DEACIDIFICATION OF CRUDE PALM OIL USING SOLVENT EXTRACTION INTEGRATED WITH MEMBRANE TECHNOLOGY

By

HENG SZE LU

A dissertation submitted to the Department of Chemical Engineering,
Lee Kong Chian Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman,
in partial fulfillment of the requirements for the degree of
Master of Engineering Science
December 2021

Specially dedicated
To my beloved husband, Boon Yap,
The wonderful people who I've ever met.

ABSTRACT

DEACIDIFICATION OF CRUDE PALM OIL USING SOLVENT EXTRACTION INTEGRATED WITH MEMBRANE TECHNOLOGY

Heng Sze Lu

Massive usage of chemicals and production of palm oil mill effluent (POME) of conventional deacidification, small difference in molecular weight between triacylglycerol and free fatty acid (FFA) as well as the state of crude palm oil (CPO) as semi-solid at room temperature make the membrane technology separation process unfavorable in CPO refining process. Therefore, this study was aimed to integrate solvent extraction and membrane technology to extract FFA from CPO with the benefit of solvent recovery. Different solvents including acetone, ethanol, hexane, methanol and propanol were used to extract palmitic acid from synthetic acidified palm oil. Then, palmitic acid and ethanol in synthetic extractant were separated via either pressurization or pervaporation membrane technology using five selected commercially available membrane including three polydimethyl siloxane (PDMS) with silicone based supported solvent resistant nanofiltration (SRNF) membranes (NF010206, NF030306 and NF030705), cellulose triacetate non-woven support forward osmosis (FO) membrane (CTA-NW), and polyamide thin-film composite reverse osmosis (RO) membrane (SW30XLE). The selected membranes underwent a series of characterization studies including scanning electron microscope (SEM), hydrophobicity, flux stability and flux recovery. The effects of different pressures and vacuum conditions on permeate flux and selectivity at 25 °C were investigated. In this study, pure ethanol was found to be the most effective solvent. It successfully reduced palmitic acid up to 81.28 ± 1.01% (mean ± standard deviation) at 55 °C with a synthetic acidified palm oil to pure ethanol mass ratio of 1: 4. It was found that the addition of water did not help to improve the palmitic acid extraction and the best equilibrium constant for ethanol extraction was found at 55 °C with the greatest oil extraction capacity. Hydrophobic membrane exhibited the highest permeate flux, but low palmitic acid rejection, whereas hydrophilic membrane was not suitable for CPO refining process with low permeate flux and low palmitic acid rejection. Surprisingly, SW30XLE with hydrophilic top layer and hydrophobic separation layer demonstrated a permeate flux of 36.88 L/m^{2}h and a rejection percentage of 100% in the pressurization membrane system, implying its potential for CPO refining process. However, the membrane pervaporation system showed a very low permeate flux (1.28 L/ m^{2}h) in most of the selected membranes which may be unfavorable for industrial usage. Therefore, further research is required to identify solvent with higher extraction ability, and membrane with higher permeation and selectivity for the integrated solvent extraction with membrane technology as an economically and environmentally friendly CPO deacidification method, followed by solvent recovery to produce high quality edible oil.

ACKNOWLEDGEMENTS

I would like to thank everyone who had contributed to the successful completion of this project. I would like to express my gratitude to my dearest research supervisor, Dr Lai Soon Onn and co-supervisor, Dr Wong Kam Huei for their invaluable advice, guidance and enormous patience throughout the development of the research.

Thousand thanks to Dr. Lau Woei Jye from Advanced Membrane Technology Research Centre (AMTEC) Universiti Teknologi Malaysia (UTM) and Dr Ong Chi Xiang from SEGi University for their guidance and advice. Nevertheless, my deep appreciation to laboratory staffs from UTAR, UTM and SEGi for their unknowing, yet remarkable contribution to this research.

In addition, I would also like to express my gratitude to my loving parent and friends who had helped and given me encouragement. Especially my wonderful husband, Tan Boon Yap who given me his full support and love.

APPROVAL SHEET

This dissertation entitled “**DEACIDIFICATION OF CRUDE PALM OIL USING SOLVENT EXTRACTION INTEGRATED WITH MEMBRANE TECHNOLOGY”** was prepared by HENG SZE LU and submitted as partial fulfillment of the requirements for the degree of Master of Engineering Science at Universiti Tunku Abdul Rahman.

Approved by:

(DR. LAI SOON ONN)
Date: 24/12/2021
Supervisor
Department of Chemical Engineering
Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

KAMHUEI
(DR. WONG KAM HUEI)
Date: 24/12/2021
Co-supervisor
Department of Chemical Engineering
Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

LEE KONG CHIAN FACULTY OF ENGINEERING AND SCIENCE

UNIVERSITI TUNKU ABDUL RAHMAN

Date: 24/12/2021

SUBMISSION OF DISSERTATION

It is hereby certified that ***Heng Sze Lu*** (ID No: ***13UEM01872***) has completed this dissertation entitled "*Deacidification Of Crude Palm Oil Using Solvent Extraction Integrated With Membrane Technology*" under the supervision of Dr. Lai Soon Onn (Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, and Dr. Wong Kam Huei (Co-Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science.

I understand that University will upload softcopy of my dissertation in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

Yours truly,

(*Heng Sze Lu*)

DECLARATION

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

Name HENG SZE LU

Date 22/12/2021

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

LIST OF SYMBOLS

K	Equilibrium constant
A	Effective filtration area, m^2
C_f	Concentration of palmitic acid in feed
C_p	Concentration of palmitic acid in permeate
J_{EtOH1}	Permeate flux for ethanol before fouling test, L/m^2h
J_{EtOH2}	Permeate flux for ethanol after washing, L/m^2h
J_{PA}	Permeate flux for palmitic acid, L/m^2h
M	Weight
Mw	Molecular weight
N	Normality
PA	Percentage of palmitic acid
PA_i	Palmitic acid concentration in synthetic acidified palm oil
PA_r	Palmitic acid concentration in raffinate phase
R	Rejection
V	Volume
V_{EtOH1}	Volume of the permeate for pure ethanol, L
V_{PA}	Volume of permeate for synthetic extractant, L
ΔT	Recorded time, hour

LIST OF ABBREVIATIONS

CPO	Crude palm oil
CTA-NW	Cellulose triacetate non-woven
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FID	Flame ionization detector
FO	Forward osmosis
GA	Glutaraldehyde
GC	Gas chromatography
GNI	Gross national income
IPA	Isopropanol
IPA	Isopropanol
KOH	Potassium hydroxide
MWCO	Molecular weight cut-off
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance
NF	Nanofiltration
PDMS	Polydimethyl siloxane
PEBAX	Poly (amide-b-ether)
PEI	Poly-etherimide
PFAD	Palm fatty acid distillate
PORMI	4, 4’-oxydiphenylene pyromellitimide
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene difluoride
RBO	Rice bran oil
RO	Reverse osmosis
SEM	Scanning electron microscope
SRNF	Solvent resistant nanofiltration
TFC	Thin- film composite
TG	Triglyceride

LIST OF APPENDICES

INTRODUCTION

1.1 Research Background

Crude palm oil (CPO) needs to further undergo a downstream process called refining to convert it into a better quality edible oil by removing the undesirable compounds such as free fatty acid (FFA). The oil and fats industry are equipped with mature and experienced technology in the refinery operation. However, the development of global health and environmental awareness urges the industry to develop more an environmentally friendly and an economical approach in the refinery operation using greener process and lesser energy as well as renewable resources (Shahidi, 2005).

Of all the refinery operations, deacidification has been known as the most critical and difficult step (Rodrigues et al., 2007). This step is mandatory to remove the FFA in order to produce favorable and quality edible oil. Besides greatly affecting economic feasibility of the refinery, deacidification brings abundant environmental impacts as well. The presence of FFA can lead to huge loss of oil during the refining process and result in the difficulty in the removal of other impurities in the following refinery operation. Moreover, it also drives to high loss of nutrients, high consumption of energy, water and non-reusable chemicals and generation of heavily polluted wastewater (Bhosle & Subramanian, 2005; Rodrigues et al., 2007).

The combination of solvent extraction and membrane technology deacidification is a remarkably simple and low-cost approach. This integrated approach can be implemented at ambient temperature which requires low consumption of energy and at the same time preserves desirable heat-sensitive components in oil. This approach also eliminates the need of wastewater treatment which is the major concern in conventional refinery operation. Hence, this suggested approach is believed to be a cleaner process with renewable resources in refinery industry (Shahidi, 2005).

1.2 Problem Statement

Conventional deacidification method involves massive volume of chemicals, high consumption of energy and huge amounts of waste generated but providing low oil yield. Many approaches have been conducted to overcome the drawbacks in the removal of FFA from oil, such as solvent extraction. However, several studies have shown some limitations of this approach including usage of hazardous and inappropriate solvent, such as hexane. Hence, a greener solvent that effectively extracts palmitic acid from palm oil is needed.

Solvent extraction integrated with membrane technology is believed to be the new promising approach for CPO deacidification. To date, numerous studies of oil refining using membrane technology have been accomplished based on the commercially existing membranes which are fabricated for other membrane processing purposes. These membranes are produced with large molecular weight cut off (MWCO) which are unable to achieve high permeate flux and selectivity. Therefore, finding a membrane with better performance for palmitic acid extraction from synthetic extractant is still an on-going work.

Other than filtration, pervaporation has become a feasible membrane separation technology for different aspect of applications. Still, there are not many studies focusing on integration of solvent extraction with membrane technology for CPO deacidification. Due to its great potential, an in-depth study is required for pervaporation to be commercially feasible in the oil and fats industry, and to be compared with filtration.

1.3 Aim and Objectives

The aim of this research project is to develop an environmentally and economically friendly deacidification method using solvent extraction integrated with membrane-based technology. The objectives of this study include:

1. To determine greener solvent that effectively extracts palmitic acid from synthetic acidified palm oil.
2. To investigate the performance of selected membranes in terms of permeate flux and membrane fouling for palmitic acid extraction from synthetic extractant.

3. To evaluate the performance of filtration and pervaporation systems on palmitic acid extraction from synthetic extractant in terms of membranes permeate flux and palmitic acid rejection percentage.

1.4 Scope of Study

In this study, palmitic acid was used to represent the FFA that is present in unrefined palm oil as it is the major FFA component found in CPO. Synthetic acidified palm oil was prepared by dissolving 5.0% w/v of palmitic acid into food-grade refined palm oil purchased from the local market. On the other hand, synthetic extractant was prepared by dissolving 3.0% w/v of palmitic acid into pure ethanol.

The selected solvents included acetone, ethanol, hexane, methanol and isopropanol (IPA). Only the solvent that exhibited the best extraction efficiency of palmitic acid was used for further studies on extraction parameters including mass ratio (solvent to synthetic acidified palm oil), water content and extraction temperature. The most suitable extraction parameters were determined based on the highest palmitic acid extraction efficiency achieved in the most cost-effective way.

Meanwhile, five selected membranes including three polydimethyl siloxane (PDMS) with silicone based supported solvent resistant nanofiltration SRNF membranes, namely NF010206, NF030306 and NF030705, cellulose triacetate non-woven support (CTA-NW) forward osmosis (FO) membrane, and polyamide thin-film composite (TFC) reverse osmosis (RO) membrane SW30XLE were characterized using scanning electron microscope (SEM) and optical tensiometer to investigate the membrane cross-sectional structure and contact angle.

Subsequently, synthetic extractant with approximately 3.0 wt% palmitic acid was treated with membrane based technology using either filtration or pervaporation system to determine permeate flux and palmitic acid rejection percentage in each membrane system. The concentration of palmitic acid in feed and permeation was determined using gas chromatography with flame ionization detector (GC-FID).

In this study, to avoid interference of the extraction and recovery, the solvent extraction and membrane technology were studied separately. In future, the integrated process can be studied in the presence of the impurities by using crude palm oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Oil Palm in Malaysia

Oil palm tree (Elaeis guneensis) originated from West Africa. It was then introduced to Malaysia in the late 1800s and early of 1900s to 1916 as an ornamental plant. Later, it was transformed into plantation development phase in 1917 right until about 1960, followed by the great expansion phase until 1966. The growth in oil palm plantation is illustrated in Figure 2.1. Now, Malaysia is well-known as the world's second biggest palm oil exporter and producer after Indonesia (Abdullah, 2003).

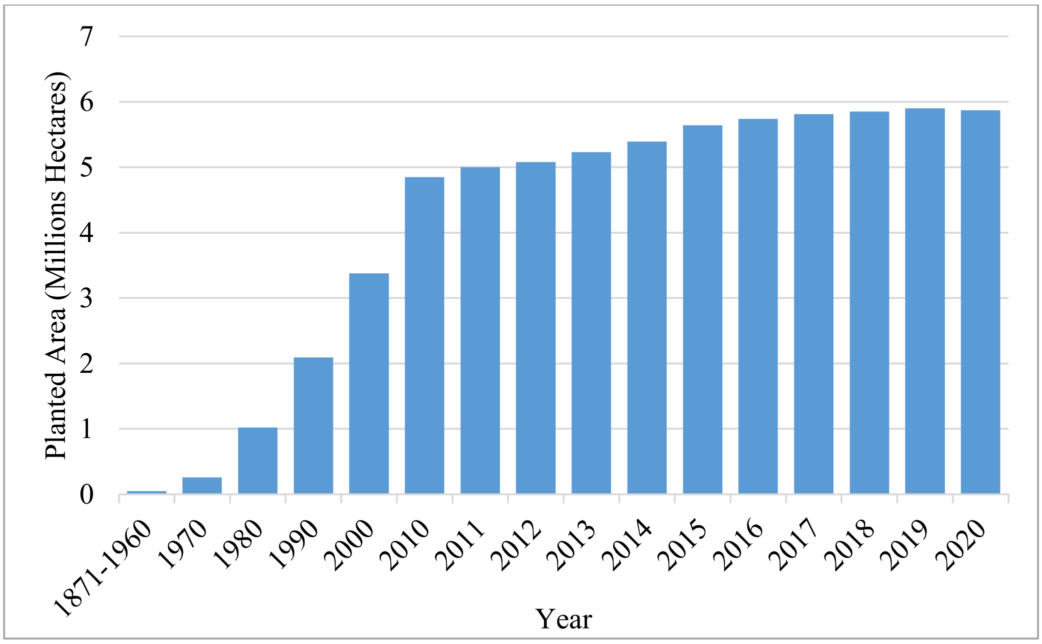


Figure 2.1: Oil Palm Plantation Area in Malaysia (MPOC, 2021)

Palm oil is one of the world's major source of oil and fats which contributes 31.4% from the world's total oil and fats production in 2020 (MPOC, 2021). In Malaysia, the agriculture sector contributes about 12% of gross national income (GNI). Within the agriculture sector, palm oil not only provides high value jobs to Malaysian, but also contributes the highest amount to the GNI. With the palm oil sector alone, it is able to generate 8 percent or over RM80 billion GNI (Rozario, 2013).

2.2 Efficient Oilseed Crop

Among the oilseed crop, oil palm is well-recognized as the most effective oil in the world in 2020 (MPOC, 2020). It is enriched with fruit after 30 months of plantation and continues to produce fruits for the next 20-30 years; thus, providing a continuous supply of oil and fats. Palm oil possesses favorable characteristics over other 17 types of oil and fats cultivated in the world, including higher yield per land area and lower production cost. Among the 4 oilseed crops that have significant share in the production of oils and fats (Figure 2.2), oil palm produced 3.35 tonnes of oil per hectare in a year making it the highest yielding oil crop (MPOC, 2020).

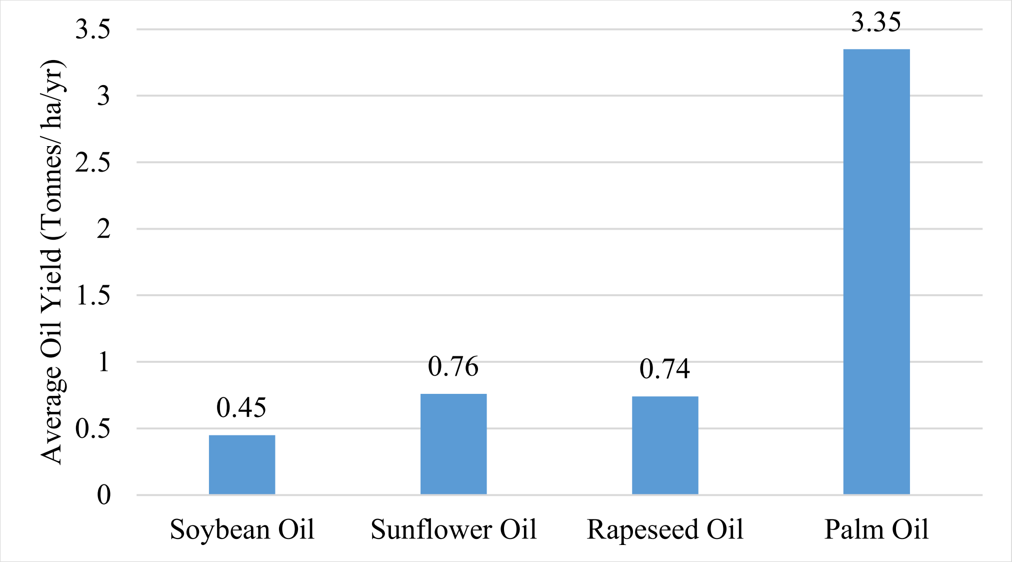


Figure 2.2: Average Palm Oil Yield (Tonnes) Per Hectare of Land in a Year Compared to Other Major Oil Crops (MPOC, 2020)

2.3 Crude Palm Oil (CPO)

Crude palm oil (CPO) is referred to the edible oil extracted from the ripened fleshy mesocarp of oil palm fruit (Figure 2.3). CPO should not be confused with palm kernel oil or coconut oil which have differences in either physical or chemical properties. CPO consists of mostly triacylglycerol and is known as red palm oil due to the abundance of carotenoids. It is also gifted with other health beneficial compounds including antioxidants (tocopherols and tocotrienols), ubiquinone and sterols. CPO appears as semi-solid naturally at ambient temperature owing to its balanced ratio of unsaturated and saturated fatty acid, resulting in high value for a variety of applications. It does not require hydrogenation for food application, making it a better substitute for butter or trans fats (Danielson, 2015).

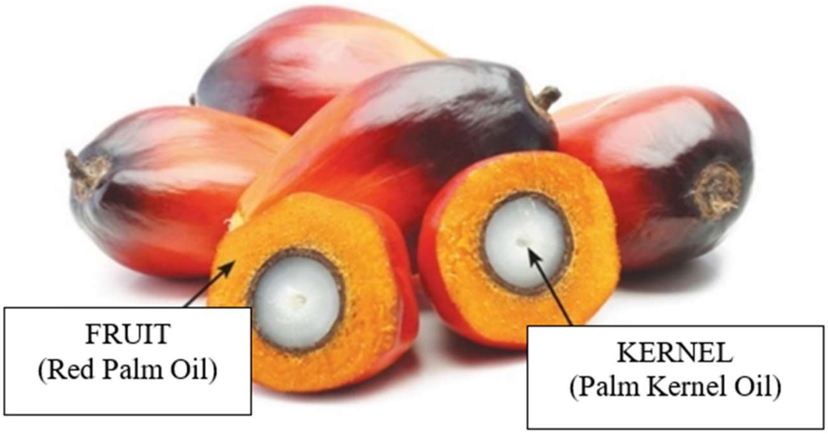


Figure 2.3: Oil Palm Fruit Cross Section (Hashim et al., 2012)

2.4 Free Fatty Acid (FFA) in Palm Oil

Palm oil contains a balanced proportion of saturated and unsaturated fatty acid. CPO predominantly contains 44% of saturated palmitic acid and 40% monounsaturated oleic acid, as well as minor amount of polyunsaturated fatty acids (Danielson, 2015). Table 2.1 lists the major FFA composition in CPO and their molar mass (Mancini et al., 2015).

Table 2.1: The Major FFA Composition of Crude Palm Oil (Mancini et al., 2015)

FFA	Name	Mass (w/w %)	Molar mass
C12:0	Lauric Acid	0.2	200.31
C14:0	Myristic Acid	1.1	228.36
C16:0	Palmitic Acid	44	256.42
C18:0	Stearic Acid	4.5	284.47
C18:1	Oleic Acid	39.2	282.44
C18:2	Linoleic Acid	10.1	280.43
	Other	0.9	NA

Triglyceride (oil) is a molecule that is built up by one glycerol backbone attached with three fatty acids. Figure 2.4 depicts the glyceryl tripalmitate, a simple triglyceride built up by three same fatty acids (palmitic acid) (University of Illinois Archives, 1999). Triglyceride can be easily hydrolyzed into FFA and glycerol either by chemical or enzyme action during harvesting, transportation and extended storage under unfavorable conditions. The hydrolysis process can become serious with the aid of heat and moisture. In a comprehensive hydrolysis, all the three fatty acids of the triglyceride are detached and released as FFA. Diglyceride (glycerol backbone attached to two fatty acids) and monoglyceride (glycerol backbone with only one fatty acid) can also be present in a partial hydrolysis (Shahidi, 2005).

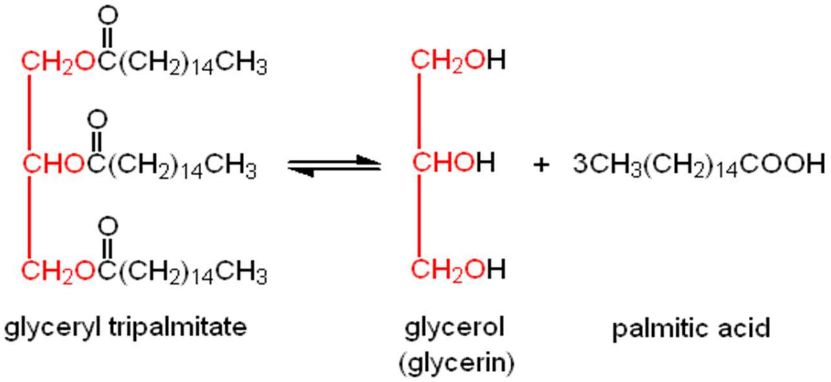


Figure 2.4: Composition of Glyceryl Tripalmitate (University of Illinois Archives, 1999)

FFA has basic structure of a hydrophobic hydrocarbon chain with a hydrophilic carboxylic acid polar head at one end (Figure 2.5). Increase of carbon chain length in FFA increases the melting point of oil. On the other hand, the melting point will be reduced when the number of unsaturated FFA increases. This property can be observed when the FFA forms part of a triglyceride. For example, a long chain saturated FFA (such as palmitic acid) will have a higher melting point than short chain FFA (such as butyric acid) and even some higher chain length unsaturated FFA (such as oleic acid). Thus, palm oil which contains about 44% saturated FFA has a higher melting point compared to other vegetable oil (Siew and Minal, 2007; Hashim et al., 2012).

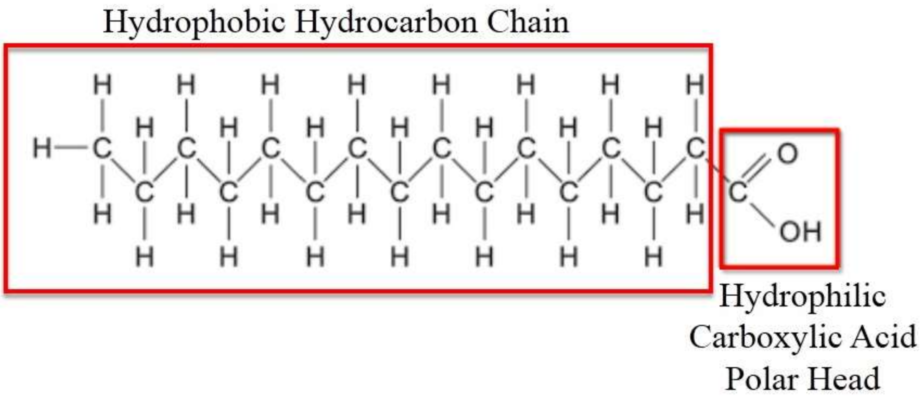


Figure 2.5: Composition of Palmitic Acid (University Of Illinois Archives, 1999)

FFA, a pro-oxidant is one of the major factors to accelerate the oil oxidation and cause deterioration in oil quality and shelf life. During the oil oxidation, undesirable flavor compounds with low molecular weight are generated, causing oil to have unpleasant rancid flavor which is less acceptable or unacceptable to be consumed. Moreover, the oil oxidation also destructs essential FFA and generates toxic compounds and oxidizes polymers that affect the nutritional quality and cause toxicity in edible oil. The natural characteristic with both hydrophobic hydrocarbon chain and hydrophilic carboxylic acid polar head at one end in the same molecule causes FFA to be prone to be accumulated on the uppermost layer of edible oils. This phenomenon tends to reduce the surface tension of edible oil and enhance the oxygen from the headspace diffused into the oil to speed up oil oxidation. The oxidation process becomes worse with the existence of trace metal (Choe and Min, 2006). Hence, it is important to minimize the FFA amount and other undesirable compounds such as trace metals in order to produce a stable and edible oil.

Besides, the existence of FFA in CPO also greatly affects the economic feasibility of the entire refinery process. The presence of FFA can lead to huge loss of oil by emulsification and saponification during the refining process and difficulty in removal of other impurities for the following refinery operation (Rodrigues et al., 2007). In deacidification, caustic soda will be added, leading to saponification. The neutral oil will be entrapped in the soap miscella and removed together with undesired compounds during centrifugation. Total refining loss is usually equal to the amount of FFA in the oil (Cheryan, 2005; Chunmsantea et al., 2012). Besides, the removal of FFA leads to high loss of nutrients, high consumption of energy, water and non-reusable chemicals and the creation of heavily polluted wastewater (Rodrigues et al., 2007).

2.5 Crude Palm Oil Refinery

CPO contains a small quantity but different amounts of undesirable compounds and impurities such as FFA, mono- and diacylglycerols, phospholipids or gum, trace metals, oxidation products, and odoriferous substances (Bhosle and Subramanian, 2005; Shahidi, 2005; Mba et al., 2015). Table 2.2 shows the minor undesired compounds and impurities present in CPO and their effects on the taste, color, odor and appearance on the oil (Čmolík and Pokorný, 2000). Thus, there is a need to undergo downstream process called refining to convert CPO into a stable and quality edible oil by removing the undesirable compounds.

Table 2.2: Typical Representatives and Deterioting Effect of Minor Undesired Compounds and Impurities in CPO (Čmolík and Pokorný, 2000)

Minor Undesired Compounds and Impurities	Typical Representatives	Deteriorating Effect
Oxidation products	Volatile aldehydes, ketones, hydrocarbons	Off-flavors
Free fatty acids	Saturated and unsaturated fatty acids	Degrade oxidative stability, impaired functional properties
Phospholipids		Degrade oxidative stability
Pigments	Chlorophylls, carotenoids, myoglobin	Degrade sensory properties
Metal salts	Iron and copper compounds	Degrade oxidative stability

CPO refinery includes operation of degumming, deacidification, bleaching and deodorization (Kale et al., 1999). Table 2.3 shows the refining operation and targeted impurities (Shahidi, 2005; Mba et al., 2015). The different impurities are fully or partially removed at different refining stages. During the CPO refinery, undesirable compounds and impurities must be diminished, if not entirely eliminated, to convert the CPO into a desirable and quality edible commodity (Azmi et al., 2015).

Table 2.3: Refining Operation and Targeted Impurities (Shahidi, 2005; Mba et al., 2015)

Refining Operation	Targeted Impurity
Degumming	Phospholipids; other polar lipids (gums)
Deacidification	Free fatty acids; residual phospholipids; metals
Bleaching	Pigments; residual soaps; oxidation products
Deodorization	Odoriferous and destabilizing impurities

Of all the undesirable compounds and impurities mentioned, deacidification, which is the removal of FFA, is the most delicate and critical stage in the refinery operation. It has the great economic impact on the CPO refining processing and determines the quality of the final oil products. Ineffectiveness in this stage will result in a huge loss of oil and off-quality of final products (Bhosle and Subramanian, 2005; Rodrigues et al., 2007). On the other hand, the health beneficial compounds should be retained as they prevent the oil from oxidation and function as a natural source of Vitamin E (Azmi et al., 2015).

2.6 Conventional Deacidification Method

Conventional deacidification process shows significant drawbacks such as massive neutral oil and nutrition loss, large quantity of water and chemical usage, huge heavily polluted wastewater generation, high energy consumption and operation cost as well as greater risk of explosion.

The usage of bleaching earth under vacuum to remove coloring compounds as well as to absorb and remove metal ions causes severe impact on environment, such as residual fat that may pollute water underground, as well as pose a fire hazard (Gonçalves et al., 2007). Spent bleaching earth clay is not recyclable and usually contains 30% to 40% oil by weight and is commonly disposed by landfill without any further treatment. In 2010, Malaysia alone has generated about 179 thousand of spent bleaching earth clay from the production of 17 million tonnes of palm oil (Wafti et al., 2017).

Conventional deacidification method can be classified into chemical deacidification and physical deacidification (Kale et al., 1999). Figure 2.6 illustrates the flow diagram of physical and chemical deacidification of CPO.

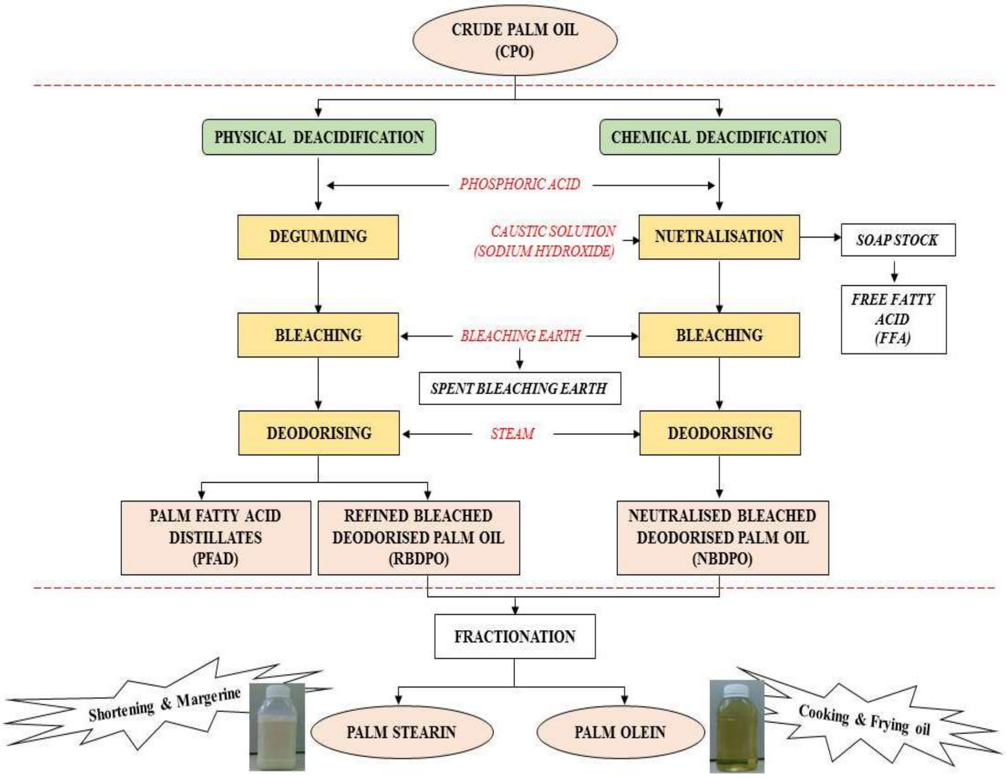


Figure 2.6: Flow Diagram of Physical and Chemical Deacidification of CPO (Kale et al., 1999)

2.6.1 Chemical Deacidification

Figure 2.7 presents the flow diagram of chemical deacidification of CPO. This method is accomplished using a large quantity of chemicals which include sodium hydroxide (NaOH) to neutralize FFA and then precipitate them as soap stock, which the latter is then followed by centrifugation to remove neutral oil (Shahidi, 2005; Mariano et al., 2011).

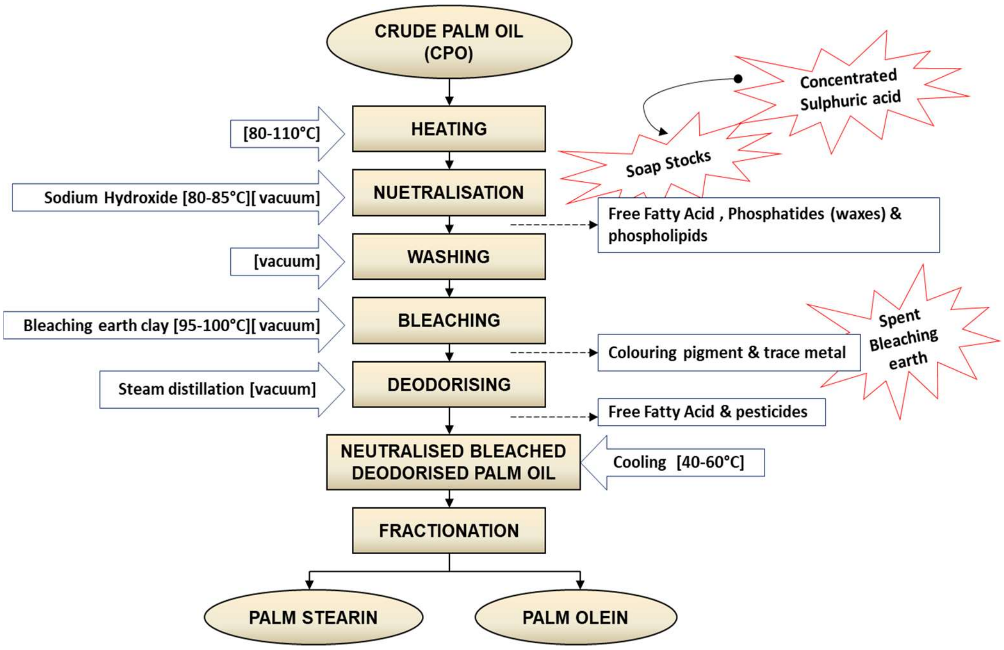


Figure 2.7: Flow Diagram of Chemical Deacidification of CPO (Shahidi, 2005; Mariano et al., 2011)

Chemical deacidification results in oil loss attributed to emulsification in soap stock. There is almost 50% of crude oil weight of neutral oil found in soap stock which leads to a reduced yield of refined oil. The neutral oil loss is proportional to the FFA amount in the raw crude oil. For the crude oil with high FFA amount such as rice bran oil (RBO), the refined oil yield will be very low (Bhosle & Subramanian, 2005). Chemical deacidification also generates large amounts of heavily polluted wastewater and soap-stock which needs further treatment process for waste discharge that meets the statutory requirements. This treatment process requires large quantities of water, energy and chemicals, leading to serious environmental pollution (Gonçalves et al., 2016). However, chemical deacidification is still applied widely in numerous industries considering the reduction of power in FFA down to the acceptable level in refined oil to produce acceptable quality oil. It is suitable for most of the crude oil and is especially applied on heat sensitive oil such as cottonseed oil.

2.6.2 Physical Deacidification

Figure 2.8 depicts the flow diagram of physical deacidification of CPO based on the volatility difference of FFA and oil. During the process, volatile compounds including FFA are volatilized at high temperatures and low pressure, while neutral oil is subjected in the stream of the stripping steam. FFA has shorter hydrocarbon chains compared to triacylglycerol, and thus it has higher volatility and can be easily refined by superheated steam. For oil with high acidity and better resistance to high temperature like crude palm oil, physical deacidification is most recommended, and therefore it is most adopted in the Malaysian oil refinery.

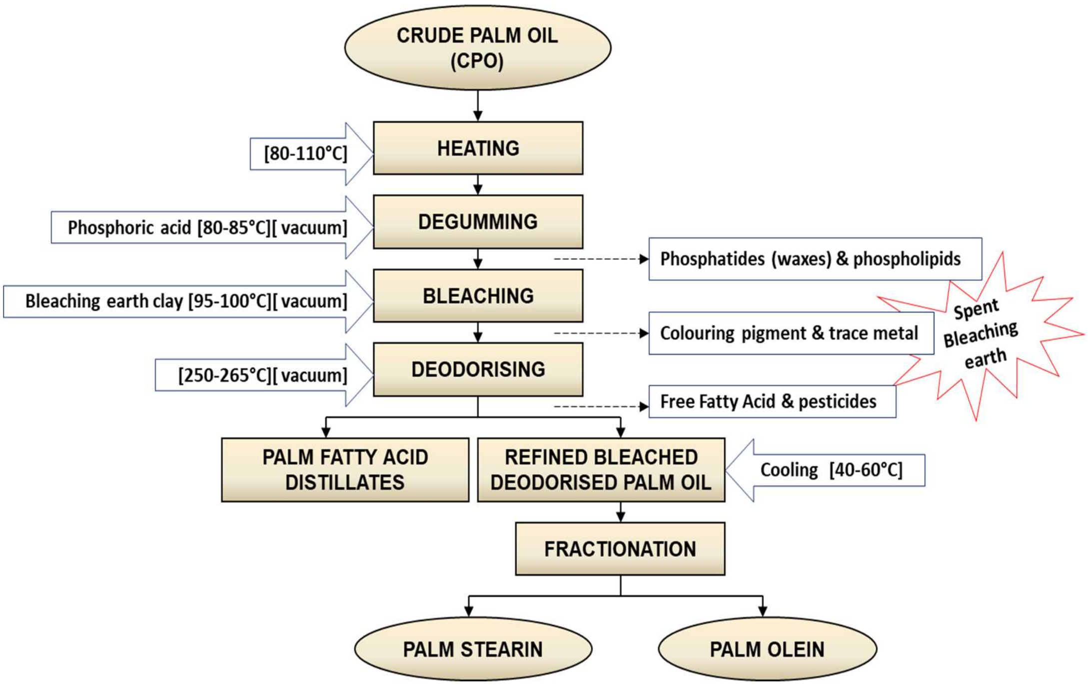


Figure 2.8: Flow Diagram of Physical Deacidification of CPO (Shahidi, 2005; Mariano et al., 2011)

Physical deacidification possesses many advantages compared to chemical deacidification. These advantages include low operating cost, high efficiency and oil recovery, low capital and operating cost, generation of less sewage as well as elimination of soap stock generation as the application does not use neutralizing chemical such as sodium hydroxide (Wafti et al., 2017). However, the pretreatment requirements are very stringent and will greatly affect the following deacidification process.

High temperature and vacuum treatment used in physical deacidification not only drives to hydrolytic, oxidative, polymerization alterations and formation of side reaction compounds (trans isomer) that affect the oil production, but also causes safety issues, such as high risk of explosion. It also drives to the great losses of nutraceutical compounds such as carotenoids in palm oil (Gonçalves et al., 2007). In physical deacidification, carotenoids, tocopherols and oryzanol concentrations are greatly reduced to half as they are entirely destroyed due to the extreme processing condition with heat and pressure. It is not suitable for heat sensitive oil such as cottonseed oil and the iron content of oil subject to the treatment must be lower than 0.2 ppm to prevent darkening of oil during the treatment (Bhosle & Subramanian, 2005; Rossi et al., 2001).

2.7 New Approach of Deacidification

Deacidification using conventional methods always lead to the losses of oils and nutrient. Furthermore, chemical deacidification process requires additional time and money on disposal and the use of soap stock creates secondary environmental contamination. Nevertheless, effective pre-treatment is very crucial in physical deacidification to produce acceptable quality edible oil. Besides, ineffectively pretreated crude oil has to be further treated with massive bleaching earth which creates additional environmental pollution issue (Bhosle & Subramanian, 2005). The quality of both chemically and physically refined edible oil is close to each other, but physical deacidification possesses smaller neutral oil loss and environmental impacts (Cmolík & Pokorny, 2000). Table 2.4 summarizes the features and drawbacks of conventional deacidification methods.

Table 2.4: Features and Limitations of Conventional Deacidification Methods (Bhosle and Subramanian, 2005)

Approaches	Features	Limitations
Chemical deacidification	- Generates desirable quality oil from crude oil. - Contains multiple effects in crude oil refining process.	- Loses neutral oil in high FFA containing crude oil - Produces soap stock that is low commercial value. - Causes loss of neutral oil due to hydrolysis.
Physical deacidification	- Accomplished on high-FFA oil - Requires minimal capital and operating costs due to lower steam and energy utilization. - Results in larger oil yield - Eliminates soap stock - Reduces effluent quantity - Improves FFA quality	- Requires stringent pretreatments - Unaccomplished for heat sensitive oil - Leads to thermal polymerization - Accomplished with controls rate of FFA removal

Due to the drawbacks of conventional deacidification methods, alternative deacidification approaches are needed. The approaches suggested by various researchers include solvent deacidification and membrane deacidification. Table 2.5 lists the features and drawbacks of these new approaches suggested by various studies (Bhosle & Subramanian, 2004). From the limitations found, some researchers tend to integrate both approaches to produce effective and efficient outcomes.

Table 2.5: Features and Limitations of New Approaches for Deacidification (Bhosle and Subramanian, 2004)

Approaches	Features	Limitations
Solvent deacidification	- Operates on atmospheric pressure and ambient temperature. - Separates easily as great difference between boiling points of solvent and fatty compounds	- Requires higher capital cost - Operates on intensive operation - Produces incomplete deacidification
Membrane deacidification	- Consumes low energy - Operates at ambient temperature - Works without chemicals - Retains desirable components, including nutrients	- Separates with difficultly due to small molecular weight difference between FFA and TG - Lacks proper membrane with high selectivity - Produces low permeate flux - Unaccomplished for high viscosity oil such as palm oil and coconut oil

2.7.1 Solvent Deacidification

Although solvent extraction has long been known as a method of separation and pre-concentration of extractant, only recently has it been recognized as a powerful and widely used separation technique. During the extraction process, the studied solution is brought into contact with a second solvent that is usually immiscible with the studied solution in order to transfer one or more compounds to be extracted into the second solvent. Deacidification using solvent extraction takes place due to the difference in the solubility of neutral oil and FFA in various solvents. This approach can be conducted at ambient temperature, thereby reducing the energy usage and the loss of essential heat-sensitive compounds. Different boiling points between FFA, neutral oil and solvents allow the solvent recovery from extractant and solvent recycling in the following usage. Solvent recovery could be operated by distillation or evaporation at low temperature with moderate vacuum (Baümler et al., 2016).

Deacidification using hexane as the solvent is widely used in the oil industry nowadays especially soybean oil due to its high oil yield and economically friendly feature. However, hexane has been banned in several countries due to its environmental and health impacts after going through several thermal or catalytic cracking process during the oil refining process. Hence, there is increased motivation in searching alternative solvents to reduce the potential traces, environmental and health impacts of hexane in refined oil (Baümler et al., 2016).

Deacidification using solvent extraction can be highly affected by several parameters including type of solvent, extraction temperature, mass ratio (solvent to oil) and water content of solvent. Although suitable solvent selection for effective separation is crucial, the ease of solvent and solute recovery is important for subsequent analytical processing. Thus, the degree of miscibility between extractant and raffinate phases, viscosity, and tendency to form emulsion should be considered. Besides, the solvent toxicity, consumers' safety, and operation safety in terms of flammability must be taken into consideration as well (Rodrigues et al., 2007).

2.7.1.1 Solvent Type

A solvent that has high solubility in increasing temperature, but low solubility at room temperature will be more favorable in the selection of solvent type as phase separation of oil from solvent will happen without the need of further treatment such as evaporation. Several researches have been carried out on laboratory scale using short chain alcohol, hydrocarbons and other green solvents to replace hexane. Among these solvents, ethanol is favorable in solvent extraction because it is immiscible with oil compared to hexane. In addition, the selected solvent should be nontoxic to users, animals or human and environment as well as have low flammability. It must be stable and nonreactive with treated solution. For example, trichloroethylene is not suitable in soybean oil extraction as it was found to form toxic compounds with proteins in soybean which becomes fatal when consumed (Johnson & Lucas, 1983).

Batista et al. (1999) demonstrated that methanol was the most selective solvent in canola oil but showed low distribution coefficient which was less than 1. Efthymiopoulos et al. (2018) study on solvent selection on extraction of oil and FFA in spent coffee grounds also concluded that polar solvents such as ethanol tend to extract a higher amount of FFAs (Figure 2.9) while non-polar solvents such as hexane were better in oil extraction. Typically, non-polar solvents are more suitable to oil extraction as oils are often miscible with non-polar solvent. Polar solvents like alcohols are seen to extract greater amounts of FFAs and other compounds such as phosphatides (Darvishmanesh et al., 2011).

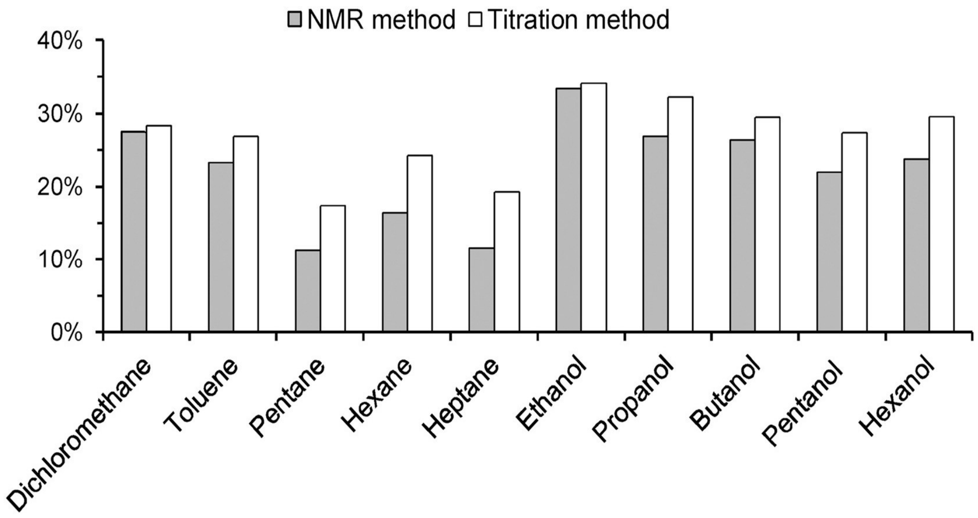


Figure 2.9 Comparison of FFA content (% w/w) of oil samples extracted with various solvents determined through titration and nuclear magnetic resonance (NMR) (Efthymiopoulos et al.,2018)

Baümler et al. (2016) demonstrated the feasibility of using ethanol in replacement of hexane as an alternative in the sunflower oil extraction. Ethanol has a comparable or even larger lipid material extraction capacity than hexane. The tocopherols and phospholipid extraction capacity in sunflower collets with ethanol is 38% greater than that of hexane. Ethanol can remove more polar lipids, including phospholipids than hexane due to the distinction between solvent polarity (Li et al., 2014). Besides, Baümler et al. (2016) reported that the yield of extracted compound using ethanol was greater than the yield that uses hexane and the extracted compound, including 69% of hexane-soluble and hexane-insoluble fractions. Both fractions were composed of partially degummed sunflower oil with a small amount of crystallizable wax content and hexane-insoluble fraction consisted of oil, pigments, phospholipids and especially sugar which was not extracted with hexane as presented in Table 2.6.

Table 2.6: Extraction Yield and Chemical Composition of the Material Extracted by Soxhlet with Ethanol and Hexane from Sunflower Collets (Baümler et al., 2016)

Analytical determination		Extraction solvent	
		Ethanol	Hexane
Yield of extracted material	(% d.b.)	32.2 ± 1.3^{b}	22.8 ± 0.6^{a}
	Hexane-soluble material (%)	69.0 ± 1.3	100
Phospholipids	(g/kg e.m.)	2.90 ± 0.01^{a}	2.52 ± 0.29^{a}
	(g/kg of solid in d.b.*)	0.93 ± 0.32 10^{-2a}	0.58 ± 6.68 10^{-2b}
	PE (%)	9.1 ± 0.8^{a}	13.3 ± 1.6^{a}
	PA (%)	16.1 ± 0.8^{b}	24.4 ± 2.2^{a}
	PI (%)	35.5 ± 1.2^{a}	30.6 ± 2.7^{a}
	PC (%)	39.3 ± 1.1^{b}	31.7 ± 2.1^{a}
Tocopherols	(mg/kg e.m.)	499 ± 125^{a}	512 ± 63^{a}
	(mg/kg of solid in d.b.*)	160.76 ± 40.21^{a}	116.95 ± 14.50^{a}
	Alpha (%)	99.0 ± 0.1^{a}	98.2 ± 0.7^{a}
	Beta (%)	1.0 ± 0.2^{a}	1.8 ± 0.9^{a}
Waxes	(mg/kg e.m.)	329 ± 8^{a}	670 ± 2^{b}
	(mg/kg of solid in d.b.*)	105.78 ± 2.50^{a}	152.93 ± 0.48^{b}
	Oil soluble (%)	24.5 ± 0.1^{b}	12.9 ± 0.04^{a}
	Partially oil soluble (%)	34.2 ± 0.3^{b}	19.3 ± 0.2^{a}
Sugars	(g/kg e.m.)	105.66 ± 11.45^{e}	-
	(g/kg of solid in d.b.*)	34.02 ± 3.69^{e}	-
	Raffinose (%)	33.3 ± 2.6^{e}	-
	Sucrose (%)	59.7 ± 3.4^{e}	-
	Glucose (%)	2.1 ± 0.3^{e}	-
	Galactose (%)	1.5 ± 0.2^{e}	-
	Fructose (%)	2.1 ± 0.3^{e}	-
	Rhamnose (%)	1.3 ± 0.8^{e}	-

Data are mean values ± standard errors.
Values in the same row with the same letter are not significantly different ($p > 0.05$) by the LSD Fisher method.
d.b. = dry basis.
e.m. = extracted material.
PE = phosphatidylethanolamine
PA = phosphatidic acid
PI = phosphatidylinositol
PC = phosphatidylcholine
*solid in d.b. means moisture-free sunflower collets.

2.7.1.2 Extraction Temperature

Temperature can be a crucial parameter and often used as manipulated variable to alter selectivity in solvent extraction. Palm oil appears naturally as semi-solid at room temperature due to the close equivalent composition of saturated fatty acids and unsaturated fatty acids. By raising the temperature, it can help to minimize the viscosity, and in this manner reduces the mass transfer resistance. The ideal deacidification temperature should not only be able to remove undesirable materials and impurities effectively, but also be able to prevent thermal decomposition of desired compounds such as heat-sensitive bioactive and beneficial compounds (Wei et al., 2015). However, most of the research was carried out in extraction of crude oil from vegetable oil seeds with solvent.

Baümler et al. (2016) research measured the degree of difficulty to extract material include oil from the sunflower collets by equilibrium studies. The equilibrium constant was determined as the ratio of the residual extractable material in the sunflower collet to the extracted material in solvent. The lower equilibrium constant value results in the greater oil extraction. It was found that the equilibrium constant of ethanol was negatively influenced by temperature. Therefore, oil extraction increased with temperature. In Efthymiopoulos et al. (2018), they also concluded that increase of extraction temperature using accelerated solvent extraction (ASE) allows the researcher to obtain higher oil extraction from the spent coffee grounds. The high temperature increased the diffusion and solubility of the oil, while decreasing viscosity.

2.7.1.3 Mass Ratio

Baümler et al. (2016) demonstrated that mass ratio of solvent to oil is very important in affecting the extraction ability. They concluded that the extraction ability rose when the solvent to oil ratio is increased. An elevated solvent to oil ratio (18 solvent to 1 oil ratio) was used in their study because oil was only miscible moderately in ethanol. The extraction abilities of ethanol and hexane were tabulated in Table 2.7. Their experimental result indicated that the extraction ability of ethanol was highly affected by the solvent to oil ratio. With the presence of higher extraction solvent volume, the residual extractable compound in the solid phase decreased, indicating better extraction. However, hexane was less influenced by the mass ratio due to the solvent nature.

Table 2.7: Comparison between Ethanol and Hexane as Extraction Solvent at Equilibrium Constant (*K*) at 50 and 60 °C and Different Collet-To-Solvent Ratios (Baümler et al., 2016)

Collet-to-solvent ratios (g/mL)	$K_{ethanol}$	K_{hexane}
50 °C		
1 : 4	17.13 ± 0.22^{c}	0.49 ± 0.01^{b}
1 : 11	10.51 ± 0.56^{b}	0.34 ± 0.04^{a}
1 : 18	7.55 ± 0.84^{a}	0.54 ± 0.03^{b}
60 °C		
1 : 4	8.17 ± 0.86^{b}	0.55 ± 0.02^{b}
1 : 11	5.14 ± 0.46^{a}	0.18 ± 0.01^{a}
1 : 18	3.52 ± 0.40^{a}	0.60 ± 0.09^{b}

In the same column and for each temperature, values with the same letter are not significantly different ($p > 0.05$) by the LSD Fisher method.

K = ratio of the residual extracted material in the solid phase to the extracted material in the bulk miscelle.

2.7.1.4 Water Content

Numerous researches have investigated the liquid-liquid extraction using aqueous alcohol solvent. All these studies revealed the addition of water in solvent could minimize the FFA level in raffinate phase (Harris et al., 1947; Johnson & Lucas, 1983). When added with water, alcohol solvent forms azeotropic mixture that possesses altered properties compared to the pure alcohol. The presence of water in solvent can increase the polarity of the solvents, subsequently increasing the extraction ability for undesired nonpolar compounds such as FFA, at the same time reducing the oil solubility (Johnson & Lucas, 1983). Gonçalves et al. (2004) even concluded that the addition of water in ethanol was able to diminish the loss of neutral palm oil and improve the selectivity.

2.7.2 Membrane Deacidification

Membrane technology which has been widely used in various industrial applications poses a promising result to overcome key downsides of conventional CPO refining process. The significant benefits of practicing membranes technology in oil extraction are efficient energy usage, operation at ambient temperature as well as retention of desirable components and nutrients in oil. Meanwhile, membrane technology proposes attractive benefits where the usage of chemicals such as NaOH and bleaching earth which are harmful to both environment and people can be avoided (Azmi et al., 2015). Membrane technology is energy efficient compared to other separation technology in many applications. Its design is simple and scalable, as well as the operation is mostly completed at ambient temperature which is suitable for heat-sensitive compounds in oil. The main cost contributors in membrane technology often involve maintenance, as well as pre- and post-treatment procedures(Strathmann, 2011).

Membrane can be described as selective semipermeable barriers that set apart a mixture of components by permitting desired compounds to pass through and the retention of others from a selected mixture, resulting in different concentrations of desired compounds in both permeate and retentate. Membrane selectivity is interconnected to the characteristics of interested components, including size, diffusivity in the matrix and associated electric charges. Meanwhile, the separation capability of a membrane is controlled by its materials and chemical composition, operation pressure, operation temperature, membrane module, feed flow including interaction between compounds in the membrane surface and the feed flow, as well as the process design and operation (Coutinho et al., 2009).

In early 20th century, the first synthetic membrane was created by infusing a filter paper into a nitrocellulose-glacial acetic acid solution. By varying the ratio of acid to nitrocellulose, membrane with different permeability and pore size can be accurately reproduced and commercialized (Strathmann, 2011). However, large scale membrane application only began in 1944 when the first functioning hemodialyzer was successfully invented by Kolff and Berk.

For water treatment, membrane technology is well-developed and equipped with high quality products with minimum environmental impacts. Yet, new emerging or potential membrane application in oil and fats industry which often involves solvent need to be further studied in terms of flux, rejection, durability and reliability.

2.7.2.1 Membrane Selectivity

Membrane separation is well-understandable based on size exclusion mechanism. However, the insignificant molecular weight difference among the FFA and oil causes the unsuccessfulness of membrane separation for CPO deacidification. The calculated average molecular weight for refined palm oil is 847.78 g/mol, while oleic acid is 282.45 g/mol and palmitic acid is only 256.43 g/mol (Gonçalves & Meirelles, 2004). Nevertheless, there is only 3-5% of FFA found in the bulk CPO, which is a relatively low amount, and therefore turning down the capability of membrane separation as well. Thus, the membrane with high selectivity and strong interaction between FFA and membrane surface is highly desired for the CPO deacidification to be feasible (Azmi et al., 2015).

Alicieo et al. (2002) studied the membrane ultrafiltration of crude soybean oil using polysulphone hollow fiber membrane with a pore size of 100 kDa and ceramic tubular membrane with a pore size of 0.01 μm. The performance of the membrane was assessed based on the influence of transmembrane pressure and temperature on the permeate flux and removal of

FFA, phosphorus, color, soaps and chlorophyll. However, the permeate flux and percent of rejection was considered low for FFA but good for phosphorus as shown in Table 2.8 with the FFA feed concentrations of 0.80 and 0.855 (%) for ceramic and polysulphone membranes respectively. The best permeate flux for ceramic tubular membrane was only 4.16 kg/m².h at 50 ºC under 6.0 bar, while for polysulfone hollow fiber membrane, the permeate flux was slightly higher with 11.58 kg/m².h at 70 ºC and 1.5 bar.

Table 2.8: Clarification of Soybean Oil in Ceramic Membrane and polysulphone Membrane (Alicieo et al., 2002)

Analysis	Rejection, R (%)	
	Polysulphone membrane	Ceramic membrane
FFA	34.39	54.45
Soaps	85.81	97.91
Phosphorus	73.37	99.14
Chlorophyll	20.91	22.34
Colour	37.50	42.00

Iyuke et al. (2004) pretreated CPO to remove FFA, carotene and phosphorus using ceramic membrane with pore sizes of 20, 50, 200 and 450 nm respectively in a crossflow filtration system to compare the quality of conventional bleached CPO (Table 2.9). Their result highlighted that FFA in both membrane-treated and conventional bleaching processes was not reduced significantly. It is known that the FFA removal in conventional refining process only happens in deodorization, but not in the bleaching process. However, the phosphorus rejection in membrane-treated process achieved 43.4% which was greater than that of conventional bleaching processed oil (34.4%). The membrane with a pore size of 450 nm was able to remove 14% of phosphorus, while the membrane with pore size of 20 nm showed 78.1% phosphorus rejection, indicating that selection of pore size is crucial in impurities removal. However, in their study, membrane process could only remove certain large impurities, such as phosphorus.

Table 2.9: Comparison of FFA, Carotene and Phosphorus Content of Microfiltration Membrane (200 nm) Permeate and Conventional Bleached Oils (Iyuke et al., 2004)

Process	Sample	FFA (%)	Carotene (ppm)	Phosphorus (ppm)
Membrane	Crude	2.94 ± 0.03	542 ± 15	11.66 ± 0.40
	Permeate	2.74 ± 0.20	558 ± 5	6.60 ± 0.20
	Retentate	2.86 ± 0.01	542 ± 3	10.32 ± 0.28
Conventional	Crude	2.82 ± 0.04	530 ± 1	11.70 ± 0.56
	Bleached	2.71 ± 0.01	418 ± 2	7.68 ± 0.55

Earlier studies (Alicieo et al., 2002; Gonçalves & Meirelles, 2004) indicated that membrane filtration in phosphorus was feasible. However, improvement was needed for FFA in terms of membrane selection, working parameter as well as more information was needed from the studies. The insignificant molecular weight difference among the FFA and oil caused the ineffectiveness of membrane separation by size exclusion, and thus membrane hydrophobicity could be the key factor for better separation as suggested by Azmi et al. (2015).

On the other hand, ultrafiltration using cellulose and cellulose acetate hollow fiber membrane was applied in a liquid-liquid extraction of FFA from soybean oil using 1, 2-butanediol as solvent (Keurentjes et al., 1992). The results revealed that the loss of triglycerides could be minimized, but a high mass transfer resistance was resulted from filtration, leading to a large membrane area required. In addition to asymmetric membrane, which consists of dense active layer and porous sublayer, it also showed potential in removing phospholipids and pigments in oil (Subramanian et al, 1998). Nonporous composite polymeric hydrophobic membrane allowed complete removal of phosphorus in CPO and palm olein while maintaining nutritional quality of oil (Arora et al., 2006). However, FFA could not be separated effectively from the oil. Hence, further improvement in separation of FFA from oil is needed. In Sarode (2009), the study also reported similar results, in which non-porous membranes were found to be able to reduce phosphorus content in rice bran oil and also substantial reduction in color value (Sarode, 2009).

2.7.2.2 Hydrophobicity

Azmi et al. (2015) found that polyvinylidene difluoride (PVDF) membranes with polyvinyl alcohol (PVA) that have been cross-linked with glutaraldehyde (GA) to produce microfiltration hollow fiber membrane concluded that the membrane-based CPO refining using PVA which possessed plenty of hydroxyl (–OH) groups was able to improve the affinity of FFA toward membrane selectivity layer which later reduce the FFA to across the membrane as permeate.

When the surface of PVDF was coated with 100 ppm of PVA, 5.93% of FFA could be promisingly rejected based upon the interaction built up between the hydroxyl (PVA layer) and carboxyl groups (FFA). PVDF was expectedly to be unsuitable to extract the FFA from the CPO bulk but could successfully remove phospholipids. In addition, Azmi et al. (2015) also highlighted that the removal of phospholipids from CPO using membrane was not by the size exclusion as the membrane presented larger pore size ranging from 60 to 360 kDa compared to the phospholipids which was only 683.83 g/mol. Thus, the removal of phospholipid was attributed to adsorption onto the polymeric membrane causing in the moderately poorer diffusion rate when compared to the triglycerides.

Darvishmanesh et al. (2011) observed that semi-hydrophobic (62° ± 1.8°) and hydrophobic (95° ± 2.7°) nanofiltration membranes had better performance in the separation of oil in polar organic solvents, including acetone, ethanol, and isopropanol compared to non-polar solvents. In case of using ethanol as solvent, this semi-hydrophobic membrane has higher flux and higher rejection compared to the hydrophobic membrane (SOLSEPP NF030306), as it was able to achieve an oil rejection of 96% with overall permeate flux of 17.4 kg/ m^2h under operating pressure of 20 bar.

2.7.2.3 Permeate Flux and Rejection

Permeate flux and rejection are the crucial parameters in improving membrane technology. High flux together with high rejection, which indicates the separation capability of the selected membrane, can minimize the capital cost (Kale et al., 1999). Koike et al. (2002) concluded that permeate flux decreased when oil concentration increased. In their study, the flux obtained for solvent-free oil was only 0.13 L/m^{2}h with hydrophobic membrane. The permeate flux was highly improved after diluting the oil with either ethanol (polar) or hexane (nonpolar) solvent. Silicon polyimide composite membrane demonstrated high permeate flux of 72 kg/ (m^2.h) with appreciable selectivity of 95% oil and 74% FFA rejection.

Arora et al. (2006) also improved the permeate flux of 0.12 kg/ (m^2.h) in solvent-free crude palm oil and 0.14 kg/ (m^2.h) in palm olein by diluting with hexane. The oil permeate flux could be improved up to 15 fold at 1 : 3 dilution as compared to solvent-free rice bran oil. In hexane diluted CPO, the permeate flux was enhanced by approximately 9-fold at 1: 1 dilution. However, by further increasing the dilution factor, it brings no significant improvement in the permeate flux but induces membrane swelling that may disturb the membrane selectivity in terms of rejection.

Darvishmanesh et al. (2011) reported that no flux was observed for the pure cooking oil when tested with selected commercial nanofiltration polymeric membranes in any case under different operating pressures (8–20 bar). However, when tested with a mixture containing 10 wt% oil in the solvents, the permeate flux and oil rejection that happened and was presented in table 2.10 concluded that oil permeability can only be improved with the presence of solvent.

Table 2.10: Overall Permeate Flux and Oil Rejection in Different Studied Systems (Darvishmanesh et al., 2011)

Solvent	Membrane	Overall flux (kg/ (m^{2}h))	Rejection (%)
Ethanol	STARMEM^{TM}122	17.4	96
	SOLSEP NF030306	4.89	78
Isopropanol	STARMEM^{TM}122	4.48	79
Acetone	STARMEM^{TM}122	56.6	70
	SOLSEP NF030306	16.6	78
Cyclohexane	SOLSEP NF030306	0.54	64
Hexane	SOLSEP NF030306	0.55	38

2.8 Solvent Extraction Integrated with Membrane Filtration System

One of the new approaches that overcomes not only the most important downsides of conventional refining processes, but also the deficiency in both solvent extraction and membrane-based refining process is integration of both approaches.

Raman et al. (1996) evaluated several commercially available flat-sheet membranes including MS 10, PZ, FT-30, NTR-729, NTR-759, and Desal-5, in the soybean oil deacidification after methanol extraction, which resulted in 35% FFA retention and less than 0.04% FFA in the permeate stream, which could be recycled to the extracted solution. Besides, Kale et al. (1999) also used commercial flat sheet membranes, DS-5 and BW-30 to recover the methanol in FFA extraction by nanofiltration in two-stage membrane system. The deacidification of crude rice bran oil with an optimal ratio of 1.8:1 methanol/oil by weight successfully reduced FFA from 16.5% to 3.7%. Subsequently, a second extraction at 1:1 ratio effectively further reduced FFA in the oil to 0.33%. Both studies had acquired no alkali, no soap-stock formation and minimal waste discharge.

Other than methanol, some studies also used hexane for FFA extraction. Flat-sheet polymeric membranes, such as polysulfone and polysulfone/ polyamide base which are normally used in reverse osmosis, nanofiltration and ultrafiltration were used in the studies. The result showed that hexane recovery from miscella can be accomplished using membrane separation, presenting a high potential for industrial application (Ribeiro et al, 2006). In Zwijnenberg et al. (1999), deacidification of oil using two types of nanofiltration membranes, one with PEBAX [poly (amide-b-ether) copolymer] top layer, and another membrane with cellulose-type top layer, was applicable. Result reported that the permeate contained almost completely of FFA in acetone with only a small amount of oil. This study was useful in removing the FFA selectively, reducing the loss of oil and enhancing the acetone recovery.

When using solvent extraction integrated with membrane-based technology in filtration system, high pressure is needed for better solvent permeate reflux. However, this will reduce the selectivity of the system and fouling tends to happen easily on selected membrane.

2.9 Deacidification using Membrane Pervaporation

In the early 19th century, pervaporation was tested at the laboratory and bench scale to separate organic mixtures. However, this process was not feasible due to poor development of membrane technology. Until the late 20th century, the improvement in membrane technology made pervaporation achievable for the removal of water from organic solvent such as ethanol. Currently, pervaporation is widely used in dehydration of food and organic solvent (e.g., bioethanol), removal of organics from solvents and separation of organic solvents mixture. Pervaporation has been demonstrated as one of the most cost-effective liquid separation technology when compared to distillation especially in separating heat sensitive, azeotropic and close boiling mixture (Findrik et al., 2012).

Pervaporation can separate a liquid mixture that contacts with one side of a membrane. This can be done by increasing the temperature in feed tank to create permeate vapor that will transport through the selected membrane due to the different permeate vapor pressure. This process is aided with a vacuum pump integrated with condenser to collect the permeate vapor. Figure 2.10 demonstrates the schematic diagram of pervaporation process (Manshad et al., 2016). The liquid is separated into two streams, i.e., permeate and retentate, where permeate is referred to solute and/or liquids that pass through the selected membrane and consists of easily transported compounds, On the other hand, retentate is referred to solute and/or liquids that remain in the feed tank and consists of compounds that are concentrated.

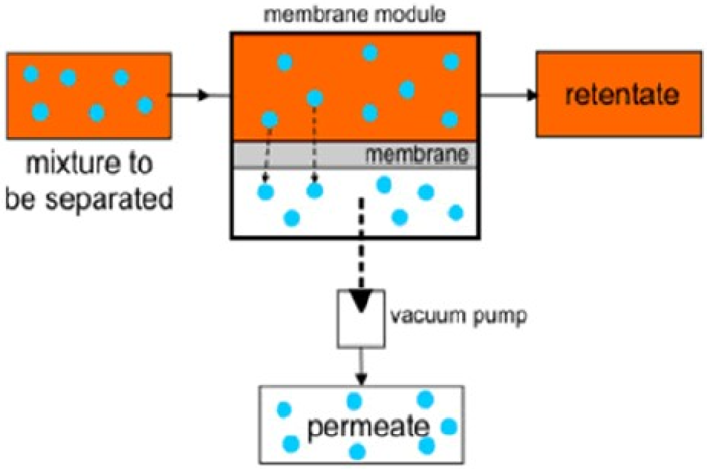


Figure 2.10: Schematic Diagram of Pervaporation Process (Manshad et al., 2016)

In pervaporation, membrane fouling can easily occur which then makes the membrane less selective and leads to an urge for replacement. Hence, a suitable membrane material is one of the key factors for the effective and efficient performance. Pervaporation is not only influenced by the membrane properties, but also permeate pressure, feed concentration and feed temperature can also affect the effectiveness of the pervaporation in terms of membrane permeability and selectivity. When the feed pressure is kept as constant, the decrease in permeate pressure with the aid of vacuum pump will increase the difference in partial pressure of the compounds between the feed and permeate sides. Hence, the increase in the driving force of the compounds transported through the membrane will then enhance the membrane flux (Findrik et al., 2012).

Membrane technology using pervaporation is believed to be able to increase the FFA selectivity regardless of the small molecular weight difference between the FFA and triglycerides. There is a phase change in the process that combines both permeation and evaporation. The separation can be done based on the permeation rate of molecules across the selected membrane. There is none of the pervaporation study focus on removal of FFA from solvent. The most related study is on biodiesel production that uses pervaporation to enhance esterification. Studies suggested that by using hydrophilic membrane, only water associated with solvent such as methanol found in permeate while hydrophobic component such as fatty acid methyl ester (FAME) and (palm fatty acid distillate (PFAD) remained as retentate (Shuit and Tan, 2019).

Okamoto et al. (1993) reported that pervaporation aided esterification of oleic acid effectively recovered ethanol and water from FFA extractant. Only water and ethanol were able to permeate through the asymmetric polyimide membrane of poly-etherimide (PEI) and poly (4, 4'-oxydiphenylene pyromellitimide) (PORMI), while oleic acid and ethyl oleate remained as retentate. However, they suggested that a membrane with better permeability and durability was needed.

Pervaporation keeps improving as a feasible membrane separation technology for different aspect of applications. Due to the lower energy consumption, easy scale-up of the process and longer production operation hour, further application development for removal of free fatty acid from solvent such as ethanol holds much promise. Hence, the objective of this study is to compare the feasiblity of both membrane technology in pressurized system and pervaporation system.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Equipment

Table 3.1 lists the equipment used throughout this study for membrane characterization and palmitic acid concentration analysis.

Table 3.1: Equipment Used in This Study

Equipment	Brand	Model	Purpose in this study
Scanning electron microscope (SEM)	Hitachi	S3400N	To examine surface morphology of membrane
Optical tensiometer	Biolin Scientific	Attension Theta	To measure contact angle of membrane
Gas chromatography with flame ionization detector (GC-FID)	PerkinElmer	Clarus® 500	To determine palmitic acid concentration

3.2 Chemicals and Gases

Table 3.2 lists the chemicals and gases that were used throughout this study for solvent extraction, synthetic acidified palm oil and synthetic extractant preparation, titration, membrane preparation prior for characterization and filtration system setup.

Table 3.2: Chemicals and Gases Used in This Study

Materials	Purity	Brand	Purpose in this study
Acetone	99.80%	Merck	Solvent extraction
Ethanol	99.98%	HmbG	Solvent extraction
Hexane	99.00%, AR Grade	Friendemann Schmidt	Solvent extraction
Methanol	99.90%, AR Grade	RCI Labscan	Solvent extraction
Isopropanol	99.70%, AR Grade	QRëC	Solvent extraction
Palmitic Acid	≥98.00%	Sigma-Aldrich	Free fatty acid (FFA) substitution
Phenolphthalein	NA	Gene Chemicals	Titration
Potassium hydroxide, 0.1 N	ACS grade	CHEMSOLn	Titration
Refined palm olein	Food-grade	Alif, Sime Darby	Part of synthetic acidified palm oil
Nitrogen, Liquid	>99%	Linde Malaysia Sdn. Bhd.	Membrane preparation for characterization
Nitrogen, Compressed	Purified	Linde Malaysia Sdn. Bhd.	Membrane filtration system

3.3 Synthetic Acidified Palm Oil Sample

In this study, palmitic acid was used to represent the FFA that is present in unrefined palm oil as it is the major FFA component found in CPO. The raw materials used for synthetic acidified palm oil preparation were food-grade refined palm olein (cooking oil) purchased from local market and commercial palmitic acid from Sigma-Aldrich. It was prepared by dissolving 5.0 wt% of palmitic acid into the refined palm oil following the quality guideline for maximum FFA acceptable to be found in CPO according to Malaysian Standards (MS 816:2007). The components were weighed using analytical balance (Model: ACJ 220-4M, KERN, Germany) with an accuracy of 0.0001 g. The mixture was then mixed homogenously at 70 °C in a water bath (Model: WNB14L1, Memmert, Germany) for 2 h until the palmitic acid was fully dissolved in the refined palm olein.

3.4 Solvent Extraction and Determination of Palmitic Acid Concentration

Figure 3.1 shows the flow chart and parameters of the study on solvent extraction. The selected solvents include acetone, ethanol, hexane, methanol and isopropanol (IPA). Only the solvent that exhibited the best extraction efficiency of palmitic acid was used for further studies on extraction parameters including mass ratio (solvent to synthetic acidified palm oil), water content and extraction temperature. The most suitable extraction parameters were determined based on the highest palmitic acid extraction efficiency achieved in the most cost-effective way.

In this study, all samples were prepared at least in three sets to obtain triplicate measurement values in the determination of palmitic acid concentration. The mean value and standard deviation of palmitic acid concentration were calculated for data analysis.

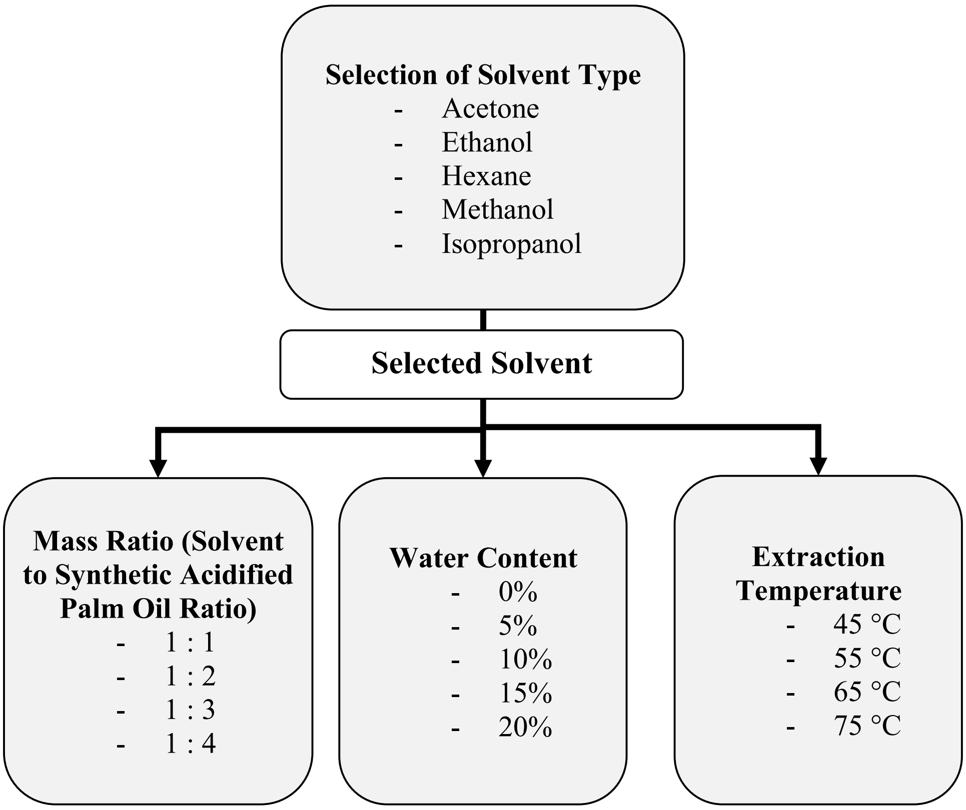


Figure 3.1 Flow Chart and Parameters of Solvent Extraction

3.4.1 Solvent Extraction

Synthetic acidified palm oil was heated to 55 °C in a water bath (Model: WNB14L1, Memmert, Germany) for 30 min until it appeared in liquid form. With the synthetic acidified palm oil to solvent mass ratio of 1: 2, 50 mL of synthetic acidified palm oil was measured into five separate conical flasks followed by 100 mL of selected solvents. The synthetic acidified palm oil with its respective solvent was placed in a shaking water bath (Model: WNB22, Memmert, Germany) at 55 °C with the shaking frequency of 135 strokes per min horizontal back/ forth for 2 h. The solvent treated synthetic acidified palm oil was then allowed to rest for another 2 h at room temperature, followed by separating the raffinate phase (ideally containing only triglyceride) from the extractant (ideally containing solvent and palmitic acid). The raffinate phase of sample that contained the smallest quantity of palmitic acid exhibited the best palmitic extraction and vice versa.

3.4.2 Parameters of Solvent Extraction Study

The synthetic acidified palm oil was prepared according to Table 3.3 into different conical flasks which are then further treated in a shaking water bath with a shaking frequency of 135 strokes per mins horizontal back/ forth for 2 h. The solvent treated synthetic acidified palm oil was then allowed to rest for another 2 h at room temperature, followed by separating the raffinate and extractant phases.

Table 3.3: Parameters of Solvent Extraction Study

Study	Parameters			
	Synthetic Acidified Palm Oil Volume (g)	Solvent Volume (mL)	Water content (%)	Temperature (°C)
Extraction Temperature				
T1	50.0	100.0	0	45
T2	50.0	100.0	0	55
T3	50.0	100.0	0	65
T4	50.0	100.0	0	75
Mass Ratio (Solvent to Synthetic Acidified Palm Oil System)				
R1	75.0	75.0	0	55
R2	50.0	100.0	0	55
R3	37.5	112.5	0	55
R4	30.0	120.0	0	55
Water Content				
W1	50.0	100.0	0	55
W2	50.0	95.0	5	55
W3	50.0	90.0	10	55
W4	50.0	85.0	15	55
W5	50.0	80.0	20	55

3.4.3 Determination of Palmitic Acid Concentration

The palmitic acid concentrations of oil samples were determined by titration method (IUPAC official method 2201) with phenolphthalein in the indicator mixture. Indicator mixture with 400 mL of IPA and 4 mL of phenolphthalein was heated until the boiling point and this followed by adding with 0.1 N potassium hydroxide (KOH) until the solution turned into pale purple. It reflects the amount of FFAs which are not attached to a glycerol backbone in the percentage by weight in the oil.

Three grams of synthetic acidified palm oil and raffinate phase (appearing at the bottom layer) in each solvent extraction study was weighed in a conical flask and mixed with 50 mL of indicator mixture. The sample was then heated until it boiled, followed by titration with KOH solution which was stopped when the sample turned reddish. Both initial and final volumes of KOH were recorded to calculate the volume of KOH consumed in titration. The percentage of palmitic acid present in the synthetic acidified palm oil and raffinate phase was recorded to calculate the sample acidity using Equation 3.1.

$$PA\ (\%) = \frac{(25.6 \times N \times V)}{M} \tag{3.1}$$

where N is the normality of KOH (mol/L), V is the volume of KOH consumed in titration (mL) and M is the weight of sample (g), whereas 25.6 is the molecular weight of palmitic acid (256 g/mol) divided by 10 due to unit conversion process and values were expressed as a fraction of 100. Meanwhile, the palmitic acid reduction percentage (%) was calculated using Equation 3.2,

$$\text{Palmitic Acid Reduction Percentage (\%)} = \left(\frac{PA_\mathrm{i} - PA_\mathrm{r}}{PA_\mathrm{i}}\right) \times 100 \tag{3.2}$$

where PA_i is palmitic acid concentration in synthetic acidified palm oil and PA_r is the palmitic acid concentration in raffinate phase.

3.5 Membrane Characterization

Five commercially available membranes were selected based on either manufacturer data on FFA filtration efficiency or pore size that is suitable for this application. The characteristics of each membrane are summarized in Table 3.4 based on the manufacturer's datasheet. These selected membranes included three polydimethyl siloxane (PDMS) with silicone based supported SRNF membranes, namely NF010206, NF030306 and NF030705 (SolSep BV, Holland), cellulose triacetate non-woven support (CTA-NW) forward osmosis (FO) membrane (Hydration Technology Innovations, USA), and polyamide thin-film composite reverse osmosis (RO) membrane SW30XLE (Dow Filmtec™, USA). All membranes were received and kept in dry condition until it was time for it to be used by pre-wetting it in ethanol. The membranes were cut into circular shape with a diameter of 49 mm, followed by pre-wetting in ethanol one day before usage. All these membranes then underwent the characterization study using scanning electron microscope (SEM) and optical tensiometer to determine the membrane cross-sectional structure and contact angle.

Table 3.4: Summarize of Characteristic of Selected Membranes (SolSep BV, Lenntech, HTI Datasheet)

Characteristic	NF010206	NF030306	NF030705	CTA-NW	SW30XLE
Pressure (max)	20 bar	40 bar	20 bar	0.69 bar (10psi)	83 bar (1200psi)
Temperature	120°C	150°C	150°C	71°C	45°C
Application	SRNF (Resistant to veggie oil, aldehydes, ketones, crude alkanes, acetone, Alcohol, hexane	SRNF (Resistant to veggie oil, aldehydes, ketones, crude alkanes, acetone, Alcohols, hexane	SRNF (Resistant to alcohols)	Forward Osmosis (No report on solvent application by manufacturer but able to withstand pH range from 2 to 12)	Reverse Osmosis (No report on solvent application by manufacturer but able to withstand pH range from 2 to 11 at 25°C)
Permeability (l/m^{2}hbar) pure solvents	acetone (20°C) ~min 1	acetone (20°C) ~2 acetone (80°C) ~5-10 veggie oil (140°C) ~2	ethanol (20°C) ~2-5	20 Lmh in FO mode and 49 Lmh in PRO mode at a test condition of 1 m NaCl as draw solute and deionized water as feed solution at 23ºC and crossflow velocity of 30 cm/s.	23-29gfd/800psi
Retention (%)	(Mw~300) 95% FA in acetone (Mw~1000 Da) 90+% oily molecule in acetone (Mw~500) 99+% colorant in ethanol-acetone	(Mw~1000 Da) 99 oily molecule in ethanol (Mw~500) 99+ colorant in ethanol (Mw~1000 Da) 99 oily molecule in acetone (Mw~500) 99+ colorant in acetone	(Mw~1000 Da) 70 oily molecule in ethanol (Mw~500) 95+ colorant in alcohol (EA)	No Data from manufacturer	91.5% Stabilized Boron 99.8% Stabilized Salt *Benchmark values are based on the following test conditions: 32,000 ppm NaCl, 5 ppm boron, 55.16 bar (800 psi), 25°C, pH 8 and 8% recovery.
MWCO (Dalton)	<300	<300	>300	<200 (0.00074um)	~100
Membrane Type	PDMS with silicon base supported	PDMS with silicon base supported	PDMS with silicon base supported	Cellulose Triacetate nonwoven asymmetric	Polyamide Thin-Film Composite (Polyester support web, microporous polysulfone interlayer, and an ultra-thin polyamide barrier layer on the top surface)

3.5.1 Membrane Cross-sectional Structure by Scanning Electron Microscope (SEM)

SEM is one of the most powerful characterization tools used to examine the sample surface morphology. It uses an electron gun to generate electrons which are later accelerated with high voltage as incident beam and focused onto a sample surface with the aid of the condenser and objective lens. Different signals are produced when the electron beam strikes the sample surface and this will be interpreted by special electron detectors that reveal information related to the sample topography in the form of high resolution image.

Figure 3.2: Scanning Electron Microscope (Hitachi, 2015)

SEM (Model: S3400N, Hitachi, Japan, Figure 3.2) was used in this study to obtain the membrane cross-sectional structure. All the membrane samples were immersed in ethanol prior to cryogenically fracture in liquid nitrogen in order to obtain their cross-sectional image with SEM scanning. The clean-fractured membranes were then mounted on the aluminium sample holder using carbon tape. As membrane is polymeric and non-conductive, all samples were coated with palladium and gold particles using a sputter coater machine (SC 7620, Emitech, United Kingdom) to increase the electron conductivity of the membrane surface. Cross-sectional and surface morphology images of each membrane were captured and recorded in an equipment-linked computer.

3.5.2 Determination of Membrane Hydrophobicity Using Contact Angle

Hydrophobicity of membranes can affect the flux and selectivity of a membrane. The effective way to determine the hydrophobicity of membrane is to measure the contact angle. Smaller contact angle is formed when the affinity between water drop and the membrane surface is higher (i.e., higher degree of surface wetting), indicating that the membrane is hydrophilic. Meanwhile, larger contact angle reveals that the membrane is hydrophobic. Optical method is the basic method to determine a substance's contact angle. This method is based on observation of a liquid drop shape that is placed on a flat solid surface captured by a camera. The drop shape is formed according to the surface tension, surface free energy, gravity and the density difference between interfaces.

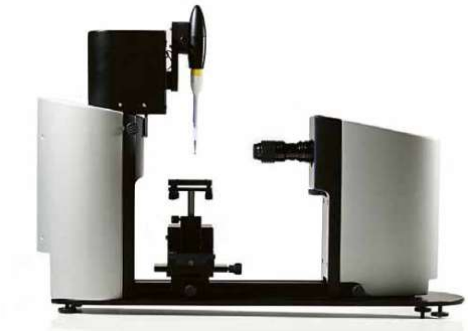


Figure 3.3: Optical Tensiometer (Model: Attension Theta, Biolin Scientific, Sweden)

The membrane contact angle was evaluated with deionized water using optical tensiometer (Model: Attension Theta, Biolin Scientific, Sweden; Figure 3.3) in this study. Deionized water droplet with the volume of 1.00 μL was dispensed automatically on top of the dry membrane. The image of droplet on the membrane surface was captured by an attached high-speed camera for 10 s. Each drop's profile was then automatically measured and analyzed with OneAttension. The mean value and standard deviation of the contact angle in 10 s were calculated and recorded for analysis. Each sample study was repeated at least three times.

3.5.3 Membrane Permeate Flux

The permeate flux study was performed using a dead-end stainless-steel stirred cell (Model: Sterlitech HP4750, Sterlitech Corporation, USA; Figure 3.4) with 14.6 cm² active membrane area and 0.3 L capacity. The stirred cell is able to withstand pressure up to 69 bar with high-pressure clamps and work at maximum temperature of 121°C at 55 bar. The stirred cell comes with Teflon magnetic stir bar to minimize concentration polarization during the experiments. The active side of selected membranes was installed towards the feed solution reservoir and the membrane was supported by a stainless steel porous membrane support disk that is located at the bottom of the stirred cell module. The membrane is sealed between an O-ring and a stainless steel porous support. Prior to both filtration and pervaporation studies, the selected membranes were pre-wetted overnight in ethanol. The membranes then underwent compact treatment with dead-end stainless-steel stirred cell at 25 bar with pure ethanol for 30 min until the flux achieved a steady state.

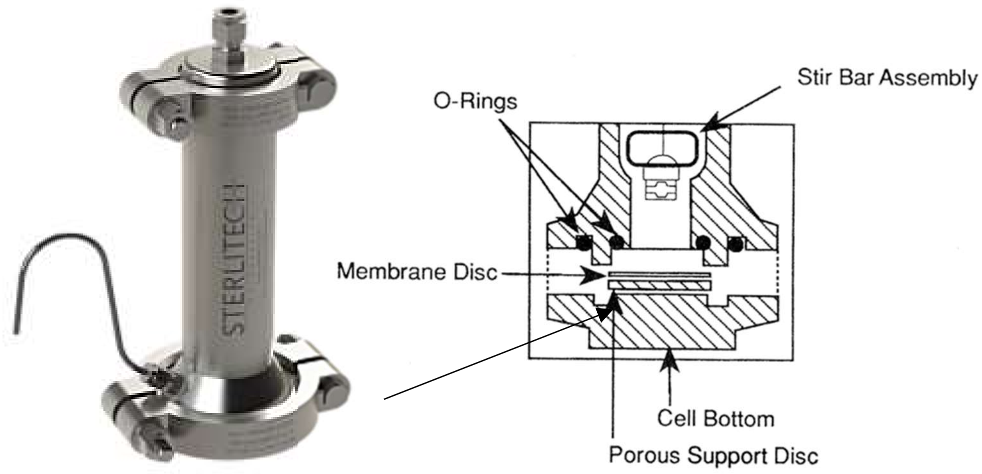


Figure 3.4: Sterlitech HP4750 Dead-End Stainless-Steel Stirred Cell

The filtration performance of the selected membranes in terms of permeate flux and membrane recovery was first determined using pure ethanol with dead end filtration cells. Permeate flux was investigated by measuring the flux, J_{EtOH1} (L/ m^{2}h) of 0.2 L of ethanol using Equation 3.3 at 20 bar, where

V_{EtOH1} is the volume of the permeation for pure ethanol (L), A is the effective filtration area (m²) and ΔT is the recorded time (hour). The result was recorded every 5 min for 40 min to observe the flux stability.

$$J_{\mathrm{EtOH1}} = \frac{V_{\mathrm{EtOH1}}}{A\Delta T} \tag{3.3}$$

Subsequently, the feed was replaced with 0.2 L of synthetic extractant which contained approximately 3.0% w/v palmitic acid in ethanol. The permeate flux for the synthetic extractant was measured at 20 bar for 30 min and named as J_{PA} as expressed in Equation 3.4.

$$J_{\mathrm{PA}} = \frac{V_{\mathrm{PA}}}{A\Delta T} \tag{3.4}$$

where V_{PA} is the volume of permeate for synthetic extractant (L), A is the effective filtration area (m²) and ΔT is the recorded time (hour). All experiments were carried out at a controlled temperature of 25 °C.

3.5.4 Flux recovery

After the filtration process, the membrane was washed thoroughly with pure ethanol. Subsequently, the pure ethanol permeate flux of the washed membrane, J_{EtOH2} (L/ m²h) was measured and calculated using Equation 3.5.

$$J_{\mathrm{EtOH2}} = \frac{V_{\mathrm{EtOH2}}}{A\Delta T} \tag{3.5}$$

Data was collected to evaluate the flux recovery of the membrane after synthetic extractant treatment. Membrane durability was also observed through visual changes of the membrane surface.

3.6 Design of Membrane Deacidification Process

The synthetic extractant was prepared by dissolving 30 g of palmitic acid into 1 L of ethanol solution to prepare an approximately 3.0 w/v% palmitic acid in ethanol. The palmitic acid was weighed using an analytical balance, while ethanol was measured by using a 1 L measuring cylinder. The mixture was homogenously stirred until the palmitic acid was fully dissolved in the ethanol. Finally, the synthetic extractant was treated with membrane filtration and pervaporation system to study selected membranes' permeate flux and palmitic acid rejection percentage in each membrane system under different operating pressures.

3.6.1 Membrane Filtration System

A nitrogen cylinder equipped with pressure regulator was connected to the top of the dead-end stainless-steel stirred cell to supply the desired pressure for the filtration tests. The stirrer speed was controlled at 1000 rpm on the top of the active side of the membrane to minimize concentration polarization during the experiments. Figure 3.5 shows the setup of the filtration system.

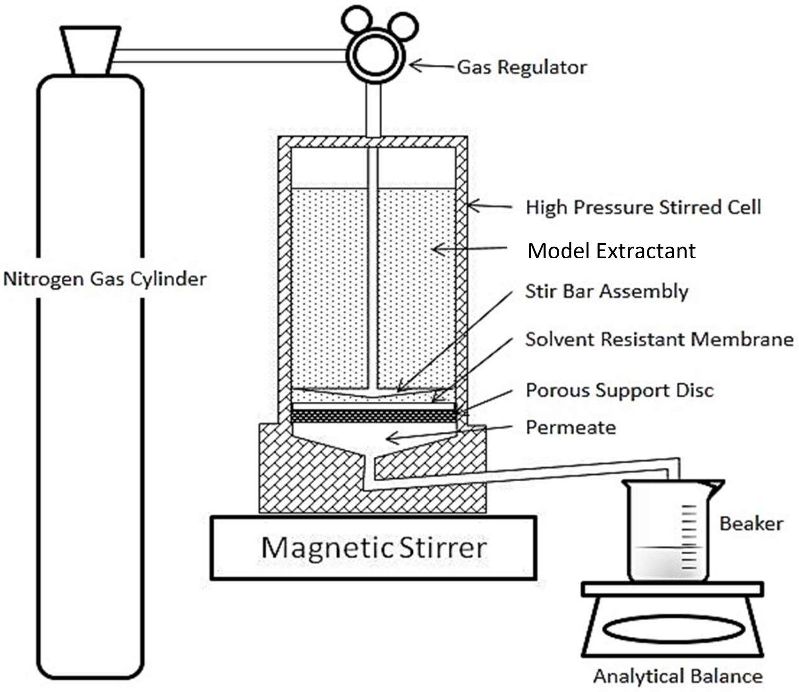


Figure 3.5: Schematic Diagram of Membrane Filtration System Setup

The feed was filled up with 0.2 L of 3 w/v% synthetic extractant. The permeated solution for the synthetic extractant was collected in a beaker at different pressure conditions of 8, 12, 16 and 20 bar at 25 °C for 30 min. The collected permeation was measured using an analytical balance to calculate the filtration flux with Equation 3.4. The rejection, *R* (%) of palmitic acid at the studied filtration pressure was calculated using Equation 3.5 after determining the concentration of palmitic acid in feed and permeate using GC-FID,

$$R\,(\%) = (1 - \frac{C_\mathrm{p}}{C_\mathrm{f}}) \times 100 \tag{3.5}$$

where C_p is the concentration of palmitic acid in permeate and C_f is the concentration of palmitic acid in feed.

3.6.2 Membrane Pervaporation System

The top connection of dead-end stainless-steel stirred cell was closed with a stainless-steel valve. The outlet piping of the dead-end stainless-steel stirred cell was connected to a three-way ball valve, where the other two outlets of the valves were connected to two high-efficiency vacuum cold-traps inside a Dewar flask that contained liquid nitrogen. For each run, the system was stabilized for 30 minutes with one of the vacuum cold-traps before switching to the other vacuum cold-trap to collect permeated vapor that was condensed by liquid nitrogen from the synthetic extractant feed. A polytetrafluoroethylene (PTFE)-coated vacuum pump (Model: 79200-05, Cole-Parmer, USA) equipped with both vacuum gauges and regulator was connected to the high-efficiency vacuum cold-trap through a three-way ball valve to supply the desired vacuum to the system for pervaporation tests. The stirrer speed was controlled at 1000 rpm on the top of the active side of the membrane to minimize concentration polarization during the experiments. Figure 3.6 shows the setup of the pervaporation system.

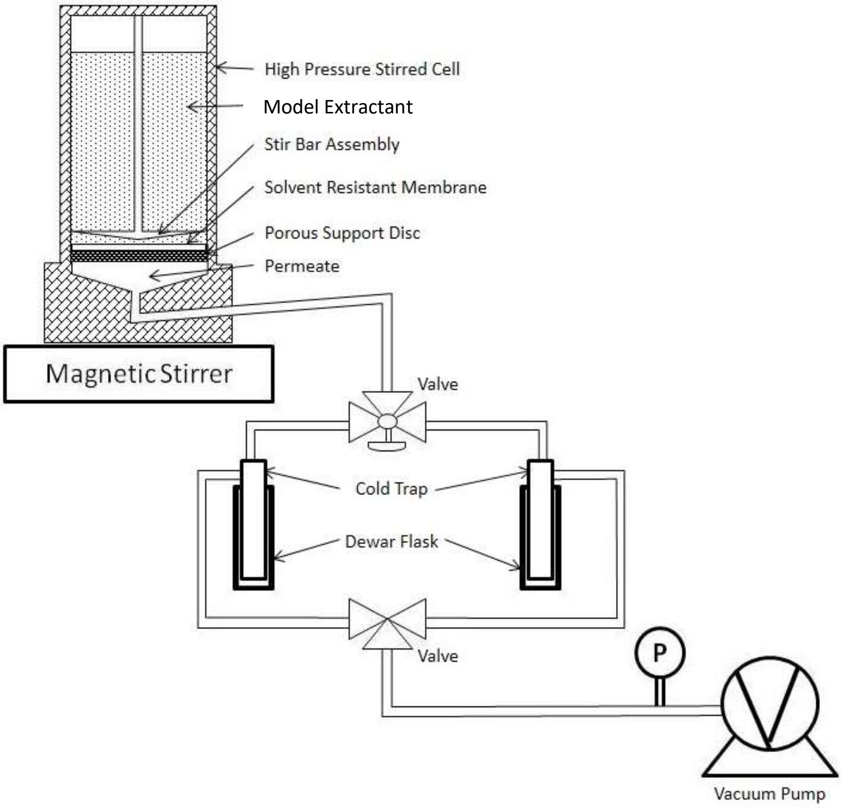


Figure 3.6: Schematic Diagram of Pervaporation System Setup

The feed was filled up with 0.2 L of 3 w/v% synthetic extractant. The permeated vapor for the synthetic extractant was condensed by the liquid nitrogen inside the Dewar flask and collected in the high-efficiency vacuum cold-trap at various vacuum conditions of 200, 300, 400, 500 mmHg at 25 °C for 1 hour. The collected permeation was weighed using an analytical balance to calculate the flux with Equation 3.4. The rejection, *R* (%) of palmitic acid, on the other hand, at studied vacuum pressure was calculated using Equation 3.6

after determining the concentration of palmitic acid in the feed and permeate using GC-FID.

3.6.3 Analysis of Free Fatty Acid by Gas Chromatography with Flame Ionization Detector (GC- FID)

Gas chromatography (GC) is an effective and efficient analytical method that is commonly used to analyse volatile compounds with the aids of inert gaseous mobile phase. The volatile compounds will be separated by the stationary phase inside the column in a way that the volatile compounds with greater affinity with the mobile phase reaches the detector faster, while the volatile compounds with greater affinity with the stationary phase moves slower through the column to the end of the detector. GC with flame ionization detector (GC-FID) (Model: Clarus 500, PerkinElmer, USA; Figure 3.7) was used in this study for the measurement of palmitic acid concentration.

Figure 3.7: Gas Chromatograph (Model : Clarus® 500, PerkinElmer, USA)

GC conditions were modified from Phenomenex (2017), to analyze palmitic acid using Zebron™ ZB-FFAP (Phenomenex, USA) as shown in Table 3.5. A palmitic acid standard with known concentration was used for calibration and peak identification before each test run. Palmitic acid standard curve was plotted from 1% to 5% to determine the sample concentration by comparing the peak retention time (appearance time) of the standard palmitic acid and areas.

Table 3.5: GC Conditions for Palmitic Acid Analysis

Component	Condition
Column	Zebron™ ZB-FFAP, GC Cap. Column 30 m × 0.25 mm × 0.25 µm
Phase	Nitroterephthalic Acid Modified Polyethylene Glycol
Dimensions	30 m × 0.25 mm × 0.25 µm
Injector	Split 10:1 1 µL at temperature 280°C
Sample Volume	1.00 µL
Oven Profile	Initial temperature 160 °C, hold for 2 minutes, increase with ramp of 8 °C/ minutes to 260 °C, hold for 3 minutes
Carrier gas	Constant Flow Helium, 2.4 mL/ minutes
Detector	Flame Ionization, Temperature 280 °C
Oven Profile	Initial temperature 160 °C, hold for 2 minutes with Ramp of 8 °C/ minutes to 260 °C, hold for 3 minutes

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Solvent Extraction Integrated with Membrane Technology

In this section, the best palmitic acid extraction solvent among acetone, ethanol, hexane, methanol and isopropanol towards synthetic acidified palm oil system was discussed. The solvent that exhibited the best palmitic acid extraction was used for subsequent studies on extraction parameters including mass ratio, water content and extraction temperature. The palmitic acid concentration in the solvent extraction study was determined by measuring the sample acidity using titration method.

Palmitic acid was selected for the preparation of synthetic acidified palm oil in this study because it is the major fatty acid composition (43.7%) in CPO. In addition, it also has smaller molecular weight of 256.42 g/mol compared to oleic acid which is the secondary fatty acid composition (39.9%) with molecular weight of 282.46 g/mol. The amount of palmitic acid in synthetic acidified palm oil was set as 5.0% because this is the standard specification for maximum free fatty acid present in palmitic acid that can be accepted in crude palm oil under the Palm Oil Refiners Association of Malaysia (PORAM) (MPOB, 2011) and Sime Darby Jomalina Sdn. Bhd (Sime Darby Plantation, 2011).

4.2 Solvent Extraction

The preliminary solvent extraction study was performed using different solvents including acetone, ethanol, hexane, methanol and isopropanol in the mass ratio of 1: 2 of synthetic acidified palm oil to solvent at 55 ± 0.1 °C (mean ± standard deviation) in a shaking water bath for 2 h. As shown in Figure 4.1, acetone, hexane and propanol appeared to be miscible with both oil and palmitic acid. This finding indicated that acetone, hexane and propanol were able to dissolve not only palmitic acid, but also high content of oil, which did not allow a clear separation of the phases as palmitic acid/ solvent-rich extractant and oil-rich raffinate phase (Fornasero et al., 2013). On the other hand, ethanol and methanol formed two clear, separate extractant and raffinate phases. These separate phases were essential for the following stage of solvent recovery using membrane technology. The raffinate phase was used to measure the remaining palmitic acid using titration method.

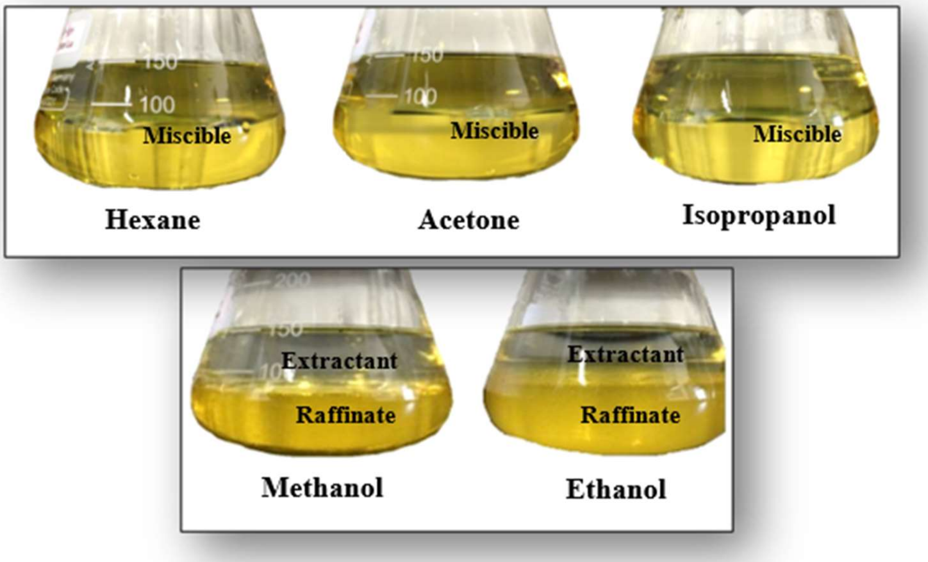


Figure 4.1: Formation of Immiscible and Miscible Mixture in Solvent Extraction by Acetone, Ethanol, Hexane, Methanol and Isopropanol

4.2.1 Solvent Type

The basic and efficiency of deacidification using solvent extraction strongly depends on the differential solubility between FFA and oil in solvent. Figure 4.2 demonstrates that ethanol had the best palmitic acid extraction which was able to extract 65.48 ± 1.71% of palmitic acid in the synthetic acidified palm oil compared with other solvent solutions evaluated in this study. Likewise, methanol demonstrated 62.49 ± 0.98% which was just inferior to ethanol. The palmitic acid reduction in raffinate of isopropanol, acetone and hexane were not able to be determined as there were no two separate phases of raffinate and extractant.

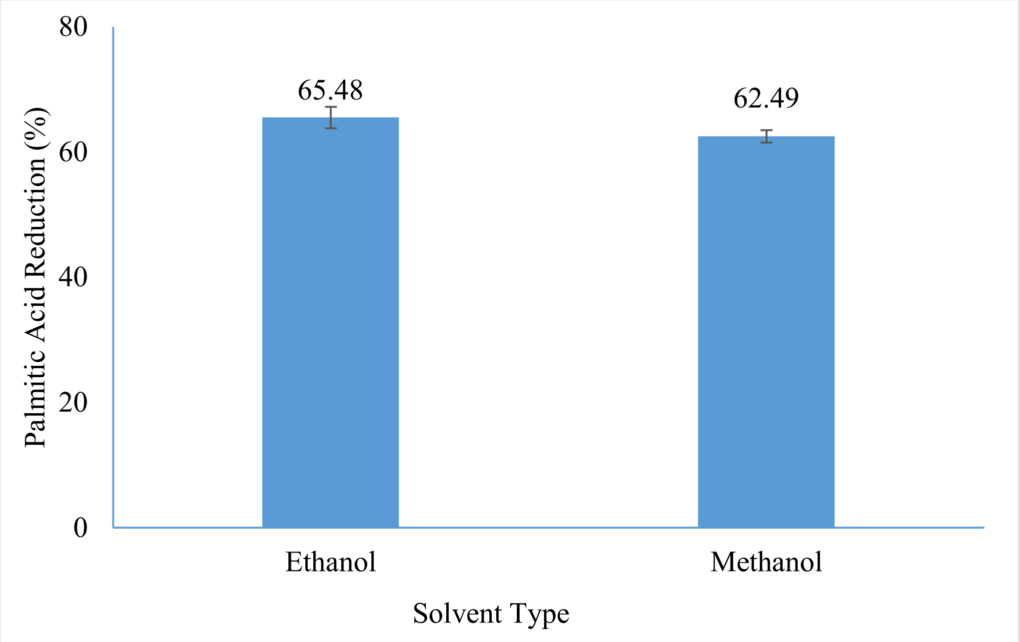


Figure 4.2: Percentage of Palmitic Acid Reduction in Different Solvents in the Mass Ratio 1: 2 of Synthetic Acidified Palm Oil to Solvent at 55 ± 0.1 °C in a Shaking Water Bath for 2 h

Johnson and Lucas (1983) emphasized that solvent type was very important in solvent-solvent extraction. Oil is more soluble in hexane due to the stronger solute-solvent interaction compared to polar solvent, making it less suitable in FFA and oil separation. Polar solvent such as ethanol will be more suitable for FFA separation from oil according to the principle of dissolution, namely ‘like dissolves like’, which indicates that polar solute such as FFA is more soluble in polar solvent, while non-polar solute such as oil will be repelled from the polar solvent layer.

Bastista et al. (1999) also found that the coefficient of distribution for fatty acid with ethanol was larger than 1 in comparison to methanol. The results indicated that ethanol had a stronger fatty acid extraction capacity. Moreover, two separate phases of raffinate and extractant allowed the recovering of solvent from extractant by separating the solvent from palmitic acid and other extracted compounds via membrane technology. However, even though methanol is polar solvent, it is able to dissolve certain nonpolar solutes such as oil because the energy earned in the solute-solvent interaction is larger than the disruption of solvent-solvent interaction (Johnson and Lucas, 1983). Hence, methanol was found to be less selective for palmitic acid and oil compared to ethanol in this study.

The desired properties of selected solvent should have great distribution coefficient, high selectivity towards palmitic acid and little or no miscibility with synthetic acidified palm oil as well as the ease of recovery. As a result, ethanol was selected for further extraction parameter study to obtain the best extraction conditions during the solvent extraction phase. Besides, ethanol has low toxicity and more cost efficiency (Fornasero et al., 2013), which also make it outstanding from other solvents in this study. Carcinogenic compounds are not present in ethanol as well (Cheryan, 2005). A previous study also supported that using ethanol as the extraction solvent allowed deacidification of crude oil to preserve great nutraceutical components with the minimum oil loss (Gonçalves et al., 2007).

4.2.2 Extraction Temperature

The percentages of palmitic acid reduction in the synthetic acidified palm oil to ethanol mass ratio of 1:2 at different temperatures of 45, 55, 65 and 75 °C, labelled as T1, T2, T3 and T4 respectively are tabulated in Table 4.1. The result in this study revealed that the best equilibrium constant value for ethanol extraction was found at 55 °C with the greatest oil extraction capacity. Baümler et al. (2016) demonstrated that the equilibrium constant of ethanol was strongly influenced by temperature. It was found that the equilibrium constant value decreased with increasing temperature, suggesting that the ethanol extraction capacity increased with temperature. The increase in temperature accelerates the diffusion and mutual solubility of the oil while at the same time decreasing viscosity (Batista et al., 1999). However, once the temperature was close to the solvent evaporation temperature, for example 78 °C for ethanol, the solvent tends to evaporate; hence, slightly reducing the extraction efficiency of the solvent.

Table 4.1: Percentage of Palmitic Acid Reduction in the Synthetic Acidified Palm Oil to Ethanol Mass Ratio of 1: 2 at Different Temperatures, T1 = 45 °C; T2 = 55 °C; T3 = 65 °C; T4 = 75 °C in a Shaking Water Bath for 2 h

Sample	Temperature (˚C)	Palmitic Acid Reduction (%)
T1	45	62.43 ± 1.18
T2	55	65.48 ± 1.71
T3	65	65.07 ± 0.77
T4	75	63.07 ± 1.49

4.2.3 Solvent to Synthetic Acidified Palm Oil Mass Ratio

The percentages of palmitic acid reduction at 55 °C with different synthetic acidified palm oil to ethanol mass ratios of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 were labelled as R1, R2, R3 and R4 respectively as shown in Figure 4.3. The result indicated that the higher solvent volume was able to reduce more palmitic acid. For the synthetic acidified palm oil to solvent mass ratio of 1: 4 in R4 sample, the palmitic acid was successfully reduced up to 81.28 ± 1.01%. This has resulted in less than 1% of palmitic acid found in the raffinate phase, indicating that the best palmitic acid reduction mass ratio. The reducing FFA reduction percentages were observed in R3, R2 and R1 samples, which were 76.99 ± 4.21%, 65.48 ± 1.71%, and 48.57 ± 1.77%,respectively. Baümler et al. (2016) also reported that the extraction ability of ethanol was highly affected by the oil to solvent ratio. With the presence of higher extraction solvent volume, the residual extractable material in the solid phase decreased, indicating better FFA extraction capacity. However, high amount of solvent usage in extraction is not favourable in the industry as this will increase the operation cost. Hence, the synthetic acidified palm oil to ethanol mass ratio of 1: 2 which was able to reduce more than 50% palmitic acid was selected in the following parameter studies.

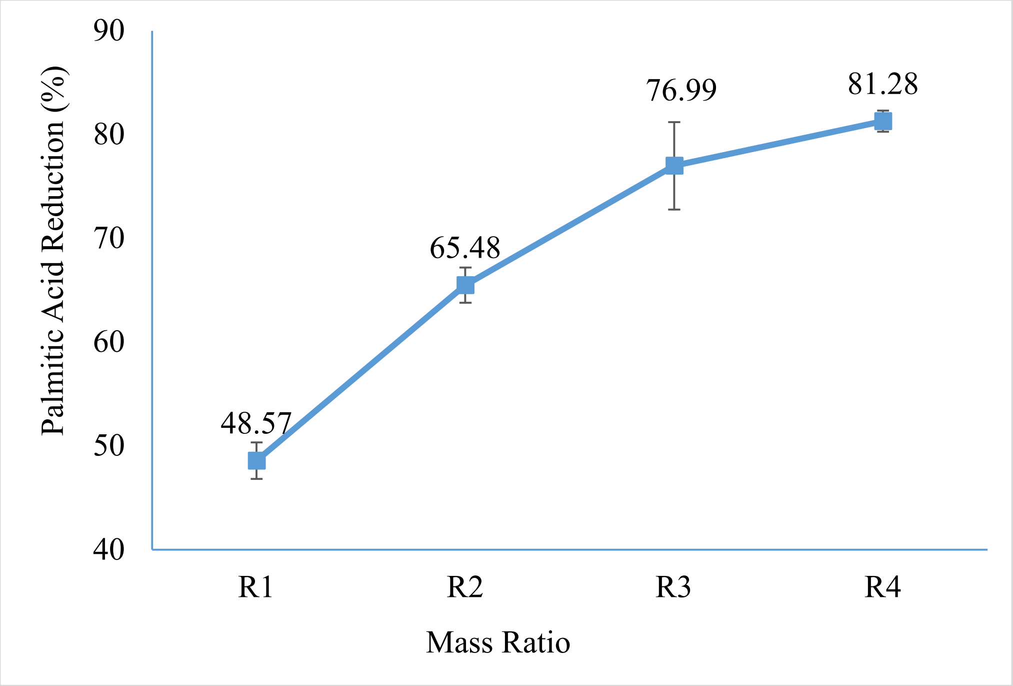


Figure 4.3: Percentage of Palmitic Acid Reduction in Ethanol with Different Mass Ratios, R1= 1: 1; R2= 1: 2; R3= 1: 3; R4= 1: 4 of Synthetic Acidified Palm Oil System to Solvent at 55 ± 0.1 °C in a Shaking Water Bath for 2 h

4.2.4 Water Content

On the other hand, the result shown in Table 4.2 demonstrated that the addition of water did not help to induce the palmitic acid extraction. Palmitic acid extraction rate decreased when water content level increased. For 80% ethanol

(W5), only 40.19 ± 6.78% of palmitic acid was extracted. The extraction rate increased from 48.52 ± 6.46% to 65.48 ± 1.71% when the water content decreased from 15% to 0%. The observation is in agreement with the study of Oliveira et al. (2012) on rice bran oil, indicating that aqueous ethanol (with water content of 6.34 to 28.29 mass %) would reduce the amount of oil solubilized in the ethanol-rich phase which then reduced the FFA extraction. Chiyoda et al. (2010) also concluded that the increase in water content in solvent reduced FFA extraction. Their study suggested that oil might become solvated in an aqueous ethanol via hydrophobic hydration due to strong interaction between water and oil, which then reduced the oil solubility in solvent, leading to low FFA extraction.

Table 4.2: Percentage of Palmitic Acid Reduction in Ethanol with Different Water Content W1 = 0%, W2 = 5%, W3 = 10%, W4 = 15% and W5 = 20% in the Mass Ratio 1: 2 of Synthetic acidified Palm Oil to Solvent at 55 ± 0.1 °C in a Shaking Water Bath for 2 h

Sample	Water Content, W (%)	Palmitic Acid Reduction (%)
W1	0	65.48±1.71
W2	5	62.17 ± 2.92
W3	10	55.37 ± 4.81
W4	15	48.52 ± 6.46
W5	20	40.19 ± 6.78

As a conclusion, the most suitable and cost effective parameters of solvent extraction for synthetic acidified palm oil in this study were determined as a synthetic acidified palm oil to ethanol mass ratio of 1: 2 at 55 ± 0.1 °C using pure ethanol. With these parameters, the palmitic acid was successfully reduced to only 1.7% which was better than the study of Kale et al. (1999) using methanol as the extraction solvent.

The solvent used in this study can be reused for subsequent extraction to fulfil the percentage of palmitic acid of not more than 0.25% in neutralized palm oil and 0.1% in commercial cooking oil set by PORAM (MPOB, 2011). Kale et al. (1999) reported that the FFA percentage of crude rice bran oil was reduced from 16.5% to 3.7% using solvent extraction with an optimal methanol/oil (by weight) ratio of 1.8: 1. Subsequently, a second extraction was performed at 1: 1 ratio, and the FFA percentage was effectively reduced to 0.33%. This finding suggested that ethanol could be reused for second extraction to improve the palmitic acid extraction in this study.

4.3 Membrane Characterization

Five commercially available membranes were selected including three PDMS with silicone based supported SRNF membranes, namely NF010206, NF030306 and NF030705, cellulose triacetate non-woven support (CTA-NW) forward osmosis (FO) membrane, and polyamide thin-film composite reverse osmosis membrane SW30XLE were studied. The selected membrane underwent a series of characterization studies including SEM, hydrophobicity, permeate flux and membrane fouling.

4.3.1 Membrane Cross-sectional Structure by Scanning Electron Microscope

SEM images of the cross section for the five selected membrane, including SRNF membrane NF010206, NF030306 and NF030705, CTA-NW membranes, as well as SW30XLE membrane were examined before and after the studies of membrane filtration and pervaporation systems. For each membrane, the images were captured for clean membrane and membrane after the membrane system study. The change in cross-sectional structures of membrane is important to observe the membrane stability under pressure condition.

As shown in Table 4.3 (a), NF010206 membrane demonstrated an outer surface layer with thin sponge-like structure extended toward thick finger-like microvoid layer, followed by a thick nonwoven fabric supportive layer. After the membrane system study, the finger-like microvoid layer collapsed and was left with only nonwoven fabric layer as observed in Table 4.3 (b).

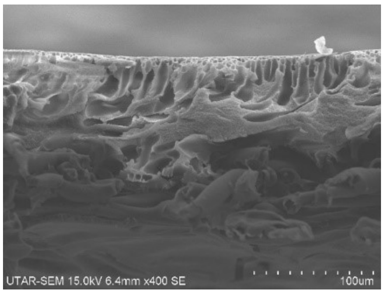
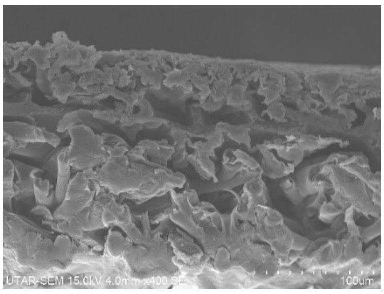
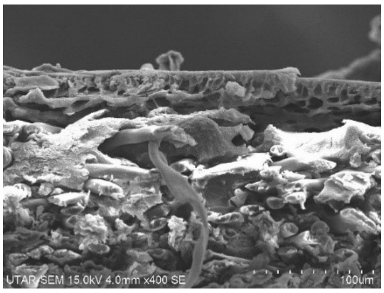
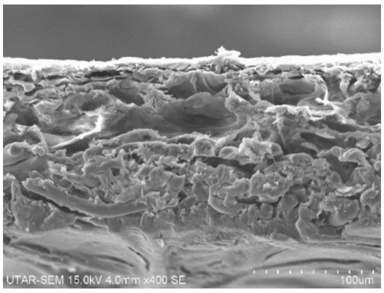
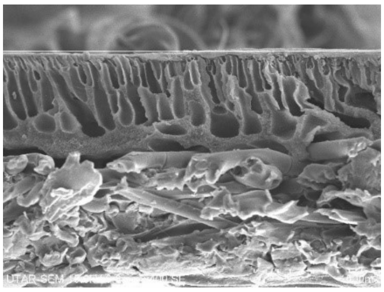
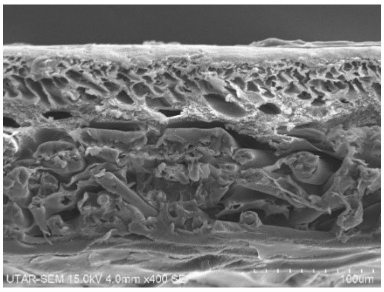
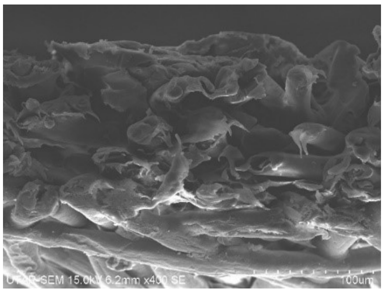
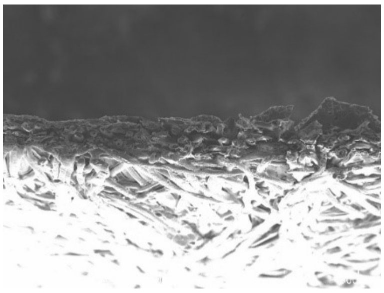
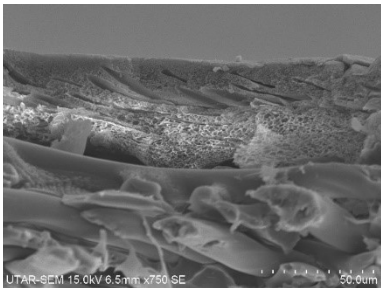
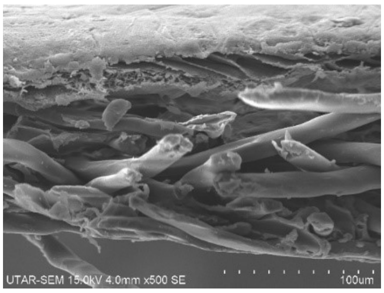
NF030306 membrane in Table 4.3 (c) displayed a thick finger-like microvoid or porous layer, followed by a thick nonwoven fabric supportive layer. However, after the membrane system study, the thick finger-like microvoid and porous layer were compressed, and only nonwoven fabric layer could be observed as in Table 4.3 (d). Besides, physical damage was also found on NF030306 membrane after the membrane system study with a slight tear-off appearance as depicted in Figure 4.4.

NF030705 membrane in Table 4.3 (e) presented a thick finger-like microvoid outer layer extended to the thin sponge-like layer. Identical to both SRNF membranes (NF010206 and NF030306 membranes), NF030705 membrane also has a thick nonwoven fabric supportive layer. However, after the membrane system study, the thick finger-like microvoid was compressed as shown in Table 4.3 (f).

CTA-NW membrane in Table 4.3 (g) exhibited an ultra-thin sponge-like morphology active layer with a thick nonwoven fabric supportive layer which was similar to SRNF membrane. CTA membrane is known to have higher resistance to chemicals such as chlorine and biological attack (Nakao et al., 2021). However, after the membrane system study, the membrane was compressed as illustrated in Table 4.3 (h). Parts of the membrane’s active and supportive layers were separated as observed in the SEM examination and severe membrane swelling was observed (Figure 4.5). This might be the reason why CTA-NW membrane demonstrated the lowest permeate flux in the membrane filtration system.

SW30XLE membrane (Table 4.3 (i)) composed of ultrathin polyamide barrier layer on the top surface and a thick microporous or sponge-like morphology polysulfone interlayer which was supported with polyester web. After the membrane system study, the ultrathin polyamide barrier layer on the top surface and the thick microporous or sponge-like polysulfone interlayer were harshly compressed and collapsed right above the polyester web supportive layer as observed in Table 4.3 (j).

Table 4.3: Cross-Sectional Image of Selected Membrane Before and After Membrane System Study using SEM

Membrane	Before	After
NF010206	 (a)	 (b)
NF030306	 (c)	 (d)
NF030705	 (e)	 (f)
CTA-NW	 (g)	 (h)
SW30XLE	 (i)	 (j)

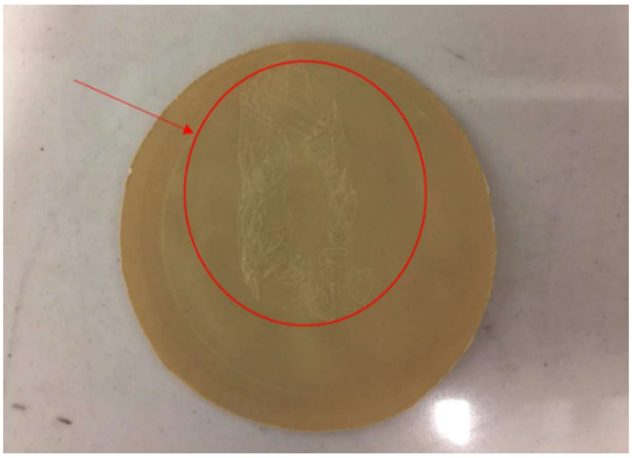


Figure 4.4: Physical Damage on NF030306 after Membrane System Study

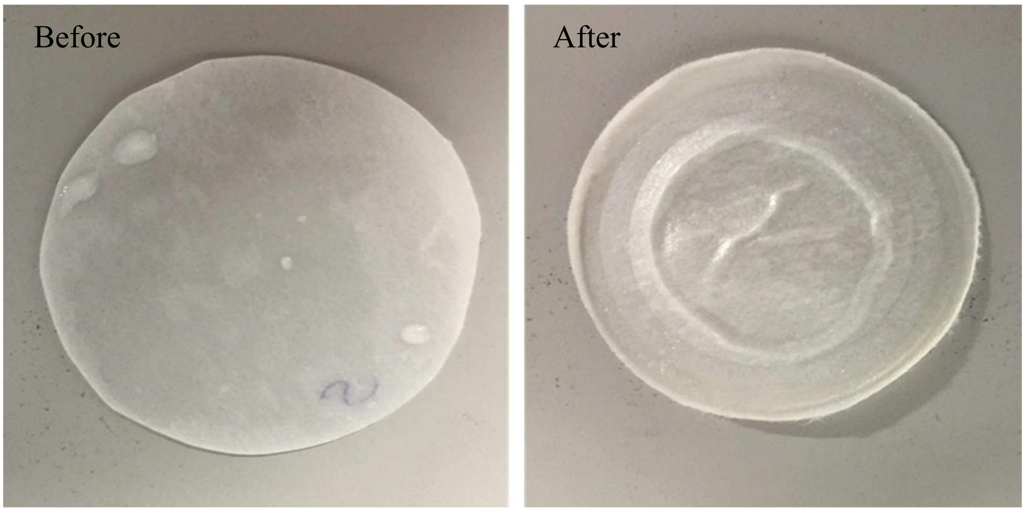


Figure 4.5: CTA-NW Membrane with Severe Swelling after Membrane System Study

4.3.2 Determination of Membrane Hydrophobicity

Generally, if the water contact angle is smaller than 90°, the membrane surface is considered as hydrophilic, while for the water contact angle greater than 90°, the membrane surface is considered as hydrophobic. Many polymers exhibit hydrophobic surfaces. Table 4.3 showed that NF030705 membrane possessed the greatest hydrophobicity with a contact angle of 108.58° ± 1.87°, followed by NF030306 membrane (94.32° ± 1.36°), while NF010206 membrane (78.84° ±

3.28º) was slightly hydrophilic. In addition, both CTA-NW and SW30XLE membranes which were originally designed for water treatment exerted great hydrophilicity.

Table 4.4: Membrane Contact Angle and Property

Membrane	Contact Angle (°)	Membrane Property
NF010206	78.84 ± 3.28	Hydrophilic
NF030306	94.32 ± 1.36	Hydrophobic
NF030705	108.58 ± 1.87	Hydrophobic
CTA-NW	65.10 ± 1.43	Hydrophilic
SW30XLE	66.72 ± 6.34	Hydrophilic

4.3.3 Membrane Permeate Flux and Fouling

As presented in Figure 4.6, all membranes presented a stable permeate flux, except NF030306 membrane. The non-linear and flux reduction trends of NF030306 in the synthetic extractant permeate flux were possibly attributed to membrane compaction and fouling effect. The membrane compaction of NF030306 membrane could be obviously viewed under SEM as shown in Table 4.3 (d) with the collapsed finger-like microvoid. Moreover, NF030306 membrane is a hydrophobic membrane with small pore size, which is less fouling-resistant than other hydrophilic membrane with similar pore size such as NF010206. For a membrane that has relatively large pores, the viscous flow may overcome the polarity effects. In the permeate flux study, NF030705 membrane expressed the highest permeate flux due to the larger pore size. When compared among membranes with almost similar pore size, hydrophilic membrane SW30XLE exhibited the highest permeate flux followed by NF010206. The poor performance of CTA-NW was anticipated since this membrane is not designed as solvent-resistant membrane and encountered a severe swelling after filtration treatment.

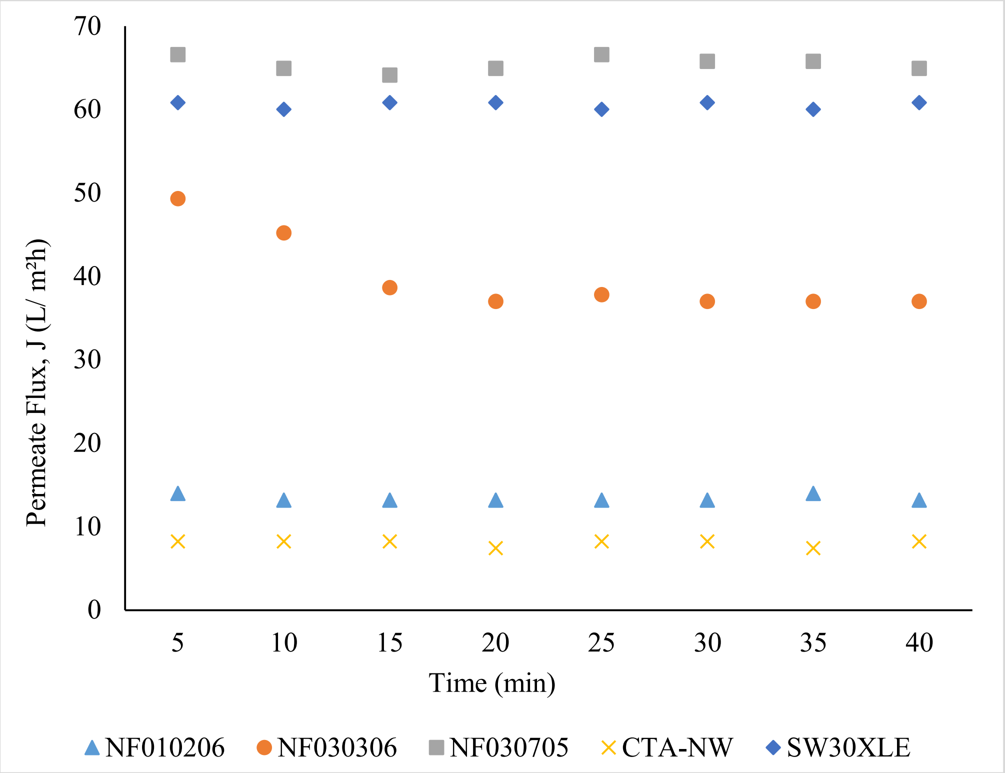


Figure 4.6: Performance in Terms of Permeate Flux Stability of Five Selected Membranes under Operating Pressure of 20 Bar for 40 min

4.3.4 Flux Recovery

NF030306 membrane was found to have drastic increase in permeate flux using pure ethanol after synthetic extractant that contained palmitic acid in Figure 4.7. In addition, this membrane was physically damaged as depicted in Figure 4.4 with slight tear-off and swelling after membrane fouling study. It is possible that the membrane was not suitable to be under high pressure. On the other hand, NF030705 membrane had the second highest ethanol flux with the best membrane stability with 100% recovery after rinsing with ethanol. Most of the membranes were found to have higher permeate flux after rinsing, except that CTA-NW indicated that all membranes were able to be recovered after treatment.

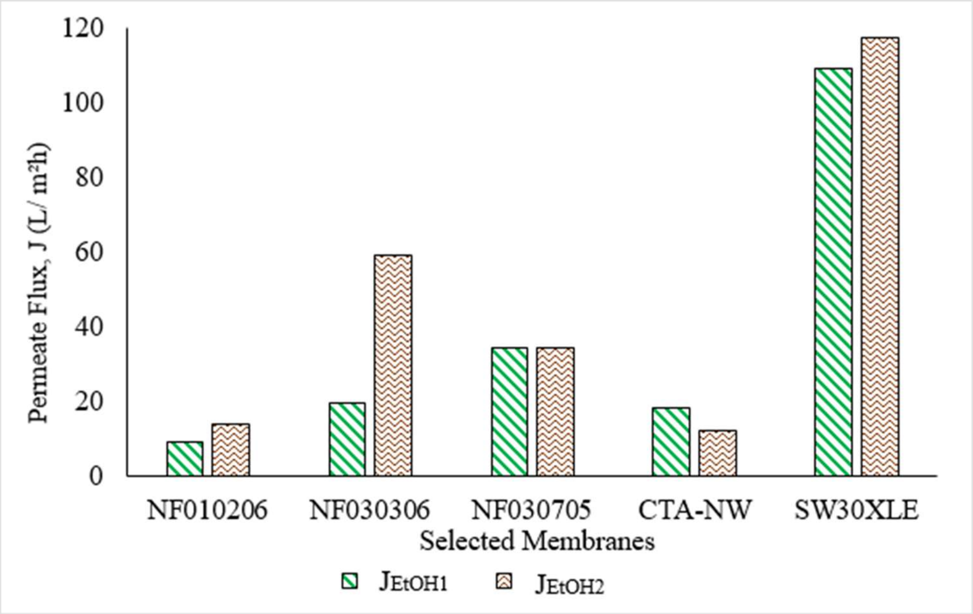


Figure 4.7: Performance in Terms of Flux Recovery of Five Selected Membranes by Compare the Pure Ethanol Permeate Flux Before ($J_{EtOH\ 1}$) and After ($J_{EtOH\ 2}$) Run with Synthetic Extractant at 20 bar for 40 min at 25 °C

4.4 Membrane Systems

For the downstream process, palmitic acid and ethanol in synthetic extractant were separated via two membrane systems, i.e., membrane filtration and pervaporation systems. The effect of different pressures of 8, 12, 16, and 20 bar on flux and selectivity at 25 °C was determined. Besides, the effect of various vacuum conditions of 200, 300, 400, 500 mmHg on flux and selectivity at 25 °C was also investigated.

4.4.1 Membrane Filtration System

Figure 4.8 and Table 4.5 show the effects of operating pressure on membrane permeation flux and palmitic acid rejection for the membrane filtration system respectively. In principle, the best membrane should be able to achieve both high permeate flux and solute rejection. Nonetheless, the increase of operating pressure was found to enhance the permeate flux, but the membrane solute rejection would be reduced (Ismail and Ghazali, 2018).

The highest permeate flux expressed by NF030705 membrane and the permeate flux increased proportionally to the operating pressure as shown in Figure 4.8. NF030705 membrane had the largest MWCO as shown in the membrane manufacturer's data sheet with only 70% oily molecule (MW ~1000 Da) rejection in ethanol. This could explaine why NF030705 membrane demonstrated the highest flux but with low palmitic acid rejection. The nonliner increase of flux versus pressure in all selected membranes could be attributed to the formation of gel layer and pore blocking of the membrane when higher pressure was applied.

Surprisingly, this study showed that SW30XLE membrane was found to possess an acceptable permeate flux which was 36.88 L/m^{2}h with 100% rejection of palmitic acid at the operating pressure of 8 bar. The increasing operating pressure could enhance the permeate flux of SW30XLE membrane, yet the membrane solute rejection reduced significantly. SW30XLE is a hydrophilic RO-membrane, that has dense structure and ultra-thin polyamide barrier layer on the top surface. Solvent transport across this membrane will experience more polarity effect at low pressure. However, high pressure will lead to convective transport across the thin active layer, which later produced high permeate flux but low selectivity as the interlayer is microporous polysulfone (Sae-Khow and Mitra, 2010). Low operating pressure with only 8 bar has resulted in acceptable permeate flux and 100% palmitic acid rejection, indicating that SW30XLE membrane has high potential in solvent recovery.

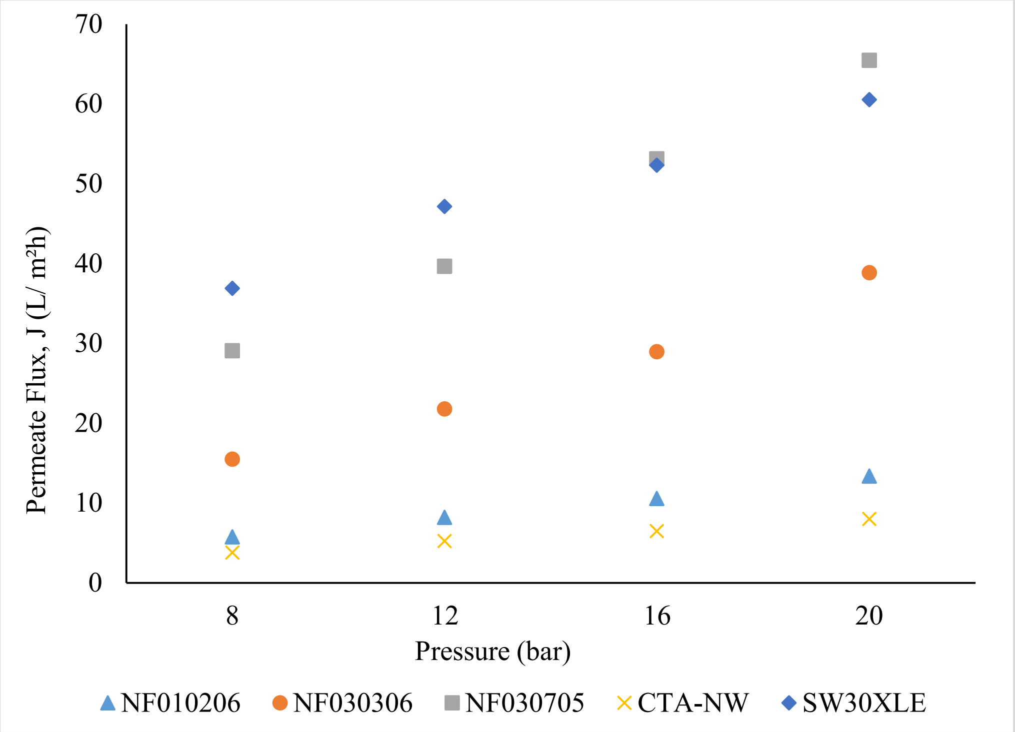


Figure 4.8: Permeate Flux (L/m².h) of Five Selected Membranes at Different Operating Pressures of 8, 12, 16 and 20 bar

Table 4.5: Effect of Operating Pressure on Palmitic Acid Rejection in Synthetic Extractant by Five Selected Membranes at 8, 12, 16 And 20 Bar

Pressure (Bar)	Palmitic Acid Rejection, R (%)				
	NF010206	NF030306	NF030705	CTA-NW	SW30XLE
8	31.59	9.56	12.56	98.44	100.00
12	27.66	8.92	11.08	59.60	17.31
16	13.50	3.79	8.22	58.38	15.47
20	11.38	1.57	1.33	51.40	14.02

4.4.2 Membrane Pervaporation System

Figure 4.9 and Table 4.6 demonstrate the effects of vacuum pressure on permeate flux and palmitic acid rejection for the membrane pervaporation system respectively. Most selected membranes exhibited 100% palmitic acid rejection under all vacuum pressure conditions, except for NF030705 and CTA-NW membranes. NF030705 membrane had exhibited > 74.99% palmitic acid rejection when the vacuum pressure was reduced to 400 mmHg. NF030705 is a porous nano-membrane; hence, the permeation is affected by size exclusion (Sae-Khow and Mitra, 2010). Both ethanol and water which are smaller than the membrane pore size will be able to permeate through the membrane, and provide higher flux but lower selectivity. Meanwhile, for CTA-NW membrane, there was no permeate flux found after the vacuum pressure of 400 mmHg, possibly due to membrane compaction and pore swelling.

In non-porous membranes, the separation of molecules is influenced by distribution coefficient as well as diffusivity of the component in the membrane. SW30XLE is a thin film composite membrane that consists of an ultra-thin polyamide dense surface layer on top of the microporous support layer. The top layer will determine the membrane selectivity, but the partial vapor pressure will determine the passage of component to the permeate part (Sae-Khow and Mitra, 2010). Ethanol has vapor pressure of 1.040 mPa, while palmitic acid has 0.051 mPa at 25 °C. Hence, ethanol will evaporate first and diffuse across the membrane, from which its selectivity can be determined. Overall, the pervaporation exhibited a very low permeate flux which was less than 1.28 L/

m²h in most of the selected membranes, making it non feasible to be used in the industry.

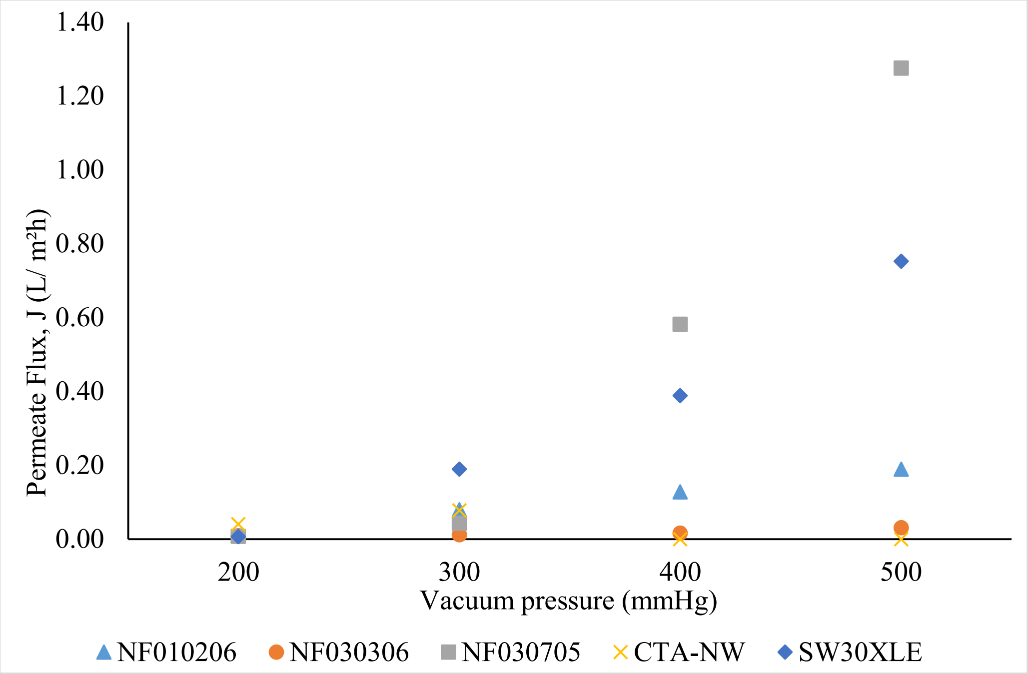


Figure 4.9: Permeate Flux (L/ m².h) of Five Selected Membranes at Different Vacuum Pressure of 200, 300, 400 and 500 mmHg

Table 4.6: Effect of Vacuum Pressure on Palmitic Acid Rejection in Synthetic Extractant by Five Selected Membranes at 200, 300, 400 And 500 mmHg

Vacuum	Palmitic Acid Rejection, R (%)				
(mmHg)	NF010206	NF030306	NF030705	CTA-NW	SW30XLE
200	100.00	100.00	100.00	100.00	100.00
300	100.00	100.00	100.00	100.00	100.00
400	100.00	100.00	74.99	NA	100.00
500	100.00	100.00	63.31	NA	100.00

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

As a conclusion, ethanol was found to be the most effective solvent for palmitic acid extraction at 55 °C with synthetic acidified palm oil to solvent mass ratio of 1: 4. The palmitic acid was successfully reduced up to 81.28 ± 1.01% without the aid of water. High amount of solvent usage in extraction is not economically feasible in industrial application as this will increase the operation cost. Membrane technology provides an alternative since the solvents are able to be reused for batch solvent extraction which helps to further improve the oil quality. This greener solvent gives rise to an environmentally and economically friendly deacidification method.

Hydrophobic membrane (such as NF030705) showed the highest permeate flux with a low palmitic acid rejection, whereas hydrophilic nanofiltration membranes demonstrated both low permeate flux and palmitic acid rejection. Meanwhile, both NF030306 and CTA-NW membranes exhibited poor filtration ability and fouling with visible defects after exposure to ethanol. In this research, SW30XLE membrane which was composed of both hydrophilic top surface and hydrophobic polysulfone interlayer was the most promising membrane to be used in the deacidification with membrane technology. This membrane exhibited acceptable permeate flux (36.88 L/m²h) and 100% FFA rejection in the filtration system.

Overall, filtration system performed better than pervaporation in separating the FFA and ethanol in this research. The filtration system was able to produce 100% FFA rejection with 30 times higher permeate flux. Pervaporation exhibited a very low permeate flux which was only less than 1.28 L/m²h in most of the selected membranes, making it to be unusable in the industry.

5.2 Recommendations

The solvent extraction integrated with membrane technology to deacidify the CPO is certainly a potential and suitable solution to be applied at laboratory scale. Most of the by-products and chemicals used can be recycled and reused through this method. The ease of this application is clearly better than conventional deacidification methods. However, to avoid interference of the extraction and recovery, the solvent extraction and membrane technology were observed separately in this study. In future, the integrated process can be studied in the presence of the impurities by using crude palm oil. The use of this integrated method in the industry will also pose a challenge, where the quantity produced are far lower compared with the conventional deacidification. Therefore, further research is required to identify the solvent with higher extraction ability, and membrane with higher permeation and selectivity for the integrated solvent extraction with membrane technology as an economically and environmentally friendly CPO deacidification method, followed by solvent recovery to produce high quality edible oil.

REFERENCES

Abdullah, R., 2003. Short-Term and Long-Term Projection of Malaysian Palm Oil Production. *Oil Palm Industry Economic Journal,* 3(1), pp. 32-36.

Alicieo, T., Mendes, E., Pereira, N. and Lima, O. M., 2002. Membrane ultrafiltration of crude soybean oil. *Desalination ,* 148, pp. 99-102.

Arora, S., Manjula, S., Krishna, A. G. and Subramaniam, R., 2006. Membrane Processing of Crude Palm Oil. *Desalination,* 191, pp. 454-466.

Azmi, R.A., Goh, P.S., Ismail, A.F., Lau, W.J., Ng, B.C., Othman, N.H., Noor, A.M., and Yusoff, M.S.A., 2015. Deacidification of crude palm oil using PVA-crosslinked PVDF membrane. *Journal of Food Engineering,* 166, pp. 165–173.

Batista, E., Monnerat, S., Kato, K., Stragevitch, L., and Meirelles A.J.A., 1999. Liquid−Liquid Equilibrium for Systems of Canola Oil, Oleic Acid, and Short-Chain Alcohols. *Journal of Chemical and Engineering Data ,* 44(6), pp. 1360-1364.

Baümler, E. R., Carrín, M. E. and Carelli, A. A., 2016. Extraction of sunflower oil using ethanol as solvent. *Journal of Food Engineering,* 178, pp. 190-197.

Bhosle, B. and Subramanian, R., 2005. New approaches in deacidification of edible oils—a review. *Journal of Food Engineering,* 69(4), pp. 481–494.

Brito Mariano, R.G., Da Silva, C.M., Freitas, S.P., Couri, S., & Nogueira, R.I., 2011. Partition of Free Fatty Acids in Deacidification of Macaúba Pulp Oil by Liquid-Liquid Extraction using Ethanol/Water as Solvent. *Defect and Diffusion Forum,* 312-315, pp. 554-559.

Cheryan, M., 2005. *Membrane technology in the vegetable oil industry,* Urbana: University of Illinois.

Chiyoda, C., Peixoto, E.C.D., Meirelles, A.J.A., and Rodrigues, C.E.C., 2010. Liquid–liquid equilibria for systems composed of refined soybean oil, free fatty acids, ethanol, and water at different temperatures. *Fluid Phase Equilibria*, 299(1), pp. 141–147. doi: 10.1016/j.fluid.2010.09.024.

Choe, E. and Min, D. B., 2006. Mechanisms and factors for edible oil oxidation. *Comprehensive Reviews In Food Science And Food Safety,* 5, pp. 169-196.

Chumsantea, S., Aryusuk, K., Jeyashoke, N., Krisnangkura, K., and Lilitchan, S., 2012. Reducing Oil Losses in Alkali Refining. *Journal of the American Oil Chemists' Society ,* 89, pp. 1913–1919.

Čmolík, J. and Pokorný, J., 2000. Physical refining of edible oils. *European Journal of Lipid Science and Technology,* 102, pp. 472–486.

Coutinho, C. d. M., Chiu, M. C., Basso, R. C. and Ribeiro, A. P. B., 2009. State of art of the application of membrane technology to vegetable oils: A review. *Food Research International,* 42 , pp. 536–550.

Danielson, M., 2015. *Malaysia Palm Oil Council.* [Online] Available at: palmoilhealth.org/news/hydrogenation-what-you-need-to-know
[Accessed 2 January 2020].

Darvishmanesha, S., Jansen, J.C., Tasselli, F., Tocci, E., Luis, P., Degrève, J., Drioli, E., and Van der Bruggen, B., 2011. Novel polyphenylsulfone membrane for potential use in solvent nanofiltration. *Journal of Membrane Science ,* 379, pp. 60-68.

Efthymiopoulos, I., Hellier, P., Ladommatos, N., Russo-Profili, A., Eveleigh, A., Aliev, A., Kay, A., and Mills-Lamptey, B., 2018. Influence of Solvent Selection and Extraction Temperature on Yield and Composition of Lipids Extracted from Spent Coffee Grounds. *Industrial Crops & Products*, 119, pp. 49–56.

Findrik, Z., Németh, G., Vasić-Rački, Đ., Bélafi-Bakó, K., Csanádi, Z., and Gubicza, L., 2012. Pervaporation-aided enzymatic esterifications in non-conventional media - Review. *Process Biochemistry ,* 47, pp. 1715–1722.

Fornasero, M. L., Marenchino, R. N. and Pagliero, C. L., 2013. Deacidification of Soybean Oil Combining Solvent Extraction and Membrane Technology. *Advances in Materials Science and Engineering 5,* pp. 1-5.

Gonçalves, C.B., Filho, P.A.P. and Meirelles, A.J., 2007. Partition of nutraceutical compounds in deacidification of palm oil by solvent extraction. *Journal of Food Engineering ,* 81, pp. 21-26.

Gonçalves, C.B., and Meirelles, A.J., 2004. Liquid–liquid equilibrium data for the system palm oil + fatty acids + ethanol + water at 318.2K. *Fluid Phase Equilibria 221 (2004) 139–150,* 221, pp. 139-150.

Gonçalves, C.B., Rodrigues, C.E.C., Marcon, E.C., and Meirelles, A.J.A., 2016. Deacidification of palm oil by solvent extraction. S*eparation and Purification Technology*, 160, pp. 106–111.

Harris, W., Bishop, F., Lyman, C. and Helpert, R., 1947. Isopropanol as a Solvent for Extraction of Cottonseed oil Preliminary Investigation. *The Journal of the American Oil Chemists' Society,* pp. 370-375.

Hashim, K., Tahiruddin, S. and Asis, A. J., 2012. Palm and Palm Kernel Oil Production and Processing in Malaysia and Indonesia. In: O. Lai, C. Tan and C. C. Akoh., eds. *Palm Oil Production, Processing, Characterization, and Uses.* United States of America: Elsevier Inc, pp. 235-250.

Ismail, D. N. F. A. and Ghazali, N. F., 2018. Separation of Fatty Acids from Palm Oil Using Organic Solvent Nanofiltration. *Malaysian Journal of Analytical Sciences,* 22(3), pp. 561-569.

Iyuke, S. E., Ahmadun, F.-R. and Majid, R. A., 2004. Process Intensification of Membrane System For Crude Palm Oil Pretreatment. *Journal of Food Process Engineering ,* 27, pp. 476–496.

Johnson, L. and Lusas, E., 1983. Comparison of Alternative Solvents for Oils Extraction. *Journal of the American Oil Chemist' Society,* 60(2), pp. 229-242.

Kale, V., Katikaneni, S. and Cheryan, M., 1999. Deacidifying Rice Bran Oil by Solvent Extraction and Membrane Technology. *Journal of the American Oil Chemist' Society,* 76(6), pp. 723-727.

Keurentjes, J. T. F., Sluijs, J. T. M., Franssen, R.-J. H. and Riet, K. v., 1992. Extraction and Fractionation of Fatty Acids from Oil Using an Ultrafiltration Membrane. *Ind. Eng. Chem. Res,* 31, pp. 581-587.

Koike, S., Subramaniana, R., Nabetania, H. and Nakajimaa, M., 2002. Separation of Oil Constituents in Organic Solvents Using Polymeric Membranes. *Journal of the American Oil Chemist' Society,* 79(9), pp. 937-941.

Li, Y., Fine, F., Fabiano-Tixier, A.-S., Abert-Vian, M., Carre, P., Pages, X., and Chemat, F., 2014. Evaluation of alternative solvents for improvement of oil extraction from rapeseeds. *Comptes Rendus Chimie,* 17, pp. 242–251.

Mancini, A., Imperlini, E., Nigro, E., Montagnese, C., Daniele, A., Orrù, S., and Buono, P., 2015. Biological and Nutritional Properties of Palm Oil and Palmitic Acid: Effects on Health. *Molecules (Basel, Switzerland)*, 20(9), pp. 17339–17361

Manshad, S., Mohd Nawawi, M.G., Sazegar, M.R., Hassan, H.B., Alamaria, A.M., 2016. Membranes with Favorable Chemical Materials for Pervaporation Process: A Review. *Journal of Membrane Science and Technology,* 6(4).

Mba, O.I., Dumont, M.-J. and Ngadi, M., 2015. Palm oil: Processing, characterization and utilization in the food industry – A review. *Food Bioscience,* 10, pp. 23-41.

MPOB (Malaysian Palm Oil Board), 2011. *About Palm Oil.* [Online] Available at: http://www.palmoilworld.org/about_palmoil.html [Accessed 20 January 2018].

MPOC (Malaysian Palm Oil Council), 2021. Monthly Stock Comparison 2021. [Online] Available at: http://mpoc.org.my/monthly-stock-comparison-2021/ [Accessed 20 May 2021].

Oliveira, C.M., Garavazo, B.R., and Rodrigues, C.E.C., 2012. Liquid–liquid equilibria for systems composed of rice bran oil and alcohol-rich solvents: Application to extraction and deacidification of oil. J*ournal of Food Engineering*, 110(3), pp. 418–427.

Okamoto, K.-I., Otoshi, Y., Semoto, T., Motoharu, M., Yano, Y., Tanaka, K., and Kita, H., 1993. Pervaporation-Aided Esterification of Oleic Acid. *Journal of Chemical Engineering of Japan,* 26(5), pp. 475-481.

PORAM (Palm Oil Refiners Association of Malaysia), 2020. *Product Specifications.* [Online] Available at: http://www.sinaranpalm.com/specifications/poram-palm-oil-refiners-association-of-malaysia/ [Accessed 20 January 2020].

Raman, L., Cheryan, M. and Rajagopalan, N., 1996. Deacidification of Soybean Oil by Membrane Technology. *Journal of the American Oil Chemist' Society,* 73, pp. 219-224.

Ribeiro, A.P.B. de Moura, J.M.L.N., Gonçalves, L.A.G., Petrus, J.C.C., and Viotto, L.A., 2006. Solvent recovery from soybean oil/hexane miscella by polymeric membranes. *Journal of Membrane Science,* 282, pp. 328–336.

Rodrigues, C. E. C., Gonçalves, C. B., Batista, E. and Meirelles, A. J. A., 2007. Deacidification of Vegetable Oils by Solvent Extraction. *Recent Patents on Engineering,* 1(1), pp. 95-102.

Rossi, M., Gianazza, M., Alamprese, C. and Stanga, F., 2001. The effect of bleaching and physical refining on color and minor components of palm oil. *Journal of the American Oil Chemist' Society,* 78, pp. 1051–1055.

Rozario, M., 2013. *National Biomass Strategy 2020: New wealth creation for Malaysia's biomass industry.* 2nd ed. Kuala Lumpur: Agensi Inovasi Malaysia.

Sae-Khow, O. and Mitra, S., 2010. Pervaporation in chemical analysis. *Journal of Chromatography A*, 1217(16), pp. 2736–2746.

Sarode, M., 2009. Simultaneous degumming, dewaxing and decolorizing crude rice bran oil using nonporous membranes. *Separation and Purification Technology,* 66, pp. 223-228.

Shahidi, F., 2005. *Bailey's Industrial Oil And Fat Products.* 6th ed. Canada: John Wiley and Sons.

Shuit, S.H. and Tan, S.H., 2019. Esterification of palm fatty acid distillate with methanol via single-step pervaporation membrane reactor: A novel biodiesel production method. *Energy Conversion and Management*, 201. doi: 10.1016/j.enconman.2019.112110.

Shukla, R. and Cheryan, M., 2002. Performance of ultrafiltration membranes in ethanol–water solutions: effect of membrane conditioning. *Journal of Membrane Science,* 198, pp. 75–85.

Siew, W.-L. and Minal, J., 2007. *Palm Oil and Fractions.* OFI Middle East: MPOB.

Sime Darby Plantation, 2011. *Annual Report 2011.* [Online] Available at: https://www.simedarby.com/sites/default/files/annualreport-pdf/sime_darby_annual_report_2011.pdf [Accessed 20 May 2021].

Strathmann, H., 2011. *Introduction to Membrane Science and Technology.* 1 ed. s.l.:Wiley-VCH.

Subramanian, R., Nakajima, M. and Kawakatsu, T., 1998. Processing of vegetable oils using polymeric composite membranes. *Journal of Food Engineering,* 38(1), pp. 41-56.

University of Illinois Archives, 1999. *Org Chem Text: Chapter 13.* [Online] Available at: archives.library.illinois.edu/erec/University%20Archives/150505/Organic/Fats/Chapter%2012/sec12-2/12-2.htm
[Accessed 20 January 2020].

Wafti, N.S.A., Lau, H.L.N., Loh, S.K., Aziz, A.A., Rahman, Z.A., and May, C.Y., 2017. Activated Carbon from Oil Palm Biomass as Potential Adsorbent for Palm Oil Mill Effluent Treatment. *Journal of Oil Palm Research,* 29(2), pp. 278-290.

Wei, J., Chen, L., Qiu, X., Hu, W., Sun, H., Chen, X., Bai, Y., Gu, X., Wang, C., Chen, H., Hu, R., Zhang, H., and Shen, G., 2015. Optimizing refining temperatures to reduce the loss of essential fatty acids and bioactive compounds in tea seed oil. *Food and Bioproducts Processing,* 94, pp. 136–146.

Zwijnenberg, H.J., Krosse, A.M., Cuperus, F.P., Ebert, K., and Peinemann, K.-V., 1999. Acetone-Stable Nanofiltration Membranes in Deacidifying Vegetable Oil. *Journal of the American Oil Chemist' Society,* 76(1).

APPENDICES

APPENDIX A

Calculation for Percentage of Palmitic Acid

The percentage of palmitic acid present in the synthetic acidified palm oil and raffinate phase

Example Hexane Sampling:

Hexane	Weight (g)	Titration			PA (%)
		V (mL)	V_f (mL)	V_{i-f} (mL)	
Initial	2.9024	40.30	48.00	7.70	6.7916
Final	2.8762	18.10	21.50	3.40	3.0262

1. Percentage of palmitic acid, *PA (%)*

$$= \frac{(25.6 \times N \times V)}{M}$$

$$= \frac{(25.6 \times 0.1 \times 3.4\ )}{2.8762}$$

$$= 3.0262$$

2. Palmitic Acid Reduction Percentage (%)

$$= (\frac{PA_\mathrm{i} - PA_\mathrm{r}}{PA_\mathrm{i}}) \times 100$$

$$= (\frac{6.7916 - 3.0262}{6.7916}) \times 100$$

$$= 55.44$$

APPENDIX B

Percentage of Palmitic Acid Reduction in Different Solvents

Solvent Type	Percentage of Palmitic Acid Reduction			
	Sampling 1	Sampling 2	Sampling 3	Average
Methanol	63.08	63.02	61.36	62.49
Ethanol	67.36	65.07	64.02	65.48

Percentage of Palmitic Acid Reduction in Ethanol at Different Temperatures

Solvent Type	Percentage of Palmitic Acid Reduction			
	Sampling 1	Sampling 2	Sampling 3	Average
T1	63.38	61.10	62.80	62.43
T2	67.36	65.07	64.02	65.48
T3	65.79	64.26	65.16	65.07
T4	63.94	63.92	61.35	63.07

Remarks: T1 = 45 °C; T2 = 55 °C; T3 = 65 °C; T4 = 75 °C

Percentage of Palmitic Acid Reduction in Ethanol with Different Mass Ratios

Solvent Type	Percentage of Palmitic Acid Reduction			
	Sampling 1	Sampling 2	Sampling 3	Average
R1	48.63	50.31	46.78	48.57
R2	67.36	65.07	64.02	65.48
R3	76.71	72.93	81.33	76.99
R4	81.23	80.29	82.31	81.28

Remarks: R1= 1: 1, R2= 1: 2, R3= 1: 3. R4= 1: 4 of Synthetic Acidified Palm Oil System to Solvent

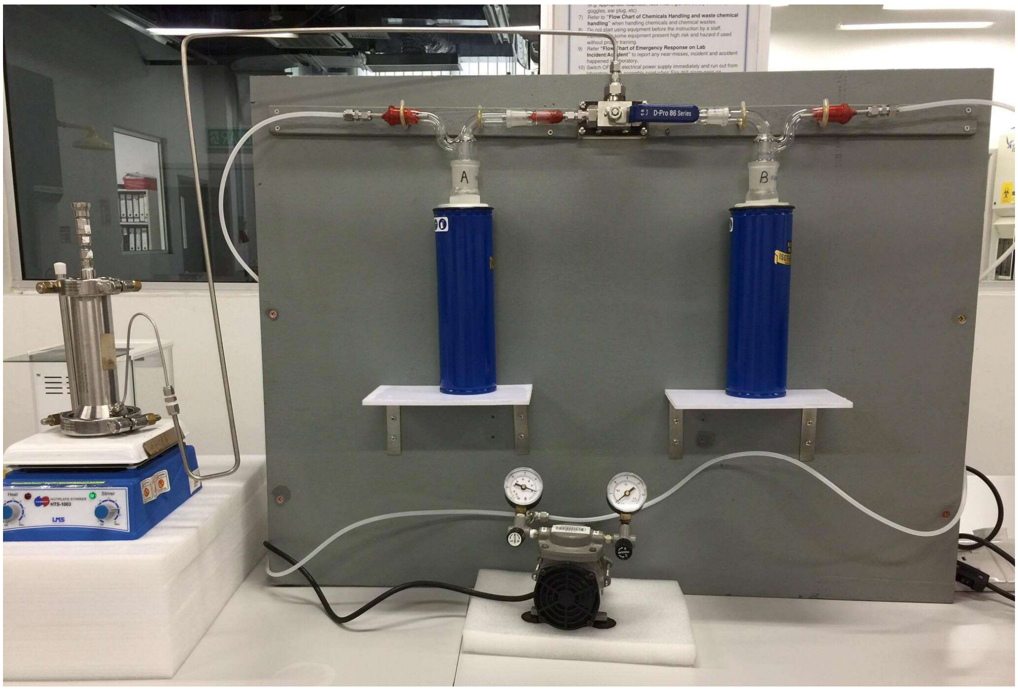
Percentage of Palmitic Acid Reduction in Ethanol with Different Water Content

Solvent Type	Percentage of Palmitic Acid Reduction			
	Sampling 1	Sampling 2	Sampling 3	Average
W1	67.36	64.02	65.07	65.48
W2	64.18	63.52	58.82	62.17
W3	59.28	50.00	56.83	55.37
W4	54.64	41.77	49.14	48.52
W5	47.95	35.46	37.15	40.19

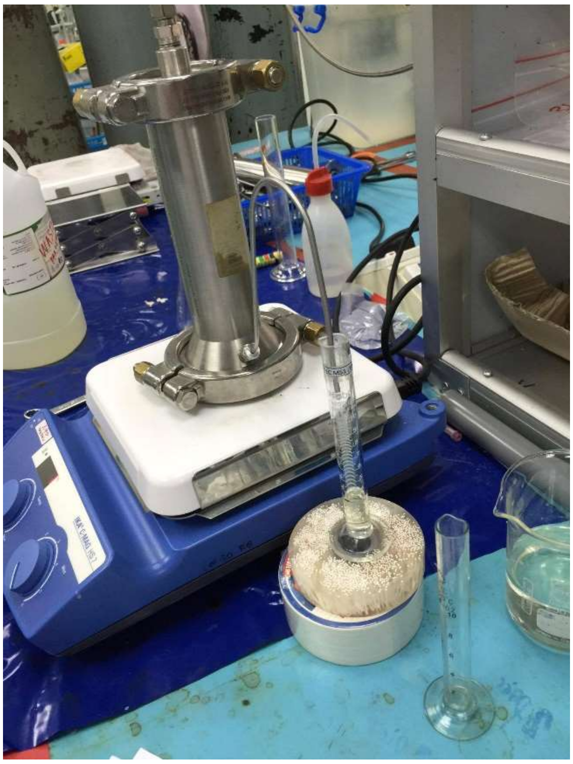
Remarks: W1 = 0%, W2 = 5%, W3 = 10%, W4 = 15% and W5 = 20%

APPENDIX C

Membrane Pervaporation Setup



Membrane Filtration Setup



APPENDIX D

Calculation for Palmitic Acid Concentration Standard Curve for GC-FID analysis

1 ppm equal to 1 mg solute per kilogram of solution. Density of ethanol is 0.789 kg/ L.

1% $= \frac{7890 \text{ mg}}{0.789 \text{ kg}}$

$= 0.0789$ g in 10 mL

2% $= \frac{15780 \text{ mg}}{0.789 \text{ kg}}$

$= 0.1578$ g in 10mL

3% $= \frac{23670 \text{ mg}}{0.789 \text{ kg}}$

$= 0.2367$ g in 10 mL

4% $= \frac{102570 \text{ mg}}{0.789 \text{ kg}}$

$= 1.0257$ g in 10 mL

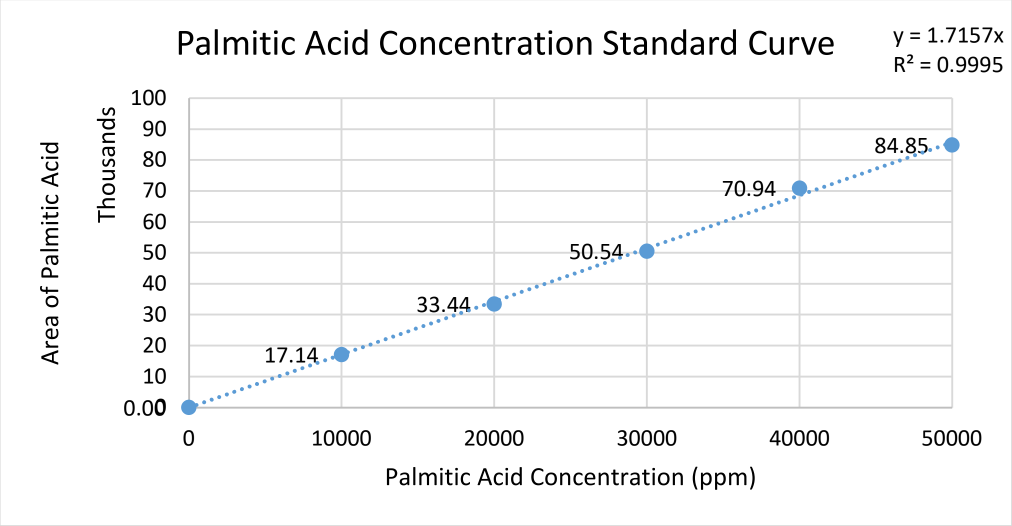
5% $= \frac{181470 \text{ mg}}{0.789 \text{ kg}}$

$= 1.8147$ g in 10 mL

Calculated amount was measured using analytical balance then transferred into 10 mL volumetric flask and dissolve by 5 mL of ethanol. Followed by top up to 10 mL to produce standard solution from 10000 to 50000 ppm. 10000ppm equal to 1%.

GC-FID Analysis

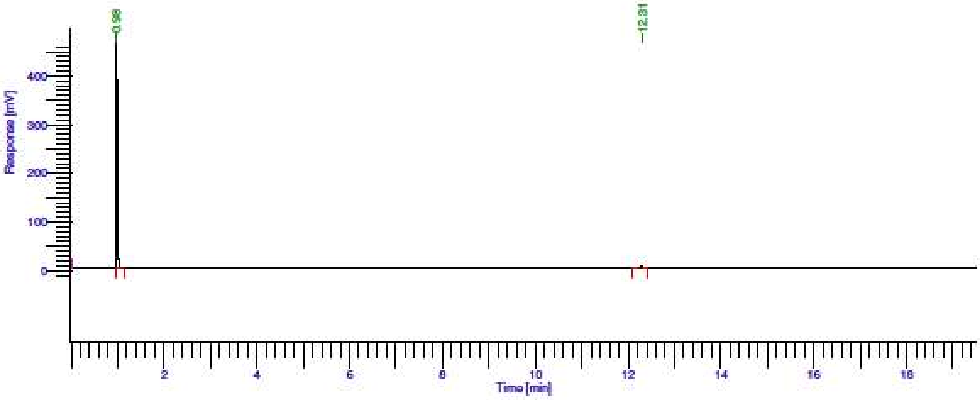
Palmitic acid concentration (%)	Palmitic acid concentration (ppm)	Palmitic Acid (g)	Area of Palmitic Acid
1	10000	0.0789	17135.77
2	20000	0.1578	33441.57
3	30000	0.2367	50537.98
4	40000	1.0257	70935.50
5	50000	1.8147	84847.95



Software Version : 6.3.1.0504
Sample Name :
Instrument Name : Clarus500
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 4/9/2016 9:56:15 AM
Data Acquisition Time : 4/6/2016 3:10:45 PM
Channel : A
Operator : FES
Dilution Factor : 1.000000

Result File : C:\Documents and Settings\FES\Desktop\ZB-FFAP\10000 ppm.rst
Sequence File : C:\GC\Method\10000 ppm.seq



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount	Component Name
1	0.977	814809.57	463234.29	0.8148	
2	12.314	17135.77	3460.29	0.0171	
		831945.35	466694.58	0.8319	

Missing Component Report

Component	Expected Retention (Calibration File)

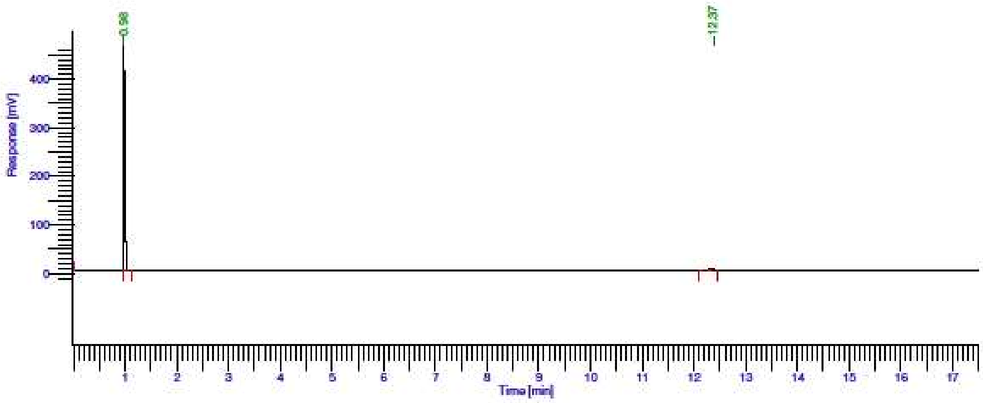
All components were found

Page 1 of 1

Software Version : 6.3.1.0504
Sample Name :
Instrument Name : Clarus500
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 4/9/2016 9:56:41 AM
Data Acquisition Time : 4/6/2016 3:57:25 PM
Channel : A
Operator : FES
Dilution Factor : 1.000000

Result File : C:\Documents and Settings\FES\Desktop\ZB-FFAP\20000 ppm.rst
Sequence File : C:\GC\Method\20000 ppm-20160406-155521.seq



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount	Component Name
1	0.977	809445.92	464374.87	0.8094	
2	12.374	33441.57	5448.95	0.0334	
		842887.49	469823.82	0.8429	

Missing Component Report

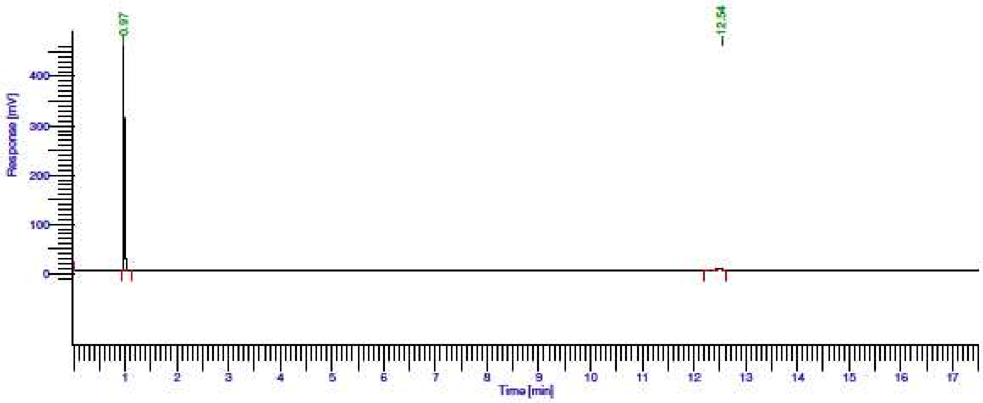
Component	Expected Retention (Calibration File)

All components were found

Software Version : 6.3.1.0504
Sample Name :
Instrument Name : Clarus500
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 4/16/2016 12:06:06 PM
Data Acquisition Time : 4/16/2016 10:45:25 AM
Channel : A
Operator : FES
Dilution Factor : 1.000000

Result File : C:\Documents and Settings\FES\Desktop\ZB-FFAP\30000 ppm.rst
Sequence File : C:\GC\Method\30000 ppm.seq



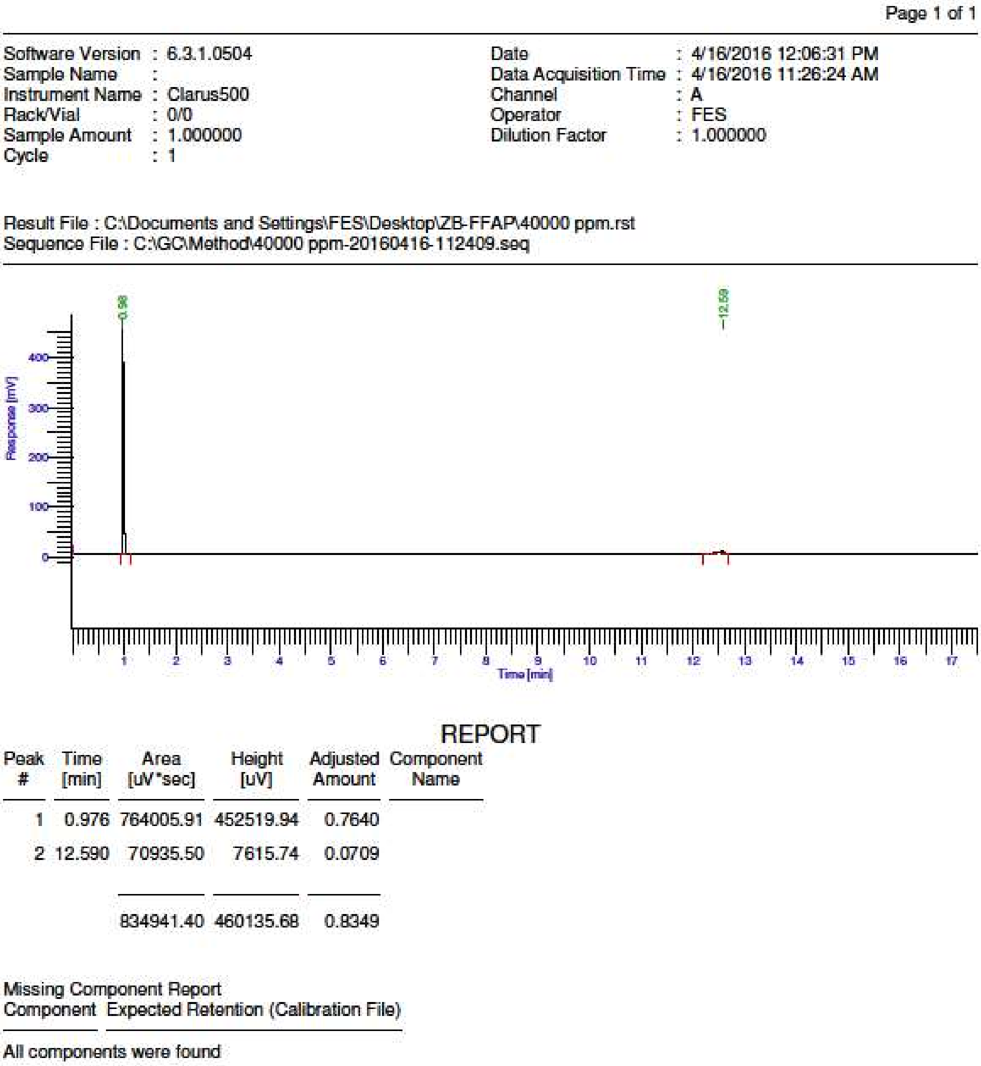
REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount	Component Name
1	0.969	796088.09	461788.75	0.7961	
2	12.541	50537.98	6342.35	0.0505	
		846626.07	468131.10	0.8466	

Missing Component Report

Component	Expected Retention (Calibration File)

All components were found



Page 1 of 1

Software Version : 6.3.1.0504
Sample Name :
Instrument Name : Clarus500
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 4/16/2016 12:06:31 PM
Data Acquisition Time : 4/16/2016 11:26:24 AM
Channel : A
Operator : FES
Dilution Factor : 1.000000

Result File : C:\Documents and Settings\FES\Desktop\ZB-FFAP\40000 ppm.rst
Sequence File : C:\GC\Method\40000 ppm-20160416-112409.seq

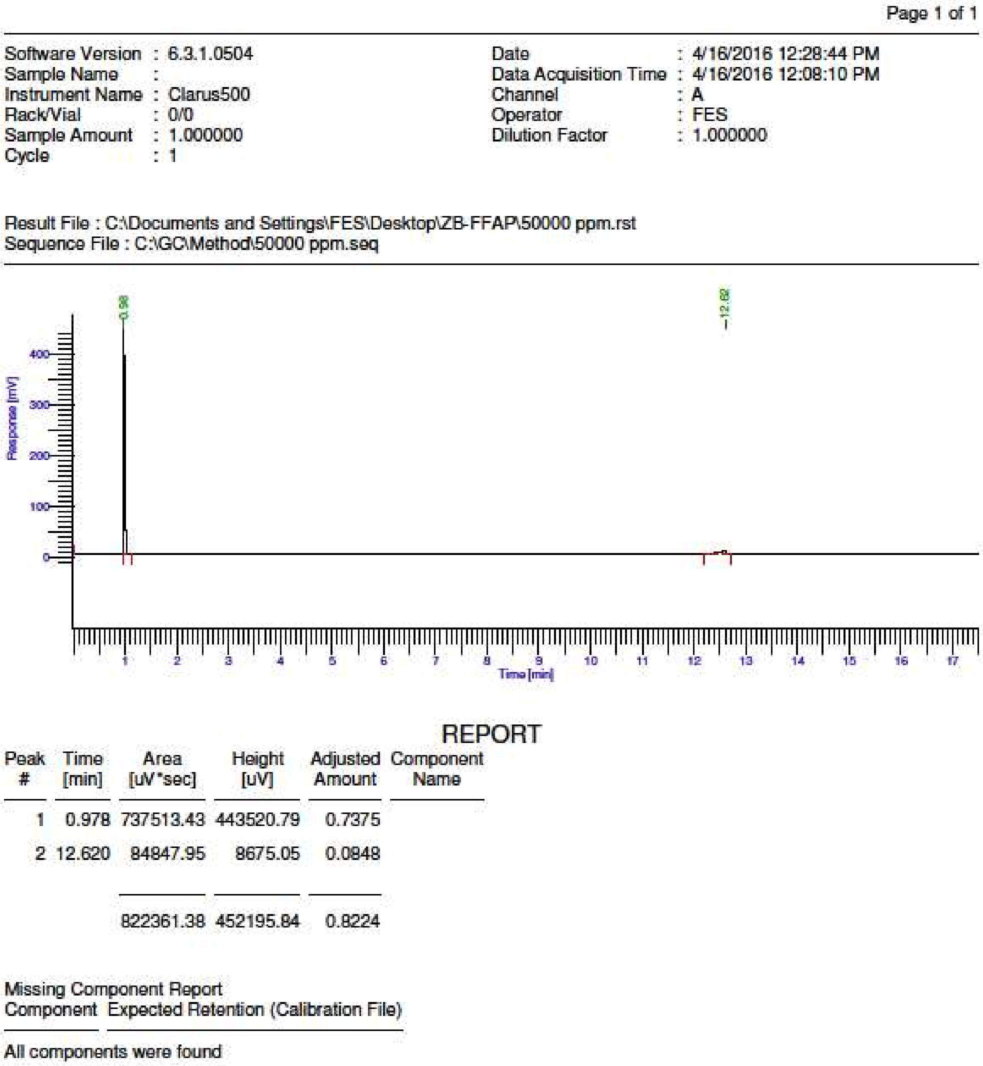
REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount	Component Name
1	0.976	764005.91	452519.94	0.7640	
2	12.590	70935.50	7615.74	0.0709	
		834941.40	460135.68	0.8349	

Missing Component Report

Component	Expected Retention (Calibration File)

All components were found



Page 1 of 1

Software Version : 6.3.1.0504
Sample Name :
Instrument Name : Clarus500
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 4/16/2016 12:28:44 PM
Data Acquisition Time : 4/16/2016 12:08:10 PM
Channel : A
Operator : FES
Dilution Factor : 1.000000

Result File : C:\Documents and Settings\FES\Desktop\ZB-FFAP\50000 ppm.rst
Sequence File : C:\GC\Method\50000 ppm.seq

REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount	Component Name
1	0.978	737513.43	443520.79	0.7375	
2	12.620	84847.95	8675.05	0.0848	
		822361.38	452195.84	0.8224	

Missing Component Report

Component	Expected Retention (Calibration File)

All components were found

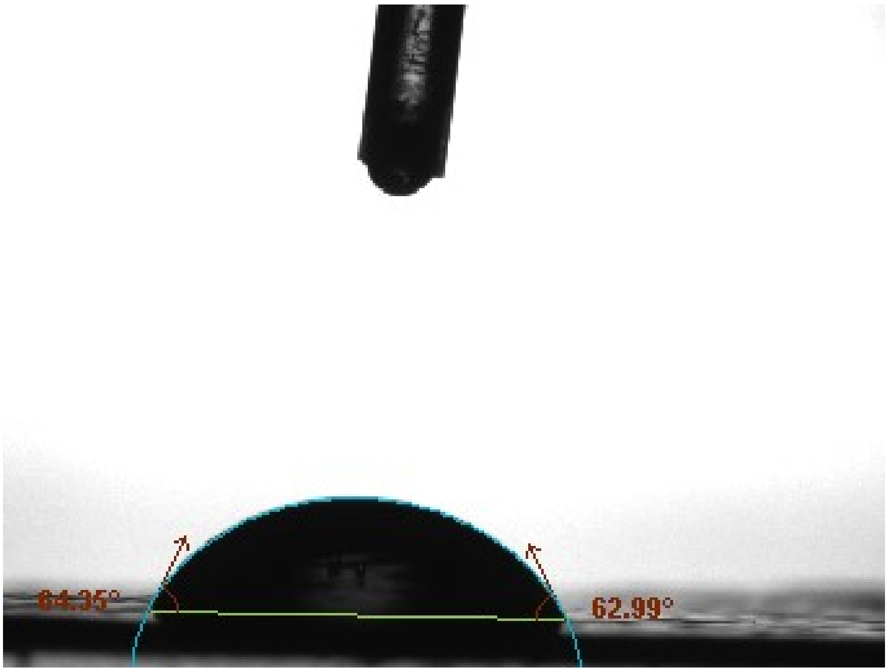
APPENDIX E

Contact Angle Result

Example CTANW membrane

Membrane	Contact Angle (°)
NF010206	78.84 ± 3.28
NF030306	94.32 ± 1.36
NF030705	108.58 ± 1.87
CTA-NW	**65.10 ± 1.43**
SW30XLE	66.72 ± 6.34

Contact Angle Image of CTANW using Optical Tensiometer



Drop's Profile measured and analyzed by OneAttension Software in 10s

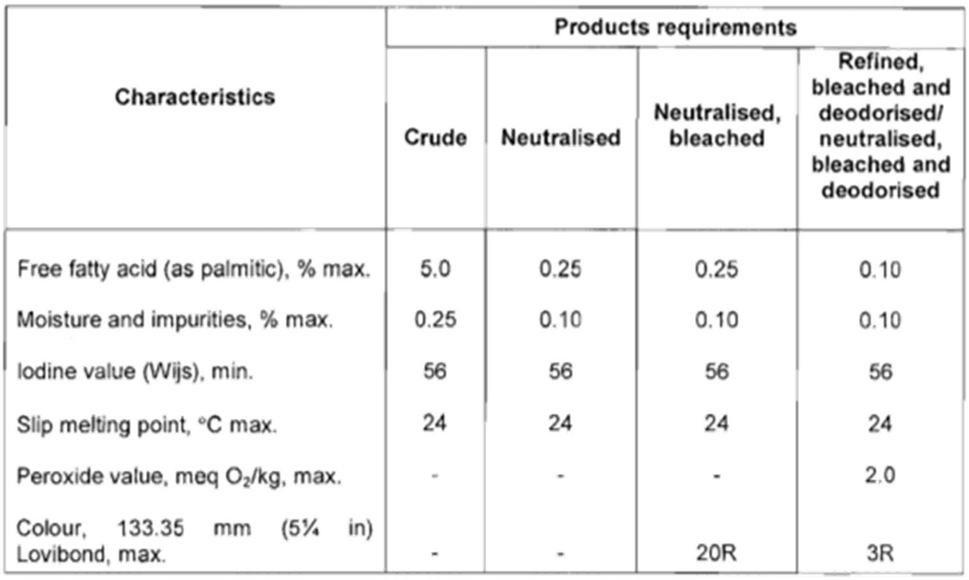
Time [s]	CA left [°]	CA right [°]	CA mean [°]	Volume [µl]	Baseline [mm]
0.00	64.74	65.10	64.92	2.70	2.68
0.08	70.20	70.83	70.51	2.93	2.72
0.17	70.42	67.91	69.16	2.90	2.72
0.25	69.29	66.07	67.68	2.93	2.73
0.33	70.35	66.63	68.49	3.03	2.75
0.42	69.41	67.28	68.34	2.98	2.75
0.50	68.73	66.50	67.61	2.88	2.74
0.67	68.35	67.54	67.94	2.95	2.76
0.75	66.69	66.34	66.51	2.83	2.75
0.83	67.57	66.79	67.18	2.91	2.76
0.92	67.37	66.53	66.95	2.88	2.76
1.00	67.10	65.76	66.43	2.85	2.75
1.08	67.21	66.04	66.62	2.86	2.76
1.17	67.96	66.38	67.17	2.91	2.76
1.25	67.06	65.72	66.39	2.85	2.76
1.33	67.01	65.77	66.39	2.85	2.76
1.42	67.15	66.12	66.64	2.88	2.76
1.50	67.41	66.14	66.78	2.89	2.77
1.58	67.31	66.10	66.70	2.89	2.77
1.67	66.75	65.32	66.03	2.80	2.75
1.75	67.38	65.74	66.56	2.86	2.76
1.83	66.94	65.70	66.32	2.85	2.76
1.92	66.71	65.34	66.02	2.82	2.76
2.00	67.07	65.94	66.50	2.87	2.76
2.08	66.49	65.61	66.05	2.85	2.76
2.25	67.57	66.03	66.80	2.90	2.77
2.33	65.37	64.90	65.13	2.77	2.75
2.42	66.31	64.81	65.56	2.80	2.76
2.50	66.77	65.59	66.18	2.86	2.77
2.58	65.26	64.57	64.92	2.74	2.75
2.67	66.01	64.62	65.32	2.77	2.75
2.75	66.42	65.21	65.82	2.83	2.76
2.83	66.02	65.29	65.66	2.82	2.76
2.92	66.08	64.95	65.52	2.81	2.76
3.00	65.13	64.62	64.87	2.74	2.75
3.08	66.47	64.60	65.53	2.79	2.76
3.25	66.03	64.90	65.47	2.79	2.76
3.33	64.53	64.25	64.39	2.70	2.75
3.42	66.39	65.21	65.80	2.84	2.77
3.50	65.57	64.90	65.23	2.79	2.76
3.58	66.32	65.15	65.73	2.83	2.77
3.67	65.56	64.44	65.00	2.76	2.76
3.75	66.19	65.00	65.59	2.81	2.76
3.83	66.14	64.97	65.56	2.82	2.77
3.92	64.84	64.36	64.60	2.74	2.76
4.00	66.03	64.95	65.49	2.83	2.77
4.08	65.70	64.86	65.28	2.81	2.77

4.17	65.73	64.85	65.29	2.81	2.77
4.25	65.87	64.85	65.36	2.80	2.77
4.33	66.13	64.94	65.53	2.82	2.77
4.42	65.54	64.22	64.88	2.75	2.76
4.50	65.77	64.72	65.25	2.81	2.77
4.58	65.44	64.27	64.85	2.74	2.76
4.67	66.40	65.08	65.74	2.84	2.77
4.75	65.56	64.35	64.95	2.77	2.76
4.83	65.98	64.64	65.31	2.81	2.77
4.92	66.33	64.87	65.60	2.83	2.77
5.00	65.99	64.70	65.35	2.83	2.77
5.08	65.81	64.54	65.18	2.80	2.77
5.16	65.05	63.57	64.31	2.71	2.76
5.25	65.86	64.61	65.24	2.82	2.77
5.33	65.46	64.33	64.89	2.78	2.77
5.41	65.49	64.22	64.86	2.80	2.77
5.50	66.28	64.67	65.47	2.83	2.77
5.58	65.64	64.38	65.01	2.80	2.77
5.67	65.29	64.29	64.79	2.79	2.77
5.75	65.13	63.36	64.24	2.73	2.76
5.83	65.45	64.10	64.77	2.77	2.77
5.91	65.20	64.06	64.63	2.77	2.77
6.00	65.06	63.53	64.30	2.72	2.76
6.08	58.64	60.08	59.36	3.23	2.86
6.16	65.62	64.26	64.94	2.81	2.78
6.25	65.58	63.93	64.76	2.79	2.77
6.33	65.11	63.90	64.51	2.78	2.77
6.41	65.36	63.91	64.64	2.78	2.77
6.50	64.49	63.20	63.85	2.70	2.76
6.59	65.57	64.17	64.87	2.80	2.77
6.66	65.55	64.27	64.91	2.81	2.78
6.75	64.96	63.82	64.39	2.77	2.77
6.83	65.47	64.43	64.95	2.82	2.78
6.91	65.12	63.93	64.52	2.78	2.77
7.00	65.10	64.00	64.55	2.77	2.77
7.08	65.54	64.45	65.00	2.83	2.78
7.16	64.89	63.67	64.28	2.76	2.77
7.25	65.18	63.89	64.53	2.78	2.77
7.33	65.46	63.92	64.69	2.79	2.78
7.42	65.41	64.06	64.74	2.79	2.78
7.50	65.03	63.35	64.19	2.74	2.77
7.58	64.55	63.55	64.05	2.74	2.77
7.66	64.78	63.72	64.25	2.76	2.77
7.75	65.10	63.88	64.49	2.77	2.77
7.83	64.51	63.36	63.94	2.74	2.77
7.91	64.39	63.45	63.92	2.74	2.77
8.00	64.68	63.46	64.07	2.76	2.78
8.08	64.87	63.60	64.23	2.76	2.77
8.16	65.31	63.83	64.57	2.79	2.78
8.25	64.52	63.31	63.91	2.74	2.77
8.33	63.70	62.32	63.01	2.65	2.76

8.42	64.88	63.58	64.23	2.76	2.78
8.50	64.69	63.48	64.09	2.75	2.77
8.58	65.18	63.47	64.33	2.77	2.78
8.66	64.81	63.21	64.01	2.74	2.77
8.75	62.67	62.19	62.43	2.61	2.75
8.83	64.89	63.60	64.25	2.76	2.78
8.92	62.73	62.34	62.53	2.62	2.76
9.00	64.32	62.82	63.57	2.69	2.77
9.08	64.11	62.85	63.48	2.72	2.77
9.16	64.20	62.96	63.58	2.73	2.77
9.25	64.91	63.40	64.16	2.76	2.78
9.33	64.71	63.42	64.07	2.75	2.78
9.41	62.67	62.29	62.48	2.62	2.76
9.50	64.28	63.27	63.78	2.73	2.78
9.58	64.65	63.09	63.87	2.75	2.78
9.66	64.28	62.75	63.52	2.69	2.77
9.75	64.42	63.13	63.78	2.74	2.78
9.83	64.46	63.13	63.80	2.73	2.77
9.91	63.78	62.51	63.14	2.69	2.77
10.00	64.35	62.99	63.67	2.74	2.78
Min	65.71	64.50	**65.10**	2.80	2.77
Standard Deviation	1.54	1.36	**1.43**	0.08	0.02

APPENDIX F

Quality Requirement for Olein Products according to MS 816:2007



Characteristics	Products requirements			
	Crude	Neutralised	Neutralised, bleached	Refined, bleached and deodorised/ neutralised, bleached and deodorised
Free fatty acid (as palmitic), % max.	5.0	0.25	0.25	0.10
Moisture and impurities, % max.	0.25	0.10	0.10	0.10
Iodine value (Wijs), min.	56	56	56	56
Slip melting point, °C max.	24	24	24	24
Peroxide value, meq O_2/kg, max.	-	-	-	2.0
Colour, 133.35 mm (5¼ in) Lovibond, max.	-	-	20R	3R