



***EVALUATION AND DEVELOPMENT OF QUALITY INDICES FOR
ADULTERATION IN PALM OIL INDUSTRY BY USED AND RECYCLED
OILS***

KHOR YIH PHING

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By

KHOR YIH PHING

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

May 2019

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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

Currently, recycled oil has emerged as a prominent food safety issue and poses a major threat to the public health. Various studies have been conducted to detect the adulteration of used and recycled palm olein in refined, bleached, and deodorized palm olein (RBDPO). The presence of polymerized triacylglycerols (PTGs), monomeric oxidized triacylglycerols (oxTAGs), or caprylic acid (C8:0) has been proposed as a potential indicator to track the adulteration. Therefore, this study investigates the presence of these compounds in commercial cooking oils, their formation during various heating and deep-frying studies, and their presence in recycled oil samples. This study can be used to justify the suitability of these compounds for use as the quality indicators to trace the adulteration of used or recycled oil.

In the first part of this study, a total of 23 commercial cooking oil samples were purchased from a market in Malaysia and were categorized into three main groups, namely, pure palm olein, blended palm olein, and packet oil. The total polar compounds (TPCs) for all fresh oil samples were within the safety limit for human consumption (< 25% polar compounds) set in many European countries. No triacylglycerol (TAG) oligomers, epoxy-, keto-, or hydroxy acids were detected in any of the fresh oil samples.

In the second part of this study, a controlled heating study was carried out, RBDPO was heated continuously for 24 h at 160 °C, 170 °C, and 180 °C, with the oil sampled at 4-hour intervals. The oxTAG, TPC, and PTG concentrations in RBDPO increased significantly ($p < 0.05$) with the temperature and heating time. At the end of the heating study, more epoxy acids were formed compared to keto and hydroxy acids. However, the TPC exceeded the limit of rejection for human consumption (>25% polar compounds). Moreover, caprylic acid, which was not present in fresh oil, was formed in significant amounts after the controlled heating study.

In the third part of this work, two different types of food products, namely, sliced potato (SP) and chicken breast meat (CBM) were fried in a total duration of 200 min/day for seven consecutive days using RBDPO at 180 °C without any oil replenishment. The amounts of TPC, PTG, and caprylic acid that formed were significantly ($p < 0.05$) higher in the RBDPO used to fry SP compared to that used for CBM. The TPC in the RBDPO used to fry SP exceeded the limit of rejection for human consumption ($> 25\%$ polar compounds) on the seventh day of frying. In addition, the amounts of epoxy, keto, and hydroxy acids that formed were significantly ($p < 0.05$) higher in the RBDPO used to fry CBM compared to that used for SP.

Following this, oil samples that underwent controlled heating and deep-frying studies were refined using the common oil refining procedure to simulate the production of recycled oil. PTG, TAG oligomers and dimers showed a significant increase ($p < 0.05$) after the refining process. The oxTAG, free fatty acid (FFA), peroxide value (PV), and *p*-anisidine value (AV) dropped significantly ($p < 0.05$) in the recycled RBDPO after the refining process. For the last part of the study, FT-NIR spectroscopy coupled with chemometrics was used to rapidly quantify the amount of thermo-oxidative products such as PTG, oxTAG, and TPC formed in used frying oil. Three separate partial least squares regression (PLS) models were built with high calibration accuracy.

In conclusion, the few proposed potential quality indicators, namely PTG, oxTAG, and caprylic acid, were all detected in recycled oil. These findings justified the suitability of these parameters to be used in the quality indices to trace the adulteration of cooking oil as these compounds were not detected in the fresh oil. It is our hope that the findings of this study will be able to control the adulteration of used and recycled palm olein in RBDPO for the protection of the health and safety of consumers.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENILAIAN DAN PEMBANGUNAN INDEKS KUALITI UNTUK MENGESAN PENYALAHGUNAAN MINYAK TERPAKAI DAN KITAR SEMULA DALAM INDUSTRI MINYAK KELAPA SAWIT

Oleh

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Pada masa kini, isu keselamatan minyak masak kitar semula telah menjadi salah satu permasalahan yang dapat meningkatkan risiko negatif kepada kesihatan pengguna. Pelbagai kajian telah dilakukan untuk mengesan penyalahgunaan minyak terpakai dan kitar semula di dalam minyak kelapa sawit tertapis, terluntur, dan ternyahbau (RBDPO). Kehadiran polimer triasilgliserol (PTG), triasilgliserol teroksidasi monomerik (oxTAG), atau asid kaprilik (C8:0) telah dicadangkan sebagai indikator yang berpotensi untuk mengesan penyalahgunaan minyak terpakai. Oleh itu, kajian ini dilakukan untuk menguji kehadiran kompaun-kompaun tersebut di dalam minyak masak komersial, pembentukannya dalam pelbagai kajian pemanasan dan penggorengan, dan juga kehadiran kompaun ini dalam minyak kitar semula. Prosedur ini digunakan dalam memastikan kesesuaian kompaun tersebut dijadikan indeks kualiti bagi mengesan penyalahgunaan minyak terpakai atau kitar semula.

Dalam kajian pertama, sejumlah 23 sampel minyak masak komersial yang diperolehi dari pasaran Malaysia telah dibeli dan dibahagikan kepada tiga kategori utama, iaitu minyak sawit olein tulen, minyak sawit olein campuran, dan minyak sawit olein dalam bungkusan plastik. Keputusan menunjukkan jumlah kompaun polar (TPC) untuk semua sampel minyak masak segar didapati berada di dalam had selamat untuk penggunaan awam (< 25% kompaun polar) seperti yang ditetapkan oleh negara-negara Eropah. Tiada triasilgliserol (TAG) oligomer, asid epoksi, asid keto, dan asid hidroksi dapat dikesan di dalam semua sampel minyak masak segar.

Dalam kajian kedua, kajian pemanasan terkawal telah dijalankan. RBDPO telah dipanaskan secara berterusan selama 24 jam pada suhu 160 °C, 170 °C, and 180 °C, dengan sebahagian minyak diambil sebagai sampel setiap selang masa 4 jam bagi proses pemanasan kawalan. Jumlah oxTAG, TPC, dan PTG didapati bertambah secara ketara ($p < 0.05$) dengan peningkatan suhu dan masa pemanasan. Selepas proses pemanasan ini,

pembentukan asid epoksi adalah lebih tinggi berbanding asid keto dan asid hidroksi. Walau bagaimanapun, kandungan TPC telah melebihi had maksimum dan tidak selamat untuk kegunaan pengguna (>25% kompaun polar). Selain itu, asid kaprilik yang tidak dijumpai dalam sampel minyak masak segar didapati telah terbentuk dalam jumlah yang ketara selepas kajian pemanasan kawalan.

Dalam kajian ketiga, dua jenis makanan telah dipilih untuk kajian penggorengan, iaitu hirisan ubi kentang (SP) dan ketulan dada ayam (CBM). Secara keseluruhannya, proses penggorengan telah dilakukan selama 200 min/sehari sepanjang 7 hari secara berterusan dengan menggunakan RBDPO pada suhu 180 °C tanpa penambahan kuantiti minyak. Pembentukan jumlah TPC, PTG, dan asid kaprilik didapati lebih tinggi dalam RBDPO yang digoreng dengan SP berbanding CBM. Jumlah TPC di dalam RBDPO juga melepasi had maksimum dan tidak selamat untuk pengguna (> 25% kompaun polar) pada hari penggorengan yang ketujuh. Di samping itu, pembentukan asid epoksi, asid keto, dan asid hidroksi adalah lebih tinggi dalam RBDPO yang digoreng dengan CBM berbanding SP.

Seterusnya, sampel minyak masak yang digunakan untuk kajian pemanasan dan penggorengan di dalam kajian kedua dan ketiga telah dihantar untuk proses penapisan minyak bagi mensimulasikan penghasilan minyak kitar semula. Selepas proses penapisan minyak, jumlah PTG, TAG oligomer, dan dimer telah menunjukkan peningkatan yang ketara ($p < 0.05$). Jumlah oxTAG, asid lemak bebas (FFA), nilai peroksida (PV), dan nilai p-anisidin (AV) telah berkurangan dalam RBDPO kitar semula selepas proses penapisan. Dalam peringkat terakhir dalam kajian ini, kombinasi spektroskopi FT-NIR dan kemometrik telah digunakan untuk menentukan kuantiti produk thermo-oksidatif yang terbentuk di dalam minyak masak terpakai seperti PTG, oxTAG, dan TPC dengan pantas. Tiga model *partial least square regression* (PLS) telah dibina dengan ketepatan penentuan yang tinggi.

Kesimpulannya, beberapa penunjuk kualiti berpotensi yang dicadangkan seperti PTG, oxTAG, dan asid kaprilik, telah dapat dijumpai di dalam sampel minyak kitar semula. Penemuan ini membuktikan kesesuaian penggunaan parameter tersebut sebagai indeks kualiti untuk mengesan penyalahgunaan minyak masak kerana kompaun-kompaun ini tidak dijumpai di dalam minyak masak segar. Melalui penemuan di dalam kajian ini, adalah diharapkan supaya kawalan penyalahgunaan minyak sawit olein terpakai dan kitar semula dapat ditingkatkan bagi melindungi kesihatan dan keselamatan pengguna.

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I certify that a Thesis Examination Committee has met on 2 May 2019 to conduct the final examination of Khor Yih Phing on her thesis entitled "Evaluation and Development of Quality Indices for Adulteration in Palm Oil Industry by Used and Recycled Oils" 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 Doctor of Philosophy.

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LIST OF ABBREVIATIONS

ANOVA	analysis of variance
AV	<i>p</i> -anisidine value
BPO	Blended palm olein
CBM	Chicken breast meat
CPO	Crude palm oil
DAG	Diacylglycerol
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FO	Fresh oil
FTIR	Fourier transform infrared
FT-NIR	Fourier transform-near infrared
GC	Gas chromatography
GC-FID	Gas chromatography-flame ionization detector
HCA	Hierarchical clustering analysis
HRGC	High resolution gas chromatography
HPLC	High-performance liquid chromatography
HPSEC	High-performance size-exclusion chromatography
KNN	K-nearest neighbor
LDA	Linear discriminant analysis
MUFA	Monounsaturated fatty acid
NMR	Nuclear magnetic resonance
oxTAG	Monomeric oxidized triacylglycerol
PAH	Polycyclic aromatic hydrocarbon
PC	Principal component

PCA	Principal component analysis
PFAD	Palm fatty acid distillate
PLS	Partial least squares
PO	Packet pure palm olein
PPO	Pure palm olein
PTG	Polymerized triacylglycerol
PTFE	Polytetrafluoroethylene
PV	Peroxide value
PUFA	Polyunsaturated fatty acid
RBDPO	Refined, bleached, and deodorized palm olein
RF	Random forest
RMSECV	Root mean square error for cross-validation
RMSEP	Root mean square error of prediction
RO	Recycled oil
ROOH	Alkyl hydroperoxides
ROOR	Dialkyl peroxides
SIMCA	Soft independent modeling of class analogy
SP	Sliced potatoes
SPE	Solid-phase extraction
SVM	Support vector machine
TAG	Triacylglycerol
TBME	<i>tert</i> -butyl methyl ether
THF	Tetrahydrofuran
TOTOX	Total oxidation value
TPC	Total polar compound



CHAPTER 1

INTRODUCTION

1.1 Research background for adulteration of used oils

Research shows that edible fats and oils are one of the foods that are most frequently counterfeited (Figure 1.1) (Moore et al., 2012). The use of adulterated edible oil in our food system is a hot topic among the food safety issues at present, as it poses a major threat toward the public health. There are many methods of adulteration, for instance, edible oil, which has a valuable composition and nutritional value, is generally expensive; therefore, to maximize profit, unscrupulous producers or manufacturers tend to adulterate the oil with cheaper or lower-quality edible oils (Akin et al., 2019).

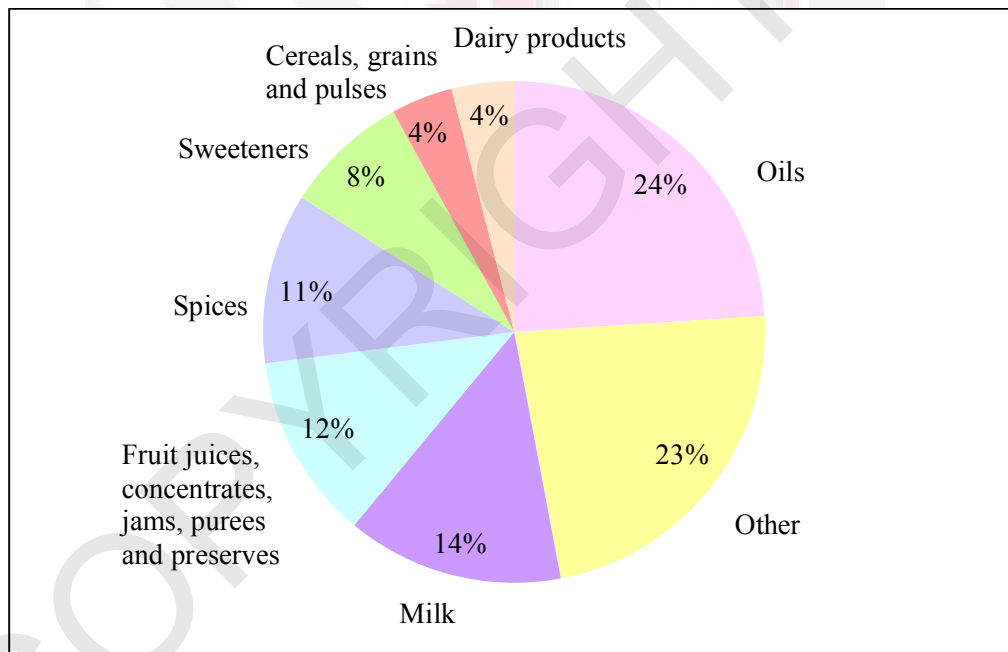


Figure 1.1: Percentage of food fraud cases from 1980 until 2010 (Moore et al., 2012).

In addition, recently there have been many cases of adulteration of refined used oil or recycled oil in our food chain system. Recycled oils are reused; in other words, the collected used oils are further subjected to a complete refining process and then repackaged and resold. The presence of recycled oil in any form of food is illegal, and the recycled oil may impose harmful effects upon humans (Lu and Wu, 2014). Used oils are found to contain a huge amount of oxidized lipids which have been claimed to exert negative biological effects. It is suggested that a substantial amount of these oxidized lipids will still retain in the oil regardless of the refining process of used oil. In general, oxidized lipids have been implicated in numerous diseases, such as atherosclerosis, liver

damage, intestinal tumours, acute inflammation or adult respiratory distress syndrome (Brühl et al., 2016; Marmesat et al., 2008a). These compounds also showed high toxicity and high digestibility (Berdeaux et al., 2008; Brühl et al., 2016). High intake of oxidation products can attribute to cancer and impairment of metabolic functions, but more data are needed on the intake of these compounds to see if the intake is sufficient to produce these adverse health effects (Kanner and Lapidot, 2001). In addition, polychlorinated biphenyls (PCBs), dioxins, arsenic, lead, aflatoxin, benzopyrene, and pesticide residue might be present in recycled oil and they may cause major public threat and will cause major disruption to the food supply.

To the best of our knowledge, currently there are still no established methods for detection of recycled oil. It is difficult to determine the degree of adulteration by simply referring to fatty acid composition and oxidation products, for example, or to free fatty acids (FFAs), peroxide values (PVs), ultraviolet specific extinction coefficients, and *p*-anisidine values (AVs) because eventually the recycled oil will go through the refining process before packaging. During the oil refining process, compounds that possess lower molecular weight or high volatility generally will be eliminated, especially during the deodorization stage (Riyadi et al., 2016), because during the deodorization step, the synergistic effects resulting from the combination of low vacuum, high temperature, and superheated steam are efficient in stripping the volatile components from the oil (FAO, 1994). Therefore, for our initial hypothesis, thermo-oxidative products that are nonvolatile and possess higher molecular weight that are generated during the oil degradation process may be proposed to be potential indicators to trace the adulteration of recycled oil.

In this scenario, special focus has been placed on three important quality parameters, which are monomeric oxidized triacylglycerols (oxTAGs), polymerized triacylglycerols (PTGs), and caprylic acid concentration because they are nonvolatile compounds formed in great amount when oils are subjected to elevated temperature for long period in the presence of oxygen. In a total of 5 working chapters, the scope of this study will basically focus on the identification and detection of these proposed quality parameters in different oil samples that underwent different treatments. As palm olein is a relatively inexpensive edible oil and is widely consumed as a major lipid source in developing countries, it was selected as the main sample for this study.

In the first stage, the safety and quality of the commercial palm olein samples were evaluated, and the emphasis was on the presence of the proposed indicators in these fresh oil samples. The PTG, oxTAG, and caprylic acid are thermo-oxidative alteration products that are formed during the oil deterioration process. Normally, these analyses are conducted on used oil samples, but now the evaluation was carried out on selected fresh oil samples as these nonvolatile compounds are not supposed to be present in fresh oil samples.

Next, palm olein was heated at various temperatures to serve as a fundamental study to provide more insight related to the extent of overall oxidative deterioration and the formation of the proposed quality parameters in the heated oil-without-food system. The correlations among all the analytical parameters were also conducted. The impacts of

different raw materials used for deep-frying on the formation of PTG, oxTAG, and caprylic acid were also investigated. The oxidation and polymerization processes were examined in depth to evaluate the discarding point of the oil. The formation of these polar products must be closely monitored, as they will affect the functional, sensory, and nutritional properties of the frying oil. A significant amount of the oxidized frying oil will be absorbed into the fried foods and eventually ingested into the human body. These thermo-oxidative products are generally recognized as threats if consumed in large quantities due to their detrimental effects.

The used oil samples in second and third stage were further subjected to an oil refining process to simulate the production of recycled oil. Then, the quality of the recycled oil was evaluated and compared with the fresh and used oil samples. Additionally, at this stage, the emphasis was on the presence of PTG, oxTAG, and caprylic acid in recycled oil samples to justify the suitability of the proposed quality parameters to be used as potential indicators to trace the adulteration of recycled oil. Furthermore, a rapid method to quantify the PTG, oxTAG, and total polar compounds (TPCs) was developed by using Fourier transform near-infrared (FT-NIR) spectroscopy coupled with the partial least squares (PLS) regression method. This rapid method is important to replace the conventional method in evaluating the polar fractions, as the common method is laborious, requires skillful operators, is less economically effective, and is not environmentally friendly.

It is our hope to develop much better indices of quality to trace the adulteration of recycled oils to safeguard the health of the general public and the rights of consumers. As a result of the advances in analytical methods, and the new challenges created by fraudsters, official methods and trade standards should be periodically revised and updated.

1.2 Research objectives

The objectives of this study were as follows:

1. To evaluate the physicochemical properties and polar lipid fraction of commercial palm olein samples available in the Malaysian market.
2. To identify the effect of different heating times and temperatures on the physicochemical properties and formation of polar lipid fraction in palm olein during a controlled heating study.
3. To investigate the effect of frying different foods on the physicochemical properties and formation of polar lipid fraction in palm olein during deep-fat frying.
4. To compare the physicochemical properties and polar lipid fraction of fresh, used, and recycled palm olein.
5. To develop a rapid method for PTG, oxTAG, and TPC quantification using FT-NIR spectroscopy coupled with chemometrics.

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