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EFFECTS OF FRYING AND STORAGE CONDITIONS ON PHYSICOCHEMICAL PROPERTIES OF PALM OLEIN AND OLIVE OIL BLENDS

MAHSA NAGHSHINEH

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By

MAHSA NAGHSHINEH

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

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Especially dedicated to my beloved father, mother, brother and my dear husband.

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfilment of the requirements for the Degree of Master of Science

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Chairman : Associate Professor Azis Ariffin, PhD

Faculty : Food Science and Technology

The main objective of this study was to investigate the effect of type and concentrations of frying oil namely palm olein (POo) (0, 10, 25, 50, 75, 90 and 100% w/w) and olive oil (OO) (0, 10, 25, 50, 75, 90 and 100% w/w) contents on physicochemical properties of the oil blends. The main physicochemical properties of frying media namely iodine value (IV), peroxide value (PV), anisidine value (AV), totox value (TV), total polar component (TPC), free fatty acid (FFA), cloud point, color and viscosity were assessed as response variables in the present study. The results indicated that the type and concentration of frying media had no significant ($p > 0.05$) effect on FFA of oil blends; whereas the magnitudes of IV, PV, AV, TV, cloud point, color and viscosity were significantly ($p < 0.05$) influenced by the type and concentration of frying media. The highest TV (6.10) was shown in the oil blend containing 10% (w/w) POo and 90% (w/w) OO; while the least TV (2.41) was observed in the oil blend containing 90%

(w/w) POo and 10% (w/w) OO. This observation could be explained by the high proportion of polyunsaturated fatty acids to monounsaturated fatty acids in former oil blend (POo:OO, 10:90) compared to latter oil blend (POo:OO, 90:10), thus indicating that the increase in the proportion of polyunsaturated/monounsaturated fatty acids led to decrease the chemical stability of the oil blend to the oxidative rancidity.

Subsequently, the influence of partial replacement of olive oil (25 and 50% w/w) on frying performance was investigated during 5 consecutive days of frying process. In general, the physiochemical properties of oil blends were significantly ($p < 0.05$) influenced by the partial replacement of olive oil. The increase in the proportion of polyunsaturated/monounsaturated fatty acid significantly ($p < 0.05$) decreased the chemical stability of the oil blend during the frying process. The highest changes in AV (79.22), PV (13.55 meq O_2/kg) and TV (103.18) were shown by the control (POo, 100% w/w); while the oil blend 2 (POo: OO, 50:50) containing higher concentration of olive oil exhibited the least changes in AV (53.17), PV (2 meq O_2/kg) and TV (52.29) during 5 days frying process. Thus, the present study offers that the chemical stability of oil to the oxidative rancidity depends on not only the saturated fatty acid content but also on the proportion of monounsaturated to polyunsaturated fatty acids. The frying time also showed the significant ($p < 0.05$) effect on TPC of frying media. TPC increased by prolonging the frying time depending on type of frying oil. During 5 days of frying process, the highest increase in TPC (16.51%) was shown by control sample (i.e. POo, 100%); while the frying process using oil blend 2 containing 50% POo and 50% OO resulted in the least increase in TPC (14.63%). Thus, the results showed that the oil blend containing higher olive oil content (i.e. higher oleic acid) provided lower TPC

(19.24%) than the TPC (20.92%) of frying media containing higher POo content.

The last part of this study was conducted to evaluate the influence of storage time and type of frying media (POo: OO, 100:0, 75:25 and 50:50) as independent variables on the physicochemical properties of oil blends during 60 consecutive days under accelerated condition (60 ºC). The physiochemical properties of oil blends were significantly ($p < 0.05$) influenced by the independent variables studied. The increase in the proportion of polyunsaturated/monounsaturated fatty acid significantly ($p < 0.05$) decreased the chemical stability of the oil blend during storage time. The highest changes in AV (38), PV (39.98 meq O_2/kg) and TV (117.26) were shown by the control (POO, 100% w/w); while the oil blend 2 (POo: OO, 50:50) containing higher concentration of olive oil (i.e. higher oleic acid content) exhibited the least changes in AV (29.31), PV (26.93 meq O_2/kg) and TV (83.38) during 60 days storage. In fact, the oil blend 2 (POo: OO, 50:50) containing higher concentration ratio of oleic acid to linoleic acid (C18:2) was found to be stable during 60 days storage. Thus, the present study suggested that blending palm olein with high monounsaturated fatty acid-contained oil e.g. olive oil can provide the oil blend which is physically more stable than regular POo and remained liquid at ambient temperature.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi sebahagian keperluan untuk Sarjana Sains

KESAN PENGGORENGAN DAN KEADAAN PENYIMPANAN KE ATAS SIFAT-SIFAT FIZIKOKIMIA ADUNAN MINYAK SAWIT OLEIN DAN MINYAK ZAITUN

Oleh

MAHSA NAGHSHINEH

Mei 2009

Pengerusi : Professor Madya Azis Ariffin, PhD

Fakulti : Sains dan Teknologi Makanan

Objektif utama kajian ini adalah untuk menyiasat kesan jenis dan kepekatan minyak menggoreng menggunakan minyak sawit olein (POo, 0, 25, 50, 75 dan 100% w/w) dan minyak zaitun (OO, 0, 25, 50, 75 dan 100% w/w) ke atas ciri-ciri fizikokimia adunan kedua-dua minyak tersebut. Dalam kajian ini, ciri-ciri fizikokimia utama media menggoreng seperti nilai iodin (IV), nilai peroksida (PV), nilai anisidina (AV), nilai totox (TV), asid lemak bebas (FFA), takat keruh, warna, jumlah komponen polar (TPC) dan kelikatan dikaji sebagai gerak balas pemboleh ubah. Keputusan menunjukkan jenis dan kepekatan media menggoreng tidak mempunyai kesan yang bererti ($p > 0.05$) ke atas asid lemak bebas adunan minyak goreng; tetapi jenis dan kepekatan media menggoreng mempunyai kesan yang signifikan ($p < 0.05$) ke atas IV, PV, AV, TV, takat keruh, warna dan kelikatan. Nilai TV yang paling tinggi (6.10) dapat dikesan apabila menggunakan adunan minyak yang mengandungi 10% (w/w) POo dan 90% (w/w) OO;

manakala nilai TV yang paling rendah (2.41) dikesan apabila adunan 90% (w/w) POo dan 10% (w/w) OO digunakan. Keputusan ini dapat dihuraikan dengan kehadiran nisbah asid lemak politaktepu terhadap asid lemak monotaktepu yang tinggi dalam adunan awal (POo:OO, 10:90) berbanding adunan yang kedua (POo:OO, 90:10). Peningkatan dalam nisbah asid lemak politaktepu/monotaktepu boleh meningkatkan kestabilan kimia adunan minyak terhadap ketengikan oksidatif.

Dalam kajian seterusnya, kesan penggantian separa minyak zaitun (25% dan 50% w/w) ke atas prestasi menggoreng dikaji melalui proses menggoreng selama 5 hari berturut-turut. Secara amnya, penggantian separa minyak zaitun memberi kesan yang signifikan ($p < 0.05$) ke atas sifat-sifat fizikokimia adunan minyak tersebut. Peningkatan nisbah asid lemak politaktepu/monotaktepu menurunkan kestabilan kimia adunan minyak secara signifikan ($p < 0.05$) semasa proses menggoreng. Seperti yang ditunjukkan dalam keputusan, perubahan yang paling tinggi dalam nilai AV (79.22), PV (13.55 meq O_2/kg) dan TV (103.18) ditunjukkan oleh kawalan (POo 100% w/w); manakala adunan minyak 2 (POo:OO, 50:50) yang mengandungi kepekatan minyak zaitun yang lebih tinggi menunjukkan perubahan paling minima dalam nilai AV (53.17), PV (2 meq O_2/kg) dan TV (52.29) semasa proses menggoreng selama 5 hari berturut-turut. Kajian ini menunjukkan bahawa kestabilan kimia minyak terhadap ketengikan oksidatif bergantung bukan sahaja kepada kandungan asid lemak tepu tetapi juga nisbah asid lemak monotaktepu/politaktepu. Keputusan juga menunjukkan bilangan hari menggoreng mempunyai kesan yang signifikan ($P < 0.05$) ke atas TPC (16.51%) media menggoreng. Seperti yang ditunjukkan, TPC (14.63%) meningkat dengan memanjangkan masa menggoreng. Semasa proses menggoreng selama 5 hari, sampel kawalan (POo 100%) menunjukkan peningkatan TPC yang paling tinggi; manakala adunan minyak 2 yang mengandungi 50% POo dan 50% OO menunjukkan peningkatan TPC yang terendah. Oleh yang demikian, keputusan menunjukkan bahawa adunan minyak yang mengandungi kandungan minyak zaitun yang lebih tinggi (i.e. kandungan asid oleik yang lebih tinggi) memberikan nilai TPC (19.24%) yang lebih rendah berbanding TPC (20.92%) aduanan media menggoreng yang mengandungi POo yang lebih tinggi.

Dalam bahagian yang terakhir kajian ini, pengaruh masa penyimpanan dan jenis adunan media menggoreng (POo:OO, 100:0, 75:25 dan 50:50) sebagai pemboleh ubah tidak bersandar ke atas sifat-sifat fizikokimia adunan minyak selama 60 hari dalam keadaan terpecut (60 ºC) telah dikaji. Seperti yang ditunjukkan dalam keputusan, ciri-ciri fizikokimia adunan minyak dipengaruhi oleh pemboleh ubah tidak bersandar secara signifikan ($p < 0.05$). Keputusan juga menunjukkan peningkatan nisbah asid lemak politaktepu/monotaktepu menurunkan kestabilan kimia adunan minyak secara signifikan ($p < 0.05$) semasa proses penyimpanan. Sampel kawalan (POo, 100% w/w) menunjukkan perubahan nilai AV (38), PV (39.98 meq O_2/kg) dan TV (117.26) yang paling besar, manakala adunan minyak 2 (POo:OO, 50:50) yang mengandungi kepekatan minyak zaitun yang lebih tinggi (i.e. kandungan asid oleik yang lebih tinggi) menunjukkan perubahan nilai AV (29.31), PV (26.93 meq O_2/kg) dan TV (83.38) yang paling minima semasa proses penyimpanan selama 60 hari. Adunan minyak 2 (POo: OO, 50:50) yang mengandungi nisbah kepekatan asid oleik/asid linoleik (C18:2) yang lebih tinggi didapati lebih stabil semasa proses penyimpanan selama 60 hari. Dengan demikian, kajian ini menunjukkan pengadunan minyak sawit olein dengan minyak yang mengandungi asid lemak monotaktepu yang tinggi, misalnya minyak zaitun boleh menghasilkan adunan minyak yang lebih stabil secara fizikal di suhu ambien berbanding POo biasa.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Azis Ariffin, PhD
Lecturer
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Chairman)

Hasanah Mohd Ghazali, PhD
Professor
Faculty of Food Science and Technology
Universiti Putra Malaysia
(Member)

AbdulKarim Sabo Mohammed, PhD
Lecturer
Faculty of Science and Technology
Universiti Putra Malaysia
(Member)

Ainie Kuntom, PhD
Lecturer
Malaysian Palm Oil Board
(Member)

HASANAH MOHD GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 9 July 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously or currently submitted for any other degree at UPM or other institutions.

MAHSA NAGHSHINEH

Date: 10 June 2009

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LIST OF ABBREVIATION

AOCS	American Oil Chemists' Society
AV	Ansidine value
CD	Cloud point
DSC	Differential scanning calorimetry
EVOO	Extra virgin olive oil
FAC	Fatty acid composition
FFA	Free fatty acids
IV	Iodine value
MPOB	Malaysian Palm Oil Board
Max	Maximum
Min	Minimum
MUFA	Mono unsaturated fatty acid
OO	Olive oil
PO	Palm oil
POo	Palm olein oil
PORIM	Palm Oil Research Institute Malaysia
PV	Peroxide value
PUFA	Poly unsaturated fatty acid
RBO	Rice bran oil
RDB	Refined bleached and deodorized
RSM	Response surface methodology
SBO	Soy been oil

SDD	Standard deviation of difference
SMP	Slip melting point
TAG	Triacylglycerol
TPC	Total polar component
TV	Totox value
VOO	Virgin olive oil

CHAPTER 1

GENERAL INTRODUCTION

Oil is a triacylglycerol (TAG) consisting of a glycerol esterified to three saturated and/or unsaturated fatty acids. Oil may be classified as hard or soft oil depending on the proportion of saturated to unsaturated fatty acids (Erickson, 1996). The term 'soft oils' is used to describe a group of oil containing TAG with two or three unsaturated fatty acids that tend to be liquid at any temperature from 0º C. Soft oils such as corn oil, olive oil, soybean oil and grape seed oil contain the high percentage of unsaturated fatty acids (> 80%) (Che Man *et al.,* 2005). The soft oils containing high concentration level of unsaturated fatty acids have low melting point, thus remaining physically stable oils. Due to high content of unsaturated fatty acids, soft oils are easily oxidized, thus showing the chemically unstable oils. Perhaps the degree of oxidation decreases with increasing the content of saturated fatty acids in the soft oils.

The term 'hard oils' is used to describe a group of oil rich in saturated fatty acid that may be in solid or semi-solid state at room temperature. Hard oils such as palm oil, palm kernel oil, coconut oil usually contain the TAGs with two or three saturated fatty acids, thus exhibiting low iodine value (IV) remaining solid at ambient temperature. The semi solid status of palm and coconut oils implicates a mixture of solid and liquid oils. Hard oils are shown to be solid at low temperatures; while they will be liquid at high temperatures. Hard oils are not physically stable due to their high melting points.

Increasing the content of unsaturated fatty acids in the hard oils may allow them to be liquid and remain in liquid form even at low temperature.

The deep fat frying method is the process in which food is cooked by immersion in hot oil. It is considered to be the oldest and most common unit operation used in food preparation, especially in the Mediterranean area. Deep fat frying is classified as a multifunctional operation that consists in immersing a wet product in a high boiling point liquid such as oil. This process leads to a double mass transfer: (i) water escape by internal vaporization and (ii) oil adhesion and drainage during cooling as a result of both water condensation and capillary pressure.

In addition, heat and mass transfer generates simultaneous food transformations: (i) texturing due to the modification of the viscoelastic characteristics and the internal mechanical properties and (ii) activation of non enzymatic browning known as Maillard reactions. In fact, the aim of deep fat frying is to seal the food by immersing it in hot oil so that all the flavours and juices are retained within the crispy crust. The quality of the fried products depends not only on the frying conditions, such as temperature of the heated oil, frying time, food weight and frying oil volume, but also on the types of oil and the kind of food used. During the frying process, there are many physicochemical changes in food as well as in oil (Valdés and García, 2006).

During the frying process, the physical, chemical, and sensory characteristics of foods will be modified. Texture, color and oil content are the main quality parameters of fried potatoes. Texture is a sensory attribute of uppermost importance for potato preference and it is a critical parameter for fried potato quality (Ross and Scanlon, 2004). Good-quality French fries must have a crispy crust of about 1-2 mm where most of the oil is located, and a wet, soft center, like a cooked potato. For potato chips, a very crispy texture is expected all way through since crispness is an indicator of freshness and high quality. The texture of potato is found to be directly related to specific gravity, total solids, starch content, cell size, and surface area and pectin (Troncoso and Pedreschi, 2007). Textural changes during frying are the result of many physical, chemical, and structural changes produced in this complex process unit operation.

Atmospheric deep-fat frying necessarily occurs at high temperatures under atmospheric pressure. Surface darkening and many adverse reactions take place at the elevated temperature before the food is fully cooked or dried. As a result of the oil deterioration during the long frying process, the oil sustains some physical changes: the color darkens, the viscosity increases, and smoke appears. This is mainly due to three different factors: the moisture of food which may cause hydrolysis with free fatty acid formation; the atmospheric oxygen that enters the oil from the surface of the container and the high temperature at which the operation takes place. For instance, color development only begins when sufficient amount of drying has occurred in potato slices and depends also on the drying rate and heat transfer coefficient during the different stages of frying. Color is visually considered as one of the most important parameters to determine the quality of fried potatoes. The color changes in fried potatoes is the result