

**REMOVAL OF FREE FATTY ACID FROM CRUDE PALM OIL USING
ORGANIC SOLVENT NANOFILTRATION (OSN)**

AZMIR BIN JAMALUDIN

UNIVERSITI TEKNOLOGI MALAYSIA

To my beloved family and friends

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ABSTRACT

The high content of free fatty acid (FFA) in crude palm oil has become a challenge in refining process due to refining losses and possible bleachability problems. Nowadays, alkaline and distillation approaches are widely used in industry to remove FFA but certain factors such as high energy consumption, environmental pollution and cost had limited the usage. Organic Solvent Nanofiltration (OSN) is being studied as an alternative due to its lower energy consumption, easy scale up, lower cost and the loss of nutrients is minimal. The objective of this research is to study the feasibility of OSN to remove FFA from palm oil based on the rejection and flux of FFA and triglyceride (TG). Two parameters which are type of solvent used and the feed concentration of FFA were studied. Based on the result, acetone shows high solubility and diffusivity towards OSN membrane leading to high selectivity of FFA and high rejection of TG compared to hexane. The rejection of FFA increases with the concentration of FFA.

ABSTRAK

Kandungan asid lemak bebas yang tinggi dalam minyak kelapa sawit mentah telah menjadi satu cabaran di dalam proses perincian disebabkan kehilangan nutrient semasa proses perincian dan masalah kelunturan. Pada hari ini, pendekatan secara pengalkalian dan penyulingan digunakan secara meluas di industri untuk menyingkirkan asid lemak bebas tetapi beberapa faktor seperti penggunaan tenaga yang tinggi, pencemaran alam dan kos telah menyekat penggunaannya. Pelarut organik nanofiltrasi (OSN) sedang dikaji sebagai alternatif kerana penggunaan tenaga yang rendah, mudah untuk dinaikkan skala, kos yang rendah dan kehilangan nutrisi adalah sedikit. Objektif kajian ini adalah untuk mengkaji kebolehan OSN untuk menyingkirkan asid lemak bebas daripada minyak kelapa sawit mentah berdasarkan penolakan dan fluks asid lemak bebas dan trigliserida. Dua parameter iaitu jenis pelarut yang digunakan dan kepekatan suapan asid lemak bebas dikaji. Berdasarkan kepada keputusan, aseton menunjukkan keterlarutan dan keserapan yang tinggi terhadap membran OSN membawa kepada pemilihan asid lemak bebas yang tinggi dan penolakan kandungan trigliserida yang tinggi berbanding heksana. Penolakan asid lemak bebas menjadi tinggi apabila kepekatan suapan asid lemak bebas tinggi.

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LIST OF ABBREVIATIONS

CPO	-	Crude Palm Oil
DOBI	-	Deterioration of bleachability index
FAARO	-	Fatty acid added to refined oil
FAME	-	Fatty acid methyl ester
FFA	-	Free Fatty Acid
FFB	-	Fresh fruit bunches
GC	-	Gas Chromatography
MJ	-	Mega Joule
MWCO	-	Molecular Weight Cutoff
OSN	-	Organic Solvent Nanofiltration
PFAD	-	Palm fatty acid distillate
PORAM	-	Palm Oil Refiners Association of Malaysia
RBD	-	Bleached and deodorized
RO	-	Reverse Osmosis
TG	-	Triglyceride

CHAPTER I

INTRODUCTION

1.1 Research background

Palm oil is an edible oil that has been used widely in food industry. It is originally produced from crude palm oil (CPO) which has gone through several treatment or refining processes. The CPO consisted of triglyceride (TG) which is the major component in palm oil, diglyceride, monoglyceride, free fatty acid (FFA) and minor components such as carotenoids, tocopherols, sterols, phosphatides, triterphenic and aliphatic alcohols. The presence of FFA in CPO has become a problem in the refining process (Kaimal *et al.* 2002). The higher content of FFA will result in higher refining losses and possible bleachability problems. These factors will affected the removal process of color pigment, dirt, trace metal and various organic impurities that promote oxidation in palm oil. In order to convert CPO into an edible form, FFA must be removed or decreased to an acceptable level.

Nowadays, there are two methods that have been used widely in refining process which are chemical approach using alkali refining and physical approach using distillation. However, these methods have been limited to several disadvantages such as high energy consumption, high cost expenditure, high neutral oil losses and also contributed to environmental pollution (Manjula *et al*, 2009). Due to these problems a new method which is Organic Solvent Nanofiltration (OSN) has been studied to remove FFA from CPO. According to Livingston, 2008, this method used only 3 MJ of energy for pump operation while in distillation method, extensive energy is required to operate the heating and cooling process leading to high energy and cost losses.

OSN is a novel method of refining palm oil. In this method, FFA will be separated from the mixture of palm oil with the presence of organic solvent using OSN membranes. These membranes have the molecular weight cutoff (MWCO) of 200 to 1000 Dalton. Solute with smaller molecular weight and high affinity to the membrane will pass to the permeate while the solute with bigger molecular weight and low affinity will be in the retentate. The flux and rejection of FFA and TG are influenced by various parameters. In this research, the concentration of FFA and type of organic solvent used are studied to determine the flux and rejection thus determining the feasibility of OSN in removing FFA from CPO.

1.2 Problem statement

FFA in CPO has given many problems in refining process. Due to this problem, various methods had been introduced purposely to remove or level down the FFA content such as alkali process (chemical method) which uses chemical to neutralize the crude oil and distillation process (physical method) that is the most common method used nowadays.

The chemical refining process also known as alkali refining is relatively simple and removes free fatty acids and residual phosphatides almost completely. During the alkali refining process however, there are always considerable losses of neutral oil, sterols, tocopherols and vitamins. Furthermore, disposal and utilization of the resulting soapstock may cause environmental pollution problems. In physical refining approach, distillation at high temperature at 260°C and pressure at 55 bar is used to evaporate the FFA from CPO, which is energy-intensive.

The usage of OSN membrane to separate FFA from palm oil has a great potential to the palm oil industry. The concept is rather simple and yet cost effective as it can be operated at ambient temperature. It also has no damage to minor compounds in palm oil. However, the separation efficiency of this method has to be studied to determine the feasibility of OSN to remove FFA from palm oil.

1.3 Objective

The objective of this research is to study the feasibility of Organic Solvent Nanofiltration (OSN) by varying the concentration of FFA in feed and the type of solvent used to remove FFA from CPO.

1.4 Scope of Study

The scopes of the study are to investigate the removal of FFA from palm oil using OSN by varying the concentration of FFA (0.0895, 0.1790, 0.2685, 0.3580 g/ml) in the feed and type of solvent used (acetone and hexane). The results of data are the rejection and flux of FFA after filtration.

REFERENCES

- Barzin, J., Madaeni, S.S., Mirzadeh, H., Mehrabzadeh, M. (2004). Effect of Polyvinylpyrrolidone on morphology and performance of hemodialysis membranes prepared from polyether sulfone, *J. Appl. Polym. Sci.*, 92, 3804.
- Beerlage, M.A.M. (1994). Polyimide ultrafiltration membranes for non-aqueous systems, PhD Thesis, University of Twente Enschede.
- Bhosle B.M., R. Subramanian, K. Ebert (2005). Deacidification of model vegetable oils using polymeric membranes, *Eur. J. Lipid Sci. Technol.* 107, 746-753
- Bockish M. (1998). *Fats and Oils Handbook*. AOCS Press.
- Che Man, Y. B., Liu, Jamilah (1999). Quality changes of RBD palm olein, soybean oil and their blends during deep-fat frying. *Journal of Food Lipids* 6 (3): 181–193.
- Cheryan, M. (1986). *Ultrafiltration Handbook*, Technomic PublishingCo., Inc., Lancaster.
- Cuperus, F. P., Smolders, C. A. (1991). Characterization of UF Membranes – Membrane characteristics and characterization techniques, *Advances in Colloid and Interface Science*, 34, 135.

Formo M. W., Jungermann E, Norris F. A., Sonntag N. O. (1979). Bailey's Industrial Oil and Fat Products. John Wiley & Sons Inc.

Goh E. M. (1991). Palm Oil Composition and Quality. PORIM International Palm Oil Conference (Chemistry and Technology). 268-278

Hashim (2004). A study of the Membrane Filtration of Whey and Palm Oil Mixtures, M. Sc., The University of Manchester, United Kingdom, 58

Hatori H., Yamada Y., Shiraishi M. (1995). Preparation of Macroporous Carbons from Phase Inversion Membranes, J. Appl. Polym. Sci., 57, 871-876

Hodgson, A. S. (1996). Refining and Bleaching, in Bailey's, Industrial Oil and Fat Products, Vol. 4, Edible Oil and Fat Products: Processing Technology, 5th edn., edited by Y.H. Hui, John Wiley & Sons, New York, 172-187.

Kaimal T.N.B, Ali S.R. V., Rao B.V.S.K., Chakrabarthy P.P., Vijayalakshmi P., Kale V., Rani K.N.P., Rajamma O., Bhasakar P.S., Rao T.C, Eur. J. (2002). Lipid Sci. Technol. 104, 203-211

Krishna Kumar N.S., Bhowmick D. N. (1996). Separation of fatty acid/triacylglycerol by membrane, 73, 3

Leong W. L (1992). The Refining and Fractionation of Palm Oil. Palm Oil Mill Engineers-Executives Training Course 14th Semester 1. PORIM Bangi, 1-6

- Lim, Jit Kang (2008). Refinery of Plam Oil. Retrieved December 12, 2010, from <http://www.andrew.cmu.edu>
- Lonsdale H, Merten U., Riley R. (1965). Transport of cellulose acetate osmotic membranes, *J. Appl. Polym. Sci.*, 9, 1341.
- Manjula S., Subramanian R. (2009). Separation and purification technology, 66, 223-228
- Noor Azian, M. (1995). The Physical Properties of Palm Oil Mixtures for Design of Process Equipment University of Leeds.Ph. D Thesis.
- Ong A. S, Goh S. H. (2002). Palm oil, A Healthful Cost-Effective Dietary Component, *Food Nutr Bull. Mar*; Vol.23, No.1, 11-22
- Paul D. R. (2004). Reformulation of the solution-diffusion theory of reverse osmosis, *J. Membr. Sci.* 241, 371–386.
- Peeva L.G, Gibbins E., Luthra S. S., White L. S., Stateva R. P., Livingston A. G. (2004). Effect of concentration polarisation and osmotic pressure on flux in organic solvent nanofiltration, *J. Membr. Sci.* 236, 121–136.
- Ping Tou Gee (2007). Analytical characteristics of crude and refined palm. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
- PORAM (2006). Palm Oil Refinery Association of Malaysia. Retrieved 2006, from <http://www.poram.org.my>

- Qiao, Xiangyi, Tai-Shung Chung (2005). Fundamental characteristics of sorption, swelling and permeation of P84 Co-polyimide Membranes for Pervaporation Dehydration of Alcohols, *Ind. Eng. Chem. Res.*, 44, 8938-8943
- Saravanan M. B.B. (2006). Processing hexane-oil miscella using a nonporous. *Journal of food engineering*, 529-535.
- Silva P., Han S., Livingston A.G. (2005). Solvent transport in organic solvent nanofiltration membranes, *J. Membr. Sci.* 262, 49–59.
- Silva P., Livingston A. G. (2006). Effect of solute concentration and mass transfer limitations on transport in organic solvent nanofiltration-partially rejected solute, *J. Membr. Sci.* 280, 889-898
- Stafie N., Stamatialis D. F., Wessling M. (2004). Insight into the transport of hexane-solute systems through tailor-made composite membranes, *J. Membr.Sci.*228, 103-116.
- Subramanian R., Nakajima M., Raghavarao K. S. M. S., Kimura T. (2004). Processing vegetable oils using nonporous denser polymeric composite membranes. *J. Am Oil Chem Soc.*, 81, 313–322.
- Subramanian R., Raghavarao K.S.M.S., Nabetani H., Nakajama M., Kimura T., Maekawa T. (2001). Differential permeation of oils constituents in nonporous denser polymeric membranes, *J. Membr. Sci.* 187, 57–69.
- White L. S., Nitsch A. R. (2000). Solvent recovery from lube oil filtrates with a polyimide membrane, *J. Membr. Sci.* 179, 267–274

- White, L. S. (2001). Polyimide membranes for hyperfiltration recovery of aromatic solvents, US 6, 180, 008,
- White, L.S. (2002). Transport properties of a polyimide solvent resistant nanofiltration membrane, *J. Membr. Sci.*, 205, 191
- Wijmans J. G., Baker R. W. (1995). The solution-diffusion model: a review, *J. Membr. Sci.* 107, 1–21.
- Zwijenburg H. J., Krosse A.M., Ebert K., Peinnemann K.V., Cuperus F. P. (1999). Acetone-stable nanofiltration membranes in deacidifying vegetable oil, *JAOSC* 76 83–87.