OPTIMISATION OF PALM OIL DEGUMMING PROCESS TOWARDS REFINED BLEACHED DEODORISED PALM OIL SAFETY AND QUALITY

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by

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LIST OF ABBREVIATIONS

3-MCPD	3-Monochloropropanediol
BPO	Bleached Palm Oil
CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
DAG	Diacylglycerides
EDTA	Ethylene Diamine Tetracetic Acid
EFSA	European Food Safety Authority
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acid
GC	Gas Chromatography
GE	Glycidyl Esters
IV	Iodine Value
MG	Monoglycerides
MAG	Monoacylglycerides
NaOH	Sodium Hydroxide
NBD	Neutralised, Bleached, and Deodorized
NBDPO	Neutralised, Bleached, and Deodorized Palm Oil
PA	Phosphatides Acids
PC	Phosphatidylcholines
PE	Phosphatidylethanolamines
PI	Phosphatidylinositol
PORAM	Palm Oil Refiners Association Malaysia
PV	Peroxide Value
RBD	Refined, Bleached, and Deodorized
RBDPO	Refined, Bleached, and Deodorized Palm Oil
RSM	Response Surface Methodology
SBE	Spent Bleaching Earth
TAG	Triacyl glycerides
TG	Triglycerides

PENGOPTIMUMAN PROSES PENYAHGAMAN MINYAK KELAPA SAWIT TERHADAP KESELAMATAN DAN KUALITI MINYAK SAWIT BERTAPIS, LUNTURAN DAN PENYAHBAUAN

ABSTRAK

Proses penapisan fizikal adalah proses yang paling banyak digunapakai di industry sawit Malaysia di mana ia melibatkan beberapa peringkat proses iaitu penyahgaman, pelunturan dan penyahbauan. Walau bagaimanapun, penyahgaman merupakan langkah penting bagi proses di dalam kilang penapisan minyak sawit kerana prestasi bagi proses penyahgaman ini memberi kesan yang besar terhadap proses penapisan yang seterusnya dan akhirnya mempengaruhi produk minyak kelapa sawit. Selain itu, proses penyahgaman minyak kelapa sawit juga merupakan penyumbang utama bagi kos operasi keseluruhan kilang penapisan minyak sawit kerana kos bagi bahan penyahgaman. Dalam penyelidikan ini, kesan proses penyahgaman asid fosforik akan dikenal pasti terhadap pembentukan ester 3-monokloropropane-1,2-diol (3-MCPD) dan ester glisidil (GE) di dalam Minyak Kelapa Sawit Bertapis, Lunturan dan Penyahbauan (RBD) yang menimbulkan kebimbangan terhadap pengguna minyak sawit. Selain itu, pengaruh proses penyahgaman asid minyak mentah kelapa sawit (CPO) and kesannya terhadap kualiti minyak kelapa sawit RBD telah dihuraikan. Kondisi eksperimen seperti dos asid (0.03 – 0.06 wt.%), suhu (70-100 °C) masa tindakbalas (15 - 45 min) telah dirancang seperti reka bentuk komposit berpusat berputar. Kondisi eksperimen yang ditentukan tersebut dioptimumkan menggunakan Kaedah Gerak Balas Permukaan (RSM) berdasarkan kemaksimuman kualiti minyak kelapa sawit RBD dan pembentukan 3-MCPD dan GE yang minimal di dalam minyak kelapa sawit RBD. Hasil kajian menunjukan bahawa pembentukan 3-MCPD dan GE di dalam minyak kelapa sawit RBD adalah 0.59 mg/kg dan 0.61 mg/kg, ketika pengotimuman masa tindakbalas proses penyahgaman selama 30 minit, 0.06 wt.% kepekatan asid fosforik dan suhu pada 90 °C. Beberapa kaedah analisis telah dijalankan untuk menentukan kualiti minyak sawit RBD termasuk warna, fosferus, asid lemak bebas (FFA), nilai peroksida, kestabilan oksidatif dan ciri-ciri asid lemak. Hasil kajian telah membuktikan bahawa asid fosforik bagi penyahgaman CPO berkesan dalam mengurangkan kandungan fosforus dan hidroperoksida tanpa menjejaskan kualiti minyak kelapa sawit. Penemuan di dalam kajian ini akan membantu untuk menyuntik industri minyak sawit Malaysia ke arah penghasilan minyak sawit yang bermutu tinggi dan premium.

THE OPTIMISATION OF PALM OIL DEGUMMING PROCESS TOWARDS REFINE BLEACHED DEODORISED PALM OIL SAFETY AND QUALITY

ABSTRACT

Physical refining is the most common refining route practiced in Malaysia palm oil industries which involves the processing stages of degumming, bleaching and deodorisation. However, degumming is one of the crucial steps of the crude palm oil refinery process since the performance of the degumming process tremendously affects the later stages of refining processes and finally affect the produced palm oil. Besides, the degumming process of crude palm oil is one of the significant contributors to the total operating cost of the palm oil refinery process due to the cost of the degumming agent. In the present study, the influence of the phosphoric acid degumming process was determined on the formation of 3-monochloropropane-1,2-diol esters (3-MCPD) and glycidyl esters (GE) in refined, bleached, and deodorised palm oil (RBDPO). Besides, the influence of the acid degumming process of crude palm oil (CPO) and its effects on the RBDPO quality was also evaluated. The experimental conditions such as acid doses (0.03 - 0.06 wt.%), temperature (70-100 °C) and reaction time (15 - 45 min) were designed following the central composite design of experiments. The drugging experimental conditions were optimised using the Response Surface Methodology (RSM) based on maximising RBDPO quality and minimal formation of 3-MCPD and GE in the RBDPO. Results showed the formation of 3-MCPD and GE in the RBDPO were 0.59 mg/kg and 0.61 mg/kg, respectively, at the optimised degumming process of the reaction time 30 min, phosphoric acid concentration 0.06 wt.%, and temperature 90 °C. Several analytical methods were employed to determine RBDPO quality, including colour, phosphorus, free fatty acids (FFAs), peroxide values, oxidative stability, and fatty acid properties. It was found that the phosphoric acid degumming of CPO effectively removed the phosphorus and hydroperoxide content without compromising the palm oil quality. The current project will assist in boosting the Malaysian palm oil industry towards premium grade palm oil production.

CHAPTER 1

INTRODUCTION

1.1 Background

The physical refining process of CPO consists of three major processes: degumming, bleaching and deodorisation Berger (1983). Generally, the degumming process is needed to eliminate the gum contained in the CPO, also known as phosphatides, that cannot be removed and does not undergo acid treatment. The presence of phosphatides in the finished product of the oil can give rapid colour reversion and low heat stability to the oil (Zulkurnain et al., 2012). The bleaching process is needed to extract the colour pigments, protein degradation, metal traces, and catalyst after the hydrogenation process. The last unit process is the deodorisation process (Zulkurnain et al., 2012). It is needed to eliminate the volatile components or the impurities that cause odour and off-flavour using steam distillation (Zulkurnain et al., 2012). Figure 1.1 shows the steps involved in the physical refining process of crude palm oil.

The physical refining process is preferable instead of the chemical refining process to prevent an excessive loss of neutral oil (Silva, 2013). Besides that, the quantity of refined palm oil produced from the physical refining process is more than the amount of chemically refined palm oil generated (Gee, 2007). The physical refining process brings substantial advantages: the higher yield of oil, minimisation of the usage of chemicals, and thus lowering the negative impact on the environment (Gibon et al., 2007).

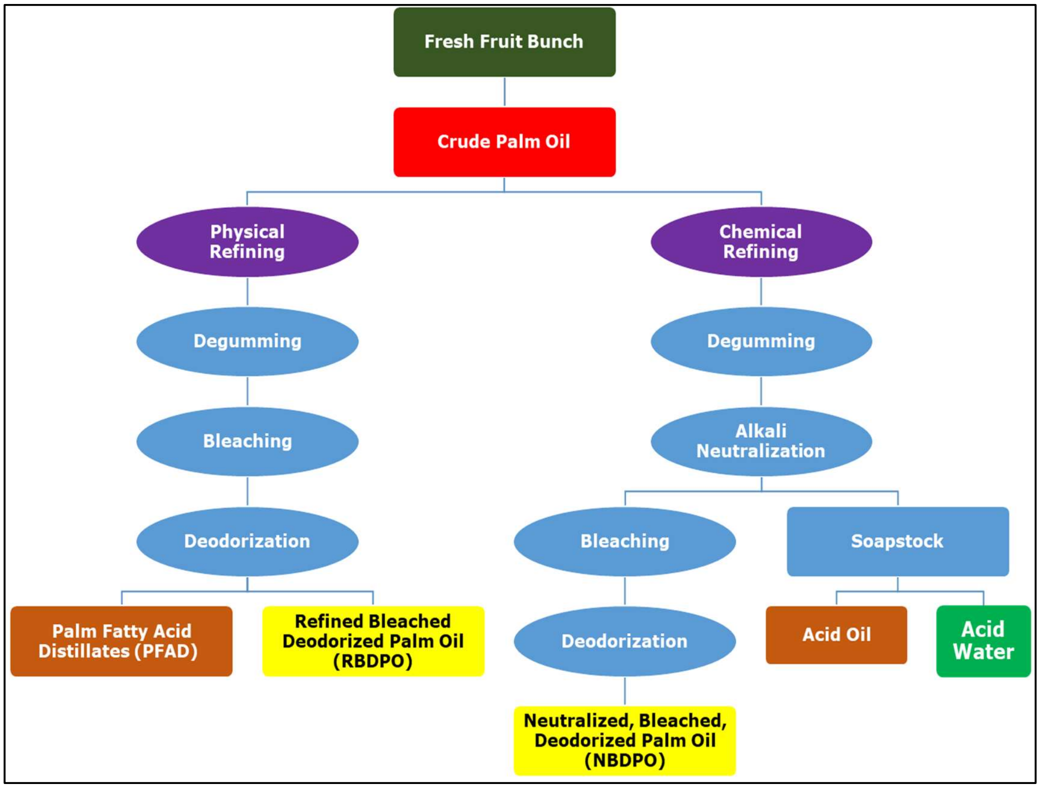

Figure 1.1 Palm Oil Physical Refining process flow (Bailey & Shahidi, 2015)

The final refining process product is refined, bleached, deodorised palm oil (RBDPO). It is crucial to determine the quality of the final product as the RBDPO that do not reach the product specification will have to go through the recycling process. (Silva, 2013). This recycling process increases the company's operational costs and leads to the loss of profit. To meet the customer standard, it is significant to know the quality of RBDPO beforehand so that it is possible to adjust the specific unit operation in the refining process. Hence, the quality of RBDPO produced will be compared with the standard specifications designated by Palm Oil Refiners Association Malaysia (PORAM) standard (Mohd Noor et al., 2017). Table 1.1 displays the standard specifications of RBDPO that are based on The Palm Oil Refiners Association of Malaysia (PORAM).

Table 1.1 Standard specifications of RBDPO based on PORAM (Gee, 2007)

Properties	RBDPO
Free Fatty Acid, FFA (%)	≤ 0.10
Moisture (%)	≤ 0.10
Iodine Value, IV	50-55
Melting Point (°C)	33-39
Colour (Red)	≤ 3

Crude oil extracted from the seeds contains phospholipids and is displayed in parts per million phosphorus. The crude palm oil initially contains phospholipid by about 0.5 to 2 %. Hence, this process eliminates the coagulated phospholipid from the gum-conditioned oil. Without the acid treatment, the gum materials will remain in the final product, and it will give rapid colour reversion and low heat stability of oil (Manan et al., 2009).

The 3-MCPD esters and GE are formed at high temperatures during edible fats and oils refining, mainly during the deodorisation step. 3-monochloropropanediol (3-MCPD) has been known as a processing contaminant, especially in foods containing acid-hydrolysed vegetable protein, such as soy and oyster sauces. On the other hand, they have found the presence of 3-MCPD esters in refined, bleached, and deodorised vegetable oil (Zelinková et al., 2006). Ramli et al. (2011) also reported that 3-MCPD esters were detected in the range of <300 (LOQ) to 2462 µg/kg in most of the refined oils. The highest levels were found in palm oils, followed by other vegetable oils (Zulkurnain et al., 2012).

1.2 Problem Statement

The degumming process is ancient and current for the oil palm industries. The process is adopted directly from the western world application on the soft oil application. However, the degumming process is the most important in refining oil palm as it can determine the final quality of the refined palm oil (Berger, 1983). Currently, Malaysian palm oil industries are conducting a degumming process using the phosphoric acid dosage of 0.05% to 0.06% and reaction time of approximately 5 to 10 minutes (Erickson, 1995). Rarely studies have been conducted to determine the influences of the degumming process of CPO on palm oil quality and its valuable fatty acid contents. Determining the best optimum and the interaction effect between the processing parameters can give industries better ideas for particular tailored research on palm oil degumming. Response surface methodology (RSM) is a statistical and mathematical procedure used to improve and optimise processes that consider the possible interactions between the parameters. RSM is usually applied to reduce the number of experiments that must be performed to determine statistically acceptable responses across dependent variable ranges (Bezerra et al., 2008). Hence, RSM reduces laborious work and time needed to optimise a process compared to other approaches.

The phosphoric acid degumming process might affect the palm oil quality since there are many degumming parameters and interactions between the parameters to affect the quality of degummed oil. Although the physical refining process may improve the quality attributes of CPO, there are limited scientific evidence in literature on the degumming of CPO. Therefore, the present study was conducted to determine the influence of the degumming process to improve the RBDPO quality. The list of problems statement would embarks the present study are listed below.

i. Although phosphoric acid used in the industries is high (0.05% to 0.06%), it is caused an inconsistency in RBDPO quality. The formation of 3-MCPD and GE is influenced by the degumming process, which is not yet understood.
ii. Optimisation of the degumming process must consider improving safety and the quality of RBDPO.
iii. Regulation on level of 3-MCPD and GE have been imposed in palm oil producers in Malaysia at 2.5ppm and 1 ppm, respectively, by the Malaysian Palm Oil Board (MPOB) and European Food Safety Authority (EFSA).

1.3 Objectives

The primary goal of the present study is to assess the influence of the phosphoric acid degumming process on the formation of 3-MCPDE and GE formation in RBDPO and its qualities which was embarked with the following objectives:

i. To determine the influence of phosphoric acid degumming parameters on the formation of 3-MCPD, GE and RBDPO qualities.
ii. To optimise the phosphoric acid degumming process parameters for reducing 3-MCPD, GE and maximising RBDPO qualities using RSM.
iii. To comply the 3-MCPD, GE and other properties of RBDPO, produced at pilot plant scale, with Palm Oil Refiners Association of Malaysia (PORAM) standard specifications.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Berger (1983) found that the fruit grown on an oil palm tree could grow up to 20 meters in height. Palm oil, known as *Elaeis guineensis*, originates from West Africa (Nambiappan et al., 2018). The oil palm tree required a humid climate to thrive. Hence, palm oil could grow best at temperatures around 24-27°C and consequently, the palm fruit that carries the oil from their fourth year onward can be harvested for 40 to 50 years (Berger, 1983). For thousands of years, the human species has used this African oil palm in many products (Nambiappan et al., 2018) Initially, palm oil was utilised as a source of vitamins for cooking and pharmaceutical usage (Nambiappan et al., 2018). In the late 1800s, it was employed as edible oil and utilised in margarine manufacturing (Nambiappan et al., 2018). The improvement of the quality of palm oil by the mechanised mills encouraged the trading of palm oil and became a significant commodity. The expanded palm oil usage resulted in 77% of palm oil is for food usage while the rest is used for non-food applications such as oleochemicals and biodiesel production (Henson, 2012).

Malaysia has become the largest producer and exporter of palm oil and their products, as 51% of world palm oil production and 62% of world exports come from our country (Berger, 1983). The palm oil industries in Malaysia plays an essential part in fulfilling the need for oils and fats globally (Abdullah & Tiong, 2008).

Extraction of palm fruit will generate two different products: crude palm oil (CPO) and crude palm kernel oil (CPKO) (Teoh, 2002). Crude palm oil is extracted from the fleshy endosperm (mesocarp), while the kernel extraction will produce crude palm kernel oil (Gunstone, 2004). Figure 2.1 displays the cross-section of oil palm fruit that contributes to palm oil and palm kernel oil generation. After the extraction process, crude palm oil will further undergo the palm oil refining processes: degumming, bleaching, and deodorisation to eliminate the contaminants in the crude palm oil (Tan et al., 2009).

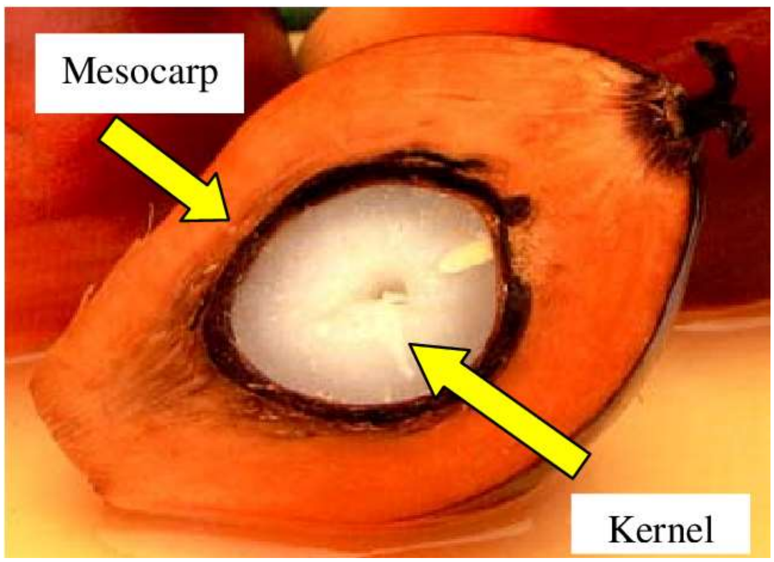

Figure 2.1 Cross-section of an oil palm fruit (Nomanbhay et al., 2017)

The palm oil produced from the mesocarp can be uses in many industrial applications. The highest percentage of palm oil and palm kernel usage is in food application, accounting for about 80% of the overall composition, while the rest, another 20% is for several non-food applications (Teoh, 2002). Refined, bleached, and deodorised (RBD) stearin is used in the production and shortenings and margarine, while the RBD olein is used in cooking and frying oils, shortenings, and margarine

(Abdullah & Tiong, 2008).The unfractionated palm oil, the RBDPO, produces margarine, shortenings, frying fats, and ice cream (Teoh, 2002).

2.2 Components in CPO and CPKO

The components in crude palm oil contain around 1% of valuable molecules beneficial to health (Ramli et al., 2011). These components include carotenoid, phospholipids, metals, tocopherols, tocotrienols and phytosterols (Silva, 2013). Table 2.1 shows minor components' compositions in crude palm oil. It cannot be directly utilised as edible oil needs to be refined. Some of these components are undesirable and considered contaminants like free fatty acids (FFAs), coloured compounds, metals, partial acyl glycerides, and odorous substances (Chang et al., 2016).

Table 2.1 Components in Crude Palm Oil (Mba et al. 2015).

Components	Crude palm oil (ppm)
Carotenoids	500-700
Tocopherol	500-600
Tocotrienols	1000-1200
Phytosterols	326-527
Phospholipids	5-130
Squalene	200-500
Ubiquinone	10-80
Aliphatic alcohols	100-200
Triterpene alcohols	40-80
Methyl sterols	40-80
Aliphatic hydrocarbons	50

The constituents in crude palm oil that are non-glyceride such as FFAs, impurities and moisture, and trace metals, are harmful to oil's stability (Berger, 1983). Besides that, the odoriferous compounds in crude palm oil decrease the tastiness of the oil. Hence, these contaminants present in the crude palm oil need to be removed by refining to attain good quality refined oil (Sambanthamurthi et al., 2000). The desirable qualities of refined oil are bland taste, good oxidative stability and light colour (Silva, 2013). On the other hand, phytonutrients are less abundant in crude palm kernel oil. The specific free fatty acid content ranges between 2.0 and 5.0%, with average values around 3.0%. Partial acylglycerols are present, but quantity is difficult to estimate (Chang et al., 2016).

2.3 Physicochemical properties in Palm Oil

Crude palm oil (CPO) must undergo refining to eliminate all the components influencing its quality, including unwanted flavours, odour, and colour (Tan et al., 2009). The components that affect CPO's quality are denoted as contaminants in the CPO, and they are free fatty acids (FFAs), lipid oxidation products and phospholipids (Tan et al., 2009). However, the desirable components in crude oils should be retained, such as vitamin E (tocotrienols and tocopherols), triacylglycerols (TAGs), phytosterols and carotenoids (Singh et al., 2019). These components function as health beneficial compounds, nutrients and antioxidants in CPO (Mba et al., 2015). The details of the wanted and unwanted compounds inside CPO and their effects on RBDPO safety and quality during the refining process (Bailey & Shahidi, 2005).

Table 2.2 Undesirable CPO minor components and their quality effects towards RBDPO quality. (Bailey & Shahidi , 2005)

Undesirable Minor Component	Origin	Quality Effect
Free Fatty Acid	Hydrolysis	Off-taste, smoke during frying
Peroxide	Oxidation	Off-taste
Phosphatides	From cell mechanism	Burns at high temperature
Moisture	From oil crop transport & storage	Microbial contaminant
Dirt	From oil crop	Appearance
Metals	Soil, milling storage & transport	Catalyst for oxidation

Crude palm oil also contains other minor components naturally present in the oil (Bailey & Shahidi, 2005). Some of the contaminants initially are not present in the CPO. However, during the refining process, these components are formed. Currently, the newest and most debatable components are the glycidyl fatty acid esters (GE) and 3-monochloropropanediol (3-MCPD) (Ramli et al., 2011). Following are the details of the contaminants in the RBDPO that need to be removed and their health effects on humans. Besides that, these minor components are essential to the nutritional properties of palm oil (Bailey & Shahidi , 2005). The orange-red colour of crude palm oil indicates the presence of carotenoids in the palm oil. These carotenoids provide oxidative protection to crude palm oil as they undergo oxidation first compared to triglycerides (Manorama & Rukmini, 1992). Tocotrienols and tocopherols are isomers of vitamin E, and they are potent antioxidants as they provide the oil oxidative stability (Singh et al., 2019).

Table 2.3 Undesirable minor components in CPO, origin, and its health effects on humans. (Bailey & Shahidi, 2005; EFSA 2016)

Undesirable Minor Component	Origin	Health Effect
Heavy metals	Soil, milling storage & transport	Toxic
Pesticides	Crop protection chemicals	Toxic
Dioxins	Environmental pollution	Highly toxic
Mycotoxins	Fungus	Toxic
Mineral oil	Process, storage, transport	Toxicity depends on chain length
Poly Aromatic Hydrocarbons	Drying of oil crop	Carcinogenic, Genotoxic
3-MCPD	High heat treatment	Carcinogenic
GE	High heat treatment	Genotoxic

2.4 Palm Oil Refining

2.4.1 Purpose of Refining

The primary purpose of the refining process is to eliminate the components inside the oil that is undesired before the consumers consume the oil. Several steps are involved in the refinery process (Dumont & Narine, 2007). The steps taken are to remove the undesired components inside the oil, with the least possible damage to the acylglycerols and minimal loss of the desirable constituents. This is because the crude oil quality affects the efficiency and yield of refining and the quality of the fully processed product. The minor components of crude palm oil that wanted to be removed is FFA, phosphatides and glycolipids, tocopherols and tocotrienols, carotenoids, sterols, methylations, triterpenes and hydrocarbons (Gibon et al., 2007). The quality of the final product from the deodorisation process, which is the last refining unit in the refinery process, will be almost bland and tasteless (Mat Dian et al., 2015).

In the industry, the core objective is to convert crude palm oil to a more edible oil with improved quality (Tan et al., 1985)This process is done by eliminating the impurities in the crude palm oil to the desired levels in a well-organised manner, which means that the losses of the desirable components are kept at a minimum and ensure that the process does not take many costs.

2.4.2 Target Quality and Stability of RBDPO

The final refining process product is refined, bleached, deodorised palm oil (RBDPO) (Bailey & Shahidi, 2005). Hence, the quality of RBDPO produced will be compared with the standard specifications designated by Palm Oil Refiners Association Malaysia (PORAM) standard (Mohd Noor et al., 2017). Table 1.1 displays the standard specifications of RBDPO that are based on PORAM.

2.4.3 RBDPO Safety Overview of 3MCPD and GE

Today's world has shifted towards demanding healthier and safer food specifications with fewer contaminants detected. Current emerging issues have been highlighted by European Food Safety Authority (EFSA), they have assessed the risks for public health of the substances: glycidyl fatty acid esters (GE), 3-monochloropropanediol (3-MCPD), and 2-monochloropropanediol (2-MCPD) and their fatty acid esters (EFSA 2016). The

3-MCPD esters and GE are formed at high temperatures during edible fats and oils refining, mainly during the deodorisation step. 3-MCPD esters and GE have been found in refined vegetable oils such as margarine and oils and in fat-containing foods, including infant formula (EFSA 2016).

The 3-MCPD and GE are categorised as carcinogenic and genotoxic, respectively (Cheng et al., 2017). Due to the nature of GE as genotoxic, EFSA has set the limit of 1 ppm for all vegetable oils coming to Europe effective from December, 2017. This has been followed by Nestle, Unilever, and many other major food producers globally. It has been studied previously that monoacylglycerol (MAG) and diacylglycerols (DAG) in vegetable oil play a significant role in the formation of GE in the refining process (Cheng et al., 2017). GE formed during a high-temperature reaction and in the CPO refining case is during the deodorisation process at 260 °C. The level of GE formed is based on the temperature and exposure time of the MAG and DAG in the vegetable oils (Cheng et al., 2017). There are four proposed reactions mechanism pathways for GE formation that have been identified in previous studies (Cheng et al., 2017). Following are the GE formation mechanism study by previous research:

The 3-MCPD limits have yet to be finalised by EFSA. However, customers have set the request 3-MCPD at 2.5 ppm for 2018 (EFSA, 2016). The limits will be revised every year by the customers (EFSA, 2016). The limits of 3-MCPD are believed to be more stringent for the future and are now expected to be at 1.25 ppm. The Malaysian Palm Oil Board (MPOB) has also given serious attention to these issues. Based on a previous study by Šmidrkal et al. (2016), the methyl esters formation mechanism is due to the dissociation of fatty acid, and the presence of free chloride ion at high temperature will result in the 3-MCPD formation. The chemistry behind the formation of 3-MCPD during the CPO refining process, as shown in Figure 2.3.

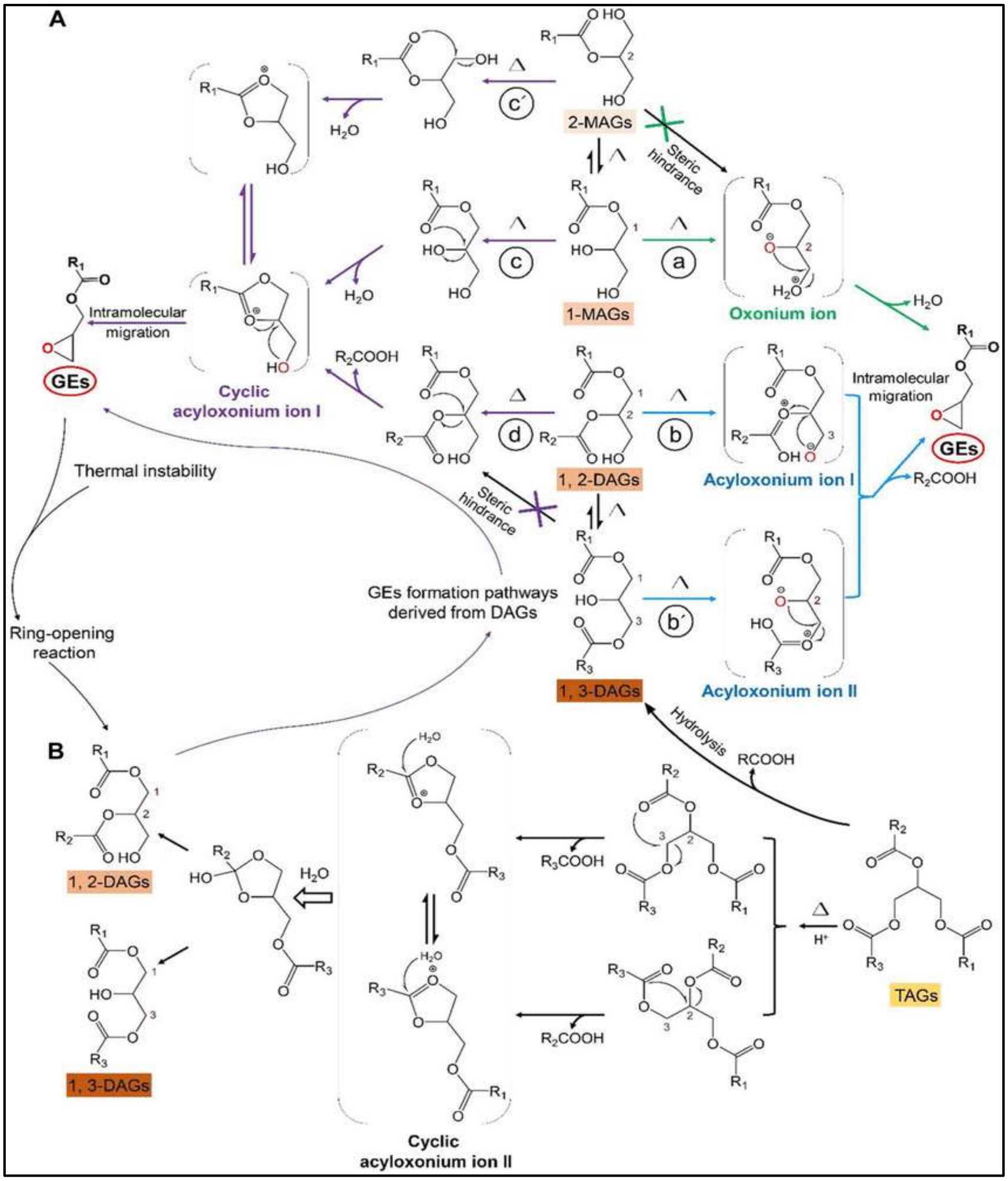

Figure 2.2 Chemistry on the formation pathway of GE with the interaction of MAG and DAG during the CPO refining process (Cheng et al., 2017).

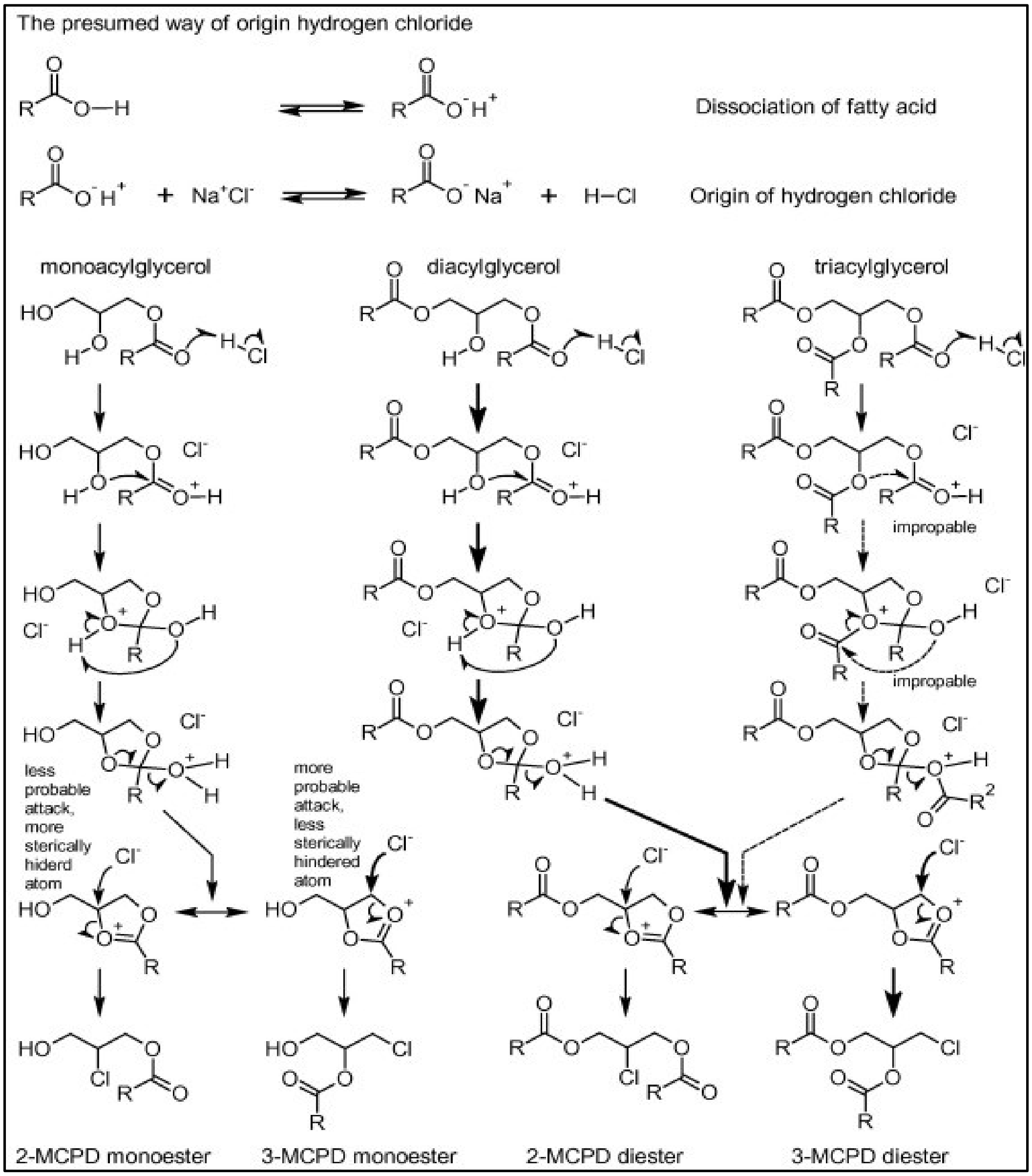

Figure 2.3 Chemistry on the formation of methyl esters under the CPO refining process (Šmidrkal et al., 2016).

Although the formation of 3-MCPD and GE in palm oil occurred during the deodorisation process, due to the high-temperature operation, an effective degumming process of the palm may minimise 3-MCPD and GE formation during the deodorisation process (Sim et al., 2020; Zulkurnain et al., 2012). Usually, the crude palm oil extract from oil palm fruits contains phospholipid by about 0.5 to 2 wt.% (Hoe et al., 2020).

Without the degumming of CPO, the phospholipids may present in the palm oil and interfere with the oil stability and undue darkening during the deodorisation process.

2.4.4 Process of Refining

The proper refining process is essential to produce a finished product that of high quality with a specified quality range and meets the users' requirements (Chompoo et al., 2019). There are two approaches to the refining process: chemical refining and physical refining (Destaillats et al., 2012). The main distinction between these approaches is the method by which the free fatty acids (FFAs) are eliminated. FFAs are eliminated during the deodorisation process for physical refining, and the operating conditions for the elimination of acids are chosen carefully (Destaillats et al., 2012). For chemical refining, the alkali neutralisation step will clean the oil from the gums and FFAs by forming soap stocks. Besides that, physical refining is different from chemical refining in terms of the unit operations involved, as the acid neutralisation step is excluded in physical refining (Gibon et al., 2007).

The chemical refining process imposes disadvantages such as high energy consumption, high expenses of equipment, the generation of large amounts of polluting environmental effluents, tedious and the losing of neutral triacylglycerols (Gibon et al., 2007). Consequently, the physical refining process is suggested (Mba et al., 2015). Moreover, over 95% of crude palm oil undergoes a physical refining process in Malaysia instead of chemical refining (Gibon et al., 2007). Palm oil refining's primary unit operations are displayed in Figure 2.4, and it shows the steps needed for both chemical refining and physical refining.

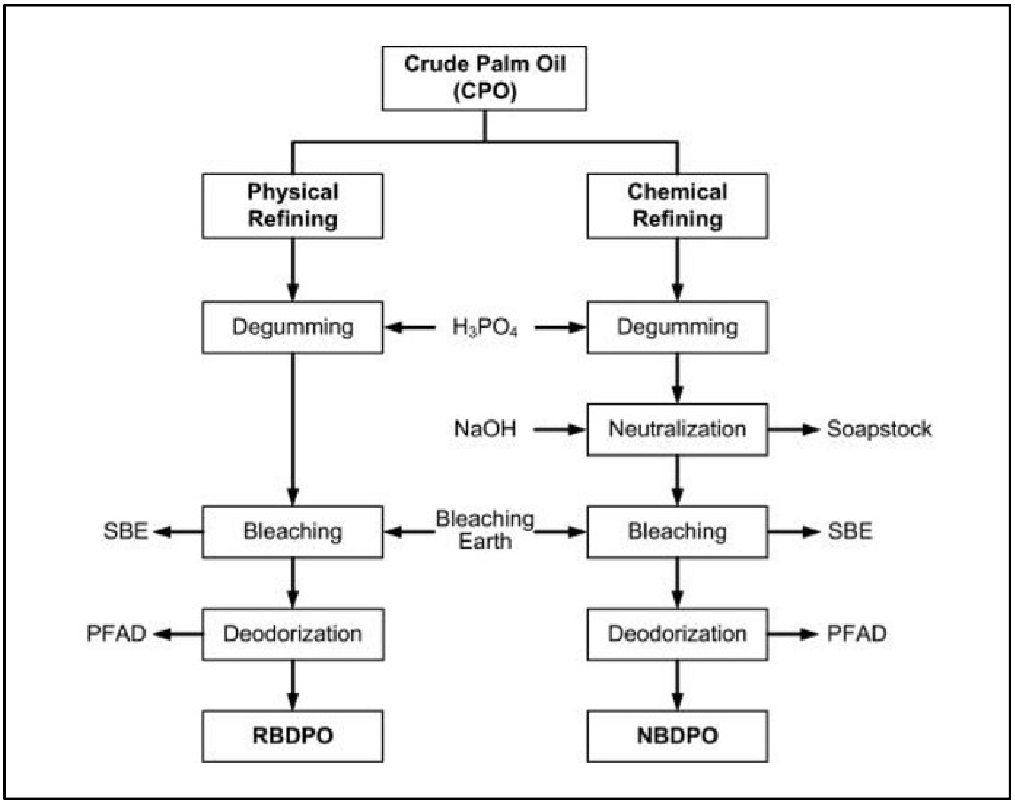

Figure 2.4 Palm Oil Refining Process (Haslenda & Jamaludin, 2011)

2.4.5 Physical Refining

The physical refinery process consists of three major processes: degumming, bleaching and deodorisation (Zulkurnain et al., 2012). Generally, the degumming process is needed to eliminate the gum contained in the oil, also known as phosphatides which cannot be removed if it is not undergoing acid treatment (Ramli et al., 2011). The presence of phosphatides in the oil's finished product will give rapid colour reversion and low heat stability. The bleaching process is needed to extract the colour pigments, protein degradation, metal traces, and catalyst after the hydrogenation process. The last unit process is the deodorisation process (Zulkurnain et al., 2012). It is needed to eliminate the volatile components or the impurities that cause odour and off-flavour using steam distillation. Figure 2.5 shows the steps involved in the physical refining process of crude palm oil.

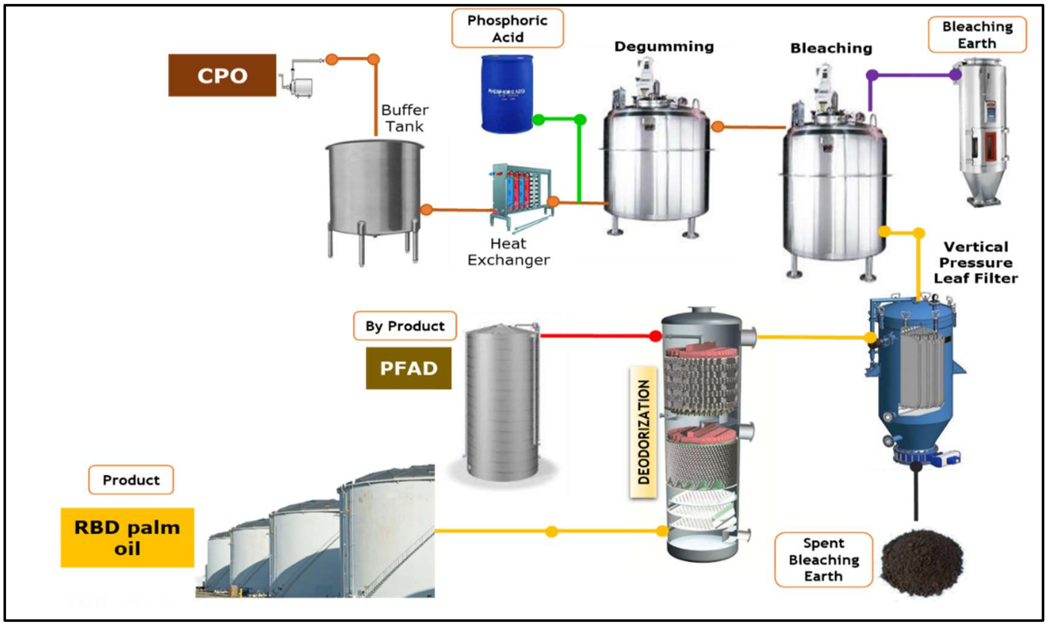

Figure 2.5 Flowchart for the physical refining of crude palm oil (Gibon et al., 2007)

The physical refining process is preferable instead of the chemical refining process to prevent an excessive loss of neutral oil (Silva, 2013). Besides that, the quantity of refined palm oil produced from the physical refining process is more than the amount of chemically refined palm oil generated (Gee, 2007). The physical refining process brings substantial advantages: the higher yield of oil, minimising the usage of chemicals, and thus lowering the negative impact on the environment (Gibon et al., 2007).

2.4.6 Chemical Refining

The final product generated in a chemical refining process is neutralised, bleached, and deodorised (NBD) palm oil (Mat Dian et al., 2015). The crude palm oil (CPO) will first undergo a degumming process, employing phosphoric acid to eliminate phospholipids from the CPO (Mat Dian et al., 2015). The excess phospholipids from the degumming process and free fatty acids (FFAs) will be removed during the neutralisation process. These are accomplished by reacting aqueous sodium hydroxide (NaOH) and palm oil (Mat Dian et al., 2015). Neutralisation transforms the phospholipids and FFAs into insoluble soaps, and these soaps will be separated through centrifugation (Mat Dian et al., 2015).

The bleaching process is conducted under a vacuum, and it utilises activated bleaching earth to eliminate colouring pigments, oxidative products, trace metal ions and excess soaps left after the neutralisation process (Lau et al., 2007). Using a filter press, the spent bleaching earth (SBE) produced from the bleaching process is removed from the bleached CPO. After that, CPO will undergo a deodorisation process, and this process is a steam distillation carried out under vacuum pressure. The deodorisation process removes the FFAs, volatile components and impurities completely (Haslenda & Jamaludin, 2011).

Compared to physical refining, chemical refining is not preferable as alkaline neutralisation will cause a massive loss of neutral oil in the form of soap (Gibon et al., 2007). The neutralisation process uses NaOH to remove the FFAs soap form in chemical refining. The soap is insoluble in water and will stay suspended in the aqueous phase. The hydrophobic and hydrophilic regions of the soap make it act as a good emulsifier. Consequently, the soap micelle, together with the trapped neutral oil, enters the aqueous phase, and this causes the losses of a substantial amount of oil. Hence, a massive amount of neutral oil will be lost if the CPO contains high FFA contents (Chumsantea et al., 2012).

2.5 Degumming

The crude palm oil initially contains phospholipid by about 1000 to 2000 ppm. Hence, this process eliminates the coagulated phospholipid from the gum-conditioned oil. Without the acid treatment, the gum materials will remain in the final product, and it will give rapid colour reversion and low heat stability of oil (Goh et al., 1982). The phospholipid molecules in oils consist of two forms, which is the hydratable phospholipid and non-hydratable phospholipid (Goh et al., 1982). It needs to be treated with acid to convert the non-hydratable phospholipid into hydrated forms. On the other hand, the hydratable phospholipid can be converted directly into hydrated forms by using water (Dumont & Narine, 2007). The reason phospholipid needs to be removed from the gums is because its presence can impact the oil's flavour and shelf life. To remove it easily during the bleaching process is by coagulating phospholipid and making it in an insoluble form (Rohani, 2006).

Crude palm oils include various amounts of impurities such as free fatty acid (FFA), gums or phospholipids, colour pigments, sterols, tocopherols, and traces of metals (Vintila et al., 2009). Phospholipids could increase refining losses. Besides that, they act as pro-oxidants that carry associated metal (Gunstone, 2004). Hence, degumming should be carried out as soon as possible where it removes completely of total oil phospholipids. Usually, crude oil contains up to 1200 ppm phosphorus, which equals three per cent of phospholipids. This level would decrease to 20-50 ppm after the degumming process (Gunstone, 2004). According to Gunstone (2004), the most common phospholipids found in crude oil are phosphatidic acids in which phosphoric acid react with hydroxyl compound. These are the name of phospholipids classes usually present in palm oil, shown in Table 2.4 and Figure 2.6.

Table 2.4 The major glycerophospholipids (Gunstone, 2004)

No.	Glycerophospholipids
1	Phosphatidic acids
2	Phosphatidylcholines
3	Phosphatidylethanolamines
4	Phosphatidylinositol

One of the characteristics of phospholipids is that they tend to form hydrates once in contact with water and then become less soluble in oil. Phosphatidylcholines (PC) and Phosphatidylinositol (PI) hydrate faster than Phosphatidic acids (PA) and Phosphatidylethanolamines (PE). This is because PA and PE react with water slowly (Gibon, 2012). These processes can be operated using two ways which are chemical refining and physical refining. The route depends on the content level of phospholipids (Gibon, 2012). For crude palm and palm kernel oils with low phosphatides content, physical refining is more preferred (Gibon, 2012). There are a few different types of degumming routes practised in vegetable oil refining industries: dry degumming, acid degumming, EDTA degumming and etc. (Deffense, 2009). Following figure 2.7 details of different degumming routes practised in the industries.

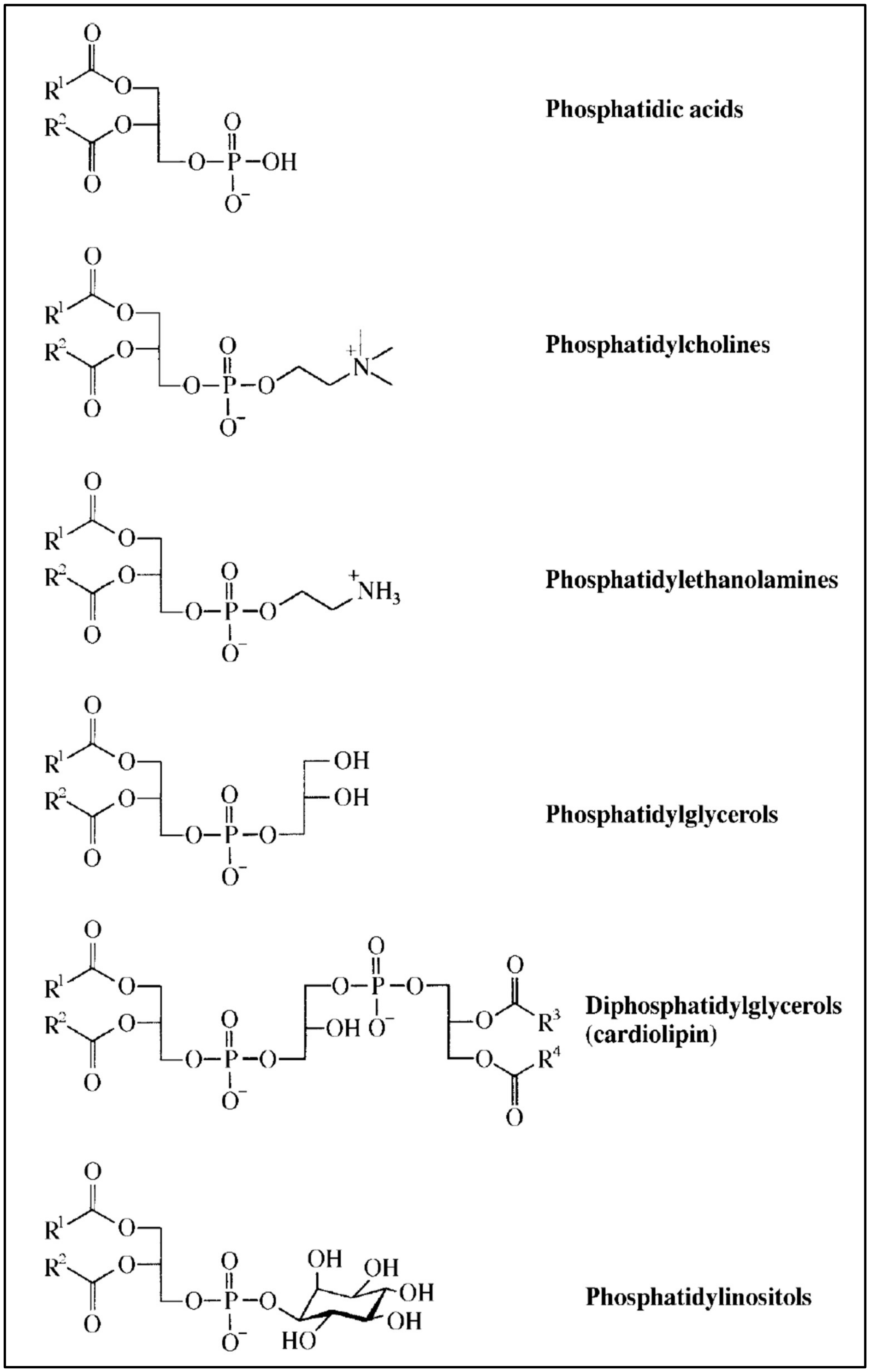

Figure 2.6 Structures of the major phospholipids (Gunstone, 2004)

The degumming processing parameters defers from different types of crude oils. The details of degumming processing parameters are defined by the characteristic of the phospholipids and other non-hydratable compounds present in the crude oils (Paisan et al., 2017). Following Figure 2.6 shows a different type of crude oils degumming processing parameters.

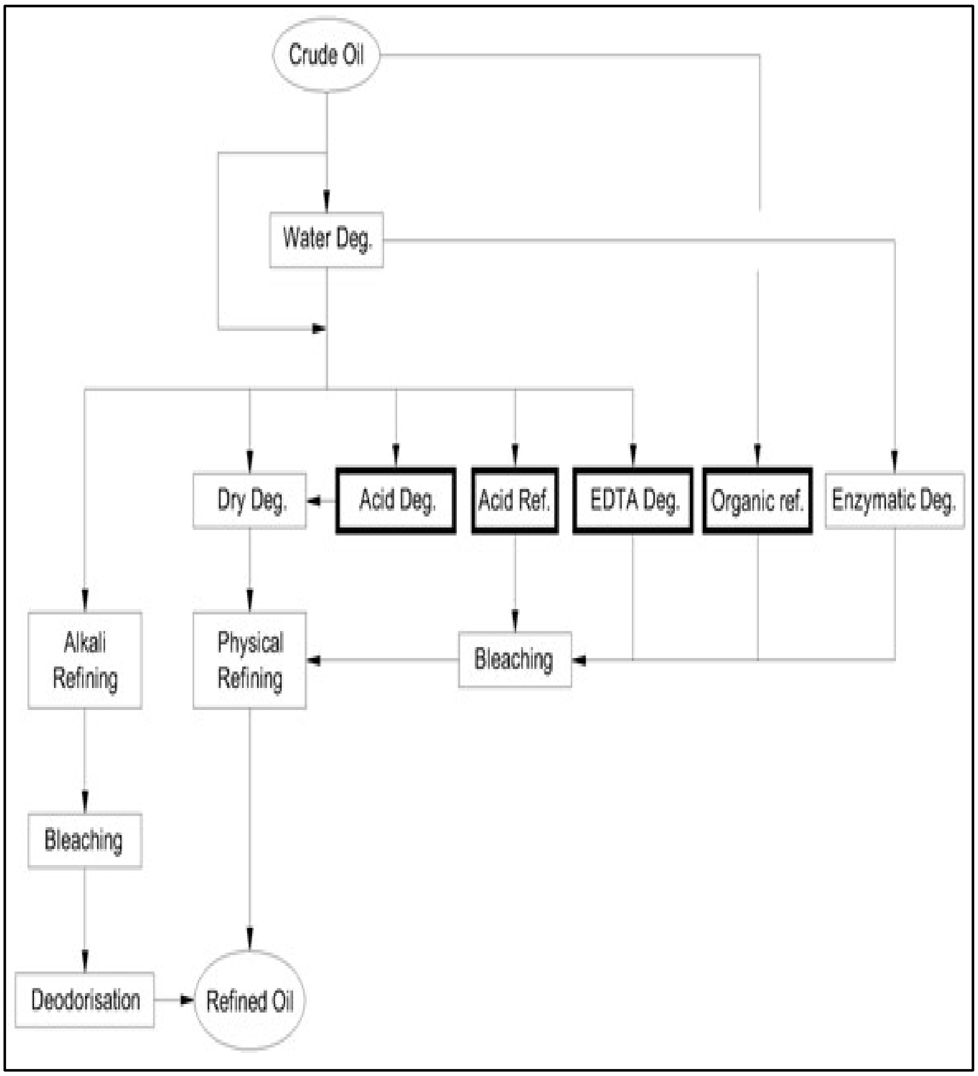

Figure 2.7 Overview of different degumming routes in refining process (Deffense, 2009).

Table 2.5 Various degumming processes applied in vegetable oil processing.

Type of Crude Oils	Degumming process	Parameters	References
Algal Oil	Water Degumming	100 °C; 30 min; 80% water	(Paisan et al., 2017)
Algal Oil	Acid Degumming	90 °C; 60 min; 0.42% phosphoric acid	(Paisan et al., 2017)
Soybean Oil	Enzymatic Degumming	40 °C; pH 4.7; phospholipase dosage 500 U/kg	(Jiang et al., 2011)
Rapeseed Oil	TOP Degumming	80 °C; 60 min; 2% Water; 0.14% phosphoric acid; 0.3% NaOH	(Zufarov et al., 2008)
Sunflower Oil	TOP Degumming	80 °C; 60 min; 2% Water; 0.14% phosphoric acid; 0.3% NaOH	(Zufarov et al., 2008)

2.5.1 Acid Degumming

Acid degumming is mainly used for crude palm oils with a higher quantity of non-hydratable phospholipid and iron contents. The addition of a strong acid can obtain this prior to hydration. Phosphoric acid is dosed at a rate of 0.05-0.2% into hot crude oil at 80-90°C (Rohani, 2006). This is to precipitate the phospholipids. The reaction between acids and non-hydratable phospholipids in the degummed oil results in the formation of hydratable phospholipids, which is readily removed by a centrifugal separator (Mei et al., 2013). As a result, the light phase contains 500-1000mg/kg of soap and moisture, whereas the heavy phase is insoluble impurities, gums, phospholipids, excess alkali, and oil loss through emulsification. It is unavoidable that a slight oil loss through saponification occurs as an excess alkali is used (Paisan et al., 2017).

The acid degumming process treats and disrupts the non-hydratable phospholipid as the phosphoric acid decomposes calcium and magnesium complexes.