# DEACIDIFICATION OF CRUDE PALM OIL USING HOLLOW FIBER MEMBRANE CONTACTOR SYSTEM

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*To My Beloved Family and Best Friends*

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# ABSTRACT

Deacidification process is one of the most critical step in vegetable oil refining. It represents the main economic impact on oil production, which determines the final quality of refined oil. This research aimed is to develop a hollow fiber membrane contactor system that is suitable for crude palm oil (CPO) deacidification. The scopes of this study included membrane fabrication, membrane characterization and membrane deacidification performance evaluation. Three batches of polyphenylsulfone (PPSU) hollow membrane were prepared by dry-jet/wet spinning method with various PPSU membrane concentration, ethylene glycol (EG) concentration in PPSU membrane dope solution and membrane bore fluid composition. All the prepared PPSU hollow fiber membranes were characterized using scanning electron microscopy, contact angle goniometer and field emission scanning electron microscopy for membrane morphology, membrane wettability and membrane pore size, respectively. The performance of hollow fiber membrane contactor was evaluated for CPO deacidification in term of percentage free fatty acid (FFA) removal and soap content. 14PPSU hollow fiber membrane without EG which fabricated using 100% distilled water as the membrane bore fluid in combination with 3N sodium hydroxide as liquid extractant demonstrated the highest FFA removal of 16.54% after 3 hours operation without soap formation. The developed membrane contactor system can be integrated to the current palm oil refining process to further improve the oil quality and stability of refined palm oil.

# ABSTRAK

Proses penyahasidan adalah merupakan salah satu langkah yang paling penting dalam penapisan minyak sayuran. Proses ini merupakan kesan ekonomi utama pada pengeluaran minyak dalam menentukan kualiti akhir minyak bertapis. Kajian ini bertujuan untuk membangunkan satu sistem penyentuh membran gentian geronggang yang sesuai untuk penyahasidan minyak sawit mentah (CPO). Skop kajian termasuk fabrikasi membran, pencirian membran dan penilaian prestasi penyahasidan membran. Tiga kelompok membran polifenilsulfona (PPSU) gentian geronggang telah disediakan melalui kaedah pemintalan jet kering/basah dengan pelbagai kepekatan membran PPSU, kepekatan etilena glikol (EG) dalam larutan dop membran PPSU dan komposisi bendalir lubang membran. Semua PPSU membran gentian geronggang yang disediakan telah dicirikan dengan menggunakan mikroskop elektron imbasan, goniometer sudut sentuh dan mikroskop elektron imbasan pancaran medan masing-masing untuk menentukan morfologi membran, kebolehbasahan membran dan saiz liang membran. Prestasi penyentuh membran gentian geronggang telah dinilai untuk proses penyahasidan CPO dari segi peratus penyingkiran asid lemak bebas (FFA) dan kandungan sabun. 14PPSU membran gentian geronggang tanpa EG yang dihasilkan dengan menggunakan 100% air suling sebagai bendalir lubang membran dengan kombinasi 3N natrium hidroksida sebagai cecair pengekstrak telah menunjukkan penyingkiran FFA tertinggi sebanyak 16.54% selepas 3 jam operasi tanpa pembentukan sabun. Sistem penyentuh membran yang dibangunkan ini boleh digabungkan dengan proses penapisan minyak sawit yang sedia ada untuk meningkatkan lagi tahap kualiti and kestabilan minyak sawit bertapis.

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# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| CEP | - | Critical Entry Pressure |
| CPO | | Crude Palm Oil |
| CA | - | Cellulose Acetate |
| DG | - | Diglycerides |
| DMF | - | Dimethylformamide |
| DMAc | - | Dimethylacetamide |
| EtOH | | Ethanol |
| EG | - | Ethylene Glycol |
| FFA | - | Free Fatty Acid |
| FS | - | Flat Sheet |
| FESEM | - | Field Emission Scanning Electron Microscopy |
| HCN | - | Cyanide |
| HF | - | Hollow Fiber |
| LiCl | - | Litoum Chloride |
| MG | - | Monoglycerides |
| MF | - | Microfiltration |
| NaOH | - | Sodium Hydroxide |
| PAN | - | Polyacronitrile |
| PEG | - | poly (ethylene glycol) |
| PEI | - | Polyether Imide |
| PHSO | - | Partially Hydrogenated Soybean Oil |
| PL | - | Phospholipid |
| PSU | - | Polysulfone |
| PPSU | - | Polyphenylsulfone |
| PVC | - | Polyvinylchloride |
| PVDF | - | Polyvinylidene Flouride |
| PVP | - | Polyvinylpyrrolidone |

| | | |
|---|---|---|
| NMP | - | N-methyl- 2-pyrrolidone |
| NF | - | Nanofiltration |
| RC | - | Regenerated Cellulose |
| RO | - | Reverse Osmosis |
| SCFE | - | Supercritical Fluid Extraction |
| SEM | - | Scnning Electron Microscope |
| TEG | - | Tetra Ethylene Glycol |
| UF | - | Ultrafiltration |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| α | - | Surface tension |
| θ | - | Contact angle |
| $d_p$ | - | Pore diameter |
| $J_i$ | - | Rate transfer of component i |
| $D_i$ | - | Diffusion coefficient |
| $K$ | - | Coefficient reflecting the nature of medium |
| Å | - | Angstrom |
| M | - | Molecular weight |
| N | - | Normality |
| W | - | Weight of sample |
| V | - | Volume |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Recently, the local palm oil industry has been hit with the presence of food contaminants specifically known as glycidyl fatty acid esters (GE) and 3-monochloropropanediol (3-MCPD) esters. GE are classify as a process contaminants and 3-MCPD is the most commonly occurring group of contaminants known as chloropropanols. Safety issues in relation to these compounds were raised in 2006 due to potential of carcinogenic and genotoxic to humans. The European Food Safety Authority (EFSA) Panel on Contaminants in the Food Chain (EPSA CONTAM Panel), 2016 had established a Tolerable Daily Intake (TDI) of 0.8 µg/kg body weight per day. Whereas a TDI of 2 μg/kg body weight had been set by the joint of Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO) expert committee on food additives (FEDIOL, 2015). However, the toxicological relevance to GE has not yet been fully elucidated. The EPSA CONTAM Panel 2016 considered the GE dose-response data inadequate for benchmark of TDI. Pertaining to the food safety issues related to GE and 3-MCPD, the food industry specially palm oil industry actively been involved in investigating how these compounds form during processing and how to decrease their content in a variety of food products including vegetable fats and oils, biscuits, pastries and cakes as well as infant formula.

3-MCPD esters represent a class of food-borne contaminants that are mainly formed during high-temperature processing of fat-based matrices. It was first detected by Velıˊsˇek et al. (1980) in acid-hydrolysed vegetable protein products, mainly soy source. In 1983, Gardner et al (1983) reported on the 3-MCPD esters formation in rapeseed oils adulterated with aniline and refined with hydrochloric acid. Two decades later their occurrence was reported in various processed foods including refined oils (Divinova et al., 2004 & Zelinkova et al., 2006). Meanwhile GE was generated during the deodorization step of edible oil refining. Diacylgycerol (DAG) present in edible oil was the main identified source to GE formation (EPSA, 2016). Destaillats et al., (2012) reported that the critical temperature for the formation of GE from DAG is approximately 200$^{o}$C. Above this temperature, direct formation of GE from DAG accelerates faster under high temperature of deodorisation that typically conducted at 260 $^{o}$ C.

The food chain that starts with planters and ends with consumers can be complex. It involves multiple stages of production from breeding, planting, harvesting, extracting, transporting, storing, importing, processing, packaging, distributing to retail market and shelf storage. Each of these practices can play a major contribution to food quality and safety due to the possibilities of contamination with the introduction of hazardous substances or constituent (Nielsen et al., 2010).

Over the last decade total production of oils and fats has grown by over 45%. Production of the major oils, derived from palm, soybean, rapeseed and sunflower seed, grew by over 64% and accounted for some 92% of the increase in world output of all oils and fats. Total production of oils and fats is 202 million tonnes in 2015 of which palm oil and soybean produced 61 million tonnes and 47 million tonnes, respectively. Production of palm oil has grown faster than any other oil or fat which surpassed soybean as the most produced oil in 2005 (R.E.A. Holding PLC, 2016a).

According to United Nations Department of Economic and Social Affairs (UN DESA) report of “World Population Prospects: The 2015 Revision”, the current world population of 7.3 billion is expected to reach 8.5 billion by 2030, 9.7 billion in 2050 and 11.2 billion in 2100 (UN DESA, 2016). Meanwhile, the world consumption of oils and fats has grown steadily during last 26 years. 'Oil World' statistics indicate that oils and fats consumption in the last 10 years has increased from 137 million tonnes in 2005 to 202 million tonnes in 2015 (R.E.A. Holding PLC, 2016b). Thus, there will be a challenges to the food producers and processors to develop new technologies, processing methods, and agricultural techniques to meet food demands of the growing population.

Production of crude oils and fats in oil mill processing had incorporation with variable amounts of minor components like free fatty acids (FFA), partial acylglycerols, phosphatides, sterols, tocopherols, tocotrienols, hydrocarbons, pigments, vitamins, sterol glycosides, protein fragments, traces of pesticides, heavy metals, etc. The used of bulk raw material for large scale operation with varying degree of oil freshness and composition contains essential components along with impurities such as FFA, phospholipid, metals ions and volatile compounds that needs to be removed because they will interfere along with further edible oil processing. However not all constituents are undesirable. For example, tocopherols and tocotrienols possess vitamin E activity that play an important function of protecting oil against oxidation. Table 1.1 shows the general composition of edible oils and overall effect on oil quality (Gibon et al., 2007 ; Chandrasekar et al., 2015).

Table 1.1: General edible oils composition and their effect on oil quality

| **Types of Components in Oil** | **Character** | **Quality** | | **Effect on Oil Quality** |
|---|---|---|---|---|
| | | **Crude** | **Refined** | |
| Acylglycerols | Desirable | 90% | > 99% | Improve |
| Tocopherols, squalene, sterols | Desirable | 200 – 800 ppm | 50 – 300 ppm | Improve oxidative stability |
| Phospholipids | Undesirable | 100 – 500 ppm | < 10 ppm | Settling at bottom during storage |
| Free fatty acids | Undesirable | 5 – 20% | < 1% | Act as pro-oxidant |
| Metal ions and metal complexes | Undesirable | 2 – 15 mg/kg | < 1 mg/kg | Harmful for consumption and act as pro-oxidant |
| Volatiles and oxidised products | Undesirable | 2 – 6 meq/kg | < 1 meq/kg | Rancidity and harmful |
| Moisture | Undesirable | 1 – 3 % | < 1% | Act as pro-oxidant |

The crude oil must undergo several treatments processes in order to become acceptable for human consumption. Refining process is a necessary step for the production of edible oils and fats products. In industry perspective, the main aim of refining is to convert the crude oil to quality edible oil by removing undesirable components as shown in Table 1.1 to the desired levels in most efficient manner. This also means where possible, losses in the desirable components are kept minimal and cost effective (Gibon et al., 2007).

In palm oil industry, refining process involves the removal of undesirable constituents such as FFA, phospholipid, colour pigment and trace elements from crude palm oil (CPO) in order to achieve an acceptable effects on color, taste, odor and stability of refined palm oil. The most commonly methods used are chemical and physical refining. Chemical refining was introduced in the early 1970s in Malaysia. It involved four refining steps known as degumming, alkali neutralization, bleaching and deodorisation. Physical refining emerged as a better alternative to chemical refining in the late of 1970s and mainly used by modern refineries in Malaysia. It involved only three refining steps known as degumming, bleaching and deodorization/deacidification (Bhosle & Subramanian, 2005). The impurities are removed or partially removed at different stages of these refining steps. The main objective of each refining steps are:

1) Degumming – to remove phospholipid/gums
2) Neutralization – to remove FFA and residual gums
3) Bleaching – to remove the colour pigment and trace metals
4) Deodorisation – to remove FFA (mainly for physical refining) and odoriferous matter for bland taste

However, several drawbacks are identified from both conventional refining. Chemical refining used a lot of chemicals such sodium hydroxide (NaOH) to neutralize FFA and removed in the form of soapstock; citric acid to breaks the oil emulsion during washing process for further soap removal; and sulfuric acid for acid oil treatment plant as by-product. Large amount of chemical and water usage had contributed to heavily contaminated effluent. Meanwhile, physical refining involved high energy consumption due to high vacuum (2 – 3 mbar) and temperature operation (260 – 265ºC) at deodorisation stage mainly to remove FFA (Gibon et al., 2007). In addition, incomplete removal of undesirable components during pre-treatment of crude oil has to be compensated by the increased use of bleaching earth which in returned will increased the operation cost (Bhosle & Subramanian, 2005).

Membrane technology is a mature industry and has been successfully applied in various food industries for separation of undesirable fractions from valuable components. The developing membrane application in vegetable oils processing includes solvent recovery, degumming, deacidification, pigment removal, wax removal and extraction of minor components (Coutinho *et al.,* 2009). Many reports on vegetable oil refining using membrane-based technology have been documented. Conceptually, membranes can be used in almost all stages of oil production and purification (Ochoa et al., 2001; Hafidi et al., 2005; Arora et al., 2006; Pagliero et al., 2007; de Morais Coutinho et al., 2009; Manjula et al., 2011). However, the used of hexane and alcohol, requires relatively high operating pressure and fouling problem are the major obstacles preventing rapid adoption of membrane technology for commercial implementation. Despite showing huge potential in removing phospholipid from the oils, the removal of FFA (deacidification) using membrane however was reported to be ineffective and strongly dependent on the chemicals used. However, at present not many works on membrane deacidification without solvent been conducted by previous researchers (Subramanian *et al*., 1998; Alicieo *et al*., 2002; Bhosle & Subramanian, 2005).

Nevertheless, looking at various inherent advantages associated with membrane process which includes low energy consumption, mild temperature operation, retention of nutrients and other desirable components that contributes to cost and energy effectiveness, an attempt has been made to further explore on membrane technology by focusing on membrane contactor (MC) for deacidification of CPO. It is mainly due to the removal of FFA is the most difficult step in palm oil refining that contributes to the maximum economic impact on overall refined oil production. MC is a device that accomplished a separation of compounds between two different stream (gas/liquid or liquid/liquid) without dispersion of one phase into another at the membrane interface by a specific driving force. In contrast to conventional membrane application such as microfiltration, utrafiltration and reverse osmosis, the driving force for separation is concentration gradient rather than a pressure gradient (Stanojevic et al., 2003, Mansourizadeh et al., 2009). The uniqueness of MC is that no flux limitation and solvent-free technology. In addition, Stankiewicz and Moulijn (2004) defined MCs as “the development of novel apparatuses and techniques that, compared to those commonly used today are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies" had explained well the associated advantages of MC for commercial implementation.

## 1.2 Problem Statement

The occurrence of GE and 3-MCPD is processes food including refined oil was due to thermally processed contaminants. Both contaminants was detected specifically in refined palm oil after deodorization process. Several claims were made on the critical effects of deodorization step in the formation of the 3-MCPD esters. Frankle et al., (2009) reported that high deodorization temperature exceeding 200$^{o}$C are considered to be the main reason for high contents of 3MCPD-esters observed in refined oil. Studied by Hrncirik and van Duijn (2011) indicated that 3-MCPD esters and the related compounds (GE) are formed during deodorization. However, it is independent of bleaching versus neutralization/bleaching and deodorization conditions. Moreover, it was observed that substantial amount of chlorides that present in refined oil after the deodorization (palm oil 2.7–5.2 mg/kg) might be decomposed and triggers 3-MCPD formation at high deodorization temperature.

One of the major concern in improving the conventional refining process is on the deacidification method. This is because high deodorisation temperature especially been practice in physical refining process by all the oil refineries was mainly to remove the FFA. The deacidification was accomplished by steam distillation in which the FFA been distilled-off based on the difference in volatility between the neutral oil at very high temperature of 260 – 265°C. Based on the current technology, only chemical refining process can produce low 3-MCPD palm oil because the oil can be deodorized at lower temperature (220 – 240°C). It is due to the deacidification process was conducted at the early refining stage (alkali neutralization) before deodorization process. Sodium hydroxide (NaOH) was used to neutralize the FFA and removed in the form of soapstock. Sometimes the excess of NaOH is required to reduce colour of the refined oil and to ensure the removal of trace elements. Any residual soap will be removed by the addition of hot water and subsequent centrifugation. However, FFA content in the CPO has direct impact in significant losses of neutral oil due to saponification and emulsification. Furthermore, high NaOH dosage is required if the CPO contains high amount of FFA that further contributed to more oil losses and even more contaminated effluent from acid oil treatment plant as the by-product from chemical refining process been produced (Snape & Nakajima, 1996; Gibon et al., 2007).

Over the years, many alternative refining processes namely biological deacidification by using specific microorganisms, chemical reesterification, supercritical fluid extraction and membrane technology have been introduced in an effort to replace the conventional deacidification processes. Out of these new approaches proposed, membrane technology seems to be the most potential alternative solution that can be further explored to overcome the abovementioned drawbacks of the current deacidification practices. However, FFA in principle is almost impossible to be removed by membranes itself due to smaller molecular size of FFA (<300 Da) than the triglycerides (~900 Da). Theoretically, the ideal process would be to use a precise membrane pores size that could effectively separate the FFAs from the triglycerides (Cheryan, 2005). Most of the previous researchers had reported the use of oil/solvent mixture (micelle) in membrane deacidification of vegetable oils (Raman, 1994; Zwijnenberga *et al.*, 1999; Koike *et al.*, 2002; Jala *et al.*, 2011).Only few studies reported on direct membrane deacidification of vegetable oils (Subramanian *et al.*, 1998; Bhosle & Subramanian, 2005; Alicieo *et al.*, 2002) but mostly resulted in negative FFA removal and low flux limitation.

Based on the abovementioned problem statements, recent research work aimed at deacidification of CPO using the principle of membrane contactor (MC) technology. MC is a new way to accomplished separation process like liquid-liquid extractant without flux limitation. The system allow two liquid phases (CPO and liquid extractant) to come into contact with each other at the mouth of membrane pores for the purpose of mass transfer without dispersion into one another. Being the two phases separate by the membrane, there is no mix of them or dispersion phenomena has occurred (Criscuoli *et al.*, 2003). Having one of the two liquid phases on one side of a microporous membrane and the other one on the back side of the membrane, phase contact occurs if one of the two liquid phases enters into the membrane pores driven by capillary force. The phase interface is immobilized in the membrane pores where extraction takes place. This could serve as a good platform for FFA removal without soap formation and prevent oil loss throughout the process as well as an attractive solution towards "solvent-free" technology. In addition, successful removal of FFA at early refining stage could give limelight towards mitigation measure within the refining process in producing low GE and 3-MCPD of refined palm oil.

## 1.2 Objectives of Research

The objectives of the present research are:

1. To evaluate the physicochemical properties of membrane contactor module at different dope composition (PPSU and EG) and bore fluid composition.
2. To identify the optimum pressure for both CPO and liquid extractant to prevent soap formation in oil phase.
3. To proposed guideline principal for the optimum FFA removal by membrane contactor system.

## 1.4 Scopes of Research

In order to achieve the above mentioned objectives, the following scopes of study are identified:

1. Fabrication of PPSU/NMP membrane at different dope solution consist of 14%PPSU / 86%NMP (14PPSU), 18%PPSU / 82%NMP (18PPSU) and 22%PPSU / 78%NMP (22PPSU) using dry-wet spinning method under fixed spinning condition.
2. Characterization of PPSU hollow fiber membranes properties using scanning electron microscope (SEM), field emission electron miscroscope (FESEM) and contact angle analyzer.
3. Fabrication of PPSU hollow fiber membrane by adding different EG concentration of 2%EG (PPSU-2EG), 6%EG (PPSU-6EG) and 10% EG (PPSU-10EG) into the optimum PPSU membrane concentration using dry/wet spinning method under fixed spinning condition.
4. Characterization of PPSU-2EG, PPSU-6EG and PPSU-10EG hollow fiber membranes properties using scanning electron microscope (SEM), contact angle analyzer and field emission electron miscroscope (FESEM).
5. Fabrication of optimized PPSU membrane concentration at different bore fluid composition (water: NMP) of 80:20 (PPSU-80:20), 70:30 (PPSU-70:30) and 60:40 (PPSU-60:40) using dry-wet spinning method.
6. Characterization of PPSU-80:20, PPSU-70:30 and PPSU-60:40 membrane properties using scanning electron microscope (SEM), contact angle analyzer and field emission electron miscroscope (FESEM).
7. Determination of the optimum pressure condition for both liquid extractant and CPO by conducting an experiment on critical entry pressure (CEP) test using 14PPSU, 18PPSU & 22PPSU hollow fiber membrane
8. Determination the optimum concentration of polymer membrane between 14PPSU, 18PPSU and 22PPSU using hollow fiber membrane

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