

SITI BALQIS CHE OTHMAN

DOCTOR OF PHILOSOPHY

2015

**EXPERIMENTAL AND THEORETICAL STUDIES ON
THE EFFECTS OF FATTY ACIDS ON THE
PERFORMANCE OF ANTIOXIDANTS IN INHIBITING
THE OXIDATION OF SELECTED VEGETABLE OILS**

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**Thesis Submitted in Fulfillment of the Requirement for the
Degree of Doctor of Philosophy in School of Fundamental Science
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DEDICATION

This thesis is dedicated to Rasimah Binti Daud

I love you.

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

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OF FATTY ACIDS ON THE PERFORMANCE OF ANTIOXIDANTS IN
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Main Supervisor : Associate Professor Ku Halim Ku Bulat, Ph. D

Co-Supervisor : Juriffah Ariffin, Ph.D

School : School of Fundamental Science

The aim of this research project was to study the effects of fatty acids on the performance of synthetic antioxidants in inhibiting the autoxidation of selected vegetable oils. In this study, four types of chain-breaking radical scavengers, BHA, BHT, TBHQ and PG, were utilized to test their performances, experimentally and theoretically in the presence or in the absence of fatty acids. Four types of fatty acids, PA, SA, OA and LA were added at several concentrations ranging from 0.25% w/w to 3.0% w/w. The samples of oils either in the presence or in the absence of other intentionally added species such as antioxidants and/or fatty acids were exposed to heat at 60°C in the oven for 15 days. Oil samples at specified days of exposure were then taken for peroxide value (PV), total acid number (TAN) tests, and for infrared analyses. For the theoretical studies, a quantum mechanical software package

of *Gaussian09* at the theoretical level of B3LYP Density Functional Theory 6-31G(d,p) were used for the optimization of the single species structures or the complex structures involving the TAGs (tripalmitic, trioleic, trilinoleic) or the hydroperoxyl radical of TAG COO• with antioxidant and/or fatty acid. Physical parameters such as SCF energy, dipole moment, distance between selected species in question, and the bond length and the bond strength of the O-H of antioxidants were collected and analyzed. Results showed that for these selected vegetable oils, palm olein, canola and safflower, the best antioxidant in reducing the TAG decomposition in the presence of fatty acids was propyl gallate and the highest (largest) negative effect was due to the presence of stearic acid. The unsaturated fatty acids (OA and LA) seem to show larger effects on palm olein in contrast to canola oil. In both oils, palm olein and canola, the performance of propyl gallate was affected very much by the presence of fatty acids. Results also showed that for palm olein, BHA was the least affected by the presence of fatty acids, while BHT and TBHQ were the best antioxidants for canola oil. BHT and TBHQ again were the best antioxidant for safflower oil either in inhibiting the hydroperoxide formation or in reducing the TAG rearrangement to produce free fatty acids. The interaction energy, corrected using the Counterpoise Procedure (CP), between TAGs and antioxidants or between TAGs and fatty acids was the main factor that can be used to determine the effect of fatty acids on the performance of antioxidants under studied. Theoretical results also showed that the interaction energy between antioxidants and TAGs were almost in the same magnitude as of fatty acids: 15 – 39 kJ/mol for H_β, and 10-26 kJ/mol with hydroperoxyl radicals (C₈ OO and C₉ OO). The presence of fatty acid had reduced the interaction between TAG and

antioxidant. The order of percentage reduction in interaction energies is: TAG trioleic H_β (59-98%) > TAG trioleic C₈OO radical (60-77%) > TAG trilinoleic C₉OO radical (7-22%). Almost in all cases, the theoretical findings always support the experimental observations.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

**KAJIAN EKSPERIMEN DAN TEORI TERHADAP KESAN ASID LEMAK
KEATAS PRESTASI ANTIOKSIDA DALAM MENGHALANG
PENGOKSIDAAN MINYAK SAYURAN TERPILIH**

SITI BALQIS CHE OTHMAN

November 2014

Penyelia Utama : Prof Madya Dr. Ku Halim Ku Bulat, Ph.D

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Pusat Pengajian : Sains Asas

Matlamat utama kajian ini adalah untuk mengkaji kesan asid lemak terhadap keberkesanan antioksidan sintetik dalam menghalang dan melambatkan proses autoperoksidaan ke atas minyak sayuran terpilih. Dalam kajian ini, empat antioksidan jenis penghapus radikal pemutus rantai iaitu BHA, BHT, TBHQ dan PG telah digunakan untuk melihat keberkesanan dan prestasinya secara eksperimen dan juga teori sama ada dalam kehadiran atau tanpa kehadiran asid lemak. Empat jenis asid lemak iaitu PA, SA, OA, LA ditambah mengikut kepekatan tertentu iaitu diantara 0.25% b/b sehingga 3.0% b/b. Sampel minyak sama ada dengan kehadiran atau tanpa kehadiran bahan yang ingin ditambah samaada antioksidan dan/atau asid lemak didedahkan kepada haba pada 60°C didalam ketuhar pemanas selama 15 hari. Sampel minyak pada hari-hari yang tertentu diambil untuk dianalisis secara kimia iaitu Nilai Peroksida (PV), Jumlah Nilai Asid (TAN) dan juga dianalisis menggunakan kaedah spektroskopi infra merah. Kajian teori pula menggunakan

pakej perisian kuantum mekanikal iaitu Gaussian 09 pada aras teori B3LYP DFT 6-31G(d,p) untuk pengoptimuman struktur spesis tunggal atau dalam keadaan kompleks yang melibatkan rantai TAG (tripalmitik, trioleik, trilinoleik) atau radikal hidroperoksil bagi TAG COO• dengan antioksidan dan/atau asid lemak. Parameter fizikal seperti tenaga SCF, momen dwikutub, jarak antara spesis, panjang ikatan dan kekuatan ikatan bagi O-H pada antioksidan dikumpul dan dianalisis. Keputusan menunjukkan bahawa bagi minyak masak yang dipilih iaitu minyak sawit, minyak canola dan minyak safflower, antioksidan yang paling berkesan dalam mengurangkan penguraian TAG dalam kehadiran asid lemak adalah PG manakala asid lemak yang memberi kesan paling negatif ialah asid stearik. Asid lemak tak tepu (OA and LA) menunjukkan kesan yang lebih besar terhadap minyak sawit berbanding minyak canola. Dalam kedua-dua kes minyak sawit dan canola, propil galat amat terkesan dengan kehadiran mana-mana asid lemak. Keputusan bagi minyak sawit juga menunjukkan BHA merupakan antioksidan yang paling kurang terkesan dengan kehadiran asid lemak, manakala BHT dan TBHQ merupakan antioksidan terbaik bagi minyak canola. BHT dan TBHQ juga merupakan antioksidan terbaik bagi minyak safflower sama ada dalam menghalang pembentukan peroksida mahupun mengurangkan penguraian TAG yang seterusnya akan membentuk asid lemak bebas. Tenaga interaksi, yang telah diperbetulkan dengan Kaedah Penyeimbangan (CP), antara TAG dan antioksidan atau antara TAG dengan asid lemak merupakan faktor utama yang boleh digunakan untuk menentukan kesan asid lemak terhadap prestasi antioksidan yang dikaji. Hasil pengiraan secara teori menunjukkan tenaga interaksi antara antioksidan dengan TAG adalah dalam magnitud yang sama dengan asid lemak: 15-39 kJ/mol bagi H_β, and 10-26 kJ/mol

dengan hydroperoksil radicals (C_8OO and C_9OO). Kehadiran asid lemak telah melemahkan interaksi antara TAG dengan antioksidan. Urutan peratus penurunan tenaga interaksi dalam tertib menurun adalah: TAG trioleik H_B (59-98%) > TAG trioleik radikal C_8OO (60-77%) > TAG trilinoleik radikal C_9OO (7-22%). Dapatan hasil pengiraan secara teori sentiasa menyokong hampir semua keputusan eksperimen.