



UNIVERSITI PUTRA MALAYSIA

**A NEW REFINING APPROACH FOR PRODUCTION OF REFINED PALM
OIL WITH REDUCED CONTENTS OF 3-MONOCHLOROPROPANE-1,2-
DIOL ESTERS AND GLYCIDYL ESTERS**

HEW KHAI SHIN

FSTM 2020 3



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By

HEW KHAI SHIN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Master of Science**

November 2019

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Dedicating this dissertation to my dearest little brother, may you only walk on flower path in your next life. I love you and miss you forever.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

**A NEW REFINING APPROACH FOR PRODUCTION OF REFINED PALM OIL
WITH REDUCED CONTENTS OF 3-MONOCHLOROPROPANE-1,2-DIOL
ESTERS AND GLYCIDYL ESTERS**

By

HEW KHAI SHIN

November 2019

Chair : Professor Tan Chin Ping, PhD
Faculty : Food Science and Technology

With the recent launch of a new legislation on the maximum limit of glycidyl esters (GE) in food products, the maximum limit of 3-monochloropropane-1,2-diol esters (3-MCPDE) in oil is expected to be introduced soon. Therefore, devising strategies to mitigate these carcinogenic esters in refined palm oil is of urgent priority now. This research aimed to firstly, revise the pre-treatment steps in palm oil refining (degumming and bleaching) in order to minimize the formation of 3-MCPDE and GE in refined, bleached, deodorized palm oil (RBDPO); and secondly, to develop and optimize a new refining approach for the production of high quality RBDPO with reduced 3-MCPDE and GE contents. For the first objective, water degumming that requires no centrifugation and decanting was incorporated into the refining process (1.0% water (w/w), 90 °C, 10 min). This modification successfully reduced 23% of 3-MCPDE and 13% of GE in RBDPO significantly ($p < 0.05$). Next, six types of bleaching earth (BE) were dosed at 0.5%, 1.0% and 1.5% (w/w) to evaluate their effects on the esters contents in RBDPO. Results showed that high dosage of BE did not promote the maximum reduction of esters contents in oil. Instead, each type of BE had their own optimal dosage to work against the esters. Pore structure, which is a typical performance indicator of BE, was unable to explain the varying capabilities of BE to control the esters formation. The surface acidity of BE was a more accurate performance marker instead. Acid-activated BE (AABE) was found to have greater esters reduction effect as compared to natural BE. AABE of low surface acidity ($\text{pH} \approx 5$) was found to be excellent for the production of RBDPO with the least amounts of 3-MCPDE and GE, while AABE of high surface acidity ($\text{pH} \approx 3$) was found to greatly promote the formations of 3-MCPDE and GE.

The modified refining method was optimized by using response surface methodology to produce RBDPO with minimum 3-MCPDE, GE and FFA contents and lowest oil color, with water dosage (0.5-1.5%), acid dosage (0.04-0.08%), pre-treatment

temperature (60-90 °C), deodorization temperature (240-260 °C) and duration (80-120 min) as the independent variables. Among all, deodorization temperature was the most critical factor that significantly affected all responses ($p < 0.05$). High pre-treatment temperature was found to exert considerable impact on the formation of both esters ($p < 0.05$), by which it significantly promoted the formation of 3-MCPDE and simultaneously decreased the formation of GE at its high level. Other than this, the interaction effect between acid and water dosage strongly impacted 3-MCPDE content too. An optimum and verified model was obtained, which resulted in 78% reduction for 3-MCPDE and 53% of reduction for GE, as compared to RBDPO that was refined conventionally. The efficiency of the new refining method was assessed on four grades of crude palm oil as the third objective of this study. Similar esters mitigation effect was observed across all grades of oil, thus confirming the ester mitigation efficiency of the new refining approach.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PROSES PENULENAN MINYAK SAWIT BAHARU UNTUK PENGHASILAN
MINYAK SAWIT TERTAPIS DENGAN KANDUNGAN 3-
MONOCHLOROPROPANE-1,2-DIOL ESTERS DAN GLYCIDYL ESTERS
YANG RENDAH**

Oleh

HEW KHAI SHIN

November 2019

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Dengan pelaksanaan undang-undang baharu mengenai kandungan maksimum *glycidyl esters* (GE) dalam makanan, undang-undang untuk had maksimum kandungan 3-*monochloropropane-1,2-diol esters* (3-MCPDE) dalam minyak dijangka akan diperkenalkan dalam masa terdekat. Oleh yang demikian, strategi-strategi untuk mengurangkan kompaun karsinogenik tersebut perlu diutamakan. Matlamat pertama penyelidikan ini adalah untuk mengkaji semula langkah-langkah pra-rawatan dalam proses penulenan minyak sawit, iaitu proses nyah gam dan proses pelunturan, untuk mengurangkan pembentukan 3-MCPDE dan GE dalam minyak sawit tertapis (RBDPO). Seterusnya, proses penulenan minyak sawit baharu akan dioptimumkan supaya RBDPO yang berkualiti tinggi dengan kandungan 3-MCPDE dan GE yang minimum boleh dihasilkan. Bagi matlamat pertama, kaedah nyah gam air yang tidak memerlukan langkah pengemparan atau pemisahan (1.0% air (w/w), 90 °C, 10 min) telah disertakan dalam proses penulenan. Modifikasi tersebut telah berjaya mengurangkan 23% 3-MCPDE dan 13% GE dalam RBDPO secara ketara ($p < 0.05$). Seterusnya, enam jenis peluntur bumi (BE) telah digunakan pada 0.5%, 1.0% and 1.5% (w/w) untuk menilai kesan-kesan mereka terhadap kandungan ester dalam RBDPO. Hasil kajian menunjukkan bahawa dos BE yang tinggi tidak membawa kepada pengurangan kandungan ester yang maksimum. Akan tetapi, setiap jenis BE berfungsi pada dos optimum masing-masing. Struktur pori yang sering dianggap sebagai petunjuk prestasi BE yang tipikal gagal menjelaskan perbezaan prestasi BE dalam pengawalan pembentukan ester. Sebaliknya, keasidan permukaan BE telah dikenalpasti sebagai petunjuk prestasi BE yang lebih tepat. BE yang diaktifkan dengan asid (AABE) didapati mempunyai kesan pengurangan kandungan ester yang lebih baik berbanding dengan BE semulajadi. AABE dengan keasidan permukaan yang rendah ($\text{pH} \approx 5$) didapati sangat berkesan untuk penghasilan RBDPO dengan kandungan 3-MCPDE dan GE yang terendah, manakala AABE dengan keasidan permukaan yang tinggi ($\text{pH} \approx 3$) didapati menggalakkan pembentukan 3-MCPDE dan GE.

Proses penulenan yang telah diubahsuai kemudian dioptimumkan dengan *response surface methodology* (RSM) untuk menghasilkan RBDPO yang mengandungi 3-MCPDE, GE dan FFA yang minimum serta warna minyak yang terang, dengan dos air (0.5-1.5%), dos asid (0.04-0.08%), suhu pra-rawatan (60-90 °C), suhu proses penyahbauan (240-260 °C) dan masa proses penyahbauan (80-120 min) sebagai pembolehubah yang dimanipulasi. Suhu proses penyahbauan merupakan faktor paling kritikal yang mempengaruhi semua pembolehubah bergerak balas secara ketara ($p < 0.05$). Suhu peringkat pra-rawatan yang tinggi turut membawa impak yang ketara ke atas kandungan kedua-dua ester ($p < 0.05$), di mana ianya didapati menggalakkan pembentukan 3-MCPDE dengan ketara dan pada masa yang sama, menurunkan kandungan GE pada suhu yang tinggi. Selain itu, interaksi antara dos air dan dos asid turut memberi kesan yang agak besar ke atas kandungan 3-MCPDE. Model yang optimum dan sah turut diperolehi, dengan kadar pengurangan sebanyak 78% bagi kandungan 3-MCPDE dan 53% bagi kandungan GE berbanding dengan RBDPO yang diproses secara konvensional. Kecekapan proses penulenan baharu ini turut dinilai dengan menggunakan minyak sawit mentah yang berlainan gred sebagai matlamat yang ketiga. Kesan pengurangan yang serupa telah didapati bagi kesemua gred minyak tersebut. Dengan ini, kecekapan dan keberkesanan proses penulenan minyak baharu ini telah dibuktikan.

ACKNOWLEDGEMENTS

The first thank you is dedicated to Yayasan Sime Darby. Without the philanthropic financial assistance, all of this would be completely impossible. Special thanks to all the staffs in Shimadzu Malaysia Sdn. Bhd. and Sime Darby Research Centre for their kind assistance in this project too. Devoting my deepest gratitude to my supervisory committee for their advices and guidance, especially the chairman of the committee, Prof. Dr. Tan Chin Ping. Not only through his professionalism in academic field, he has always inspired me through the way he thinks and deals with different people and problems. I am fortunate to have him as my mentor. To my laboratory mates, I feel grateful to have all of you along this journey. I am deeply in debt for all the love, care, and joy you shared to me. Every obstacles and disappointments faced in this research would be difficult and lonely to get through without all of you.

To my dearest family, thank you for your understanding and support. You own all the glory of my achievements, for I can sail freely with you anchoring me in this rough water. My late little brother, I can't thank you enough for all the love, strength and inner peace that you gave to me. I wish you could be anything you want to be in your next life. And my dear friends, thanks for being with me and bearing with me for all the good times and bad. For all the encounters along this journey, be it a blessing or a lesson, I would not be able to register my appreciation to each of you but they are all in me. I extend the last appreciation to God, for all the rains and shines, for the opened windows you left for me despite of all the shut doors of life, and thanks for not giving up on me. I am forever mortified for all my free thoughts over the past few years.

I certify that a Thesis Examination Committee has met on 27th November 2019 to conduct the final examination of Hew Khai Shin on her thesis entitled “A New Refining Approach for the Production of Refined Palm Oil with Reduced Contents of 3-Monochloropropane-1,2-Diol Esters and Glycidyl Esters” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

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LIST OF ABBREVIATIONS

2-MCPD	2-monochloropropane-1,2-diol
2-MCPDE	2-monochloropropane-1,2-diol esters
3-MCPD	3-monochloropropane-1,2-diol
3-MCPDE	3-monochloropropane-1,2-diol esters
AABE	Acid-activated bleaching earth
Adj MS	Adjusted mean of square
Adj SS	Adjusted sum of square
ANOVA	Analysis of variance
AOCS	American Oil Chemists' Society
AV	Anisidine value
BE	Bleaching earth
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BPO	Bleached palm oil
CCD	Central composite design
Coef.	Regression coefficient
CONTAM	Contaminants in the Food Chain
CPO	Crude palm oil
D	Composite desirability
d5	Deuterated
DAG	Diacylglycerol
df	Degree of freedom
DOBI	Deterioration of the bleachability index

EC	European Commission
EFSA	European Food Safety Authority
ELSD	Evaporative light scattering detector
EU	European Union
FESEM	Field emission scanning electron microscope
FFA	Free fatty acids
GC-MS	Gas chromatography-mass spectrometry
GE	Glycidyl esters
HP	Hydratable phosphatides
IARC	International Agency for Research on Cancer
JECFA	Joint FAO/WHO Expert Committee on Food Additives
LOD	Limit of detection
LOQ	Limit of quantification
m/z	Mass-to-charge ratio
MAG	Monoacylglycerol
max	Maximum
MB	Middle bound
min	Minimum
MPOB	Malaysian Palm Oil Board
MPOC	Malaysian Palm Oil Council
NHP	Non-hydratable phosphatides
PFAD	Palm fatty acid distillate
pH	Potential of hydrogen
PORAM	Palm Oil Refiners Association of Malaysia
PQ	Premium quality

PV	Peroxide value
R	Coefficient of correlation
R	Redness
rac	racemate
R ²	Coefficient of determination
RBDPO	Refined, bleached and deodorized palm oil
RP-HPLC	Reverse phase-high performance liquid chromatography
RSD	Relative standard deviation
RSM	Response surface methodology
RSPO	Roundtable on Sustainable Palm Oil
S _N	Nucleophilic substitution
SQ	Superior quality
STQ	Standard quality
TAG	Triacylglycerides
TDI	Tolerable daily intake
TIC	Total ion count
UV-vis	Ultraviolet visible
w/v	Volume concentration
w/w	Mass fraction (mass/mass)

CHAPTER 1

INTRODUCTION

3-monochloropropane-1,2-diol esters (3-MCPDE) is not something new. It was first identified in its free form in acid-hydrolyzed vegetable protein and soy sauce by Velišek et al. in 1978, and its ester form was subsequently reported in 1980 (Davidek, Velišek, Kubelka, Janiček, & Šimicová, 1980; Velišek et al., 1980). Corresponding regulation was then introduced in order to control the maximum limit of this carcinogenic compound in food. Years later, high level of 3-MCPDE was discovered again but in edible fats and oils instead, particularly in refined palm oil (Zelinková, Svejkovská, Velišek, & Doležal, 2006). Further studies have subsequently revealed a new type of process contaminant named glycidyl esters (GE) as a result of overestimation of 3-MCPDE analyzed by indirect methods in edible oils (Weiðhaar & Perz, 2010). 3-MCPDE and GE, are both proven to be carcinogenic when they are completely hydrolyzed into their free form in human body (EFSA CONTAM Panel (European Food Safety Authority Panel on Contaminants in the Food Chain), 2016). 3-MCPD has been identified as a non-genotoxic threshold carcinogen that primarily affects kidneys and male fertility, while glycidol is known as a genotoxic non-threshold carcinogen in animal studies. As of now, the mechanisms and factors that affect the formation of both esters are still not clearly understood.

However, even with limited knowledge on these esters, new regulations regarding the maximum levels of GE in food have already been put in place since 2018. Regulation (EU) 2018/290 by the European Commission has established a maximum level of 1.0 mg/kg for GE in vegetable oils and fats, 0.5 mg/kg in infants and young children food, 0.05 mg/kg and 0.006 mg/kg in powdered and liquid infant formula, respectively, as of 1st July 2019. For 3-MCPDE, the related regulation has yet to be launched, but the European Commission has suggested two possible maximum levels for 3-MCPDE in refined vegetable oils, which are 1.25 mg/kg for oils and fats from coconut, maize, rapeseed, sunflower, soybean and palm kernel oil and the mixture of aforementioned oils and fats, and 2.50 mg/kg for other vegetable oils and fish oil and mixture of oils in this category. Palm oil falls in the second group with 2.50 mg/kg as the maximum level, but based on a survey on the commercial refined, bleached and deodorized palm olein in Malaysia market, high levels of 3-MCPDE and GE in were found, ranging from 0.34-4.45 mg/kg and 0.34-10.98 mg/kg, respectively (Sim, 2016). Refined palm oil is the major vegetable oil in the world due to its low-cost production, high oil yield and versatility in food application. It is a unique food ingredient, especially in infant formula, because of its balanced composition of different classes of fatty acids and high nutritional value. To date, no substitute ingredient has been found to replace the functions of palm oil in infant formula. As the second most consumed oil in the world after soybean oil, its genotoxicity and carcinogenicity thus bring up public health concerns and drive the need for mitigation strategies.

Generally, palm oil refining aims to remove undesirable minor constituents in oil with the least possible damage to the acylglycerols and minimal loss of the desirable constituents. Typical palm oil refining process employs physical refining process which

involves three main steps, namely degumming, bleaching and deodorization. Although it was proven that the formation of both contaminants is strongly associated with the high temperature of deodorization process, other stages of refining, such as degumming and bleaching, could affect the formation of 3-MCPDE and GE as well (WO2010063450A1, 2010). Although each stage of the physical refining process was carefully inspected via various studies, the resulting findings and suggestions proposed were not always consistent. Besides, it is even perplexing for industries as researchers believe that both 3-MCPDE and GE, are of different structural profiles and toxicology significances and therefore should be treated independently when formulating mitigation measures. This results in the development of various mitigation strategies which only take one contaminant into consideration. This makes it difficult for the industries to adopt the suggestions if both esters require different refining approaches. Most importantly, high cost incurred by the proposed strategies sets the industry back. Refiners are challenged by cost-efficient refining approach which is sustainable to produce high quality oils with guarantees of low level of contaminants, excellent nutritional quality and the least possible side-streams.

Limited knowledge, contradictory findings, lack of comprehensive mitigation approach and high cost incurred by the modified process are believed to be the main obstacles faced by current industries. Therefore, the objectives of this study were:

- To improve the pre-treatment steps (degumming and bleaching) of physical palm oil refining process for the minimal formation of 3-MCPDE and GE in RBDPO; and
- To develop and optimize a new refining process for the production of high quality RBDPO with reduced levels of 3-MCPDE and GE, while maintaining the oil qualities at the same time; and
- To evaluate the mitigation efficiency of the new refining approach.

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BIODATA OF STUDENT

Born on October 17th 1992, Hew Khai Shin received her primary education and higher education in Seremban, Negeri Sembilan. She then completed her pre-university programme and obtained the Malaysian Higher Education Certificate (STPM). With that, she enrolled in Universiti Putra Malaysia (UPM) for the programme of Bachelor of Food Science and Technology. Graduated as a first class recipient, she was awarded with “*Hadiah Dewina*” in faculty level, which is an award for potential researcher award for her final year project titled “Effect of Mild Heat Treatment and Types of Adsorbent on the Odour Removal of Virgin Coconut Oil” in 2016. In the same year, she received the Royal Education Award/ *Anugerah Pelajaran Diraja* awarded by the Conference of Rulers/ *Majlis Raja-Raja* for her excellent performance in academic and extracurricular field throughout her bachelor degree. Before she further her postgraduate studies in 2018, she joined the working industry as a management trainee in research and development department to gain some industrial exposure. After a year, she was funded by Yayasan Sime Darby to pursue the Master of Science programme in the field of Food Technology in UPM.

LIST OF PUBLICATIONS

Hew, K. S., Asis, A. J., Tan, T. B., Yusoff, M. M., Lai, O. M., Nehdi, I. A., & Tan, C. P. (2020). Revising degumming and bleaching processes of palm oil refining for the mitigation of 3-monochloropropane-1,2-diol esters (3-MCPDE) and glycidyl esters (GE) contents in refined palm oil. *Food Chemistry*, 307. <https://doi.org/10.1016/j.foodchem.2019.125545>

Hew, K. S., Asis, A. J., Tan, T. B., Yusoff, M. M., Lai, O. M., Nehdi, I. A., & Tan, C. P. (2020). Optimization of modified palm oil refining process for the reduction of 3-monochloropropane-1,2-diol esters (3-MCPDE) and glycidyl esters (GE) contents in refined palm oil. (Under review).



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