery hardware, to formulate heavy duty disinfectant for domestic and hospital use and to sterilize food bottle or containers, particularly in the dairy and beverage industries.

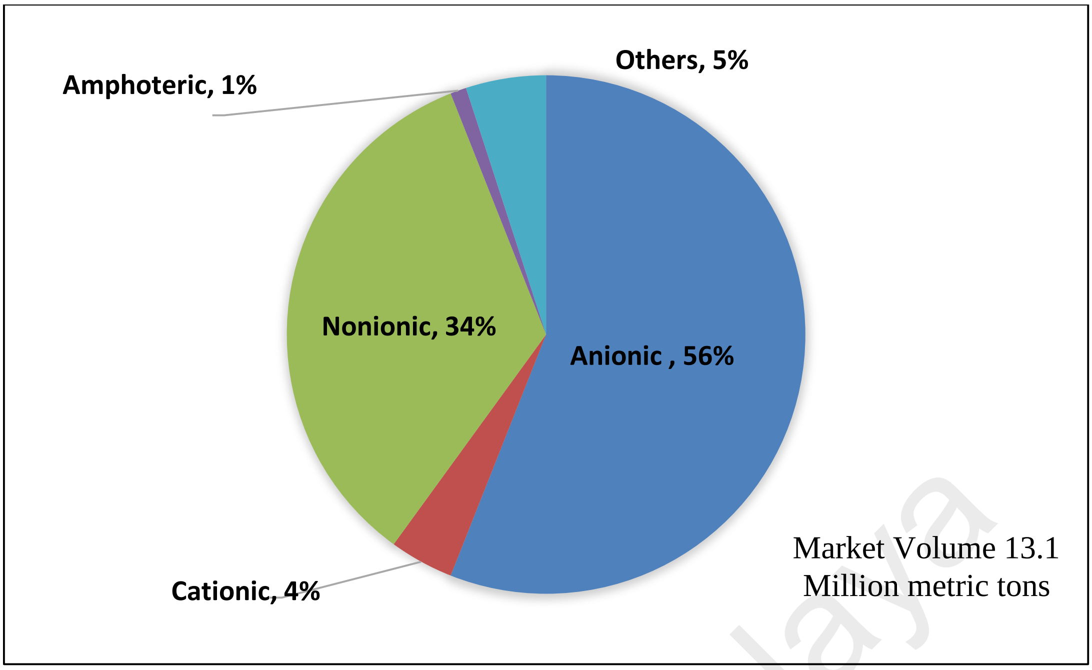


Figure 2.6: Global Surfactant Market by Ionic Type (Colin A. Houston & Associates, Inc. CESIO 2011)

Most used cationic surfactants are fatty amines, their salts and quaternary derivatives as shown in Figure 2.7. The amine is labeled as primary, secondary or tertiary respectively when the nitrogen is linked with 1, 2 our 3 alkyl groups. If the nitrogen possesses 4 bonds with C atoms, the compound is called a quaternary ammonium. In an ammonium structure, the nitrogen atom gives two electrons to ensure the fourth bond and thus remains with a positive charge.

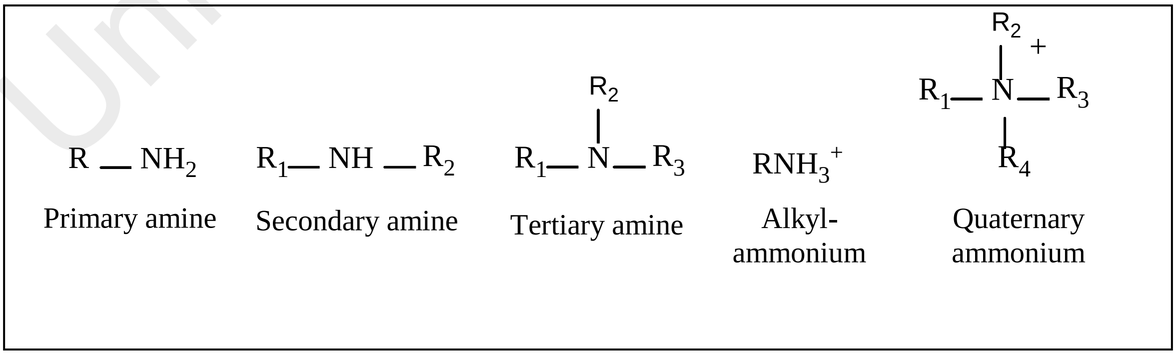
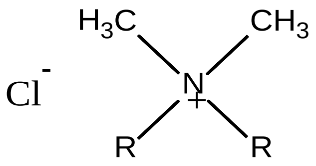


Figure 2.7: Fatty Amines, Their Salts and Quaternary Derivatives (Salager, 2002)

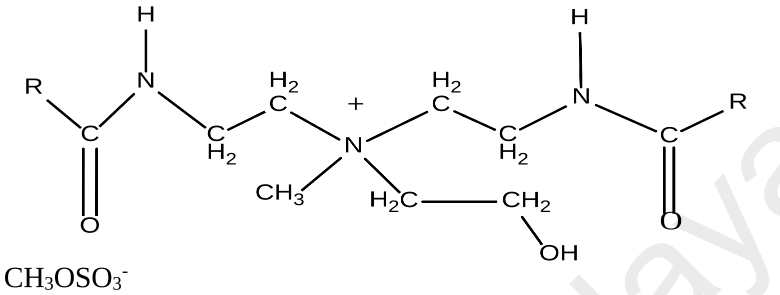
Quaternary ammonium compounds are the largest class of nitrogen-based cationic surfactant (Billenstein *et al.*, 1984). They contain at least one nitrogen atom that is covalently bonded to four alkyl or aryl substituents. Friedli *et al*. (2001) described that dehydrogenated tallow dimethyl ammonium chloride (Structure 1), ditallow amidoamine quat (Structure 2), ditallow imidazoline quat (Structure 3) shown in Figure 2.8 are traditionally used as an active ingredient in fabric softener. For environmental reasons, esterquats (Structure 4) have been the main ingredient in fabric softener replacing these traditional quats.

2.4 Esterquats

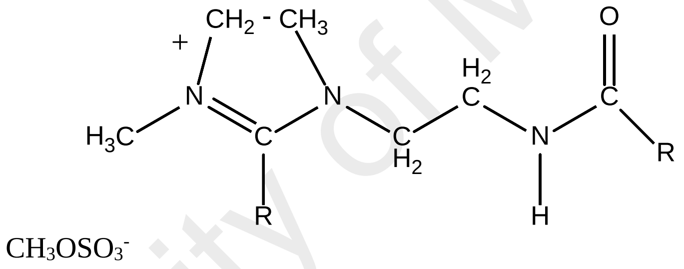
Esterquats is an interesting class of quaternaries, whereby they are characterized by the presence of hydrophobic alkyl chains that link to the positively charged nitrogen molecule via ester bonds as shown in Figure 2.9. Esterquats are replacing the conventional distearyl dimethyl ammonium compounds due to their excellent biodegradability (Friedli *et al*., 2001). This ester link provides site for easy hydrolysis to fatty acids and short chain quats where subsequently microorganism will be able to digest the fatty acid to give carbon dioxide and water (Puchta *et al*., 1993). The positive charge on the nitrogen atom confers to the compounds the ability to adsorb onto surface, most of which are negatively charged and can easily attract a positively charged molecule (Idris *et al.*, 1995).



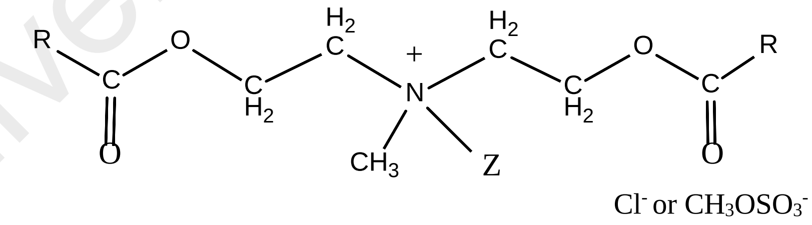
Structure 1: Dihydrogenated tallow dimethyl ammonium chloride



Structure 2: Ditallow amidoamine quat



Structure 3: Ditallow imidazoline quat



Where R = C_{11} to C_{17}, Z = CH_3 or CH_2CH_2OH

Structure 4: Esterquats

Figure 2.8: Examples of Quaternaries (Friedli *et al.*, 2001)

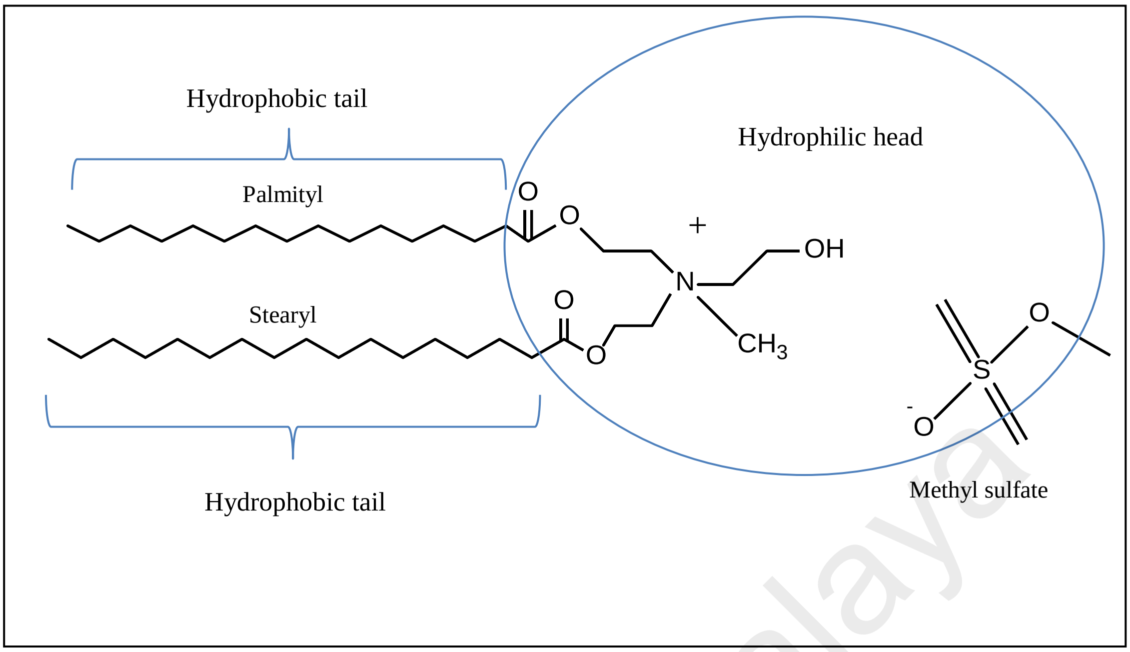


Figure 2.9: Esterquats Chemical Structure (Idris *et al.*, 1995)

Cationic materials having two long alkyl chains used as active softening compounds are substantially water insoluble. Hence, textile softening products are conventionally prepared with only 3–5% content of distearyl dimethyl ammonium compounds as the softening agent since aqueous preparations with more than 10% cationic active ingredient would results in high viscosity and stability problems (Chang, 1991). With esterquats, however, it is possible to prepare stable and low viscosity dispersions containing up to 50% active softening compounds. This will reduce the storage space, packaging and transportation costs and utilizes smaller and easier-to-handle containers (Keys, 1995).

Generally, esterquats are produced via a two-stage process in which fatty acid or ester is first esterified or transesterified with triethanolamine in the presence of catalyst to produce fatty esteramine. Fatty esteramine, an intermediate for esterquats which consist of mixtures of mono, di and tri-esteramine is then quaternized with an alkylating agent in monohydric solution to introduce the positive charge onto the esterquats molecule. The synthesis route for esterquats production as illustrated in Figure 2.10 has been developed by the Malaysian Palm Oil Board in 1995 by Idris and co-workers, whereby the process consists of two steps. The first step involves formation of esteramine by esterification of fatty acid with triethanolamine. The second step followed by the reaction of esteramine with dimethyl sulfate (quaternizing agent) in the presence of solvent.

Higher formation of mono-esteramine will exhibit good formulation stability but give low softening effects. Higher tri-esteramine content results in better softening but give poor formulation stability. Therefore, it is preferable to have higher di-esteramine content as it will exhibits both excellent softening and good stability of fabric softeners formulation (Mishra *et al*, 2007).

The direct esterification process to produce esterquats normally requires high temperatures and vacuum as well as corrosion- resistant equipment. These extreme conditions of direct esterification can be replaced with a milder process conditions for esterquats production. A milder process through transesterification between triethanolamine and methyl ester was patented by Haliza *et al.* (2006) in 2006 as an alternative to the direct esterification route from fatty acid. The esterquats production involves a two-step process, in which the fatty acid is replaced by methyl ester, which are transesterified with triethanolamine to produce esteramine and subsequently quaternized with dimethyl sulfate to introduce the positive charge onto the esterquats molecule. Overall, optimization of the esterification or transesterification process for maximum conversion into esteramine is the key step in the preparation of esterquats.

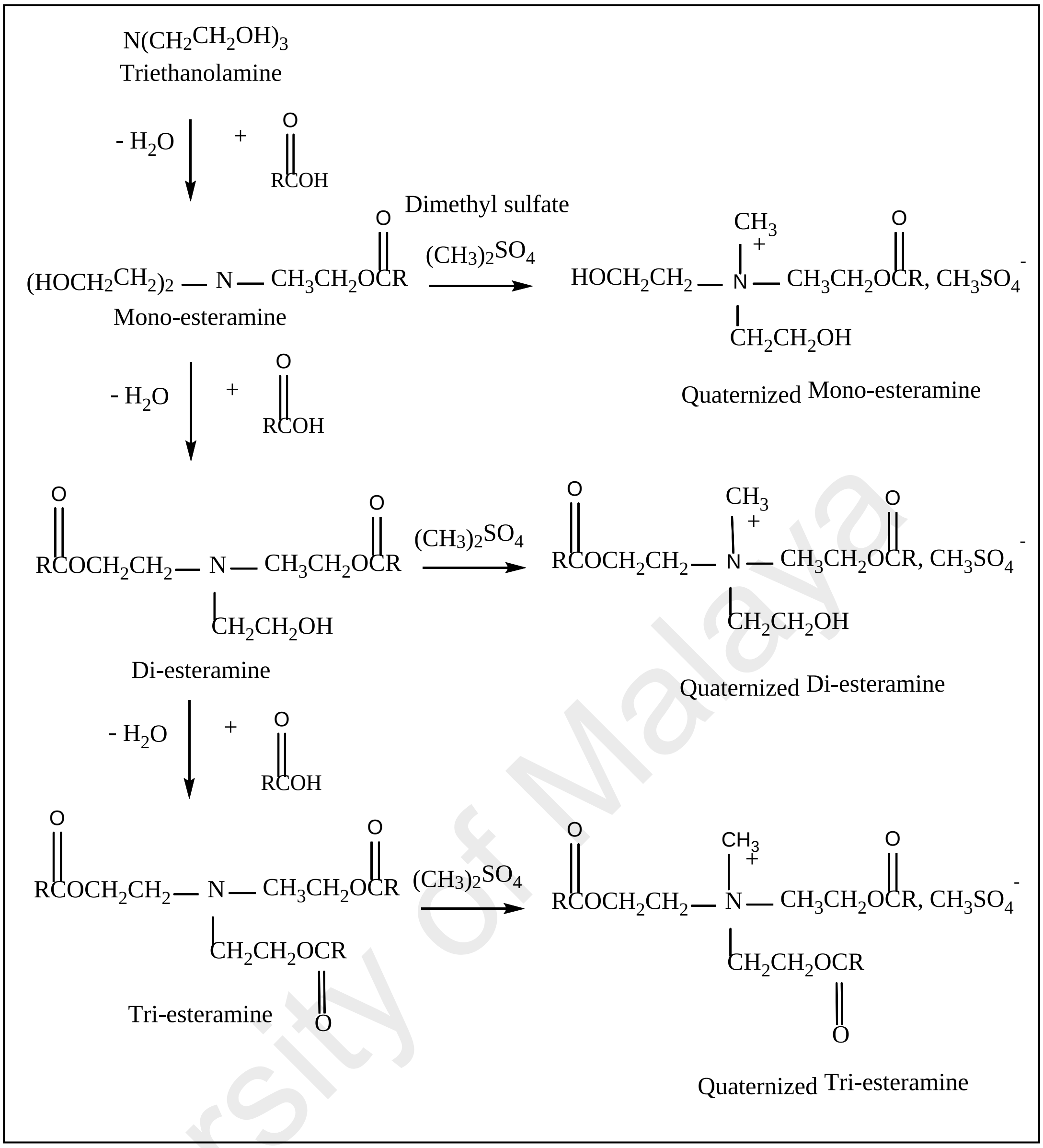


Figure 2.10: Preparation of Quaternized Esteramine (Idris *et al*.,1995)

2.4.1 Applications of Esterquats

Fabric Softeners

Esterquats are cationic surfactant, which are mainly used as an active ingredient in fabric softener due to their significance softening effect and their excellent biodegradability. The positively charged molecules of esterquats is adsorbed onto a surface that are normally negatively charged. Once adsorbed onto the surface, the long hydrocarbon chain (hydrophobic tail) present in the molecule will extend outwards from the surface. Such configuration of the hydrocarbon chain provides both softening and lubricity, giving soft and fluffy feels to the fabrics. An anti-static effect will also be exhibited due to the neutralization of the surface charge (Idris *et al.*, 1995). An illustrative diagram on the function of esterquats molecule on solid surface is shown in Figure 2.11. The search for renewable resources, specific requirements by certain ethnic communities and growing concern for environmentally friendly products have put vegetable-based raw materials in the growing market trend for household consumer products around the world. In line with the development of new types of washing machines, which include separate automatic dispenser for detergent and fabric softener, consumers are becoming attracted to the use of this commodity in addition to their basic laundry process because it imparts softness, comfort and fragrance and sometimes ease of ironing to their laundry. The general trends in fabric softeners include an overall movement towards concentrated products (15%), although regular product (3% - 8%) predominates in many markets and co-exist with ultra-concentrate (25% - 35%) (Matthew, 1999).

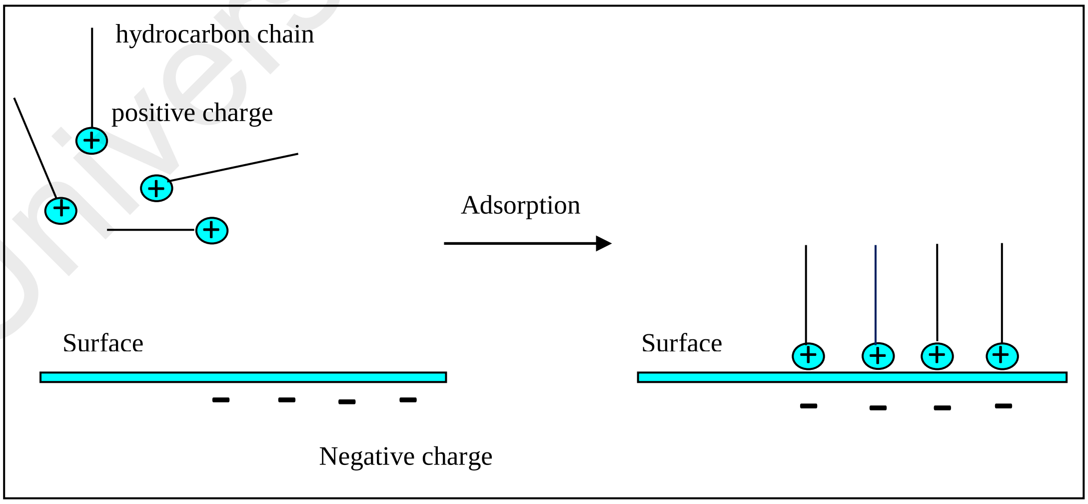


Figure 2.11: Illustration on the Adsorption of Positively Charged Esterquats Molecule on Negatively Charged Surface (Idris *et al.*, 1995)

2.5 Process for Fatty Esteramine Production

2.5.1 Esterification via Homogeneous Catalysis

There are several studies reported on the process which utilizes fatty acid as the starting materials to produce esteramine. The esterification of fatty acids with triethanolamine has been conventionally catalyzed with homogeneous acid catalyst, such as para toluene sulfonic acid, phosphorous acid and sulfuric acid. Trius *et al*. (1991) had developed a process to produce esteramine from esterification of fatty acid having chain lengths of C_6 – C_{22} and triethanolamine in the presence of acid catalysts. In his study, several types of acid catalysts were employed including sulfonic acid, such as para-toluene sulfonic acid or methane sulfonic acid, phosphoric acid, phosphorous acid, hypophosphorous acid and oxalic acid. According to his patent, the esterification aided by these homogeneous catalysts was performed at 160 ^{o}C, vacuum of 1.33 mbar and catalyst dosage of 0.15%. Idris *et al*. (1995) studied the production of esteramine from palm-based myristic acid that esterified with triethanolamine and catalyzed by phosphinic acid of 50% concentration in the presence of xylene as a solvent. The esterification performed at 140 ^{o}C, mole ratio of myristic acid to triethanolamine of 2:1 and duration of 4 hours successfully yielded the desired mono, di and tri-esteramine. Another process developed and patented by Idris *et al*. (2003) was on the esterification reaction between distilled palm-stearin fatty acid and triethanolamine catalyzed by acid catalysts (MY 138148) for fatty esteramine production. According to the patent, acid catalysts such as hypophosphorous acid, sulfuric acid and para-toluene sulfonic acid were employed in the esterification process performed at 160 ^{o}C and vacuum between 1 – 40 mbar to form the desired esteramine prior to the production of esterquats. Meanwhile, Nepras *et al*. (2012) had employed divalent zinc as the homogeneous catalyst to produce esteramine through esterification processing between alkanolamines and fatty acids. According to him, the process utilizing divalent zinc catalyst can facilitate and accelerate the esterification process as well as produce esteramine that has a good color and stable upon storage.

2.5.2 Transesterification via Homogeneous Catalysis

Several literatures reported on the processes that used triglycerides or methyl ester as the starting materials for the production of esterquats. These feedstocks are transesterified with triethanolamine under the action of base catalyst such as sodium or potassium alkoxides (e.g. methoxides) in the first step of the esterquats production. European patent EP 0 750 606 B1 (Cognis) described the process in which, the fatty acids are replaced by triglycerides as the starting materials to produce esteramine. Potassium hydroxide and sodium methylate was employed as the homogeneous alkaline catalyst for the transesterification process. However, according to Pi Subirana *et al.* (1999), this process involved longer reaction time which leads to formation of discolored product, which required bleaching of the product in the post-treatment process. Thus, resulted in increase of cost of production. Due to this problem, Pi Subirana *et al*. (1999) had demonstrated the used of sodium borohydride and hypophosphorous acid as the homogeneous catalyst in the transesterification of triglycerides with triethanolamine. It was reported that the use of borohydrides as opposed to other conventional transestericication catalysts leads to faster reaction completion and in addition, produce esteramine with high color quality. The reaction was reported to be carried out at mole ratio of triglycerides to triethanolamine between 1.2:1 to 2.2:1, sodium borohydride dosage of 0.01 to 0.1% by weight of triglycerides, temperature of 120 – 180 ^{o}C with duration of 1 to 12 hours.

Previous works on the production of fatty esteramine was conducted by Idris *et al*. (1995) via transesterification of palm-based methyl ester and triethanolamine that employed 1% sodium methoxide as the homogeneous catalyst. Unlike the esterification process, transesterification of methyl myristate with triethanolamine studied by Idris *et al*. (1995) could be accomplished at milder temperature between 80 to 100 ^{o}C within 2 hours reaction without the presence of solvent. A milder process for esterquats production through transesterification between triethanolamine and palm stearin methyl ester catalyzed by 1% sodium methoxide as the alkaline homogeneous catalyst was performed at 100 ^{o}C, 200 mbar, 5% catalyst dosage, 540 rpm and mole ratio of 2:1 (methyl ester : triethanolamine). This transesterification process was reported as the alternative route for esterquats production replacing the extreme process conditions from direct esterification from fatty acids.

However, homogeneous catalysts conventionally used for esteramine production have several disadvantages, which include complex separation process as well as environmental issue due to high toxicity and corrosiveness. Due to these limitations, a process employing heterogeneous catalysts have been proposed as an alternative to the homogeneous catalysts for the production of esteramine.

2.5.3 Esterification via Heterogeneous Catalysis

Few studies reported on the use of heterogeneous acid catalysts in direct esterification of fatty acids to produce esteramine. The use of supported zirconium sulfate on HZSM-5 as the heterogeneous catalyst in the esterification of stearic acid with triethanolamine was reported by Jiang *et al.* (2007). However, his study revealed that the pore diameter of HZSM-5 was too small to produce the esteramine. The geometric size of mono plus di-esteramine was reported to be of approximately 4 nm whereas tri-esteramine molecules are approximately 7 nm. Esterification of stearic acid with triethanolamine to produce triethanolamine ester using zirconium sulphate supported on MCM-41, SBA-15 (9) (pore diameter 9 nm) and SBA-15 (6) (pore diameter 6 nm) mesoporous molecular sieves has been demonstrated by Geng *et al.* (2011). Among those catalysts, 20% loaded zirconium sulphate supported on SBA-15 (with pore diameter 6 nm) was claimed to exhibit better catalytic activity and selectivity towards mono and di-esteramine compared to the conventionally used H_3PO_3 homogeneous catalyst. Moreover, this catalyst has good stability and can be reused at least five times. The optimum operating conditions for esterification of stearic acid and triethanolamine catalyzed by these zirconium sulfate supported on SBA-15 mesoporous materials were reported at temperature of 190 ^{o}C, catalyst dosage of 0.25 %, mole ratio of 1.8:1 (stearic acid : triethanolamine) and 6 hours reaction time. Jiang *et al* (2012) used aluminium supported on SBA-15 mesoporous molecular sieves in esterification of stearic acid with triethanolamine under the same reaction conditions reported by Geng *et al* (2011). The findings indicated that aluminium supported on SBA-15 was an efficient catalyst in which their activity and selectivity is comparable to zirconium sulfate supported on SBA-15 (pore diameter 6 nm) and better than zirconium sulphate supported on MCM-41 and SBA-15 (pore diameter 9 nm). Furthermore, aluminium supported on SBA-15 can be reused for six times, suggesting that this catalyst has an excellent stability.

Masoumi *et al* (2013) had investigated a milder process for the production of esteramine as opposed to direct esterification of fatty acids and triethanolamine in the presence of solid acid catalyst. He revealed that the study involved lipase-catalyzed esterification of oleic acid and triethanolamine for the esteramine production. In their work, lipase from Candida Antarctica (Novozyme 435) was used as the biocatalyst in the organic solvent system. Response surface methodology (RSM) was used to optimize the enzymatic process conditions. The optimum conditions were established at enzyme of 4.8wt %, reaction time of 24 hours, temperature of 61.9 ^{o}C, mole ratio of 1:1 (oleic acid to triethanolamine) and agitation speed of 480 rpm with the highest conversion of 63.6%.

2.5.4 Transesterification via Heterogeneous Catalysis (Hydrotalcite – like Compounds)

In this study, the employment of heterogeneous basic catalyst in transesterification of methyl ester and triethanolamine for the production of esteramine has been explored. There is no research has been reported on transesterification from methyl ester aided by heterogeneous catalyst, specifically hydrotalcite-like compounds (HTLC) and as such, this current work can be considered as the first experimental investigation to produce esteramine via heterogeneous catalysis.

Hydrotalcite-like compounds (HTLC) 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. Cavani *et al.* (1991) explained that 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 (Figure 2.11a). 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 (Figure 2.11b).When Mg^{2+} ions are substituted by a trivalent ion having almost similar radius (such as $A1^{3+}$ 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 (Figure 2.11c).

Cavani *et al.* (1991) reported that upon calcination, HTLC 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.

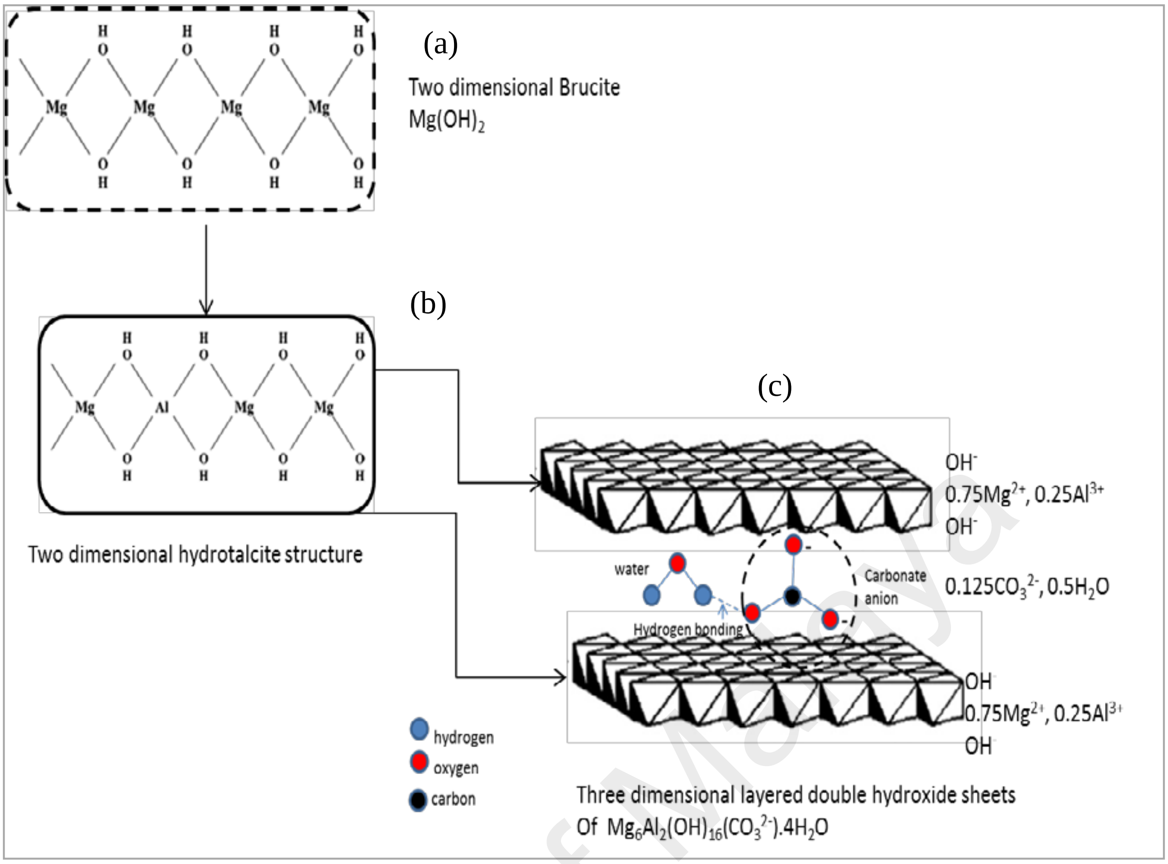


Figure 2.12: Two-dimensional Representation of the Structure of Hydroxide Layers in: (a) Brucite-Mg $(OH)_2$; (b) Hydrotalcite-$Mg_6Al_2(OH)_{16}(CO_3^{2-}).4H_2O$; (c) Atom positions (Cavani *et al.*, 1991)

There are several studies reported on the use of HTLC as catalysts in transesterification processes. Ca-Al (HTLC) has been reported by Simonetti *et al*, (2014) as solid base catalyst for biodiesel production from transesterification of soybean oil in methanol and ethanol. The calcined Ca-Al catalyst is considered as an effective catalysts for transesterification of soybean oil with ethanol and methanol. When the reaction was carried out with the Ca-Al catalyst, the conversion of soybean oil was reported to be 94% with ethanol and 100% with methanol. Simonetti *et al*, (2014) also mentioned that in his study, the Ca-Al catalyst was impregnated with KOH. However, the impregnated Ca-Al catalysts gave much lower yields as compared to the non-impregnated Ca-Al catalyst. The maximum conversion for ethanolysis employing the impregnated

Ca-Al was 58%, whereby the maximum conversion obtained with methanolysis was reported to be 90-95%. According to Simonetti *et al*, (2014), the catalytic performance of the catalysts is related to the acid properties determined in isopropanol decomposition reaction. The higher acid activity on the impregnated catalysts gave unfavorable transesterification reaction.

Kocik *et al.* (2015) also investigated the catalytic activity of Ca–Al for biodiesel production from rapeseed oil. In his study, it was found that the calcination temperature of the catalyst affected the conversion and leaching of the active species (Ca^{2+}). The catalyst was synthesized from hydrocalumite as a precursor at constant molar ratio of 2 of Ca-Al and different calcination conditions (temperature from 250 to 950 °C and in the flow of air or nitrogen). It was reported that the conversion rapidly increases when the catalyst was calcined at temperatures more than 650 °C in the flow of air because mixed oxide was formed. However, the amount of leached calcium into the reaction products (the ester and glycerol phase) also increases. When the catalyst was calcined at temperature of 450 °C in the flow of nitrogen, maximum conversion was observed. However, slightly decrease in conversion was observed at calcination temperature between 450 to 950 °C. In the case of calcination in a flow of nitrogen, the leaching also increases at catalyst calcination temperature of 450 °C. Kocik *et al.* (2015) also reported that the catalytic activity of Ca-Al is significantly influenced by the mixed oxides present in the catalyst and not influenced by the CaO content in the catalyst. Conversion of 92% was obtained after 90 min of reaction when the reaction was performed at temperature of 60 °C, 4% catalyst dosage, molar ratio of 24:1 (methanol to oil) and agitator speed of 320 rpm.

Gao *et al*. (2010) has reported the use of KF/Ca-Al solid base catalyst in the transesterification of methanol with palm oil to produce biodiesel. It was found that the yield was much higher when catalyzed by KF/Ca-Al than Ca-Al (without the incorporation of KF), implying that loading of KF largely had increased the activity of the catalyst. KF mass ratio of 80% showed a high catalytic activity of the catalyst after only one hour reaction with yields of 85%.

It was also reported that increase in reaction time will increase the yield, whereby 4 hours appeared to be the optimal reaction time that give maximum yield of 99.7%. Higher reaction temperature had increased the reaction rate, whereby the optimum reaction temperature was established at methanol boiling point of 65 ^{o}C. Increase in catalyst dosage had increased the contact opportunity of the catalyst with the reactants, which directly influenced the reaction rate, eventually the conversion and yield. In this study, it was found that the biodiesel yields was increased as the mole ratio of methanol to oil increased with maximum yield of of 80% at molar ratio of 12:1(methanol:oil). Increasing mole ratio up to 12:1 could be explained by the forward reaction effect of the excess methanol on the reaction equilibrium. However, a decrease in yield was observed as the mole ratio was increase higher than 12:1 and this could be due to the large amount of methanol that diluting the oil and reducing the reaction rate. According to Gao *et al*. (2010), for the mass ratio 80 wt% ($KF.6H_2O$ to Ca-Al mixed-oxides) catalyst, under the optimal condition at 65 ^{o}C, 5% catalyst, methanol to oil molar ratio of 12:1 and 5 hours reaction time, the highest biodiesel yield obtained was 98%.

Another study on the application of HTLC as catalyst in biodiesel production was also reported by Wang *et al*. (2011). According to him, HTLC containing Mg^{2+}, Ni^{2+} and Al^{3+} layered double hydroxide (LDH) provide suitable base catalyst for transesterification of soybean oil with methanol to produce biodiesel. It was reported that several process parameters including the basicity and acidity of catalyst, the mole ratio of methanol to oil, reaction temperature and reaction time can affect the transesterification. In this study, the optimum reaction temperature was reported at 65 ^{o}C because it is close to the boiling point of methanol. The conversion into fatty acid methyl ester (FAME) was influenced by the basicity and Mg content of the catalysts with Mg/Ni molar ratio of 16 showing the highest basicity. His study suggested that the rate of FAME formation is lower at lower molar ratios of methanol to oil and increases when the molar ratio reached maximum value of 21. The reaction time also affects the transesterification process, whereby the maximum conversion of 87% can be reached within 4 hours reaction time. The optimum conditions for this study was obtained at methanol/oil molar ratio of 21, 0.3% catalyst and 1200 rpm stirring speed for 4 hours at 65 ^{o}C, which results in the highest methyl ester conversion of 87%.

Studies on the utilization of HTLC as catalyst in the production of monoglycerides have been reported in several literatures. Corma *et al* (2005) reported that Li-Al mixed oxide and rehydrated Mg-Al mixed oxides appeared to be a promising catalysts for the transesterification of methyl oleate with glycerol for the production of monoglycerides. Rehydration of the calcined Al–Mg hydrotalcite notably enhances the catalytic activity of the corresponding Mg-Al mixed oxide and this catalyst exhibit Brönsted basic sites, which appeared to be an effective catalysts for the transesterification process. The selectivity towards monoglycerides was higher than that obtained with other solid Lewis base catalysts. According to this study, the higher selectivity towards monoester was mainly due to the ability of this catalyst to perform the subsequent transesterification of the diglycerides during the reaction. Corma *et al* (2005) also claimed in his study that Li-Al mixed oxide is an active Lewis base catalyst with better performance than MgO and Mg-Al in transesterification of methyl oleate with glycerol for the production of monoglycerides.

In 2006, Climent and co-worker studied the possibility of using Li-Al and Mg-Al for the production of polyoxyethylene glycol monoester via transesterification of methyl oleate and polyethylene glycol. Climent et al. (2006) mentioned that although Mg-Al mixed oxides exhibit lower catalytic activity than MgO, they are very stable and mechanically strong catalysts. Li-Al was also reported as a replacement to Mg-Al as the density of negative charge on the oxygen will increase with Li $^{2+}$, leading to an increase of the base strength and consequently increase the catalytic activity. Li-Al performed efficiently in the transesterification reaction than Mg-Al mixed oxides, however its activity was still lower than MgO. Rehydrated Mg-Al catalysts and MgO exhibited similar selectivities towards monoester formation. In this study, the influence of reaction temperature and mole ratio of PEG to methyl oleate were investigated. Reduce the reaction temperature had improved the transesterification process, whereby temperature of 453K gave higher selectivity of 95% towards monoester than at 493K, for 65% conversion within after 3 hours reaction time. Increase in mole ratio of PEG to methyl oleate from 1:1 to 4:1 gave a good conversion to monoester and selectivity of 98%.

A series of Mg-Al layered double hydroxides intercalated with various alkoxide ions such as methoxide, ethoxide, *iso*-propoxide and *tert*-butoxide applied as the heterogeneous catalysts in the transesterification of methyl laurate with glycerol to selectively synthesize monolaurins was reported by Nuchanart *et al.* (2016). According to his study, the initial rate of the transesterification was increased with increasing content of the intercalated catalytically active alkoxide ions. This study also revealed higher basic strength enhanced the methyl laurate conversion, selectivity and yield. It was reported that Mg-Al (LDH) intercalated with butoxide ion (t-$C_4H_9O^-$ – MgAl) was the most suitable catalyst and exhibited superior performance, which gave the highest yield and selectivity of monolaurin of 86.6 and 87.3%, respectively with methyl laurate conversion of 99%. High selectivity towards monolaurin was influenced by the molecular size of the *tert*-butoxide ions rather than the basicity of the alkoxide. Nuchanart *et al.* (2016) mentioned that the larger molecular size of the *tert*-butoxide reduced the spatial volume in the interlayer space of the intercalated Mg-Al, limiting the consecutive transesterification of manolaurin to di and trilaurin. Several process parameters were found to give a significant impact on the transesterification as mentioned in this study. It appeared that increase in temperature from 130 to 150 ^{o}C had increased the monolourin conversion and selectivity. The conversion and selectivity increase when catalyst loading increase from 2 – 4%. More than 4% catalyst loading reduced the conversion and selectivity, due to the mass transfer problem at higher level of catalyst loading. When the mole ratio (glycerol: methyl laurate) was reduced from 6:1 to 4:1, the selectivity was significantly reduced, as the increase in the proportion of methyl laurate promoted the consecutive transesterification to di and trilaurin. Increased the mole ration from

6:1 to 8:1 had reduced the conversion and selectivity due to the increased in mass transfer limitation caused by the high viscosity of glycerol.

Alvarez *et al,* (2010) also reported on the use of Mg-Al mixed oxide in transesterification of glycerol (biodiesel by-product) using diethyl carbonate as co-substrate to produce glycerol carbonate and glycerol dicarbonate. This green, efficient and selective process described in his study involving different hydrotalcite-like compounds containing Mg-Al molar ratio of 4:1 that were activated by calcination and followed by rehydration under ultrasound. According to Alvarez *et al,* (2010), the rehydrated Mg-Al gave 99% glycerol conversion after 10 hours reaction time, whereas the Mg-Al mixed oxide catalyst achieved only a 76% glycerol conversion eventhough after 50 hours of reaction. This study revealed that eventhough these two catalysts exhibited similar total number of basic sites and the rehydrated catalyst has significantly lower surface area compared to the Mg-Al mixed oxide, the rehydrated Mg-Al catalyst (Brønsted basic sites) shows better catalytic properties than Mg-Al catalyst (Lewis basic sites). The study concluded that the type of basicity of the solid catalyst has more influence on the activity of the catalyst than number of base sites.

2.6 Optimization Study

The primary goal of optimization is to find the operating conditions that maximize (or minimize) the system responses.Traditionally, reaction optimization involves changing the value of one reaction parameter at a time for each experimental run in a series of reactions, while keeping the others at fixed level, known as the one-factor-at-a-time (OFAT) experimental approach (Moos *et al*., 1997). However, OFAT experimental approach has various drawbacks. The major disadvantage is that it fails to consider any possible interaction between factors (independent variables) studied. Consequently, this technique does not depict the complete effects of the factors on the response (dependent variables) (Montgomery, 2009). Another disadvantage of OFAT approach is the increase in the number of experiments necessary to conduct the research, which leads to an increase of time and cost as well as an increase in the consumption of reagents and materials (Moos *et al.*, 1997). Therefore, this conventional optimization methods are found to be inefficient. In order to overcome this problem, the optimization of chemical processes has been carried out by using multivariate statistic techniques. A far more comprehensive and reliable optimization method is the design of experiments (DOE) approach.

Some of the most popular multivariate optimization tools are Artificial Neural Network (ANN), Taguchi Robust Design Method, Factorial design, Wavelet Neural Network (WNN) and Response Surface Methodology (RSM). Among these optimization tools, Response Surface Methodology (RSM) is the most relevant multivariate techniques used in analytical optimization. The application of RSM as optimization tools and its reliability to generate a model equation and to calculate optimum condition have been reported in many chemical and environmental processes (Zabeti *et al.,* 2009b)

2.6.1 Response Surface Methodology (RSM) Optimization Method

In the field of chemical reaction and synthesis, RSM optimization method has been applied by numerous researchers to optimize the reaction conditions in order to achieve certain product's quality. Masoumi *et al.* (2011) employed RSM optimization method to determine the optimum reaction conditions for the lipase-catalyzed synthesis of oleic acid and triethanolamine for the production of fatty esteramine. The reaction parameters chosen are enzyme amount, reaction temperature, reaction time, agitator speed and molar ratio of oleic acid to triethanolamine and the response was the esterification conversion percentage. They conducted experiments based on central composite design (CCD) by varying each reaction parameter at five levels. Masoumi *et al.* (2011) also compared the RSM optimization technique with artificial neural network (ANN) and discovered that RSM had lower percentage of error (2.32%) compared to ANN method (3.98%). In 2014, Aziz and co-worker conducted a study on transesterification reaction of palm oil methyl ester and pentaerythritol adopting RSM for optimization of the process conditions. Central composite design (CCD) was used to evaluate four factors which were temperature, amount of catalyst (sodium methoxide), molar ratio (palm oil methyl ester: pentaerythritol) and the duration of the reaction using a five-level-factor.

RSM in combination with Central Composite Design (CCD) was used to optimize the activity of CaO/Al_2O_3 solid catalysts for the production of biodiesel conducted by Zabeti *et al* (2009). His study revealed that both the calcination temperature and amount of calcium oxide loaded on the support had significant effects on the biodiesel yield. In 2010, Zabeti and co-worker also performed an optimization study adopting RSM in conjunction with Central Composite Design (CCD) to optimize the operating parameters in transesterification of palm oil using the optimum CaO/Al_2O_3 solid base catalyst developed in his earlier study for biodiesel production. Alcohol to oil molar ratio, catalyst content and reaction temperature were chosen as the independent variables while the response selected was the amount of methyl ester yields. He also reported the interaction effects between these independent variables on the amount of methyl ester yields.

RSM optimization method has also been applied in the optimization of reaction conditions for biodiesel production conducted by Mahdavi *et al* (2014). Transesterification of cottonseed oil with ethanol over a novel catalyst CaO–MgO supported on Al_2O_3, conducted in this study involved three independent variables such as loading of CaO–MgO on Al_2O_3 catalyst, reaction temperature and molar ratio of ethanol to cottonseed oil and the response chosen was cottonseed oil conversion. They conducted the experiments based on the Box–Behnken design by varying each of the operating parameters at three levels.

Norhazimah *et al* (2012) adopted RSM optimization of fermentation parameters for the production of bio-ethanol from oil palm trunks sap using face-centered cube design (CCD). Effects of process parameters such as temperature, initial pH, agitation rate and percentage inoculums on ethanol yield were studied by using RSM. The results showed that temperature was the most significant factor that influenced the ethanol yield, followed by the interaction effect of temperature-initial pH, quadratic effect of initial pH and interaction effects of initial pH and agitation.

Other previous works that employed RSM approach as a medium in optimizing the reaction conditions are Jose *et al*. (2011), who studied transesterification of glycerol and dimethyl carbonate to produce glycerol carbonate and also Maadyrad *et al*. (2011), who investigated the vacuum deep-fat frying process to reduce the oil content in fried snacks, maintaining the product nutritional quality and reducing the oil deterioration.

2.7 Summary

Fatty esteramine is an intermediate for esterquats, a cationic surfactant used as an active ingredient in fabric softeners. Conventionally, production of esteramine aided by homogeneous catalysts was reported with major contribution by Trius *et al*.(1991), Pi Subirana *et al*. (1999) and in European patent EP 0 750 606 B1 (Cognis). Due to complex separation process and significant environmental impact, the use of homogeneous catalyst has been substituted by the employment of heterogeneous catalyst for the production of esteramine.

Few studies on the production of fatty esteramine via direct esterification utilizing fatty acids as feedstock, employing heterogeneous catalysts were reported by, Jiang *et al.* (2007), Geng *et al.* (2011), Jiang *et al.* (2012) and Masoumi *et al.* (2014). No research has been reported on transesterification of methyl ester as the starting material for esteramine production employing heterogeneous catalyst, specifically HTLC as catalyst. RSM optimization method was used by Masoumi *et al.* (2011) in his work on lipase-catalyzed synthesis of oleic acid and triethanolamine for the production of fatty esteramine. As such, this present study will be adopting the RSM approach to obtain the optimum operating condition towards maximum di-esteramine yield.

Due to no study was reported on the process to produce fatty esteramine via transesterification of methyl ester using HTLC as catalyst, the present research intents to investigate thoroughly on this new route, based on the research methodology discussed in Chapter 3.

CHAPTER 3: RESEARCH METHODOLOGY

In order to achieve the objectives and the scopes of the research, the experimental and analytical procedures used in this study are presented and discussed with more details in this chapter.

3.1 Materials for the Production of Fatty Esteramine

Palm-based methyl palmitate (98% purity) was purchased from Carotino Sdn. Bhd. and triethanolamine (99.5% purity) was purchased from Bumi-Pharma Sdn. Bhd. Hydrotalcite-like compound (HTLC) was developed in house by the Malaysian Palm Oil Board. Sodium methoxide as a 1% solution was freshly prepared, according to method reported by Idris *et al*. (1995) in which the sodium metal was supplied by Bumi-Pharma Sdn. Bhd and methanol was obtained from Fisher Scientific (M) Sdn. Bhd.

3. 2 Fatty Acid Composition of Palm-based Methyl Palmitate

Fatty acid composition of palm-based methyl palmitate used in the study was characterized using gas chromatography (GC) analysis according to AOCS Ce 1-62 and Ce 2-66 Test Method. For sample preparation, about 0.4 g of sample and 6 mL methanolic sodium hydroxide were mixed in a round bottom flask and refluxed for 10 minutes continuously. Boron trifluoride-methanol complex of 7 mL was added from the top of the condenser into the reaction mixture and the sample underwent refluxed for another 3 minutes. 5 mL of heptane was added into the reaction mixture, followed by continuous refluxed for additional 1 minute. Subsequently, the reaction mixture was cooled down to room temperature (28 ^{o}C) for 10 minutes. In the round bottom flask containing cooled sample, a saturated sodium chloride was added until the solution reached to the neck level of the flask. The sample in the upper layer was transferred into a vial containing sodium sulphate anhydrous for drying purposes. The dried sample (0.5 mL) was further transferred into a gas chromatography vial and the sample was diluted with heptane to 1.5 mL About 1 μL sample was then injected into the gas chromatography. A Hewlett Packard HP 6890 series gas chromatography equipped with auto-injector 6890 series and flame ionization detector (FID) was used. Gas chromatography analysis was accomplished using capillary column Agilent 112-8867 HP-88 (60 m; 0.25 mm; 0.20 μm), a split injection mode with ratio of 100:1 at 250 °C and helium was used as a mobile phase at a flow rate of 20 mLmin^{-1}. The oven temperature was ramped over a linear gradient from 150 to 210 °C at 3 °C min^{-1}. The detector temperature was set at 250 °C. The fatty acid composition of the palm-based methyl palmitate is shown in Table 3.1.

Table 3.1: Fatty Acid Composition of Methyl Palmitate

Fatty acid	Structure	Composition (wt.%)
Myristic	C 14	0.8
Palmitic	C 16	98.8
Stearic	C18:0	0.4

3.3 Preparation of Catalyst

Hydrotalcite-like compound (HTLC) was developed in house by the Malaysian Palm Oil Board and used as the heterogeneous catalyst for the transesterification process in this present study. 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 (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 ^{o}C), resistance to mass transfer (zeolites), and loss of active sites in the presence of a polar support (HPA/silica) (Barros *et al*, 2013).

The HTLC catalyst system was prepared by a continuous precipitation technique as reported by Reichle (1985) at high supersaturation in a single container of two diluted solutions A and B, in which solution A contained divalent cation (67 g) and trivalent cation (150 g) dissolved in 1 L deionized water. Solution B acting as precipitating reagent was prepared by dissolving Na_2CO_3 (42.4 g) and NaOH (16 g) in 0.5 L deionized water. The prepared solutions A and B were then mixed with a high supersaturation technique for 18 hours at 80 ^{o}C with vigorous stirring. Finally, the precipitate was filtered, washed with deoinized water up to pH 7 and dried overnight at 120 ^{o}C (Figure 3.1). All reagents used in Solution A, such as magnesium nitrate, calcium nitrate, zinc nitrate, copper nitrate and aluminium nitrate were purchased from Bendosen Laboratory Chemical. The precipitating reagents used in Solution B were purchased from Sigma Aldrich.

Figure 3.1: Hydrotalcite-Like Compound (HTLC) as Heterogeneous Catalyst

3.4. Screening of Heterogeneous Catalysts

Various types of heterogeneous catalysts as shown in Table 3.2 were screened to find the suitable catalyst for the transesterification of methyl palmitate and triethanolamine. Non-catalytic transesterification were also conducted in this study. The process conditions for this screening experiment were at reaction temperature of 150 ^{o}C, vacuum of 10 mbar, 1% catalyst dosage, 250 rpm and mole ratio of 1.8:1 (methyl palmitate to triethanolamine). The process parameters was determined based on literatures reported on the application of heterogeneous catalysis for esteramine production (Bonhorst *et al.*,1948, Jiang *et al.*,2012) and earlier study on the process to produce esteramine via methyl ester route (Haliza *et al*., 2006). Transesterification employing conventional homogeneous sodium methoxide catalyst was conducted as comparison to the reaction catalyzed by these HTLC catalysts. The process conditions for the conventional approach using sodium methoxide is at temperature of 100 ^{o}C, 10 mbar, mole ratio of 1.8:1 (methyl palmitate:triethanolamine) and 5% sodium methoxide (1% solution in methanol) and 2 hours duration. The conversion of methyl palmitate and mono, di and tri-esteramine compositions obtained from the reactions were determined by gas chromatography analysis. Based on the screening result, the selected catalyst that gave the highest conversion of methyl palmitate as well as di-esteramine content was further characterized.

Table 3.2: Screening of Various Types of HTLC Catalysts

Heterogeneous Catalyst	Catalyst
Hydrotalcite compound	Mg-Al
Hydrotalcite-like compound (HTLC)	Ca-Al
	Zn-Al
	Cu-Al
	Cu/Zn-Al

3.5 Characterization of Catalyst

Characterization of the heterogeneous catalyst was performed on X-ray diffraction (XRD), specific surface area, pore sizes and pore volume determination as well as scanning electron microscopy (SEM) analysis.

3.5.1 X-ray diffraction (XRD)

XRD profiles of the HTLC catalyst was determined using Bruker D8 Advance diffractometer (secondary monochromator, using Cu Ka radiation, two theta–theta modes) equipped with linear position sensitive detector (scintillation counter) at room temperature.

3.5.2 Specific Surface Area, Pore Sizes and Pore Volume Determination

Textural properties of the HTLC catalyst such as specific surface area, pore sizes and pore volume were determined using Micromeritics apparatus (Model: ASAP 2010, USA) after pretreating the samples under vacuum at 400 ^{o}C overnight, with a surface area obtained using the Brunauer-Emmett-Teller (BET) technique over the pressure range P/P_0 = 0.02–0.2, where a linear relationship was maintained. The pore volume and pore size distributions were obtained according to the Barret-Joyner-Halenda (BJH) method from the adsorption branch data.

3.5.3 Scanning Electron Microscopy (SEM) Analysis

The morphology of the heterogeneous catalyst was examined using scanning electron microscope (SEM) analysis. The SEM measurement was performed using FEI Quanta 200 modal with an accelerate voltage of 2 – 30 kV.

3.5.4 Particle Size Measurement

The particle size of the solid catalyst was measured using sieve analysis with a stack of sieves arranged in decreasing mesh size (850, 355, 250, 125 and 75 µm respectively) and shaken for 10–15 minutes on an Automatic Sieve Shaker D403 (Milano, Italy) to separate the catalyst into various size ranges. The particle size of the heterogeneous catalyst (Ca-Al) used in the transesterification process was approximately 850 µm.

3.6 Experimental Procedures for the Production of Fatty Esteramine

3.6.1 Reactor Set-up

Transesterification process was carried out in a 3-neck spherical flask (500 mL capacity) made of Pyrex glass, acting as a batch reactor (Figure 3.2). The glass reactor allowed visual inspection of the reactor content during reaction. This flexibility is important incase of any complication in the reactor, such as sudden failure in mechanical agitation can be detected as early as possible. The reactor was equipped with a magnetically driven agitator and the impeller is a 4-bladed pitched-blade turbine. The reactor was also equipped with a thermometer as a temperature sensor and a distillation condenser. Vacuum in the system was supplied by a rotary vane vacuum pump and the reactor was jacketed with thermal oil to provide heating on the system.

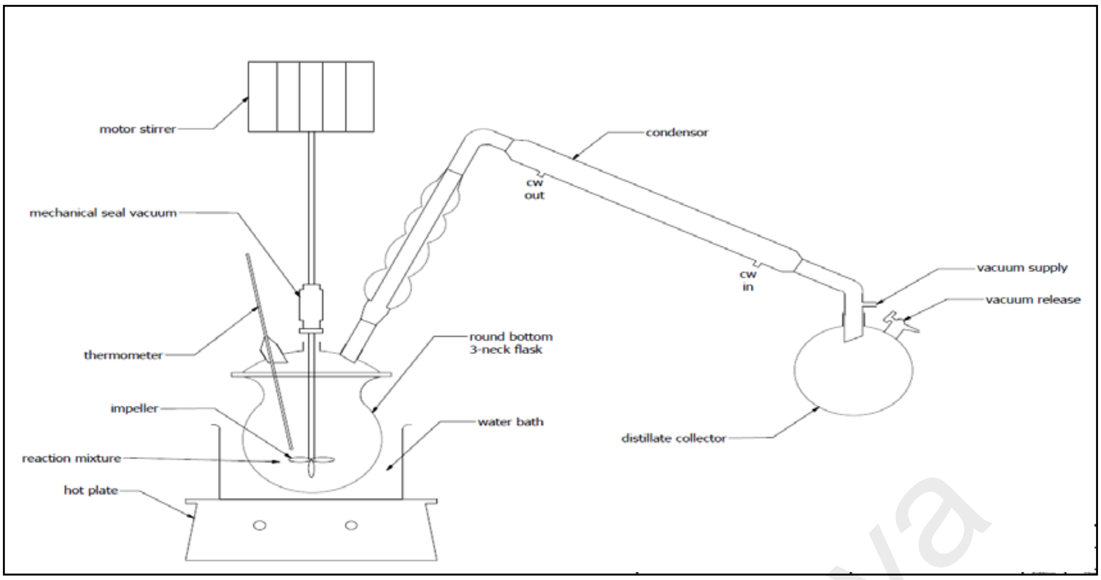


Figure 3.2: Transesterification Set–up

3.6.2 Reaction Procedure

Palm-based methyl palmitate (C16), triethanolamine and HTLC as heterogeneous catalyst, with catalyst composition ranging from 0.1 to 1% of the weight of methyl palmitate were introduced into the reactor followed by continuous stirring. The reactants were mixed and heated to the desired reaction temperature (ranging 130 to 170 ^{o}C) and vacuum (ranging 500 to 10 mbar). A rotary vane vacuum pump will be used to remove the methanol released as the by-product. Removal of methanol is important, as its removal will favour the forward reaction. The reaction mixture was stirred at agitator speed ranging from 150 to 250 rpm. These conditions are maintained for 2 hours. The product was then cooled to 60 ^{o}C with continuous stirring and under vacuum. After the reaction was completed, the heterogeneous catalyst was separated by vacuum filtration and the product mixtures (Figure 3.3) were then analyzed using gas chromatography. Further characterization of the fatty esteramine was performed using gas chromatography-mass spectroscopy (GC-MS) analysis.

Figure 3.3: Fatty Esteramine

3.7 Analytical Procedures for Characterization of Fatty Esteramine

3.7.1 Gas Chromatography Analysis

Gas chromatography analysis was performed using HP 6890 series equipped with auto-injector 6890 from Hewlett Packard and Agilent 6890N equipped with 7683B series auto-injector from Agilent Technologies.

3.7.1.1 Instrument Set-up

The separation on the gas chromatography system was performed using the capillary column ZB-5HT inferno (12 m x 530 µm x 15 µm). The oven temperature was set initially at 100 ºC, held for 3 min, then increase at 6 ºC/min to 350 ºC. Helium is used as the carrier gas at a flow rate of 20 mL/min. Injector temperature is set at 350 ºC with split ratio is set at 10:1. Detector type is flame ionization detector (FID) with temperature set at 360 ºC.

3.7.1.2 Sample Preparation

The fatty esteramine sample will be subjected to undergo sylation process prior to injection into the gas chromatography. The sylation process was carried out by preparing the trimethylsilyl (TMS) derivatives of fatty esteramine as shown in the procedure below:

1. About 0.01 g of fatty esteramine sample was weighted into a vial and the weight was recorded.
2. 2 mL of gas chromatography grade N,N-dimethylformamide (DMF) and 1 mL of N,O-*bis*-trimethylsilyl acetamide (BTSFA) were then added into the vial.
3. The vial was then shaked vigorously for 30 seconds to ensure homogeneity of the mixture before incubated at 60 ^{o}C for 30 minutes. The mixture was allowed to cool down for a few minutes.
4. About 1.5 mL of the derivatives mixture was then transferred into a 2 mL clear wide opening vial laced with a very small amount of sodium sulphate anhydrous.
5. Finally, the vial was sealed off and the derivatives mixture was injected into the gas chromatography. The volume of injection was recorded.

3.7.2 Gas Chromatography/Mass Spectrometry (GC/MS) Analysis

For structure confirmation of fatty esteramine, a gas chromatography 7890A series equipped with auto-injector 7683B series and inert MSD 5975C series from Agilent Technologies was used. Chromatographic separation was accomplished using a rugged high temperature gas chromatography capillary column Zebron ZB-5HT Inferno (15 m; 0.25 mm; 0.25 μm), a split injection mode with ratio of 50:1 at 350 °C and helium as a mobile phase at a flow rate of 0.8 mL min^{-1}. The oven temperature was initially set at 100 ^{o}C , then increased to 360 ^{o}C at a ramping rate of 6 °C min^{-1} and held at that temperature for 15 min. The mass spectrometry temperature was set at 230 °C for the ion source and 150 ^{o}C for the mass spectrometry quadrupole magnet. Electron impact mass spectra were obtained at acceleration energy of 70 eV. As for sample preparation, the sample was dissolved in DCM and DMF, followed by derivatization with BSTFA and heating the sample at 60 ^{o}C for 30 minutes prior to analysis. Fragment ions were analyzed over 0-600 *m/z* mass range in the full scan.

3.8 Effect of Process Parameters on Transesterification of Methyl Palmitate

The effect of process parameters in transesterification of methyl palmitate and triethanolamine such as reaction temperature, vacuum, catalyst dosage, agitator speed and reaction time on the conversion of methyl palmitate was investigated while the mole ratios of methyl palmitate to triethanolamine were varied in order to study the effect of this parameter on the composition of mono, di and tri-esteramine (Table 3.3). All measurements of conversion as well as compositions of mono, di and tri-esteramine were performed in duplicate with data reported representing average values ± standard errors. The percentage of conversion was calculated using the equation (3.1).

Table 3.3: Range of Process Conditions Investigated for the Reaction

Reaction Parameter	Range	Unit
Mole ratio (methyl palmitate:triethanolamine)	1.2:1 – 2:1	-
Temperature	100 - 170	^{o}C
Vacuum	10 - 500	mbar
Catalyst Dosage	0.1 – 1.0	%
Agitator Speed	150 - 250	rpm
Reaction Time	2 - 6	hour

$$\text{Conversion of methyl palmitate (\%)} = \left\{ \frac{\text{Weight of methyl palmitate reacted}}{\text{Initial weight of methyl palmitate}} \right\} \times 100 \qquad (3.1)$$

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

These preliminary experiments on the effects of process parameters on conversion of methyl palmitate were carried out to screen the appropriate process parameters and experimental regions to investigate the levels of each process parameters for optimization using RSM, which will be performed in the next part of this study. The selection of range of each process parameters was determined based on various literature reported on the application of heterogeneous catalysis for transesterification reaction. The effect of these process parameters on the transesterification reaction as discussed above were studied based on the manual one-factor-at-a-time (OFAT) experimental approach.

Mole Ratio of Reactants

Mole ratios of methyl palmitate to triethanolamine were varied at 1.2:1, 1.4:1, 1.6:1, 1.8:1 and 2:1 in order to study the effect of this parameter on the composition of mono, di and tri-esteramine. Other reaction conditions were held constant at reaction temperature of 150 ^{o}C, vacuum of 10 mbar, 1% catalyst dosage and agitator speed of 250 rpm.

Reaction Temperature

Effect of temperature on conversion of methyl palmitate was investigated by varying the temperature at 100, 130, 150 and 170 ^{o}C while keeping all the other reaction conditions at constant values. The process parameters were held at reaction vacuum of 10 mbar, 1% catalyst dosage, agitator speed of 250 rpm and mole ratio of 1.8:1 (methyl palmitate:triethanolamine). The lowest temperature was chosen at 100 ^{o}C as lower than that, no reaction was observed. The maximum temperature studied was at 170 ^{o}C as the boiling point of methyl palmitate reported by Bonhorst *et al* (1948) is at 185 ^{o}C under maximum vacuum of 10 mbar.

Vacuum

Effect of vacuum on conversion of methyl palmitate was studied by varying the vacuum at 500, 200, 100, 50 and 10 mbar, while keeping the other process parameters constant at reaction temperature of 170 ^{o}C, 1% catalyst dosage, agitator speed of 250 rpm and mole ratio of 1.8:1 (methyl palmitate to triethanolamine). The range of vacuum levels investigated was with reference to the previous study (Haliza *et al*., 2006). Transesterification reaction without applying any vacuum in the system for methanol removal was also performed as control experiment.

Catalyst Dosage

Effect of catalyst dosage on conversion of methyl palmitate was studied by varying the dosage at 0.1, 0.3, 0.5, 0.7 and 1%. Other process parameters were held constant at reaction temperature of 170 ^{o}C, vacuum of 10 mbar, 250 rpm and mole ratio of 1.8:1 (methyl palmitate to triethanolamine). The minimum catalyst dosage of 0.1% was chosen as lower than that, the reaction rate was very slow. Maximum catalyst dosage of

1% was chosen based on the results reported by Jiang *et al.* (2012) on the use of solid acid catalyst to produce the esteramine.

Agitation Speed

Effect of agitation speed on conversion of methyl palmitate was studied by varying the mechanical stirrer speed at 150, 170, 200 and 250 rpm. Other process parameters were held constant at reaction temperature of 170 ^{o}C, vacuum of 10 mbar, 0.5% catalyst dosage and mole ratio of 1.8:1 (methyl palmitate:triethanolamine). Non-catalytic transesterification reaction was performed as control experiment.

Reaction Time

Effect of reaction time on conversion of methyl palmitate was studied by varying the duration for 0.5, 1, 2, 3, 4, 5 and 6 hours. Other process parameters were held constant at reaction temperature of 170 ^{o}C, vacuum of 10 mbar, and 0.5% catalyst dosage and mole ratio of 1.8:1 (methyl palmitate:triethanolamine).

3.9 Optimization of Process Conditions Using Response Surface Methodology (RSM)

Optimization of the process conditions for the transesterification of palm-based methyl palmitate with triethanolamine aided by HTLC as heterogeneous catalyst using response surface methodology (RSM) approach was carried out. The experiments were designed using the Design-Expert® version 8 (DX) software and optimum operating conditions were determined for maximum di-esteramine content. Selection of the experimental regions for the process parameters involved in the optimization using RSM was based on the preliminary experiments performed in the earlier part of this study (section 3.8).

3.9.1 Experimental Design

Central composite design (CCD) is the most widely used response surface design and has desirable rotatability property. In this study, a modified CCD called face-centered central composite design was employed to design the experiments based on a three-level design and according to Norhazimah *et al.* (2012), this design is usually used in order to avoid the experimental regions over the process limit.

Four chosen independent variables (factor) were reaction temperature, vacuum, agitator speed and catalyst dosage while di-esteramine content was chosen as the response. For this optimization study, the transesterification was performed at optimum mole ratio of 1.8:1 (methyl palmitate: triethanolamine) with duration of two hours. These independent variables were studied at three levels as shown in Table 3.4 with the range of process parameters being determined based on literature review and preliminary experiments as described in section 3.8.

Table 3.4 : Studied Range of Each Independent Variable in Actual and Coded Levels

Independent variable	**Variation levels**		
	Low level (-1)	**Center (0)**	**High Level (+1)**
Temperature (^oC)	130	150	170
Vacuum (mbar)	500	255	10
Catalyst Dosage (%)	0.1	0.55	1
Agitator Speed (rpm)	150	200	250

Four factors in two-level full factorial face-centered design (2^4) resulted in total of 30 experiments ($2^k + 2k + 6$), where k represented the independent variables or factors selected. There was six replications at the center points (zero level) in order to obtain a good estimation of errors with eight axial and sixteen factorial experimental runs. All experiments were carried out in randomized order. Alpha (α) is defined as a distance from the center point, in which its value depend on the number of variables. For two, three and four variables, the value of α are 1.41, 1.68, and 2.00 respectively. For face-centered CCD used in this study, the value of alpha was set at 1 ($\alpha = 1$). For statistical computation, the variables are coded according to equation (3.2) below:

$$X_i = \frac{Ui - U_i^o}{\Delta U_i} \tag{3.2}$$

where, Xi is the independent variable coded value, U_i is the independent variable real value and U_i^o is the independent variable real value at the center point (Bezerra *et al.*, 2008).

Face-centered CCD experimental design matrix generated using the Design-Expert® version 8 are shown in Table 3.5. All the trials were repeated at least twice to ensure reproducibility of the results. The response measured was di-esteramine content, obtained from the peak area (%) of gas chromatography analysis.

Table 3.5: Face-centered CCD Design Layout

Run Order	Type of Factor	Coded Value			
		A (ºC)	B (mbar)	C (%)	D (rpm)
5	Center	0	0	0	0
6	Center	0	0	0	0
11	Center	0	0	0	0
13	Center	0	0	0	0
20	Center	0	0	0	0
21	Center	0	0	0	0
7	Axial	0	0	1	0
14	Axial	0	-1	0	0
16	Axial	1	0	0	0
17	Axial	-1	0	0	0
22	Axial	0	0	-1	0
25	Axial	0	0	0	-1
26	Axial	0	0	0	1
28	Axial	0	1	0	0
1	Factorial	1	-1	-1	1
2	Factorial	1	-1	1	-1
3	Factorial	-1	-1	1	-1
4	Factorial	-1	-1	-1	-1
8	Factorial	-1	1	1	1
9	Factorial	1	-1	1	1
10	Factorial	-1	1	-1	1
12	Factorial	1	-1	-1	-1
15	Factorial	1	1	-1	1
18	Factorial	1	1	-1	-1
19	Factorial	-1	1	-1	-1
23	Factorial	1	1	1	-1
24	Factorial	1	1	1	1
27	Factorial	-1	-1	1	1
29	Factorial	-1	1	1	-1
30	Factorial	-1	-1	-1	1

Note: A, temperature; B, vacuum; C, catalyst dosage; D, agitator speed

The experimental data obtained were subjected to analysis of variance (ANOVA). The response values were fitted by the second order model in order to describe the relationship between independent variables and response. The coded mathematical model for the quadratic model is expressed as in equation (3.3).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x^2{}_i + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3.3}$$

where, y is the predicted response, $x_i x_j$ represents the independent variables, β_o is the constant, βi represents the linear coefficient, β_{ii} represents the quadratic coefficient and β_{ij} represents the interaction coefficient and ε is the residual associated to the experiment (Bezerra *et al*., 2008).

The quality of the fit of polynomial model was expressed by the coefficient of determination R^2 and its statistical significance was checked by the *F*-test in the same programme. The validation of the model was performed by conducting the confirmation runs based on the recommended optimized conditions by RSM.

3.10 Reusability and Leaching Tests of Catalyst

For the reusability test of the catalyst, several reactions were performed under the optimum operating conditions by recycling the catalyst from one cycle to the subsequent cycle without washing or drying the catalyst cake after its separation from the reaction mixture. The reusability test was performed under the optimum reaction conditions obtained from RSM.

Leaching of the active species of the catalyst into the reaction medium was determined by measuring the metal content in fatty esteramine 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, 1g of fatty esteramine sample was added into 10 ml nitric acid (50%

concentration) and the sample mixture was heated for 10 minutes at 95 ^oC. Then, 5 ml of concentrated nitric acid (HNO_3) was added to the mixture and heated for another 30 minutes at 95 ^oC. 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 ^oC. 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 minutes at 95 ^oC. Finally, the sample mixture was cooled down, filtered and marked up to 100 mL with deionized water.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Preliminary Evaluation on the Production of Fatty Esteramine via Heterogeneous Catalysis

The feasibility of producing the fatty esteramine via the novel heterogeneous transesterification process employing hydrotalcite-like compounds (HTLC), as an alternative to the conventional approach using homogeneous catalyst was evaluated in this present study. No research has been reported on the use of heterogeneous catalysts for transesterification of methyl palmitate and triethanolamine for the production of esteramine. As such, the present study can be considered as the first experimental investigation to produce esteramine via heterogeneous catalysis for the production of esterquats. The reaction scheme for the production of fatty esteramine is depicted in Figure 4.1, whereby methanol was produced as the by-product along with the formation of mono-esteramine, di-esteramine and tri-esteramine.

Preliminary results indicated that besides the reactants peaks (methyl palmitate and triethanolamine), three possible product peaks (mono, di and tri-esteramine) were detected from the gas chromatography (GC) analysis using this new process. The palm-based methyl palmitate peak was detected at retention time of 9.18 min (Figure 4.2a), while triethanolamine peak appeared at retention time of 5.32 min. The fatty esteramine peaks, which consist of mixtures of mono-esteramine, di-esteramine and tri-esteramine appeared at retention time of 22 min., 34 min and 42 min respectively. The formation of mono, di and tri-esteramine were subjected to further confirmation via gas chromatography – mass spectrometer analysis.

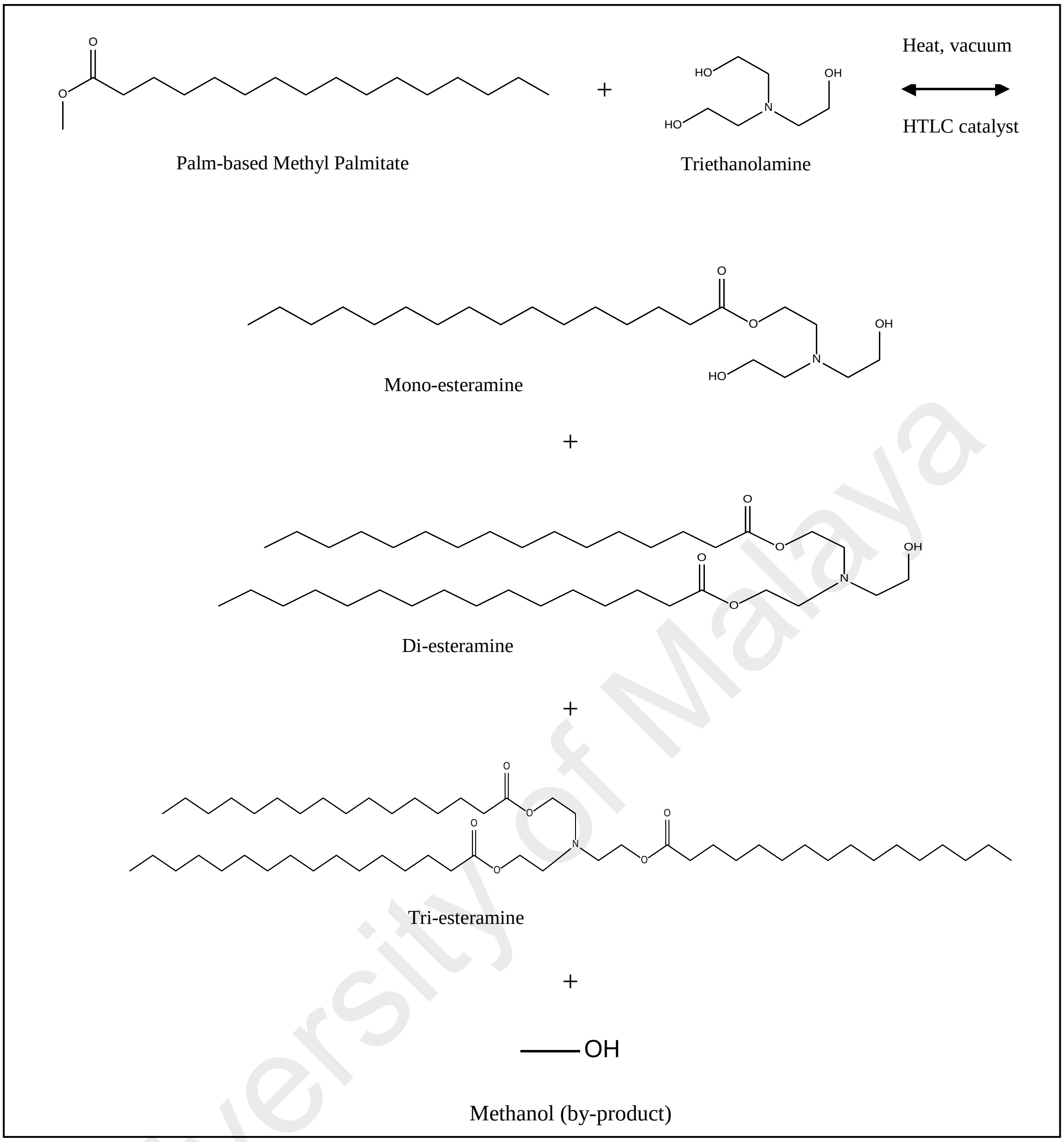


Figure 4.1: Transesterification Reaction for Fatty Esteramine Production

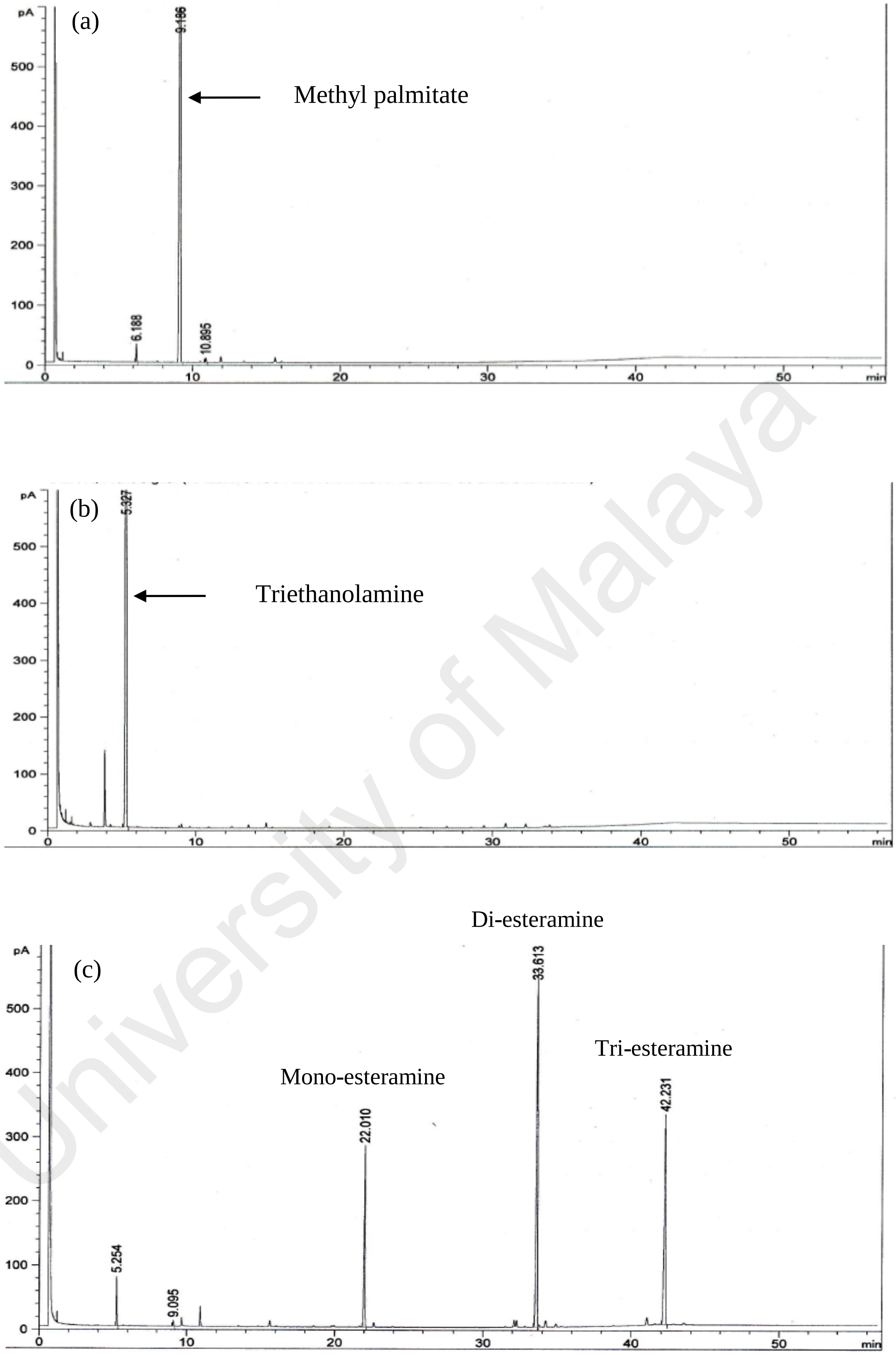


Figure 4.2: GC Chromatograms for (a) Palm-Based Methyl Palmitate, (b) Triethanolamine and (c) Fatty Esteramine Mixtures

The total ion chromatogram of the reaction mixture obtained from the GC-MS analysis shown in Figure 4.3 illustrates the appearance of several peaks at retention time of 5.69, 7.54, 11.46, 15.58 and 29.22 min. Through the instrumental library search, fragment ions for the peak at retention time of 5.69 min. strongly matched the fragment ions profiles for triethanolamine with *m/z* 350.2 (Figure 4.4) whereas, peak at retention time of 7.54 min. matched the fragment ions profiles for palm-based methyl palmitate with *m/z* 269.3 (Figure 4.5). Meanwhile, fragment ions at retention time 11.46 (Figure 4.6) matched the fragment ions for mono-esteramine (mono-palmitate) with *m/z* 516.5. Figure 4.7 show the proposed fragment ions for mono-esteramine. For peak existed at retention time 15.58 min., the fragment ions appeared at this retention time (Figure 4.8) matched the fragment ions of di-esteramine (di-palmitate) with m/z 594.6. The proposed fragment ions for di-esteramine is shown in Figure 4.9 The fragment ions observed at retention time 29.22 min. as shown in Figure 4.10 were found to be tri-esteramine (tri-palmitate) with m/z 863, in which the proposed fragment ions for tri-esteramine is illustrated in Figure 4.11.

In summary, the transesterification of palm-based methyl palmitate and triethanolamine employing HTLC catalyst is a potential route for the production of mono, di and tri-esteramine and the structures of fatty esteramine mixtures were confirmed by GC-MS analysis.

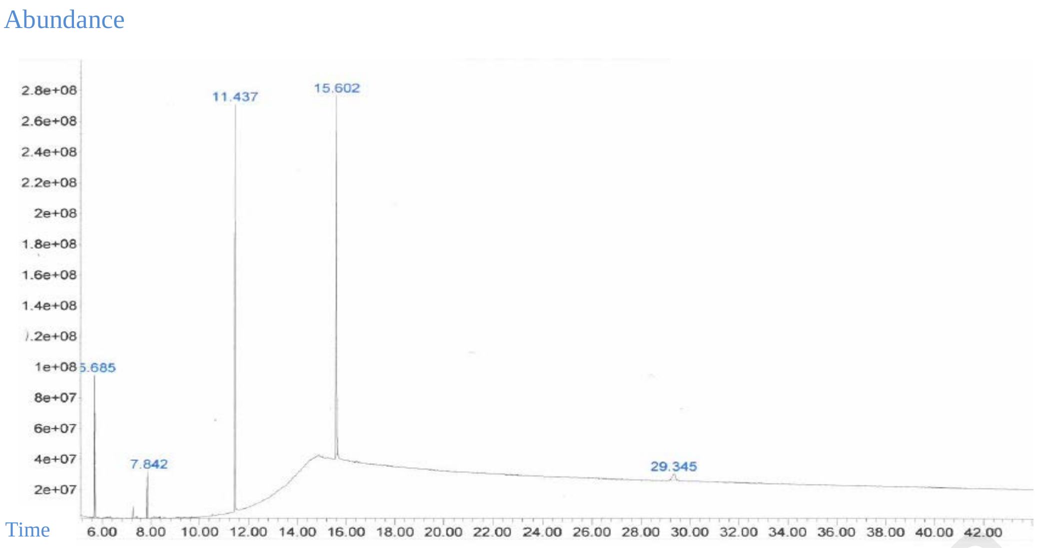


Figure 4.3: Total Ion Chromatogram of Reaction Mixture

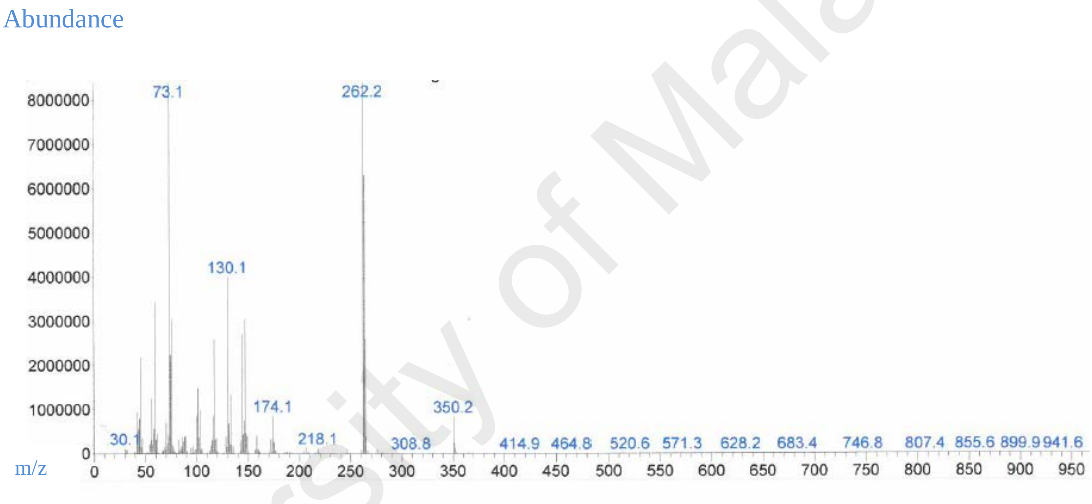


Figure 4.4: Fragment Ions at Retention Time 5.69 min

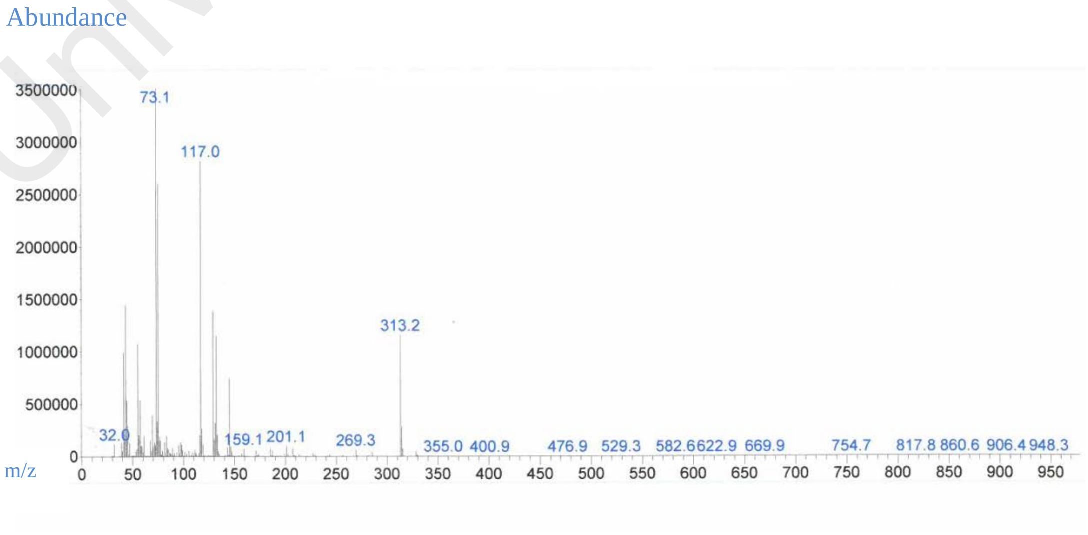


Figure 4.5: Fragment Ions at Retention Time 7.54 min.

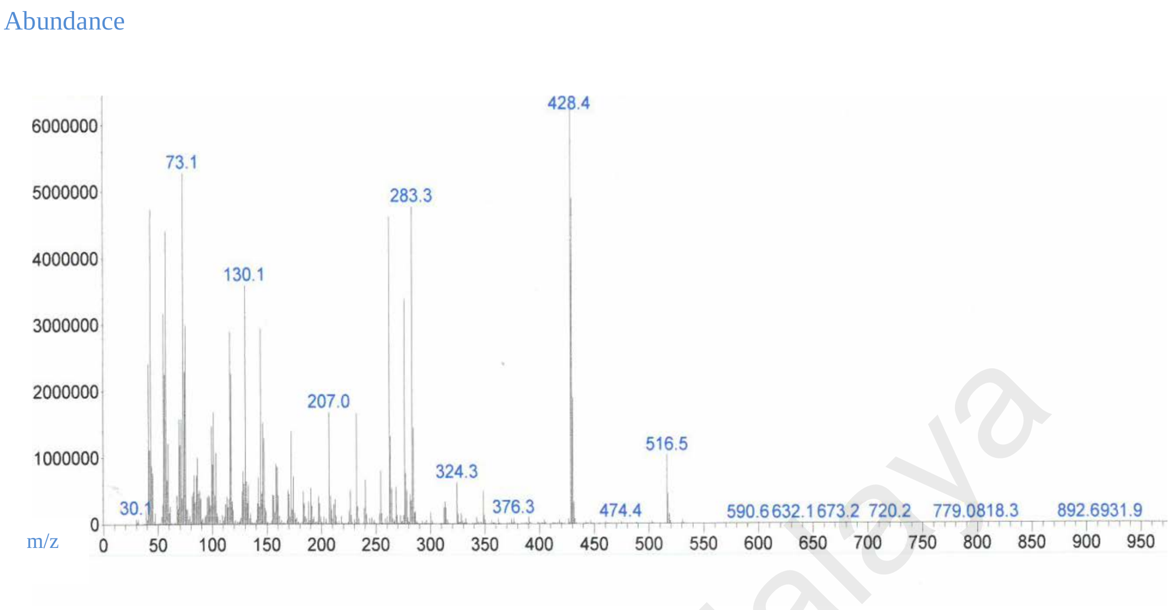


Figure 4.6: Fragment Ions at Retention Time 11.46 min.

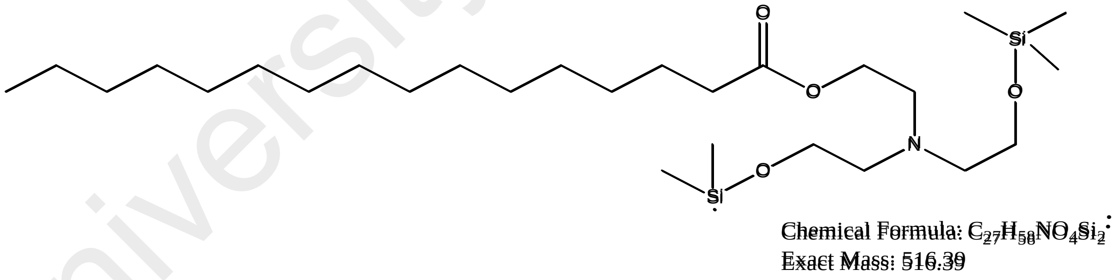


Figure 4.7: Proposed Fragment Ions for Mono-esteramine (mono-palmitate)

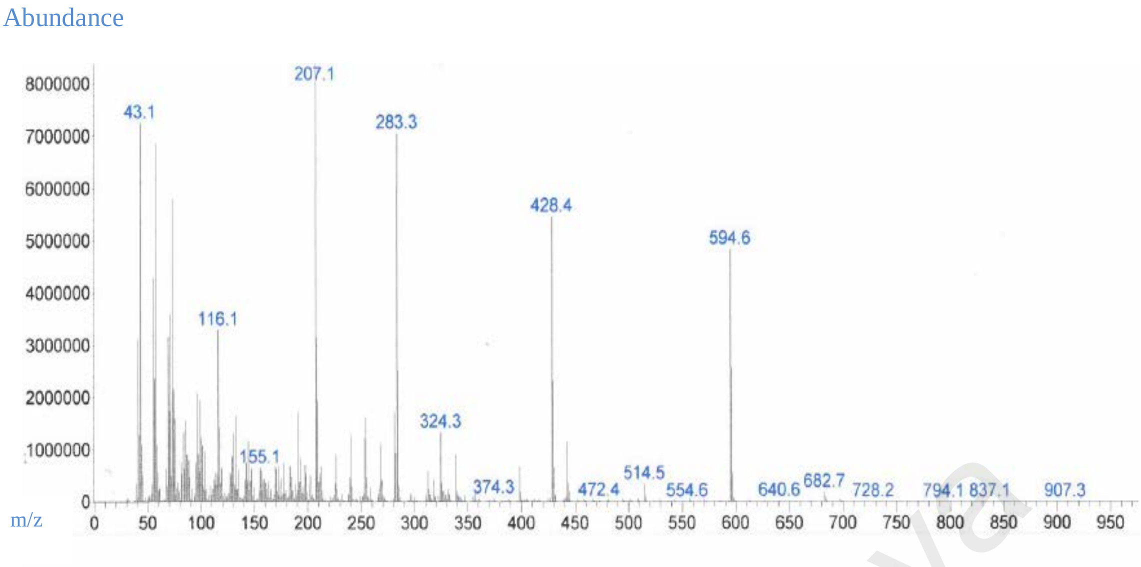
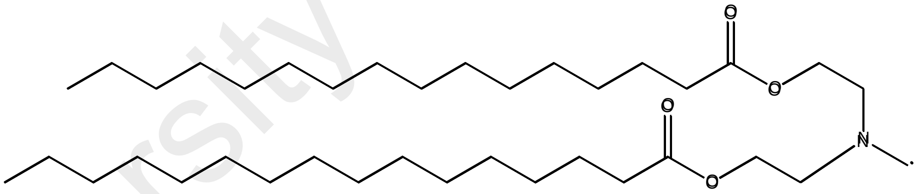


Figure 4.8: Fragment Ions at Retention Time 15.58 min.



Chemical Formula: $C_{37}H_{72}NO_4^-$
Exact Mass: 594.55

Figure 4.9: Proposed Fragment Ions for Di-esteramine (di-palmitate)

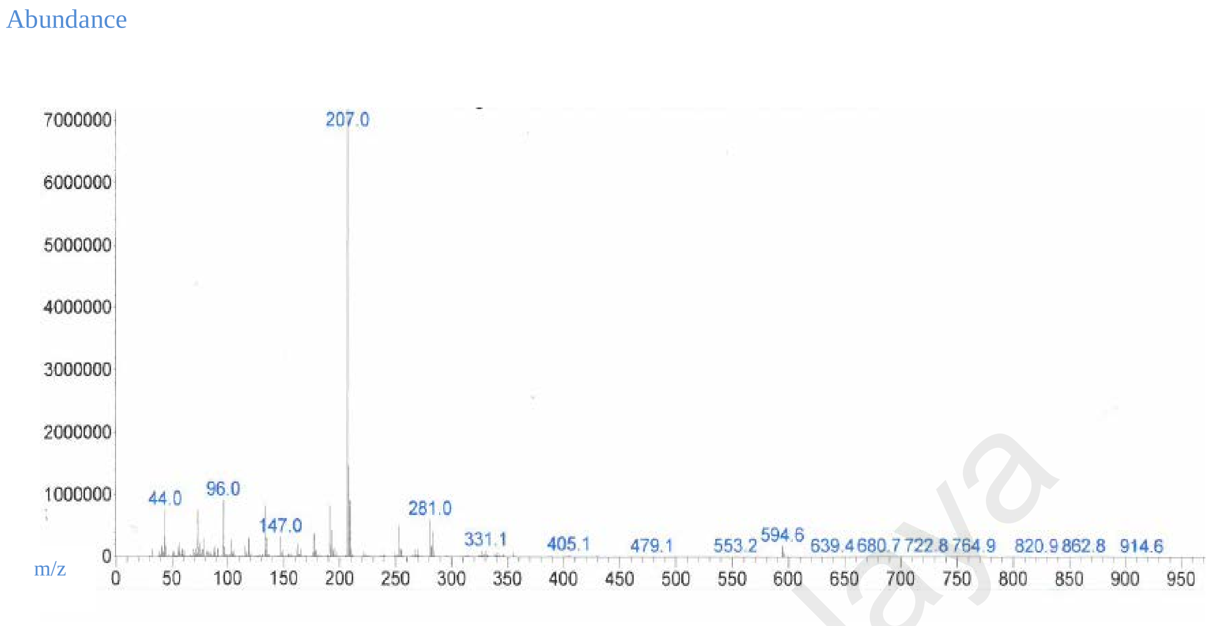
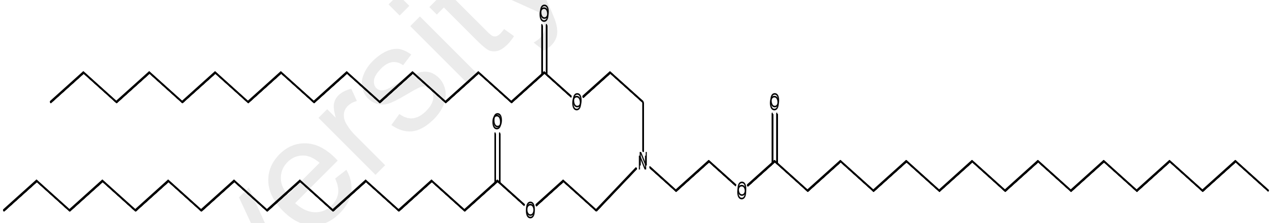


Figure 4.10: Fragment Ion at Retention Time 29.22 min.



m/z :863

Figure 4.11: Proposed Fragment Ions for Tri-esteramine (tri-palmitate)

4.2 Screening of Heterogeneous Catalysts

Hydrotalcite-like compounds (HTLC) of various metals ions were screened to find the suitable catalyst for the transesterification of methyl palmitate and triethanolamine. Table 4.1 illustrates the conversion of methyl palmitate and fatty esteramine compositions aided by the heterogeneous catalysts (HTLC) and the results were compared with the conventional sodium methoxide catalyst. All reactions were performed by employing uncalcined catalysts, due to the high energy consumption in the calcination process. Furthermore, preliminary evaluation shows that the uncalcined HTLC appeared to be more active than the calcined HTLC, as no reaction took place using the calcined HTLC. This clearly indicates that the mixed hydroxide structure was advantageous for the transesterification of methyl pamitate with triethanolamine.

According to Table 4.1, the non-catalytic transesterification gave low conversion of palm-based methyl palmitate into fatty esteramine with only 5.24% of mono-esteramine formation within 6 hours reaction time. When the reaction was performed using Mg–Al catalyst, conversion of 86.4% with compositions of mono, di and tri-esteramine of 24.96 40.64 and 18.4% respectively were obtained. As for the reactions aided by HTLC, the conversion follows the following order: Ca–Al>Zn–Al >Cu/Zn–Al>Cu–Al. Methyl palmitate conversions of more than 90% was observed when the reaction was aided by both Zn–Al and Ca–Al. It appears that Ca–Al catalyst gave both highest conversion of 98% and maximum di-esteramine content of 47% in the transesterification process. Hence, this catalyst was selected as the best catalyst for this study. Reactions employing Ca–Al demonstrated similar methyl ester conversion and fatty esteramine compositions with the conventional approach using sodium methoxide. Besides, Ca–Al is preferred as it derived from a cheap source of calcium nitrate. Transesterification using Ca–Al can be a potential green process over the conventional approach using sodium methoxide for the esterquats production because according to Akhihiero *et al.* (2010), the conventional catalyst can be a serious health hazard to humans upon contact.

4.3. Characterization of Ca-Al Catalyst

4.3.1 X-ray diffraction (XRD) of Ca-Al

The characteristic features of a well crystallized hydrotalcite compound on XRD analyses can be represented by sharp and symmetric peaks on the diffractograms (Cavani *et al.*, 1991). The XRD of Ca–Al, which was specifically dried at 120 ^{o}C overnight, was found to exhibit characteristic features of the hydrotalcite-like materials. The structure pattern on the XRD as shown in Figure 4.12 demonstrated peaks corresponding to (003), (006), (012), (015) and (018) planes that matched with the calcium aluminium hydroxide carbonate hydrate pattern, a hydrotalcite-like compound with chemical formula of $Ca_{0.67}$ $Al_{0.33}$ $(OH)_2$ $(CO3)_{0.167}$ $(H2O)_{0.5.}$ (Vaccari, 1998).

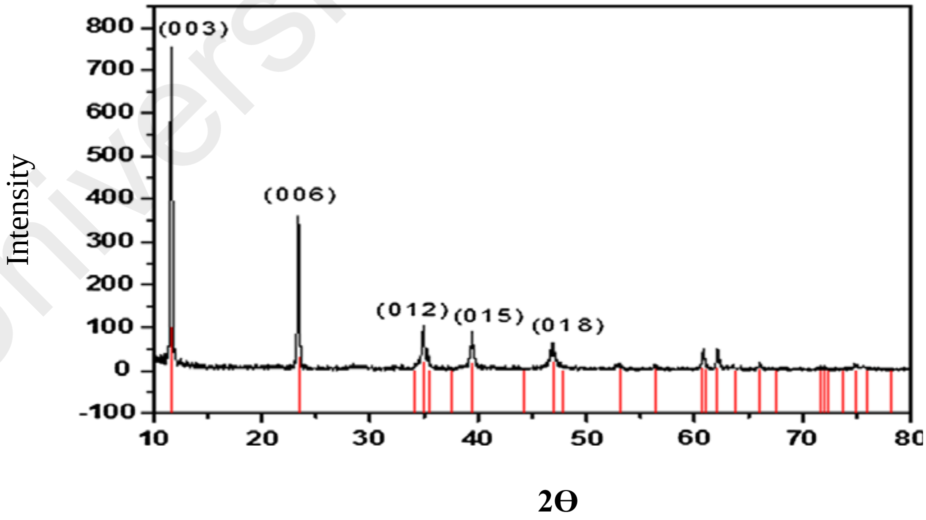


Figure 4.12: XRD Pattern of Ca–Al

Table 4.1: Conversion and Compositions of Fatty Esteramine using Various Heterogeneous Catalysts

Catalyst Type	Conversion of methyl palmitate (%)	Product Composition (%)				
		Mono esteramine	Di esteramine	Tri esteramine	Methyl Palmitate	Triethanolamine
Blank[a]	8.0	5.24	-	-	93.02	1.74
Mg-Al [a]	86.4	24.96	40.64	18.40	11.17	4.83
Zn-Al [a]	94.1	24.20	46.20	22.10	4.93	2.57
Ca-Al[a]	98.0	23.50	47.0	23.90	1.70	3.90
Cu-Al [a]	9.0	6.0	-	-	92.0	2.0
Cu/Zn-Al [a]	70.3	28.37	33.04	7.05	24.09	7.45
Sodium Methoxide[b]	99.0	19.60	49.0	28.50	0.3	2.60

Notes: a: 150 ºC, 10 mbar, mole ratio of 1.8:1 (methyl palmitate: triethanolamine) and 1% catalyst composition, 6 hours duration

b: 100 ºC, 10 mbar, mole ratio of 1.8:1 (methyl palmitate: triethanolamine) and 5% of sodium methoxide (1% solution in methanol) and 2 hours duration

4.3.2 Specific Surface Area, Pore Sizes and Pore Volume of Ca-Al

The BET surface area, total pore volume and mesopore size of Ca–Al are summarized in Table 4.2. The large surface area of Ca–Al of 256 m^2g^{-1} could provide enough active sites for palm-based methyl palmitate and triethanolamine molecules to react effectively. Ca–Al with a pore diameter of 10 nm could be a potential heterogeneous catalyst for the production of esteramine, attributed to its mesoporous structure (pore diameter ranging from 2 to 50 nm). This was based on the published works reported by Jiang *et al.* (2012) described that the geometric size of mono plus di-esteramine and tri-esteramine molecules are approximately 4 nm and 7 nm respectively.

Table 4.2: Surface Area, Total Pore Volume and Pore Size of Ca–Al

Catalyst properties	Unit	Value
BET surface area	m^2/ g	256
Pore volume	cm^3/g	0.27
Pore diameter	nm	10

4.3.3 Scanning Electron Microscopy (SEM) of Ca-Al

The SEM image shown in Figure 4.13 indicates that Ca-Al particles exhibit a hexagonal shape. However, needle shape forms are also observed. The morphology of Ca-Al obtained from the SEM technique is similar to the Ca-Al solid catalyst reported by Savita *et al*. (2008).

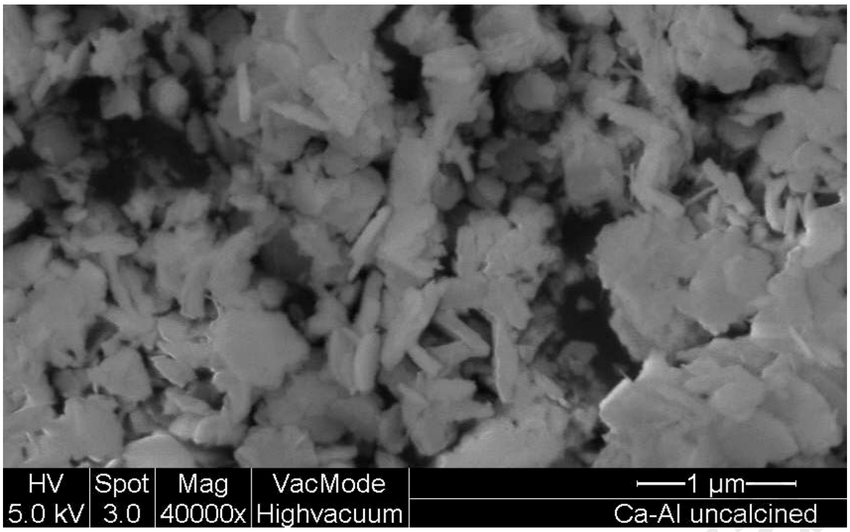


Figure 4.13: SEM Image of Ca-Al

4.4. Effect of Process Parameters on Transesterification Process

4.4.1 Effect of Reactants Mole Ratio on Composition of Fatty Esteramine

To investigate the effect of mole ratio of methyl palmitate to triethanolamine on product composition, five mole ratios ranging from 1.2:1 to 2:1 were investigated. In this study, higher formation of di-esteramine is desirable for an ideal performance in fabric softeners. According to Mishra *et al.,* (2007), higher formation of mono-esteramine would give better dispersibility and formulation stability, whereas higher tri-esteramine content results in better softening due to the presence of more hydrocarbon chains (hydrophobic tails) linked to the ester group but exhibits poor formulation stability. Figure 4.14 shows that as the mole ratio of methyl palmitate to triethanolamine is increased from 1.2:1 to 2:1, the mono-esteramine content decreased, di-esteramine content did not change significantly and tri-esteramine content increased. A maximum percentage composition of di-esteramine of 47.9% was observed at a mole ratio of 2:1, with tri-esteramine content of 29%. However, according to Franklin *et al* (2002), for better fabric softener formulation stability, tri-esteramine composition should be < 25%. Therefore, mole ratio of 2:1 is not suitable for fabric softener formulation. The next highest di-esteramine composition of 47% was obtained at a mole ratio of 1.8:1 with tri-esteramine composition of 23.9% and minimal amount of methyl palmitate and triethanolamine residuals. Therefore, mole ratio of 1.8:1 was chosen as the optimum ratio.

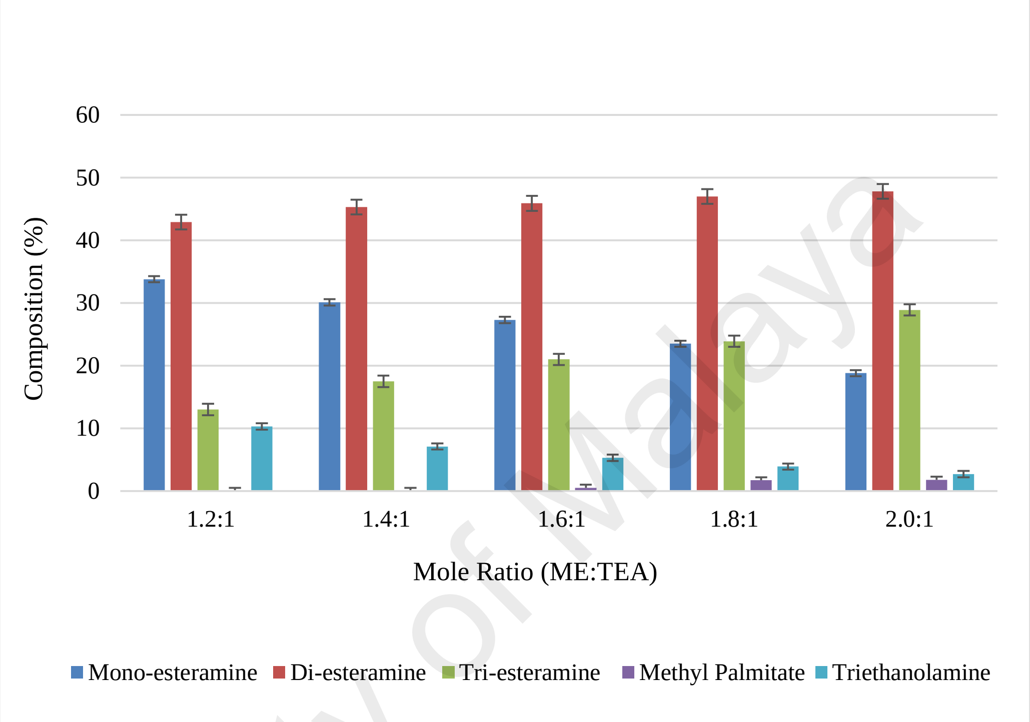


Figure 4.14: Effect of Mole Ratio (Methyl Palmitate: Triethanolamine) on Mono, Di and Tri-esteramine Compositions. Reaction Conditions: 150 °C, 10 mbar, 1% Catalyst Dosage, 250 rpm and Duration of 6 hours

4.4.2 Effect of Temperature

The effect of temperature on conversion of methyl palmitate shown in Figure 4.15 was studied at 100, 130, 150 and 170 °C. From the plot, it can be observed that the conversion increases with temperature. Initially, at the reaction time of 0 min (t = 0), 40% conversion of methyl palmitate was achieved at 170 °C, whereas minimal conversion was observed for lower temperatures. Reaction time t=0 refers to the time at which the desired reaction temperature of the transesterification process began to be realized. The conversion obtained by performing the reaction at the lowest temperature of 100 °C was only 10% throughout the 6 hours duration. Higher conversion was observed when conducting the reaction at 130 °C than that obtained at 100 °C, with maximum conversion of 89.7% within 6 hours reaction time. Increasing the temperature to 150 °C resulted in a significant increase of conversion in the beginning and approached a plateau after 4 hours reaction time with maximum conversion of 98%. A similar trend was observed when performing the reaction at a high temperature of 170 °C, whereby the conversion increased rapidly, starting from 40% to a maximum conversion of 98.6% within 2 hours and reaching a plateau thereafter. Hence, 170 °C was found to be the best temperature to perform the transesterification process.

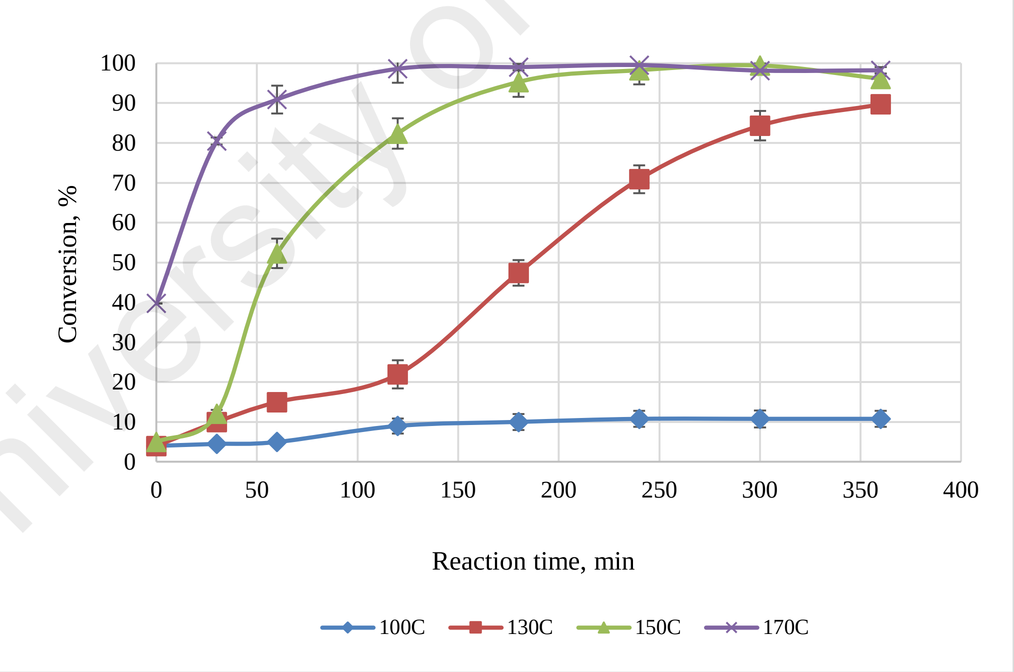


Figure 4.15: Effect of Temperature on Conversion of Methyl Palmitate. Reaction Conditions: 10 mbar, 1% Catalyst Dosage, 250 rpm, Mole Ratio of 1.8:1 (Methyl Palmitate:Triethanolamine) and Duration of 6 hours

This temperature was found to be lower than the temperature of 190 °C studied by Jiang *et al.* (2012) for the production of esteramine via esterification of stearic acid and triethanolamine using Al-SBA-15 solid acid catalyst. The operating temperature of 190 °C was not selected for this investigation, due to the limitation of the boiling point of methyl palmitate reported by Bonhorst *et al* (1948) at approximately 185 °C under a high vacuum of 10 mbar.

4.4.3 Effect of Vacuum

Effective methanol removal by the application of vacuum to the system promotes higher conversion of methyl palmitate in the transesterification process. Several vacuum conditions were applied in the reaction to investigate the effect of vacuum on the conversion of methyl palmitate. As indicated in Figure 4.16, a higher vacuum level resulted in higher conversion of methyl palmitate. At the starting point, where t=0, it was observed that some reaction had taken place for all vacuum levels. Reaction performed at the highest vacuum of 10 mbar shows a significant increase in the conversion from 40% at the starting point (t=0) to the highest conversion of 98.6% achieved at 2 hours reaction time. After 2 hours, no further increase in the conversion was observed. This trend suggests that an efficient methanol removal system favored the conversion of methyl palmitate into fatty esteramine. A lower initial conversion (t=0) was observed when the reaction was performed at 200 mbar than that obtained at 10 mbar. The initial conversion gradually increased from 15% to the maximum conversion of 95% within the first 2 hours and the conversion reached plateau after 2 hours reaction time. When applying a vacuum of 200 mbar, the conversion obtained was slightly lower than that performed at 10 mbar, due to the lower amount of methanol removed from the reaction. Accumulation of methanol in the system tends to promote a reversible reaction causing decomposition of esteramine into methyl palmitate. This finding was in agreement with results reported by Yunus *et al* (2003) in her study related to transesterification of palm oil methyl ester and trimethylolpropane.

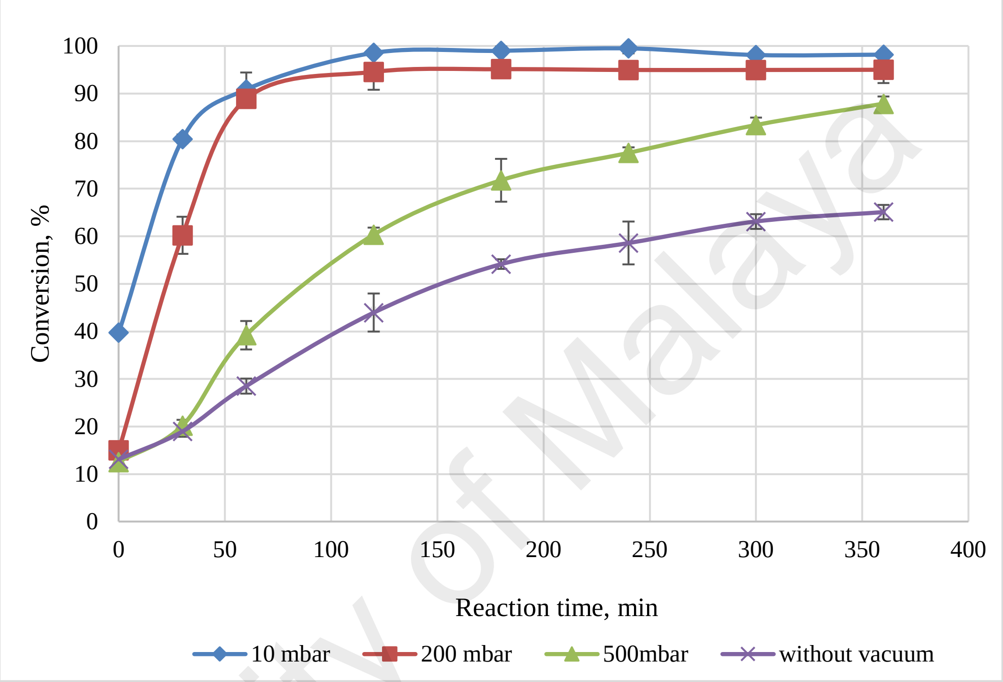


Figure 4.16: Effect of Vacuum on Conversion of Methyl Palmitate. Reaction Conditions: 170 ºC, 1% Catalyst Dosage, Mole Ratio of 1.8:1 (Methyl Palmitate: Triethanolamine), 250 rpm and Duration of 6 hours

As a result, slightly higher amount of unreacted methyl palmitate was present in the final product. At a low vacuum of 500 mbar, the conversion obtained was only up to 87.9% after 6 hours reaction time. This reveals that under very low vacuum, excessive accumulation of methanol vapour was observed in the system. This could lead to reverse reaction, whereby higher decomposition of esteramine into methyl palmitate could occurred. Hence resulting in a higher percentage of unconverted methyl palmitate. It is also interesting to observe that by not applying any vacuum to the reaction (free evaporation), a conversion of

65% was achievable after 6 hours reaction time. Therefore, in this study, a high vacuum of 10 mbar was selected to enhance the methanol removal in transesterification reaction. This result is in agreement with the work reported by Trius *et al* (1991) whereby in his study, a high vacuum system between 1.33 to 6.7 mbar was utilized for the production of esteramine via esterification of fatty acids and triethanolamine in the presence of homogeneous acid catalyst. However, an extremely high vacuum is costly as it requires considerable amount of energy.

4.4.4 Effect of Catalyst Dosage

A catalyst is known to lower the activation energy, hence increasing the reaction rate, which indirectly lowers the operational cost attributed to a prolonged reaction period. Previous works on the production of esteramine via transesterification of palm stearin methyl ester and triethanolamine employing sodium methoxide requires an optimum catalyst dosage of 5%. Masoumi and co-workers, who investigated the enzymatic synthesis of esteramine using lipase, reported that the catalyst dosage ranging from 3 to 7% were employed in their study. In this present study, the effect of catalyst dosage on transesterification process was investigated by incorporating the Ca-Al catalyst at 0.1, 0.3, 0.5, 0.7 and 1%. Figure 4.17 shows that the reaction rate increased with the increase in Ca–Al dosage. When the reaction was performed in the presence of only 0.1% of Ca–Al, the maximum conversion achieved was up to 97.4% after a 6 hours reaction period. For the reaction employing 0.3% of Ca–Al, the maximum conversion of 98.2% was achieved within 3 hours and remained constant after the 3 hours reaction period. Increasing the Ca–Al dosage to 0.5% led to an increase in the reaction rate as the maximum conversion of 98.5% was obtained within 2 hours reaction time and the conversion reached plateau thereafter. There was no significant difference on the overall reaction rate was observed when Ca–Al dosage was further increased to 0.7 and 1% as the equilibrium reached almost at the time. This indicates that catalyst dosage higher than 0.5% is not necessary to speed up the reaction of the process

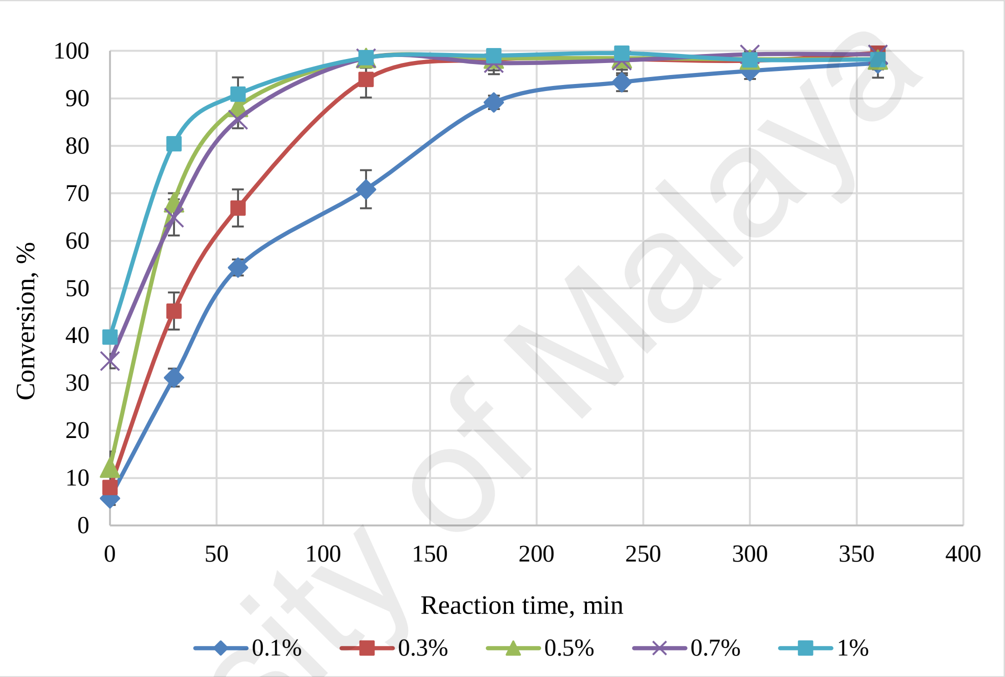


Figure 4.17: Effect of Catalyst Dosage on Conversion of Methyl Palmitate. Reaction Conditions: 170 ^{o}C, 10 mbar, 250 rpm, Mole Ratio of 1.8:1 (Methyl Palmitate:Triethanolamine) and Duration of 6 hours

Thus, Ca–Al dosage of 0.5% is sufficient to give maximum conversion at a high reaction rate. This is in agreement with the published data reported by Jiang *et al.* (2010), which utilized low dosage of aluminium supported on SBA-15 solid acid catalyst of only 0.25% for the esteramine production via esterification of stearic acid and triethanolamine. Based on his work, there were no further changes in the reaction rates when the catalyst dosage was further increased from 0.25 to 0.5, 0.75 and 1%.

4.4.5 Effect of Agitator Speed

Adequate agitation is required to create a circulatory flow induced by agitator in order to ensure homogeneous state between the two immiscible reactants of palm-based methyl palmitate and triethanolamine. Theoretically, the greater the agitation, the more the reactants come into contact with each other to facilitate the chemical reaction. Increasing agitation speed will increase the external mass transfer rates between bulk phases of the reactants towards the surface of heterogeneous catalyst. The influence of agitation on conversion of methyl palmitate was studied by varying the impeller speed at 150, 170, 200 and 250 rpm. Figure 4.18 demonstrates that at 150 rpm, an apparent increase in conversion was observed within the first hour and after 2 hours, the reaction reached equilibrium with a maximum conversion of approximately 98%. Similar trends were observed when the reaction was performed at higher agitator speeds of 170, 200 and 250 rpm. No significant changes on the reaction rate were experienced when the agitator speeds were increased. This indicates that the effect of agitator speed on conversion was not significant. The reaction was observed to be free from the external mass transfer limitation, thus favoring the kinetic control mechanism. In this present study, the transesterification can be performed at lower agitator speed of 150 rpm. Agitator speed of 150 rpm is considered low compared to the one studied by Masoumi *et al.* (2013), that utilizes an optimum mechanical speed agitation of 480 rpm in lipase-catalyzed production of esteramine via esterification of oleic acid and triethanolamine. Nevertheless, agitation at 150 rpm is preferred in this study as rates higher than 250 rpm resulted in crushing of Ca–Al into very fine particles at the end of the reaction, making it difficult to reuse it for the next reaction cycle. A great extent of size reduction of Ca–Al was experienced from 850 µm initially to approximately 75 µm after performing the reaction under an agitation speed of 250 rpm.

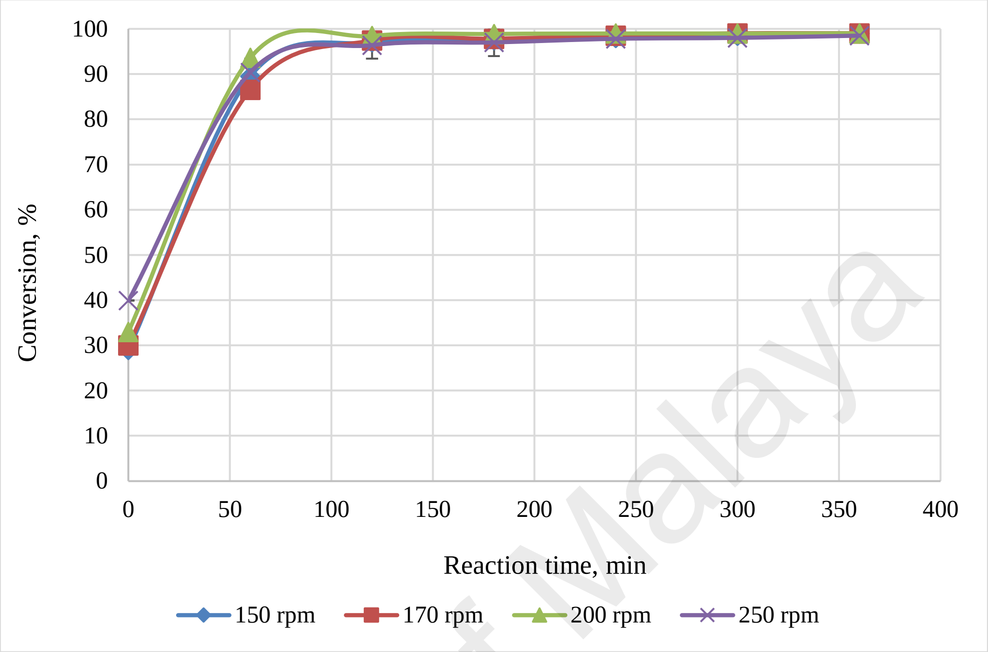


Figure 4.18: Effect of Agitator Speed on Conversion of Methyl Palmitate. Reaction Conditions: 170 °C, 10 mbar, 0.5% Catalyst Dosage, Mole Ratio of 1.8:1 (Methyl Palmitate: Triethanolamine) and Duration of 6 hours

4.4.6 Effect of Reaction Time

The influence of reaction time on the percentage of conversion of methyl palmitate was investigated. Based on the plot shown in Figure 4.19, a minimal conversion of approximately 8% was observed at the initial stage of the reaction (t=0). Rapid increment from 8% conversion to the maximum conversion of 98.5% was observed at 2 hours reaction time, suggesting that increasing the reaction time promoted more collisions between reactants and the heterogeneous catalyst, leading to an increase in conversion. However, the increment of the conversion was minor when the reaction time was extended from 2 to 6 hours. Hence, the time course of this transesterification can be established for 2 hours. Studies conducted by Jiang *et al.* (2012) reported that the aluminium supported on SBA-15 solid acid-catalyzed esterification for esteramine production requires a longer duration of 6 hours compared to reaction time used in this present study. The transesterification process aided by Ca-Al experienced a shorter reaction time, presumably due to utilization of high vacuum in the system compared to the published work by Jiang *et al.* (2012), where he claimed that the removal of water (by product) from the system was performed only by purging of nitrogen.

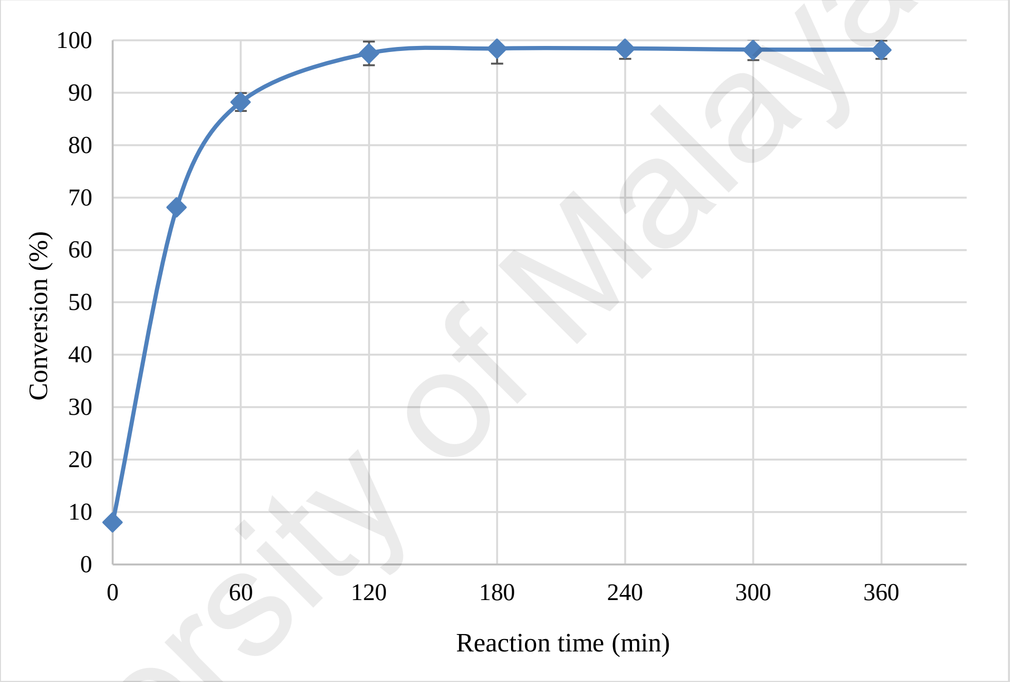


Figure 4.19: Effect of Reaction Time on Conversion of Methyl Palmitate. Reaction Conditions: 170 ºC, 10 mbar, Mole Ratio of 1.8:1 (Methyl Palmitate: Triethanolamine), 150 rpm and 0.5% Catalyst Dosage

4.5 Optimization of Operating Conditions using Response Surface Methodology (RSM)

Based on the preliminary data on the effects of process parameters on transesterification process investigated in the earlier section, it was found that reaction temperature, vacuum, catalyst dosage and agitator speed were regarded as an important operating variables, which influenced the transesterification of methyl palmitate into fatty esteramine. Therefore, for optimization using RSM, the experimental regions of study to locate the optimum operating conditions were selected as follows; 130 – 170 ^{o}C for temperature, 500 – 10 mbar for vacuum, 0.1 – 1% for catalyst dosage and 150 – 250 rpm for agitator speed, a range containing the minimum and maximum values of investigation. This study was carried out under the optimum mole ratio of 1.8:1 (methyl palmitate: triethanolamine) and duration of 2 hours as discussed in earlier section.

Fatty esteramine derived from triethanolamine will consists of a mixture of mono, di and tri-esteramine. Formation of higher mono-esteramine shall facilitates the dispersibility and formulation stability but exhibits low softening effects, whereas higher formation of tri-esteramine will give better softening properties but poor formulation stability. Ideally, higher di-esteramine content is desirable as it exhibits both excellent softening and good stability in fabric softeners formulation (Mishra *et al*, 2007). As such, the di-esteramine content was chosen as the response for the process optimization. In the face-centered design, 30 experimental observations were undertaken at random orders for the optimization of the operating conditions for fatty esteramine production. The face-centered design matrix represents in terms of coded value of the independent variables and the experimental results of di-esteramine yield (response) resulting from the effect of four process parameters (independent variables): temperature (A), vacuum (B), catalyst dosage (C) and agitator speed (D) are tabulated in Table 4.3.

Table 4.3: Face-centered CCD Design Layout and Experimental Results

Run Order	Type of Factor	Coded Value				Response (Di-esteramine Content, %)
		A (°C)	B (mbar)	C (%)	D (rpm)	
5	Center	0	0	0	0	32.82
6	Center	0	0	0	0	38.52
11	Center	0	0	0	0	38.45
13	Center	0	0	0	0	32.52
20	Center	0	0	0	0	39.79
21	Center	0	0	0	0	42.31
7	Axial	0	0	1	0	30.40
14	Axial	0	-1	0	0	27.40
16	Axial	1	0	0	0	43.26
17	Axial	-1	0	0	0	4.78
22	Axial	0	0	-1	0	7.16
25	Axial	0	0	0	-1	35.55
26	Axial	0	0	0	1	37.69
28	Axial	0	1	0	0	43.30
1	Factorial	1	-1	-1	1	14.85
2	Factorial	1	-1	1	-1	33.16
3	Factorial	-1	-1	1	-1	4.67
4	Factorial	-1	-1	-1	-1	3.00
8	Factorial	-1	1	1	1	41.25
9	Factorial	1	-1	1	1	40.12
10	Factorial	-1	1	-1	1	1.85
12	Factorial	1	-1	-1	-1	22.96
15	Factorial	1	1	-1	1	27.13
18	Factorial	1	1	-1	-1	36.68
19	Factorial	-1	1	-1	-1	1.00
23	Factorial	1	1	1	-1	45.00
24	Factorial	1	1	1	1	45.62
27	Factorial	-1	-1	1	1	5.55
29	Factorial	-1	1	1	-1	40.10
30	Factorial	-1	-1	-1	1	1.4

Note: A, temperature; B, vacuum; C, catalyst dosage; D, agitator speed

4.5.1. Data Analysis

Statistical analysis of variance (ANOVA) was performed to investigate the significance and fitness of the quadratic model as well as the effects of the individual independent variables and their interaction on the response. Fitting of the experimental data to various models (i.e.linear, quadratic and cubic model) by the RSM software and their subsequent analysis of variance showed that this heterogeneous transesterification process was most suitably described with a quadratic model. The model was used to describe the mathematical relationship between the independent variables and response. The following equation (4.1) and (4.2) in terms of coded and actual independent variables respectively were generated to predict the di-esteramine content:

Equation in terms of coded independent variables:

$Y_{\text{di-ester}}$

$$= 35.34 + 12.57\,A + 7.75\,B + 9.33\,C + 4.47\,BC - 13.92\,C^2 \qquad (4.1)$$

where, Y: di-esteramine content , A: temperature, B: vacuum, C: catalyst dosage, BC: interaction between vacuum and catalyst dosage and C^2: quadratic effect of catalyst dosage.

Equation in terms of actual independent variables:

Di-esteramine content (%)

$$= -\ 88.78 + 0.63{*}\text{Temperature} + 0.0093{*}\text{Vacuum} + 106.7{*}\text{Catalyst Dosage} + 0.04{*}\ \text{Vacuum}{*}\text{Catalyst Dosage} - 68.74{*}\text{Catalyst Dosage}^2 \qquad (4.2)$$

From the ANOVA analysis shown in Table 4.4, it was observed that the model is significant as the *p*-value (probability of error value) of the model is less than 0.0001 to predict the di-esteramine content. The lack of fit *p*-value of 0.0551 (lack of fit *p*-value > 0.05 is not significant) implies that the model fitted to all experimental data (not significant lack of fit is good). In this study, temperature (A), vacuum (B) and catalyst dosage (C), interaction between vacuum and catalyst dosage (BC) and quadratic effect of catalyst dosage (C^2) are the significant model terms with *p*-value less than 0.05 (*p*-value < 0.05 indicates that the model terms are significant for 95% confidence interval). Statistically, the larger the magnitude of the F-value from the ANOVA indicated that the corresponding model term is more significant. By referring to the individual model term from ANOVA shown in Table 4.4, temperature has the highest F-value of 45.84, implying that this process parameter has the most significance influence towards maximum formation of di-esteramine. Ca-Al catalyst dosage observed to be the next most significance process parameter with F-value of 25.26 that can promote the formation of di-esteramine. Vacuum level of the system has the least influence towards promoting the maximum formation of di-esteramine with F-value of 17.41. Agitator speed was found not to have significant impact on the formation of di-esteramine and thus this variable was excluded in the analysis in order to improve the model and optimization results. The ranking of the overall significance terms from the ANOVA shown in Table 4.4 are as follow; temperature > catalyst dosage > quadratic effect of catalyst dosage > vacuum > interaction of vacuum and catalyst dosage. Meanwhile, the insignificant model terms were found to be agitator speed (D), interactions of temperature – vacuum (AB), temperature – catalyst dosage (AC) and temperature – agitator speed (AD), quadratic effect of temperature (A^2), vacuum (B^2) and agitator speed (D^2).

Table 4.4: ANOVA Results for the Model and Model Terms

Source	**F-value**	***p*-value**	
Model	23.23	<0.0001	Significant
A-temperature	45.84	<0.0001	
B-vacuum	17.41	0.0003	
C-catalyst dosage	25.26	<0.0001	
BC	5.16	0.0324	
C^2	22.48	<0.0001	
Lack of fit	4.35	0.0551	not significant

R-squared = 0.8287, Adjusted R-squared = 0.7931, Predicted R-squared= 0.7218, Adequate Precision = 16.832

The value of R-squared of 0.8287 indicates that the model fits the experimental data as the value of $R^2 > 0.75$ indicates fitness of the model (Reddy *et al.*, 2008). Predicted R-squared of 0.7218 is in agreement with the adjusted R-squared of 0.7931 as the adjusted and predicted R-squared values are within 0.2 of each other. This confirms the precision of the experimental data and model. Adequate precision measures the signal to noise ratio and a value greater than 4 is desirable. Result shows that the adequate precision value was 16.832, indicating that the model can be used to navigate the design space (Zabeti *et al.*, 2009b).

The plot of predicted versus actual di-esteramine content shown in Figure 4.20 verified that the predicted value is in agreement with the experimental data (actual) in the range of the operating conditions. The value $R^2 = 0.8287$ indicated that the model fits the experimental data.

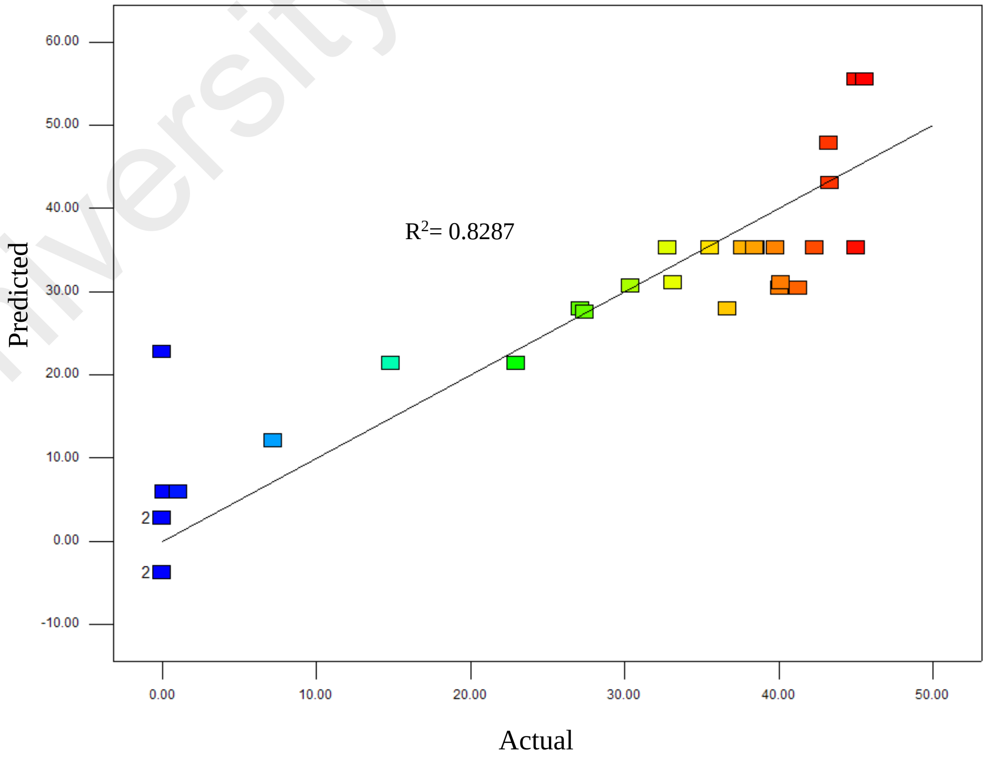


Figure 4.20: Scatter Plot of Predicted Di-esteramine Content (%) Against Actual Di-esteramine Content (%)

Correlation between empirical equation and surface response

Correlation between empirical equation and the response surface was investigated. The response surface 3D plot of di-esteramine content versus vacuum and catalyst dosage shown in Figure 4.21 was generated based on equation (4.1) and (4.2) and by having the temperature and agitator speed at their center points. The response surface indicates that at low vacuum, the di-esteramine content increase with an increase in catalyst dosage. However, higher catalyst dosage leads to a slight reduction in the formation of di-esteramine, due to the fact that the quadratic term of the catalyst dosage is more significant with a negative effect. Considerable increment in di-esteramine content was observed with increasing catalyst dosage at higher vacuum. This is due to the fact that the interaction term of vacuum – catalyst dosage, BC, is more significant with a positive effect on the response (equation 4.1 and 4.2).

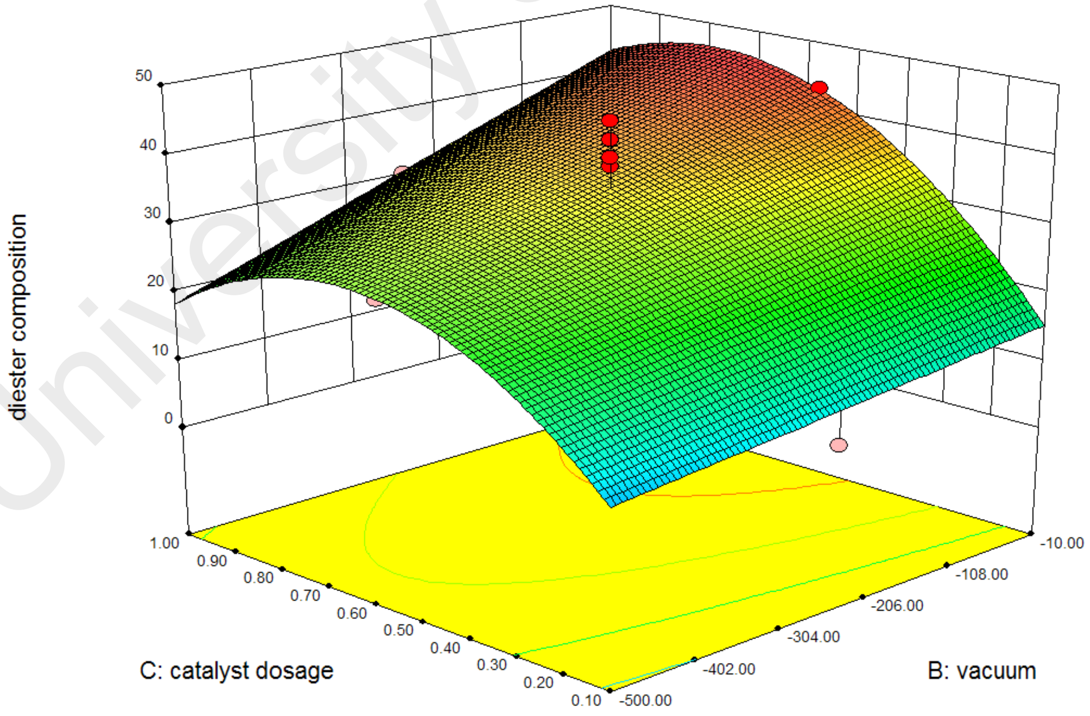
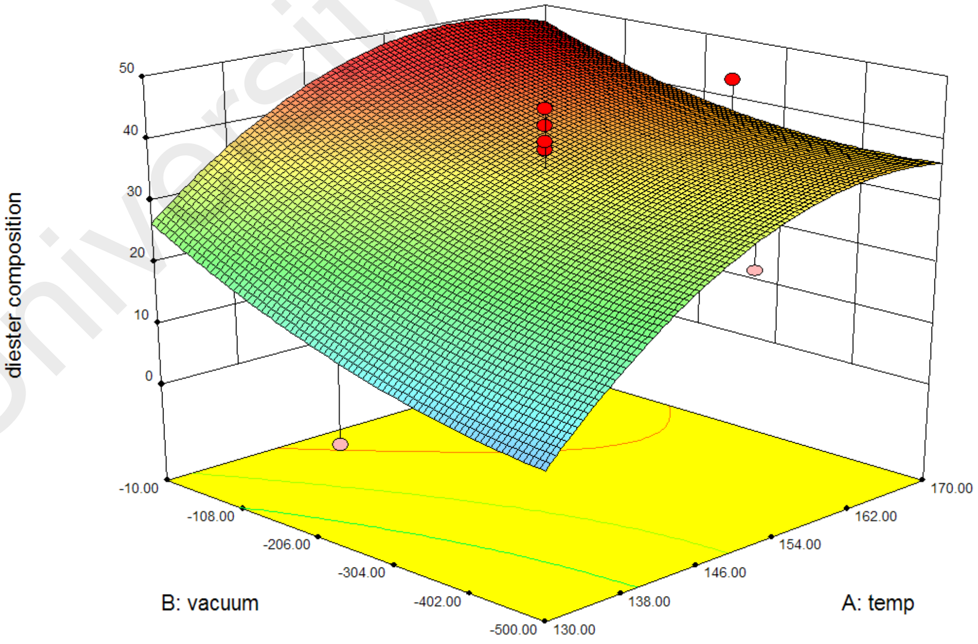


Figure 4.21: Response Surface 3D Plot of Di-esteramine Content versus Catalyst Dosage and Vacuum at Temperature of 150 °C and Agitator Speed of 200 rpm

4.5.2 Interaction Effects of Process Parameters on Di-esteramine Content

In order to determine the optimum levels of each process variables for maximum di-esteramine content, a 3D response surface and contour plots were constructed by plotting the response (di-esteramine content) against any two independent variables, while maintaining the third variable at their center points. 3D response surface and contour plot of di-esteramine content versus temperature and vacuum shown in Figure 4.22 at fixed catalyst dosage of 0.55% and agitator speed of 200 rpm reveals that generally, increase in both variables yielded in an increase in di-esteramine formation. However, the di-esteramine content was more affected by temperature compared to vacuum. Temperature gave a profound impact on transesterification, in which the rate of reaction increases as the temperature is increased. Higher di-esteramine content was obtained at higher temperature from 150 to 170 °C and higher vacuum from 150 to 10 mbar.



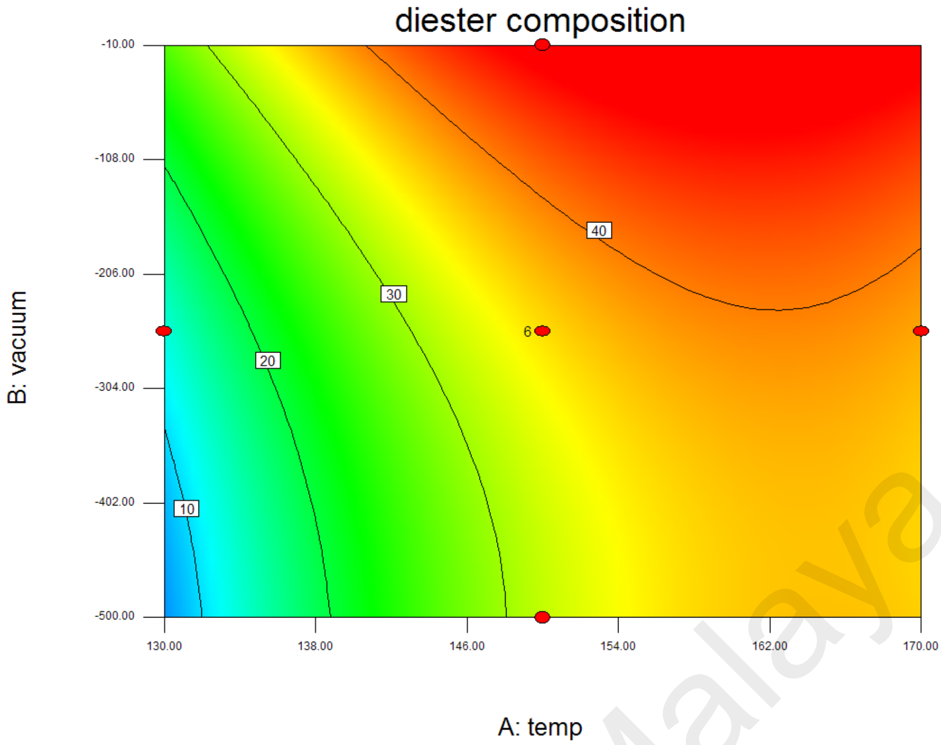


Figure 4.22: 3D Response Surface and Contour Plots of Di-esteramine Content versus Temperature and Vacuum at Catalyst Dosage of 0.55% and Agitator Speed of 200 rpm

Figure 4.23 demonstrates the plots of di-esteramine content versus temperature and Ca-Al catalyst dosage with vacuum fixed at 255 mbar and agitator speed of 200 rpm. It was observed from the figure that minimal di-esteramine was obtained at low temperature and low amount of catalyst dosage. An increase in temperature resulted in increase in di-esteramine content and it appeared that the di-esteramine content increased with increase in catalyst dosage from 0.5 to 0.8%. When the catalyst dosage was increased beyond 0.8%, a reduction in the formation of di-esteramine was experienced, presumably due to increase in viscosity of the reaction mixture when higher amount of Ca-Al catalyst was incorporated. Increase in viscosity of the reaction mixture will reduce the external mass transfer rates between bulk phases of the reactants towards the surface of the solid catalyst. This finding is in agreement with the work published by Wenlei *et al*. (2015), where similar trend on the effect of catalyst dosage was reported.

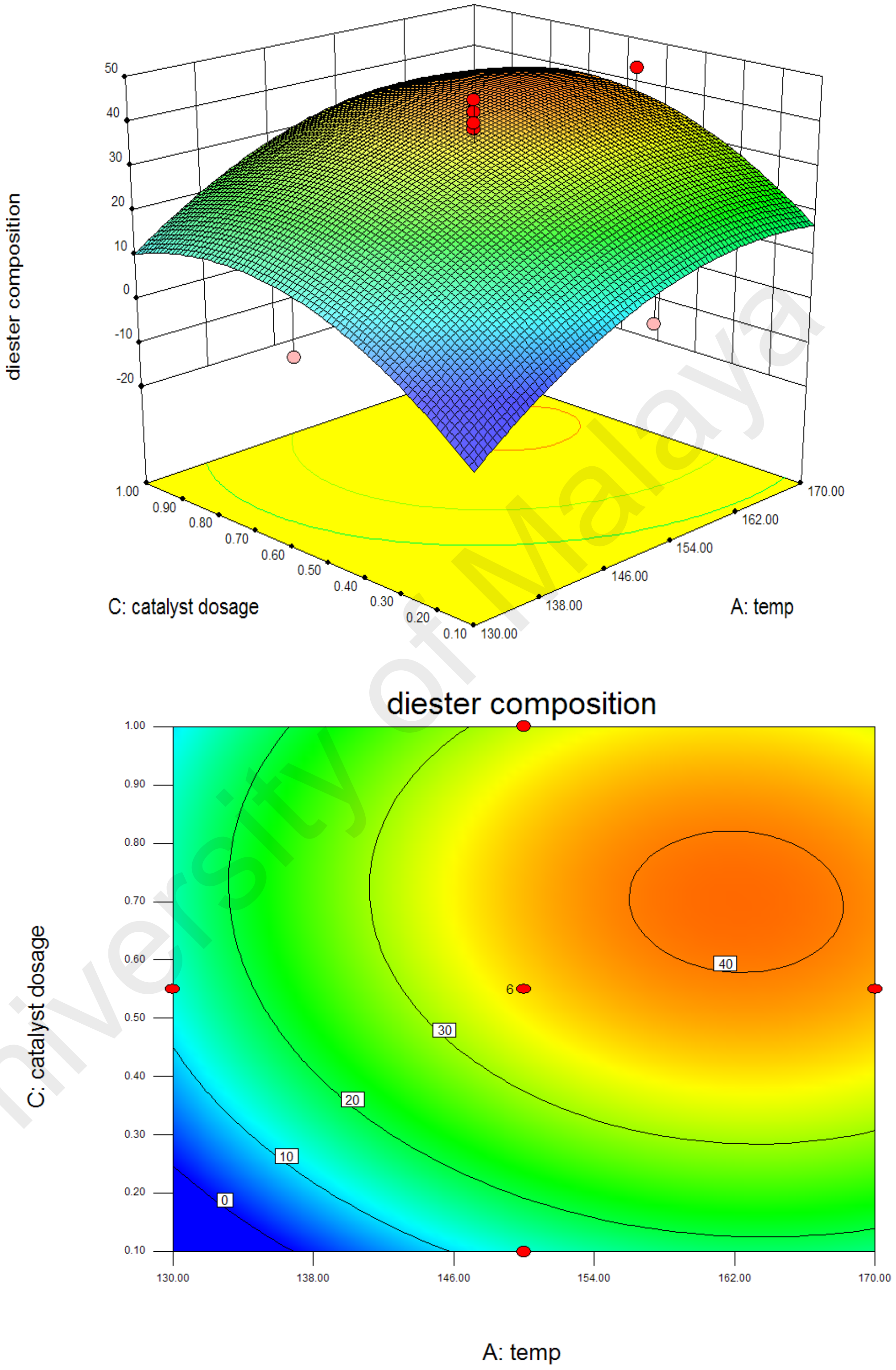


Figure 4.23: 3D Response Surface and Contour Plots of Di-esteramine Content versus Temperature and Catalyst Dosage at Vacuum of 255 mbar and Agitator Speed of 200 rpm.

Yigang and co-worker (2015) revealed that in the biodiesel production from *Styrax confuses Hemsl* seed oil, the yield started to reduce when the solid acid catalyst concentration was more than 5 g/L. The higher amount of catalyst resulted in agglomeration and settled out from reaction mixture and thus, reduces the catalyst surface area. Other study conducted by Masoumi *et a*l (2013) also described similar trend as present work whereby, the percentage of conversion was increased by increasing the catalyst dosage from 3.0 to 5.8% and decreased with further increase to 7% catalyst dosage. Unlike the heterogeneous transesterification, higher reaction temperatures were reported to induce the inactivation of the enzyme used in the study performed by Masoumi and co-workers (2013).

The plot of di-esteramine content versus vacuum and Ca-Al catalyst dosage at fixed temperature 150 ^{o}C and agitator speed of 200 rpm is demonstrated in Figure 4.24. It was found that the formation of di-esteramine was more affected by the Ca-Al catalyst dosage than vacuum. Increase in catalyst dosage resulted in an increase in di-esteramine content until it reached 0.8%, whereas, an increase in vacuum did not significantly increase the di-esteramine content. High vacuum of 10 mbar gave maximum formation of di-esteramine when the catalyst dosage was at 0.8%, suggesting that an efficient methanol removal system via vacuum favored the formation of di-esteramine. Lower di-esteramine content was observed at vacuum lower than 200 mbar when 0.8% catalyst dosage was incorporated, presumably due to insufficient energy to pull the methanol away from the system. The excessive accumulation of methanol could lead to higher decomposition of di-esteramine into mono-esteramine, hence resulting in lower percentage of di-esteramine in the product mixture.

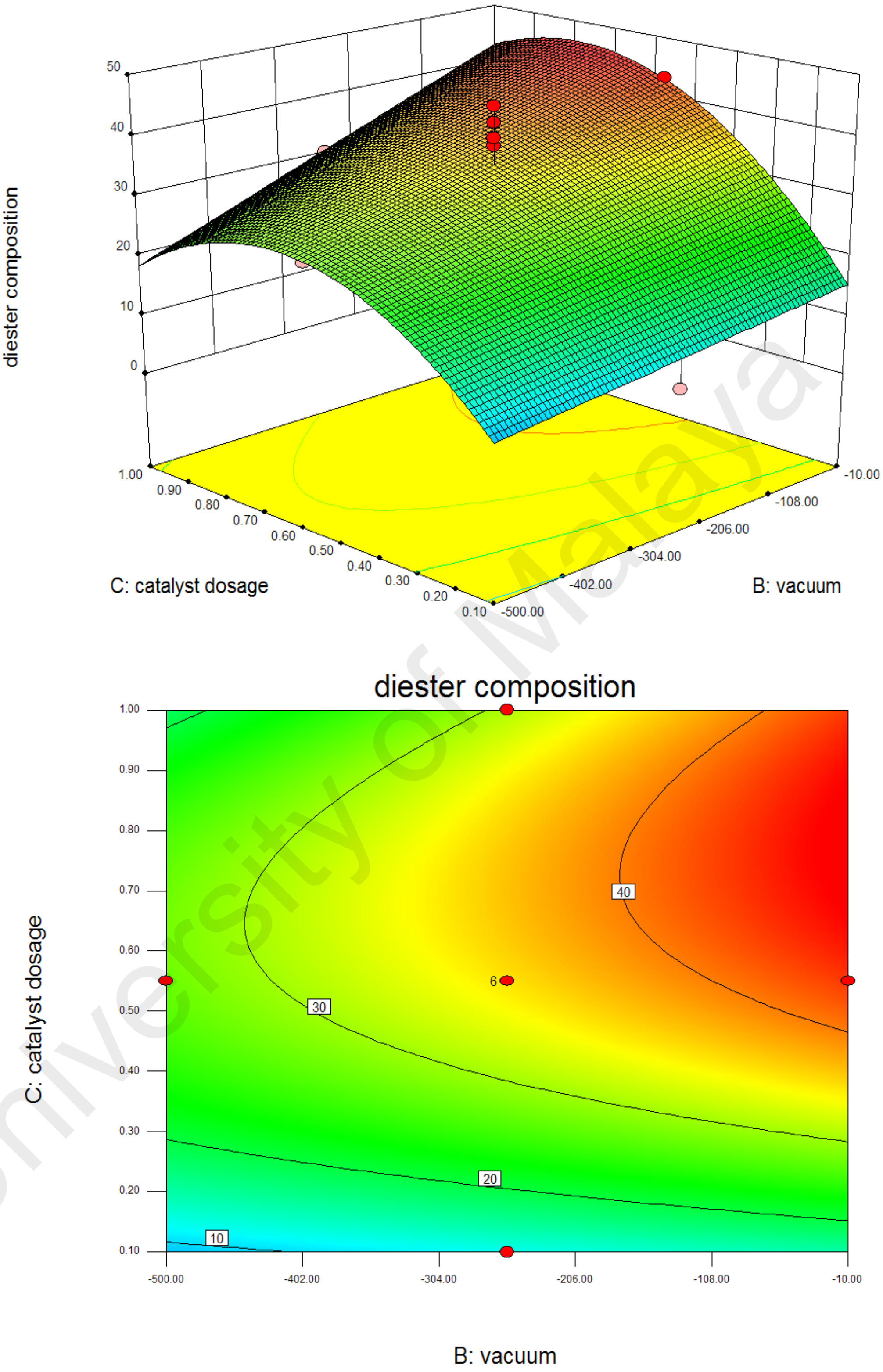
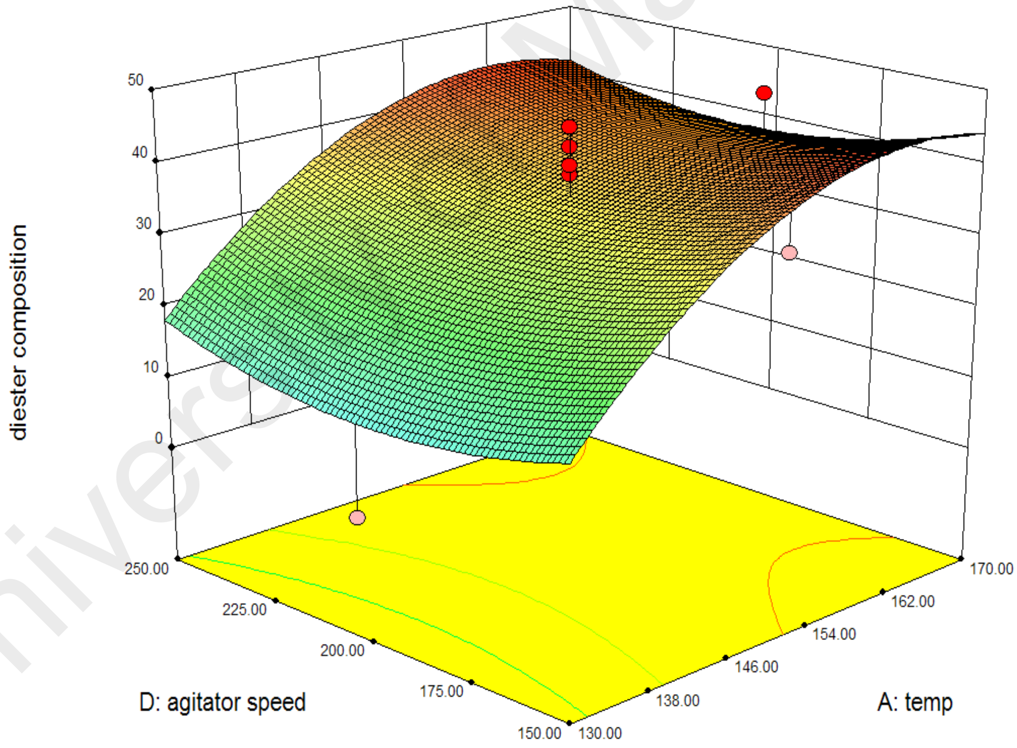


Figure 4.24: 3D Response Surface and Contour Plots of Di-esteramine Content versus Vacuum and Catalyst Dosage at Temperature of 150 °C and Agitator Speed of 200 rpm

The effect of agitator speed and temperature on the formation of di-esteramine at fixed vacuum level of 255 mbar and catalyst dosage of 0.55% was demonstrated in Figure 4.25. It was observed that temperature of the transesterification process has a more significant effect towards formation of di-esteramine compared to that of the agitator speed. The di-esteramine yield obtained increased as the reaction temperature increased, in which higher di-esteramine content was observed at temperature between 150 °C to 170 °C. As for the effect of agitator speed, insignificant increment of the di-esteramine content was observed with increase in agitation.



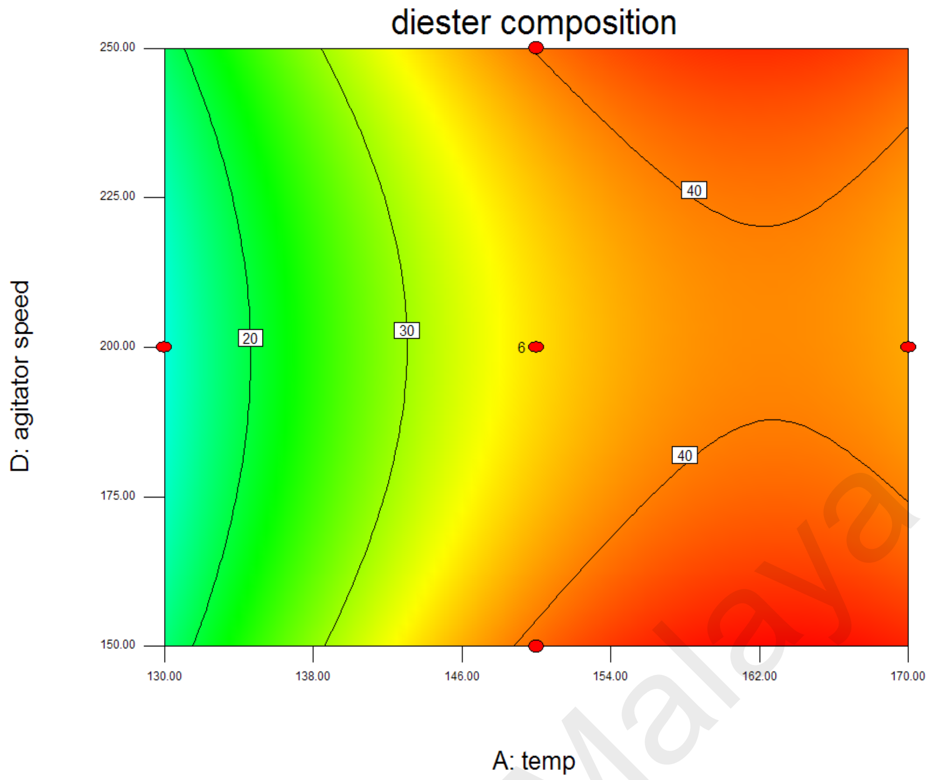


Figure 4.25: 3D Response Surface and Contour Plots of Di-esteramine Content versus Agitator Speed and Temperature at Catalyst Dosage of 0.55% and Vacuum of 255 mbar

Figure 4.26 demonstrates the 3D response surface and contour plots of di-esteramine content versus agitator speed and vacuum at fixed catalyst dosage of 0.55% and temperature of 150 °C. Similarly, the effect of the agitator speed towards formation of di-esteramine was minimal. The response was more affected by the vacuum applied in the system. As the vacuum level in the system increased, the di-esteramine content increased. The response value reached the highest level at vacuum of approximately 10 mbar.

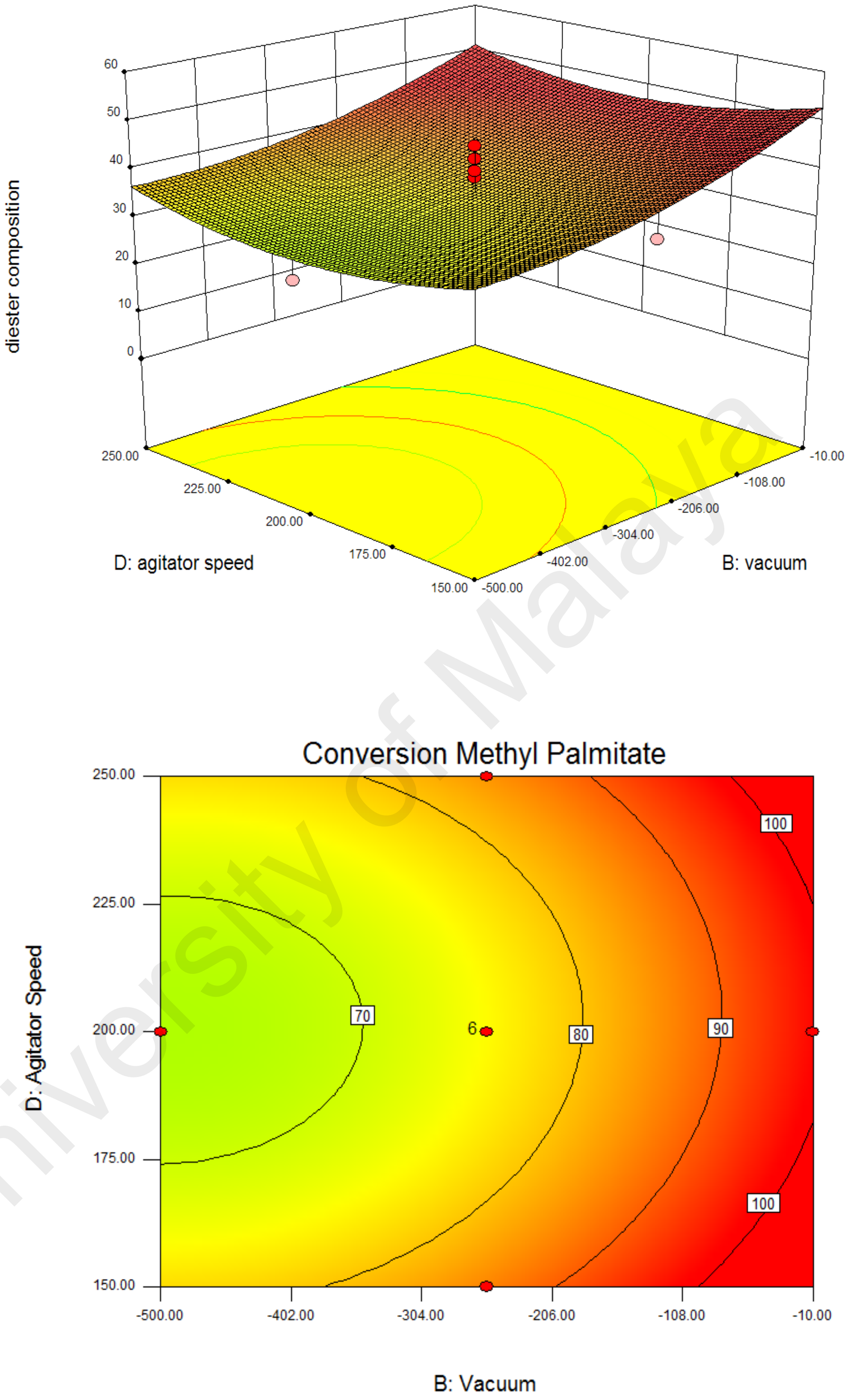
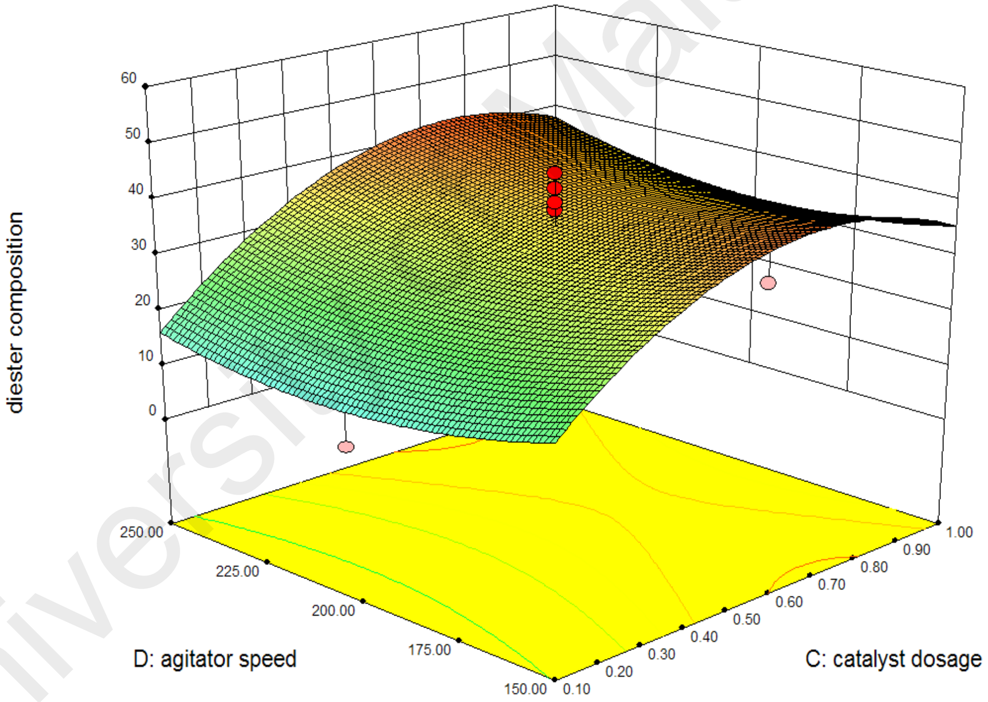


Figure 4.26: 3D Response Surface and Contour Plots of Di-esteramine Content versus Agitator Speed and Vacuum at Catalyst Dosage of 0.55% and Temperature of 150 °C.

The 3D response surface and contour plots of effect of agitator speed and catalyst dosage on the response at fixed reaction temperature of 150 ^{o}C and vacuum level of 255 mbar are illustrated in Figure 4.27. Increase in agitator speed did not give significant impact to the formation of di-esteramine. It appears that increase Ca-Al catalyst dosage led to increase in the response surface until one point and further increment of this variable (above 0.8%) resulted in a gradual decrease in the response surface. Therefore, the transesterification should be performed at Ca-Al dosage less than 0.8% and stirring speed of 200 rpm (mid-point).



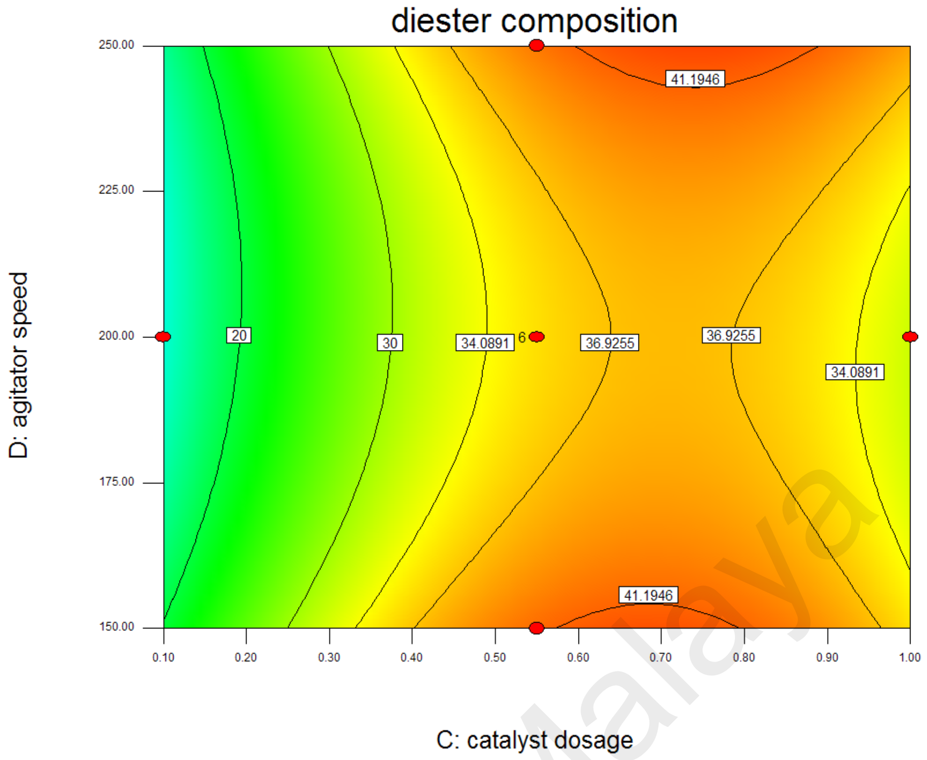


Figure 4.27: 3D Response Surface and Contour Plots of Di-esteramine Content versus Agitator Speed and Catalyst Dosage at Vacuum of 255 mbar and Temperature of 150 ^oC.

4.5.3 Optimization of Operating Conditions and Validation of Model

For optimization, the transesterification reaction was performed under the recommended conditions by RSM and the experimental results were compared with the predicted values. The software suggested that the optimized conditions for maximum di-esteramine content are temperature of 169 ^oC, vacuum of 278.6 mbar, Ca-Al catalyst dosage of 0.74% and agitator speed of 200 rpm (Table 4.5). The di-esteramine content under the optimum reaction conditions was predicted to be 47.9%. After a triple run of the experiments, it was found that the actual di-esteramine content obtained under the optimum operating conditions suggested was 45.5%, which is in agreement with the predicted value. Therefore, this implies that the generated quadratic model derived from RSM experimental design has sufficient accuracy to predict the di-esteramine content. The conversion of methyl palmitate obtained under the optimum operating conditions was 97%, which was slightly lower than 98%, as reported in previous section. This might be due to the lower vacuum level of 278.6 mbar applied under the optimum condition suggested by RSM.

Table 4.5: Optimum Operating Conditions and Di-esteramine Content using RSM

Temperature (°C)	**Vacuum (mbar)**	**Catalyst Dosage (%)**	**Agitator Speed (rpm)**	**Di-esteramine Content (%)**	
				Experimental	Predicted
169	278.6	0.74	200	45.5 *	47.9

* Experimental data are mean values from three replicates measurement (SD ≤ 0.3)

The reaction performed under this optimized condition yielded 21% mono-esteramine and 27% tri-esteramine (Figure 4.28). The tri-esteramine content obtained from RSM optimization was 27%, which was slightly higher than the reported composition of ≤ 25% by Franklin *et al*. (2002) for experiencing a better fabric softening formulation stability. This might be overcome by performing the reaction at mole ratio lower than 1.8:1 (methyl palmitate: triethanolamine) or employing more selective solid catalyst with suitable pore diameters.

Studies conducted by Jiang and co-workers in 2012 on esterification of stearic acid and triethanolamine, revealed that suitable pore diameters of acid catalyst could improve selectivity to mono and di-esteramine and minimize tri-esteramine content. Their studies proved that pore diameter of solid acid catalyst Al-25 supported on SBA-15 having pore diameter of approximately 6 nm, exhibited higher selectivity to mono and di-esteramine as the pore size of these catalysts was larger than the size of di-esteramine molecules (about 4 nm) and smaller than the size of tri-esteramine (about 7 nm). The reported di-esteramine content produced using Al-25 supported on SBA-15 was 68%, higher than other solid catalyst studied, such as 20 wt% zirconium sulfate supported on SBA-15 (with pore diameter of 9 nm), 20 wt% zirconium sulfate supported on MCM-41 and the homogeneous catalyst of H_3PO_3.

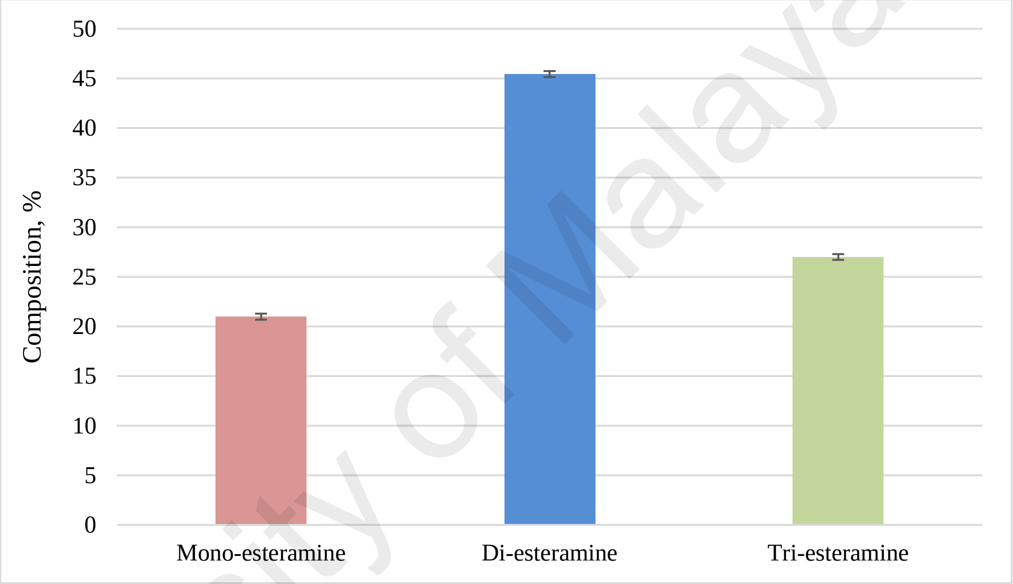


Figure 4.28: Composition of Fatty Esteramine Obtained from Optimized Condition using RSM (Optimum Conditions: 169 °C, 278.6 mbar, 0.74% Ca-Al Dosage, Mole Ratio of 1.8:1 (Methyl Palmitate: Triethanolamine) and 200 rpm

4.6 Reusability of Ca-Al Catalyst

In conventional process, sodium methoxide was commonly used as the catalyst for transesterification of methyl ester and triethanolamine. However, the catalyst was difficult to be separated from the product and could not be reused. Reusability is an important property for heterogeneous catalyst as it can reduce the production cost through recycling of the catalyst and elimination of the regeneration process. Therefore, heterogeneous catalyst that has a potential for industrial application should have a good stability. Reusability experiments were carried in this present study to test the stability of the Ca-Al catalyst. Based on Figure 4.29, the reusability of Ca–Al was successfully tested for three subsequent cycles, where the conversion and fatty esteramine compositions obtained for the second and third cycles were close to the first cycle using fresh catalyst. However, Ca-Al catalyst suffered a significant drop in conversion of methyl palmitate and dramatic change in fatty esteramine compositions in the fourth cycle, whereby only 22% di-esteramine was obtained compared to approximately 46% formed in the first, second and third cycles of the recycling process. It was noticeable that higher composition of mono-esteramine of approximately 33% obtained in the fourth cycle, indicating that the catalytic activity of Ca-Al catalyst in converting the mono-esteramine into di-esteramine was reduced.

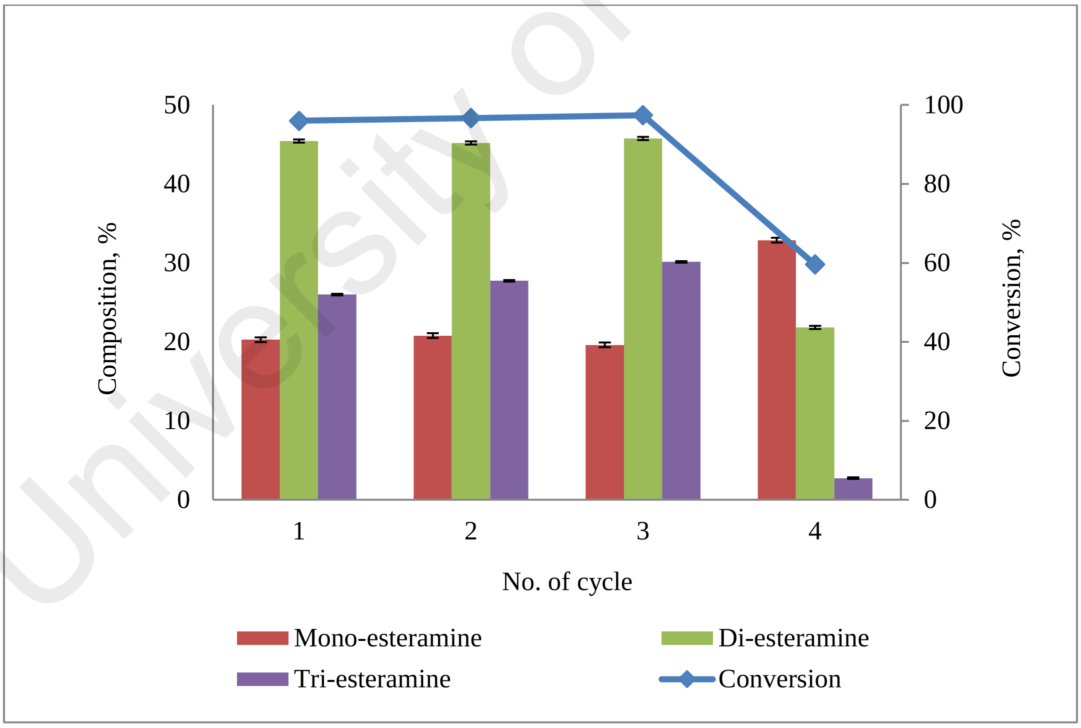


Figure 4.29: Reusability of Ca–Al Catalyst.
(Optimum Conditions: 169 ºC, 278.6 mbar, 0.74% Ca-Al Dosage, Mole Ratio of 1.8:1 (Methyl Palmitate: Triethanolamine) and 200 rpm

The dramatic decrease of conversion and fatty esteramine compositions probably due to the mechanical stress of the catalyst particles that collide against each other and also against the walls of the reaction unit caused by continuous agitation from one cycle to another in the reusability study. Moreover, the mass loss of Ca-Al catalyst in the recycling process might also lead to decrease in conversion and fatty acid composition in the forth cycle. The reusability of Ca-Al catalyst performed under the optimum operating conditions established in this study were compared with reported reusability study of other solid catalysts in transesterification processes. Ca-Al catalyst was used in methanolysis and ethanolysis of soybean oil for biodiesel production as reported by Simonetti *et al* (2014), however, the reusability of this catalyst for the process was not reported. Similarly, research work conducted by Kocik *et al* (2015) employing Ca-Al mixed oxide for biodiesel production from transesterification of rapeseed oil did not mentioned on the stability in terms of reusability of this catalyst in his study. Reusability of other catalyst such as CaO supported on Al_2O_3 employed in transesterification of palm oil for biodiesel production was reported by Zabeti *et al*. (2010) whereby, the catalyst was reused for only two subsequent cycles at optimum condition of 65 °C, catalyst content of 6 wt% and alcohol/oil molar ratio of 12:1. Meanwhile, Jose *et al*. (2009) also reported his study on the reusability of CaO catalyst employed in the production of glycerol carbonate via transesterification of glycerol and dimethyl carbonate. The catalyst showed a weak catalytic activity in the second cycle of the reaction conducted at 95 ^{o}C, catalyst to glycerol molar ratio of 0.06 and dimethyl carbonate to glycerol molar ratio of 3.5. Jose and co-workers revealed that the rapid decrease in both conversion and yield presumably due to deactivation of CaO caused by the exposure with air between the catalytic runs and reduction of its surface area as the catalyst was lump together when it was reused in the subsequent cycles.

4.7 Leaching of Ca-Al Catalyst Active Species into Reaction System

Leaching of active sites into the reaction medium is one of the causes for deactivation of the heterogeneous catalyst in chemical processes. According to Refaat (2011), the deactivation mechanism heterogeneous transesterification process specifically for biodiesel production can be classified into the leaching of the active species as well as adsorption of acidic hydrocarbon onto the basic sites. The deactivation mechanism affects the industrial application as extensive leaching may threaten the reusability of the heterogeneous catalyst. The degree of leaching directly influences the number of cycles the catalyst can be reused. Besides leaching, possible main causes for heterogeneous catalyst deactivation are poisoning of the active sites, fouling and thermal degradation.

The work in this section will focus on leaching of Ca-Al catalyst active species into fatty esteramine, whereby the Ca and Al metals content in the product were measured after first, second, third and forth cycles in the reusability study conducted in previous section. Figure 4.30 shows insignificant amount of Ca metal of 32 mg/L was detected in the fatty esteramine sample from the first cycle. It is noticeable that only minor amount of Ca active species were leached into the product from second, third and forth cycles of approximately 5, 6 and 6.2 mg/L respectively and thus they were found to be negligible. Similarly, the leaching of Al active species was also found to be minimal. The trace amount Al metal of ≤ 5 mg/L detected in the fatty esteramine samples from the first, second, third and forth cycles are depicted in Figure 4.31. Overall, it was observed that leaching of Ca and Al active species into fatty esteramine samples were insignificant and this finding were in agreement with the catalytic activity of Ca-Al catalyst shown in the previous section, which capable of maintaining its activity for three subsequent cycles. However, leaching of Ca and Al metals was not the main reason for the deactivation of the catalyst causing the decrease in conversion and change in fatty esteramine compositions from the forth cycles as insignificant amount of the actives species were detected in fatty esteramine sample from the forth cycle. This findings strongly supports that the weak catalytic activity of Ca-Al in the forth cycle presumably due to mechanical stress of the catalyst and weight loss upon recycling process as discussed in the previous section.

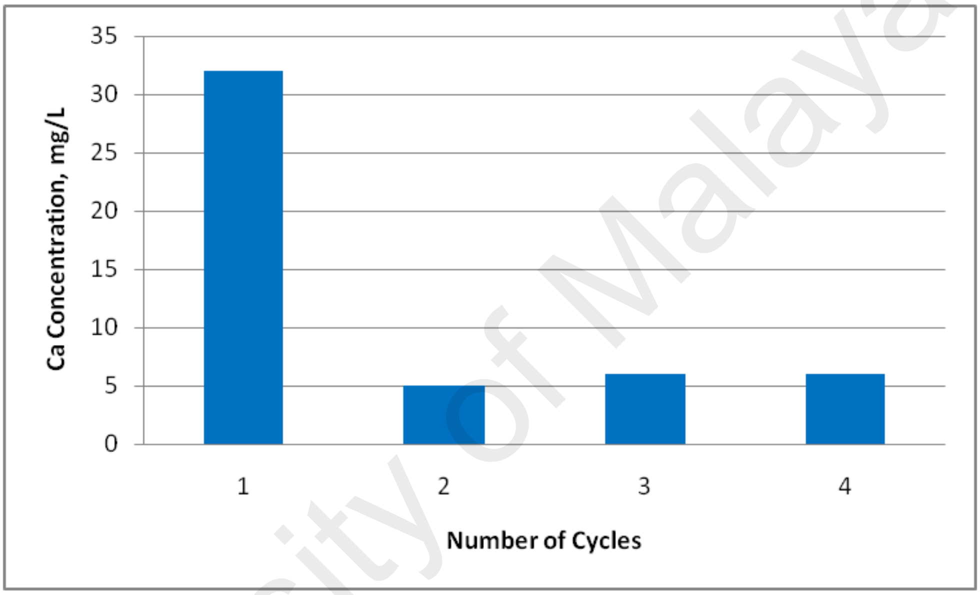


Figure 4.30: Leaching Test Profile for Ca Metal in Fatty Esteramine

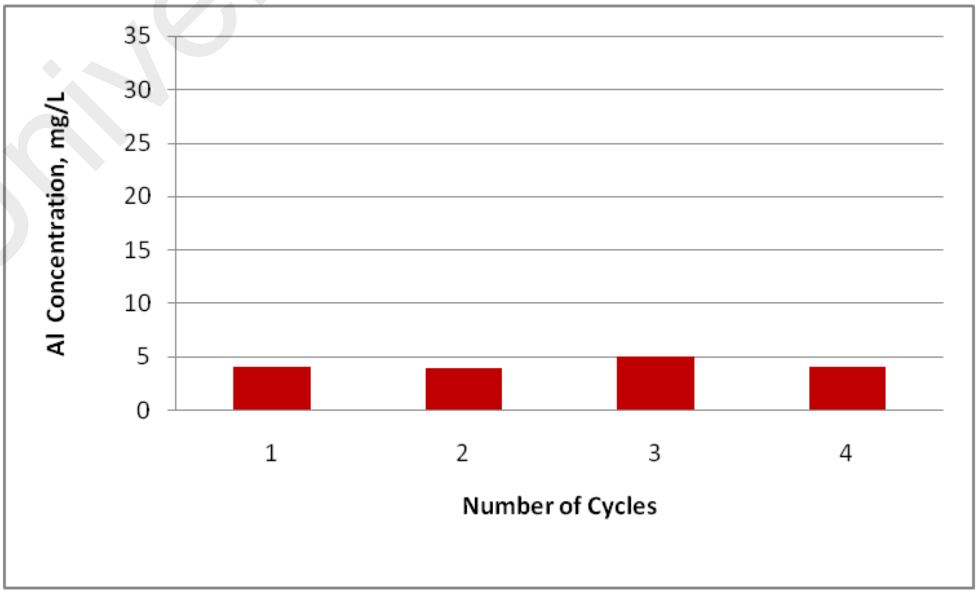


Figure 4.31: Leaching Test Profile for Al Metal in Fatty Esteramine

The leaching profile of Ca-Al catalyst obtained in this present study was compared with findings reported in heterogeneous transesterification processes. Kocik and co-workers (2015) studied the Ca leaching in Ca-Al mixed oxide in transesterification of rapeseed oil for biodiesel production. They pointed out that the leaching of Ca actives species into product started to increase rapidly when the conversion was high as more glycerol was formed. High conversion of 92% was achieved within 90 minutes reaction time and almost no Ca metal (~5 mg/L) was detected in the reaction mixtures within this period. When the transesterification was prolonged to more than 90 minutes, the leaching of the Ca metal increased rapidly up to 75 mg/L. Kocik and co-workers (2015) also investigated the leaching of Ca metal from Ca-Al mixed oxides catalyst in each reaction components such as methanol, rapeseed oil, methyl ester and glycerol. They found that the maximum content of Ca active species of approximately 70.8 mg/L was detected in glycerol. They also reported that the degree of leaching of the Ca actives species affected by the calcination conditions (e.g. nitrogen or air flow, calcination temperature) of the Ca-Al mixed oxide catalyst. Zabeti *et al.* (2010) has evaluated the stability of CaO supported on alumina catalyst in transesterification of palm oil for biodiesel production, concluding that the leaching of Ca active species into biodiesel phase was insignificant. The amount of Ca metal in the biodiesel samples after the first and second cycles were measured at 31 mg/L and 12 mg/L respectively. Overall, the amount of Ca active species leached into fatty esteramine detected in this present study were observed to be lower than that of the reported literature and the leaching of Al active species into fatty esteramine was also found to be minimal.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

This final chapter summarizes all the major findings based on the main objectives of this study. This chapter also provides recommendations for future works in gaining better understanding on the heterogeneous transesterification reaction specifically for the production of palm fatty esteramine, the intermediate of esterquats.

5.1 Conclusion

Preliminary evaluation on the production of fatty esteramine from the novel heterogeneous catalysis was evaluated in the first part of this research. The attempts in transesterification of palm-based methyl palmitate and triethanolamine employing hydrotalcite-like compounds (HTLC) solid catalyst successfully produced the desired products mixtures of mono-esteramine, di-esteramine and tri-esteramine. The structures of the desired product were confirmed via gas chromatography – mass spectrometer analysis, whereby the fragment ions for peaks existed at retention time of 11.46, 15.58 and 29.22 min. matched the fragment ions of mono-esteramine (m/z 516.4), di-esteramine (m/z 594.6) and tri-esteramine (m/z 863).

Five types of HTLC catalyst were screened to find the suitable catalyst for the transesterification of methyl palmitate and triethanolamine. The order of the catalytic activity of these catalysts is as follows: Ca–Al > Zn–Al > Mg-Al > Cu/Zn–Al > Cu–Al. Among the five types of HTLC catalysts studied, Ca-Al and Zn-Al gave conversion of methyl palmitate more than 90%. Ca-Al was selected as the best catalyst for the transesterification of methyl palmitate and triethanolamine as it gave the highest conversion of methyl palmitate of approximately 98% and maximum di-esteramine content of 47%. The transesterification process employing Ca–Al demonstrated similar conversion and fatty esteramine compositions with the conventional approach using sodium methoxide. Moreover, the use of Ca-Al is preferred as it is less hazardous than the homogeneous catalyst, can be recycled and simplifies the downstream separation process.

Preliminary study on the effects of process parameters on transesterification of methyl palmitate was conducted prior to the optimization using Response Surface Methodology (RSM) approach. It appears that increasing the mole ratio of methyl palmitate to triethanolamine from 1.2:1 to 2:1 resulted in decrease of mono-esteramine content, insignificant changes in di-esteramine content and increase in tri-esteramine content. The influence of temperature on the methyl palmitate conversion was profound as higher conversion was obtained with increase in temperature up to 170 ^{o}C. The vacuum level in the system affected the transesterification process as high vacuum of 10 mbar enhanced the removal of methanol in the process, led to higher conversion of methyl palmitate. The effect of Ca-Al dosage on conversion of methyl palmitate was profoundly observed as the conversion increased when the catalyst dosage was increased from 0.1 to 0.5%. Further increment of the catalyst dosage to 0.7 and 1% only gave a marginal impact on the conversion. It is noticeable that the transesterification process is free from the external mass transfer limitation as the influence of agitator speed on conversion of methyl palmitate seemed to be minimal. The reaction time for this transesterification process was established for 2 hours.

Based on RSM optimization method, the optimum conditions leading to maximum di-esteramine yield was established at reaction temperature of 169 ^{o}C, vacuum of 278.6 mbar, catalyst dosage of 0.74% and agitator speed of 200 rpm. The statistical analysis from ANOVA revealed that the reaction temperature was observed to be the most significant variable affecting the formation of di-esteramine, followed by catalyst dosage, quadratic effect of catalyst dosage, vacuum and interaction of vacuum and catalyst dosage. Experimental di-esteramine content obtained under the optimum operating conditions was 45.5%, which was in good agreement with the predicted value of 47.9 %. The optimized operating conditions yielded 21% mono-esteramine and 27% tri-esteramine.

The reusability of Ca–Al catalyst was successfully tested for three subsequent cycles, in which the conversion and fatty esteramine compositions obtained for the second and third cycles were close to the first cycle using fresh Ca-Al catalyst. After the third cycle, conversion was reduced and fatty esteramine compositions seemed to change dramatically. Hence, Ca–Al was found to have good stability as its catalytic activity was unchanged for three subsequent cycles in the production of fatty esteramine via transesterification of palm-based methyl palmitate and triethanolamine. Leaching of Ca active species from Ca-Al catalyst into the fatty esteramine samples appeared to be insignificant as Ca metal content of 32 mg/L was detected from the first cycles, whereas only a trace amount of Ca active species were leached into the product from the second, third and forth cycles. Similarly, leaching of Al active species into the product were almost negligible as ≤ 5 mg/L of Al metal content was measured in fatty esteramine samples from all cycles.

5.2 Recommendations for Future Studies

In this present research, the transesterification of palm-based methyl palmitate and triethanolamine employing HTLC catalyst specifically the Ca-Al catalyst performed under the optimized operating condition yielded 21% mono-esteramine, 46% di-esteramine and 27% tri-esteramine. Higher di-esteramine content is desirable for excellent performance of esterquats. As such, it is recommended to develop a heterogeneous catalyst that can improved the selectivity of di-esteramine content and minimize the tri-esteramine formation and subsequently optimize the operating conditions of the transesterification of methyl palmitate and triethanolamine using this catalyst.

From the reusability test results, it appears that the catalytic activity of Ca-Al catalyst dropped in the forth cycles. This might be due to the loss of catalyst active species caused by mechanical stress as well as mass loss of the catalyst upon recycling process. To overcome this limitation, the transesterification process can be conducted in a packed bed reactor, where the Ca-Al catalyst particles are immobilized inside the reactor, eliminates all the above mentioned problem.

In this present research, the optimum operating conditions for the transesterification of methyl palmitate and triethanolamine using HTLC catalyst, specifically the Ca-Al catalyst was established. Therefore, it is recommended to further expend the research scope to kinetic investigation on the transesterification reactions of palm-based methyl ester into fatty esteramine, as no kinetic data of the reaction is available. It is also recommended to investigate on the possible mechanism of the transesterification of methyl palmitate into mono, di and tri-esteramine and deactivation of the Ca-Al catalyst upon recycling process.

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List of Publications and Papers Presented

1. Haliza, A.A., Aroua, M.K., & Yusoff, R, Abas, N.A., Idris, Z., & Hazimah, A.H. (2016). Production of palm-based esteramine through heterogeneous catalysis. *Journal of Surfactant Detergent*, *19*,11–18.

2. Haliza, A.A., Aroua, M.K., & Yusoff, R, Abas, N.A., Idris, Z., & Hazimah, A.H. (2016). Production of esterquats aided by hydrotalcite-like compounds as solid catalyst. Paper presented at Global Conference on Engineering and Technology at Pullman Hotel, Bangsar, Kuala Lumpur 1-2 June 2016.

3. Haliza, A.A., Aroua, M.K., & Yusoff, R, Abas, N.A., & Idris, Z., (2017). Optimization of palm-based methyl palmitate and triethanolamine towards maximum di-esteramine content. *Journal of Biocatalysis and Agricultural Biotechnology*, *10*,352-359.