DEEP-FAT FRYING CHARACTERISTICS OF BLENDS OF PALM AND CANOLA OILS

By

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DEDICATION

This thesis is dedicated to these my loved ones: **Hon. Mba Anyaele**, my father, foremost teacher, and mentor. **Mrs. Cherish Ogan Mba**, my amiable wife. And the memories of **Madam Ijeoma Mba Anyaele** and **Chidumga Mba** my mother and sister respectively.

ABSTRACT

Selecting an appropriate oil for deep-fat frying can be challenging, since oils undergo irreversible thermo-degradation as frying progresses. Highly-saturated and *trans*-fat oils have adverse public health consequences. Virgin palm oil (VPO) has a balanced fatty acid composition. It is very rich in phytonutrients that possess health-promoting functions such as carotenoids, tocopherols and tocotrienols. This study investigated the stability of these phytonutrients and their migration into fried products when VPO is used either alone or as the major portion in blends of oils in deep-fat frying. Refined canola oil (RCO) was the second oil sample in the binary blends.

Firstly, Fourier transform near-infrared spectroscopy (FTNIRS) was used to characterize the palm, canola, and their blends oil samples. Partial Least Squares (PLS) regression was used to correlate spectral data with iodine value (IV), free fatty acid (FFA) and peroxide value (PV) data of the oil samples obtained by the reference AOCS wet methods. First derivative and first derivative + straight line subtraction spectra pre-processing methods gave the most reproducible and robust predictions of the PLS-NIR models developed. The study achieved simultaneous characterization of the essential quality parameters of VPO, RCO and their blends using the FTNIRS.

The VPO, RCO and blend samples were used in deep-fat frying of ripe and unripe plantain crisps at 180 °C for different times. The moisture loss rate and the crispness of the crisps fried in VPO and RCO were similar ($p > 0.05$). Significant differences ($p < 0.05$) were observed in the oil uptake and color properties of the crisps. The unripe and ripe plantain crisps absorbed 14% and 26% less oil, respectively, when fried in VPO than RCO. The browning index showed that the VPO crisps had greater color changes than the crisps fried using RCO. The qualities of the crisps fried in the 70:30 and 50:50 (VPO: RCO) blends were also statistically ($p < 0.05$) different and improved the quality of the crisps better than RCO alone.

The deterioration of VPO, RCO and VPO: RCO (1:1 w/w) blend during 20 h of successive deep-fat frying at 170, 180 and 190 ºC was investigated. Kinetics of changes in FFA, PV, anisidine value (*p*-AV), total polar compounds (TPC) and color index (CI) were monitored. The results showed that FFA and PV accumulation followed the first order reaction model, while *p*-AV, TPC and CI followed the zero-order reaction model. The concentration and deterioration rate constants

increased with increasing temperatures and was modeled by the Arrhenius equation. The overall activation energy (E_a) values showed that during thermo-oxidation, the PV build-up was the fastest while the blend oil sample was the most stable.

Frying potato slices at 170 ºC for different times was used to assess the migration and retention of the endogenous phytonutrients from VPO, RCO and blend (VPO: RCO 1:1 w/w). The French fries produced using VPO and the blend were significantly enriched with phytonutrients, absorbed less oil and had more pronounced color changes. Over 50% of the total carotenoids, 40 – 45% of tocotrienols and 3 – 16% of tocopherols were absorbed from the oils. The biphasic first order model was applied as a predictor model of changes in the concentration of the phytonutrients in the French fries. The carotenoid level in French fries influenced the overall color change (ΔE).

The thermostability of the tocopherols, tocotrienols and carotenoids in VPO, RCO and their blends used in deep-fat frying at 170 to 190 ºC for 20 h was evaluated. The deterioration kinetic rate of each homolog followed a reaction order >1. The Arrhenius relationship adequately modeled the temperature dependent deterioration rates. The E_a showed that the least stable homologs were γ-tocopherol and γ-tocotrienol while δ-tocotrienol and carotenoids were the most stable. The rate for α-tocopherol, α-tocotrienol and δ-tocopherol were similar and intermediate. The E_a values also showed that carotenoids were more retained in VPO (E_a of 71±5 kJ/mol), while the tocopherols and tocotrienols were more stable in the blend oil samples.

This work further broadened the scientific knowledge on the behavior of VPO alone or in blend with other unsaturated oils during deep-fat frying. The blended oil samples performed best in terms of stability of oil and phytonutrients, and fried products enrichment with bioactive phytonutrients. The results also elucidated the reaction rates with respect to individual quality parameters, phytonutrients and frying medium. VPO and blends offer great advantages as choice frying oils and can be adopted in domestic and commercial deep-fat frying protocols.

RÉSUMÉ

La sélection d'une huile appropriée pour la friture commerciale peut être difficile puisque lors du procédé de friture, l'huile subit des réactions de thermo-oxydation menant à sa dégradation. Les graisses animales très saturées et les acides gras *trans* ont des effets néfastes sur la santé. L'huile de palme vierge (HPV) a une composition balancée en acides gras. De plus, elle est très riche en phytonutriments ayant des propriétés bénéfiques sur la santé tels que les caroténoïdes, les tocophérols et les tocotriénols. Cette étude a examiné la stabilité de ces phytonutriments et l'ampleur de la migration des phytonutriments vers les produits frits lorsque HPV est utilisée seule en friture, ou en mélange avec une l'huile de canola (HCO).

Tout d'abord, la spectroscopie dans le proche infrarouge à transformée de Fourier (FT-NIR) fut utilisée pour caractériser l'huile de palme et l'huile de canola seuls ou en combinaison. Les analyses chimiométriques par régression des moindres carrés partiels (PLS) ont été utilisées pour corréler les données spectrales avec l'indice d'iode (IV), les acides gras libres (FFA) et l'indice de peroxydes (PV) des échantillons de référence. Les effets des différentes méthodes de prétraitement des spectres ont été étudiés afin de prédire la reproductibilité et la robustesse du modèle PLS-NIR développé. Les modèles les plus adéquats étaient ceux de la dérivée première ainsi que la dérivée première + soustraction de la ligne droite. Dans l'ensemble, les résultats de cette étude ont démontrés la pertinence de la spectroscopie FT-NIR pour la caractérisation simultanée des paramètres essentiels des huiles végétales.

Les huiles HPV, HCO et le mélange de ces huiles en friture a été testée sur des tranches de plantains mûrs et immatures. La température de friture était de 180 °C. Aucune différence significative ($p > 0,05$) du taux de perte de l'humidité ou de la croustillance des échantillons ne fut observée. Par contre, des différences significatives ($p < 0,05$) ont été observées dans les propriétés d'absorption et de la couleur. Les tranches de plantains frittes dans HPV ont absorbé 14 % moins d'huile dans les échantillons immatures et 26 % moins d'huile dans les échantillons mûrs que lorsque HCO fut utilisé comme huile. L'indice de brunissage a révélé que les tranches de plantain ont subi un changement de couleur plus prononcé lorsque HPV fut utilisé comme huile. Les paramètres de qualité des plantains tranchés après friture étaient également statistiquement différents. Les mélanges 70 : 30 et 50 :50 (HPV : HCO) ont amélioré la qualité des chips par rapport à l'utilisation

de HCO. Les résultats obtenus ont encouragé l'utilisation de l'huile de palme brute lors de la friture.

La détérioration du HPV, HCO, et du mélange HPV:HCO (1:1 w/w) pendant une période de friture de 20 h successives à 170, 180 et 190 ºC a été étudiée. Les changements cinétiques portant sur les FFA, PV, l'indice d'anisidine (*p*-AV), les composés polaires totaux (TPC) et l'indice de couleur (CI) furent étudiés. Les résultats ont montré que l'accumulation des FFA et PV ont suivi un modèle cinétique de premier ordre alors que *p*-AV, TPC et CI ont suivi un modèle cinétique d'ordre zéro. Les constantes de concentration et de la vitesse de détérioration *k* ont augmentées avec l'augmentation de la température. La modélisation fut effectuée avec l'équation d'Arrhénius. Les résultats ont montré que l'accumulation de PV était la plus rapide pendant la thermo-oxydation. Les valeurs d'énergie d'activation (E_a) ont démontré que la stabilité du mélange était supérieure et pas juste intermédiaire au HPV et HCO.

Des pommes de terre frites furent produites en utilisant HPV, HCO et un mélange de HPV : HCO (1:1 w/w) à 170 °C. Les frites produites à l'aide de HPV et du mélange d'huiles ont été considérablement enrichies de phytonutriments, ont absorbé moins d'huile et avait un changement de couleur plus prononcé. Plus de 50 % des caroténoïdes, 40 à 45 % des tocotriénols et 3 à 16 % des tocophérols ont été absorbés. L'ordre d'enrichissement basé sur l'huile utilisée pendant la friture était HPV : HCO > HPV > HCO. Le modèle biphasique de premier ordre était valide et satisfaisant comme modèle de prédiction des changements dans la concentration de phytonutriments dans les frites. Le niveau de caroténoïdes contenu dans les frites à influencé le changement de la couleur (ΔE) de celles-ci.

La thermostabilité des tocophérols, tocotriénols (tocochromanols) et caroténoïdes pendant la fritures en utilisant les huiles HPV, HCO et un mélange de ces deux huiles à des températures allant de 170 à 190 °C pendant une période de 20 h a été évaluée. Les résultats ont montré que la cinétique de dégradation de chaque homologue a suivi une réaction d'ordre supérieure à 1. Le taux dépend de la température de friture et a été correctement modélisé par l'équation d'Arrhenius. Le taux de détérioration a révélé que les homologues les moins stables étaient le γ-tocophérols et le γ-tocotrienol tandis que le δ-tocotrienol et les caroténoïdes ont été les plus stables. Alors que les homologues de tocochromanols étaient moins stables dans l'huile de palme, les caroténoïdes y étaient le plus retenu. L'E_a élevée des caroténoïdes dans HPV (E_a de 71±5 kJ/mol) confirme ce

résultat. Les tocochromanols sont plus stables dans les mélanges de HPV et HCO. Ceci fut confirmé par la valeur de l'E_a qui était plus élevée que lorsque les huiles furent utilisées de façon individuelle.

Les résultats obtenus dans cette étude ont démontré que l'huile de palme seule ou en mélange avec d'autres huiles moins saturées peut être utilisée pour la friture. Il fut démontré que le mélange des huiles est plus stable à haute température. De plus, les frites produites dans le mélange d'huiles ont absorbé la plupart phytonutriments. Les résultats donnent également une meilleure compréhension des taux de réaction en ce qui concerne les paramètres de qualité individuelle, homologues bioactifs et le milieu de friture. Il s'agit d'un grand avantage dans le choix de l'huile et des protocoles de friture à adopter lors des opérations de friture.

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CONTRIBUTIONS OF AUTHORS

All the manuscripts in this thesis have been authored by **Ogan I. Mba**, as the principal author. He is the Ph.D. candidate who was responsible for the design of experiment, experimental setup, analytical work in the laboratory, data analysis, modeling and preparing the manuscripts and revisions for scientific publications and the thesis. **Dr. Michael Ngadi** is the primary thesis supervisor. Dr. Ngadi provided scientific advice and technical supervision during the entire program. He was directly involved with editing, correcting, and reviewing the manuscripts. **Dr. Marie-Josée Dumont** is the thesis co-supervisor. She provided direction, scientific and technical advice during the entire program. She was enthusiastically involved with the editing, correcting, and revisions of the manuscripts. **Dr. Peter Adewale** was a Ph.D. candidate in Bioresource Engineering Department, McGill University, Canada. He collaborated technically on the use of MPA FT-NIR equipment and helped in experimental and data analysis.

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NOMENCLATURE

Abbreviation/Acronym	Meaning
ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
AOCS	American Oil Chemists' Society
ASTM	American Society for Testing of Materials
AV	Acid Value
BHA	Butylated hydroxyl anisole
BHT	Butylated hydroxyl toluene
BI	Browning Index
BLFF	Blend oil French fries
CAC	Codex Alimentarius Commission
CHD	Coronary heart diseases
CI	Color Index
Cox	Calculated oxidizability
CPO	Crude Palm Oil
CPOFF	Crude Palm Oil French fries
DAG	Diacylglycerols
DFF	Deep-fat frying
DGF	German Society for Fat Research
DMPS	Dimethyl polysiloxane
DMRT	Duncan's Multiple Range Test
DSC	Differential Scanning Calorimetry
E_a	Activation Energy
FA	Fatty acids
FAC	Fatty Acid Composition
FAME	Fatty Acid Methyl Esters
FAO	Food and Agricultural Organization
FD	First Derivative
FFA	Free Fatty Acids

FID	Flame Ionization Detector
FRP	Fully Ripened Plantain
FTIR	Fourier Transform Infrared
FTMIR	Fourier Transform Mid-Infrared
FTNIR	Fourier Transform Near-Infrared
g/100 g	gram per 100 grams
GC	Gas Chromatography
GRAS	Generally Regarded as Safe
HDL	High density lipo-protein
HDPE	High-density Polyethylene
HEAR	High erucic acid rapeseed
HPLC	High-Performance Liquid Chromatography
IOS	International Organization for Standardization
IR	Infra-red
IUPAC	International Union of Pure and Applied Chemists
IV	Iodine value
JECFA	Joint Expert Committee on Food Additives
LDL	Low density lipo-protein
LOD	Limits of Detection
LOQ	Limits of Quantification
MAG	Monoacylglycerols
meq O_2/Kg	milliequivalent oxygen per kilogram
MR	Moisture Ratio
MS	Mass Spectroscopy
MSC	Multiplicative Scatter Correction
MT	Metric tons
MUFA	Monounsaturated fatty acids
NIRS	Near Infra-Red Spectroscopy
OVP	Optics Validation Protocol
p-AV	*para*-Anisidine value
PDAD	Photodiode Array Detector

PG	Propyl gallate
PKO	Palm Kernel Oil
PL	Phospholipids
PLS	Partial Least Squares
PMF	Palm mid-fractions
POP	Phytosterol oxidation products
PORIM	Palm Oil Research Institute of Malaysia
ppm	Parts per million
PUFA	Polyunsaturated Fatty Acids
PV	Peroxide Value
R^2	Coefficient of Determination
RBD	Refined, Bleached, and Deodorized
RCO	Refined Canola Oil
RCOFF	Refined Canola Oil French fries
RMSEE	Root Mean Square Error of Estimation
RMSEP	Root Mean Square Error of Prediction
RPD	Residual Predictive Deviation
RT	Retention Time
SAM	Standard analytical methods
SAS	Statistical Analysis System
SB-ATR	Single Bounce Attenuated Total Reflectance
SD	Standard Deviation
SECV	Standard Error of Cross Validation
SED	Second Derivative
SEM	Standard error of the Mean
SEP	Standard Error of Prediction
SFA	Saturated Fatty Acids
SLS	Straight Line Subtraction
TAG	Triacylglycerol
TBHQ	Tert-butyl hydroquinone
TGA	Thermogravimetric Analysis

TPC	Total Polar Compounds
TV	Total Oxidation Value
UFA	Unsaturated Fatty Acids
UGP	Unripe Green Plantain
UP	Un-fried Potato
USDA	United States Department of Agriculture
UV	Ultra-Violet
VN	Vector Normalization
VPO	Virgin palm oil
WET	Water Emulsion Titratables
WHO	World Health Organization
α-T3	Alpha-tocotrienol
α-TP	Alpha-tocopherol
β-T3	Beta-tocotrienol
β-TP	Beta-tocopherol
γ-T3	Gamma-tocotrienol
γ-TP	Gamma-tocopherol
δ-T3	Delta-tocotrienol
δ-TP	Delta-tocopherol
ΔE	Overall Color Change

THESIS FORMAT

This thesis is submitted in the format of papers suitable for journal publication. This thesis format has been approved by the Faculty of Graduate and Postdoctoral Studies, McGill University, and follows the conditions outlined in the Guidelines: Concerning Thesis Preparation, which are as follows:

"As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research". The structure for the manuscript based thesis must conform to the following:

1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis).

2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges between the different papers are mandatory.

3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts. The thesis must include the following:

(a) A table of contents;
(b) An abstract in English and French;
(c) An introduction which clearly states the rational and objectives of the research;
(d) A comprehensive review of the literature (in addition to that covered in the introduction to each paper);
(e) A final conclusion and summary;

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.
5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers".

THESIS ORGANIZATION

Chapter 1: General introduction to the research work, including the scope and research objectives.

Chapter 2: Review of relevant literatures pertaining to palm oil utilization, deep-fat frying and kinetic models used to describe frying operations.

Chapter 3: Characterization of crude palm oil, refined canola oil and their binary blends by Near-Infrared Spectroscopy.

Chapter 4: Impact of palm oil, canola oil and blends on characteristics of fried plantain crisps.

Chapter 5: Deterioration kinetics of palm oil, canola oil, and blend during repeated deep-fat frying.

Chapter 6: Migration and retention of valuable phytonutrients during deep-fat frying of French fries in palm oil and blend.

Chapter 7: Thermostability and degradation kinetics of phytonutrients in palm and canola oil blends used in deep-fat frying.

Chapter 8: General summary and conclusions.

Chapter 9: Contributions to knowledge and future research.

Chapter 10: Bibliography

CHAPTER 1

1. GENERAL INTRODUCTION

1.1 Background

Deep-fat frying is the process of cooking by completely immersing foods in hot oil. It is a simultaneous heat and mass transfer process. Frying oils are usually maintained at elevated temperatures ranging from 150 to 200 ^{o}C. The hot oil serves as a medium of heat transfer into the food, while the moisture migrates out and the oil is absorbed (Moyano and Pedreschi 2006; Moreira 2014). Frying causes complex physicochemical reactions such as starch gelatinization, protein denaturation, browning, crust formation, textural and flavor changes. These depend on either the frying process itself or the nature of the food or type of frying oil (Marikkar et al. 2011). Atmospheric deep-fat frying is usually practiced. At high frying temperatures and in the presence of oxygen, thermo-oxidation and breakdown occur especially if the oil is polyunsaturated. These reactions lead to the formation of volatile and non-volatile oxidative compounds that affect the quality of frying oil and fried products. Foaming also occurs when products with high initial moisture content are fried. Repeated and continuous use of frying oils produces undesirable compounds that may compromise the quality of the food and pose a potential risk to human health and nutrition (Andrikopoulos et al. 2003). The popularity of fried foods has at no time been reported to decrease. This is certainly due to the smooth mouthfeel, distinct flavor, palatability, and aesthetic appeal of fried foods.

The choice of the frying oil is important for two reasons. First, the oil is used as a heat transfer medium during frying. Therefore, the oil must be reasonably stable at high temperature and must stay stable for multiple heating cycles. Secondly, since the fried products absorb some of the oil during frying, this requires the oil to maintain high oxidative stability throughout the life of the product and remain nutritious (Alireza et al. 2010a). Unrefined oils are usually least chosen because of the presence of some impurities, pro-oxidants, and sometimes high levels of free fatty acids. However, refining in addition to removing or lowering these, also removes the natural nutrients from the oils and create a final product that is bland and oxidizes easily (May and Nesaretnam 2014). Overall, healthy unrefined oils are better alternatives to refined oils as they permit consumers to “eat naturally”.

Oxidation of polyunsaturated molecules leads to reactive free radicals, which are harmful to human cells and genetic materials. Although polyunsaturated oils can be stabilized by hydrogenation or partial hydrogenation, the hydrogenation reaction produces *trans*-fatty acids, which have been shown to cause undesirable effects. These effects include a raise in the "bad" low-density lipoprotein (LDL) cholesterol and lowering the "good" high-density lipoprotein (HDL) cholesterol in the body. Both effects increase the risk of cardiovascular disease in the long term (Berger 2007; Ribeiro et al. 2009). In general, the optimum frying oil should be non-hydrogenated (for nutritional reasons) and have a high oxidative stability (for frying life reasons). The oil must also be available and relatively cheap. Palm oil meets all these requirements (Gunstone 2011; Stier 2013).

Palm oil is extracted from the fleshy orange-red mesocarp of oil palm fruits (*Elaeis guineensis*) which contain 45 – 50% by weight oil. The oil palm fruit gives the highest yield of oil per unit of cultivated area among oil crops. The oil palm is a perennial crop, and its high oil yield per planted hectare provides sufficient and reliable supplies at economic prices (Daud et al. 2012). Crude palm oil (CPO), also known as virgin palm oil (VPO), is nature's richest source of carotenoids. The total carotenoids content of VPO varies from 500 – 700 mg/kg and is responsible for the orange-red color of the oil. It is also rich in vitamin E (1,200 ppm) especially tocopherol and tocotrienol (Sarmidi et al. 2009). VPO is naturally semi-solid at room temperature. It is the only vegetable oil with a balanced composition of saturated and unsaturated fatty acids both in the crude and refined forms (Edem 2002). Other minor components that stabilize palm oil include phytosterols, squalene, and diacylglycerols (Ping and May 2000; Pande et al. 2012). Palm oil does not require hydrogenation in much of food applications, therefore, *trans*-fats are not present (Rossell 2001). However, despite these excellent qualities, VPO has a negative image mainly due to the hitherto unfavorable media campaign, classifying it as 'bad tropical oil' that raises LDL and lowers HDL.

Canola is used as the name for rapeseed with substantially reduced amounts of erucic acid (C22:1 $\leq$ 2%) and glucosinolates. The term ''canola'' is used mainly in the American continent and Australia, while rapeseed is commonly used in Europe. The rapeseed species used to produce canola oil and meal belong to the genus *Brassica* and the family, *Cruciferae* (Przybylski and Eskin 2011). The conversion from high erucic acid rapeseed (HEAR) to canola resulted in an oil with very low levels of saturated fatty acids (SFA) (6%), high levels of monounsaturated fatty acid (MUFA) particularly, oleic acid (58 – 61%) and moderate levels of polyunsaturated fatty acids

(PUFA) (36%). The fatty acid composition of canola oil is favorable in terms of health benefits. However, high levels of oleic acid and PUFA makes canola oil highly susceptible to oxidative rancidity and thermo-oxidation (Ackman 1990; Aachary et al. 2014).

Oils and fats for commercial frying applications must be stabilized to delay or prevent any changes caused by oxidation, polymerization, or hydrolysis during high-temperature processing. Synthetic antioxidants are usually added to improve the stability of the oils. The most commonly used antioxidants are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and tert-butyl hydroquinone (TBHQ) (Ardabili et al. 2010). Blending is also carried out to give oils with the recommended ratios of SFA, MUFA, and PUFA (Mobin Siddique et al. 2010). Blending can modify the fatty acid levels of the frying oils. For instance, mixing high-oleic sunflower oil with corn oil, hydrogenated soybean oil with soybean oil, palm olein with sunflower oil and sunflower oil with palm oil have been reported (Frankel and Huang 1994; Gulla et al. 2010; Li et al. 2014). In these cases, blending decreased the rate of evolution of free fatty acids and total polar compounds during discontinuous prolonged frying. The food and vegetable oil industries have continued to search for alternative sources of frying oils that combine thermostability with proven health benefits to consumers. Also, while many studies have been conducted on the auto- and thermal oxidation of fats and oils, the mechanism and by-products of oxidation, the kinetics of deterioration and/or accumulation of each breakdown products and the different homologs of the phytonutrients have not been well elucidated.

1.2 Hypothesis

The quality of deep-fat fried food is directly correlated to the quality of the oil used in the frying operation. Taste, flavor, shelf life, consumer acceptance, and safety of fried foods essentially depend on the quality of the frying oil. Since high temperatures used in frying lead to complex degradation of both saturated and unsaturated oils, the monitoring of the frying oil quality degradation, therefore, is an important issue for both food frying operators and food control/regulatory agencies. Once heating is initiated, the oil begins an irreversible degradation process. This leads to the build-up of breakdown products in the oil. It is important to carefully choose the right oil for frying and to monitor the oil quality changes during frying. The aim is to prolong the optimum useful life of the oil without compromising the quality of the fried product. This present study sought to further deepen the understanding of the characteristics, behavior and

stability of virgin palm oil (VPO), refined canola oil (RCO) and blends of VPO and RCO during repeated deep-fat frying of foods. It was assumed that by blending VPO and RCO, the result would be a frying medium with enhanced nutritional and essential physicochemical properties. It was also assumed that the thermostability of the blends of palm and canola oils would improve by the availability of natural antioxidants present in VPO. It was equally anticipated that the carotenes, tocopherols, and tocotrienols would be relatively stable and migrate into the fried food products.

1.3 Overall Objective

The overall objective of this study was to monitor the behavior of VPO and its major phytonutrients during multiple deep-fat frying cycles. To modify the physicochemical properties of VPO and RCO by blending and comparing the frying characteristics of the blends with those of VPO and RCO alone. The experimental data obtained was used to explore the characterization of the oil samples by near-infrared spectroscopy and kinetic models will be applied to predict the thermo-stability of the oil as well as the uptake of the phytonutrients by the fried products. The findings from this study are important in promoting the greater utilization and inclusion of VPO as a frying medium. Increasing the phytonutrients level in so called 'junk foods' such as fried snack foods and French fries means desirable product enrichment with health promoting antioxidants and bioactives that will benefit consumers. The absorbed antioxidants will also extend the shelf stability of par-fried and frozen retail fries on supermarket shelves.

1.4 Specific Objectives

This study has the following specific objectives:

1. Non-destructive characterization and prediction of the basic chemical properties of virgin palm oil (VPO), refined canola oil (RCO) and their binary blends using Fourier transform near-infrared (FTNIR) spectroscopy.

2. Evaluation of the behavior and thermostability of VPO, RCO and blends as media for repeated deep-fat frying.

3. To model the degradation kinetics of VPO, RCO, and blends at different frying temperatures and times.

4. To assess the migration and retention of the carotenoids, tocopherols, and tocotrienols into the fried food.

5. To determine the thermostability and degradation kinetics of the phytonutrients in the oil samples at elevated frying temperatures and times.

CHAPTER 2

2. LITERATURE REVIEW

2.1 The art of food frying

Since ancient times, plant, and animal products are cooked, baked, roasted, or fried, to make them more palatable and to improve their digestibility. The heat can be transferred from air, water, or oil to the product. Frying as a cooking method started probably around the 6th Century BC. It is the process of using oil as the cooking medium (Gertz et al. 2014). The range of temperatures used for frying is 150 – 200 °C. Heat transfer during frying can be by conduction, convection, or both (Moreira 2014). High temperatures promote reactions between food components such as proteins and carbohydrates, moisture loss, oil uptake, surface dehydration, and crust formation. The elevated temperatures used during frying do not exceed the boiling point of water inside the food. In contrast to boiling in hot water, the frying of foods results in desirable appearance (color), texture (crispness), flavor, and taste. Compared to the other cooking methods, frying is a more efficient process and has grown in popularity not just in home cooking, but also in commercial food preparations because of its speed and operational simplicity (Gertz 2014). Though fried foods have a negative view in the Western diet, frying is considered to have almost the same or even less effect on nutrient losses as compared to other cooking methods. It also results in product enrichment (Chiou et al. 2009). Frying also leads to oil decomposition. The nature, rate, and products of decomposition are influenced by the composition of the oil (fatty acids pattern, unsaponifiable matter content), the mode of frying (intermittent or continuous, shallow- or deep-frying), applied frying temperature, the length of the frying process, and type of food being fried.

2.2 Deep-fat frying

Deep-fat frying (DFF) is one of the most popular methods for the preparation of food. DFF is the process of cooking by completely immersing foods in oil heated to a pre-determined temperature. It is an easy, fast, and relatively cheap cooking method that results in palatable foods with wonderful flavors and aromas. Most deep-fat frying operations are done at temperatures between 165 – 180 ºC under atmospheric conditions (Moreira 2014). During deep-fat frying, the product undergoes two correlated mass transfers: water loss and oil uptake. The outcome is a cooked, dried, and crispy product (Bassama et al. 2015). Most foods that undergo DFF are solids with pores filled with water and air. When food is introduced into the hot oil, sudden evaporation of free moisture

on the surface causes a violent bubbling action. This action enlarges the contact area between air and oil and may accelerate oil degradation (Gertz 2014). During DFF, heat transfer is by convection from the oil to the surface of the product and by conduction to the center of the product. As the water inside the product reaches the boiling point, pressure is increased. Thus, as surface water leaves the product, moisture from the interior of the food migrates from the central position radially outward to the walls. This water transport is responsible for cooling in the external region of the product during early periods of frying, ensuring that the food does not get burnt or charred. The moisture in the inner part on reaching boiling point also induces starch gelatinization and proteins denaturation (cooking) (Vitrac et al. 2002). As DFF progresses, other reactions such as caramelization, Maillard reaction, crust formation, textural and flavor changes occur. These depend on either the frying process itself or the nature of the food or type of frying oil (Marrikar et al. 2003). The high frying temperatures, the presence of oxygen, moisture, trace elements and free radicals lead to thermo-oxidation reactions and oil breakdown. Consequently, volatile and non-volatile oxidative compounds are formed. These breakdown compounds affect the quality of frying oil and fried product. Foaming also occurs when products with high initial moisture content are fried. Repeated and continuous use of degraded oils compromises the quality of the food and pose a potential risk to human health and nutrition (Andrikopoulos et al. 2003; Kita 2014). In frying technology, like in other fields, there is a continuous need for innovation in terms of process efficiency and product quality (Blumenthal and Stier 1991). Thus, split frying and vacuum frying have been proposed to help reduce oil uptake by fried foods and oil breakdown during frying (Moreira 2014).

2.3 Frying oils

The essential role of frying oil is to serve as an efficient heat transfer medium. The oil transmits the heat rapidly and evenly to the surface of the foods. At the same time, some of the oil/fat absorbed by the food becomes a source of flavor, nutrition, and energy (Boskou 2011; Taha et al. 2014). It is difficult to give an accurate definition of the “ideal oil” for the many applications and products available in the frying industry. Selecting a suitable frying oil must be based on the process of interest, food being fried, storage/shelf life of the finished product, and the cost. However, for nutritional reasons, a good frying oil should be low in free fatty acids (FFA), saturated and *trans*-fatty acids and high in *cis*-monounsaturated acids. Unsaturated fats are more susceptible to oxidative degradation reactions. Therefore, despite the nutritional value of essential polyunsaturated fatty acids, frying oil should be low in poly-unsaturation (≤ 2 % linolenic acid is

recommended) to have higher oxidative stability. The fatty acids composition (FAC) of the oil is also important (Boskou 2011). The aggressive heating over a longer period in the presence of moisture from the food and atmospheric oxygen lead to a series of chemical reactions, such as, oxidation and polymerization of unsaturated fatty acids. The result is an array of reaction products namely, volatile chain-scission products, non-volatile oxidized derivatives, and dimeric, polymeric, or cyclic substances which ultimately changes the composition of the triacylglycerol (TAG) (Stier 2013; Taha et al. 2014). Since oil becomes an important component of the fried product, changes and degradations in the frying oil affects the quality of the product. Therefore, understanding the individual oil chemistry and behavior during frying is crucial in optimizing the frying process and to ensure that the fried food meets public health expectations.

2.4 Oil chemistry

As shown in Figure 2.1, frying fats or oils are predominantly composed of three fatty acid molecules esterified to glycerol. They are hydrophobic (Scrimgeour 2005). The esterification of glycerol with the fatty acids forms mono-, di-, and triacylglycerols. The fatty acid (FA) present in the TAG is the basis of characterizing frying oils. These molecules may be long, medium, or short chain fatty acids (FA). FA with no double bond are termed saturated fatty acids (SFA) such as palmitic acid (C16:0) and stearic acid (C18:0). Those with one double bond are monounsaturated fatty acids (MUFA) (e.g. oleic acid C18:1). Those with more than one double bond are polyunsaturated fatty acids (PUFA), such as linoleic acid (C18:2) and linolenic acid (C18:3). Double bonds can be sited at different places in an unsaturated fatty acid. The position of double bonds has a greater role in determining the stability of fatty acid more than the number of them. Fatty acid molecules with closer double bonds are more unstable. An increasing number of double bonds in the fatty acid chain means a less stable oil, and the more likely the oil is to undergo degradation reactions. Good quality oil must be carefully chosen since it is difficult to control the degradation reactions that take place during frying. Oxidation of oil during heating and frying induces a significant loss of quality. This, in turn, leads to changes in functional, sensory, nutritional values and safety of the fried foods (Sambanthamurthi et al. 2000; Choe and Min 2007). Oxidation will further promote the formation of new compounds such as diacylglycerols, monoglycerols, monomers, polymers, free fatty acids, and other oxidative substances that are unsafe for humans (Scrimgeour 2005; Choe and Min 2007).

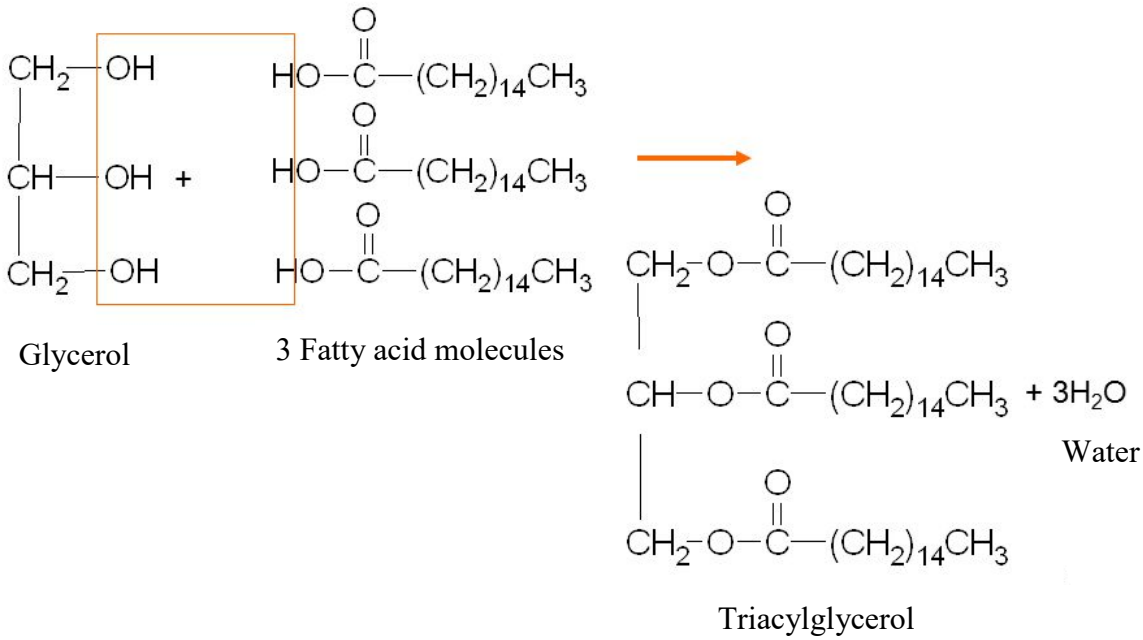


Figure 2.1: Formation of triacylglycerol from esterification of one glycerol molecule with three fatty acids.

2.5 Types of frying oil

In the early years of frying, animal fats dominated the industry due their stability and exceptional flavor properties conferred to foods fried using animal fats. In the 1980s, consumer advocacy groups began a campaign against using saturated fat for frying in fast food establishments. In response, the industry began using partially hydrogenated oils instead of tallow, lard, butter, and tropical oils. By the 1990s, numerous research studies linked *trans*-fatty acids to increased LDL cholesterol levels and a higher incidence of heart disease and most recently diabetes. In 2002, food policy makers, governments and researchers agree for the first time, that there is no safe level of *trans*-fats (Menaa et al. 2013). In recent times, the food frying industry relies more on different types of vegetable oils, blends of vegetable oils or blends of vegetable and animal oils (Boskou 2011). However, not all frying fats and oils can be used for all purposes (Choe and Min 2007). Over 40 types of vegetable oils have been mentioned in frying applications and studies all over the world. The most prominent ones are canola oil, soybean oil, corn oil, cottonseed oil, palm oil, palm olein, peanut oil, rice bran oil, safflower oil, sesame oil, coconut oil, palm kernel oil, olive oil, and sunflower seed oil (Gunstone 2011; Sebastian et al. 2014). The process of selecting the best frying oil is a balancing act. Health perceptions and stability considerations must be balanced. Also, to be considered is the odor, flavor, texture, and mouthfeel along with consumer satisfaction. Palm

oil is suitable for DFF due to the high level of natural antioxidants present, its composition and stability (Matthaus 2007). Canola oil is also widely used in DFF because of its high level of beneficial MUFA (Aladedunye and Przybylski 2012).

2.6 Virgin palm oil (VPO)

Palm oil is extracted from the ripened mesocarp of the fruits of oil palm tree (*Elaeis guineensis*). The oil palm fruit is a drupe formed in spiky tight bunches. The five leading producing countries are, Indonesia, Malaysia, Thailand, Colombia, and Nigeria. The oil palm tree gives the highest yield of oil per unit area of cultivated land, an estimated 58.431 million metric tons (MT) per year. One hectare of oil palm plantation can produce up to ten times more oil than other leading oilseed crops. Palm fruit produces two distinct types of oils: virgin palm oil (VPO) also known as crude palm oil (CPO) from the mesocarp and palm kernel oil (PKO) from the inside kernel (Gourichon 2013). Both CPO and PKO are important in world vegetable oil trade (Oil World 2013). A chart showing the recent trend in supply of vegetable oils in the world's market is shown in Figure 2.2.

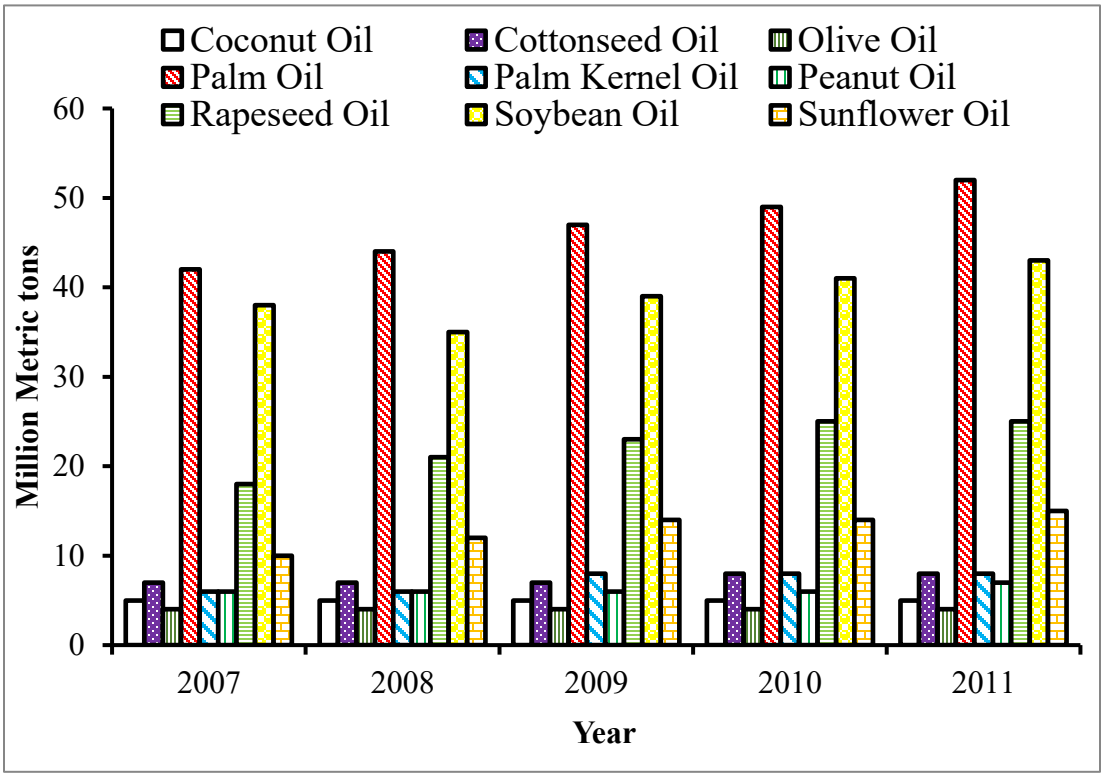


Figure 2.2: World supply of vegetable oils Gourichon (2013) and Oil World (2013).

VPO is also called red palm oil because of its high content of carotenoids. It is a rich source of vitamin E (600 – 1000 ppm); coenzyme Q10 (ubiquinone) (18 – 25 mg/kg) and sterols (325 – 365 mg/kg) (Akoh and Min 2010; Gunstone 2011). The edible food industry utilizes about 90% of palm oil while the remaining 10% finds application in soap and oleo-chemical manufacturing (Oil World, 2013). Palm oil has a unique FA and TAG profile which makes it suitable for numerous food applications. It is the only vegetable oil with almost 50 – 50 composition of saturated and unsaturated fatty acids. VPO is top prime among frying oils. In addition to its unique fatty acid composition, it has a high smoke point of about 230 ^{o}C (Akoh and Min 2010). VPO is also a source of vitamins. It has been reported in the literature that VPO and its fractionation products have beneficial health effects (Sambanthamurthi et al. 2000; Atkinson et al. 2008; Daud et al. 2013), are suitable and stable for restaurant batch frying and continuous frying in the manufacture of various snack foods (Berger 2005; Ismail 2005; Pande et al. 2012), and have similar frying performance as high oleic oils (Matthaus 2007). Palm oil has largely replaced beef tallow and lard in large scale industrial frying. Palm oil and palm olein are mostly used to fry foods like French fries, fried chicken, instant noodles, snack foods (Fan and Eskin 2012) and chicken fillets (Chen et al. 2014). Palm oil is resistant to oxidation, polymerization, and foaming. Palm oil does not produce any gummy or sticky residues in the fryer. Kochhar (2001), reported that palm oil's good performance and high oxidative stability is making it the oil of choice for the major snack food manufacturers in most European Union (EU) countries.

2.6.1 VPO processing, refining, and fractionation

The mesocarp of palm fruits contains about 56 – 70% edible oil when fully ripened. This oil can be extracted using different methods. These methods are grouped into four categories based on their throughput and degree of complexity. They are the traditional methods, small-scale mechanical units, medium-scale mills, and large industrial mills (Poku 2002). The basic unit operations associated with palm oil processing include fruit sterilization, fruit loosening/stripping, digestion, oil extraction, and clarification. The major oil extraction procedures employed are mechanical pressing and solvent extraction, either method can have extraction efficiency range of 75 – 90% (Owolarafe et al. 2002; Poku 2002). VPO obtained by either mechanical pressing or solvent extraction contains desirable and undesirable compounds. Desirable compounds include the TAG (neutral lipids) and health beneficial compounds such as the vitamins E (tocopherols and tocotrienols), carotenoids and phytosterols. The desired compounds serve as nutrients, antioxidants, and bioactive compounds. On the other hand, free fatty acids (FFA), phospholipids

(PL) or gums, and lipid oxidation products are the major undesirable compounds or impurities. The impurities are objectionable from a sensory point of view and are removed during the oil refining process (Čmolík and Pokorný 2000; Dunford 2012).

After extraction, the crude oil is usually washed with a solution of sodium hydroxide or sodium carbonate to reduce the FFA content, remove the PL and other polar lipids. This operation is generally referred to as alkali refining (Čmolík and Pokorný 2000). Other refining methods include physical, hydration/degumming, neutralization, bleaching and deodorization (Poku 2002). The gums are subsequently removed by centrifugation. Pigments are removed by bleaching with activated clay or charcoal while volatile oxidation products are removed through steam distillation at high temperatures and reduced pressure. The resulting oil is usually colorless, bland, and has good storage stability (Dunford 2012). Čmolík and Pokorný (2000), reported that the disadvantages of alkali refining include: losses of the neutral lipids, high energy requirement, and the high cost of equipment, time-consuming, and generates large amounts of effluents that pollutes the environment. For these reasons, physical methods of refining are recommended. Physical refining is based on the higher volatility of FFA and TAG at high temperatures and low pressures. During physical refining, volatile compounds including FFA are volatilized and neutral oil droplets are carried in the current of the stripping steam. These methods include steam refining, inert gas stripping, molecular distillation, membrane refining, hermetic system, supercritical carbon dioxide etc. (Gunstone 2011; Dunford 2012).

The quality of palm oil dictates and directs its use. Broadly speaking, high-quality palm oils are used in the edible oil industry while lower quality oils are used in the non-edible industry for biofuels, candles, cosmetics, and soap (Henson 2012). The good quality oil contains more than 95% neutral TAG and 0.5% or less FFA. As an industry rule, the FFA content of refined oils must be $\leq 0.1\%$. Most crude oils usually contain 1 – 3% FFA. Where the oil has high FFA, physical refining is recommended (Gunstone, 2011; Dunford, 2012). However, care must be taken since high temperatures lead to the destruction of carotenes. The consumers generally accept the red color of palm oil. High carotene content is desirable because of its pro-vitamin A and antioxidant activities (Chong 2012). The major unit operations in CPO refining are shown in Figure 2.3.

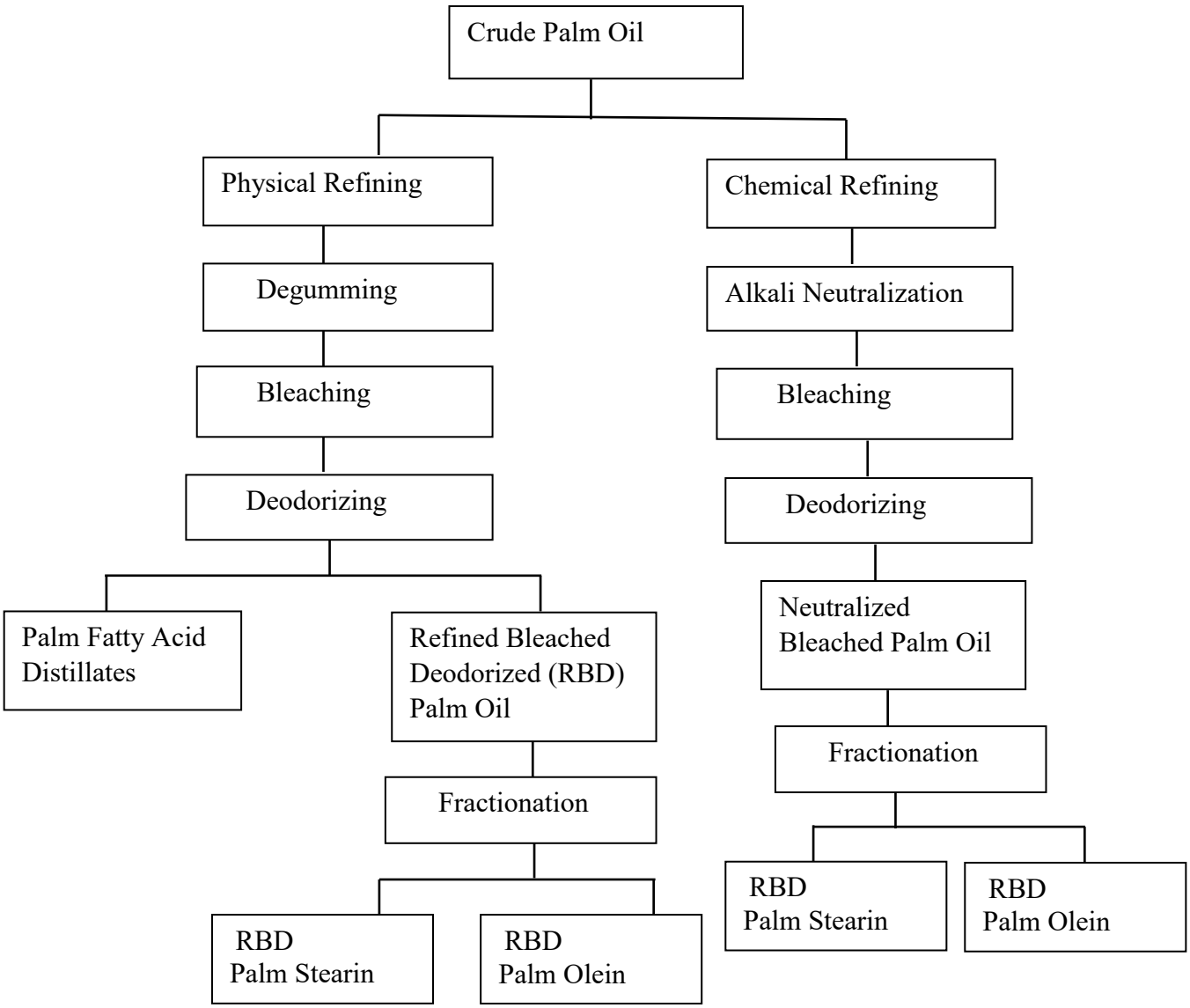


Figure 2.3: The major unit operations in CPO refining.

The utilization of most natural vegetable oils can be diversified through physical and chemical modification procedures. One such modification process is fractionation. Fractionation is a selective physical and/or thermo-mechanical process that separates a mixture into two or more fractions with distinct physical and chemical properties. It is a fully reversible modification process. Oils are fractionated to change the physicochemical properties of the oil such as reducing the degree of unsaturation of the acyl groups. This is done by redistributing the fatty acids chains using different selective crystallization and filtration methods (Kellens et al. 2007). The separation is based on differences in solidification, solubility, or volatility of the constituents. CPO is fractionated based on the differences in the crystallization behavior of the TAG. CPO easily separates into a low melting liquid fraction (65 – 70% palm olein) and a high melting solid fraction (30 – 35% palm stearin). The products mainly have different iodine values (IV). There are three different types of fractionation: dry fractionation, detergent fractionation, and solvent fractionation (Kellens et al. 2007; Pande et al. 2012). The major fractions of CPO can also be refined, bleached and deodorized (RBD). RBD palm olein is used for frying, cooking, shortenings, and margarine. RBD palm stearin is used mainly in food applications that require higher solid fats content such as shortenings, margarine, and Vanaspati. Other fractions such as palm mid-fractions (PMF) are used as cocoa butter equivalents in confectioneries while super olein is used in mayonnaise and salad dressings. Fractionation adds value to the oil and creates no undesirable by-products (Sarmidi et al. 2009). A summary of the advantages and disadvantages of the refining and fractionation methods is given in Table 2.1.

Table 2.1: Advantages and disadvantages of different refining and fractionation methods

Operation	Advantages	Disadvantages
Refining:		
Chemical	1. Functional Process 2. Great reduction of FFA	1. Losses of neutral TAGs 2. High energy requirement 3. Very expensive 4. Time consuming 5. Generates polluting effluents
Physical	1. Less energy requirement 2. Fewer by-products generated 3. Reduced Cost	1. High temperature destroys carotenes 2. Loss of deep red color 3. Oxidative damage more pronounced 4. Likely loss of the Vitamins E 5. Lower storage stability of oil 6. Strong time-temperature effect
Fractionation:		
Dry	1. Simple 2. Cheap 3. No chemicals 4. No effluent 5. No losses 6. No additional substance 7. Multi-step operation possible	1. Viscosity problems 2. Limited degree of crystallization
Detergent	1. Wetting agents allow the crystals to be easily suspended in the aqueous phase	1. Very expensive 2. Contamination of the end products by the detergent 3. Requires additional accessories
Solvent	1. Reduced viscosity 2. Short process time 3. High separation efficiency 4. Improved yield 5. Higher purity of products	1. High capital investments 2. High production costs 3. Possible fire hazards 4. Hazardous Chemicals and effluents

2.6.2 Physicochemical characteristics of CPO

Earlier CPO quality characterization was mainly defined in terms of total percentage of FFA, moisture, and impurities. This was followed by a five-point quality grading system that regulated oil production by cottage industries. 'Grade 1' oils must have FFA < 1% while 'grade 5' oils had FFA > 36%. 'Grades 2, 3 and 4' oils had FFA ranges of 9 – 18%, 18 – 27%, and 27 – 36%, respectively. This grading system stimulated the small-scale producers to improve their oil quality. Later, the specification 'Special Grade' palm oil with maximum FFA level of 4.5% at the point of sale was introduced. Further adjustment put the maximum FFA at 3.5%. Trade reports showed that by 1965 more than 80% of CPO export from Africa was of the 'Special Grade' quality (Iwuchukwu 1965; Berger 2007). Since the 1990s, some countries such as Malaysia have the set limits of FFA to ≤ 5% and a maximum of 0.25% for moisture and impurities for locally produced CPO (Chong 2012).

The physicochemical properties of palm oil and its fractions were extensively studied during the 1980s and 1990s. Research findings on the physicochemical properties of palm oil and its fractions have been published (Tan and Oh 1981; Tan and Che Man 2000; Tan and Nehdi 2012). CPO is classified as saturated oil with an iodine value (IV) range of 51 – 58 g/100g oil. Palm oils with a wider IV range of 46 – 63 g/100g oil have been reported. These types of palm oil may be mixtures of oils from different species of oil palm tree or oil mixed with various proportions of palm stearin (Edem 2002; O'brien 2010). The major physicochemical characteristics of palm oil are presented in Table 2.2.

Table 2.2: Physicochemical properties of palm oil

Characteristics	Typical	Range
Apparent density at 50ºC (g/ml)	-	0.892 – 0.899[a]
AOM Stability (hr)	54.0	53.0 – 60.0[b]
Melting Point (ºC)	37.5	33.0 – 45.0[b]
Oxidative Stability Index at 110ºC (hr)	16.9	16.6 – 19.0[b]
Refractive Index at 50ºC	-	1.449 – 1.456[b]
Smoke Point (ºC)	-	230.0 – 235.0[c]
Solidification Point (ºC)	-	35.0 – 42.0[b]
Solid Fat Content: 10ºC	34.5	30.0 – 39.0[b]
21.1ºC	14.0	11.5 – 17.0[b]
26.7ºC	11.0	8.0 – 14.0[b]
33.3ºC	7.4	4.0 – 11.0[b]
37.8ºC	5.6	2.5 – 9.0[b]
40.0ºC	4.7	2.0 – 7.0[b]
Specific gravity at 50ºC	-	0.888 – 0.889[b]
Viscosity (cP)	45.0	45.0 – 49.0[d]
Iodine Value (g/100g)	53.0	46.0 – 56.0[b]
Free Fatty Acid (% FFA as Palmitic)	-	3.17 – 5.0[e]
Peroxide Value ($mEqO_2/Kg$)	-	0.1 – 10.0[b]
Anisidine Value (mg KOH/g)	-	0.6 – 4.65[e]
Saponification Value (mg KOH/g)	196.0	190.0 – 209.0[e]
Unsaponifiable Matter (%)	0.5	0.15 – 0.99[b]
Total Polar Compounds (%)	13.5	9.47 – 19.50[d]
Total Polymer Materials (%)	0.5	0.4 – 15.0[d]
Saturated Fatty Acids SFA (%)	-	49.9 – 54.7[f]
Mono-unsaturated Fatty Acids MUFA (%)	-	37.1 – 39.2[f]
Poly-unsaturated Fatty Acids PUFA (%)	-	8.1 – 10.5[f]
Crystal Habit	β'[b]	-

Source : [a] (Codex Alimentarius Commission (CAC) 1999); [b] (O'brien 2010); [c] (Gunstone 2011); [d] (Berger 2005); [e] (Chong 2012); [f] (Tan and Nehdi 2012).

2.6.3 Phytonutrients and natural antioxidants of VPO

VPO contains minor components that demonstrate considerable nutritional and health benefits. The phytonutrients also referred to as micronutrients are listed in Table 2.3. These micronutrients include carotenoids, tocopherols, tocotrienols, sterols, phospholipids, and squalene (O'brien 2010). The carotenoids, tocopherols and tocotrienols maintain the stability and quality of palm oil and act as natural antioxidants (Wu and Ng 2007). The tocopherols and tocotrienols act as anti-cancer, anti-inflammatory agents (Luna et al. 2011; Daud et al. 2013), control atherosclerosis, and decrease cholesterol (Atkinson et al. 2008; Fu et al. 2014). The growing interest in the bioactivities of these micronutrients has led to the development of functional foods or nutraceuticals incorporating these phytonutrients (Zou et al. 2012).

Carotenoids are responsible for the diversity of color in nature. Alpha-carotene, β-carotene, and cryptoxanthin have demonstrated pro-vitamin A activity. Beta-carotene is the most potent pro-vitamin A carotenoid. The others are the α- and γ-carotenoids (Figure 2.4). Vitamin A is necessary for vision, growth, cellular differentiation, and other physiologic functions (Perera and Yen 2007; Fernández-García et al. 2012). VPO contains 500 – 700 ppm of carotenoids and is thus the natural richest source of carotenoids. VPO contains 33% α-carotene, 65% β-carotene and 2% other carotenoids such as γ-carotene and lycopene (Ng et al. 2012). The carotenes are responsible for the rich orange-red color of CPO. They act as antioxidants by trapping free radicals, neutralize thiyl radicals, chelate peroxy radicals and quench singlet oxygen in lipids. Stated simply, carotenoids protect the oil against oxidation by themselves being first oxidized before the oxidative attack on the TAG (Maiani et al. 2009; Böhm et al. 2012). In 1992, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) accepted and included palm oil carotenoids as a permissible food colorant (Zou et al. 2012). VPO has been proposed as an alternative treatment for vitamin A deficiency. The digestibility of α- and β-carotene found in VPO is high and this enhances their bioavailability (Maiani et al. 2009; Böhm et al. 2012). Rice & Burns (2010) reviewed a series of key intervention studies designed to investigate the impact of using red palm oil to improve the status of vitamin A. The review's focus was related to the use of palm oil in dietary supplementation and food fortification studies. They concluded that red palm oil increased dietary intake of pro-vitamin A carotenoids especially β-carotenes which are more abundant and better converted than α-carotenes. Palm oil is highly effective in improving vitamin A status amongst populations at risk of vitamin A deficiency.

Tocopherols and tocotrienols (termed tocochromanols) are usually called vitamin E. They are fat soluble. They have a chromanol head, formed by phenolic and heterocyclic rings, and a phytyl tail. The number and position of methyl substitutions on the chromanol nucleus give rise to the homologs α-, β-, γ-, and δ-tocopherols/tocotrienols (Figure 2.5). The difference in the structure of tocopherols and tocotrienols is only in the phytyl tail. The tocopherols have a saturated tail while the tocotrienols have an unsaturated chain with three isolated double bonds (Atkinson et al. 2008; Fu et al. 2014). The tocopherols and tocotrienols are present at different concentrations depending on the type of vegetable oil and its origin (Pinheiro-Sant'Ana et al. 2011). Palm oil is one of the richest sources of vitamin E in nature. The vitamin E in palm oil is unique since it is composed of both tocopherols and tocotrienols. CPO contains 600 – 1200 ppm vitamin E. Tocopherols account for 18 – 22% while tocotrienols account for 78 – 82%. Amongst the tocotrienols, the major ones are γ-tocotrienol, α-tocotrienol and δ-tocotrienol (Atkinson et al. 2008; Fu et al. 2014; Ahsan et al. 2015). Some vitamins E in CPO are lost during processing and refining. During fractionation, vitamin E tends to partition preferentially into the olein fraction (Sundram et al. 2002; Pacifico et al. 2012). Recent findings showed that palm oil's tocotrienols significantly inhibited debilitating illnesses such as diabetes, Crohn syndrome, Alzheimer's etc. (Zaiden et al. 2010; Luna et al. 2011; Fu et al. 2014). The stability of the different tocopherols and tocotrienols present in the refined vegetable oils basically depend on the fatty acid composition of the oil, and the type of tocopherol and tocotrienol homologs present. As antioxidants, tocopherols and tocotrienols act as free radical quenchers which contribute to the stability of palm oil. Tocopherols can interrupt lipid oxidation by inhibiting peroxide formation in the chain propagation step, or the decomposition process by inhibiting aldehyde formation (Schrøder et al. 2006; Rossi et al. 2007). Vitamin E as antioxidants are capable of neutralizing free radicals directly by donating hydrogen from its chromanol ring. In addition to fighting cancer, vitamin E has also been shown to be protective in bone, cardiovascular, eye, nephrological and neurological diseases; with α-tocopherol being regarded as the homolog with the highest biological activity (Peh et al. 2015). Tocotrienols have greater and unique anti-oxidant and anti-inflammatory properties than tocopherol. However, compared to tocopherols, the concentration of tocotrienols in human plasma is lower and needs to be supplemented (Fu et al. 2014). Carotenoids, along with vitamin E, protect the oil from thermal oxidation. During thermal oxidation carotene radicals are formed which are converted back to active carotene in the presence of tocotrienols. Schrøder et al. (2006) reported that this synergistic relationship decreased the oxidation of oil during frying of potato slices at 163 °C.

Other minor components of palm oil such as the sterols, higher aliphatic alcohols and hydrocarbons are found in the unsaponifiable fraction. Like all other edible oils of vegetable origin, the cholesterol content of palm oil is negligible. Refining decreases the phytosterols, ketones, wax and methyl esters present (Čmolík and Pokorný 2000; Edem 2002). Generally, the minor components act as antioxidants, boost energy, enhance the immune system and provide benefits in the prevention and treatment of coronary heart diseases (CHD). Palm oil also contains low levels (< 100 mg/L) of phenolic compounds (Sundram et al. 2002). The phenolic compounds are responsible for the initial darkening of palm oil during frying (Berger 2005). Like all vegetable oils, a mixture of sterols is found in CPO, palm olein, and their refined products. The sterols found in palm oil include β-sitosterol, campesterol, stigmasterol, and avenasterols. Amongst them, avenasterols exhibit antioxidant activity (Berger 2005; Lin 2011). The sterols of plant origin are referred to as phytosterols. Phytosterols are susceptible to oxidative degradation during food processing operations such as frying. During frying, phytosterols degradation occurs due to auto-oxidation. The products of this degradation are termed phytosterol oxidation products (POP). The POP can be found in both frying oil and the fried products (Tabee et al. 2008). These workers also reported that the POP found in palm olein used in frying French fries at 180 ^{o}C for 5 hours increased from 1.9 µg/g to 5.3 µg/g in the final batch. The degradation of phytosterols depends on the type of oil and polyunsaturated fatty acids present. Phytosterols appear to degrade faster in oils with high content of linoleic and linolenic acids. The rate of POP formation is also influenced by the type of sterol and the tocopherols content of the oil (Chirinos et al. 2013; Igoumenidis et al. 2011).

Table 2.3: Phytonutrients and other minor components of palm oil

Phytonutrient/Component	Range (ppm)
Carotenoids:	
α-carotene	30.0 – 35.16[b]
β-carotene	50.0 – 56.02[b]
Lycopene	1.0 – 1.30[b]
Total Carotenoids	500 – 700[b]
Tocopherol:	
α-tocopherol	129 – 215[a]
β-tocopherol	22 – 37[a]
γ-tocopherol	19 – 32[a]
δ-tocopherol	10 – 16[a]
Total Tocopherol	500 – 600[a]
Tocotrienols:	
α-tocotrienol	44 – 73[a]
β-tocotrienol	44 – 73[a]
γ-tocotrienol	262 – 437[a]
δ-tocotrienol	70 – 117[a]
Total Tocotrienols	1000 – 1200[a]
Phytosterols	326 – 527[b]
Phospholipids	5 – 130[b]
Squalene	200 – 500[b]
Ubiquinones	10 – 80[b]
Aliphatic alcohols	100 – 200[b]
Triterpene alcohols	40 – 80[b]
Methyl sterols	40 – 80[b]
Aliphatic hydrocarbons	50[b]

Source : (a) O'brien (2010) (b) Zou et al. (2012).

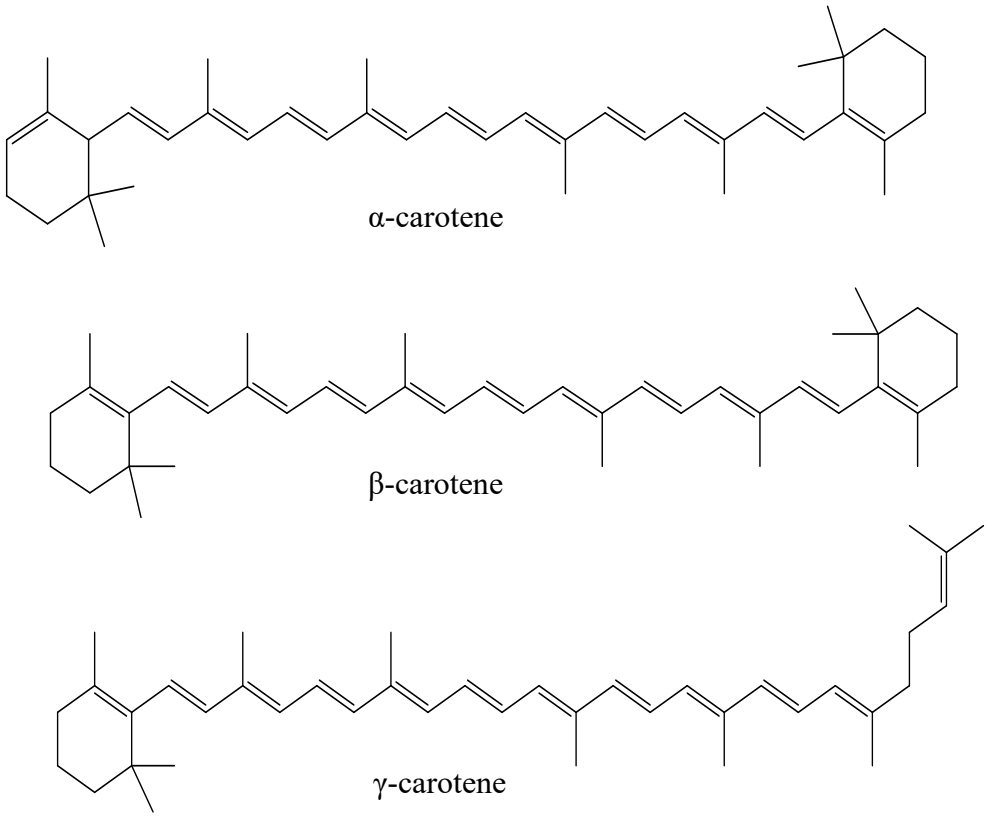
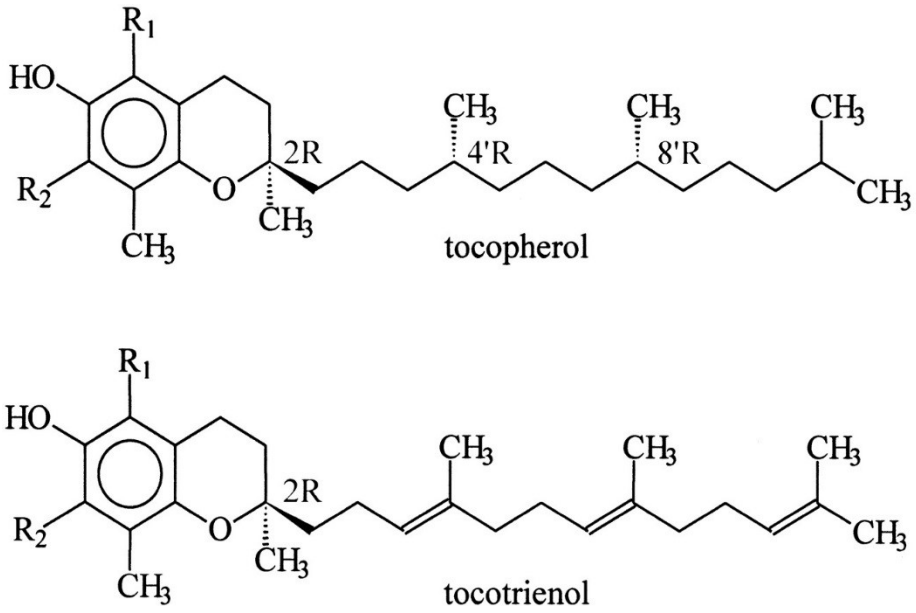


Figure 2.4: Major carotenoids in palm oil.



R_1	R_2	
CH_3	CH_3	α
CH_3	H	β
H	CH_3	γ
H	H	δ

Figure 2.5: Tocopherols and tocotrienols present in palm oil

2.7 Refined canola oil (RCO)

Canola oil comes from the seeds of *Brassica napus* (rapeseed, oilseed rape). Canola cultivars are a specific type of rapeseed with reduced glucosinolates (< 30 mmol/g) and erucic acid (< 2%) (Przybylski et al. 2005). Within the last forty years, work and studies on canola have rapidly developed to the extent that canola oil is now the third highest vegetable oil consumed globally, after palm and soybean oils (Oil World 2013). Canola oil is considered a healthy vegetable oil in terms of the FAC. It is a rich source of MUFA (especially oleic acid), PUFA, and distinctively low level of SFA (Gunstone 2011). The FAC profile shows that SFA is 6%, MUFA (62%), and PUFA (32%). It is a valuable source of ω-3 FA with ω-6/ω-3 ratio of 2:1 that allows canola oil to be considered an appropriate food source to improve current dietary patterns (Flakelar et al. 2015).

Canola is also a rich source of health beneficial bioactive phytonutrients including tocopherols and carotenoids. Crude canola oil contains high concentrations of α- and γ-tocopherol, approximately 270 and 420 mg/kg, respectively. The range of concentrations of carotenoids reported in the literature is 10 - 130 mg/kg. The variations could largely be due to the use of different extraction and detection methods (Przybylski et al. 2005; Li et al. 2011; Flakelar et al. 2015). However, current commercial processing and refining operations almost eliminate the carotenoids. To a lesser extent, tocopherol concentrations are also reduced during oil extraction and refining (Ghazani and Marangoni 2013). Thus, it is highly desirable to enrich refined canola with these valuable phytonutrients.

2.8 Blending and its effects

The blending of two or more oils with different characteristics is among the techniques to make new specific oil products. Mixing different kinds of vegetable oils not only changes the FA profile but also enhances the levels of bioactive phytonutrients and natural antioxidants in the blends and give better quality oils. The nutritional status of the oil is also improved at affordable prices (Marmesat et al. 2012; Aladedunye and Przybylski 2013). The food frying industry has adopted blending two or more oils with different characteristics to making new specific frying oils (De Leonardis and Macciola 2012; Tiwari et al. 2014).

In blending, the composite oils share advantages and disadvantages depending on the blend ratio. It is important that the blend complies with all the food laws and guidelines as well as meets consumer's expectations. For instance, oil blending is avoided if it causes foaming. The objective of blending can be commercial, technical, functional, nutritional or their interactions depending

on the intended application. Blending is widely accepted because it does not increase processing cost (Boskou 2011; Waghray and Gulla 2011). The blending of polyunsaturated oils with highly saturated oils reduces the content of linoleic and linolenic acids to the desirable level where the effect is similar to partial hydrogenation without worrying about the formation of *trans*-fatty acid isomers (Naghshineh and Mirhosseini 2010; Tiwari et al. 2014). It may be necessary to interesterify oil blends. Interesterification is a procedure for rearranging the fatty acids in oil or in a blend of oils so that triacylglycerol composition is changed. The FAC of the single oil or the blend remains unchanged and do not interact with triacylglycerol as they are of similar chemical composition (Benjumea et al. 2008; Christie and Han 2010).

The oxidation stability of a blend highly depends on those of the individual oils in the mix (Isbell et al. 1999; Tiwari et al. 2014). The oxidative stability of palm oil in a blend is principally due to its high saturation and heavy presence of natural antioxidants especially γ-tocotrienol (De Marco et al. 2007; Bansal et al. 2010b; De Leonardis and Macciola 2012). Different researchers have evaluated the frying characteristics of blends of other vegetable oils and palm oil/palm olein (Naghshineh and Mirhosseini 2010; Del Carmen Flores-Alvarez et al. 2012; Kupongsak and Kansuwan 2012; Tiwari et al. 2014). De Leonardis and Macciola (2012) reported that the fatty acid composition of oils and blends appeared to be the most decisive factor influencing oxidation stability. The saturated/unsaturated fatty acid ratio near to 1 offers optimally stable condition. The American Heart Association/ WHO guideline for smart blend ratio is 1:1:1 for SFA, MUFA and PUFA vegetable oils. Some important findings in the literature concerning blends of palm oil or palm olein are summarized in Table 2.4. Hayes and Khosla (2007) reported that palm oil (or palm olein) is the oil of choice for blending with unsaturated oils to provide specific functional characteristics without compromising health. This is because partially hydrogenated fats contain *trans*-fatty acids which have proven adverse health effects. Blending tailors and improves frying properties of oil by fine tuning the fatty acid composition and antioxidant balancing. It improves the fried product quality, improves appearance, and enhances the shelf life of the product. Blending also helps moderate the retail prices of oil for the consumers' benefit.

Table 2.4: Summary of effects of blending palm oil/palm olein and other vegetable oils

Oil Blends	Blend Ratio % (palm oil: other oil)	Effect	Reference
Palm oil: Sunflower oil	80:20 60:40	Palm olein with much higher IV. 40% blends reduced olein's cloud point.	(Nor Aini et al. 2005)
Palm olein: Olive oil	75:25 50:50	Oil remained liquid at ambient temperature. Increased oxidative stability.	(Naghshineh et al. 2009)
Palm olein: Canola oil	50:50	Better PV after repeated frying at 180ºC; French fries had reduced fat content than olein alone.	(Enriquez-Fernandez et al. 2011)
Palm olein:	50:50	Stable against oxidation; depressed melting point	(Mobin Siddique et al. 2010)
Palm oil: Extra virgin Olive oil	88:20	Induction time and oxidative stability like pure palm oil at 120, 130 and 140ºC	(De Leonardis and Macciola 2012)
Palm olein: Sunflower oil	50:50	Exhibited very high radical scavenging activity	(Ramadan et al. 2006)
Palm olein: Peanut oil	90:10 to 60:40	Increasing peanut imparted a pleasant nutty flavor; significant changes in percentage of C16:0 and C18:2	(Myat et al. 2009)
Palm oil: Sunflower oil	65:35	Decreased rate of evolution of FFA and polar compounds during 8 h of discontinuous frying; reduced degradation rate of tocopherols and tocotrienols	(De Marco et al. 2007)
Palm olein: Canola oil	75:25;	Frying stability of canola oil significantly improved by the blending.	(Farhoosh et al. 2009)
Palm olein: Olive oil: Corn oil	75:15:10	Frying performance of ternary blends better than binary blends	(Farhoosh et al. 2009)
Palm oil: Sesame oil	52: 48	Resulted in ideal fatty acid composition of 1:1:1 (SUFA: MUFA: PUFA) Stable to oxidative deterioration Enhanced nutritional qualities	(Tiwari et al. 2014)

2.9 Deterioration of frying oils

During frying, several chemical reactions such as hydrolysis, oxidation, polymerization, fission and isomerization take place. The presence of oxygen, moisture, trace elements and free radicals at the high temperatures used in frying accelerate the breakdown process. These reactions change the oil from a medium that is almost pure triacylglycerol when fresh to one that contains literally thousands of different degradation compounds. These can compromise the texture, taste, flavor, and the overall perception of the fried product. Additionally, potential risk to human health and nutrition may arise (Naghshineh and Mirhosseini 2010; Stier 2013). Oils with higher amounts of PUFA are not stable to oxidation and the products fried using such oils have shorter shelf-life. PUFA oils quickly break down at frying temperatures to form gums. Some physical changes such as increased viscosity and foaming, color changes and decreased smoke-point, also occur (Boskou 2011). Also, a vast number of volatile compounds are formed during the frying process, depending on the nature of the oil used and the frying conditions employed. The volatiles cover different classes of compounds, like alkanes, alkenes, alcohols, saturated and unsaturated aldehydes/ketones, and short chain fatty acids. These compounds are responsible for the distinctive pleasant odor and the unpleasant flavor of abused frying oil and can be used as markers of frying oil quality (Weisshaar 2014).

2.11.1 Hydrolysis

The extent of hydrolysis of oils during deep-fat frying is influenced by the moisture from the food. When the food material, usually at room temperature, meets the frying oil that has been preheated to a target frying temperature, the water within the food is almost immediately heated to boiling point. The steam so produced partially hydrolyzes the TAG by attacking the ester linkages in a relatively short period of about 5 – 10 min of deep-fat frying. Diacylglycerols (DAG), monoacylglycerols (MAG), glycerol and free fatty acids (FFA) are produced (Scrimgeour 2005; Bhattacharya et al. 2008). FFA are more volatile and decrease the smoke point of the oil. FFA levels in frying oil increase with the number of frying cycles and are therefore used to monitor the quality of the frying oil. MAG and DAG are polar and increase the oil's tendency to foam. Glycerol evaporates at 150 ^{o}C and the remaining glycerol in the oil promotes the production of FFA (Zeb and Murkovic 2013).

Thermal hydrolysis proceeds mainly within the oil phase rather than the water-oil interface. Water from foods is easily accessible to short chain and unsaturated fats and oils for hydrolysis because they are more soluble in water than long chain and saturated fatty acids. Large amounts of water

hydrolyze the oil rapidly. Water hydrolyzes the oil faster than steam. Large contact between the oil and the aqueous phase of food increases hydrolysis of oil (Scrimgeour 2005). Frequent replenishing of frying oil with fresh oil slows down the hydrolysis process. Sodium hydroxide and other alkalis used for cleaning a fryer increase the oil hydrolysis (Silvagni et al. 2012).

2.11.2 Oxidation

Most of the reactions that occur during frying that directly affects flavor, aroma, color, nutrition, and health-related properties of the oil are by means of oxidation. The oxygen within the frying oil and environment reacts with the oil. The chemical mechanism of thermal oxidation is principally the same as the autoxidation mechanism only that thermal oxidation is faster. The mechanism of thermal oxidation involves 3 steps: initiation, propagation, and termination (Choe and Min 2007; Choe and Min 2009).

Atmospheric oxygen is a di-radical compound. Radical oxygen requires radical oil for the oxidation of the oil. Oil assumes a radical state to react with radical oxygen in oxidation reactions. A radical oil is formed when the hydrogen on the weakest carbon-hydrogen bond of the TAG is removed (Scrimgeour 2005). Heat, light, metals, and reactive oxygen species facilitate radicals' formation in the oil. Polyvalent metals such as $Fe^{3+}$and Cu^{2+} remove hydrogen atoms from oil to form alkyl radicals by redox mechanism even at low temperatures. The site of radical formation in SFA is different from those of UFA. The alkyl radical of saturated fatty acids is formed at alpha position of the carboxyl group having electron-withdrawing property (Choe and Min 2009; Menaa et al. 2013).

Lipid peroxidation is initiated by an attack on a fatty acid's side chain by a radical abstracting a hydrogen atom from a methylene carbon. The more double bonds present in the fatty acid the easier it is to remove hydrogen atoms and consequently form a radical, making saturated fatty acids (SFA) and monounsaturated fatty acids (MUFA) more resistant to radicals than polyunsaturated fatty acids (PUFA). After the removal, the carbon-centered lipid radical then undergoes molecular rearrangement and react with oxygen forming a peroxyl radical. These highly reactive molecules can then abstract hydrogen atoms from surrounding molecules and propagate a chain reaction of lipid peroxidation (Carocho and Ferreira 2013). The hydroperoxides are not generally stable during the deep-fat frying. Hydroperoxides are decomposed to alkoxy radicals and hydroxy radicals by homolysis of the peroxide bond. The hydroperoxides are decomposed to produce oxy- and hydroxy-radicals. The alkoxy radical reacts with other alkoxy radicals or is

decomposed to form non-radical products. The formation of non-radical volatile and nonvolatile compounds at the end of oxidation is called the termination step (Silvagni et al. 2012; Menaa et al. 2013).

The 3 stages of thermoxidation can be summarized as follows:

Initiation phase: $RH \rightarrow R^{\cdot} + H^{\cdot}$

$$RCH{=}CHR + O_2 \rightarrow RCH - CHR\text{-}O\text{-}O^{\cdot}$$

Propagation phase: $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$$

Termination phase: $R^{\cdot} + R^{\cdot} \rightarrow RR$

$$ROO^{\cdot} + ROO^{\cdot} \rightarrow ROOR + O_2$$

$$ROO^{\cdot} + R^{\cdot} \rightarrow ROOR$$

$$RO^{\cdot} + R^{\cdot} \rightarrow ROR$$

2.11.3 Polymerization

At elevated temperatures and limited oxygen supply as deep-fat frying progresses, the main reactions lead to polymerization. The major decomposition products of frying oil are nonvolatile polar compounds, triacylglycerol dimers, and polymers. Dimers and polymers are large molecules with a molecular weight range of 692 – 1600 Daltons. They are formed by a combination of —C—C—, —C—O—C—, and —C—O—O—C— bonds. Dimers and polymers have hydroperoxy, epoxy, hydroxyl, and carbonyl groups linkages (Scrimgeour 2005).

Dimers and polymers are either acyclic or cyclic depending on the reaction process and kinds of fatty acids that make up the oil. Dimerization and polymerization in deep-fat frying are radical reactions. Alkyl radicals are formed preferably at the methylene carbons alpha to the double bonds. Dimers are formed from the reactions of allyl radicals by C—C linkage. TAG react with oxygen and produce alkyl hydroperoxides (ROOH) or dialkyl peroxides (ROOR). They are readily decomposed to alkoxy and peroxy radicals by RO—OH and ROO—R scission, respectively. Alkoxy radicals can abstract hydrogen from the oil molecule to produce hydroxyl compounds, or combine with other alkyl radicals to produce oxy-dimers. Peroxy radicals can combine with alkyl

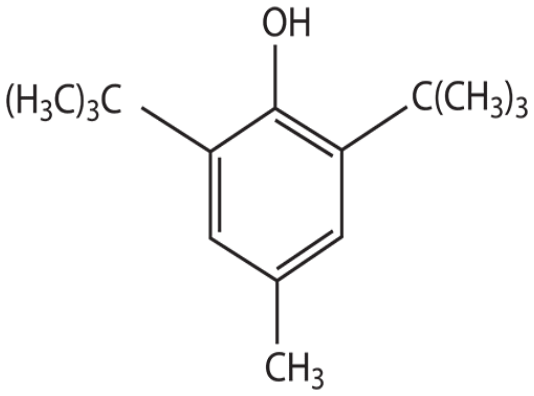
radicals to produce peroxy dimers (Scrimgeour 2005; Choe and Min 2007). Formation of dimers and polymers depends on the oil type, frying temperature, and number of frying cycles. As the number of frying cycles and frying temperature increase, the amounts of polymers increase. Oil rich in linoleic acid (C18:2) is more easily polymerized during deep-fat frying than the oil rich in oleic acid (C18:1) (Boskou 2011; Zhang et al. 2012).

Polymers formed during deep-fat frying are rich in oxygen. Oxidized polymer compounds accelerate further degradation of the oil, increase oil viscosity, reduce the heat transfer, increase oil absorption by fried product, and induce foaming and development of undesirable color in the food. Polymers produce the brown resin-like residues along the sides of the fryer and the coil of the heating elements (Enriquez-Fernandez et al. 2012; Menaa et al. 2013).

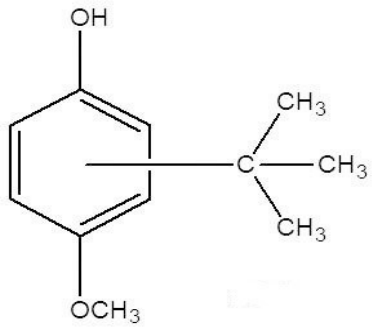
2.10 Use of synthetic antioxidants

Oxidation in foods can be minimized by removing pro-oxidants such as FFA, metals, and oxidized compounds, and by protecting foods from light. Limiting the availability of oxygen or adding oxygen scavengers can also lower the rate of oxidation reactions. However, it is very difficult to completely remove all the pro-oxidants and oxygen. Therefore, antioxidants are added to the oil or food. Antioxidants significantly delay or inhibit oxidation of the oxidizable substrates at low concentrations (Choe and Min 2009). Resistance to oxidation of oils during deep-frying depends mainly on the fatty acid composition, the type and amount of antioxidants present (Taha et al. 2014). Besides the endogenous antioxidants that are naturally present in the oils, some synthetic antioxidants have long been used in the oil industry to prolong the "useful life" of the oil. They include compounds like butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA), tert-butyl hydroquinone (TBHQ), and propyl gallate (PG) (Figure 2.6). BHT and BHA are the most widely used to prevent the oxidation of fatty acids while TBHQ is used to stabilize and preserve the freshness, nutritive value, flavor, and color of animal food products (Carocho and Ferreira 2013).

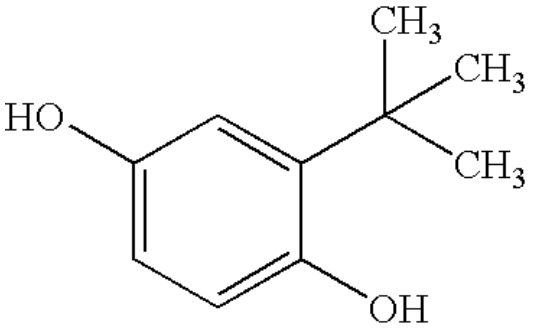
As reported by Pokorný (2007) and Carocho and Ferreira (2013), the antioxidant mechanisms include: inhibition of free radical oxidation reactions (preventive oxidants) by inhibiting the formation of free lipid radicals; interruption of the propagation autoxidation chain reactions (chain breaking antioxidants); quenching singlet oxygen; synergism with other antioxidants; reduction of hydroperoxides into stable compounds; chelating metals (converting metal pro-oxidants, Fe^{3+} and Cu^{2+}, into stable products); and inhibition of pro-oxidative enzymes (lipoxygenases).



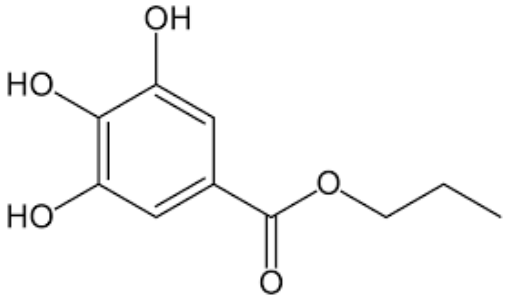
Butylated hydroxyl toluene (BHT)



Butylated hydroxyl anisole (BHA)



Tert-Butyl hydroquinone (TBHQ)



Propyl gallate (PG)

Figure 2.6: Important synthetic antioxidants used in the vegetable oil industry

2.11 Quality evaluation of frying oils

Various indices are used to evaluate the quality of frying oils. Different quantitative analytical methods for systematic evaluation of the quality of used and unused fats and oils have been proposed. International organizations such as those listed below provide similar but not identical techniques, methods, procedures, and protocols for the analysis of lipid samples. The guidelines differ as efforts continue to be made to ensure accuracy and precision of outcomes, and more sensitive test tools continue to evolve. The procedures require that the test sample must be a true representative of the target oil sample(s). Guidelines also exist for transport and storage of the lipid samples before analysis. To ensure the reliability of the analytical results, care must be given to

details such as the storage temperature, the type of container and the possible addition of antioxidants (Stier 2004 ; Gunstone 2011). The organizations providing guidelines include:

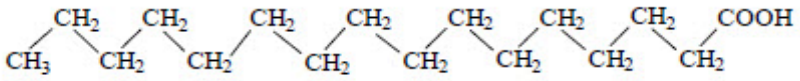
- The Association of Official Analytical Chemists (AOAC)
- The American Oil Chemists' Society (AOCS)
- The British Standards Institution (BSI)
- The International Organization for Standardization (IOS)
- The International Union of Pure and Applied Chemists (IUPAC)
- German Society for Fat Research (DGF)
- Palm Oil Research Institute of Malaysia (PORIM)
- American Society for Testing of Materials (ASTM)
- Codex Alimentarius Commission for Oils and Fats

The parameters usually measured as indicators of frying oil quality and degree of degradation are discussed in the following sections.

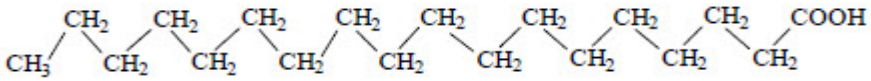
2.11.1 Fatty acid composition

Fatty acids esterified to glycerol are the main constituents of oils and fats. They are almost entirely straight-chain aliphatic carboxylic acids. The most common fatty acids contain 16 to 18 carbon chain length (C16 – C18). Below this range, they are characterized as short or medium chain and above C18; they are characterized as long chain fatty acids. Most vegetable oils contain fatty acids with chain lengths between C16 and C22, with C18 fatty acids dominating (Boskou 2011). The most reactive sites in fatty acids are the carboxyl group, the double bonds, and methylenes adjacent to them. Only rarely do saturated chains show reactivity. Carboxyl groups and unsaturated centers react independently, but when near, both may react through neighboring group participation (Scrimgeour 2005; Choe and Min 2007). Vegetable oils consist of 98% TAG, with the fatty acids distributed among different molecular species. They mainly consist of unsaturated fatty acids and are liquid at room temperature (Gunstone 2011). In general, deep-fat frying leads to loss of unsaturation in frying oils. For instance, relative loss of C18:2 has been reported (Alireza et al. 2010a). The rate of oxidation is approximately proportional to the degree of unsaturation of the fatty acids present in the frying oil (O'brien 2010). Linolenic acid (C18:3), with three double bonds, is more susceptible to oxidation than oleic acid (C18:1) that has only one double bond. Canola and soybean oils are examples of vegetable oils that contain high proportions of linolenic acid. This is one of the reasons why canola and soybean oils are not considered satisfactory for frying. Oils

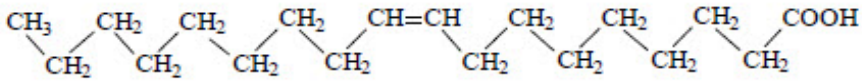
with a high degree of unsaturation have a greater tendency to form polymeric degradation products rather than highly polar materials. Oils and fats that contain more saturated fatty acids demonstrate higher resistance to oxidative alterations (O'brien 2010; Bittman 2013). The most important fatty acids common to CPO and RCO are shown in Figure 2.7.



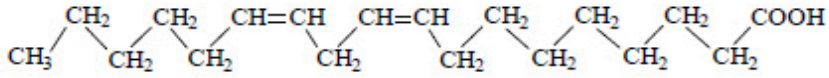
Palmitic acid (C16: 0)



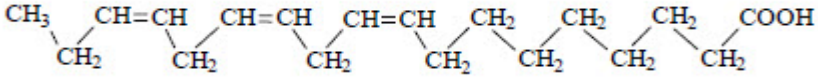
Stearic acid (C18: 0)



Oleic acid (C18: 1)



Linoleic acid (C18: 2)



Alpha-Linolenic acid (C18: 3)

Figure 2.7: Major fatty acids present in palm and canola oils

2.11.2 Iodine value (IV)

IV is a measure of the degree of unsaturation. It is expressed as the weight percent of iodine consumed by the oil in a reaction with iodine (Scrimgeour 2005). Researchers have found a decrease in the IV of oil after heating due to intensive thermo-oxidative transformations. The decrease in IV can be attributed to the destruction of double bonds by oxidation, scission, and polymerization (Alireza et al. 2010a; Aladedunye and Przybylski 2012). Frying oils are considered

spoiled if the decrease in IV compared with the IV of unused oil is greater than 16 (Firestone 2007).

2.11.3 Free fatty acids (FFA)

Lipases hydrolyze fatty acids from lipid species such as TAG. Lipase-catalyzed reactions take place at even low temperatures releasing mainly FFA (Scrimgeour 2005). Heat treatment increases oxidative rancidity resulting in an increase in the evolution of FFA. The formation of FFA is mainly due to the hydrolysis of TAG at frying temperatures in the presence of moisture (Azizian et al. 2007; Brühl 2014). Total FFA depends on the amount of water introduced into the frying medium by the food, the food composition, the frying temperature, the oil turnover time, and the accumulation of burnt food particles (Choe and Min 2007; Bou et al. 2012). Also, greater amounts of free fatty acids form if the initial levels of FFA present in the fresh oil are higher. Thus, heated and unheated oils must be monitored by means of analysis (Alireza et al. 2010a). However, FFA only reflects hydrolytic changes, comprising only part of the complex degradation process that occurs during frying.

2.11.4 Peroxide value (PV), *p*-Anisidine value (*p*-AV) and Total oxidation value (TV)

Both auto- and thermo-oxidations produce hydroperoxides from unsaturation points of the FA chain. The rate of auto-oxidation generally increases with increasing unsaturation. In higher polyenes, the rate doubles for each additional double bond (Cox et al. 2000). The PV is a widely used analytical measure of oxidative deterioration of edible oils. It is a measure of the hydroperoxides content by iodine titration. The PV is expressed in terms of milliequivalents of peroxides per kilogram of the sample, which oxidize saturated potassium iodide. As oil degradation progresses and more degradation products are formed, the PV increases. The critical limits for PV are 2 meq/kg. (Setiowaty et al. 2000). As oxidation advances, the unstable hydroperoxides soon break down to more stable aldehyde and ketone products (Choe and Min 2007). The amount aldehydic compounds formed is determined by reacting with anisidine reagent. This is known as *para*-anisidine value (*p*-AV) determination (Gotoh et al. 2011). Oxidation is better assessed by a combination of PV and *p*-AV, referred to as the Totox Value (TV). Where TV = (2 × PV) + *p*-AV. TV is a better index of oxidation than either PV or *p*-AV alone (Scrimgeour 2005).

2.11.5 Total polymer compounds

Dimers and polymers are formed at methylene carbons α to the double bonds during deep-fat frying. As the number of frying cycles and the frying temperature increase, the amounts of

polymers formed increase (Choe and Min 2007). The degree of polymerization is dependent on the unsaturation of oils and time of reaction. The reaction requires the presence of diene in the FA structure, which form a cyclic structure with a double bond. Thus, the oil rich in linoleic acid is more easily polymerized during deep-fat frying than the oil rich in oleic acid (Petrović 2010). Polymer compounds formed during deep-fat frying are rich in oxygen, accelerate further degradation of the oil, increase the oil viscosity, reduce the heat transfer capacity, produce foam, and develop undesirable color in the food. Polymers formation also lead to increased oil absorption by the fried food. They also produce brown resin-like residue along the sides of the fryer, where the oil and metals come in contact with atmospheric oxygen (Choe and Min 2007).

2.11.6 Total polar compounds (TPC)

These are low volatile deterioration compounds with higher polarity than the native TAG. They are basically modified TAG with at least one altered fatty acyl chain (Velasco et al. 2004; Marmesat et al. 2012). The determination of total polar compounds in frying oil provides a more robust measurement on the extent of deterioration due to its higher accuracy and reproducibility (Chen et al. 2013). The assessment of total polar compounds is independent of the type of oil used in frying since initial values of polar compounds are similar in unused oils (Velasco et al. 2004). Due to health concerns, guidelines, and regulatory limits by official food control agencies have established the maximum range of polar compounds in used frying fats and oils for human consumption to 24 – 27% (Stier 2013). Choe and Min (2007) surmised that frequent addition of fresh oil rejuvenates the oil in the fryer, decreases the formation of polar compounds, diacylglycerols, and free fatty acids.

2.11.7 Color properties

The color of the frying oil is a major parameter of acceptance to be evaluated on a daily basis (Berger 2005). Che Man et al. (1999), listed color as the most important index of oil quality assessment. They further stated that the darkening of frying oil is a useful indicator of excessive deterioration. Such darkened oils must be rejected as unfit for frying (Gunstone 2011). Color deterioration during frying has been attributed to FFA produced during hydrolysis, overheated pieces of food that stick to the surface of the fryer, amino-carbonyl reaction between thermally oxidized oil and amino acids exuded by foodstuffs and influence of coloring pigments, phytonutrients and minerals that may be present (Totani et al. 2006; Aladedunye 2015). Even though color changes are the most noticeable alteration of frying oils when in use, there is no correlation between color and frying oil quality. Good oil can be dark and bad oil can be light in

color (Stier 2013). However, the degree of darkening can be helpful if a consistent assemblage of frying oils and fried products are available. If a defined level of dark color is reached the oil is then considered unfit for use and should be discarded (Weisshaar 2014). For this purpose, schemes for color comparison must be provided by both vegetable oil producers and end users in the frying industry.

2.12 Methods of evaluating frying oil quality

Accurate measurement of lipid oxidation is a challenging task as the process is complex and depends on the type of oil, the oxidation agents, and the environmental factors. Choosing just one parameter to analyze oil quality is not sufficient and could be misleading. Thus, a combination of parameters is most suitable to describe oil quality and deterioration (Barriuso et al. 2013). The determination of total fats and quality of the fat in fried food samples begins with Soxhlet extraction. There are also instrumental techniques and procedures adapted from pharmaceutical and chemical engineering analysis protocols. The extraction technique is simpler, more accurate and more generally applied in lipid analysis than the instrumental methods. However, extraction techniques are time consuming, destructive and generate large volumes of laboratory effluents that lead to disposal challenges. On the other hand, instrumental techniques are non-destructive, give rapid useful results for online quality measurements in laboratories and food factories.

Over the years, the determination of the quality of used and unused oils has witnessed the development, implementation, and revision of a variety of methodologies. The methodologies include those involving use of organic solvents, spectroscopy, gas chromatography (GC), high-performance liquid chromatography (HPLC) (Gunstone 2011); thermogravimetric analysis (TGA) (Debnath et al. 2011); differential scanning calorimetry (DSC) (Tan and Che Man 2000; Marquez and Maza 2003); Fourier transform infrared (FTIR) and Fourier transform near-infra red (FTNIR) (Azizian et al. 2007; Casale et al. 2008; Mba et al. 2014). The most common methods are discussed below under the headings: volumetric analytical methods, non-volumetric analytical methods, and recent analytical methods.

2.12.1 Volumetric analytical methods

This refers to conventional standard analytical methods (SAM) used to determine both primary and secondary oxidation products that rely on the use of organic solvents. It includes iodometric titration procedures used to determine hydroperoxides (PV), degree of unsaturation (IV); ferrous oxidation method for peroxides; alkali based titration used for determination of free fatty acids

(FFA); derivatization into methyl or silyl esters respectively before other analyses that follow (Dumont and Narine 2007; Nuchi et al. 2009; Barriuso et al. 2013). These SAM have been used over the years as effective quality control and analytical tools to monitor frying fats and oils (Bansal et al. 2010a). While some are easy to determine by titration, others are laborious and involve large amounts of organic solvents and effluents (Weisshaar 2014).

2.12.2 Non-volumetric analytical methods

This refers to analytical techniques not requiring titration for direct determination such as ultraviolet-visible (UV-VIS) Spectroscopy and Chromatography. They are used to measure complex mixtures of lipid oxidation molecules of aldehydes, ketones, epoxides, hydroxyl compounds, oligomers, and polymers (Márquez-Ruiz et al. 2007).

Ultraviolet and visible radiation interacts with matter and leads to electronic transitions. The UV region is in the range of 190 – 380 nm while the visible region falls between 380 – 750 nm. In lipid quality management, a spectrophotometric determination is used for the *p*-AV test, malondialdehyde (MDA) test, tests for carbonyl compounds, and non-volatile unsaturated aldehydes (Nuchi et al. 2009). Spectrophotometric tests are simple but could lead to under- or over-estimation as well as variability in the results as a result of low-to-moderate selectivity and sensitivity (Barriuso et al. 2013; Weisshaar 2014).

A far more accurate, sensible, and specific for target compounds of interest is chromatography. Chromatographic techniques have been used to separate, purify, and identify oxidized monomeric and dimeric fatty acid methyl esters (FAME), MDA, and individual fatty acids. The techniques include gas chromatography (GC) and high-performance liquid chromatography (HPLC) (Aguirre-González et al. 2010). Morales et al. (2010) reported that silica gel column chromatography (SGCC) and high-performance size exclusion chromatography (HPSEC) have proved satisfactory in determining polar compounds and fatty acid polymers in degraded refined vegetable oils. After separation of the compounds of interest, detection can be by flame ionization detector (FID), mass spectrometer (MS), photodiode array (PDA), fluorescence detector (FD), refractive index detector (RID) and variable wavelength detector (VWD) (Barriuso et al. 2013). Chromatographic methods require long and meticulous experimental work, precise control of experimental conditions and a certain level of complexity in data processing (Weisshaar 2014).

2.12.3 Advanced and recent analytical methods

The techniques discussed so far are too empirical. They highly depend on many experimental factors such as the extent of lighting and oxygen in the environment where the experiments are carried out, and the skill of the analyst. They are also generally time-consuming. Recently, various techniques have been reported for oil quality analysis. They are based on direct spectroscopic analyses of the samples like magnetic resonance-, fluorescence-, and vibrational- spectroscopy. Some other techniques are based on chemiluminescent properties of the products of oxidation. In most of these techniques, preliminary treatments are minimal or eliminated, require a small quantity of sample, are often non-destructive and give rapid, highly accurate and specific results (Ozaki et al. 2007; Barriuso et al. 2013; Du et al. 2012).

Some chemical reactions emit low-intensity light when they absorb electromagnetic energy. This light can be amplified and detected by a spectrometer. This is the basis of chemiluminescence (CL). CL has been used to detect lipid hydroperoxides using luminol to amplify the emitted light (Navas and Jiménez 1996). Fluorescence is the emission of light by a chemical compound that has been excited by absorbing light or other electromagnetic energy. It is a form of luminescence. Commonly, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. In fluorescence spectroscopy, the excitation wavelength range is 250 – 500 nm while the emission wavelength range is 280 – 600 nm. The interaction between proteins and aldehyde products of lipid oxidation produces fluorescent pigments which are used as markers of lipid oxidation (Karoui and Blecker 2010; Barrett et al. 2011).

Techniques based on the assessment of fundamental vibrational transitions of functional groups after absorption of discrete energy levels in the infrared (IR) spectrum have been developed. IR spectrophotometers measure electromagnetic energy absorption in the mid-infrared (MIR) region of wavenumber range 4000 – 400 cm^{-1} (2500 – 25000 nm) and near-infrared region of wavenumber range 12500 – 4000 cm^{-1} (800 – 2500 nm). Different kinds of bonds in a molecule exhibit different absorption bands or characteristic absorption in IR region where the fundamental vibrations occur. Each of these vibrations then raises overtones and combination bands that are observed in the IR region of the spectrum. Knowledge of IR absorption wavelength bands for each functional group is, therefore, necessary to be able to locate the corresponding bands in the NIR region. Mathematical tools such as Fourier transform (FT) or multivariate chemometric algorithms, such as partial least square regression (PLSR) and principal component analysis (PCA), are used correlate spectral changes to the changes of a specific functional group (Ozaki et al. 2007; Barriuso

et al. 2013). Fourier transform infrared (FTIR) and Fourier transform near-infrared (FTNIR) has been used to study the quality of palm and olive oils (Rohman and Man 2010), fatty acid classes (Sherazi et al. 2009), IV, FFA and PV of vegetable oils (Cox et al. 2000; Li et al. 2000; Mba et al. 2014), oil degradation (Ng et al. 2007; Falco et al. 2012) and polymerized TAG (Kuligowski et al. 2012).

Fourier transform Raman spectroscopy (FTRS) has been used to detect the formation of aldehydes, conjugated double bond systems, and isomerized *cis* to *trans* double bonds in vegetable oils (Muik et al. 2005), and fatty acid content of olive oil (El-Abassy et al. 2009). Simultaneous analysis of the oxidation of edible oils by infrared and Raman techniques has also been reported (Muik et al. 2007). Other techniques such as thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) are also alternative lipid analysis methodologies that show interesting and promising results (Debnath et al. 2011; Barriuso et al. 2013).

For restaurant and food service oil quality control, several test kits have been developed to measure the degradation state of in-process frying oils. They include the gel-based Veri-Fry® that measures FFA and TPC; the solvent-based Merck Oxifrit-Test that estimates TPC; the Merck Fritest that estimates carbonyl compounds; and the Policontrol Oil Test that estimates oxidized compounds. Also available is the water emulsion titratables (WET) kits mainly used by regulatory agencies and industrial frying plants (Bansal et al. 2010a; Sanibal and Mancini-Filho 2004).

2.13 Fried food products

Various types of fried foods of vegetable and animal origin are commonly consumed worldwide. Though fried products are often associated with "junk food" that aggravates the risk of overweight and obesity (Li et al. 2009), and sources of various thermo-oxidized compounds with significant health concerns (Ghidurus et al. 2013). The benefits offered by frying such as faster cooking time, peculiar flavor, crispy texture, crunchy mouthfeel, unique taste, attractive color, palatability, and satiety, still make fried foods popular (Albert and Mittal 2002; Bou et al. 2012; Vauvre et al. 2014).

2.13.1 Plantain chips

In tropical countries, plantains, cooking bananas and dessert bananas (*Musa spp*) are major fruit crops that have achieved the status of staple food in the producing countries (Yomeni et al. 2004). The *Musa spp* is low in sodium and fat content, and can be consumed by people who are intolerant to salt. They are rich in carbohydrate, antioxidants like dopamine and minerals like potassium and

calcium. They are also used to satisfy the calorific need of many developing countries (Mohapatra et al. 2011). They are consumed at maturity between the mature green and yellow stages of ripening after boiling, roasting, and frying. Flour can also be produced from the *Musa* fruits (Yomeni et al. 2004). The plantain especially is used in making fried chips or crisps after washing, peeling, and cutting to uniform slices. The slices can be pan-fried or deep-fat fried to produce plantain chips. Salting, spicing and sweetening can be pre- or post- the frying process, depending on the consumers' preference. The cooled plantain chips can be consumed immediately or packed in hermetically sealed plastic sachets for retail or delayed consumption (Aurore et al. 2009).

2.13.2 French fries and crisps

French fries and crisps are among the most popular snack products obtained from potatoes. The term "French fries" refers to an intermediate product or a ready-to-eat product reaching the consumer in a fried form. They are prepared by blanching strip-shaped potatoes of different thickness, sliced potatoes, crescent-shaped potatoes, and frying in preheated oil. Crisps are thin slices of potato, fried in oil or fat until their moisture is below 2% (Lisinska and Leszczynski 1989). The production of French fries could be a single stage deep-fat frying process or two immersion stage processes, par-frying and finish-frying. The par-frying process is usually followed by freezing and freezer storage, while the finish-frying process follow later (Agblor and Scanlon 2000; Vauvre et al. 2014). Potato is low in fat content and is a significant source of phenolic compounds, anthocyanins, and ascorbic acid (Nassar et al. 2014). In most cases, the lipid content of the French fries and crisps comes from the oil absorbed during the frying process. Therefore, the nutritional characteristics of the fried products can be modified by the type of frying oil selected and the frying conditions. Suitable conditions must be maintained in each frying cycle, to have well-controlled production and products (Bou et al. 2012).

2.14 Quality of fried products

Each step of the unit operations in frying, type of oil used and the type of raw material fried play crucial roles in the final quality of fried products (Agblor and Scanlon 2000). The optimization of the quality of the fried products depends on careful modification of the processing conditions in the various unit operations. The modifications must be cautious as changing the processing conditions may positively influence the outcome of one quality attribute while at the same time negatively affect another attribute (Vauvre et al. 2014). The quality of fried products is primarily determined by the amount of oil absorbed, color and texture characteristics.

2.14.1 Moisture loss and oil uptake

Deep-fat frying temperatures (150 – 190 ºC) is above the boiling point of water (Aladedunye 2015). These high temperatures lead to the formation of water vapor during frying. The water vapor escapes to the surrounding atmosphere due to pressure and concentration gradients. The escaping vapors leave behind a porous network of open channels that allow oil to enter the food being fried (Mellema 2003). It has been reported that oil absorption by fried foods is highly dependent on the amount of moisture lost (Pedreschi et al. 2005). Other factors that affect oil uptake by fried foods include: pre-frying treatments, surface treatments, porosity, characteristics of food being fried, type of oil, oil quality, initial interfacial tension, frying procedure, temperature, and time (Lalam et al. 2013; Moreira 2014). Foods usually have complex and heterogeneous porous structure that makes studying and understanding the mechanism of oil uptake very challenging.

Recent studies have shown that oil uptake is largely a surface phenomenon. The dry matter content of food, the surface characteristics and microstructure have more pronounced influence on oil uptake (Pedreschi 2012; Aladedunye 2015). Durán et al. (2007) reported that a large fraction of oil is absorbed after frying and during cooling of the fried products. Therefore, post-frying management such as quick drainage of adhering oil by vigorous shaking of the products after it leaves the frying medium and quickly wiping off any adhering surface oil helps reduce the amount of post-frying oil taken up by the product. However, most studies on reducing fat or oil uptake during frying, targets pre-frying treatments that alters the surface and microstructure of the food prior to frying (Rahimi and Ngadi 2016). Some of these techniques reported in literature include immersion in sugar, brine and other aqueous solutions, blanching followed by drying using hot air, oven, microwave and freeze-drying, the use of different coating materials such as batter, breading, hydrocolloids, and proteins (Alvarez et al. 2000; Pedreschi 2012; Rahimi and Ngadi 2016).

2.14.2 Sensory characteristics

Sensory characteristics refer to the appearance, taste, odor, flavor, texture and sound associated with foods as perceived by the human senses. Researchers aim to understand how human senses work and respond to stimuli both from natural and processed foods and added ingredients. The understanding helps to improve processing and testing methods. The most important and distinguishing sensory attributes of fried foods are the texture and the color (Krokida et al. 2001a, c). Collectively, the mouthfeel, sound, and consistency of a food all contribute to the texture of the food. For fried products, this generally refers to increase in the firmness, crispiness, and hardness

because of crust formation and protein denaturation (Krokida et al. 2001c). Kita (2014) reported that the texture of fried potato products correlated positively with the fat content and composition of the frying medium. Higher frying temperatures decreased hardness of French fries and potato crisps. Also, compared to products fried at lower temperatures, those fried at higher temperatures were more crispy and delicate.

Two major approaches namely, descriptive sensory (subjective) and instrumental (objective), have been used to evaluate the sensory attribute of texture of fried foods (Segnini et al. 1999). However, it costs a lot of money and time to organize panelists and prepare foods for the highly subjective descriptive sensory panel evaluation. This limits the use of sensory panels (Chen and Opara 2013). In recent times laboratory texture evaluation involves instrumental measurement. These are more objective tests using a wide range of texture measurement instruments ranging from simple hand-held devices to the Instron universal testing machine and texture analyzers. The instruments provide time-series data of product deformation thereby allowing a wide range of texture attributes to be calculated from force–time or force–displacement data (Kita 2014). The application of novel and emerging non-invasive technologies such as near-infrared spectroscopy and hyper-spectral imaging to determine the textural attributes of both fresh and processed foods has also been reported (Chen and Opara 2013).

Visual appearance and color of food surface is the foremost quality attribute evaluated by the consumers. The color of foods has a strong influence on consumers' acceptance or rejection of the food. Most often the consumers relate the color of the product to other quality aspects such as sensory, nutritional, and even health benefits (León et al. 2006; Nisha et al. 2011). The measurement of the color of food products can be used as an indirect measure of the level of food pigmentation. Color measurement is simpler and faster than pigments measurements (Pathare et al. 2013).

The crust color of fried products such as potato and plantain is usually associated with Maillard, non-enzymatic reactions at high temperatures between the reducing sugars and proteins present (Pedreschi 2012) and frying time (Pathare et al. 2013). Low reducing sugar content is required to minimize color development during frying. In the case of French fries, the recommended reducing sugar limit for the chosen potato variety is 5 mg/g of potato (Yamsaengsung and Moreira 2002). Krokida et al. (2001a) measured the lightness (L*), redness (a*) and yellowness (b*) of fried potato strips in a CIELAB color space using spectrophotometer. They reported that L* increased in the

early stages of frying and in the later stages remained constant; while a* and b* values increased with increasing frying temperature and time. The authors also noted that strips with smaller thickness had lower L* values for the same frying temperature and time; and temperatures below 170 ^{o}C resulted in fried products with less redness and more yellowness.

2.15 Nutrient loss and uptake during frying

Fats and oils used in frying contain different kinds of bioactive phytonutrients depending on the source of the lipid. These phytonutrients contribute actively to the taste and color of foods and the normal functions and regulations of the human body (Fine et al. 2016). The bioactive compounds are known to chelate metals (such as iron and cupper), donate hydrogen atom, and scavenge harmful free radicals that can cause chronic diseases. Thus, they protect human tissues and cells from oxidative damages (Karam et al. 2016). Phytonutrients play an important role in human health as anti-oxidants, anti-bacterial, anti-fungal, anti-inflammatory, anti-allergic, anti-spasmodic, chemo-preventive, hepato-protective, hypo-lipidemic, neuro-protective, and hypotensive agents. They also help in preventing aging, diabetes, osteoporosis, cancer, and heart diseases. Dietary intake of phytochemicals promotes health benefits and protects against chronic degenerative disorders (Gupta and Prakash 2014).

Many of these phytonutrients are present in CPO (Table 2.3). Although these minor components constitute less than 1% of the oil, they nevertheless play an important role in the stability and quality of the oil. In addition, all these phytonutrients have antioxidant properties and some of them exhibit nutritional and health benefits beyond their antioxidant function (May and Nesaretnam 2014). Tocopherols and Phytosterols are important lipid-soluble minor constituents of canola seed that are also found in canola oil (Zhang et al. 2007). Some Australian cultivars of canola are reported to contain small levels of carotenoids (Flakelar et al. 2015). The presence of phytonutrients contributes to the stability of vegetable oils (Przybylski and Eskin 2006).

Regardless of negative viewpoints, deep-fat frying is said to have almost the same or even less effect on nutrient losses compared to other cooking methods (Bognar 1998). Since frying does not involve added water, leaching out of water soluble nutrients does not occur, instead some frying oil and its phytonutrients are absorbed in partial replacement of the in-situ moisture lost due to evaporation. The uptake of fats and oils by the fried product contribute to palatability, high energy density, increased nutritional, and sensory values (Saguy and Dana 2003; Pedreschi 2012). Fillion and Henry (1998) reported that while frying has little or no impact on the protein or mineral content

of fried foods, the dietary fiber content of potato is increased due to the formation of resistant starch. They also reported lesser loss of heat labile vitamins since process time is shorter when frying is compared to cooking and baking. However, oxidation and leaching of fat soluble nutrients can lead to loss of nutrients. For instance, some carotenoids initially present in the food being fried may be lost into the frying oil. But most often β-carotene losses are compensated if the oil used for frying is initially rich in β-carotene or enriched with vitamin E. Loizzo et al. (2013) reported a drastic loss of polyphenols originally present in bell peppers fried using olive oil. On the other hand, Kalogeropoulos et al. (2007) reported an overall polyphenols retention of 38.5% when green pepper is fried in extra virgin olive oil. Salta et al. (2008) reported that French-fries were enriched with phytosterols due to the absorption of frying oil, with β-sitosterol predominating in both fried oils and potatoes. The authors also reported that the amount of phytosterols decreased during frying, with retentions of 9.5 – 22.8% and 29.4 – 51.2% after eight successive pan-frying and deep-frying sessions, respectively. Phytosterols deterioration was found to be affected by frying time, frying method used, being more pronounced during pan-frying. Phytosterols were uniformly distributed between the fried oil and the fried potatoes. Similarly, Chiou et al. (2012) stated that presence of vitamin E, phytosterols, polyphenols, squalene, triterpenes, and carotenoids in French fries depend on the type of oil used in the frying. Tocopherols and phytosterols content of French fries follows the respective oil content. They also reported that polyphenols seem to survive better inside the food tissue than in the oil, thus presenting higher concentrations in the former. The concentrations of these compounds in French fries are mainly affected by the oil type, oil quality, and the frying procedure adopted. Carotenoids are extremely susceptible to degradation. Their highly unsaturated structure makes them sensitive to heat, oxygen, and light. The β-carotene retention depends on the species of vegetable and the type of cooking method. For vegetables, blanching resulted in 7 – 11% loss of β-carotene, while steaming, frying, and boiling showed losses of 15%, 18%, and 43%, respectively (Lešková et al. 2006).

The loss of phytonutrients from frying oil appears to be due to chemical degradation at high temperatures as total heating time accumulates. Other routes through which losses may occur include volatilization and steam distillation due to the combined effect of high temperature and large amount of steam escaping from the food being fried (Marmesat et al. 2010). The relative stability of the tocopherol isomers during oil storage have been studied. It was reported that α-tocopherol is the least stable, followed by δ-tocopherol. The β- and γ-tocopherols degrade at intermediate rates. The γ-tocopherol gives higher protection than α-tocopherol irrespective of the

oil used (Barrera-Arellano et al. 2002; Schwartz et al. 2008). Though tocotrienols have been less studied, the stability of α-tocotrienol is said to be like α-tocopherol in palm olein and purified oils in which both homologs were added (Simonne and Eitenmiller 1998; Schrøder et al. 2006). Some researchers have concluded that the order of the stability of the different homologs of tocotrienol was different from those of the tocopherols. The γ-tocotrienols was reported to be least stable in double fractionated super olein (Simonne and Eitenmiller 1998; Rossi et al. 2007). The stability of the polyphenolic compounds, hydroxytyrosol, tyrosol and lignans have been studied in virgin olive oil. It was reported that during frying, the highest rate of degradation occurred in the hydroxytyrosol, similar to α-tocopherol. While tyrosol and lignan was more stable (Andrikopoulos et al. 2002b; Daskalaki et al. 2009). Recent studies have shown that a significant increase in oil thermostability, and higher retention of natural tocopherols are observed when blends of different oils are used in deep-fat frying (Farhoosh et al. 2009; De Leonardis and Macciola 2012). The studies on the thermostability of tocotrienols, carotenoids and other phytonutrients is scanty. In general, the action of the natural antioxidants and other phytonutrients at frying temperatures cannot be presumed from their behavior at low or moderate temperatures. The phytonutrients may also be exhausted from the frying oil long before the recommended total polar compounds discard point of the used frying oil (Marmesat et al. 2010).

2.16 Kinetic models applied to the phytonutrients stability studies

Food quality degradation during thermal treatments is a major concern. Optimization of thermal processes depends on appropriate kinetic models. Kinetic studies and mathematical models on food quality changes are essential in proper design of the thermal process to ensure environmental and health safety (Ling et al. 2014). This is important in oil refining, production of oil with high level of bioactive nutrients, storage and end use of the oil involving high temperature processes (Sampaio et al. 2013). Chemical reaction kinetics can be applied to quantify individual attribute of model, ideal and real food system by applying the general rate law (Van Boekel 2008):

$$\frac{dP}{dt} = \pm kP^n \tag{2.1}$$

(k = rate constant (time^{-1}), t = reaction time and n = the order of reaction. P represents a measured quantitative value for a quality attribute or its concentration).

Usually the changes in the quality parameter of the food is monitored as a function of heating and frying time at chosen temperatures using temperature-dependent reaction rate constants after the

reaction order has been decided. The order of kinetics can be determined based on regression analysis or the goodness of fit of the observations to a preselected reaction order model. According to Van Boekel (2008) and Ling et al. (2014), kinetics of food quality changes generally follows zero-, first- or second-order reactions. Some researchers have also reported that third-order or fractional order best describes the loss of phytonutrients from the food matrix during thermal processing (Dhuique-Mayer et al. 2007; Achir et al. 2010; Sampaio et al. 2013).

These kinetic models are shown below:

$$P = P_0 * -kt \qquad (n = 0) \tag{2.2}$$

$$P = P_0 * e^{-kt} \qquad (n = 1) \tag{2.3}$$

$$P = (P_0^{1-n} - (1-n) * kt)^{1/1-n} \qquad (n \neq 1) \tag{2.4}$$

(P_0 is the initial value of the quality attribute at $t = 0$).

In thermal processing, *D*-value (min) is also used for convenience in describing the heating time in minutes to give 90% or one log reduction in food quality in a semi-log scale at a constant temperature. The *D*-value is directly related to the first-order reaction rate constant *k* (Van Boekel 2008):

$$D = \frac{2.303}{k} \tag{2.5}$$

The Arrhenius equation is the most commonly used model to describe the effect of temperature (*T*) on the reaction rate constant (*k*):

$$k = k_0 * e^{\frac{-E_a}{RT}} \tag{2.6}$$

(k_0 = pre-exponential factor, R = ideal gas constant (8.314 J/mol. K), T = absolute temperature (K) and E_a = activation energy (J/mol). Activation energy is the minimum energy required to start a chemical reaction).

CONNECTING TEXT TO CHAPTER 3

Chapter two of this dissertation reviewed the recent literature on frying oils, frying procedures and techniques for monitoring the qualities of both the oil and fried products. It was noted that selecting a frying oil could be challenging. However, virgin palm oil (VPO) also known as crude palm oil (CPO) is a rich source of beneficial bioactive phytonutrients. The need still exists for a much fuller utilization of VPO either alone or as the major component of a composite oil in deep-fat frying. It was also noted that the application of non-destructive techniques in characterizing frying oil quality is not yet widely practiced in the vegetable oil and frying industries, information on direct use of VPO and blends of VPO with other polyunsaturated vegetable oils to prolong useful life of frying oil and fried products enrichment with phytonutrients is scarce. These identified areas were further investigated in this study. The portions of chapter 2 that dealt directly with CPO and its benefits was published as a review article in Food Bioscience. The review manuscript was co-authored by Dr. Dumont, M-J., and Dr. Ngadi, M. All literature cited in chapter 2 has been listed in the reference section at the end of this thesis.

Ogan I. Mba, Marie-Josée Dumont, and Michael Ngadi (2015). Palm oil: Processing, characterization, and utilization in the food industry – A review. Food BioScience, 10 (1), 26 – 41. dx.doi.org/10.1016/j.fbio.2015.01.003.

Chapter 3 of this thesis explored the characterization of crude palm oil (CPO), refined canola oil (RCO) and different blend ratios of CPO and RCO using a non-destructive technique, Fourier Transform Near-Infrared (FTNIR) spectroscopy. Three important frying oil quality indices namely, iodine value (IV), free fatty acid (FFA) and peroxide value (PV) were determined using FTNIR as the first objective of this dissertation. This chapter 3 was published in the peer-reviewed journal 'Industrial Crops and Products' (doi.org/10.1016/j.indcrop.2014.07.037). The format of the manuscript has been altered to be consistent with the thesis format. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER 3

3. CHARACTERIZATION OF PALM OIL, CANOLA OIL AND THEIR BINARY BLENDS BY NEAR-INFRARED SPECTROSCOPY

3.1 Abstract

The essential quality parameters of binary blends of vegetable oils were evaluated using a rapid and non-destructive technique namely Fourier transform near-infrared (FTNIR) spectroscopy. Crude palm oil and canola oil from different vendors were blended at different ratios to obtain 40 oil samples with wide ranges of iodine values (IV), free fatty acids (FFA) and peroxide values (PV). FTNIR spectra of these oil samples were acquired and used in the calibration and test validation steps. The IV, FFA and PV of the oil samples were analyzed by AOCS methods. The FTNIR spectra were correlated to the AOCS data using partial least squares regression (PLSR). Calibration models were developed after test validation. The chemometric models were further improved through spectral processing. The optimal models were first derivative and first derivative + straight line subtraction. For IV, coefficient of determination (R^2) = 0.98; root mean square error of prediction (RMSEP) = 2.54 and residual predictive deviation (RPD) = 6.11. The values for FFA were R^2 = 0.9927; RMSEP = 0.35 and RPD = 11.6. While the values for PV were R^2 = 0.9722; RMSEP = 0.49 and RPD = 6.4. The simultaneous characterization of the essential chemical quality parameters of CPO, RCO and blends by FTNIR spectroscopy is reported.

3.2 Introduction

Palm oil is extracted from the fleshy orange-red mesocarp of oil palm fruits *Elaeis guineensis*. It is a vegetable oil with a balanced composition of saturated and unsaturated fatty acids both in the crude and processed forms. Palm oil is important in the world's vegetable oil trade. It is mainly used for edible purposes such as in cooking, margarine production, deep-fat frying, shortening, ice creams and cocoa butter substitutes in chocolate. Palm oil is also used in soap and oleo-chemical industries (Schrøder et al. 2006; Barriuso et al. 2013). Oilseed rape species used to produce canola oil are from the *Brassica* genus in the *Cruciferae* family. The conversion from high erucic acid rapeseed (HEAR) to canola resulted in an oil with very low levels of saturated fatty acids (6%), high levels of the monounsaturated fatty acid where oleic acid is predominant (58 – 61%) and moderate levels of polyunsaturated fatty acids (36%) (Farag et al. 2010). It has been reported that

blending vegetable oils improved nutrition and physical properties as well as the stability of the mixture of oils (Tyagi and Vasishtha 1996; Curvelo et al. 2011). Oils are also blended to obtain the desired mix with appropriate fatty acid composition and effective antioxidants at minimum cost (Kochhar 2000). To improve the handling properties of palm oil at low temperatures, blending with canola oil and enzymatic modification improved the fluidity of the blend (Ramírez and Cava 2005). Blending palm olein and canola oil has been used to produce oil samples with increased levels of essential fatty acids, tocopherols, tocotrienols and improved frying stability (Zou et al. 2012). Rapid and online investigation and monitoring of the quality of binary blends of palm oil and canola oil during storage and application in foods is important to ensure the safety and functionality of the oil samples and the wholesomeness of food products.

The current standard chemical methods such as AOCS, AOAC and IUPAC used to evaluate the quality of oils are among the most diversified ones for food safety and quality analyses issues (Du et al. 2012). Although some of the methods are relatively simple, others are complicated and require expensive instruments and hazardous chemicals. Each method targets only part of reactions. Several methods are normally required to evaluate the quality of culinary oil. This makes the analyses of fats and oils costly and time consuming. The development and integration of rapid methods for accurately evaluating the quality of fats and oils is of significant importance in ensuring its safety and quality. In 2001, FTNIR was approved by the American Oil Chemists' Society (AOCS) as an official method for the determination of the iodine value of fats and oils (Azizian et al. 2007). NIRS has gained importance as a tool for the investigation of vegetable oil samples. Using infrared and near-infrared spectroscopy in combination with different chemometric tools, adulteration of oil, such as extra virgin olive oil and palm oil, has been detected and quantified (Christy et al. 2004; Rohman and Man 2010). The classification of oils with different geographic (Casale et al. 2010) and botanic (Yang et al. 2005) origin or quality parameters (Lankmayr et al. 2004) has been demonstrated. Furthermore, NIRS and single bounce attenuated total reflectance (SB-ATR) FTIR have been used for the quantification of fatty acids and triacylglycerols of different edible oils and partially hydrogenated vegetable oils (Galtier et al. 2007; Sherazi et al. 2009; Dupuy et al. 2010). Other non-destructive techniques for oil authentication and analysis are differential scanning calorimetry and electronic nose (Man and Rohman 2013).

Near Infrared Spectroscopy (NIRS) is an analytical technique using a source of emitting radiations of the known wavenumber 12,500 – 4,000 cm^{-1} (wavelength 800 – 2,500 nm). NIRS makes it possible to obtain a complete image of major organic components of the material being analyzed (Van Kempen 2001). The principle behind the method is the absorption or reflection of different wavelengths of incident radiation, which depends on the chemical composition of the sample (Mlček et al. 2006). For the determination of the components in the samples, it is nevertheless necessary to perform an accurate calibration of the NIR spectrometer using an appropriate file of calibration standards of the known composition or using appropriate analytical methods known as the reference methods. The dependence of NIRS on reference methods is one of the major disadvantages. Other disadvantages include its low sensitivity to minor components and complicated interpretation of spectral data (Büning-Pfaue 2003). The combination of NIRS and chemometrics can be applied to many foods and agricultural commodities. It is widely used in the cereal, dairy, pharmaceutical, and other processing industries to predict the chemical composition of biological products with high accuracy. Both Fourier transform near-infrared (FTNIR) and Fourier transform infrared (FTIR) are fast and non-destructive methods which only require minimal or no sample preparation (Rohman and Man 2010; Ferrer-Gallego et al. 2011; Bala and Singh 2013). FTNIR is an excellent tool in industrial quality assurance/quality control because it has large path length that permits analysis of more samples. It can pass through glass and plastic materials to analyze the samples inside. The spectrum gives accurate, precise, and fast results in a few seconds. FTNIR has remote sampling capabilities. While mid-infrared spectroscopy makes use of fundamental vibrations, NIR spectroscopy uses overtones and combination bands. Combination bands are the sum of several fundamentals from different vibrations which contributes to greater analysis, repeatability and accuracy that meet standard laboratory testing protocols. Thus, one single spectrum may contain qualitative and quantitative (chemical and physical) information (De Beer et al. 2011).

Concerning the analysis of edible oils, Li et al. (1999) have demonstrated the use of FTNIR spectroscopy for the determination of IV. They reported that even though the near-IR spectra show considerable variation for oils and fats of different origin, the near-IR signature for unsaturation (IV) in the second overtone region, 9,100 – 7,500 cm^{-1} (1,333 – 1,099 nm) is remarkably uniform for a wide variety of oils and fats. Sato et al. (1991) reported that NIRS absorption bands between 6,250 – 5,555.56 cm^{-1} and 4,761.9 – 4,545.45 cm^{-1} contain useful information regarding fatty acid

compositions in various fats and oils. Man and Moh (1998) obtained an optimized calibration model for the free fatty acids of palm oil based on C=O overtone regions from 5,504.41 to 4,878.05 cm^{-1}. They reported that the best wavenumber combinations were 5,313.5, 4,975.12 and 4,901.96 cm^{-1} (i.e. wavelengths of 1,882, 2,010 and 2,040 nm). PLS calibration model for predicting the PV of triacylglycerols at levels of PV 10 – 100 was developed using the spectral region from 4,710 to 4,550 cm^{-1} (Dong et al. 1997). Li et al. (2000) further described the upgrading of the FTNIR PV method for the determination of PV in the range 0 – 10 PV based on the quantitation of triphenyl phosphine oxide using the region 4,695 – 4,553 cm^{-1}.

Our research group has recently utilized FTNIR to evaluate and predict the iodine value and free fatty acid contents of animal fats waste and their binary blends (Adewale et al. 2014). The objectives of this work were to use FTNIR spectroscopy to evaluate and monitor the essential quality attributes of crude palm oil, refined canola oil and binary blends of palm and canola oils as well as determine which spectra preprocessing method gave the best fit model. The work focused on simultaneously evaluating iodine value (IV), free fatty acid (FFA) and peroxide value (PV) of the of oil samples. The NIR spectra of the oil samples were preprocessed to improve the PLS results. IV, FFA and PV were chosen for this evaluation because they are among the topmost important chemical quality indices monitored in both fresh and used oils by food service and industrial frying operators (Chong 2012). This study will assist rapid detection of quality of vegetable oils in research and industrial applications.

3.3 Materials and Methods

3.3.1 Samples collection and calibration standards

Crude palm oil and canola oil were purchased from different vendors in Abia State Nigeria, Montreal QC and Richmond BC, Canada. Analytical grade reagents were purchased from Fischer Scientific, New Jersey, USA. Forty samples comprising of palm, canola and blend oil samples were used for the development of the calibration model. Each oil sample was prepared in triplicates for both the chemical analysis and spectral acquisition. Total number of calibration spectra was 90 while the test validation spectra were 30. Blending palm and canola oil in different ratios (w/w) was done in order to obtain oil samples with a wide range of IV, FFA and PV. IV is a measure of degree of unsaturation of fats and oils. It is expressed as the weight percent of iodine consumed by the oil in a reaction with iodine (Wij's solution). The formation of FFA in lipids is due to the hydrolysis of the triacylglycerol in the presence of moisture in the immediate environment of the

oil. FFA was determined by dissolving a portion of the oil sample in hot ethyl alcohol and titrating against 0.25 M sodium hydroxide. Phenolphthalein was used as the indicator. PV is the most widely used analytical measurement of oxidative deterioration. Iodine titration was used to measure the PV, with 0.01 M sodium thiosulphate as titrant. The IV, FFA and PV were determined in triplicates using the AOCS methods Tg1 – 64, Ca 5a – 40 and Ja 8–87, respectively (Firestone 2009). The data was used to develop the PLS calibration models used for the prediction of the IV, FFA and PV of the of oil samples.

3.3.2 FTNIR spectral acquisition

After calibration, about 1.0 mL aliquot of each oil sample was pipetted into 2 mm glass cuvettes, with a 1 cm^{-1} spectra resolution and set into the sample compartment of the spectrometer. NIR spectra were acquired using a Bruker Optics MPA FTNIR Spectrometer. The spectrometer was equipped with the optics validation protocol (OVP), which is an instrument validation tool that includes comprehensive instrument test protocols and a PC workstation based on Opus Quant 2 software, an all-in-one spectroscopy software. The Opus Quant 2 software was used to automatically perform the spectra preprocessing, making model development less time consuming. It is based on the multivariate algorithm, Partial Least Squares regression (PLSR). The NIR spectra of the samples were acquired in absorbance mode at a wavenumber range of 12,000 – 4,000 cm^{-1}. Background spectra were first obtained by running the spectrometer with empty cuvettes (air absorbance). Absorbance spectra of completely melted oil samples at 50±2 ˚C were collected in 16 scans at a resolution of 8 cm^{-1}. Three different spectral images were acquired for each oil sample. A total of 120 calibration and test validation spectra were used. Sample single beam was ratioed against the open-air reference single beam to generate a typical absorbance spectrum of the oil samples. Spectra were stored on the hard disc of the computer workstation for subsequent PLSR.

3.3.3 Spectral data pre-processing and validation

Applying the Opus Quant 2 software (version 7.2, Bruker Optics, GmbH) the PLS analysis was performed within the optimal spectral regions and the mathematical pre-treatments. This allowed the optimal use of spectral data in constructing a linear predictive model. The purpose of data preprocessing was to ensure a good correlation between the spectral data and the concentration values, enhance spectral features and remove or reduce unwanted sources of variation, such as instrument noise. The spectral data sets were correlated with the calculated iodine value (IV), free

fatty acid (FFA) and peroxide value (PV) using the PLSR algorithm. The FFA content and PV values of oils are not linearly related, therefore separate calibration and prediction sets of samples were used for development of FFA and PV models (Du et al. 2012). The same principle was applied to IV. Optimized concentration values were used to set up the calibration design. In order to evaluate the calibration performance of the developed models and minimize prediction error, the method was validated with the independent test validation samples set, made of binary blends from different sources. The predicted values were compared with the references. Multivariate variables such as the coefficient of correlation (R^2), the root-mean-square-error of prediction (RMSEP), residual predictive deviation (RPD) and root mean-square-error of estimation (RMSEE) were computed to judge the quality of the model. The RPD is defined as the ratio between the standard deviation of the population's reference values and the standard error of prediction (RPD = SD/SEP). RPD was used to verify the accuracy of the calibration models developed. Models that gave the lowest possible rank (latent variable) with the highest coefficient of determination (R^2), lowest root mean square error of estimation (RMSEE), lowest root mean square error of prediction (RMSEP) and the highest value of residual prediction deviation (RPD) were chosen. RMSEE measures the model's ability to predict new or future samples.

3.4 Results and discussions

3.4.1 Chemical analysis

The range of values of the chemical data obtained from the AOCS analytical methods are shown in Table 3.1. The minimum and maximum IV values were 31.48 and 101.02 g/100 g, respectively. The IV kept increasing in the blends as the weight ratio of canola oil was increasing. The mean IV was 61.56 g/100 g. The values obtained are similar to values reported in the literature. Mamat et al. (2005) had reported that blending and fractionating olein at lower temperatures resulted in a blend with more unsaturated fatty acids, which contributed to higher iodine values. Similarly, Alireza et al. (2010a) reported an increased IV of 77.97 and PV of 1.37 for a 1:1 (w/w) blend of refined, bleached and deodorized (RBD) palm olein and canola oil. The minimum and maximum FFA values were 0.23% and 12.23%; while the minimum and maximum values for PV were 0.13 and 7.73 meq O_2/kg. These represented increased mean FFA of 4.22% and PV of 2.44 meq O_2/kg. The results agreed with the reported increases of blending a saturated vegetable oil such as palm oil and unsaturated oil such as canola oil (Alireza et al. 2010a; Du et al. 2012).

Table 3.1: Iodine value (IV), free fatty acid (FFA) and peroxide value (PV) of the oil samples

Batch	Palm: Canola Blend (w/w)	IV (g 100/g oil)	FFA (%)	PV (meq O_2/Kg oil)	Spectral Usage
A	100: 0	38.78	12.23	0.13	Validation
	90: 10	44.58	11.00	0.93	Calibration
	85: 15	48.98	10.64	1.13	Calibration
	80: 20	50.71	10.20	1.60	Calibration
	75: 25	51.72	9.99	1.93	Calibration
	70: 30	52.08	9.06	2.13	Validation
	65: 35	52.46	8.59	2.53	Calibration
	60: 40	55.51	7.86	2.80	Calibration
	55: 45	57.40	7.37	3.20	Calibration
	50: 50	63.32	6.69	3.53	Calibration
	45: 55	64.03	6.03	3.66	Validation
	40: 60	67.47	5.19	4.06	Calibration
	35: 65	71.99	4.69	4.33	Calibration
	30: 70	76.56	3.89	5.06	Validation
	25: 75	78.64	3.49	5.19	Calibration
	20: 80	81.82	2.77	5.59	Calibration
	15: 85	85.13	2.13	5.93	Validation
	10: 90	94.14	1.53	6.26	Calibration
	5: 95	97.50	0.95	6.53	Calibration
	0: 100	101.02	0.30	7.73	Calibration
B	100: 0	31.48	2.83	0.26	Calibration
	95: 5	33.45	2.79	0.26	Calibration
	90: 10	36.64	2.57	0.27	Validation
	85: 15	41.27	2.45	0.30	Calibration
	80: 20	42.23	2.30	0.33	Calibration
	75: 25	45.98	2.20	0.39	Calibration
	70: 30	46.79	2.13	0.40	Calibration
	65: 35	48.27	1.96	0.47	Calibration
	60: 40	51.72	1.70	0.53	Calibration
	50: 50	56.09	1.50	0.59	Validation
	45: 55	57.98	1.33	0.59	Calibration
	40: 60	60.20	1.20	0.60	Calibration
	35: 65	61.18	1.17	0.67	Calibration
	30: 70	64.46	1.00	0.73	Validation
	25: 75	66.74	0.90	0.93	Calibration
	20: 80	68.34	0.83	1.20	Validation
	15: 85	69.30	0.77	1.25	Calibration
	10:90	71.04	0.63	1.53	Calibration
	5: 95	74.22	0.34	2.00	Calibration
	0: 100	77.87	0.23	2.13	Validation

A and B = palm, canola and blend oil samples from different vendors worked on at different times.

3.4.2 FTNIR spectral analysis

The NIR spectra of the oil samples collected in the entire available spectral range 12,000 – 4,000 cm^{-1} is shown in Figure 3.1. The spectral patterns of all the samples were found to be similar across the whole wavenumber range along the X-axis. However, along the absorbance (Y) axis some changes are noticeable. Workman and Weyer (2007) reported that bands at around 5,796 and 5,678 cm^{-1} are due to the combination bands and first overtone of C—H of methylene of aliphatic groups of oil and their second overtone is observed at 8,264 cm^{-1}. The bands at around 4,663 and 4,591 cm^{-1} may be attributed to combination bands of C═C and C—H stretching vibrations of cis unsaturated fatty acids, and at 7,074 and 7,180 $cm^{-1}$are attributed to C—H combination band of methylene (Cozzolino et al. 2005).

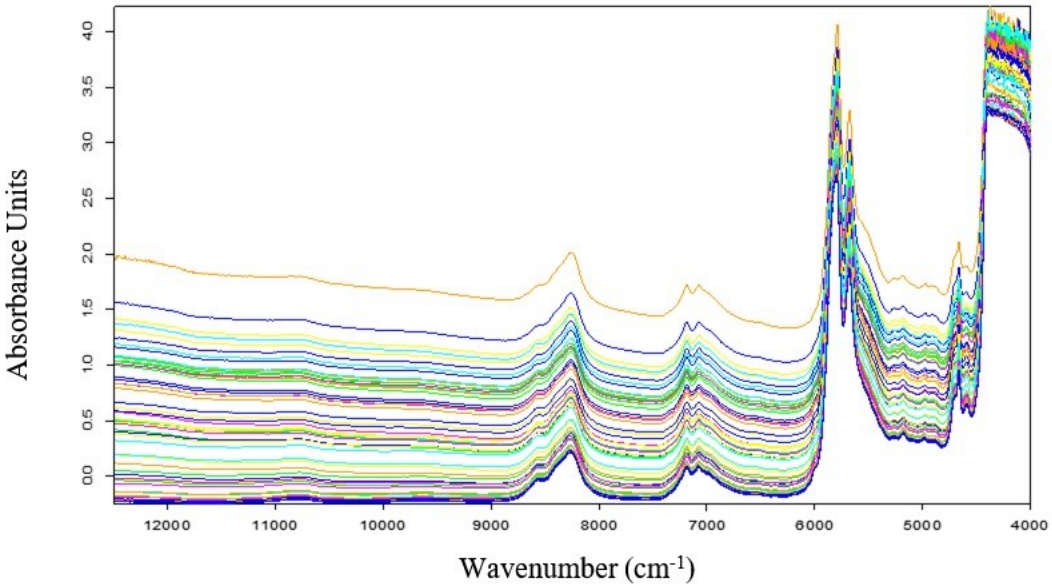


Figure 3.1: Raw FTNIR spectra of palm, canola, and blend oil samples.

The analysis showed that the best preprocessing model for the parameters investigated were First Derivative for FFA and PV, and First Derivative + Straight Line Subtraction for the IV (Table 3.2). The Quant 2 software package had the capability of smoothing the spectral data. Prediction equations were developed for the IV, FFA and PV using the OPUS Quant 2 PLSR algorithm and presented in Table 3.3. The higher the RPD value, the greater the probability of the model to accurately predict the chemical composition of the samples set. When RPD values range between 2.4 and 3.0, it is considered poor and the models could be applied to very rough screenings. RPD range of 3.1 – 4.9 is considered fair for screening purposes, while RPD >5 is considered good for

quality control (Williams and Norris 1987; Cen and He 2007). The RPD values obtained were above 5.0.

Table 3.2: Comparison of the preprocessing models of the oil spectra

	Validation			Calibration			Rank
Parameter/Preprocessing Model	R^2	RMSEP	RPD	R^2	RMSEE	RPD	
Iodine Value:							
No Preprocessing	0.9652	2.76	5.47	0.9830	2.38	7.66	5
First Derivative	0.9673	2.68	5.82	0.9777	2.71	6.70	4
First Derivative + SLS [a]	0.9800	2.54	6.11	0.9868	2.51	7.21	4
Second Derivative	0.9645	2.79	5.49	0.9760	2.81	6.46	4
Multiplicative Scatter Correction	0.9640	2.81	5.64	0.9770	2.73	6.59	3
Vector Normalization	0.9503	3.30	4.76	0.9656	3.34	5.39	3
Free Fatty Acid:							
No Preprocessing	0.9792	0.55	7.17	0.9973	0.20	19.30	9
First Derivative [a]	0.9927	0.35	11.60	0.9966	0.22	19.30	10
First Derivative + SLS	0.9905	0.34	10.50	0.9961	0.21	17.10	10
Second Derivative	0.8501	1.46	2.59	0.8754	1.26	2.87	3
Multiplicative Scatter Correction	0.9841	0.45	8.82	0.9973	0.19	18.10	8
Vector Normalization	0.9778	0.56	7.29	0.9962	0.23	16.20	7
Peroxide Value:							
No Preprocessing	0.9542	0.49	4.68	0.9877	0.27	9.03	9
First Derivative [a]	0.9722	0.49	6.40	0.9885	0.37	9.32	5
First Derivative + SLS	0.9704	0.49	5.82	0.9746	0.38	6.27	5
Second Derivative	0.9494	0.48	4.45	0.9740	0.26	6.20	9
Multiplicative Scatter Correction	0.9428	0.49	4.18	0.9808	0.33	7.22	7
Vector Normalization	0.9439	0.51	4.23	0.9618	0.46	5.12	6

R^2 = Coefficient of determination; RMSEP = Root mean square error of prediction;
RPD = Residual predictive deviation; RMSEE = Root mean square error of estimation;
SLS = Straight line subtraction; [a] Best fit model

Table 3.3: Prediction results for the oil quality parameters measured

Parameter	Prediction Equation	R^2	RMSEP	RPD	Rank	Spectral Range of Prediction (cm^{-1})
Iodine Value [a]	Y=1.0618X-3.0109	0.9800	2.54	6.11	4	9,403.8 – 7,498.3
Free Fatty Acid [b]	Y=0.9797X+0.1966	0.9927	0.347	11.60	10	7,502.2 – 6,098.2
Peroxide Value [b]	Y=0.9390X+0.1147	0.9722	0.488	6.40	5	6,102 – 5,446.3

[a] = First Derivative + Straight Line Subtraction Preprocessing; [b] = First Derivative Preprocessing;
R^2 = Coefficient of Determination; RMSEP = Root Mean Square of error of prediction;
RPD = Residual Predictive Deviation; Y = Predicted value; X = Chemical value.

3.4.3 Calibration for iodine value (IV)

Table 3.2 shows that the best statistical result for IV was obtained when data were preprocessed using First Derivative + Straight Line Subtraction. In Table 3.3, the IV prediction equation obtained from the AOCS method (the calibration data) and the NIRS predicted values obtained from the test validation is shown. Validation of the calibration model was done to assess its predicting abilities in routine application. Different prediction variables were used to test the validity of the calibration (Table 3.3). The high value of determination coefficient ($R^2 = 0.98$) and low RMSEP (2.54) indicated a good correlation between FTNIR predicted and calculated iodine values from standard methods. The RPD value of 6.11 obtained from the test validation indicated a high predictability of IV by FTNIR and the robustness of the developed model. The ability to predict IV in vegetable oils had been reported by Li et al. (1999). Cox et al. (2000) also reported a good predictability of IV in the range of 30 – 90.1 with R^2 of 0.99 and standard error of cross validation (SECV) between 0.523 and 0.808. Also, as shown in Figure 3.2, the predicted wave number range was 9,018 – 7,594.7 cm^{-1}. This range falls within the documented near-infrared signature for IV in the second overtone region of 9,100 – 7,500 cm^{-1} (Cox et al. 2000). The PLS algorithm multiplies (weights) each of the original spectra by the normalized concentrations of the IV. These weighted spectra were added together and the total spectral area was normalized to 1.0 to produce a weight loading vector. The optimum PLS rank was 4. The regression vector plot (Figure 3.3) represents the contribution of IV to the model. The regression vector for IV is not noisy and the absorbance between 8,800 and 8,200 cm^{-1} had important weight for the IV calibration. This corresponds to the asymmetric aromatic, methylene, and methyl C—H stretching of second overtone and strong —CH=CH— (cis double bond) overtones.

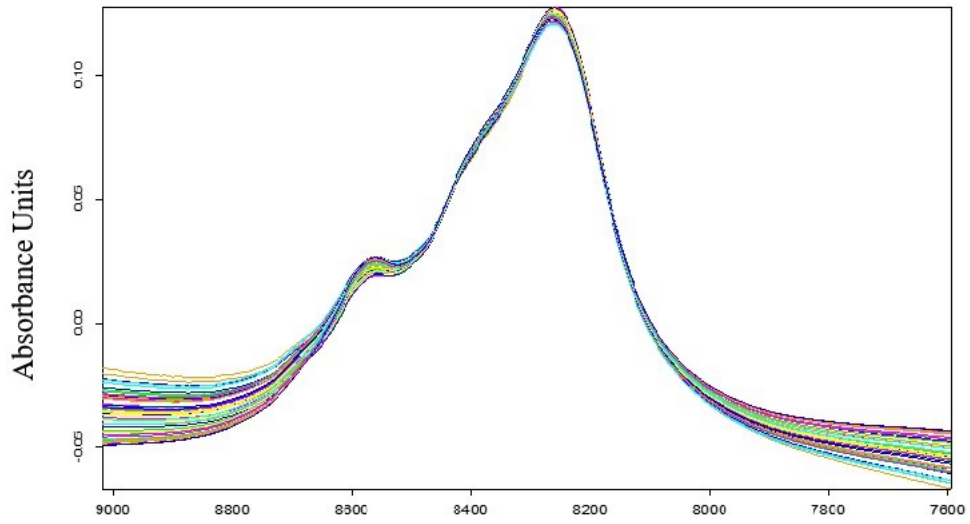


Figure 3.2: Pre-processed spectra for the iodine value (IV).

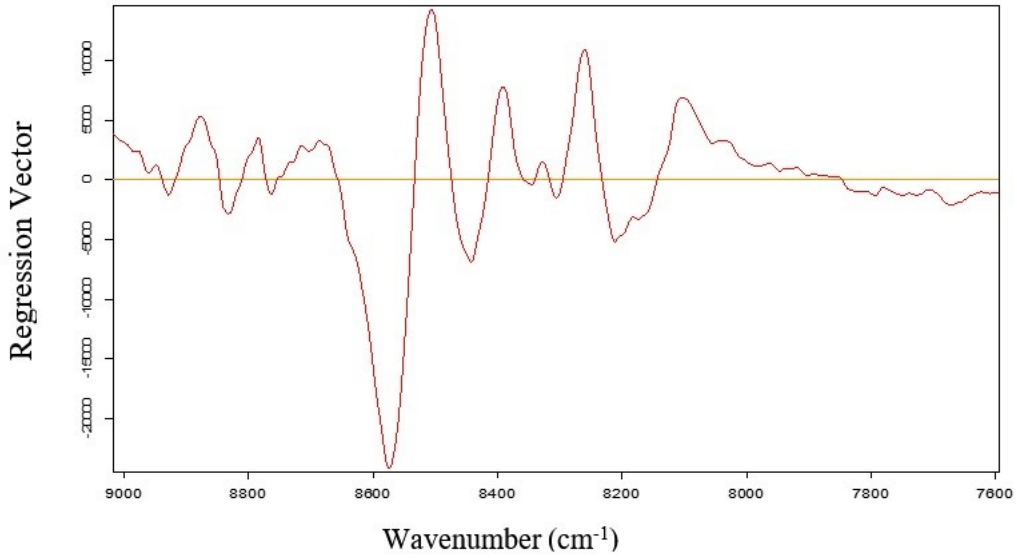


Figure 3.3: Regression vector plot for iodine value (IV).

3.4.4 Calibration for free fatty acid (FFA)

The best preprocessing model for FFA was first derivative (Table 3.2). The prediction equation obtained from the calibration for FFA and the NIR predicted values obtained from the test validation is shown in Table 3.3. Validation of the calibration model was also done to assess its predicting abilities in routine application. Different prediction variables were used to test the validity of the calibration (Table 3.3). The R^2 obtained for FFA (0.9927) and RMSEP (0.347)

indicated an excellent correlation between FTNIR predicted and calculated FFA values. The RPD obtained from the test validation and calibrations were 11.6 and 19.3, respectively, an indication of very high predictability of free fatty acid by FTNIR and the robustness of the developed model. Du et al. (2012) had reported R^2 of 0.948 and standard error of prediction of 0.14 for the FFA of frying oil. Figure 3.4 showed that the wavenumber of our prediction ranged between 7,502.2 and 6,098.2 cm^{-1}. This range differs from the FFA absorption band intensity range of 5,850 – 5,800 cm^{-1} reported by Azizian et al. (2007). The authors also pointed out that the FTNIR absorption band is affected by the chain length of the fatty acid molecule. The samples we worked on came from various sources which could be a source of variation. The weighted spectral information was based on the first derivative preprocessing and optimum PLS rank of 5. First derivative preprocessing was used to remove baseline offsets and slope variations among spectra. The regression vector representing the contribution of FFA to the model is shown in Figure 3.5. The regression vector of the FFA was not noisy and the absorbance around 7,000 – 5,450.2 cm^{-1} conformed to the absorbance range said to have important weight on the FFA model calibration (Du et al. 2012). This corresponds to the methyl C—H combination of the first overtone and carbonyl C═O stretching of the second overtone.

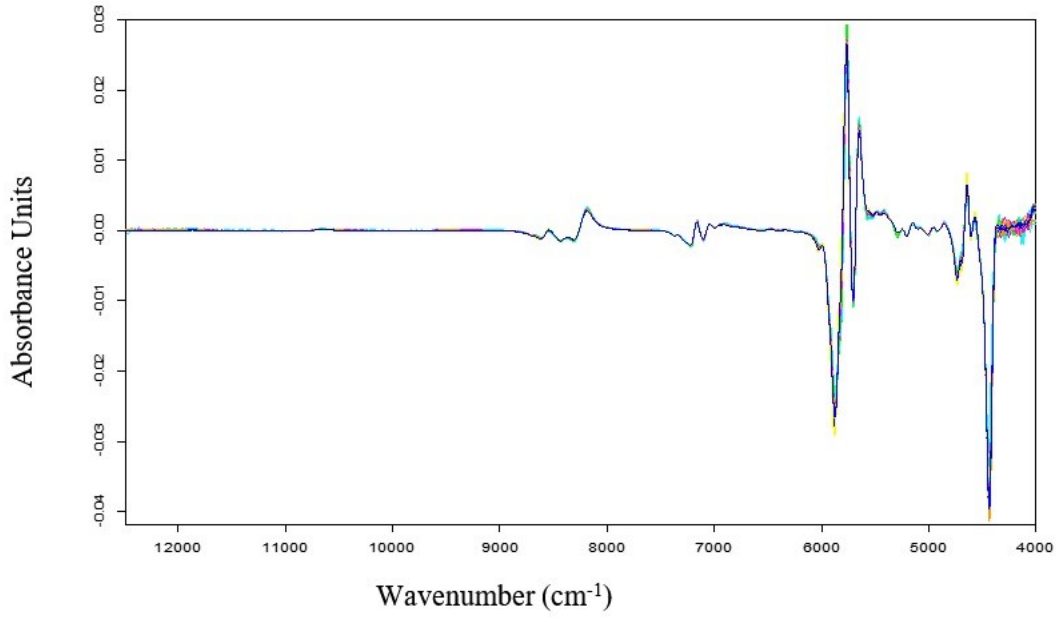


Figure 3.4: First Derivative spectra for the free fatty acid (FFA) and peroxide value (PV).

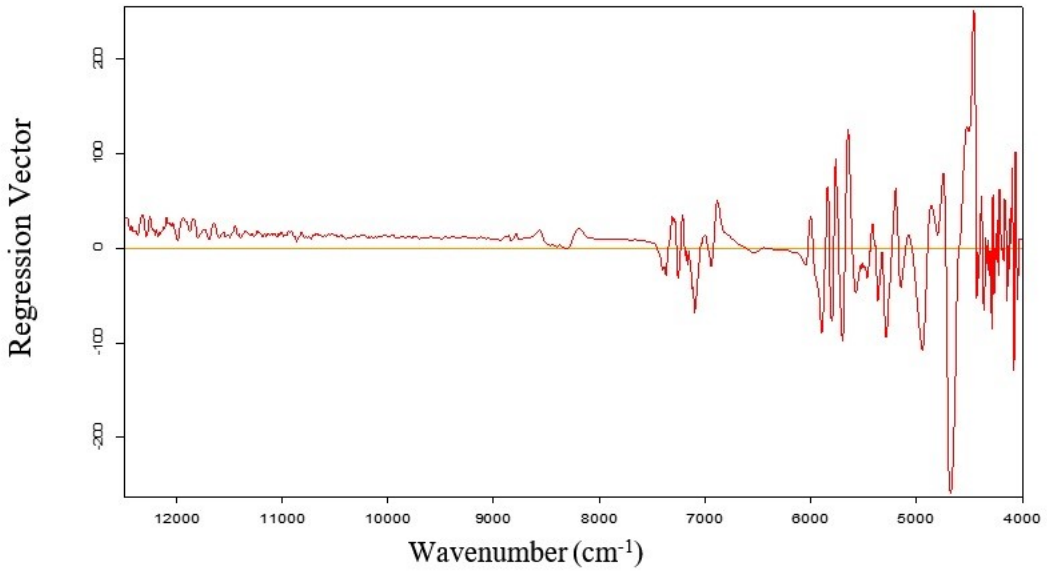


Figure 3.5: Regression vector plot for free fatty acid (FFA).

3.4.5 Calibration for peroxide value (PV)

The FTNIR spectral data had a similar predictability for peroxide value as free fatty acid, the best preprocessing model being the first derivative (Table 3.2). The prediction equation relating the AOCS chemical data and the NIR predicted values obtained from the test validation is shown in Table 3.3. Validation of the calibration model was also done to assess its predicting abilities in routine applications. To test the validity of the calibration, different prediction variables were used (Table 3.3). The R^2 obtained for PV was 0.9722 and RMSEP was 0.49. These values indicated an excellent correlation between the FTNIR predicted and calculated PV values. The RPD obtained from the test validation and calibrations were 6.40 and 9.32 respectively, an indication of very high predictability of PV by FTNIR and the robustness of the developed model. The R^2 and RPD values obtained were higher than the R^2 of 0.953 and the RPD of 4.36, reported by Du et al. (2012), but lower than the R^2 of 0.996 reported by Moh et al. (1999) for the PV of thermally oxidized crude palm oil. No spectral outlier was found in the calibration data set and this shows that the PV of the samples selected were accurately determined. As shown in Figure 3.4, the first derivative spectral image for PV and FFA are similar.

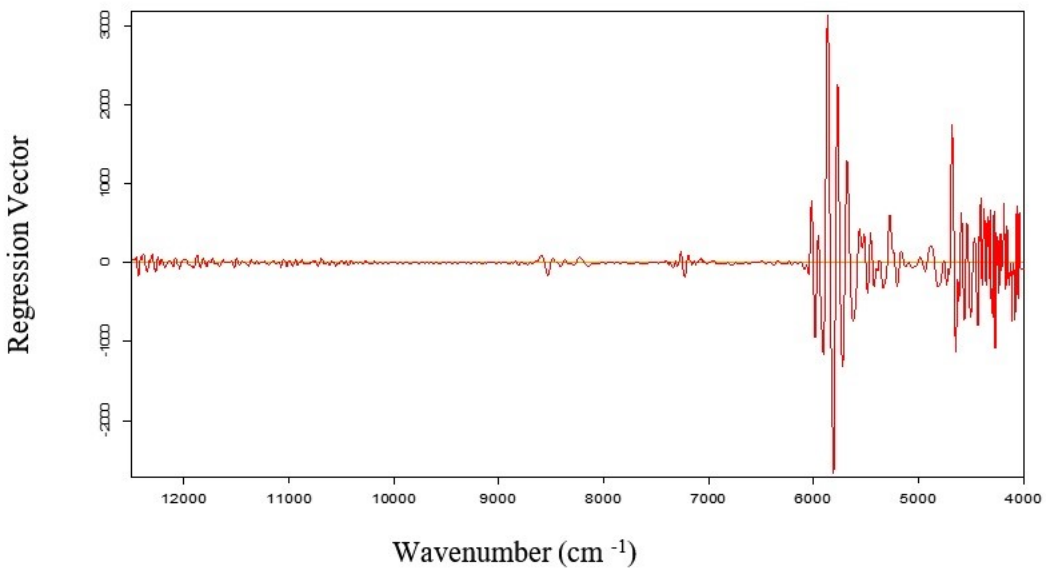


Figure 3.6: Regression vector plot for peroxide value (PV).

Figure 3.6 above shows the regression vector representing the contribution of PV to the model. It can also be seen that the regression vector of the PV was not noisy and the absorbance range was 6,102 – 5,446.3 cm^{-1} in the first overtone combination and 4,601.6 – 4,246.7 cm^{-1} in the first overtone C—H. The optimum PLS rank was 5. This result is in agreement with reported NIR spectral region for predicting PV as reported by Li et al. (2000). Similarly, Du et al. (2012) reported absorption at 6,780 cm^{-1} for the PV of frying oil. Also, Dong et al. (1997) reported a PV prediction range of 4,710 – 4,550 cm^{-1} for high erucic rapeseed oil. This region corresponds to the methylene C—H combination and O—H stretching bands of the first overtone (Moh et al. 1999).

3.5 Conclusion

Absorptions in the NIR region mainly arise from the overtone and combination vibrations of functional groups containing hydrogen bonds. NIRS measurements allow the use of large sample size. The spectra mainly consist of broad bands that make this method more adequate for non-homogeneous samples and less affected by the changes in the test environment. The results obtained from this study has demonstrated that FTNIR spectroscopy can be used for online monitoring of the iodine value (IV), free fatty acid (FFA) and peroxide value (PV) simultaneously in intact palm oil, canola oil and their blends. When RPD is greater than 5 in all the test parameters of the oil samples, it suggests that the models were very good for quality control of the oil samples studied. The prediction model equations are as follows: IV = 1.062X - 3.011; FFA = 0.98X + 0.197 and PV = 0.939X + 0.115. The wavenumber ranges for the evaluation of IV, FFA and PV of the

oil samples were found to be 9,403.8 – 7,498.3 cm^{-1}; 7,502.2 – 6,098.2 cm^{-1} and 6,102 – 5,446.3 cm^{-1} respectively. It was a rapid method that greatly reduced analysis time, reagent use and disposal problems associated with the wet chemical methods. It can reduce the cost of analysing large number of samples. FTNIR is a powerful technique for the routine analysis of the studied parameters in vegetable oils before and after utilization.

CONNECTING TEXT TO CHAPTER 4

The applicability of FTNIR spectroscopy to evaluate and predict simultaneously the iodine value (IV), free fatty acid (FFA) and peroxide value (PV) of vegetable oils was given a further boost by this research finding. The developed calibration equations can be useful in predicting the PV, FFA and PV profile on spectra of crude palm oil (CPO), refined canola oil (RCO) and blends of CPO/RCO oils rapidly and on-line in the vegetable oil, food service and food manufacturing industries. The chapter 3 of this dissertation was published in a peer-reviewed journal 'Industrial Crops and Products'. The authors and article information is as follows:

Ogan Mba, Peter Adewale, Marie-Josée Dumont, and Michael Ngadi (2014). Application of near-infrared spectroscopy to characterize binary blends of palm and canola oils. Industrial Crops and Products, 61, 472 – 478; doi.org/10.1016/j.indcrop.2014.07.037.

Both conventional chemical and non-destructive techniques have been used to establish that the basic quality indices of CPO, RCO and blends met regulatory standards for frying oils. The utilization of these oil samples and the characteristics they impart to foods during deep-fat frying was further studied. The blend oil samples with qualities closest to CPO, were used in deep-fat frying of plantain crisps. The impact of the blend oil samples was compared with those of the CPO and the RCO. This is the focus of chapter 4. The findings from this study was published in 'British Food Journal'. The format of the manuscript has been altered to be consistent with this thesis. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER 4

4. IMPACT OF PALM OIL, CANOLA OIL, AND BLENDS ON CHARACTERISTICS OF FRIED PLANTAIN CRISPS

4.1 Abstract

This work studied the influence of crude palm oil (CPO), refine canola oil (RCO) and their blends on characteristics of fried plantain crisps at two different stages of ripening. There was no significant difference ($p > 0.05$) in the moisture loss rate and the crispness of the crisps produced using CPO and RCO. Significant differences ($p < 0.05$) existed in the oil uptake and color properties of the crisps fried in the two oils. CPO fried crisps absorbed 14% less oil in the unripe crisps samples and 26% less oil in the fully ripened crisps than RCO. The browning index showed that the CPO crisps had greater color changes than the crisps fried using RCO. The 50:50 and 70:30 blends improved the qualities of the crisps better than RCO alone. Analysis of kinetics data showed that moisture loss, oil uptake and browning index followed a first order kinetics model. Understanding the interactions between ripening and processing methods was enhanced and use of crude (virgin) palm oil for commercial deep-fat frying is encouraged.

4.2 Introduction

Plantain (*Musa paradisiaca L*) ranks among the leading cultivated crops like cereals and citrus fruits. The current annual world production of bananas and plantains is estimated to be approximately 145 million tons. About 85% of this global production comes from small holder farmers in Sub-Saharan Africa, tropical Asia, and Latin America (FAO 2013; Ortiz and Swennen 2014). The matured green plantain has the following proximate composition per 100 g: water (65.28 g); carbohydrate (31.89 g); total dietary fiber (2.3 g); protein (1.30 g); total fat (0.37 g); total sugars (15.0 g); and the total energy value is 122 kcal. The fruit pulp is also a rich source of potassium, magnesium, phosphorus vitamin C and niacin (USDA, 2013). The plantain fruits are usually consumed between the mature green stage and the yellow stages of ripeness using the peel color as index of ripening (Yomeni et al. 2004). The various methods of preparation are boiling, frying, roasting, and baking. The stage of fruit maturity at harvest determines their post-harvest life. In order to utilize the abundant harvest during the season, the plantain can be processed into dehydrated chips, flour/powder, fried chips (crisps) and plantain pulp or puree made from the ripened fruits. There is also increasing interest in plantain starch and plantain bars (Mohapatra et

al. 2009). Aboua (1991) reported that plantain is a climacteric fruit that continues to ripen even after harvesting from the parent plant due to evolution of ethylene. Plantain ripening involves irreversible series of physical, chemical, biochemical, and organoleptic changes in the fruit (Suntharalingam and Ravindran 1993). During ripening, the peel changes from green to yellow and finally to dark brown. The stage of ripeness of the plantain affects the quality of any product made from it. For chips or crisps, the choicest are made from plantain at either the green stage or yellow stage of ripening (Yomeni et al. 2004; Mba et al. 2013). The two stages correspond to the "harvest stage greenness" and "more- yellow-than green" described in the banana ripening guide (Conie and Young 2003). In order to ensure production of nutritious and healthy products from plantain, the processing methods have to be optimized.

One of the most popular processing routes for plantain is deep-fat frying. Frying is an efficient means of transferring heat and cooking food. It is a process of immersing food pieces in hot vegetable oil or fat between 150 ºC and 190 ºC (Moyano and Pedreschi 2006). Fried foods are very popular because of their unique quality characteristics like smooth mouthfeel, distinct flavor, enticing aroma, palatability and aesthetic appeal. These have been attributed to the texture, color and flavor of fried foods. Frying also provides satiety and increases the calorific count of fried products as the frying oil becomes part of the fried product (Ziaiifar et al. 2008; Farhoosh et al. 2009; Boskou 2011; Stier 2013). The kinetics of the frying process, including the mechanism of oil diffusion and absorption has been studied for a range of fried products such as potato, tortillas, plantains and chicken nuggets (Diaz et al. 1999; Moyano and Pedreschi 2006; Adedeji et al. 2009).

Different types of oils are used in frying. They include: soybean oil, sunflower oil, cottonseed oil, canola oil, rice bran oil, safflower oil, palm oil, palm olein, animal tallows and lard as well as binary and ternary blends of animal/vegetable oils or vegetable oils (Blumenthal and Stier 1991; Alireza et al. 2010b). The functionality of a particular oil can impact on its uses. These functionalities include: heat transfer, textural qualities, and carriers of vitamins, colors and antioxidants. For instance, polyunsaturated oils are not good enough for frying because of poor thermostability (Bouchon 2009). Because of increasing consumer health consciousness and regulations requiring a shift away from *trans*-fats, the oils with poor thermostability and those that are hydrogenated are no longer popular in the frying industry. The use of naturally stable oils such as crude palm oil (CPO) or blends of CPO and other vegetable oils has reengaged the attention of

the frying industry. CPO and its fraction palm olein have been reported to offer excellent frying characteristics (Ong and Goh 2002). CPO has an almost equal composition of saturated and unsaturated fatty acids. Linolenic acid is absent in the fatty acid profile, and it has high concentrations of antioxidants such as tocopherols and tocotrienols (Lin 2011). CPO also is nature's richest source of β-carotene which acts synergistically with tocopherols as antioxidants. Beta-carotene is also a pre-cursor of vitamin A and natural food colorant. CPO does not contain short-chain fatty acids that give rise to smoking problems (De Leonardis and Macciola 2012). The frying performance of polyunsaturated oils such as canola, soybean and sunflower seed oils can be improved by blending them with the saturated and stable palm oil. The objective of the present work is to study the effect of, crude palm oil (CPO), refined canola oil (RCO) and their blends on the qualities of fried unripe green plantain (UGP) and fully ripened plantain (FRP) and model the kinetics of their frying characteristics. The crisps were evaluated for their moisture and fat content and changes in the color and texture characteristics. The result contributed to understanding the interactions between natural processes such as ripening and processing methods and encourage use of crude or virgin palm oil for commercial deep-fat frying.

4.3 Materials and Methods

4.3.1 Samples preparation

Commercially unripe plantain fruits with peel still completely green were purchased from a grocery shop in Montréal, Canada. Some of the plantain fingers were kept in the laboratory up to the fully ripened stage (peel completely yellow). Crude palm oil (CPO) was supplied by an oil mill based in Nigeria and refined canola oil (RCO) was sourced from an oil refinery in Montréal. In the laboratory, two different blends of CPO: RCO was prepared in the weight ratio of 70:30 (Blend-1) and 50:50 (Blend-2). The blends as well as CPO alone and RCO alone were used for the frying experiments. On each frying day, unripe green plantain (UGP) and fully ripened plantain (FRP) were washed and distributed into 4 lots for the four different frying oil samples. Each lot was peeled by hand and the pulps sliced into fine discs of 3 ± 0.2 mm thickness using Rival precision mechanical slicer (model C1105). The plantain discs were blanched by immersing in a hot water bath at 70 ºC for 3 min and then dried on absorbent paper. The samples were equally distributed into previously weighed pans ready for the frying experiment that followed.

4.3.2 Deep-fat frying experiment

The oil samples were labeled as follows: A = 100% CPO; B = CPO: RCO 70:30 w/w (Blend-1); C = CPO: RCO 50:50 w/w (Blend-2); and D = 100% RCO. Approximately 4 L of each oil sample was used for the frying operation in a bench-top temperature controlled fryer (Délonghi D24527DZ). Each oil sample was preheated for 2 h at 180 ± 2 ^{o}C before commencement of frying at the same temperature. Frying was done for 1, 2, 3, and 4 min. A set of un-fried slices was used as the control and regarded as 0 min fried samples. Previously weighed plantain slices were completely immersed in the hot oil and fried to produce plantain crisps. After frying the fryer basket was well shaken to remove adhering oil. The plantain crisps were quickly blotted with absorbent paper to remove as quickly as possible oil adhering to the surface of the crisps. The crisps were allowed to cool at room temperature. After cooling they were weighed again and stored in a sealed polyethylene bags and stored under vacuum for the analyses that followed. Frying was done in triplicates for each of the frying times.

4.3.3 Moisture content determination

The moisture content (dry basis) of the un-fried and fried plantain crisps was determined gravimetrically. The weighed fried samples were dried to a constant weight using forced air convention oven (Isotemp 700, Fischer Scientific, Pittsburgh, USA) at 105 °C for 24 h (AOAC 1990). The measurements were done in triplicates.

4.3.4 Oil extraction and oil content determination

The AOAC method 960.39 was used for the oil extraction and oil content determination (AOAC 1990). Oil content and uptake was determined after frying and cooling the crisps. An electric grinder was used to grind the oven dried crisp samples. Approximately 5.0 g of each ground sample in a thimble was used for the oil extraction, using auto extraction unit (SER 148, Velp Scientifica, Usmate, Italy). The following operating conditions were used: temperature, 130 ^{o}C; immersion time, 30 min; washing time, 30 min; and recovery time, 20 min. The solvent used for oil extraction was petroleum ether (b.p. 40 – 60 °C) in pre-weighed flask. Any residual solvent in the flask after was removed by allowing the flask and content to stand in the oven at 105 ^{o}C for 30 min. The mean of triplicate determinations of the oil content was reported on dry weight basis.

4.3.5 Measurement of crisps color properties

The color properties of both the UGP and FRP crisp samples were measured before oven drying using Konica Minolta spectrophotometer (model CM-3500d, Osaka, Japan) in the reflectance

mode, following the protocols described by Dadali et al. (2007). The instrument was calibrated before the measurements, first with a black plate followed by a white ceramic plate. The color values were expressed as L* (brightness/darkness), a* (redness/greenness) and b*(yellowness/blueness). The average of 10 scans at different locations of the crisps were used to determine the L* a* b* parameters. The Chroma (C*) was calculated internally by the instrument. In addition, the total color change (*ΔE*) and the browning index were calculated using equations (4.1) and (4.2) respectively.

$$\text{Total color change } \Delta E = [(L_0 - L_t)^2 + (a_0 - a_t)^2 + (b_0 - b_t)^2]^{0.5} \quad (4.1)$$

$$\text{Browning index} \quad BI = \frac{[100(X - 0.31)]}{0.17} \quad (4.2)$$

$$\text{Where} \quad X = \frac{(a_t + 1.75L_t)}{(5.645L_t + a_t - 3.012b_t)} \quad (4.3)$$

(L_0, a_0 and b_0 are L a b values at time 0; L_t, a_t and b_t are L a b values at any other frying time).

4.3.6 Measurement of texture parameters

The compression/puncture test described by Pedreschi and Moyano (2005) with slight modification was used to measure the hardness and crispiness of the UGP and FRP crisps fried in different oils. The instrument used was Instron Universal Testing Machine (Model 4502, Canton MA, USA). Force vs displacement (F/D) curves were generated with the puncture test by mounting the sample on a flat rigid support where the distance between the support and a cylindrical punch was 15 mm. The punch diameter and the crosshead speed were 5 mm $min^{-1}$and 25 mm min^{-1}, respectively. The hardness (equals maximum force) and crispiness (equals the slope of the linear section of the F/D curve) was obtained from the plot generated. Each parameter was measured five times and their mean values were reported.

4.3.7 Statistical analysis and kinetics models

All the data collected were analyzed using the SAS system software (Version 9.2, SAS Institute, Inc., 1999, Cary, NC, USA). Differences among means were estimated using Duncan's multiple range test (DMRT) at 5% probability level. The rate of moisture loss, oil uptake and changes in color of the plantain crisps fried in different oils as a function of frying time were determined. Generally, the rate of change of a food quality factor C is usually represented by equation (4.4):

$$\frac{dC}{dt} = -kC^n \tag{4.4}$$

Where *k* is the kinetic rate constant and *n* is the order of reaction. Integrating equation (4.4) gives

$$C = C_0 exp^{(-kt)} \tag{4.5}$$

Equation (4.5) is a first order kinetic model where C_0 is the initial concentration and *C* is the concentration at time *t*.

For most foods, the time-dependence relationships are said to be described by either zero-order or first-order kinetic models (Chen and Ramaswamy 2002; Dadali et al. 2007). In this work, the first order kinetic models proposed for moisture ratio (Pedreschi et al. 2005); oil uptake (Moyano and Pedreschi 2006) and non-enzymatic browning (Ibarz et al. 2000) with slight modifications were used respectively to determine the rates of change of these parameters in the products:

$$MR = \frac{M_t}{M_0} = A_1 * Exp^{(-kt)} + C_1 \tag{4.6}$$

(Where moisture ratio (MR) is the ratio of moisture at a given time (M_t) and initial moisture (M_0) on dry basis (g/g), *k* is the drying rate constant, *t* is frying time, and A_1 and C_1 are constants).

$$OC = O_{eq} * [1 - exp^{(-kt)}] \tag{4.7}$$

(Where *OC* is the oil content on dry basis (g/g), O_{eq} is the oil content at equilibrium (or maximum oil content on dry basis per treatment), *k* is the oil uptake rate constant and *t* is the frying time).

$$BI = B_{max} - B_{eq} * exp^{(-kt)} \tag{4.8}$$

(Where *BI* is the browning index, B_{max} is the maximum browning per treatment B_{eq} is the equilibrium browning per treatment, *k* is the browning index rate constant and *t* is the frying time). Equation (4.8) was also used to model the total color change ΔE.

Non-linear regression analysis was performed using MATLAB R2015b computer program. The goodness of fit of the tested mathematical model to the experimental data was evaluated from the coefficients of determination (R^2) which represents the proportion of variability that has been accounted for by the prediction equation. The quality of the mathematical models was also evaluated by calculating the root mean square error (RMSE) between the experimental results and

the results predicted by the models. In each case kinetic parameters and the kinetic rate constant that gave the best fit was selected.

4.4 Results and Discussion

4.4.1 Moisture loss

As shown in Figure 4.1, the moisture loss during frying of the UGP and FRP crisp samples followed the classical drying profile.

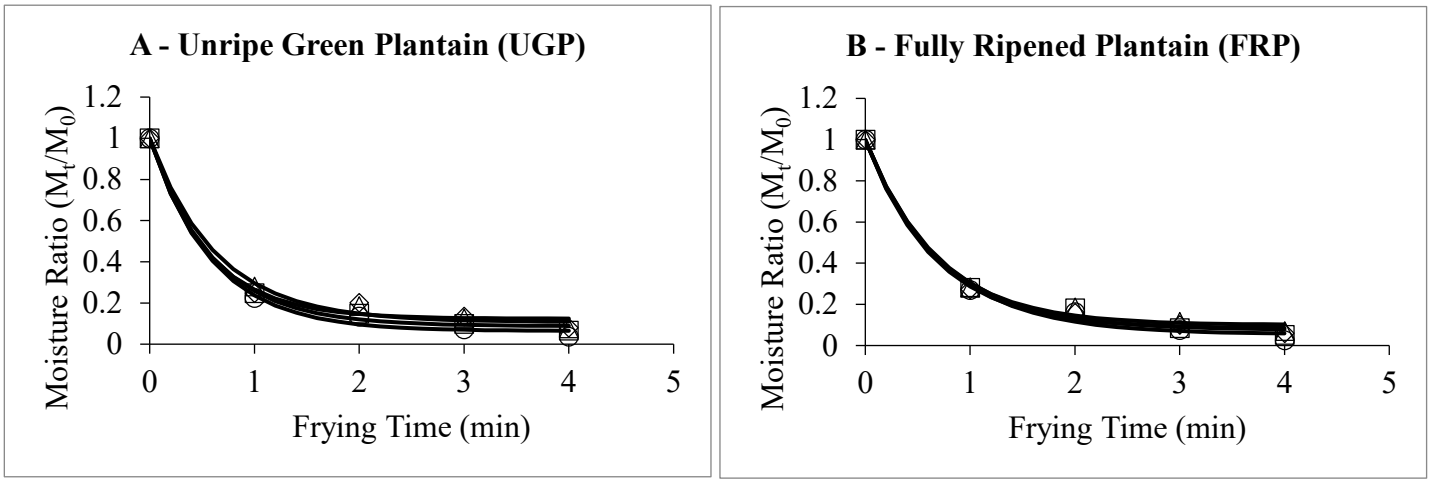


Figure 4.1: Moisture loss of plantain crisps fried using different oils. ◊= 100% Crude palm oil (CPO); Δ = Blend-1 (CPO: RCO – 70:30); ○ = Blend-2 (CPO: RCO – 50:50); □ = 100% Canola oil (RCO); Continuous line = Predicted values.

The crisps were heated up from their initial temperature to the frying temperature where the moisture begins to evaporate. Frying time and the stage of ripening significantly ($p < 0.05$) affected the rate of moisture loss. There was not much significant difference ($p > 0.05$) when considering the effect of type of oil used in the frying operation. The mean moisture content of the plantain was initially 63.78% which was considerably reduced to a mean moisture content of 9.57% after 4 min of frying. Frying time had more influence on the moisture loss than the type of oil used in the frying. This trend is in harmony with literature reports (Blumenthal and Stier 1991; Pedreschi et al. 2005). In both Figures 4.1 A and B, the effect of the oil samples followed a similar trend. In UGP samples, the mean moisture content of crisps fried in 100% CPO was18.74 %; while crisps fried in 100% RCO had 19.10%. There was no significant difference in the moisture loss rate of the two oils. Even when the plantain became softer due to ripening (Figure 4.1B), the moisture loss rate of the crisps fried in different oils was relatively higher but not statistically significant. The differences in the rheological behavior of CPO and RCO such as kinematic viscosity,

recrystallization upon cooling and density could account for any slight variation in their moisture loss trend (Fountain et al. 1997; Abdulkarim et al. 2007). Increased rate of moisture loss can be expected in the softer and more porous tissues of the ripened plantain.

4.4.2 Fat uptake

The initial total fat content of the UGP samples used was 0.34 % (db), which decreased to 0.26% (db) at the fully ripened stage. There was a significant difference ($p < 0.05$) in the mean fat content of UGP samples after frying, 12.02% (db), while FRP samples had a mean fat content of 14.72% (db). Less oil uptake in UGP crisps can be attributed to rapid starch gelatinization and swelling which make the cells dense with no rupture to allow easy oil diffusion (Aguilera et al. 2001). The increased oil absorption during deep-fat frying of ripe plantains could be due to changes in porosity and pore size redistribution as starch is hydrolyzed to sugars during ripening (Yomeni et al. 2004; Baiyeri et al. 2011). Ripening is a natural process that results in the breakdown of adhesive forces between cells creating voids. Oil does not penetrate into intact cells but enters the voids when moisture evaporates from the product. The capillary effect of the porous microstructures then provides the driving force that pushes the oil deposits at the surface of the fried products into the open voids (Ziaiifar et al. 2010; He et al. 2012).

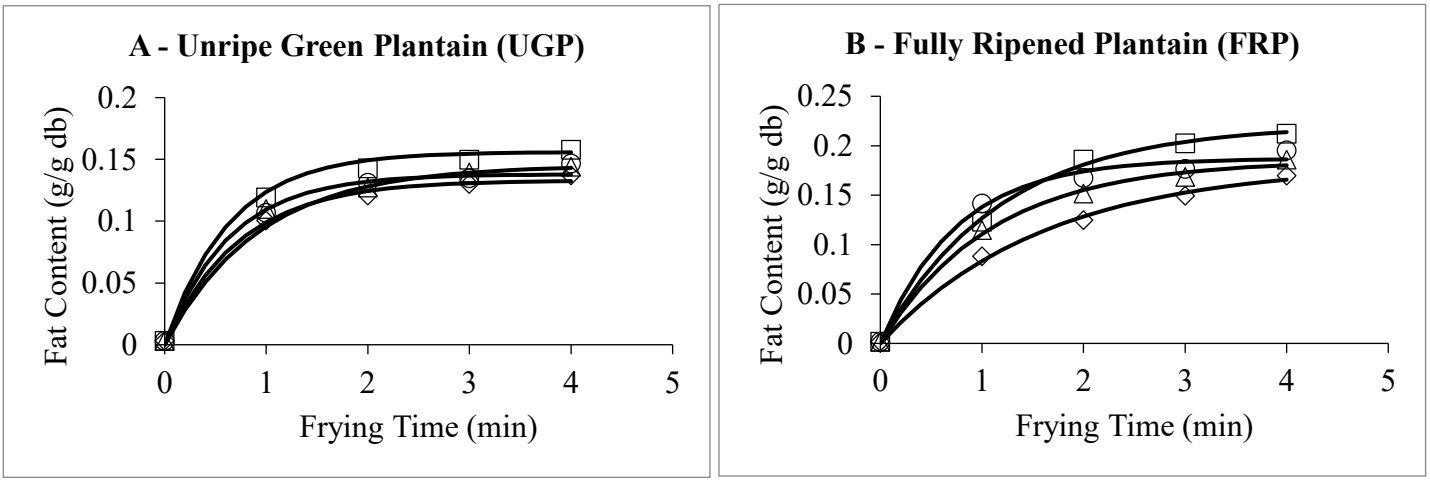


Figure 4.2: Oil uptake trend in plantain crisps fried using different oil samples. ◊ = 100% Crude palm oil (CPO); Δ = Blend-1 (CPO: RCO – 70:30); ○ = Blend-2 (CPO: RCO – 50:50); □ = 100% refined canola oil (RCO); Continuous line = Predicted values.

As seen in Figure 4.2 above, the type of oil used and frying time had significant effect ($p < 0.05$) on the oil uptake of the fried plantain crisps. Good deep-fat frying practice and health considerations demand the production of low fat chips (Boskou 2011). In the UGP samples the

percentage mean fat content (on dry basis) in ascending order of magnitude was 9.85, 10.45, 10.49 and 11.46 for oil samples CPO, Blend-1, Blend-2 and RCO respectively. CPO fried crisps showed the least oil uptake which was significantly different from the other three oil samples. CPO fried crisps absorbed 14% less oil than the crisps fried in RCO. The crisps fried in Blend-1 and Blend-2 also had significantly different oil uptake from the crisps fried using RCO. This showed that there was less oil absorption when UGP crisps were fried in palm oil. A similar but more distinct trend was observed for the FRP fried crisp samples (Figure 4.2B). CPO crisps had a mean oil content of 10.68% (db) while RCO crisps had 14.52% (d.b.). This represented a 26% more oil uptake for the crisps fried in RCO. Crisps fried in Blend-1 had a mean fat content of 12.45% (d.b.) which is between the values obtained for CPO and RCO. Crisps fried in Blend-2 had fat content of 13.66% d.b. which was not significantly different from RCO samples. CPO consistently performed better than RCO and the blends in terms of oil uptake. The trend suggests that the higher the CPO inclusion in the blend the lower the oil uptake. This result is in line with Ong and Goh (2002) who reported that potato chips have less oil retention when fried in palm olein than when fried in polyunsaturated oils. Although, Rimac-Brncic et al. (2004) reported that the kind of oil had no significant effect on the fat uptake they still observed a 2% reduction in the fat content of potato strips fried in palm oil when compared to sunflower and vegetable oils.

In both UGP and FRP crisps, the oil uptake continued to increase with increase in frying time reaching a maximum of 14.65% (d.b.) and 19.07% (d.b.) respectively after 4 min of frying. Our result also showed that increased oil uptake started after the second minute of frying as there was no significant difference ($p > 0.05$) in the mean oil content of crisps fried for 1 min and 2 min. This agrees with literature report that fried products initially have to be heated from its initial temperature when it enters the fryer until it reaches the boiling point of water. As time passes the moisture content decreases and the oil content increases; a threshold point was when the rate of moisture loss becomes negligible and the crisps are sensibly heated to the frying oil temperature, then structural oil uptake begins to occur (Southern et al. 2000; He et al. 2012).

4.4.3 Crisps color properties

The L* a* b* color changes in the UGP and FRP crisps were represented by the lightness, browning index, and total color change (ΔE) (Figures 4.3A – F).

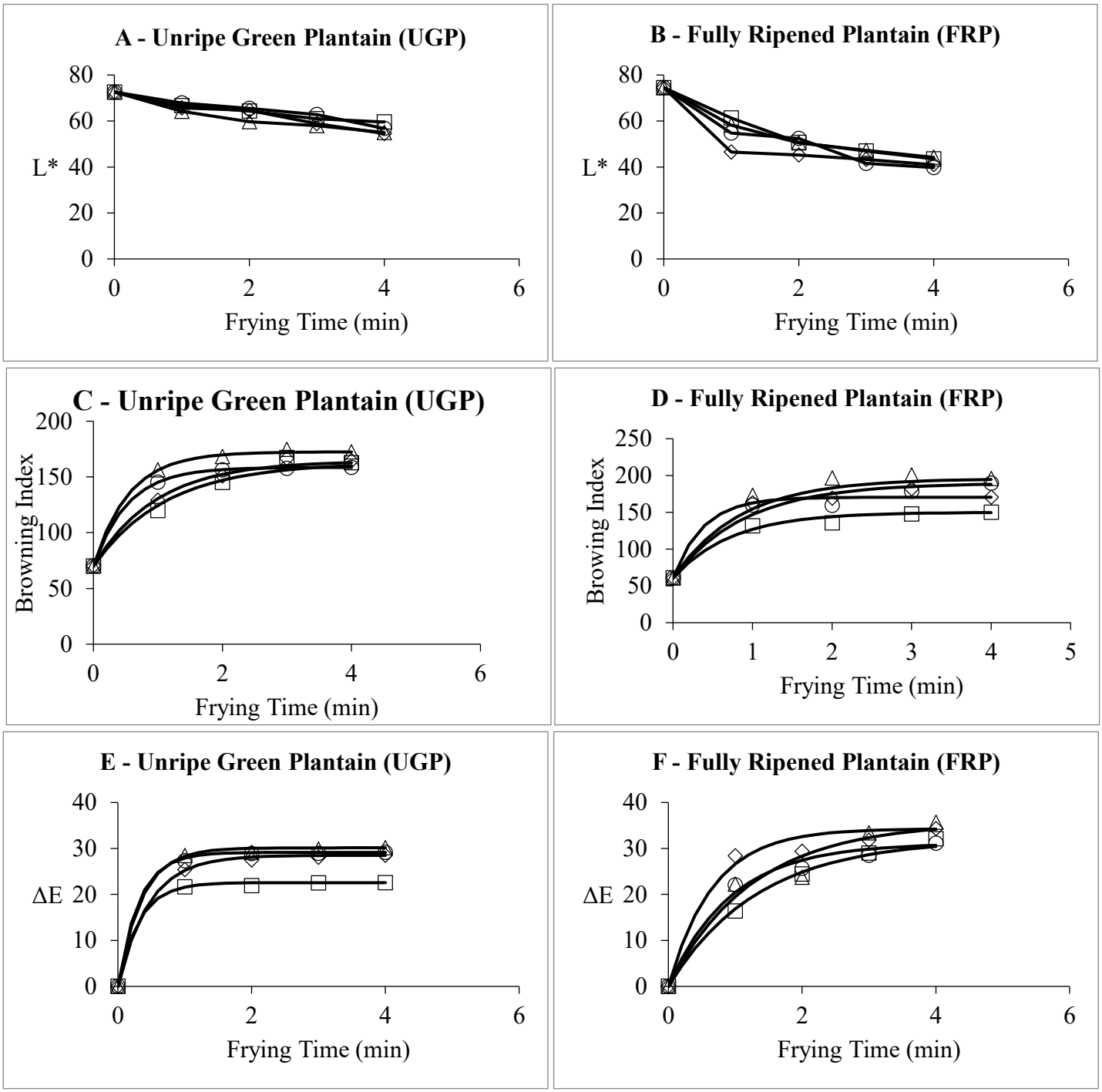


Figure 4.3: Color parameters of the fried plantain crisps using different oil samples. ◊ = 100% Crude palm oil (CPO); Δ = Blend-1 (CPO: RCO – 70:30); ○ = Blend-2 (CPO: RCO – 50:50); □ = 100% Refined canola oil (RCO); Continuous line = Predicted values.

It has been reported that the color of French fries is the result of the Maillard reactions. Maillard reactions depend on the amount of reducing sugars and certain amino acids or proteins at the surface of the food being fried, as well as the temperature and time of frying (Pedreschi et al. 2007;

Andreu-Sevilla et al. 2009). Figures 4.3A and 4.3B showed that the lightness (L*) values decreased with frying time reaching below 50 after 4 min of frying especially in the FRP crisps. The decrease in lightness positively correlated with the observed increases in the redness (a*) and yellowness (b*) of the fried crisps with time. These changes represent a measurement of browning (Dadali et al. 2007). As shown in Figures 4.3C and 4.3D, the browning index (BI) increased from 65.36 ± 6.47 in the fresh state to 170.52 ± 5.46 after 4 min frying. There was more browning in the FRP crisp samples than in the UGP crisp samples. This was expected since there are 10.42% more reducing sugars in ripened than in un-ripened plantain pulp (Adewole and Duruji 2010), and higher concentration of amino acids in the ripened plantain pulp (Pedreschi 2012; Matiacevich et al. 2014).

CPO is naturally yellowish in color and significantly changes the color of food when used in foods preparations due to abundance of β-carotene (Andreu-Sevilla et al. 2009). Among the frying oils, the CPO fried crisps showed the least L* value of 52.53 ± 9.84 which was not significantly different from the L* value of Blend-1 crisps (54.55 ± 6.77). The maximum L* value was observed for crisps fried in Blend-2 (59.15 ± 11.9); while RCO crisp samples had L* value of 56.4 ± 8.46. The very lightly colored RCO produced crisps with the least mean browning index (144.95 ± 5.8) which was more evident in the FRP crisp samples (Figure 4.3D). The browning index of CPO crisps was 161.83 ± 5.8 and continued to rise as the level of CPO increased in the blends, reaching a maximum of 179.76 ± 5.93 in Blend-1 crisp samples. The overall color changes in the plantain crisp samples are shown in Figures 4.3E and 4.3F. The observed trend confirmed that frying time significantly ($p < 0.05$) affected the color properties of the crisps. In the UGP samples RCO crisps showed the least total color changes while Blend-1 crisps showed the maximum changes. In the FRP samples, RCO crisps again showed the least total color change while CPO crisps showed the maximum, thus leading to the conclusion that CPO and its blends influenced significantly the color and perception of the fried plantain crisps.

4.4.4 Hardness and crispiness

As shown in Figures 4.4A – 4.4D, the stage of ripening and the frying time had greater significant ($p < 0.05$) influence on hardness and crispness than the type of oil used in frying the crisps. The maximum force used to break the UGP samples, 17.67±2.83 N was much greater than the 7.49±1.09 N used to break the FRP samples. The effect of frying time on hardness can be seen from the increase in breaking force 3.83±0.92 N in the un-fried samples to 18.73±2.81 N after 4

min frying of the UGP samples. However, in the FRP samples it was observed that there was no significant difference between the hardness of the un-fried samples and crisps fried for 1 min. Differences became noticeable after 2 min of frying reaching a maximum of 13.70±3.1 N after 4 min of frying. The crisps fried in oil Blend-1 showed the least hardness as indicated in the mean maximum force used to break them which was 14.25±2.49 N in UGP and 6.46±2.45 N in FRP. CPO fried UGP crisps demonstrated the maximum hardness of 19.74±2.91 N, while in the FRP crisps it had a force of 8.27±2.98 N. The force used to break the crisps fried in RCO was not significantly different from Blend-2 in both UGP and FRP crisp samples.

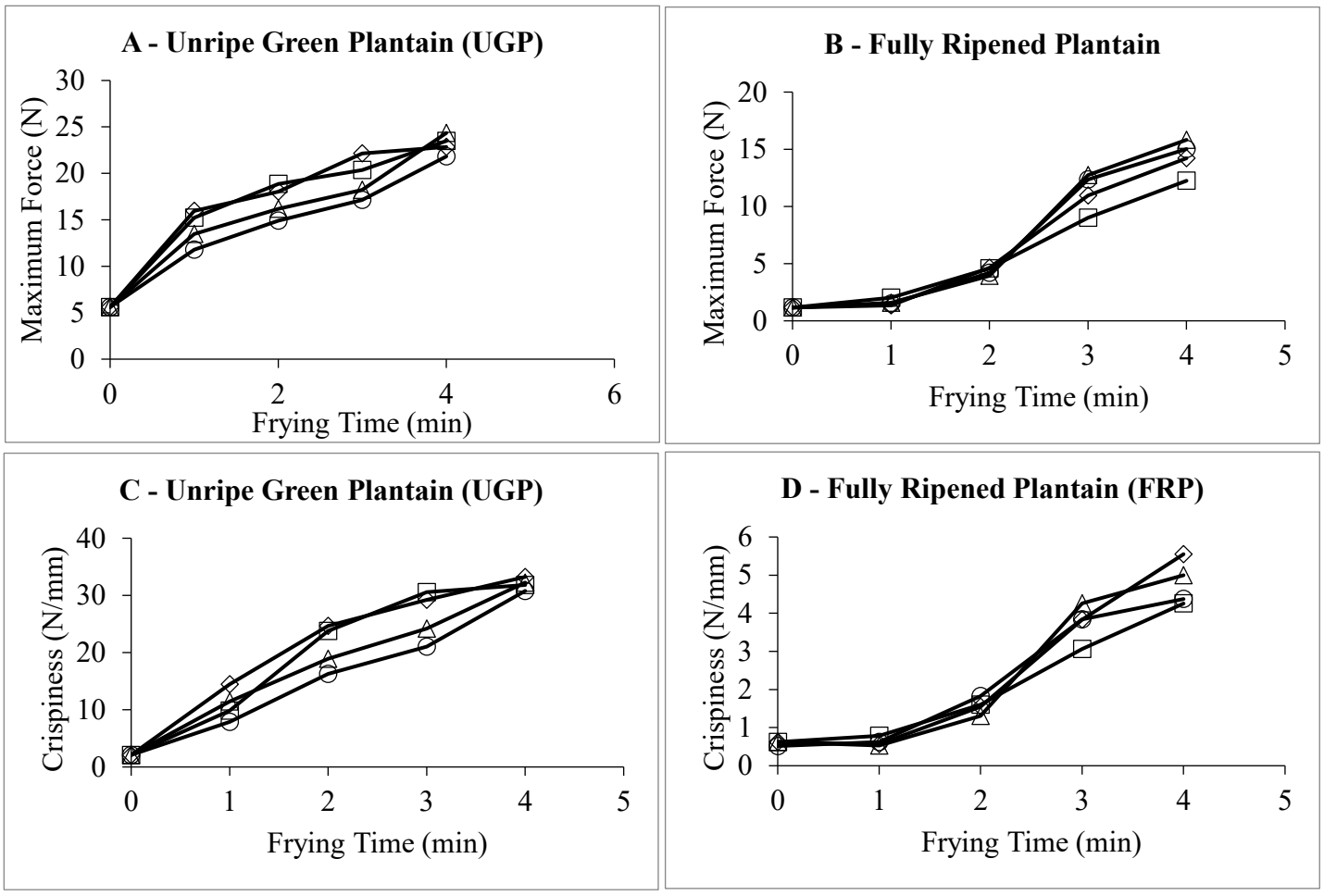


Figure 4.4: Textural characteristics of fried plantain crisps using different oil samples. ◊ = 100% Crude palm oil (CPO); Δ = Blend-1 (CPO: RCO – 70:30); ○ = Blend-2 (CPO: RCO – 50:50); □ = 100% Canola oil (RCO). Continuous line links samples from the same oil.

A similar trend was observed for the crispness of the fried crisps just as ripening stage and frying time had a significant ($p < 0.05$) effect on texture. The type of oil used had very minimal effect (Figures 4.4C and 4.4D). The mean crispiness value of UGP (21.32±3.89 N mm^{-1}) was higher than that of the FRP samples (2.58±0.36 N mm^{-1}). Overall the crispness of CPO crisp samples was 13.8±1.65 N mm^{-1}. The difference in the texture of UGP and FRP is attributed to softening due to pectin mediated degradation of cell wall and middle lamella during ripening (Suntharalingam and Ravindran 1993). The textural characteristics of the UGP and FRP crisps can be due to the development of crust as frying time progressed (Kita 2014). The crystalline nature of an oil, the fineness and stability of the crystals can contribute to the firmness of a fried product on cooling (Ghotra et al. 2002). CPO is noted for maintaining a fine and stable β` crystal structure at room temperature (O'brien 2010; Lin 2011).

4.4.5 Kinetic parameters

The parameters of the first order kinetic model for moisture loss, fat uptake, and browning index of the UGP and FRP crisp samples fried using CPO, RCO and blends are presented in Table 4.1. The experimental data of the parameters were adequately modeled by the first-order kinetic equations used. This is shown by the high coefficient of determination ($R^2 \geq 0.96$) and low root mean square error (RMSE) calculated for all the samples. In all the samples, the rate of moisture loss was higher than the rate of oil uptake. The rate of browning was higher in the oil samples containing CPO than the oil samples not containing CPO (RCO alone). The kinetic results are in agreement with model fits reported in the literature for moisture loss, fat uptake and browning index (Debnath et al. 2003; Moyano and Pedreschi 2006; Dadali et al. 2007).

Table 4.1: The first order kinetic parameters of the models used for moisture loss, oil uptake, and browning index of plantain crisp samples fried in different oil samples

	Moisture ratio				Oil uptake				Browning index		
Sample	k_m (min^{-1})	R^2	RMSE	O_{eq} (% d.b)	k_{ou} (min^{-1})	R^2	RMSE	B_{eq}	k_{bi} (min^{-1})	R^2	RMSE
UGPA	1.826	0.9907	0.052	0.133	1.368	0.9852	0.015	94.49	1.355	0.9926	3.438
UGPB	1.755	0.9951	0.038	0.138	1.455	0.9863	0.014	102.52	1.830	0.9988	1.549
UGPC	1.684	0.9962	0.035	0.145	1.077	0.9816	0.013	88.60	1.888	0.9999	0.312
UGPD	1.677	0.9976	0.027	0.156	1.573	0.9971	0.011	89.22	1.028	0.9829	4.815
FRPA	1.504	0.9969	0.030	0.181	0.617	0.9961	0.005	109.74	2.643	0.9873	5.608
FRPB	1.492	0.9949	0.039	0.185	0.912	0.9967	0.006	135.07	1.861	0.9968	3.384
FRPC	1.375	0.9940	0.044	0.187	1.338	0.9919	0.008	128.85	1.105	0.9589	1.051
FRPD	1.395	0.9939	0.043	0.221	0.853	0.9983	0.004	92.75	0.888	0.9754	6.256

UGPA = unripe green plantain fried in 100% crude palm oil (CPO); UGPB = unripe green plantain fried in Blend-1 (CPO: RCO - 70:30); UGPC = unripe green plantain fried in Blend-2 (CPO: RCO - 50:50);
UGPD = unripe green plantain fried in 100% refined canola oil (RCO); FRPA = fully ripened plantain fried in 100% CPO; FRPB = fully ripened plantain fried in CPO: RCO - 70:30; FRPC = fully ripened plantain fried in CPO: RCO - 50:50; FRPD = fully ripened plantain fried in 100% RCO; k_m = drying rate constant;
R^2 = Coefficient of determination; RMSE = Root mean square error; O_{eq} = oil content at equilibrium;
k_{ou} = oil uptake rate constant; B_{eq} = browning index equilibrium; kbi = Browning index rate constant.

4.5 Conclusion

Expectedly, frying time and ripening stages significantly influenced the quality of the plantain crisps produced. Using crude palm oil (CPO) in frying the crisps resulted in significant less oil uptake and more color changes when compared to using refined canola oil RCO. While the hardness and crispness values were higher in the crisps produced using CPO than the other oils, the values were not statistically significant. Overall, the quality characteristics of the crisps produced using the 70:30 blend of CPO: RCO oil sample were not significantly different in quality from CPO fried crisps. The color of the crisps produced using RCO were very different from the color of the crisps produced in CPO containing oil samples. The moisture loss, oil uptake and color changes that took place during the frying process in each of the oil samples were satisfactorily described by the first order kinetic model. Good quality plantain crisps can be produced using CPO and other oils containing higher amounts of CPO in the blend ratio.

CONNECTING TEXT TO CHAPTER 5

In chapter 4 the use of crude or virgin palm oil as a medium for deep-fat frying as well as blends of crude palm oil and polyunsaturated vegetable oil such as refined canola oil to produce quality products was given added impetus. The quality characteristics of the plantain crisps produced met the quality of similar snack products reported in literature. The chapter 4 of this dissertation was published in a peer-reviewed journal 'British Food Journal'. The authors and article information is as follows:

Ogan I. Mba, Marie-Josée Dumont, and Michael Ngadi, (2015). Influence of palm oil, canola oil, and blends on characteristics of fried plantain crisps. British Food Journal, 117 (6), 1793 – 1807; doi: 10.1108/BFJ-04-2014-0155.

The frying of the plantain crisps was done at just one temperature (180 ^{o}C) and the total frying time was relatively small. Whereas, commercial frying involves multiple frying cycles using the same oil. The discard and change of thermo-oxidized frying oil is an aspect of good manufacturing practice in the frying industry. Using oils highly susceptible to thermo-oxidation and frequent discard of oxidized oils or otherwise still useful oil can unnecessarily add to the cost of production. The findings in chapter 4 helped to select and test the behavior of 50:50 (1: 1 w/w) blend of CPO: RCO, CPO and RCO when used in repeated deep-fat frying cycles with extended process time. The thermostability of the selected oil samples at elevated temperature and time was studied. The rate of accumulation in the concentration of each of the most conventional oil deterioration parameters when the oil samples are used in deep-fat frying operations and using kinetic models to predict the useful life of frying oil became the focus of chapter 5. The frying studies was done without any partial replacement of the frying medium with fresh oils. The findings of this investigation have been published in the peer reviewed journal, 'Journal of the American Oil Chemists' Society'. The format of the manuscript has been altered to be consistent with this thesis. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER 5

5. DETERIORATION KINETICS OF PALM OIL, CANOLA OIL, AND BLEND DURING REPEATED DEEP-FAT FRYING

5.1 Abstract

The oxidation of vegetable oils is generally treated as an apparent first order kinetic reaction. This study investigated the deterioration of crude palm oil (CPO), refined canola oil (RCO) and their blend (CPO: RCO 1:1 w/w) during 20 h of successive deep-fat frying of potato at 170, 180 and 190 ºC. Kinetics of changes in oil quality indices, namely, free fatty acid (FFA), peroxide value (PV), *para*-anisidine value (*p*-AV), total polar compounds (TPC) and color index (CI) were monitored. The results showed that FFA and PV accumulation followed the kinetic first order model, while *p*-AV, TPC, and CI followed the kinetic zero order model. The concentration and deterioration rate constants *k* increased with increasing temperatures. This effect of temperature was modeled by the Arrhenius equation. The results showed that PV had the least activation energies E_a (kJ/mol) values of 5.4±1 (RCO), 6.6±0.7 (CPO) and 11.4±1 (blend). The highest E_a requirement was exhibited by FFA with a range of 31.7±3 – 76.5±7 kJ/mol in the oil samples. The overall E_a values showed that the stability of the blend was superior and not just intermediate of CPO and RCO. The correlation of the other oil quality indices with TPC indicated a positive linear correlation. The *p*-AV displayed the most correlation, with mean correlation coefficient r_s of 0.998±0.00, 0.994±0.00 and 0.999±0.00 for CPO, RCO and blend, respectively.

5.2 Introduction

The thermostability of frying oils during deep fat frying is most desirable. This depends on factors such as the type of oil and its composition, the frying procedure and the type of food being fried (Aladedunye 2015). Other conditions that affect the rate of thermal degradation of oils include the presence of pro-oxidants (such as water, oxygen, salt, iron and cupper) and anti-oxidants (natural and synthetic) (Aniołowska and Kita 2016). The mechanism of thermal oxidation mainly comes from free radical mediated breakages of the unsaturated sites of the triacylglycerols (TAG) (Houhoula et al. 2003; Zhang et al. 2012). Oil degradation reactions that occur during deep-fat frying are hydrolysis, oxidation, isomerization, and polymerization (Choe and Min 2007). Frying oil degradation results in the generation of free fatty acids, small molecular weight alcohols aldehydes, ketone, lactone, and hydrocarbons (Zhang et al. 2012). Other compounds that have

been identified in degraded oils include polymerized diacylglycerols, monoacylglycerols, oligomeric, cyclic, and epoxy compounds (Sebastian et al. 2014) as well as t*rans*-fats and volatile short-chain aldehyde compounds such as acrolein (Wang et al. 2015). Some of these degradation products affect the quality of the fried products and can potentially harm the consumers' health (Firestone 2007). It is necessary that any frying oil be reasonably stable to thermoxidation during extended exposure to the high temperatures (150 – 190 ºC) used in frying different kinds of foods. Chemical indicators such as the free fatty acid (FFA), peroxide value (PV), *para*-anisidine value (*p*-AV), and total polar compounds (TPC) are used in monitoring frying fats and oils. The TPC and polymeric triacylglycerols are among the most reliable frying oil degradation indicators used in regulations by many countries (Firestone 2007; Stier 2013). In the year 2000, the DGF (German Society for Fat Research) recommended TPC level of < 24 % for used frying oils as TPC levels above 19 % result in fried products with poor sensory characteristics (DGF (German Society for Fat Research) 2000).

Palm oil has near equal composition of saturated and unsaturated fatty acids, moderate amounts of linoleic acid and a trace amount of linolenic acid (Mba et al. 2015b). Crude palm oil (CPO), also known as virgin palm oil (VPO), contains high levels of beneficial phytonutrients such as β-carotene, tocopherols and tocotrienols. These antioxidants make the oil less prone to oxidation and deterioration. CPO has a long history of direct use in cooking and food preparations in tropical Africa, Southeast Asia, and South America. The oil is readily available and is used as a major component of some processed foods or as a minor ingredient in a variety of food products (Mba et al. 2015b). Canola oil is commonly utilized in cooking and frying. It is very rich in oleic acid and is among the vegetable oils with very low concentration of saturated fatty acids (Aachary et al. 2014). These characteristics make canola oil perform poorly during prolonged frying (Farhoosh et al. 2009; Aladedunye and Przybylski 2012). Natural antioxidants of frying oils are lost during the refining process, some natural and synthetic antioxidants such as tocopherol, butylated hydroxytoluene (BHT), and butylated hydroxyanisole (BHA) are always added into the frying oil to slow down the oxidation process and especially reduce the formation and accumulation of TPC (Aachary et al. 2014; Aladedunye 2015). Frying operators sometimes blend polyunsaturated oils with a more saturated or monounsaturated oil as a cost-effective way of reducing the amounts of linolenic and linoleic acids in the frying medium and thus increasing its thermostability (Alireza

et al. 2010b; Tiwari et al. 2014). In addition to controlling oil oxidation, blending can be used to attain better sensory properties in fried foods (Ramadan 2013).

The maximum 'fry life' of oils, the various chemical reactions, and the extent of thermo-oxidative degradation during deep-fat frying has continued to engage the attention of researchers (Abdulkarim et al. 2007; Petersen et al. 2013; Aladedunye and Przybylski 2014). Frying oils differ in their rate of deterioration and formation of breakdown products (Aniołowska and Kita 2016). Mathematical models and kinetic studies of food quality changes during thermal processes is very important in estimating the performance and suitability of the applied thermal treatment. This ensures the selection of optimum processing variables. The controllable variables in deep fat frying are the oil type, the frying temperature, and the frying time (Hindra and Baik 2006). Furthermore, the oil's chemical composition, the proportion of unsaturated fatty acids, the presence of pro- or anti- oxidant compounds and the initial oxidative state of the oil needs to be controlled. According to Van Boekel (2008), the oxidation of vegetable oils can generally be treated as an apparent first order reaction. The need for further studies to determine if each individual oil quality index follows this apparent order during actual frying still exists. The knowledge of the kinetics of quality indices (like the FFA, PV, *p*-AV, TPC, and color index (CI)) changes in palm oil, canola oil and blend will make it possible to predict the threshold reject point due to safety or quality reasons. The application of kinetics will make it possible to design frying procedures that can maintain the quality of the oils studied for a reasonable time and produce fried products with minimal undesirable breakdown products, enhanced sensory characteristics, and elimination of potential hazards. Some studies on repeated heating of oil samples without food, deep-fat frying of model systems and the presence of food in the frying oil reported that while polar and polymerization products are generated due to oil breakdown, the presence of food and some metals in the oil significantly increased the concentration of these breakdown products (Kalogianni et al. 2009; Kalogianni et al. 2010; Lioumbas et al. 2012). However, the conditions encountered in actual frying are different from heating oil samples with no food and model systems. Refined vegetable oils mostly used in frying have significantly low amounts of natural phytonutrients and antioxidants. However, unrefined virgin oils are rich in various kinds of beneficial phytonutrients and antioxidants (Fine et al. 2016). Therefore, the need still exists to investigate the potentials of virgin oils for deep-fat frying and fried products enrichment. The objectives of this work are to evaluate the kinetics driving the deterioration of crude palm oil (CPO), refined canola oil (RCO)

and a binary blend (CPO: RCO 1:1 w/w) during deep-fat frying of potato strips using established kinetic equations and to compare the deterioration rates of the oils determined quality indices based on their activation energies. The strength of the relationships between these quality indices of oil deterioration will also be investigated.

5.3 Materials and Methods

5.3.1 Materials

Crude palm oil (CPO) was obtained from a local palm oil mill in Abia State, Nigeria. A qualified industry based oil chemist supervised the CPO production and packaging. The fresh CPO was filled into dark high-density polyethylene (HDPE) barrels. The bulk CPO cargo in wooden crates was transported by air within 2 weeks of production. The refined canola oil (RCO) (labelled as containing BHA, BHT and dimethyl polysiloxane (DMPS)) was obtained from Titan Oils Inc. Montréal, Canada. A binary blend was formulated by mixing and vortexing CPO and RCO (1:1 w/w) to a homogenous blend. The oils were kept in a dark cool place. Russets potatoes were purchased from a local grocery shop. All chemicals and solvents used were of analytical grade and purchased from Fisher Scientific, Fair Lawn, NJ, USA.

5.3.2 Frying and oil sampling procedures

About 4.5 L of CPO, RCO and blend were heated from an initial temperature of 23 ºC to the chosen frying temperature for 2 h in a batch electric fryer (D24527DZ Délonghi Inc. USA). The frying temperatures used were 170, 180 and 190 ºC for 5 h per day. These temperatures are commonly used for commercial and industrial deep-fat frying operations. Successive batches of 100 ± 2.0 g potato strips (≈ 10 cm long and 1.2 cm thick) were deep-fat fried for 10 min. The interval between frying the batches was 30 min. The frying procedure was repeated 3 more consecutive days, to give a total heating and frying time of 20 h. Each oil sample and frying temperature was treated the same way. K-type thermocouple interfaced with Hotmux data logger was used to monitor the oil temperature during the frying process. The end of each 5 h frying cycle was followed by cooling to room temperature, then aliquots of the fried and fresh (unused) oil samples (250 mL) were drained into HDPE dark amber bottles and kept frozen at -20 ºC until analyzed. Frying was done without oil replacement, however the oil in the fryer was kept in a dark cold place and filtered at the beginning of each successive frying day to remove solid debris.

5.3.3 Analytical procedure

Before each analysis, the frozen oil samples were allowed to revert to their liquid state by briefly holding in warm water at 50 ^{o}C.

5.3.4 Physicochemical analysis

5.3.4.1 Free fatty acids (FFA), Peroxide value (PV) and Iodine value (IV)

The FFA, PV and IV of the oil samples were determined by following the AOCS Official Methods Ca 5a-40, Ja 8-87 and Tg 1-64 respectively (Firestone 2009). FFA was expressed as percentage (%) oleic acid while PV was expressed as milliequivalents of oxygen per kilogram of oil (meqv. O_2/kg) and IV as grams of iodine absorbed per 100 grams of oil (g/100 g).

5.3.4.2 Anisidine value (*p*-AV)

The Anisidine Value (*p*-AV) measures the extent of secondary oxidation in heated oil samples. The *p*-AV was determined and calculated using the ISO Method 6885 (ISO 2006) as shown in equation (5.1).

$$p - AV = \frac{25*1.2*(A_r - A_b - A_u)}{Oil\ mass\ (g)} \quad (5.1)$$

(A_r = absorbance of the test oil samples after reacting with anisidine reagent; A_b = blank absorbance; and A_u = absorbance of the test oil samples that were not reacted with anisidine reagent).

5.3.4.3 Total polar compounds (TPC)

The estimation and calculation of the TPC of the oil samples were done according to the method and equation (5.2) described by Schulte (2004).

$$TPC\ (\%) = \frac{Oil\ mass\ (mg) - nonpolar\ componds\ (mg)}{Oil\ mass\ (mg)} * 100 \quad (5.2)$$

5.3.4.4 Color Index (CI)

The overall color changes related to the degradation processes in the oil samples were measured and calculated as CI (equation 5.3) following the AOCS Official Method Cc 13c – 50 (Firestone 2009). Briefly, the absorbance of clear free flowing oil samples in 10 mm cuvettes was read at 460, 550, 620 and 670 nm using Unicam-UV1 Spectrophotometer (Thermospectronic Inc., NY).

$$CI = 1.29(A_{460}) + 69.7(A_{550}) + 41.2(A_{620}) - 56.4(A_{670}) \quad (5.3)$$

5.4 Kinetic data analysis

Oil deterioration was based on the accumulation of FFA, PV, *p*-AV, TPC and CI. The reaction kinetics were analyzed as described by Van Boekel (2008). Firstly, the most suitable kinetic reaction order model for each quality index data was established by pre-fitting the experimental data with different kinetic models. The kinetic model that gave the coefficient of determination R^2 closest to 1 was chosen as the reaction order kinetics for the index.

As reported by Hindra and Baik (2006), a model for the rate of food quality changes that degrade by accumulation in concentration with time is shown in equation (5.4).

$$rate\ (molL^{-1}s^{-1}) = \frac{dP}{dt} = k[P]^n \tag{5.4}$$

(*P* = food property (in this case, FFA, PV, *p*-AV, TPC and CI), *dp/dt* = rate of deterioration, *k* = deterioration rate constant ($time^{-1}$); [*P*] = concentration and *n* = apparent order of reaction).

If P_0 = initial value and P_t = value at any time *t;* integrating and rearranging equation (5.4) give equations (5.5) and (5.6) for zero- and first-order reactions respectively:

$$[P_t] = kt + [P_0] \tag{5.5}$$

$$[P_t] = [P_0] * exp^{(kt)} \tag{5.6}$$

Taking natural logarithm of equation (5.6) and rearranging, gives the linearized form (equation 5.7):

$$Ln[P_t] = kt + Ln[P_0] \tag{5.7}$$

The effect of temperature on the *k* was described by the Arrhenius equation:

$$k = A * exp^{(\frac{-E_a}{RT})} \tag{5.8}$$

(*k* = deterioration rate constant; *A* = frequency factor (h^{-1}); E_a = activation energy (kJ mol^{-1}); *R* = universal gas constant (0.008314 kJ mol^{-1} K^{-1}) and *T* = absolute temperature (K)).

To reduce correlation between *A* and E_a, a reference temperature T_{ref} was chosen. The T_{ref} was the mean of the temperatures *T* studied (Van Boekel 2008). The Arrhenius equation was then reformulated:

$$k = A_r * \exp[-\frac{E_a}{R} * \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)] \quad (5.9)$$

(A_r = reparametrized frequency factor (h^{-1})).

The predicted data were obtained by substituting for k in equations (5.5) and (5.7) using equation (5.9):

$$[P_t] = A_r * \exp[-\frac{E_a}{R} * \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)] * t + [P_0] \qquad (n = 0) \quad (5.10)$$

$$Ln\,[P_t] = A_r * \exp[-\frac{E_a}{R} * \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)] * t + Ln\,[P_0] \quad (n = 1) \quad (5.11)$$

5.5 Statistical analysis

All the experiments and measurements were performed in triplicates. The significant effects of factors were assessed by analysis of variance (ANOVA) and the differences between mean values of parameters were evaluated by Tukey's LSD test (α = 0.05). The kinetic parameters were estimated by non-linear regression of the kinetic equations and the quality indices were also correlated (Statistical Analysis System (SAS) version 9.4). Model discrimination was based on pseudo-R^2 values and the correlation coefficient r. The validity of the kinetic models for each oil quality index was verified by the mean relative percentage deviation P (%) between experimental and calculated values (Kaymak-Ertekin and Gedik 2005), using equation (5.12).

$$P\,(\%) = \frac{100}{N}\sum_{i=1}^{N}(C_{ex} - C_{pr})/\,C_{ex} \quad (5.12)$$

(C_{ex} = experimental concentration; C_{pr} = predicted concentration and N = number of experimental data points. A model is considered acceptable if P values are below 10%).

5.6 Results and Discussion

5.6.1 Free fatty acid (FFA) variations

The initial free fatty acid (FFA) content expressed as % oleic acid and the acid value (AV) of the oil samples are shown in Table 5.1. The AV was 8.26 ± 1.00 mg KOH/g for CPO, 0.54 ± 0.06 mg KOH/g for RCO and 4.20 ± 0.28 mg KOH/g for the blend. These values are within the AV range of 0.60, 4.00 and 10.00 mg KOH/g recommended for refined oils, cold pressed/virgin oils and virgin palm oils respectively by the CODEX commission (Codex Alimentarius Commission

(CAC) 1999). Our earlier characterization study showed that the amount of FFA in CPO was higher than RCO because it was not refined (Mba et al. 2014).

Table 5.1: Quality parameters of fresh crude palm oil, refined canola oil and blend used in the frying experiment

Quality Index	Crude Palm oil	Refined Canola oil	Blend (1:1w/w)
Free Fatty Acid (FFA) (%)	4.15±0.50	0.27±0.06	2.11±0.14
Acid Value (AV) (mg KOH/g)	8.26±1.00	0.54±0.12	4.20±0.28
Peroxide Value (PV) (meqv. O_2/kg)	1.18±0.12	0.42±0.11	0.78±0.14
p-Anisidine Value (*p*-AV)	2.87±0.07	2.42±0.01	3.88±0.01
Total Polar Compounds (TPC) (%)	5.83±0.40	6.10±0.44	5.63±0.61
Color Index (CI)	92.07±0.70	2.38±0.40	42.37±0.60
Iodine Value (IV) (g/100 g)	54.82±0.15	101.27±0.41	85.41±0.83

Measured values ± std. dev.; AV = %FFA *1.99

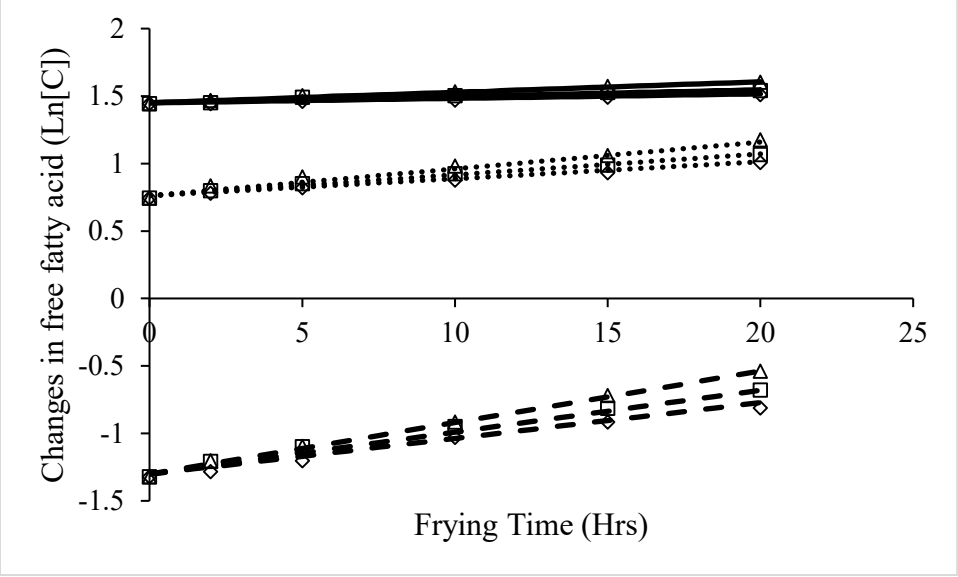


Figure 5.1: Results for free fatty acid (FFA) accumulation *vs* time on a natural log scale. Experimental data corresponds to ◊ at 170 °C, □ at 180 °C and Δ at 190 °C. Lines represent the first order fit: CPO (solid line), RCO (broken line), and Blend (dotted line).

As shown in Figure 5.1 above, the FFA of the oils significantly ($P<0.05$) increased with frying temperature and time. The maximum percentage changes in FFA over the temperature range studied were 1.59%, 2.21% and 1.09% for CPO, RCO and blend, respectively. RCO showed the most noticeable FFA deterioration despite its initial low levels. This can be attributed to the polyunsaturated nature of the oil which made it exhibit more sensitivity to the moisture released by the potato strips. These observations are in line with literature reports on RCO (Azmil Haizam Ahmad and Siew Wai 2008; Aladedunye and Przybylski 2012; Xu et al. 2014). The increase in FFA of the blend samples was not an intermediate between the observed increases in CPO and RCO. This is due to slower hydrolytic degradation in the blends, possibly because of alteration of the triacylglycerol composition and reduction in polyunsaturated C18 fatty acids (Tiwari et al. 2014; Aladedunye 2015).

Figure 5.1 also shows the results of the kinetic study of the FFA accumulation. FFA concentration increased with time and became more rapid at higher temperatures. This was also reflected by the increase in deterioration rate constants k with temperature (Table 5.2). The first-order kinetic model was adequate in describing the FFA accumulation in CPO, RCO and blend. This was evidenced by the values of the regression coefficient R^2 and the percentage deviation P also shown in Table 5.2. The Pr > F values which correspond to the p-values (Meier 2014) were less than 0.05 which indicated that the model was statistically significant and robust as predictor of changes in FFA during deep-fat frying.

The activation energies E_a obtained from the non-linear regression of the Arrhenius equation at $\alpha = 0.05$ is presented in Table 5.3 below. The high pseudo-R^2 values were evidence of the goodness of fit of the model. The E_a (kJ/mol) values obtained were 76.5±7, 31.7±3 and 39.6±3 for CPO, RCO and blend, respectively. The E_a for RCO was the most significantly low. These results are in accordance with findings, that hydrolytic reactions that break the ester bonds of the TAG require high activation energy (Laguerre et al. 2007). Moisture attacks more readily the ester linkage of short and unsaturated fatty acids because they are more soluble in water than long and saturated fatty acids, releasing FFA, glycerol, di- and mono-acylglycerols. Also, RCO with higher amounts of unsaturated C18 fatty acids is more amenable to hydrolysis (Choe and Min 2007; Laguerre et al. 2007).

Table 5.2: Deterioration rate constants for quality changes in palm oil, canola oil and blend during deep-fat frying

Index	Temp. (ºC)	k (h^{-1})	R^2	Apparent Reaction Order	Pr > F	Relative Error P (%)
		Crude Palm Oil (CPO)				
Free Fatty Acid (%)	170	0.0033	0.9757	1	0.0254	0.63
	180	0.0048	0.9823			0.01
	190	0.0078	0.9852			0.09
Peroxide Value (meqv. O_2/kg)	170	0.0670	0.9963	1	0.0033	3.20
	180	0.0702	0.9977			0.26
	190	0.0724	0.9944			4.50
p-Anisidine Value	170	0.7674	0.9975	0	0.0036	3.08
	180	0.8281	0.997			2.00
	190	0.9042	0.9971			0.92
Total Polar Compounds (%)	170	0.5768	0.9873	0	0.0160	3.10
	180	0.6672	0.9878			0.60
	190	0.8215	0.9882			0.23
Color Index	170	0.7177	0.9994	0	0.0080	6.16
	180	0.7616	0.9878			6.89
	190	0.7797	0.9972			3.59
		Refined Canola Oil (RCO)				
Free Fatty Acid (%)	170	0.0265	0.9929	1	0.0122	2.18
	180	0.0311	0.9891			2.02
	190	0.0382	0.9975			0.48
Peroxide Value (meqv. O_2/kg)	170	0.0861	0.9970	1	0.0052	9.09
	180	0.0899	0.9864			5.21
	190	0.0917	0.9962			9.48
p-Anisidine Value	170	1.4908	0.9866	0	0.0031	5.04
	180	1.5560	0.9836			6.17
	190	1.6422	0.9825			3.88
Total Polar Compounds (%)	170	0.8290	0.9843	0	0.0130	1.13
	180	0.9436	0.9903			3.00
	190	1.2260	0.9921			0.95
Color Index	170	0.0772	0.9999	0	0.0020	6.39
	180	0.0787	0.9997			4.18
	190	0.0795	0.9987			3.41

Table 5.2: Deterioration rate constants for quality changes in palm oil, canola oil and blend during deep-fat frying (Continued)

Index	Temp. (ºC)	k (h^{-1})	R^2	Apparent Reaction Order	Pr > F	Relative Error P (%)
	CPO: RCO blend (1:1 w/w)					
Free Fatty Acid (%)	170	0.0126	0.9960	1	0.0118	1.39
	180	0.0155	0.9917			0.19
	190	0.0199	0.9812			1.51
Peroxide Value (meqv. O_2/kg)	170	0.0519	0.9968	1	0.0058	8.03
	180	0.0563	0.9964			0.90
	190	0.0594	0.9927			6.52
p-Anisidine Value	170	0.6554	0.9965	0	0.0086	1.77
	180	0.7819	0.9974			1.64
	190	0.8929	0.9965			1.17
Total Polar Compounds (%)	170	0.7322	0.9971	0	0.0320	3.62
	180	0.8844	0.9939			0.39
	190	1.1289	0.9920			1.05
Color Index	170	0.4440	0.9993	0	0.0087	2.32
	180	0.4665	0.9979			3.15
	190	0.5064	0.9999			3.02

Table 5.3: Activation energies of the quality indices of oil deterioration

Parameter	Crude Palm Oil			Refined Canola Oil			Blend (1:1 w/w)		
	E_a (KJ/mol)	A_r	R^2_{pseud}	E_a (KJ/mol)	A_r	R^2_{pseud}	E_a (KJ/mol)	A_r	R^2_{pseud}
Free Fatty Acid	76.5±7.0	0.01±0.00	0.9994	31.7±3.0	0.03±0.00	0.9999	39.6±3.0	0.02±0.00	0.9956
Peroxide Value	6.6±0.7	0.07±0.00	0.9999	5.4±1.0	0.09±0.00	0.9979	11.4±1.0	0.06±0.00	0.9992
p-Anisidine Value	14.1±0.8	0.83±0.00	0.9997	8.3±0.7	1.56±0.01	0.9999	26.4±2.0	0.77±0.01	0.9995
Total Polar Compounds	30.8±4.0	0.68±0.01	0.9997	26.8±3.0	0.95±0.01	0.9998	45.8±7.0	0.92±0.03	0.9990
Color Index	7.0±2.0	0.75±0.01	0.9999	2.5±0.4	0.08±0.00	0.9999	11.2±2.0	0.47±0.00	0.9992

E_a = activation energy (± standard error of regression); A_r = reparametrized pre-exponential factor (± standard error of regression); R^2_{pseud} = pseudo-regression coefficient of determination.

5.6.2 Peroxide value (PV) variations

The initial PV values (meqv. O_2/kg) of CPO, RCO and blend were 1.18±0.12, 0.43±0.11 and 0.78±0.14, respectively (Table 5.1). These values are within the range of guidelines which recommended initial PV of ≤ 2 meqv. O_2/kg for good quality vegetable oil and discard level PV of 10 meqv. O_2/kg (DGF (German Society for Fat Research) 2000) and upto 15 meqv. O_2/kg for cold pressed and virgin oils (Codex Alimentarius Commission (CAC) 1999). There was no evidence of advanced auto-oxidation in the three oils as their initial PV were within the recommended range.

The kinetic study of the changes in hydroperoxides was expressed relative to the initial mean value of the unused oil on a natural log scale (Fig. 5.2). The PV values progressively increased with studied frying time and temperature in the three oils. Though RCO showed an accelerated rate of PV formation especially at 190 ºC reaching up to 4.87%, it did not reach the oil reject points specified by the DGF (German Society for Fat Research) (2000) and the Codex Alimentarius Commission (CAC) (1999). Tiwari et al. (2014) obtained a similar result while frying potato chips at 180 ºC in palm oil, sesame oil, and palm-sesame oil blend. This trend was also reported for unrefined Pollock oil (Sathivel et al. 2008) and choibá oil containing antioxidants from *Rosmarinus officinalis* (Piedrahita et al. 2015). The first-order kinetic model gave a good fit in describing the changes in the PV of the oil samples as shown by the high R^2 and low P of the model (Table 5.2). The Pr > F values were 0.0033, 0.0052 and 0.0058 for CPO, RCO and blend respectively. These values gave further proof that the models for predicting changes in PV of the oil samples were statistically significant ($P<0.05$). The same order of reaction for lipid peroxidation was reported by Piedrahita et al. (2015) for choibá fruit oil and Sathivel et al. (2008) for Pollock oil.

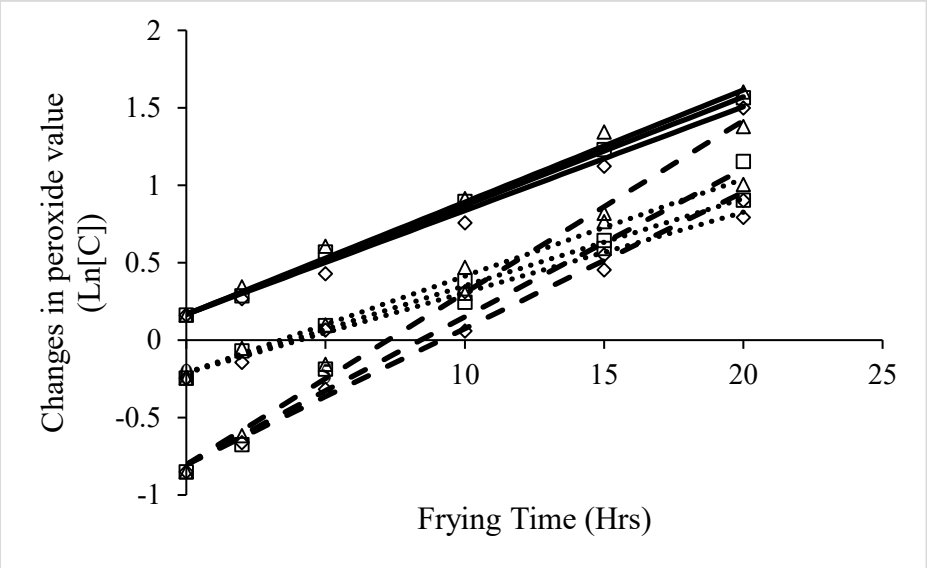


Figure 5.2: Results for peroxide value (PV) accumulation *vs* time on a natural log scale. Experimental data corresponds to ◊ at 170 °C, □ at 180 °C and Δ at 190 °C. Lines represent the first order fit: CPO (solid line), RCO (broken line), and Blend (dotted line).

The Arrhenius equation was used to describe the temperature dependence of k of the oil samples. Non-linear regressions were performed, and the values obtained for the E_a and the pseudo-R^2 are shown in Table 5.3. The resulting E_a values (kJ/mol) were 6.6±0.7, 5.4±1 and 11.4±1 for CPO, RCO and blend, respectively. The E_a values for PV are in line with earlier findings that the E_a required for the formation and accumulation of lipid peroxides and hydroperoxides is very low since peroxyl radicals' formation and decomposition take place simultaneously during thermal processing of oils (Laguerre et al. 2007). Low E_a values imply that the reaction takes place very quickly as the buildup of aldehydes and carbonyls soon dominates (Aniołowska and Kita 2016). The very low E_a values obtained for the PV of the RCO can be attributed to the presence of more double bonds that led to greater spontaneous reaction between carbon-centered lipid radicals and molecular oxygen. Another polyunsaturated oil, choibá fruit oil, was reported to have shown PV E_a range of 4.6 – 7.4 kJ/mol by Piedrahita et al. (2015). The blend oil sample had the highest PV E_a. This confirmed that the rate of formation of peroxide radicals in the blend was the slowest. This can be attributed to the effect of reduced double bond strength as saturation level increased combined with the synergistic radical scavenging activity of both natural and synthetic antioxidants (Goburdhun and Jhurree 1995; Ramadan 2013).

5.6.3 Anisidine value (*p*-AV) variations

The *p*-AV test is one of the most common tests for monitoring oil thermostability because the aldehydes formed during secondary oxidation and the non-volatile portion of the carbonyls linger in the frying oil (Abdulkarim et al. 2007; Aniołowska and Kita 2016). As seen from Table 5.1, the initial *p*-AV for CPO, RCO and blend were 2.87±0.07, 2.42±0.01 and 3.88± 0.01, respectively. This variation in the *p*-AV of the fresh oil samples was not significant and could be due to inherent experimental errors within the chemical analysis method. Laguerre et al. (2007), observed that because of auto-oxidation, some non-volatile aldehydes can be present in unused oils. However, the initial *p*-AV obtained were below 10 units in the three oil samples, indicating near absence of secondary oxidation (Petersen et al. 2013). In the oil samples, the *p*-AV increased as the frying temperature and time increased. In this study, RCO showed 41% higher *p*-AV than the CPO and 5 – 18% higher than the blend. The highest values observed in RCO can be due to higher proportions of linolenic and linoleic acids in the oil. These unsaturated C18 fatty acids decompose more readily after initial oxidation and yield more aldehydes, particularly 2-alkenals and 2, 4-dienals (Tompkins and Perkins 2000; Aladedunye 2015). The changes in *p*-AV of the oil samples as a function of time at different temperatures are shown in Figure 5.3.

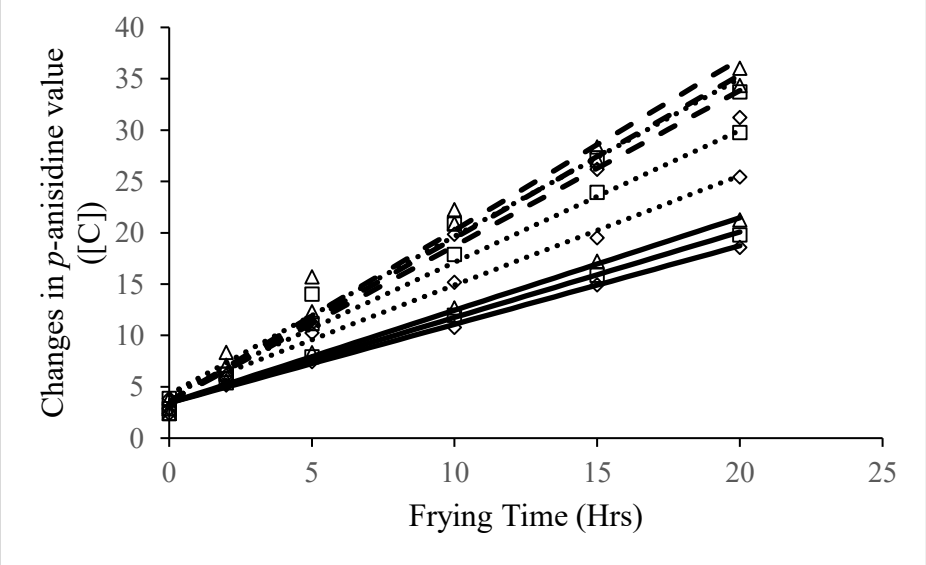


Figure 5.3: Results for p-anisidine value (p-AV) accumulation *vs* time. Experimental data corresponds to ◊ at 170 °C, □ at 180 °C and Δ at 190 °C. Lines represent the zero-order fit: CPO (solid line), RCO (broken line), and Blend (dotted line).

The *p*-anisidine values significantly ($P < 0.05$) increased with increased time and temperature. The observed trend correlated with the iodine value (IV) of the oils, 54.82±0.15 g/100 g (CPO), 101.27±0.41 g/100 g (RCO) and 85.41±0.83 g/100 g (blend) shown in Table 1. The CPO with the least number of double bonds showed the lowest reactivity of radicals and formation of secondary breakdown products. A similar trend has been reported for different lipid media by some researchers (Houhoula et al. 2003; Laguerre et al. 2007; Aladedunye and Przybylski 2014). The deterioration rates *k* with respect to *p*-AV were well fitted by the zero-order kinetic model. This is evidenced by the values for Pr > F, R^2 and *P* at different temperatures shown in Table 5.2. Some workers have also used zero-order kinetic model to satisfactorily fit the increase in *p*-AV in lipids and blends of oils (Farhoosh et al. 2009).

Non-linear regression analysis showed that *k* for *p*-AV, which is temperature dependent, was also well described by the Arrhenius equation. The results obtained are presented in Table 5.3. The result showed that the order of E_a for *p*-AV is RCO < CPO < Blend (8.3±0.7 < 14.1±0.8 < 26.4±2 kJ/mol). The E_a results confirmed that RCO was most susceptible to secondary oxidation than CPO and blend. This is due to the presence of a high concentration of polyunsaturated fatty acids in RCO (Aladedunye and Przybylski 2012). The altered TAG composition of the blend resulted in a reduction in the level of unsaturation, intermediate IV and reduced rate of aldehyde accumulation. The reduced accumulation of aldehydes in the blend oil sample could be due to the presence of both natural and synthetic antioxidants. This antioxidant synergism likely inhibited the rapid evolution and accumulation of the aldehydes (Laguerre et al. 2007; Alireza et al. 2010b).

5.6.4 Total polar compounds (TPC) variation

The percentage TPC is the commonly authorized criterion for the appraisal of deterioration of fats and oils during frying (DGF (German Society for Fat Research) 2000). Theoretically, fresh oils are non-polar. However, the reported levels of TPC (%) in fresh oils ranged between 2.77 – 3.98 in hazelnut, corn, soybean, and olive oils (Karakaya and Şimşek 2011); 2.40 – 2.80 in sunflower oil, tigernut oil and blend (1:1) of sunflower/tigernut oil (Ali and El-Anany 2012); 4.80 – 8.00 in soybean oil, beef tallow, shortening and double fractionated palm oil (Gil et al. 2004); and 6.20 in extra virgin olive oil (Benedito et al. 2002). The initial TPC (%) values of the three oils used in this frying study were 5.83±0.40, 6.10±0.44, and 5.63±0.61 for the CPO, RCO and blend respectively (Table 5.1). These TPC values mean that the oils have not been adversely altered by auto-oxidation. The recommended range of TPC in unused oils is 0.4 – 6.4% (Lumley 1988; Ali

and El-Anany 2012). As the oil breakdown progresses, polymerization products with polarity greater than the native TAG are increasingly formed (Sebastian et al. 2014; Aniołowska and Kita 2016). The level of TPC in the three oil samples significantly ($P < 0.05$) increased linearly with frying time and temperature as shown in Figure 5.4.

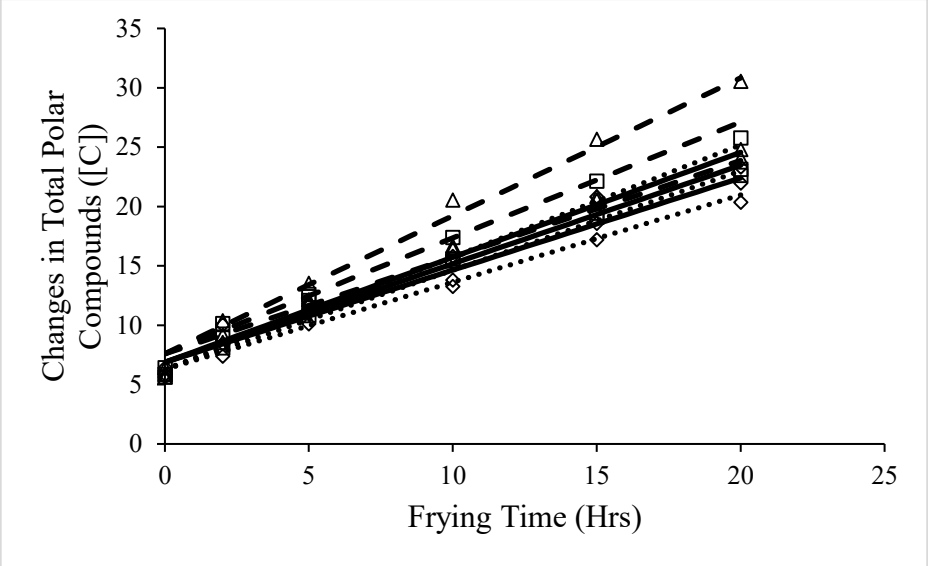


Figure 5.4: Results of total polar compounds (TPC) accumulation *vs* time. Experimental data corresponds to ◊ at 170 °C, □ at 180 °C and Δ at 190 °C. Lines represent the zero-order fit: CPO (solid line), RCO (broken line), and Blend (dotted line).

The TPC variation trend shown in Figure 5.4 agrees with literature reports (Houhoula et al. 2003; Gil et al. 2004; Karakaya and Şimşek 2011; Ali and El-Anany 2012; Petersen et al. 2013). TPC accumulation in CPO, RCO and blend were well fitted by the zero-order kinetic model. This is also shown by the values for, R^2 and P at different temperatures reported in Table 5.2. The table also shows that the Pr > F values range from 0.0130 – 0.0320 in the three oils which gave evidence of the significance ($P<0.05$) of the models. The zero-order model was also used to estimate the theoretical frying hours until TPC reached the critical 25% level in the seed oil of *Moringa stenopetala* (Lalas et al. 2006). In this study, the type of oil significantly ($P<0.05$) influenced the accumulation of TPC during frying. The highest rates of TPC accumulation were observed in the RCO. This is because among the three oils, RCO has the highest linolenic acid content whose breakdown and further polymerization is a critical factor that affects the formation of polar compounds in frying oils (Xu et al. 1999; Chen et al. 2013). RCO fatty acids had higher rate of

secondary oxidation and polymerization reactions. It was only RCO at 190 ºC and 20 h frying that exceeded the 24 % TPC discard limit endorsed by the German Society for Fat Science.

Table 5.3 shows E_a and pseudo-R^2 obtained from the non-linear regression of the Arrhenius equation. The E_a values were 30.8±4 kJ/mol, 26.8±3 kJ/mol and 45.8±7 kJ/mol for CPO, RCO and blend, respectively. The E_a for RCO was expectedly the lowest since it is the oil sample that was the most unsaturated. As seen from the IV of the three oils (Table 5.1), RCO had 45.87 % and 35.82 % greater degree of unsaturation than CPO and the blend respectively. The blend had the highest TPC E_a. Blending canola and palm oils at 1:1 ratio affected the fatty acid composition and significantly altered the triacylglycerol (TAG) composition. These can hugely affect the frying performance of the blend (Aladedunye 2015). In addition, antioxidant synergism and altered chemical composition contributed to reduce the rate of formation of oxidized TAG, oligomers and new polymeric compounds (Aniołowska and Kita 2016). Based on TPC values in a work that used synthetic antioxidants, Farhoosh (2011) reported that an oil medium that had a mix of TBHQ and α-tocopherol lasted up to 44 h of frying. In this work, frying with progressively reduced oil level in the fryer may have increased the relative formation of polar compounds especially at higher frying temperatures and time (Aladedunye and Przybylski 2009; Kalogianni et al. 2009). However, maximum reject point based on TPC was largely not exceeded and the result is similar to the report of Omar et al. (2010) that the TPC content in standard palm olein and palm-based shortening were 19.60 % and 15.3 % respectively after 40 h of frying potato chips at 180 ºC.

5.6.5 Variations in color index (CI)

The composition of the oil, the accumulation of highly conjugated oxidation products, the formation of polymers in frying oil, reactions between glucose and glycine, the oil's in-situ pigments and the leached pigments from the fried products are all involved in oil color changes during frying (Aladedunye 2015). Color index (CI) is a measure of the totality of the degradation products that led to oil darkening (Firestone 2007; Petersen et al. 2013). The initial CI values as presented in Table 5.1 showed the following values, 92.07±0.70 (CPO), 2.38±0.40 (RCO) and 42.37±0.60. There were significant ($P<0.05$) changes in the CI of CPO and blend as frying temperature and time changed. CI changes in RCO was not significant. The darkening of CPO and blend was not necessarily an indication of instant deterioration. The darkening of the CPO based oils can be due to the degradation of β-carotene, transformation of phenols and tocotrienols and an increase of UV absorbance of polymerized acylglycerols (Petersen et al. 2013). After heating

induced lightening of the oils, the CI began to increase with an increase in frying time and temperature. The increase in CI was modeled with a zero-order kinetic equation (Figure 5.5).

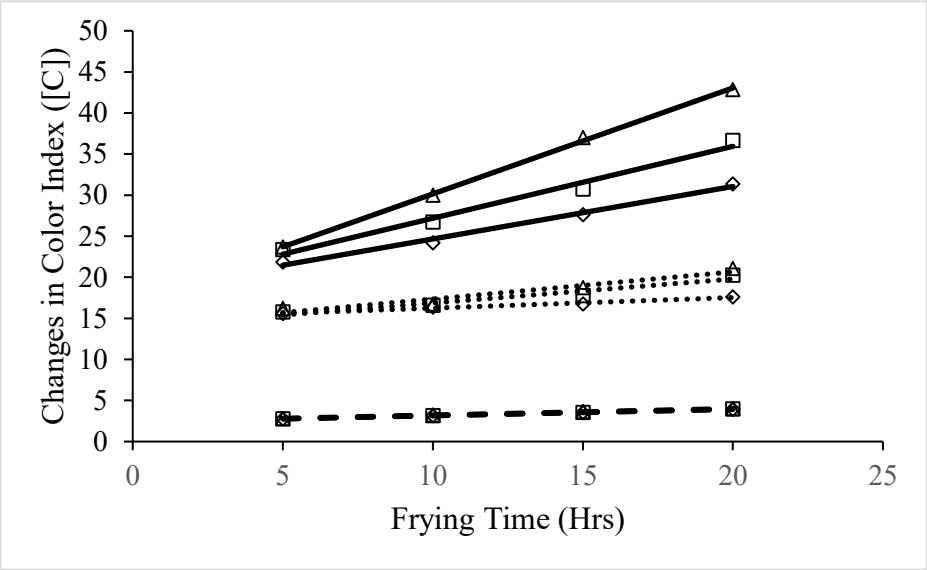


Figure 5.5: Results for color index (CI) changes *vs* time. Experimental data corresponds to ◊ at 170 °C, □ at 180 °C and Δ at 190 °C. Lines represent the zero-order fit: CPO (solid line), RCO (broken line), and Blend (dotted line).

The goodness of fit of the model was shown by the high R^2 for the three temperatures and low Pr > F as well as low *P* values (Table 2). The zero-order model was also proposed for color changes in corn and canola oils (in CIELAB color space) during frying by Wenstrup et al. (2014). The E_a and pseudo-R^2 results obtained from the non-linear regression of the Arrhenius equation is shown in Table 5.3. The high pseudo-R^2 gave evidence of the goodness of fit. The E_a (kJ/mol) values obtained were 7.0±2 (CPO), 2.5±0.4 (RCO) and 11.2±2 (blend). The E_a for RCO was most significantly low. Most publications on frying color kinetics are focused on the fried products and not the frying oil. The reported E_a are based on color parameters such as lightness, redness, yellowness and total color change ratios. The E_a from such evaluations ranges from 71.95 – 174.55 kJ/mol at temperatures between 170 – 190 ºC for different products (Hindra and Baik 2006). This result showed that it takes far lesser E_a for the colors of the frying oils to undergo changes. Though the frying temperature has more effect on the color of fried products than the oil type (Choe and Min 2007), it is also necessary to monitor the color of the frying oil as the fried products likely

pick up some of the pigments and nutrients responsible for the oil color, especially at the early stages of frying.

5.6.6 Correlation between TPC and other quality indices measured

Conventionally, TPC is used to establish oil deterioration (DGF (German Society for Fat Research) 2000). The method of assessment of TPC is laborious and time-consuming and so efforts were made to correlate the strength of the relationships between TPC and the other quality indices. The Spearman's correlation coefficient r_s values obtained are presented in Table 5.4. In the three oils, at all the temperatures, TPC showed a strong positive linear correlation with the other quality indices ($\alpha = 0.05$). The order of magnitude of correlation was *p*-AV > FFA > CI > PV. This trend agrees with the oil quality indices correlation results reported by Houhoula et al. (2003). The TPC's significant positive correlation to the other degradation parameters is expected since TPC is a measure of the totality of the non-volatile oil decomposition compounds such as thermal scission products, hydroperoxides, aldehydes, polymerized TAG, DAG, MAG, acids, alcohols, ketones and epoxides present in the frying oil (Sebastian et al. 2014). The relatively lower correlation with PV (r_s range = 0.9374 – 0.9900) and higher correlation with *p*-AV (r_s range = 0.9933 – 0.9989) could be attributed to the ease with which hydroperoxides decompose to form more stable carbonyls, alcohols, and aldehydes. The *p*-AV analysis targets secondary oxidation products that are retained in the oil and subsequently undergo polymerization reactions as frying time and temperature increased. The *p*-AV, FFA and CI could be used for the estimation of deterioration of CPO, RCO and blend (1:1 w/w) in deep-fat frying operation.

Table 5.4: Spearman's correlations between total polar compounds (TPC) and other quality indices

	Crude Palm Oil			Refined Canola Oil			Blend (1:1 w/w)		
	170°C	180°C	190°C	170°C	180°C	190°C	170°C	180°C	190°C
FFA	0.9958^{a}	0.9809^{a}	0.9966^{a}	0.9869^{b}	0.9961^{a}	0.9864^{b}	0.9952^{a}	0.9971^{a}	0.9921^{a}
PV	0.9589^{b}	0.9694^{b}	0.9718^{b}	0.9499^{b}	0.9610^{b}	0.9374^{b}	0.9900^{a}	0.9830^{b}	0.9828^{b}
p-AV	0.9974^{a}	0.9983^{a}	0.9983^{a}	0.9933^{a}	0.9943^{a}	0.9940^{a}	0.9981^{a}	0.9989^{a}	0.9985^{a}
CI	0.9962^{b}	0.9920^{b}	0.9995^{b}	0.9908^{a}	0.9938^{a}	0.9964^{a}	0.9829^{b}	0.9514^{b}	0.9610^{b}

Spearman's correlation coefficient r_s values with superscript ^{a} = significant at ($P \leq 0.0001$); superscript ^{b} = significant at ($0.0001 \leq P \leq 0.05$).

5.7 Conclusion

This study provided kinetic information on the deterioration in quality parameters of CPO, RCO and blend (CPO: RPO 1:1 w/w) during repeated deep-fat frying operations. The study showed that first-order kinetic model adequately predicted changes in FFA and PV; while zero-order kinetic model fittingly predicted changes in *p*-AV, TPC and CI. The rate of changes in the quality indices of the oils and the activation energies were well described by the Arrhenius equation. The study showed that activation energy E_a was least for PV and highest for FFA. The quality of the blend oil sample (CPO: RCO 1:1 w/w) was not just additive of the qualities of CPO and RCO. The blend had its own character and was more stable than CPO and RCO. This can be attributed to the dilution effect of blending which weakened any pro-oxidant likely present in CPO and induced lag in the oxidation of the blend during frying. The blend oil sample had altered fatty acid and TAG composition as shown by the IV of the fresh oil blend that affected the rate of deterioration. The blend oil sample also benefited from the combined effect of reduced double bond strength as saturation level increased and synergistic radical scavenging activity of both natural and synthetic antioxidants present in CPO and RCO. TPC had a significant linear positive correlation with the other oil quality indices especially *p*-AV.

CONNECTING TEXT TO CHAPTER 6

The kinetics driving the thermostability of CPO, RCO and blend (1:1 w/w) oils sample when used in repeated cycles of deep-fat frying at 170, 180 and 190 ºC was studied. The rate of deterioration and activation energy required at these frying temperatures after 20 h of frying without oil replacement was established. The blend oil sample and CPO performed better than RCO in all the quality indices studied. The outcome of this research effort has been published in a peer reviewed journal. The author and article information of chapter 5 is as follows:

Ogan I. Mba, Marie-Josée Dumont, and Michael Ngadi, (2016). Deterioration kinetics of crude palm oil, canola oil and blend during repeated deep-fat frying. Journal of the American Oil Chemists' Society, 93 (9), 1243 – 1253; doi: 10.1007/s11746-016-2872-z.

This research has so far broadened the knowledge on the practicality of utilization (Chapter 4) and the thermostability and kinetics of deterioration (Chapter 5) of CPO and blend of oil sample(s) where CPO is the major component as media for repeated deep-fat frying cycles. Since CPO is very rich in bioactive phytonutrients, it is expected that blend samples containing CPO will be enriched with the phytonutrients from the oil. However, when these nutrient rich and stable oils are used in deep-fat frying, do the fried products pick up these nutrients from the oils? What is the rate of transfer of the valuable nutrients into the fried products? Does the phytonutrient uptake result in significant product enrichment with natural bioactive compounds? These were investigated in chapter 6. The outcome of this research study has been submitted to the peer reviewed journal 'Food and Bioprocess Technology'. The format of the manuscript has been altered to be consistent with this thesis. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER 6

6. MIGRATION AND RETENTION OF VALUABLE PHYTONUTRIENTS DURING DEEP-FAT FRYING OF FRENCH FRIES IN PALM OIL AND BLEND

6.1 Abstract

French fries were produced by deep-fat frying sliced potato in crude palm oil (CPO), refined canola oil (RCO) and a blend of CPO/RCO (1:1 w/w) at170 ^{o}C for different times. The presence of some phytonutrients in the fries originating from the frying oils was investigated. The French fries produced using CPO and the blend of CPO/RCO were significantly enriched with phytonutrients, absorbed less oil and had more pronounced color changes. Over 50 % of the total carotenoids, 40 – 45 % of tocotrienols and 3 – 16 % of tocopherols originating from the oils were absorbed. The order of enrichment based on the oil used during frying was CPO/RCO blend > CPO > RCO. The biphasic first order model was valid and satisfactory as a predictor model of changes in the concentration of the phytonutrients in the French fries. For each phytonutrient, the coefficient of determination (R^2) was ≥ 0.92. Additionally, differences were recorded in the reaction rates and the associated D-values of the fast phase and the slow phase of the reactions. The moisture ratio, oil uptake and changes in color were also modeled with a first order kinetic model with R^2 above 0.98 for all the French fries' samples. The carotenoid level in French fries influenced the overall color change (ΔE) as shown by the strong positive correlation with the yellowness color parameter.

6.2 Introduction

Consumers' escalating interest in healthy eating has revived attention to the potential health benefits of bioactive phytonutrients. The careful choice of raw materials, process controls, and optimizations have led to the creation of functional ingredients and food products that serve as carriers for bioactive compounds (Boon et al. 2010). It has been reported that vegetable oils are among nature's richest source of bioactive compounds such as vitamin E, phenolic compounds, and carotenoids (Azlan et al. 2010). These phytonutrients and the fatty acid composition are responsible for the rich organoleptic values, antioxidant properties, and thermostability of vegetable oils (Choo et al. 2004).

The carotenoids and all the isomers of vitamin E, namely, α-, β-, γ-, δ-tocopherols and α-, β-, γ-, δ-tocotrienols, have demonstrated a high biological activity and are considered as natural antioxidants (Pinheiro-Sant'Ana et al. 2011). They are essential phytonutrients that must be obtained from the diet. Crude palm oil (CPO) is rich in tocotrienols, tocopherols, and carotenoids (Mba et al. 2015b). Recent studies have shown that palm-derived tocotrienols lower the plasma triacylglycerol levels and have cardiovascular benefits (Zaiden et al. 2010; Daud et al. 2013). Carotenoids contribute to the color of media and foods. They are antioxidants that can modulate other cellular antioxidants (Melendez-Martinez et al. 2013; Flakelar et al. 2015). It has also been reported that carotenoids and tocopherols act synergistically to provide enhanced antioxidant activity (Sampaio et al. 2013; Zhang et al. 2014). Beta-carotene (a carotenoid homolog), has been reported to possess pro-vitamin A activity. Vitamin A is required for epithelial maintenance, reproduction, and vision (Fernández-García et al. 2012).

A great variety of fried foods is available worldwide. Nowadays, fried foods are regularly associated with "junk food" that aggravates the risk of obesity (Li et al. 2009). Fried foods can also contain various thermo-oxidized compounds with significant health concerns (Ghidurus et al. 2013). However, the benefits offered by frying foods such as faster cooking time, peculiar flavor, crispy texture, crunchy mouthfeel, distinctive color, and satiety feeling, still make fried foods popular (Bou et al. 2012; Vauvre et al. 2014). In addition, the nutritive value of fried foods increases due to the absorption of frying oils and phytonutrients. For instance, the oil content of fresh raw potato is low (Nassar et al. 2014). Therefore, the oil present in French fries is mainly the oil absorbed during frying (Chiou et al. 2012), and the composition and phytonutrients level of the absorbed oil does not significantly differ from the composition of the oils used in the frying process (Dobarganes et al. 2000; Chiou et al. 2009; Chiou et al. 2012). However, these same useful bioactive phytonutrients are susceptible to thermal degradation. Thus, there is the need to monitor the extent of migration of the phytonutrients in fried foods, their retention, and stability. The changes in the phytonutrients levels should be quantified based on the temperature dependent rate constants (Ling et al. 2014). Generally, the changes in food quality are described by zero-, first- or second-order reaction kinetics. Other kinetic models such as the biphasic first-order and the fractional conversion models have been used to explain the thermal degradation trend of phytonutrients (Vieira et al. 2000; Hiwilepo-van Hal et al. 2012; Ling et al. 2014). The objectives of this study are to monitor the enrichment of French fries that can provide additional nutritional

benefits besides energy and macronutrients, and to determine the presence and level of the phytonutrients that migrated into the French fries after deep-fat frying in CPO, RCO, and CPO/RCO blend. The application of the biphasic model to predict the changes in the concentration of the phytonutrients in the French fries' samples was also evaluated. The findings from this study are important in promoting the use of CPO in deep-fat frying and highlight the possibility of nutritional enrichment through careful selection of the frying oil. Increasing the phytonutrients level in snack foods such as French fries will add up to increasing the phytonutrients in the diet. It will also promote the shelf stability of par-fried and frozen fries on supermarket shelves as the absorbed phytonutrients are also effective antioxidants.

6.3 Materials and Methods

6.3.1 Materials and Reagents

Fresh crude palm oil (CPO) was imported from Nigeria. Commercially refined canola oil (RCO) (labeled as containing, butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and dimethylpolysiloxane (DMPS)) was supplied by Titan Oils Inc. Montréal Canada. A blend of the two oils, CPO: RCO 1:1 w/w (blend) was prepared in the lab at room temperature. Russet potatoes (*Solanum tuberosum L.*) were purchased from a local grocery shop. HPLC grade n-hexane, methanol, ethyl acetate, acetic acid and ascorbic acid were purchased from Fisher Scientific, Fair Lawn, New Jersey. Stock standard solutions of α-, β-, γ-, δ-tocopherols, were obtained from Sigma-Aldrich, St Louis, MO. The tocol calibration kit, internal standard and standard α-, β-, γ-, δ-tocotrienols samples were gifts from ExcelVite Sdn. Bhd. Perak, Malaysia.

6.3.2 Frying Protocol

Each of the oil samples (CPO, RCO, and blend) was preheated at 170 ºC for 2 h, in a temperature controlled laboratory deep-fryer (D24527DZ, Délonghi Inc. USA) of 5 L capacity. Batonnet cuts (≈ 10 cm long and 1.6 cm thick) of peeled potatoes were washed to remove surface starch and then quickly dried with a light stream of warm air. About 100 g of potato slices were deep-fat fried for 1, 3, 5, 7, 9 and 11 min. K-type thermocouple interfaced with 'Hotmux' data logger was used to monitor the oil temperature during the frying process. At the end of each frying time, adhering surface oil on the French fries was quickly drained and wiped out using paper towels. The fries were allowed to cool at room temperature. A set of un-fried potato cuts was used as the reference sample and termed 0 min fries. The weight of the French fries' samples was also taken before

packing them in non-transparent self-sealing polyethylene pouches. The un-fried and fried French fries' samples were kept frozen at -80 ºC until freeze-drying.

6.3.3 Samples Preparation

The lyophilized French fries' samples were dried in a freeze dryer (ThermoSavant VLP200; Savant Instruments Inc. NY). Freeze-drying was chosen to limit the degradation and loss of the phytonutrients to that which may have occurred during frying. After the freeze-drying step, the moisture loss was calculated. The oil extraction method described by AOAC (1990) and Manirakiza et al. (2001) was followed for extracting oil from the French fries' samples. Briefly, the samples were ground using a pestle and a mortar. About 5.0 g of each ground sample in thimbles were attached to an auto-extraction unit (Velp Scientifica, SER 148; Usmate, Italy) used for the Soxhlet extraction. The extraction solvent was petroleum ether containing 0.05% ascorbic acid to prevent oxidation during the extraction cycle. The total run time for each sample was 75 min. Any residual solvent in the extracted oil was allowed to completely evaporate by allowing the flasks containing the oil samples to stand in a vacuum hood for 30 min. The oil in the flask was weighed and siphoned into amber colored vials. The oil extraction was done in triplicates and the oil uptake by the French fries' samples at different times was calculated from this step. All the oil samples were subjected to phytonutrient content analysis.

6.3.4 Analysis of vitamin E isomers

One percent stock solutions of α-, β-, γ-, δ-tocopherol, and α-, β-, γ-, δ-tocotrienol standards were prepared using n-hexane. The internal standard was also diluted to obtain 1% stock solution using n-hexane. All the stock standard solutions were kept in amber colored bottles and stored at -20 ºC. Working standard solutions for each isomer were prepared by diluting the stock standard solutions in n-hexane containing 1% isopropanol. The concentrations used for each isomer are shown in Table 6.1. After this step, 10 µL of each concentration was injected in triplicate. The calibration curves were obtained through linear correlation between peak areas and concentrations of the injected external standards. The linear regression equation obtained for each isomer was the basis for the quantification of the bioactive phytonutrients in the French fries and to calculate the limits of detection (LOD) and the limits of quantification (LOQ). The weighted linear regressions were performed using SAS 9.4.

Table 6.1: Different concentrations (µg/mL) of vitamin E homologs used for the calibration curve

Sample #	α-TP	β-TP	γ-TP	δ-TP	α-T3	β-T3	γ-T3	δ-T3
1	0.7676	0.0833	3.8322	1.2675	0.5825	0.1144	0.8735	0.3265
2	1.5353	0.1666	7.6644	2.5350	1.1650	0.2287	1.7470	0.6529
3	2.3029	0.2499	11.4966	3.8024	1.7475	0.3430	2.6206	0.9793
4	3.0705	0.3332	15.3287	5.0691	2.3299	0.4574	3.4941	1.3058
5	3.8381	0.4165	19.1609	6.3374	2.9125	0.5717	4.3676	1.6322
6	4.6058	0.4999	22.9931	7.6049	3.4950	0.6861	5.2411	1.9587

α-TP = Alpha-tocopherol, β-TP = Beta-tocopherol, γ-TP = Gamma-tocopherol, δ-TP = Delta-tocopherol, α-T3 = Alpha-tocotrienol, β-T3 = Beta-tocotrienol, γ-T3 = Gamma-tocotrienol, and δ-T3 = Delta-tocotrienol.

The method described by Chen and Bergman (2005) was used to extract the vitamin E isomers from the fresh oil samples and the oil samples extracted from the French fries. In brief, 7 mL of methanol containing 0.05% ascorbic acid was added to 0.1 g of the oil samples in a centrifuge tube. The tubes with samples immersed in the solvent were continuously shaken in a horizontal shaker at 200 oscillations/min for 30 min. This was followed by centrifugation at 3500 rpm for 8 min. The solvent layers were collected in another set of clean tubes. Another 7 mL of the extraction solvent was added to the residual oil samples in the first set of tubes. The shaking and centrifugation steps were repeated. The solvent layers were collected and combined with the first set of extracts. The tubes were vortexed for 30 sec and the methanol was evaporated using a stream of nitrogen. The resultant dry matter was dissolved in 2 mL of the mobile phase, and filtered through 0.22 µm PTFE micro filter into amber colored HPLC vials. All the steps were carried out in a restrained light environment.

Normal phase HPLC protocol described by Andersson et al. (2012) and Ahsan et al. (2015) was used for the analysis of the vitamin E isomers using a Varian Prostar HPLC unit equipped with a photodiode array detector (PDAD), an autosampler (Varian, model 410), a Luna® 5 µm silica (2) LC column (100 Å × 250 mm × 4.6 mm i.d., Phenomenex, Torrance CA, USA) and a guard column (10 × 4.6 mm, Phenomenex). The wavelength used for the detection of the vitamin E isomers was 295 nm. The mobile phase was n-hexane: ethyl acetate: acetic acid (97.3: 1.8: 0.9). An isocratic

flow rate of 1.5 mL/min at an ambient temperature of 23 ºC was used. The vitamin E isomers in the fresh and French fries' oil samples were identified by comparing the retention times (RT) and peak spectra with those of the external standards. The standards calibration curves were used for the quantification.

6.3.5 Spectrophotometric analysis of Carotenoids

The total carotenoids in the un-fried potato cuts and French fries were determined according to the procedure described by Gao et al. (2007) with slight modifications. A spectrophotometer (Unicam UV1 – 091309, Thermo Spectronic, Rochester, NY) was used. Briefly, 9 mL of n-hexane was added to 0.3 g of ground French fries' samples in centrifugation tubes. The samples were soaked in the solvent at ambient temperature for 6 h inside a darkened shaker (Series 25 Incubator Shaker, New Brunswick Scientific, NJ) oscillating at 100 rpm. After centrifuging at 3500 rpm for 8.5 min, the supernatants were collected and their absorbance was measured at 445 nm. Fresh oil samples (1.0 g) were also treated the same way and their absorbance was also measured. The absorbance of n-hexane served as blank value and was deducted from the absorbance value of the samples. Total carotenoid values were calculated using equation (6.1) and further converted to parts per million (ppm).

$$X(mg/100g) = \frac{A_s * Y * 10^6}{A^{\%}_{1cm} * W_s * 1000} \tag{6.1}$$

(X = total carotenoid content; A_s = absorbance value of sample at 445 nm; Y = volume of hexane used in extraction (mL); $A^{\%}_{1cm}$ = average absorption coefficient of carotenoid molecule (= 2500); and W_s = mass of sample (g)).

6.3.6 Measurement of the French fries' colors

The tridimensional CIELAB chromatic ordinates L* a* b* of the absorption spectrum described in a previous work (Mba et al. 2015a) was used to determine the color values. The spectrophotometer used was a Konica Minolta spectrophotometer (model CM-3500d, Osaka, Japan) in the reflectance mode. In this classification, L* is the lightness on a 0 – 100 scale from black to white; a* is the redness or the greenness, and b* is the yellowness or the blueness. The total color change (ΔE) was calculated using equation (6.2).

$$\Delta E = \sqrt{[(L_0 - L_t)^2 + (a_0 - a_t)^2 + (b_0 - b_t)^2} \tag{6.2}$$

(L_0, a_0, and b_0 are the respective color values at frying time t = 0; L_t. a_t, and b_t are respective color values at any other frying time t).

6.3.7 Kinetic Analysis

The mechanism of phytonutrient migration from the frying oil into the French fries was separated into two, namely, the fast phase and the slow/decline phase as shown in equation (6.3). On the other hand, the pseudo-first-order model shown in equations (6.4) and (6.5) were used to estimate the moisture loss ratio (Pedreschi et al. 2005), oil uptake (Krokida et al. 2001a) and the changes in color properties of the French fries' samples. The phytonutrients were expected to continue to migrate into the fries as long as they remain in the frying oil. Therefore, the D-value which is the heating time (min) required to achieve 90 % or one log change in food quality on a semi-log scale at a constant temperature, was calculated using equation (6.6) (Ling et al. 2014).

$$P = (P_f * \exp^{-kft} + P_s * \exp^{-k_s t}) \tag{6.3}$$

$$MR = \frac{M_t}{M_0} = A * \exp^{-kt} + C \tag{6.4}$$

$$X = x_{eq} * (1 - \exp^{-kt}) \tag{6.5}$$

$$D = \frac{2.303}{k} \tag{6.6}$$

Where P is the value of any of the phytonutrients (ppm), P_f and P_s are quality attributes at the beginning of the fast and slow phases respectively, k_f and k_s are the corresponding first-order rate constants (min^{-1}), t is the frying time (min.), M_t is the moisture content (g/g d.b.) at time t and M_0 is the initial moisture content (g/g d.b.), k is the rate constant (min^{-1}.), A and C are constants, X represents oil uptake (g/g d.b.) and overall color change (ΔE), x_{eq} represents the equilibrium oil content and equilibrium color change per oil treatment. The coefficient of determination R^2 and root mean square error (RMSE) were the basis of the model acceptability.

6.3.8 Statistical Analysis

The differences in the absorption of the bioactive phytonutrients by the French fries in CPO, RCO, and blend, as well as the physicochemical characteristics evaluated, were statistically analyzed using ANOVA. The means were compared using Duncan's multiple range test (SAS version 9.4 software). The correlation between the total carotenoids absorbed and the color variables were also

determined. The kinetic model parameters of equations (6.3), (6.4) and (6.5) were estimated by non-linear regression using MATLAB R2015b software.

6.4 Results and Discussion

6.4.1 Moisture Loss

The moisture ratio trend observed in the French fries' samples is shown in Figure 6.1. The moisture loss in the fries made with the three oil samples followed the classical drying curve which also applies to deep-fat frying operations (Pedreschi et al. 2005).

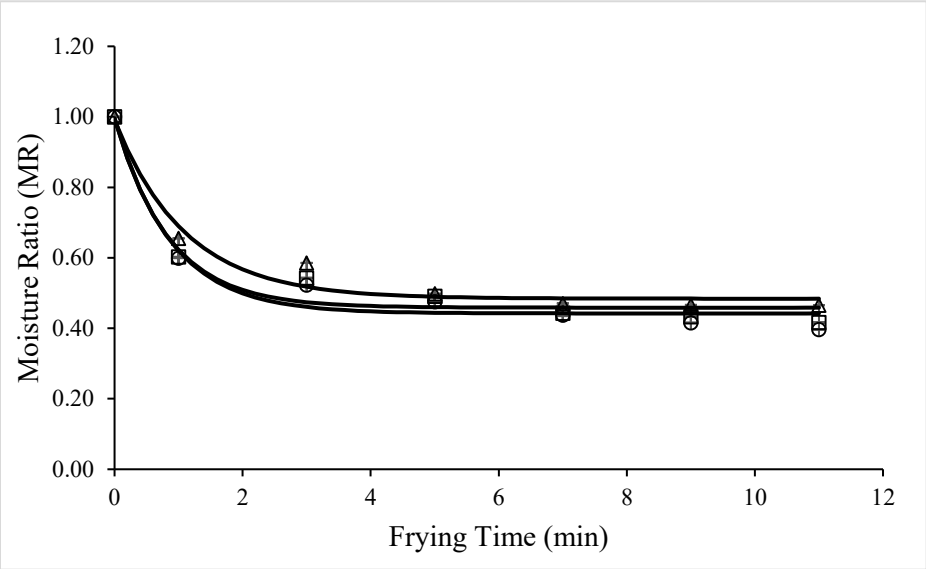


Figure 6.1: Moisture ratio in French fries produced using crude palm oil (CPO), refined canola oil (RCO) and blend (BL). ○ = CPOFF, Δ = RCOFF, □ = BLFF, and line = predicted values.

The initial moisture content of the fresh un-fried potato was 78.17%. The type of oil used in the frying significantly ($P<0.05$) influenced the moisture loss rate of the French fries' samples. At the maximum frying time, the mean moisture loss was 46.91% for CPO fried French fries (CPOFF), 42.95% for RCO fried French fries (RCOFF), and 45.35% for CPO/RCO (1:1 w/w) blend fried French fries (BLFF). The differences in the moisture loss values in the French fries' samples could be due to variations in the heat flux and heat transfer coefficients in heated oils (Orthoefer and List 2007). In the three oil samples, the moisture loss rate was very rapid within the first minute of frying and fell below 5% after 5 min of frying. As shown in Table 6.2, the apparent moisture loss rates (min^{-1}) were 1.185, 1.135 and 0.903 for CPOFF, BLFF, and RCOFF, respectively. This confirmed that moisture content of the CPOFF samples was lower compared to BLFF and RCOFF.

Table 6.2: Estimation parameters of the models used for some properties of French fries produced using crude palm oil, refined canola oil, and blend

Estimated parameter	Sample	Equilibrium value	k (min^{-1})	R^2	Adj. R^2	RMSE
Moisture Ratio (MR)	CPOFF	-	1.1850	0.9696	0.9544	0.044
	BLFF	-	1.1350	0.9646	0.9469	0.047
	RCOFF	-	0.9028	0.9698	0.9547	0.041
Oil Uptake (OU)	CPOFF	0.1203	0.3324	0.9911	0.9894	0.006
	BLFF	0.1283	0.3748	0.9975	0.9970	0.003
	RCOFF	0.1459	0.3984	0.9941	0.9930	0.005
Total Color Change (ΔE)	CPOFF	59.4100	5.0410	0.9866	0.9839	2.863
	BLFF	55.2200	2.5280	0.9986	0.9983	0.852
	RCOFF	70.1600	0.1140	0.9880	0.9856	2.271

k = Apparent reaction rate constant; R^2 = Coefficient of determination; Adj. R^2 = Adjusted coefficient of determination; RMSE = Root mean square error; CPOFF = Crude palm oil French fries; BLFF = Blend French fries; RCOFF = Refined canola French fries.

It is possible that during deep-fat frying, CPO retained more heat than either RCO or the blend. The retained energy likely provided additional driving force, hence the higher moisture loss in CPOFF samples. As expected, the frying time had a more significant effect on moisture loss than frying oils. There was a progressive decline in the moisture content of the French fries' samples as the frying time increased. This trend agrees with the reported moisture loss trends during deep fat frying (Pedreschi et al. 2005). Figure 6.1 also shows that the fit of the moisture ratio with the time data using equation (6.4) was adequate for the experimental data. As seen in Table 6.2, the adjusted R^2 range was 0.9469 – 0.9646 while the RMSE range was 0.041 – 0.047. The values obtained for the parameters of the model are like those reported during frying of potato products at ≤ 180 ^oC (Costa and Oliveira 1999; Huang and Yi-Chung 2014).

6.4.2 Oil Absorption

The quantity of oil absorbed during frying has been reported to be proportional to the amount of moisture lost (Gamble et al. 1987). In general, low moisture content correlated to high oil absorption during frying (Moyano and Pedreschi 2006). However, Bouchon (2009) reported that

oil uptake and water removal during deep-fat frying are not synchronous phenomena. The plots of oil uptake *vs* moisture loss and oil uptake *vs* frying time in the French fries' samples are shown in Figure 6.2.

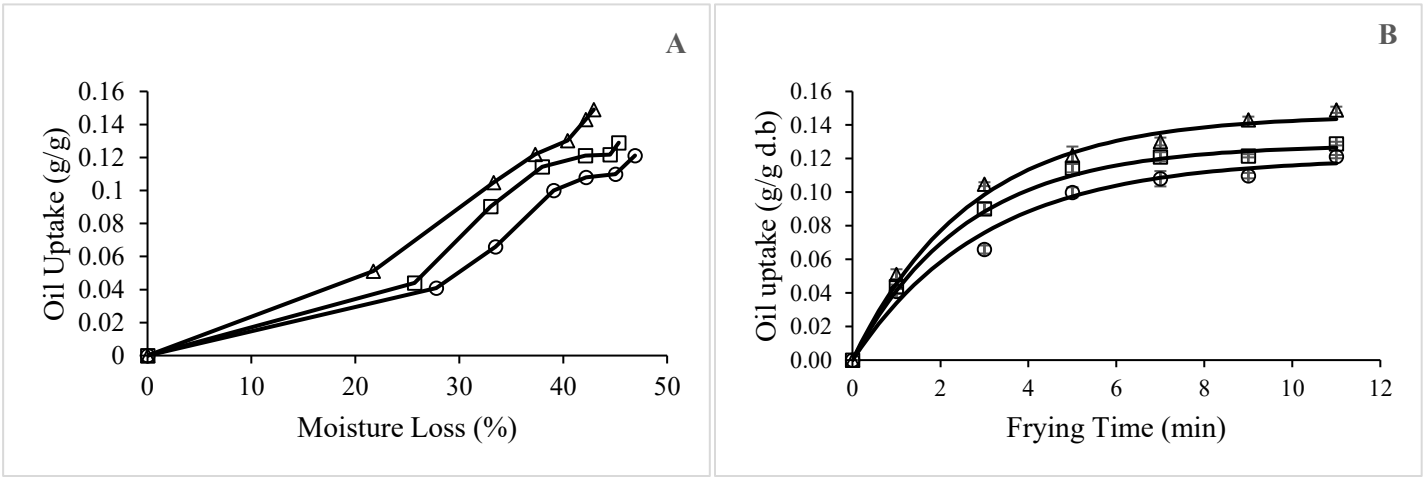


Figure 6.2: Effect of oil type and frying time on oil uptake in French fries produced using crude palm oil (CPO), refined canola oil (RCO), and blend (BL). ○ = CPOFF, Δ = RCOFF, □ = BLFF, line = predicted values, and connects experimental data corresponding to the same fries' sample

The type of oil used had a significant ($P<0.05$) effect on the amount of oil absorbed and the rate of the absorption (Figure 6.2a). The maximum oil uptake (g/g d.b) for the French fries produced using CPO, RCO, and CPO/RCO blend was 0.12±0.001, 0.15±0.002 and 0.13±0.002, respectively. The CPOFF samples which had the least moisture content also had the least rate of oil uptake. This can be attributed to the higher saturated nature of the CPO and possibly the solidification of the stearin portion of CPO upon cooling which made the oil less likely to penetrate deeply into the crusted pores of the French fries (Ziaiifar et al. 2008). A similar result was reported by Kita and Lisińska (2005) for French fries fried above 150 ^{o}C in different oils. The authors reported that fat absorption was higher when the amount of unsaturated fatty acids increases in a frying oil. Other authors have also reported that convective heat transfer coefficient and heat flux are higher in saturated than unsaturated oils (Hubbard and Farkas 2000; Orthoefer and List 2007). The higher energy density in saturated CPO can cause more rapid gelatinization of the potato starch, thus reducing the porosity of the fries and oil intake into the CPOFF samples (Aguilera et al. 2001; Durán et al. 2007; Yusop et al. 2008). Ong and Goh (2002) and Mba et al. (2015a) had also reported

a significant reduction in oil absorption when palm oil is the medium for deep-fat frying. Generally, consumers prefer low-fat content fried foods (Pedreschi 2012).

There was also a significant ($P<0.05$) increase in oil absorption as frying progressed (Figure 6.2b). The peak oil uptake (0.15±0.002 g/g d.b) observed is similar to the values reported in the literature for French fries (Odenigbo et al. 2012). The degree of oil deterioration also affects oil uptake (Kita et al. 2005), the faster rate of degradation of the polyunsaturated RCO might be responsible for the highest oil uptake recorded in RCOFF samples. The French fries' oil uptake rate (min^{-1}) was 0.332 for CPO, 0.398 for RCO and 0.375 for the blended oils (Table 6.2). These values confirmed that RCOFF had the highest fat content. The values also showed that the oil uptake rate was 2 – 4 times lower than the moisture loss rate. Figure 6.2b also shows that the fit of oil uptake with time data using model equation (6.5) was adequate for the experimental data. As shown in Table 6.2, CPOFF had the smallest equilibrium value, followed by BLFF and RCOFF. The high adjusted R^2 values (0.99) and low RMSE values for the three samples gave evidence of the robustness of the model. Odenigbo et al. (2012), Moyano and Pedreschi (2006) and Krokida et al. (2001b) used a similar model for predicting oil uptake during deep-fat frying.

6.4.3 Vitamin E Isomers Absorption

The initial concentration (ppm) of each phytonutrient is shown in Figure 6.3. The phytonutrients were present in VPO and the oil blend (VPO: RCO) in high amounts. Tocotrienols were not found in RCO but γ- and α-tocopherol were detected. The distribution, concentration, and range presented in this study are in line with regulatory and literature reports (Codex Alimentarius Commission (CAC) 1999; Flakelar et al. 2015). The un-fried potato had very small amount of α-tocopherol (5.06±0.00 ppm), and γ-tocopherol (2.17±0.21 ppm). These levels were above the quantities reported for some commercial un-fried potato varieties (Chun et al. 2006), but within the range reported for genetically improved varieties (Ramadan and Elsanhoty 2012).

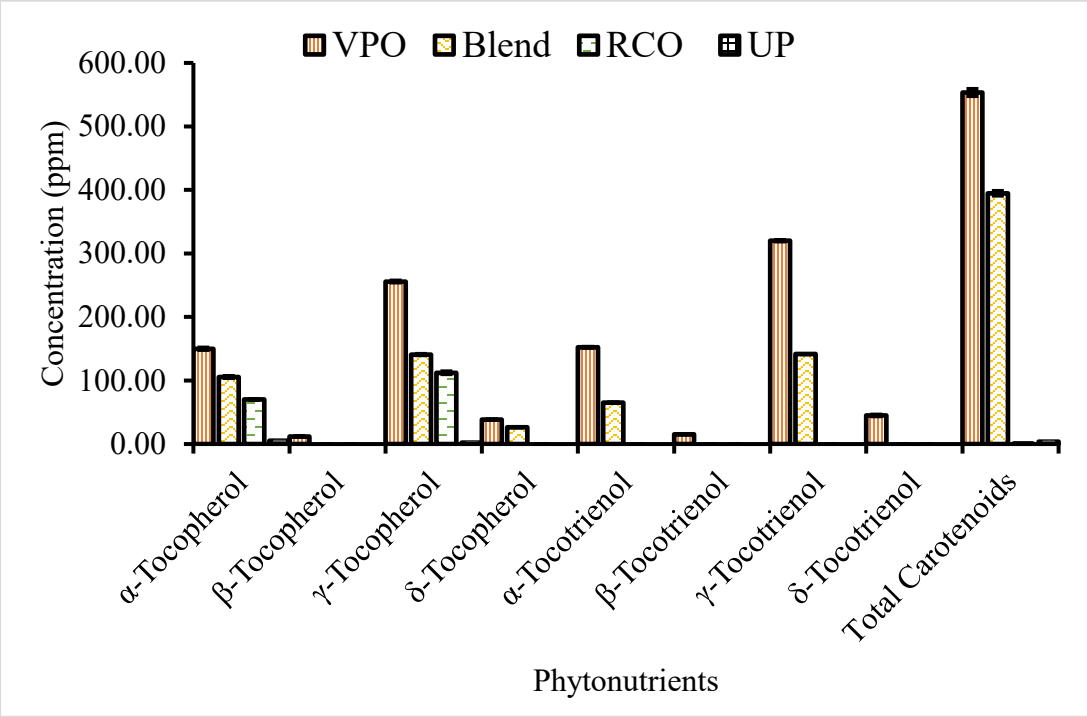


Figure 6.3: Phytonutrients concentration in raw samples.

VPO = virgin palm oil, RCO = refined canola oil, Blend = VPO/RCO (1:1 w/w), and UP = un-fried potato.

Deep-fat frying resulted in a significant ($P<0.05$) enrichment of the French fries' samples. The mean percentage migration of the vitamin E isomers is presented in Table 6.3. These were calculated from the amount of the phytonutrients originally present in the oils and French fries' samples before and after deep-fat frying. The initial proportions of the endogenous phytonutrients in the oils influenced the type of phytonutrient found in the French fries. Thus, both the tocopherol and tocotrienol homologs in CPO were found in CPOFF and BLFF; while α- and γ-tocopherol homologs of RCO were present in RCOFF. Table 6.3 also shows that considering the ratio of initial amounts of phytonutrients present in the fresh oil samples to the amount taken up by the fries, the BLFF samples absorbed more vitamers from the oil blend than either CPOFF or RCOFF did from CPO and RCO, respectively. This could also be due to the enhanced stability of the vitamers in the oil blend. This observation represented another useful advantage of blending CPO and RCO.

Table 6.3: Mean percentage (%) migration* of phytonutrients into French fries deep-fat fried in crude palm oil, refined canola oil, and blend

Phytonutrient	CPOFF	BLFF	RCOFF
α-Tocopherol	3.18	3.67	2.87
β-Tocopherol	-	-	-
γ-Tocopherol	14.86	15.57	14.58
δ-Tocopherol	16.22	-	-
α-Tocotrienol	49.08	55.85	-
β-Tocotrienol	-	-	-
γ-Tocotrienol	41.60	50.90	-
δ-Tocotrienol	16.84	-	-
Total Carotenoids	57.56	54.84	16.53

CPOFF = Crude palm oil French fries; BLFF = Blend (CPO: RCO 1:1 w/w) French fries; RCOFF = Refined canola French fries; - = Not detected. * Calculated from the amount of phytonutrient present in the French fries after deep-fat frying less initial value in the raw potato, divided by the amount in fresh oil samples and multiplied by 100.

The variation in the concentration of the vitamin E isomers for the French fries' samples as a function of time at 170 ^{o}C is shown in Figure 6.4. The type of oil used and the frying time were all highly significant ($P<0.05$) for the amount of isomers absorbed and the rate of absorption. The tocopherols uptake was rapid and showed a marked turning point after 5 minutes of frying when concentration began to steadily decline (Figures 4 A – C). This could be related to the depletion and degradation of the tocopherols in the native oil because of thermal processing. The maximum percentage absorption of the tocopherols by the French fries' samples was 3.67% for α-tocopherol, 15.57% for γ-tocopherol and 16.22% for δ-tocopherol. The α-tocopherol had the lowest migration into the French fries. This can be due to a rapid loss of the α-tocopherol possibly due to initial higher anti-oxidant activity (Barrera-Arellano et al. 2002; Schrøder et al. 2006; Pinheiro-Sant'Ana et al. 2011). The initial migration of the tocotrienols into the French fries was even more rapid. However, after 3 minutes of frying, the tocotrienol absorption became stabilized (Figures 4 D – F). The highest percentage migrations were 50.90% for α-tocotrienol, 55.85% for γ-tocotrienol and 16.84% for δ-tocotrienol.

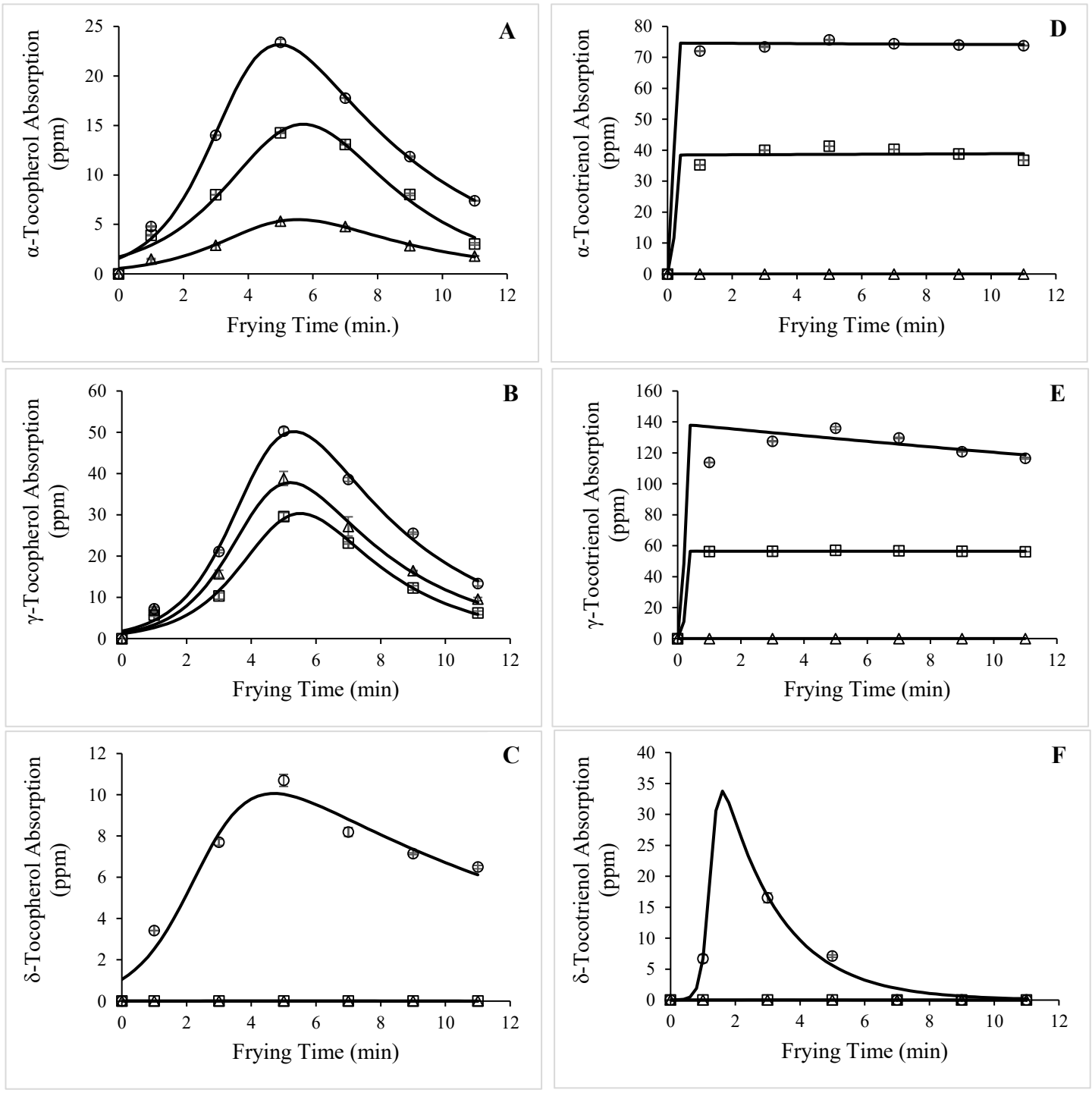


Figure 6.4: Concentration of vitamin E isomers in French fries produced using crude palm oil (CPO), refined canola oil (RCO) and blend (BL). ○ = CPOFF; Δ = RCOFF; □ = BLFF; line = predicted values.

Overall, the tocotrienols migrated more into the French fries than the tocopherols. These results agreed with the report of Pacifico et al. (2012) that unsaturation in the side chain attached to the chromanol rings of tocotrienols has a positive influence on their solubility in membranes, which also improves their antioxidant capacity. Earlier studies by Packer et al. (2001) showed that tocotrienols penetrate rapidly through the skin and efficiently combats oxidative stress. The initial concentrations of β-tocopherol (11.82±0.25 ppm) and β-tocotrienol (15.35±0.18 ppm) in the CPO were very low. This could explain why they were not detected in the French fries' samples. The δ-tocotrienol with an initial concentration of 45.01 ± 1.36 ppm in the CPO could not be quantified after 5 minutes of frying. Pinheiro-Sant'Ana et al. (2011) had reported that detection and quantification difficulties arise when a homolog is in a trace amount or present in very low concentration.

The concentration of vitamin E isomers in CPOFF, BLFF and RCOFF followed a trend that was adequately modeled by the biphasic apparent first order reaction (equation (6.3)). The biphasic first order path has different rate constants k_f and k_s occurring concurrently, one at a faster rate than the other. The rate constants calculated from the regression of equation (6.3) for all the French fries' samples are shown in Table 6.4. The results largely confirmed the first order nature of the two phases as indicated by the high adjusted R^2 values (0.9159 – 0.9996) and low RMSE values (0.40 – 3.67). The D-values (Table 6.4) associated with the slow phase (6.22 – 24.74 min.) were 2 – 5 times greater than the D-value range of the fast phase in the tocopherols. Similarly, the range of D-values for the slow phase of the tocotrienols (161.05 – 11515.00) was $3.2 \times 10^3 – 4.6 \times 10^4$ times greater than the D-values of the fast phase. The kinetics data also showed that the tocotrienols' absorption was more sustained over the frying period than the tocopherols. The values of the reaction rate constant of the fast phase (k_f) are also higher than the rate constant of the slow phase (k_s). This provided a strong support for the proposed biphasic mode of absorption of vitamin E isomers. The k values also showed that the absorption is $2.0 – 5.5 \times 10^4$ times faster in the fast phase than the slow phase. While Simonne and Eitenmiller (1998) reported that the depletion of vitamin E homologs did not follow first-order kinetics, no model was proposed. However, the biphasic first order kinetics has been applied to model the changes in the concentration of vitamin C in strawberries and raspberries (Verbeyst et al. 2012); and marula, mango and guava (Hiwilepo-van Hal et al. 2012) during different thermal treatments.

Table 6.4: Estimation parameters and D-values of the phytonutrients absorbed by French fries produced using crude palm oil, refined canola oil and blend

Phytonutrient	Sample	Fast Phase			Slow Phase			R^2	Adj. R^2	RMSE
		P_f	k_f (min^{-1})	D (min)	P_s	k_s (min^{-1})	D (min)			
α-Tocopherol	CPOFF	0.6281	0.8541	2.70	0.011	-0.2279	6.22	0.9892	0.9784	1.173
	RCOFF	1.7850	0.6250	3.69	0.027	-0.2786	6.35	0.9723	0.9446	0.439
	BLFF	0.5786	0.5407	4.26	0.005	-0.3629	8.27	0.9706	0.9412	1.127
γ-Tocopherol	CPOFF	0.5457	0.8959	2.57	0.0036	-0.2718	8.47	0.9909	0.9817	2.385
	RCOFF	0.7199	0.9001	2.56	0.0041	-0.3025	7.61	0.9803	0.9605	2.596
	BLFF	0.8272	0.7899	2.92	0.0029	-0.3704	10.11	0.9795	0.9591	2.108
δ-Tocopherol	CPOFF	0.8946	0.9924	2.32	0.0587	-0.0931	24.74	0.9580	0.9159	1.016
	RCOFF	-	-	-	-	-	-	-	-	-
	BLFF	-	-	-	-	-	-	-	-	-
α-Tocotrienol	CPOFF	648.80	54.81	0.16	0.0177	-0.0002	11515	0.9998	0.9996	0.400
	RCOFF	-	-	-	-	-	-	-	-	-
	BLFF	198.90	40.56	0.06	0.026	-0.0010	2303	0.9798	0.9696	2.971
γ-Tocotrienol	CPOFF	351.30	42.36	0.05	0.0134	-0.0006	3838	0.9994	0.9988	0.985
	RCOFF	-	-	-	-	-	-	-	-	-
	BLFF	15.53	35.26	0.25	0.0072	-0.0143	161.1	0.9929	0.9858	3.665
δ-Tocotrienol	CPOFF	135.60	6.963	0.33	0.0115	-0.5483	4.20	0.9737	0.9474	1.442
	RCOFF	-	-	-	-	-	-	-	-	-
	BLFF	-	-	-	-	-	-	-	-	-
Total carotenoids	CPOFF	66.45	12.16	0.19	0.0023	-0.0266	86.58	0.9932	0.9863	1.677
	RCOFF	147.60	0.4499	5.12	0.0352	-0.8578	2.69	0.8857	0.7714	0.012
	BLFF	135.20	14.10	0.16	0.0039	2.6E-5	0.01	0.9994	0.9989	3.203

P_f and P_s = Phytonutrient attribute during the fast and slow phases respectively; k_f and k_s = Apparent rate constant for the fast and slow phases respectively; D = Decimal reduction time; R^2 = Coefficient of determination; Adj. R^2 = Adjusted coefficient of determination; RMSE = Root mean square error; CPOFF = Crude palm oil French fries; BLFF = Blend (CPO: RCO 1:1 w/w) French fries; RCOFF = Refined canola French fries; - = not detected

6.4.4 Carotenoids Absorption

The initial total carotenoid concentrations (ppm) were CPO (553.44±5.62), blend (394.01±3.66), un-fried potato (3.72±0.22), and RCO (0.08±0.02) (Figure 6.3). These values are within the range of values reported in the literature for palm oil (Sampaio et al. 2013), un-fried potatoes (Konschuh et al. 2005) and refined canola oil (Flakelar et al. 2015). As shown in Table 6.3, the mean percentages of absorbance were 57.56%, 54.84% and 16.53% in CPOFF, BLFF, and RCOFF respectively. As the raw potato did not contain any appreciable quantity of carotenoids, there was over 50% enrichment of the French fries samples after frying in CPO and the blend containing CPO. Expectedly, the initial concentration of carotenoids in the frying oil affected the availability and the amount of nutrients that can be released and absorbed by the fried samples. With respect to the changes in concentration as frying time increased, the biphasic model also fitted very well with the experimental results (Figure 6.5).

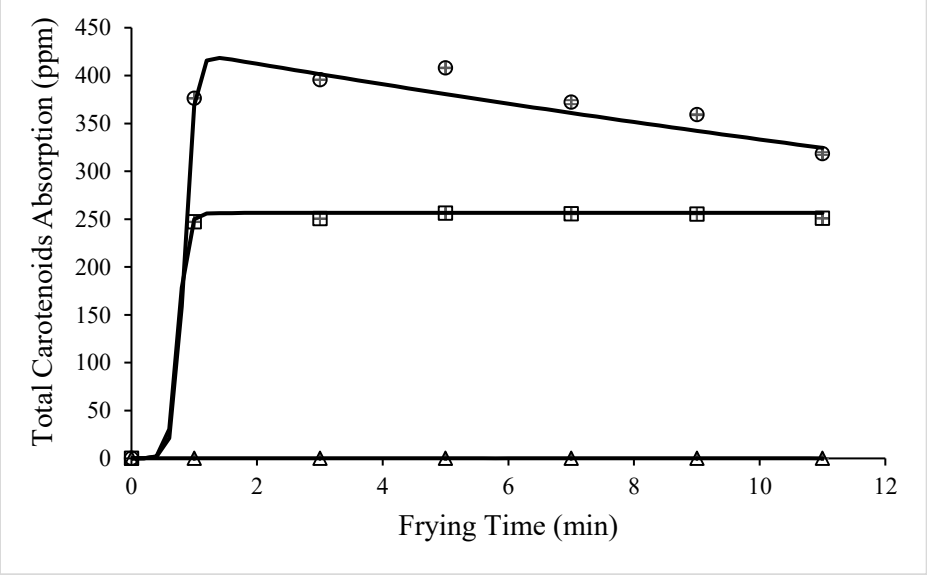


Figure 6.5: Total carotenoids concentration in French fries produced using crude palm oil (CPO), refined canola oil (RCO), and blend (BL). ○ = CPOFF; Δ = RCOFF; □ = BLFF; line = predicted values.

The type of oil used and the first few minutes of frying had a significant ($P<0.05$) effect on the migration of the carotenoids into the French fries' samples. The model parameters obtained showed that the reaction rate constant of the fast phase (k_f) was 0.52 – 5.42 × 10^5 times higher than the rate constant of the slow phase (k_s) (Table 6.4). The D-values showed that the slow phase of carotenoids absorption was 27.22 – 32.25 times greater than in the fast phase. Greater evidence of absorption related to continuous availability in the native frying oil was shown by BLFF, even though the blending resulted in an initial dilution of the total carotenoids in CPO. This trend is in line with the reported behavior of β-carotene the dominant carotenoid in palm oil. Schrøder et al. (2006) reported that in a model system containing a mixture of 100 ppm β-carotene and 1000 ppm of vitamin E homologs (α-tocopherol, α-tocotrienol, and γ-tocotrienol), the antioxidants interacted synergistically to improve the stability of each other. However, the synergy decreased for all combinations when β-carotene levels increased to 500 ppm and above. Some authors have used the apparent first order kinetic model to describe the thermal stability of carotenoids in oil (Qiu et al. 2012). This study successfully applied the biphasic first order model to describe the migration and changes in the concentration of total carotenoids in French fries during deep-fat frying. The R^2 values for CPOFF and BLFF were 0.9932 and 0.9994 respectively. The R^2 for RCOFF was 0.8857 which was not a reflection of the model misfit but rather that RCO is not a significant source of carotenoids (Franke et al. 2010).

6.4.5 Color Properties of the French fries

The color of French fries begins to develop when a sufficient amount of drying has occurred as frying progressed. The Maillard reaction between the reducing sugars and amino acids or proteins at the surface of the cut potato slices during frying also play some role in the color of fries. The changes in the L* a* b* properties are shown in Figures 6.6 A – C. There was a significant difference ($P<0.05$) in the color properties of CPOFF, BLFF, and RCOFF. The raw potato cuts had the following color characteristics: L* (90.32±1.22), a* (-0.63±0.00) and b* (13.57±1.01).

The overall color change ΔE, which was modeled using the first order kinetic equation (equation 6.5), is shown in Fig. 6.6D. The values obtained showed that both the type of oil used and the frying time significantly ($P<0.05$) affected the color changes observed in the fries as earlier reported by (Pedreschi 2012). For all the sets of fries' samples, the change in color was a function of the combined changes in the L*, a* and b* color values with time. The overall change in color of the fries was of the order RCOFF < BLFF < CPOFF. It was observed that at the maximum time

of frying, there was a slight shift towards the redness index. The values were 15.66±0.95, 17.32±0.61 and 20.12±1.14 for RCOFF, BLFF and CPOFF, respectively. There was a more significant increase in the yellowness (b*) values of CPOFF (50.11±1.24) and BLFF (42.99±1.83) than for RCOFF (33.59±1.67). There was a rapid increase in ΔE values during the early stages of frying and became nearly constant as the frying time increased for CPOFF and BLFF. For RCOFF, a progressive increase in ΔE was observed. This trend in color change agrees with literature reports for products fried in palm oil or composite oils containing palm oil (Andreu-Sevilla et al. 2009; Mba et al. 2015a).

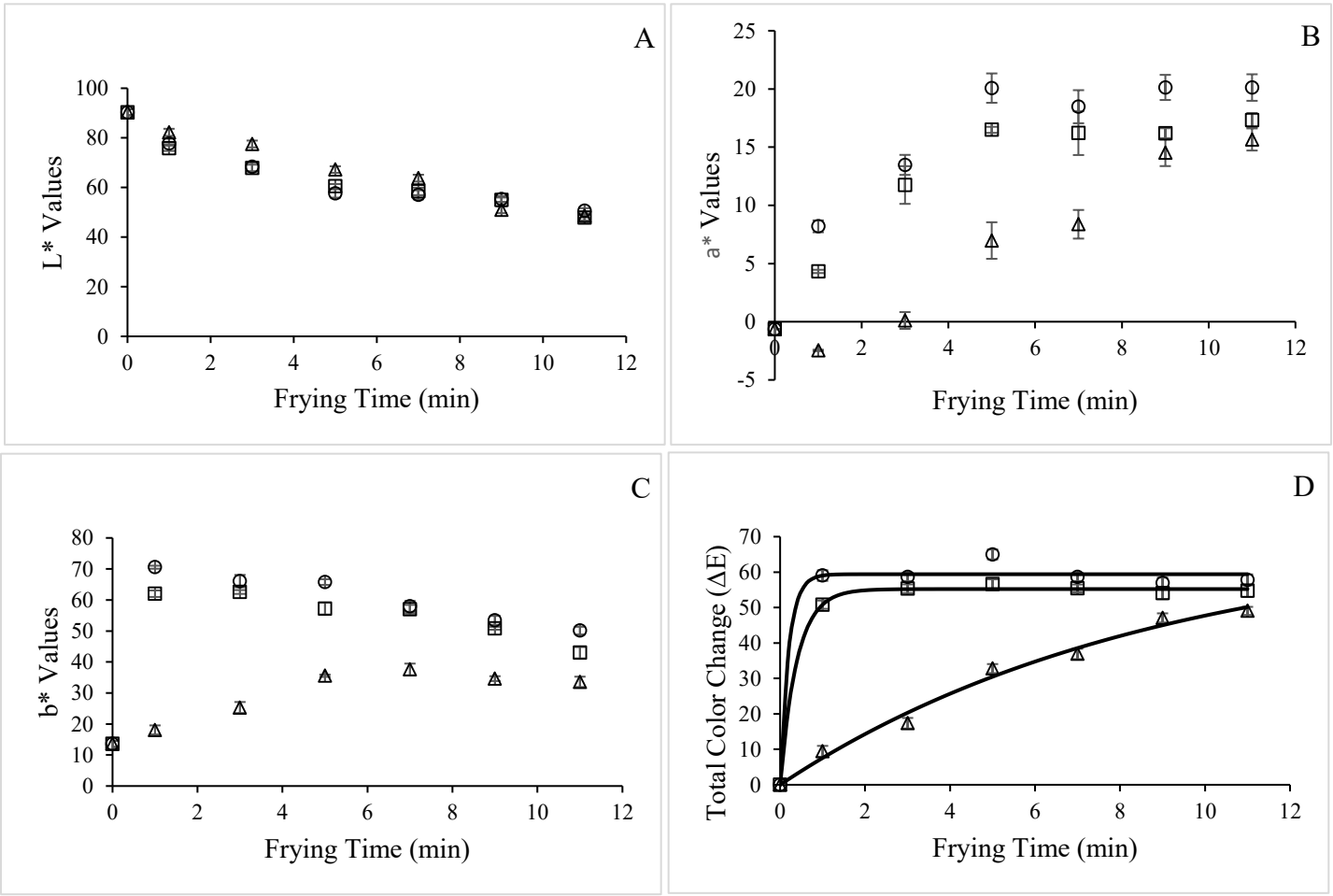


Figure 6.6: CIELAB color properties of French fries produced using crude palm oil (CPO), refined canola oil (RCO), and blend (BL). ○ = CPOFF; Δ = RCOFF; □ = BLFF; line = predicted values.

The model parameters (Table 6.2) confirmed that the rate of ΔE in CPOFF was approximately 2 times higher than in BLFF and 44 times higher than in RCOFF. The equilibrium values also showed that the CPOFF samples were the most yellowish, while RCOFF samples were the lightest in color. The high R^2 values ≥ 0.98 and low RMSE in the three French fries' samples showed that the first-order model was adequate in estimating the color changes in the fries. The first order kinetic model has been used to predict the color changes during frying (Krokida et al. 2001a; Ling et al. 2014).

6.4.6 Correlation between the French fries color and absorbed Carotenoids

Carotenoids have been reported to be responsible for the attractive color of fruits and vegetables. It is abundant in CPO and largely responsible for the color of the oil (Mba et al. 2015b; Fernández-García et al. 2012). The color is the first attribute that consumers assess when determining the quality and appearance of a product and therefore conditions its acceptability (Pathare et al. 2013). The relationship between total carotenoids in French fries' samples and the measured color parameters was investigated to highlight which color property was most influenced by the carotenoid content.

The relationships obtained for the color variables and carotenoid absorption is shown in Table 6.5. In all the samples, the order of correlation observed was b* > a* > L*. The strong positive Spearman's correlation (r_s) between b* and the total carotenoids in CPOFF and BLFF was very high (0.9666 and 0.9156, respectively). This proved that the relationship between b* and the carotenoid level was the most established. This also implied that the carotenoid level in the French fries strongly influenced the overall color change (ΔE) observed. This is evident from the high r_s and low p values obtained. These findings agree with the results reported by Minguez-Mosquera et al. (1991) that among the color variables, the b* and the carotenoid content has one of the best correlation coefficients in virgin olive oil.

Table 6.5: Spearman's correlation between total carotenoids and color variables of French fries produced in crude palm oil, refined canola oil, and blend (α = 0.05)

	L*		a*		b*		ΔE	
Sample	r	P	r	P	r	P	r	P
CPOFF	-0.6947	0.0832	0.7774	0.0397	0.9666	0.0040	0.9988	<0.0001
BLFF	-0.7899	0.0346	0.7822	0.0377	0.9156	0.0038	0.9887	<0.0001
RCOFF	-0.0888	0.8498	0.0344	0.9417	0.5803	0.1720	0.2176	0.6393

L* = Lightness/darkness; a* = Redness/greenness; b* = Yellowness/blueness; ΔE = Overall color change; r = Spearman's correlation coefficient; P = Probability value; CPOFF = Crude palm oil French fries; BLFF = Blend (CPO: RCO 1:1 w/w) French fries; RCOFF = Refined canola French fries.

6.5 Conclusion

The results obtained in this study showed that deep-fat frying of French fries in CPO and CPO: RCO blend resulted in substantial enrichment of the fries with bioactive phytonutrients considering the initial very low levels of the phytonutrients in the un-fried potato. The type and amount of phytonutrients present in French fries samples depend on the type of oil, the solubility, and the stability of the phytonutrient in the native oil. The order of magnitude found in the fries showed that carotenoids were the most absorbed, followed by the tocotrienols and tocopherols. The first order kinetic model with slight parameter modification was used to adequately predict the moisture loss, oil uptake and total change in color of the French fries' samples. The oil uptake rate was 2 – 4 times lower than the moisture loss rate in the frying oils studied. The biphasic apparent first order model was successfully used to estimate the migration and concentration of the phytonutrients in the fried product. In all cases, the reaction rates of the fast phase were greater than the reaction rates of the slow phase. This model was further confirmed by the higher range of D-values associated with the slow phase than the D-values of the fast phase. Even though blending resulted in a dilution and reduction in the initial amount of phytonutrients in the blend oil sample, the blend oil products had the greatest percentage migration of the original phytonutrients in the native oil. A very strong positive correlation was found between the total carotenoids content and the b* color parameter and the overall color change of the fried samples. Despite differences in the amount of phytonutrients absorbed by the French fries, the potential of enriching the fries by frying in CPO and blend of oils containing CPO has been established.

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Significant enrichment of French fries was observed when the frying oil used was CPO or composite oils containing CPO in their formulation. In the case of total carotenoids over 50%, tocotrienol isomers over 40% and tocopherol isomers 3 – 16% absorption from the frying media took place during deep-fat frying at 170 ^{o}C and frying time ≤ 11 min. These findings have been submitted and is being reviewed for publication by a scientific journal. The author and article information of chapter 6 is as follows:

Ogan I. Mba, Marie-Josée Dumont, and Michael Ngadi, (2016). Migration and concentration of valuable phytonutrients in French fries during deep-fat frying in palm oil, canola oil and blend. Food and Bioprocess Technology, (Submitted).

Chapter 6 documented that the bioactive phytonutrients in the frying oil can be transferred to the fried products at short frying time periods. However, commercial deep-fat frying involves large number of frying cycles, longer frying periods and oil reuse under varying temperatures. These phytonutrients also are degraded and lost from the oil as frying continues. We formulated the hypothesis that the phytonutrients are quickly depleted from the frying oil as frying time and temperature increases. The test of this hypothesis was the last objective of this research and the findings are presented in Chapter 7 of this thesis. The results of this research objective have been written up (with the title: 'Thermostability and degradation kinetics of phytonutrients in palm and canola oil blends used in deep-fat frying') and submitted to the peer reviewed journal 'LWT- Food Science and Technology'. The format of the manuscript has been altered to be consistent with this thesis. All the literatures cited in this chapter are listed in the references section of this thesis.

CHAPTER 7

7. THERMOSTABILITY AND DEGRADATION KINETICS OF PHYTONUTRIENTS IN PALM AND CANOLA OIL BLENDS USED IN DEEP FAT FRYING

7.1 Abstract

The thermostability of tocochromanols (tocopherols and tocotrienols) and carotenoids in virgin palm oil (VPO), refined canola oil (RCO) and blends of the two oils under deep-fat frying conditions at 170 – 190 ºC was investigated. Normal-phase HPLC was used to monitor the tocochromanols variation over frying time at each temperature. The changes in total carotenoids content was analyzed spectrophotometrically. The deterioration kinetic rate of each homolog detected followed a reaction order greater than 1. The rates were dependent on frying temperatures and were satisfactorily modeled by the Arrhenius relationship. The rate of deterioration and the activation energy showed that the least stable homologs were γ-tocopherol and γ-tocotrienol while δ-tocotrienol and carotenoids were the most stable. In VPO, the carotenoids were more retained while the tocochromanols were less stable. This was further evidenced by the high activation energy (E_a of 71±5 kJ/mol) for carotenoids in VPO. The tocopherol and tocotrienol homologs had greater stability in the blends as shown by their comparatively higher E_a values. The E_a for γ-tocopherol, γ-tocotrienol, α-tocopherol and α-tocotrienol in the blend were 20±2, 47±16, 48±9, and 74±4 kJ/mol, respectively. These behaviors are related to the initial composition of the oils and their calculated oxidizability (Cox) value.

7.2 Introduction

Deep-fat frying leads to the formation of deterioration compounds that alters the chemical, nutritional and sensory properties of the oil and the fried products. Some breakdown products decrease the nutritional value of the oil, limit the shelf life of fried food, and raise health concerns (Sanches-Silva et al. 2014). To improve the oil's stability, the practice is to add synthetic antioxidants. The most commonly used antioxidants are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and tert-butyl hydroquinone (TBHQ). They are categorized as 'generally regarded as safe' (GRAS) compounds (Ardabili et al. 2010). However, some studies suggest that they can be potential human carcinogens (Taghvaei and Jafari 2015). Therefore, their use is regulated in most countries. The maximum permitted level

recommended by regulatory agencies is 0.02% or 200 ppm of the total lipids present in food (Shahidi and Zhong 2005; Taghvaei and Jafari 2015).

Increasing attention is being given to natural bioactive phytonutrients such as carotenoids and tocochromanols (tocopherols and tocotrienols) present in vegetable oils. These phytonutrients contribute actively to the taste and color of the unrefined virgin oils (Berger 2005; Fine et al. 2016). Most importantly, they are known to significantly delay or prevent the oxidation of fats and oils by chelating redox metals (such as iron and copper), donating hydrogen atom, and scavenging harmful free radicals. They protect human tissues and cells from oxidative damages and chronic degenerative illnesses (Karam et al. 2016). An ideal antioxidant is also readily absorbed by the body. Carotenoids, tocopherols, and tocotrienols are the major lipophilic phytonutrients found in crude palm oil with concentrations > 500 ppm (Berger 2005; Mba et al. 2015b). Tocopherols and phytosterols are important minor constituents of canola seed that are also found in canola oil (Zhang et al. 2007). These phytonutrients have isomers and homologs with distinctive biological value, bioactivity and antioxidant potency. Though bioactive phytonutrients constitute < 1% of the oils' composition, they play important roles in the quality of the oil. They exhibit nutritional, health and physiological benefits beyond their antioxidant function (May and Nesaretnam 2014).

Significant losses of the phytonutrients occur during conventional refining of virgin oils (Gallina Toschi et al. 2013). Losses of phytonutrients present in oils during frying and other thermal processes have also been widely reported in the literature (Simonne and Eitenmiller 1998; Barrera-Arellano et al. 2002; Kalogeropoulos et al. 2007; Rossi et al. 2007; Vaidya and Choe 2011; Chiou et al. 2012). Marmesat et al. (2010) suggested that the loss of phytonutrients from frying oils is due to chemical degradation at high temperatures as total heating time accumulates. Other routes through which losses may occur include volatilization and steam distillation due to the combined effect of high temperature and a large amount of steam escaping from the food being fried (Gallina Toschi et al. 2013). Nevertheless, the optimization of thermal processes depends on suitable degradation kinetic models (Sampaio et al. 2013). Kinetic modeling is used to predict the influence of processing on critical quality parameters. Data on deterioration kinetics, including reaction order, rate constants and activation energies, are very important in predicting food quality loss during thermal processing and product storage (Patras et al. 2010). In deep-fat frying, kinetic studies are needed to minimize oil breakdown, optimize the frying process and enhance the quality

of the fried products. Previous kinetic analysis reporting on carotenoid and tocopherol losses were performed mainly at temperatures ≤ 100 ºC (Dhuique-Mayer et al. 2007), in model oil systems (Henry et al. 1998; Chung 2007), and in refined palm olein which is a fraction of palm oil with a different fatty acid composition (Achir et al. 2010). Similarly, Sampaio et al. (2013) studied only carotenoid degradation in pre-treated palm oil with a high level of antioxidants for a period not exceeding 2.3 h at 170 – 230 ºC. They reported that the degradation kinetics followed an order greater than 1. On the other hand, Qiu et al. (2012) reported that the loss of β-carotene in oils heated at 140 – 180 ºC followed a first-order kinetics. Information on the kinetics of tocotrienol degradation is very limited. In this work, the thermo-stability of natural tocopherols, tocotrienols and total carotenoids at frying temperatures in virgin palm oil (VPO or crude palm oil (CPO)), refined canola oil (RCO), and VPO/RCO blend (1:1 w/w) was investigated. The effect of the presence of the homologs together on the stability and losses of the phytonutrients during deep-fat frying was simultaneously analyzed. The reaction orders, degradation rates and activation energies of each homolog was calculated by applying degradation kinetics models. This study will contribute to better characterization of loss in nutritional quality and stability of frying oils.

7.3 Materials and Methods

7.3.1 Materials

The external standards of fatty acid methyl esters (FAME, purity > 98%), the internal standard (C19:0), standard solutions of α-, β-, γ-, δ-tocopherols, were purchased from Sigma-Aldrich (St Louis, MO, USA). The standard α-, β-, γ-, δ-tocotrienols as well as a tocol calibration kit were gifts from ExcelVite Sdn. Bhd. (Perak, Malaysia). HPLC grade n-hexane and other reagents were purchased from Fisher Scientific (Fair Lawn, NJ, USA).

Refined canola oil (RCO) (labelled as containing BHA, BHT and dimethyl polysiloxane (DMPS)) was supplied by Titan Oils Inc. Montréal, Canada. The virgin palm oil (VPO) was supplied by a palm oil mill in Abia State, Nigeria. The VPO was produced, packaged, and controlled according to quality standards. High-density polyethylene (HDPE) barrels containing the fresh VPO were air lifted to Canada within 2 weeks of production. The binary blend was made in the laboratory (just before frying) by mixing and vortexing VPO and RCO (1:1 w/w) to a homogenous blend. Russets potato (*Solanum tuberosum L.)* variety was purchased from a local grocery shop and used for the frying experiments.

7.3.2 Frying Experiment

The potatoes were peeled, sliced (≈ 16 mm × 16 mm × 100 mm) and washed to remove surface starch. The slices were quickly dried with a light stream of warm air. About 4.5 L of VPO, RCO and blend were heated from an initial temperature of 23 ºC to the target frying temperature for 2 h in a batch electric fryer (D24527DZ Délonghi Inc. USA). The frying temperatures used were 170, 180 and 190 ºC. These temperatures are widely used for domestic and commercial deep-fat frying operations. At 30 min intervals, successive batches of 100±2.0 g potato slices were fried for 10 min within 5 h/day of heating. The frying procedure was repeated 3 more consecutive days, to give a total heating and frying time of 20 h. This frying protocol was followed for each oil sample and temperature. The temperature of the frying oil was monitored by a K-type thermocouple attached to a digital data logger (Hotmux). The end of each 5 h frying cycle was followed by cooling to room temperature. Aliquots of the fried and unused oil samples were decanted into screw-capped amber HDPE bottles and kept frozen at -20 ºC until analysis that followed. Frying was done without oil replacement, however the oil in the fryer was kept in a cool dark cabinet and filtered at the beginning of each successive frying day to remove solid debris.

7.3.3 Fatty acid profile

The proportion of fatty acids in the unused oil samples was determined by capillary gas chromatography (GC). First, the external FAME standards were used to prepare standard calibration curves at a concentration range of 0.1 – 2.5 mg mL^{-1}. Next, the methylation procedure described by O'Fallon et al. (2007), but using C19:0 as the internal standard, was used to derivatize the FAME from the oil samples. Subsequently, GC analysis of FAME was carried out using a Hewlett Packard 5890 Series II instrument equipped with a Phenomenex ZB-WAX capillary column (30 m × 0.25 mm (internal diameter) × 0.25 µm (film thickness)). The GC unit was fitted with an auto-injector (model HP 7673) and flame ionization detector (FID). The carrier gas used was helium (40 mL min^{-1}), while the FID gases were hydrogen (30 mL min^{-1}) and compressed air (430 mL min^{-1}). Other GC conditions were as follows: FAME injection volume, 1 µL; oven temperature, 80 ºC for 3 min, increased to 150 ºC (10 ºC min^{-1}), 150 ºC for 3 min, increased to 250 ºC (10 ºC min^{-1}), and 250 ºC for 20 min. The injection and FID temperatures were both set at 250 ºC. Each FAME sample was injected in triplicates. The fatty acids were identified by comparing retention times (RT) with the RT of the pure FAME standards and quantified using the calibration curves.

7.3.4 Calculated Oxidizability Value of the Oils

The Cox value of VPO, RCO, and the blend oil samples was calculated based on the relative percentage of the unsaturated C18 fatty acids by using the formula proposed by Fatemi and Hammond (1980).

$$Cox\ value = \frac{((1*C18{:}1\%)+(10.3*C18{:}2\%)+(21.6*C18{:}3\%))}{100} \quad (7.1)$$

7.3.5 Tocopherol and Tocotrienol Determination

The concentrations of the different tocopherol and tocotrienol homologs in the used and unused oil samples were determined by normal phase HPLC analysis by following the method described by López Ortíz et al. (2006). Each homolog standard and the internal standard, were used to prepare individual 1% stock solutions in n-hexane. Different concentrations of working solutions were made and used to prepare the calibration curves. The calibration curves were prepared through linear correlation between mean peak areas and concentrations of the injected homolog standards. The tocopherol and tocotrienol homologs were extracted from the oil samples using methanol containing 0.05% ascorbic acid as described by Chen and Bergman (2005). Each homolog was identified by comparing retention times with the corresponding standard solution and the photodiode array detector scanning was used to confirm the characteristic spectra of each homolog. The linear regression equation obtained for each homolog ($r \geq 0.987$) was used for the quantification and calculation of the limits of detection (LOD) and the limits of quantification (LOQ). The weighted linear regressions were performed using SAS 9.4.

7.3.6 Total Carotenoids Determination

The total carotenoids in the oil samples were determined according to the procedure described by Gao et al. (2007). The spectrophotometer used was Unicam UV series (model UV1 – 091309, Thermo Spectronic, Rochester, NY). The absorbance of diluted n-hexane extracts of 1.0 g oil samples was measured at 445 nm using n-hexane as blank. The total carotenoid (TC) values in per million (ppm) were calculated based on TC specific absorption coefficient in n-hexane of 2500 dL g^{-1} cm^{-1} (Luterotti et al. 2013) as shown in equation (7.2).

$$TC_{(ppm)} = \frac{A_s*Y*10^6}{2500*W_s*1000} \quad (7.2)$$

(A_s = absorbance value of sample at 445 nm; Y = volume (mL) of n-hexane used in the extraction and W_s = mass of oil sample (g)).

7.3.7 Statistical and Kinetics Analysis

The significant effects of factors were assessed by analysis of variance (ANOVA) and the differences between mean values of parameters were evaluated by Tukey's LSD test ($\alpha = 0.05$). Data handling were done using Statistical Analysis System (SAS version 9.4). The results presented are the mean of the obtained values ± standard deviation (SD), n = 3. The degradation kinetics of each vitamin E homolog and carotenoids was analyzed by determining the rate constants of their degradation during deep-fat frying.

The kinetics of the experimental data were evaluated using the dimensionless normalized concentration C/C_0 at the different frying temperatures and time; where C and C_0 are the concentrations of the phytonutrient in the frying oil at any time during the frying and in the unused oil samples, respectively. Each phytonutrient deterioration rate k (s^{-1}) was calculated from the slope of the plot of C/C_0 *vs* frying time at the different frying temperatures. The general kinetic equation of food quality deterioration proposed by Van Boekel (2008) shown in equation (7.3) was used in the study.

$$\frac{dC}{dt} = -kC^n \tag{7.3}$$

Where dC/dt = deterioration rate, C = concentration of each phytonutrient (*ppm*) at any time t, k = reaction rate constant (s^{-1}), and n = order of the reaction. Integrating equation (7.3) between C_0 and C from time zero to time interval t gives:

$$\int_{C_0}^{C} \frac{dC}{C^n} = -\int_0^t k * dt \tag{7.4}$$

Since the term $1/(1-n)$ would be indeterminate, equation (7.4) does not apply to $n = 1$, therefore

$$C = [{C_0}^{1-n} - (1-n)kt]^{1/1-n} \quad (n \neq 1) \tag{7.5}$$

$$C = C_0 * exp^{(-kt)} \quad (n = 1) \tag{7.6}$$

The order of the reaction n and the rate constants k were estimated through nonlinear regression using SAS. The Arrhenius equation was used to explore the temperature-dependence of the reaction rate k:

$$k = k_0 exp^{(\frac{-E_a}{RT})} \tag{7.7}$$

(k_0 = pre-exponential factor (s^{-1}), E_a = activation energy (kJ/mol), T = frying temperature (K), R = gas constant (8.314 J/mol/K)). As explained by Peleg et al. (2012), processes which have optimal temperature, chemical reactions that start at elevated temperatures and complex processes where the isothermal rate constant is a function of both temperature and time can be described by the modified Arrhenius model shown in equation (7.8):

$$k_{ref} = k_0 * exp^{(\frac{-E_a}{RT_{ref}})} \quad (7.8)$$

$$k = k_{ref} * exp^{(\frac{-E_a}{R}(\frac{1}{T} - \frac{1}{T_{ref}}))} \quad (7.9)$$

(k_{ref} = the rate constant at chosen reference temperature, T_{ref} = chosen reference temperature (180 ^oC) which was the mid-point of the frying temperatures studied).

The k values were replaced by equation (7.3) and fitted to all the data at once by nonlinear regression using SAS. Using this approach, a much superior accuracy in final estimates was achieved than first deriving the rate constant and then fitting them to the Arrhenius model equation (Van Boekel 2008; Peleg et al. 2012).

7.4 Results and Discussions

7.4.1 Fatty Acid Composition and Initial Phytonutrients Content of the Fresh Oil Samples

The fatty acid composition (FAC) of lipid systems is important in their oxidative stability. The FAC, the ratio of unsaturated and saturated fatty acids and the Cox value of unused VPO, RCO and the blend of the two oils is shown in Table 7.1. The values are in agreement with literature reports for these fresh oils (Edem 2002; Alireza et al. 2010b; Azlan et al. 2010). The VPO has the distinction of being high in saturated fatty acids (SFA) particularly, palmitic acid (C16:0). Thus, it has the lowest unsaturated and saturated fatty acid ratio (1.07) and Cox value (1.29). These values show that VPO has the greatest thermostability potentials during deep fat frying (Rossi et al. 2007). The RCO had a high concentration of oleic acid (C18:1) and is low in SFA. The FAC values of the blend while not just the additive mean of the FAC of the of the original oils that make up the blend, showed intermediate values. The ratio of unsaturated acid to saturated acid in RCO and blend was 19.54 and 3.18, respectively. The Cox values were 4.46 in RCO and 3.11 in the blend. Though the percentage unsaturation in the RCO and the blend was high and RCO had the highest ratio of unsaturation versus saturation, their Cox values were below 5.0. This was due to

the predominance of the monounsaturated C18:1 which has a lower weight in the Cox index calculation than the polyunsaturated linoleic (C18:2) and linolenic (C18:3) acids. The oxidation rate of C18:1 is far below the rate of the other C18 unsaturated fatty acids (Rossi et al. 2007; Brühl 2014).

Table 7.1: Fatty acid composition (%) of the oils used in the frying experiment

Fatty acids	VPO	RCO	Blend (1:1 w/w)
C14:0	0.51±0.04	0.03±0.00	0.33±0.09
C16:0	44.32±0.21	3.20±0.06	20.54±0.12
C16:1	0.12±0.03	0.09±0.04	0.04±0.02
C18:0	2.85±0.16	1.41±0.07	2.97±0.07
C18:1	42.16±0.19	64.08±0.40	54.26±0.07
C18:2	7.76±0.11	20.84±0.20	16.19±0.30
C18:3	0.34±0.07	7.75±0.09	4.16±0.16
C20:0	0.09±0.03	0.18±0.02	0.11±0.08
C20:5	0.88±0.16	1.43±0.12	1.39±0.09
∑SFA	47.77±0.44	4.82±0.15	23.95±0.36
∑MUFA	48.28±0.22	64.17±0.44	54.30±0.09
∑PUFA	8.98±0.34	30.02±0.41	21.74±0.55
∑UFA/∑SFA	1.07	19.54	3.18
Cox Value	1.29	4.46	3.11

VPO = Virgin palm oil, RCO = Refined canola oil, Blend = VPO/RCO (1:1 w/w), ∑SFA = Total saturated fatty acids, ∑MUFA = Total monounsaturated fatty acids, ∑PUFA = Total polyunsaturated fatty acids, ∑UFA = Total unsaturated fatty acids. Values are means ± std.

From Table 7.2 below, it can be seen that all the phytonutrients homologs were found in VPO in different amounts. The dominant ones being total carotenoids (553.44±5.62 ppm) and γ-tocotrienol (320.11±1.16 ppm). While tocotrienols were absent in RCO, α- and γ-tocopherols concentration was 70.17±0.47 ppm and 112.27±2.19 ppm, respectively. The total carotenoids content of RCO (0.084±0.02 ppm) was very low. The total concentration of tocopherols, tocotrienols and carotenoids in the fresh blend oil sample represents a significant nutritional improvement and balancing of the bioactive components. These concentrations of the phytonutrients are within the range of values reported in the literature (Ng et al. 2004; Rossi et al. 2007; Przybylski and Eskin

2011; Ghazani and Marangoni 2013). The ratio of vitamin E to unsaturation was 2.21 in RCO, 5.98 in the blend and 19.23 in VPO. This showed that supplementary vitamin E requirement will increase with an increase in the consumption of RCO and RCO based foods in the diet (Raederstorff et al. 2015).

Table 7.2: Phytonutrients content (ppm) of the fresh oils used in the deep-fat frying experiment

Characteristic	VPO	RCO	Blend (1:1 w/w)
α-Tocopherol	150.03±1.81	70.17±0.47	105.53±1.57
β-Tocopherol	11.82±0.25	-	-
γ-Tocopherol	255.87±1.55	112.27±2.19	140.90±0.99
δ-Tocopherol	38.44±0.02	-	26.56±0.01
α-Tocotrienol	152.28±0.75	-	65.21±0.24
β-Tocotrienol	15.35±0.18	-	-
γ-Tocotrienol	320.11±1.16	-	141.55±0.22
δ-Tocotrienol	45.01±1.36	-	-
Total carotenoids	553.44±5.62	0.084±0.02	394.80±3.66
∑Tocopherol	456.16±3.63	182.44±2.66	272.99±2.57
∑Tocotrienol	532.75±3.89	-	206.76±0.46
Vitamin E/Unsaturated	19.23	2.21	5.98

7.4.2 Deterioration Kinetics of Tocopherols

As frying progressed, the β-homologs of the tocochromanols were not detected in the analysis. This could be due to their low initial levels in the fresh oil (Pinheiro-Sant'Ana et al. 2011). It has also been reported that the α- and γ-tocopherols are the main homologs in unrefined oils, while δ-tocopherol content is highly limited (Bonvehi et al. 2000; Seppanen et al. 2010). Aladedunye and Przybylski (2012) reported that while tocochromanols mixtures significantly inhibited the thermo-oxidation of canola oil during frying at 185 ^{o}C, there was no significant difference in the performance of the mixtures despite the differences in their isomeric composition, suggesting an absence of synergies among the tocopherol and tocotrienol homologs. This implies that the homologs have different antioxidant potencies, thermostability and kinetics behavior. As shown

in Table 4, a range of 1.4 to 1.6 was obtained as the order of reaction for the tocopherol homologs after the nonlinear regression of equation (7.5). The kinetic orders being greater than 1 suggests that multiple steps were involved in the degradation process, and that temperature mediated autocatalytic and acid catalyzed decomposition reactions contributed to the changes in the homolog concentration during deep-fat frying (Achir et al. 2010; Aladedunye 2014). Chung (2007) reported that degradation of tocopherols followed a first order kinetics during heating of tocopherol mixtures in a temperature controlled muffle furnace. However, the chemical reactions occurring during deep-fat frying of foods are different from reactions during continuous heating or even frying with model systems (Kalogianni et al. 2010; Aladedunye et al. 2015). Thus, the results reported in this work were from data obtained from real food frying experiments.

Figure 7.1 below, shows the thermal deterioration of the tocopherol homologs as frying temperature and time increased. The trend shows a continuous reduction in the concentration of each homolog relative to their initial concentration. The highest percentage losses were observed in VPO while the opposite effects were observed in the blend. It has been reported that tocopherols and tocotrienols seem to degrade more rapidly in oils with high saturated fatty acid content. Whereas, in polyunsaturated oils, the double bonds of the fatty acids compete with the tocopherols and tocotrienols as oxidation substrates, resulting in a less rapid decrease of the antioxidants in the frying oils (Simonne and Eitenmiller 1998; Rossi et al. 2007). Rossi et al. (2007) further stated that during the propagation phase of thermo-oxidation, the fatty acid peroxy free radicals react preferentially with the phenolic hydrogen of the tocopherol molecule. At the maximum temperature, the loss of α-tocopherol was 87% in VPO, 60% in RCO and 71% in the blend. These results agree with reported trend of losses of tocopherols and tocotrienols encountered during deep-fat frying. For instance, Juárez et al. (2011) reported that loss of tocopherols reached 76% after 14 h of frying at 180 ºC using soybean oil, sunflower oil and partially hydrogenated mixture of vegetable oils. Andrikopoulos et al. (2002a) reported 70 – 80% loss of α-tocopherol in virgin olive oil, sunflower oil, and vegetable shortening after eight cycles of potato deep-frying session at 170 ºC. In both VPO and RCO, the highest loss of α-tocopherol at all the temperatures studied was observed after 15 h of frying, while in the blend the highest loss was after 20 h. As shown in Table 7.3, the rate of deterioration k (s^{-1}) of α-tocopherol increased with frying temperature, from 6.58×10^{-6} to 11.81×10^{-6} in VPO, 5.76×10^{-6} to 9.50×10^{-6} in RCO, and 5.44×10^{-6} to 8.39×10^{-6} in the blend. Thus, the rate constant was the lowest ($p<0.05$) in the blend oil sample.

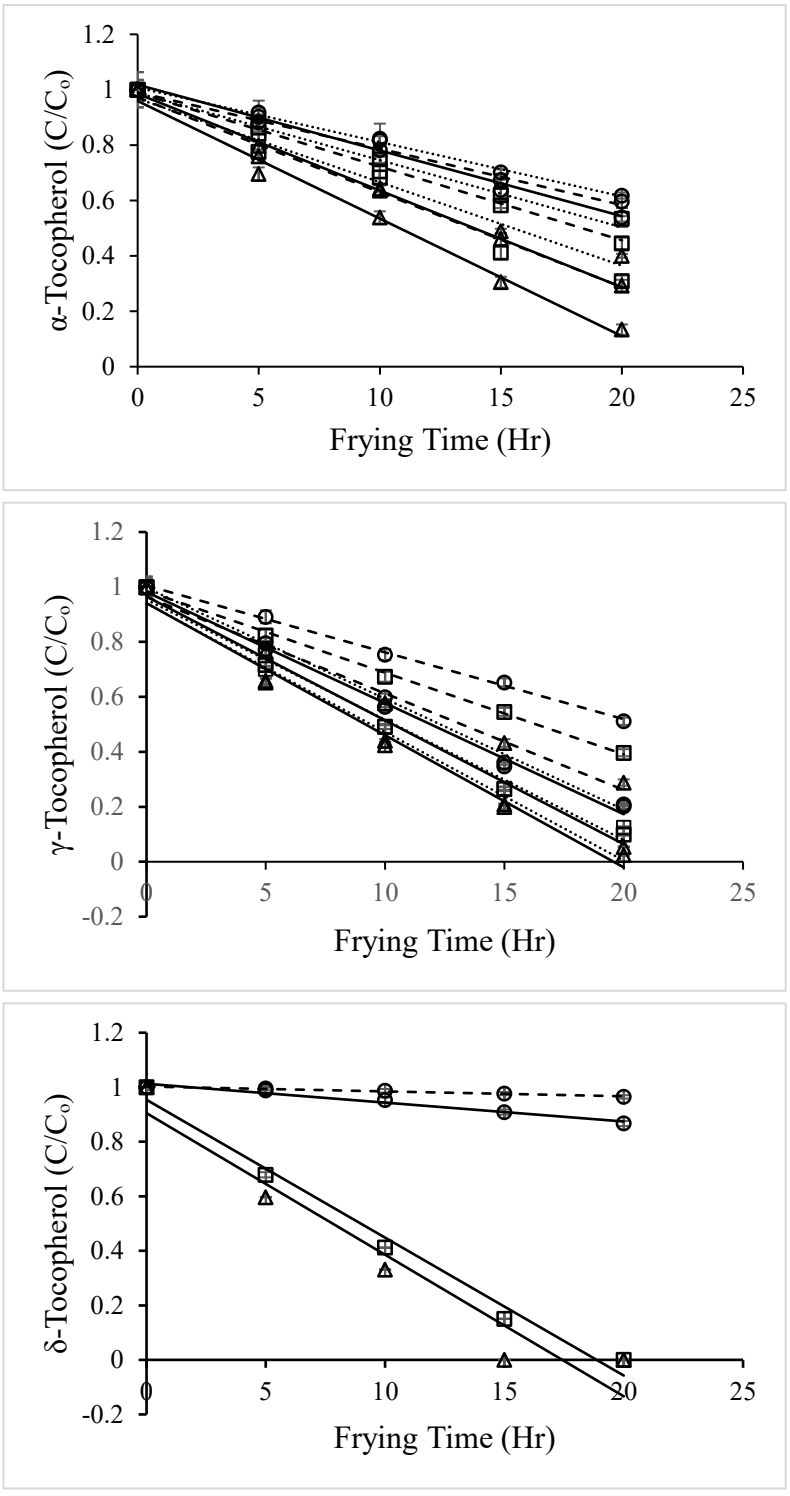

Figure 7.1: Plots of tocopherol homologs deterioration kinetics in oil samples used for deep-fat frying. 170 ºC (circle), 180 ºC (square) and 190 ºC (triangle). VPO (solid line), RCO (dotted line) and blend (broken line)

The kinetic data obtained in this study is presented in Table 7.4. The activation energies E_a (kJ/mol) calculated were 44±14 in VPO, 44±2 in RCO and 48±9 in the blend. Table 7.4 also shows that α-tocopherol had the highest E_a among the tocopherol homologs. This confirms the higher stability of α-tocopherol during frying and agrees with literature reports (Bansal et al. 2010b). The thermal stability of α-tocopherol is attributed to increased steric hindrance due to the extra methyl group(s) reducing the rate of addition and polymerization reactions (Al-Khusaibi et al. 2012).

Table 7.3: Initial deterioration rate of the phytonutrients during deep-fat frying

Phytonutrient	Temp. (°C)	Virgin palm oil		Refined Canola oil		Blend (1:1)	
		k [$k\times10^{-6}$ (s^{-1})]	R^2	k [$k\times10^{-6}$ (s^{-1})]	R^2	k [$k\times10^{-6}$ (s^{-1})]	R^2
α-Tocopherol:	170	6.58	0.99	5.76	0.99	5.44	0.99
	180	9.69	0.99	7.39	0.99	6.72	0.99
	190	11.81	0.98	9.50	0.98	8.39	0.99
γ-Tocopherol:	170	11.22	0.98	11.22	0.99	6.75	0.99
	180	12.53	0.98	12.14	0.98	8.25	0.99
	190	13.36	0.99	13.00	0.96	9.75	0.99
δ-Tocopherol:	170	2.25	0.98	-	-	1.92	0.97
	180	4.06	0.99	-	-	-	-
	190	4.42	0.93	-	-	-	-
α-Tocotrienol:	170	1.94	0.96	-	-	1.00	0.96
	180	3.17	0.98	-	-	2.17	0.95
	190	4.72	0.99	-	-	3.67	0.99
γ-Tocotrienol:	170	10.31	0.99	-	-	6.58	0.99
	180	11.06	0.99	-	-	7.58	0.98
	190	12.92	0.99	-	-	9.42	0.99
δ-Tocotrienol:	170	1.36	0.99	-	-	-	-
	180	1.38	0.99	-	-	-	-
	190	1.39	0.98	-	-	-	-
Total Carotenoids:	170	0.71	0.99	1.18	0.99	0.88	0.99
	180	0.94	0.99	1.26	0.99	1.04	0.99
	190	1.16	0.98	1.34	0.98	1.23	0.99

k = rate constant (s^{-1}), R^2 = coefficient of determination.

Table 7.4: Apparent kinetic order and activation energy of phytonutrients deterioration in frying oils

	Virgin palm oil				Refined canola oil				Blend			
Phytonutrient	n	E_a	p-R^2	SEM	n	E_a	p-R^2	SEM	n	E_a	p-R^2	SEM
α-Tocopherol	1.6	44±14	0.9999	0.064	1.6	44±2	0.9998	0.018	1.6	48±9	0.9934	0.036
γ-Tocopherol	1.4	13±2	0.9999	0.038	1.4	15±2	0.9959	0.028	1.6	20±2	0.9982	0.027
δ-Tocopherol	1.5	46±2	0.9993	0.010	-	-	-	-	1.3	-	-	-
α-Tocotrienol	1.8	52±7	0.9996	0.038	-	-	-	-	1.8	74±4	0.9947	0.033
γ-Tocotrienol	1.5	20±4	0.9998	0.080	-	-	-	-	1.6	47±16	0.9986	0.036
δ-Tocotrienol	1.3	103±11	0.9868	0.012	-	-	-	-	-	-	-	-
Total carotenoids	1.5	71±5	0.9991	0.324	1.5	56±6	0.9989	0.001	1.5	65±5	0.9996	0.211

n = apparent order, E_a = activation energy (kJ/mol) with confidence interval (p=0.05), p-R^2 = pseudo coefficient of determination, SEM = Standard error of the mean of the concentration.

Gamma-tocopherol showed the greatest loss, 80 – 95% in VPO, 79 – 95% in RCO and 49 – 71% in the blend. As seen from Table 7.3, the k (s^{-1}) range is 11.22×10^{-6} to 13.36×10^{-6} in VPO, 11.22×10^{-6} to 13.00×10^{-6} in RCO and 6.75×10^{-6} to 9.75×10^{-6} in the blend. These correspond to E_a (kJ/mol) values of 13±2, 15±2 and 20±2 for VPO, RCO and blend, respectively. The rate of thermal deterioration of γ-tocopherol in VPO and RCO was similar but significantly different from the deterioration in the blend. The γ-tocopherol had the highest initial concentration (Table 7.2) which also affected its rate of loss. This trend agrees with literature report (Warner and Moser 2009; Ghazani and Marangoni 2013). Also, Aladedunye and Przybylski (2009) reported that although the relative stability of α- and γ-tocopherols is temperature dependent, γ-tocopherols exhibited greater losses than α-tocopherols during frying at 180 ºC and 215 ºC.

Delta-tocopherol was not detected in RCO but was found in VPO and the blend in concentrations below 40 ppm (Table 7.2). At 170 ºC, the k (s^{-1}) were 2.25×10^{-6} in VPO and 1.92×10^{-6} in the blend, and losses were below 15% in the two oils. At the higher temperature studied, δ-tocopherol was not detected in the blend and was barely detected in the VPO after 10 h of frying. This could be due to their low levels in the unused oil samples. In the VPO, the E_a was 46±2 kJ/mol which was not significantly different from the E_a of α-tocopherol. The result of δ-tocopherol degradation is in agreement with literature reports. Andrikopoulos et al. (2002b) had reported that the deterioration rate of δ-tocopherol is similar to the rate of α-tocopherol in virgin olive oil and sunflower oil. Warner and Moser (2009) also reported that α- and γ-tocopherols are mostly lost preferentially to δ-tocopherol in oils during frying. Their study also showed that added δ-tocopherol was usually more retained. They also reported that lower concentrations of added δ-tocopherol (10 ppm) resulted in significantly higher retention (74%) than higher concentration (160 ppm) which gave only 34% retention in sunflower oil after 6 h of deep-frying tortilla chips. In this study, the E_a results showed that the deterioration of the tocopherol homologs detected in the RCO was the fastest. This suggests that the unsaturation of the native oil has some influence on the thermal stability of the endogenous antioxidants deep-fat frying.

7.4.3 Deterioration Kinetics of Tocotrienols

None of the tocotrienol homologs was detected in RCO. The deterioration curve of tocotrienol in VPO and the blend oil samples is shown in Figure 7.2 below.

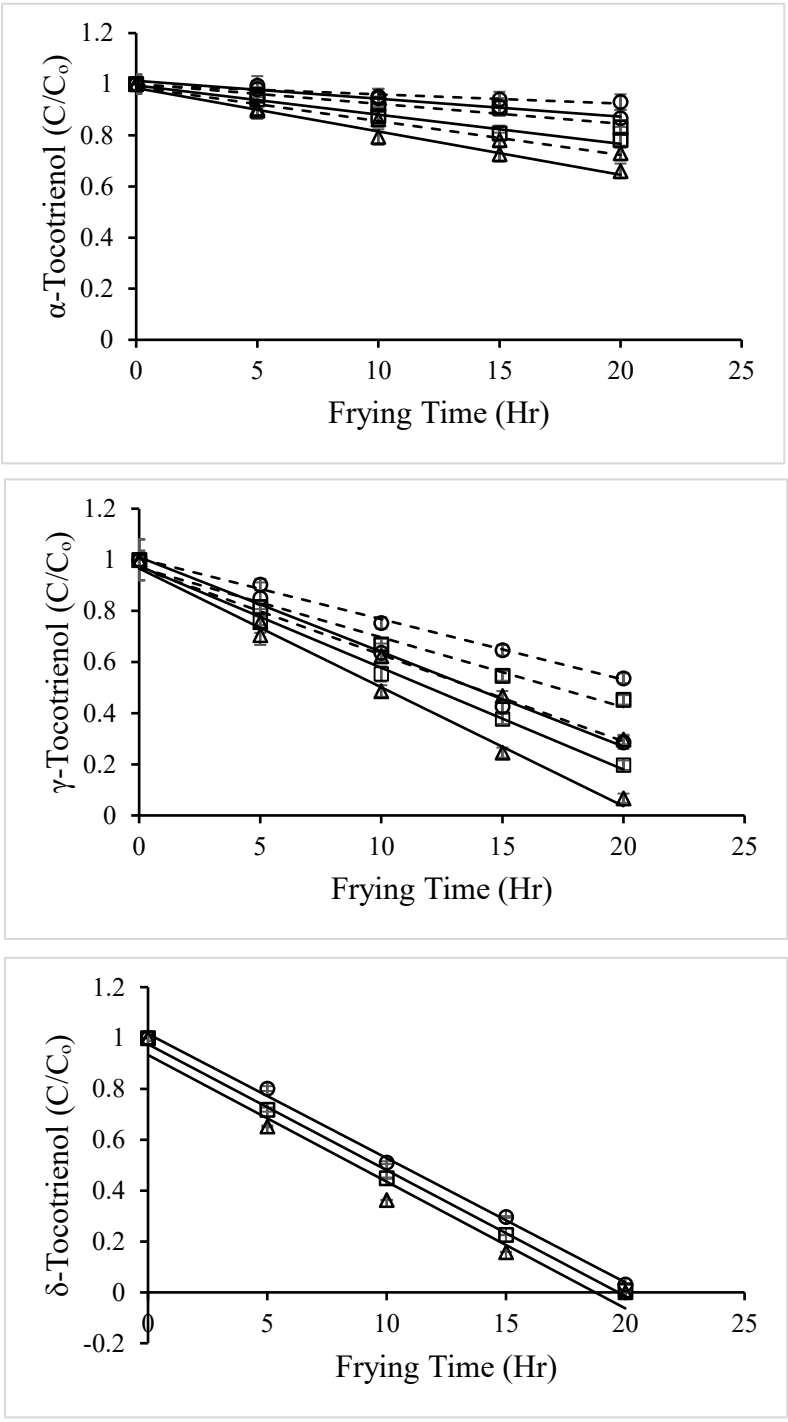

Figure 7.2: Plots of tocotrienol homologs deterioration kinetics in oil samples used for deep-fat frying. 170 ºC (circle), 180 ºC (square) and 190 ºC (triangle). VPO (solid line) and blend (broken line)

Compared with tocopherols, the multiple double bonds on the phytyl side chain of tocotrienols enable it to quench free radical reactions more readily (Packer et al. 2001; Aladedunye et al. 2015). The protective effects of tocotrienols are dose dependent and appear to increase with increasing concentration. The γ- and δ-tocotrienols show significantly more active antioxidant potentials than their tocopherol counterparts even at higher temperatures (Wagner et al. 2001). At $\alpha = 0.05$, the concentration of the tocotrienol homologs decreased linearly as a function of frying temperature and time. Also, as shown in Table 4, the thermal deterioration and the kinetic parameters were better described by reaction orders greater than 1 (ranging from 1.3 to 1.8). The goodness of fit of the model was shown by the values of the pseudo-coefficient of determination and the standard error of the mean (SEM) of the concentration of each of the homolog.

The rate of deterioration k (s^{-1}) for α-tocotrienol was 1.94×10^{-6} to 4.72×10^{-6} in VPO and 1.00×10^{-6} to 3.67×10^{-6} in the blend. The corresponding activation energy E_a (kJ/mol) was 52±7 and 74±4. The maximum α-tocotrienol loss was 35% in VPO and 27% in the blend. This also showed that loss of α-tocotrienol is influenced by the level of saturation of the fresh oil (Seppanen et al. 2010). Among the tocotrienols, the alpha homolog showed the least deterioration rate and is similar to α-tocopherol in its stability. This result is in line with literature reports (Wagner et al. 2001; Schrøder et al. 2006; Seppanen et al. 2010).

The range of loss observed for γ-tocotrienol was 72 – 94% in VPO and 46 – 70% in the blend. With a high k (s^{-1}) rate of 10.31×10^{-6} to 12.92×10^{-6} in VPO and 6.58×10^{-6} to 9.42×10^{-6} in the blend, γ-tocotrienol was the most rapidly lost homolog. It was reported that after 60 fryings at 163 ^{o}C, γ-tocotrienol showed the most significant decrease than α- and δ-tocotrienol in red palm olein and is the most effective tocochromanols homolog (Schrøder et al. 2006). In general, in oils and fats, γ-tocotrienol has been reported to be a better antioxidant than α-tocotrienol and tocopherols. This also explains its rapid disappearance during deep-fat frying (Seppanen et al. 2010; Aladedunye et al. 2015).

It was only in VPO that δ-tocotrienol was detected in small concentration. It's high E_a 103±11 kJ/mol and very low reaction rate $1.36 \times 10^{-6} – 1.39 \times 10^{-6}$ s^{-1} suggests relative stability compared to the other tocotrienol homologs. This result is slightly different from the result reported by Gapor et al. (1989), who studied the stabilizing effects of palm-derived tocotrienol homologs in a model system containing refined, bleached and deodorized palm olein and palm oil methyl ester. They

reported the order antioxidant activity as γ-tocotrienol > δ-tocotrienol > α-tocotrienol. The deterioration pattern of the tocotrienols in VPO during real deep-fat frying could have been affected by the quality and quantity of the many other phytonutrients present in the fresh oil (Berger 2005).

7.4.4 Deterioration Kinetics of Total Carotenoids

The carotenoids data obtained from the fresh and used oil samples with respect to its deterioration was treated by nonlinear regression using the parameters of equation (7.5). The decrease in concentration as a function of frying temperature and time is shown in Figure 7.3.

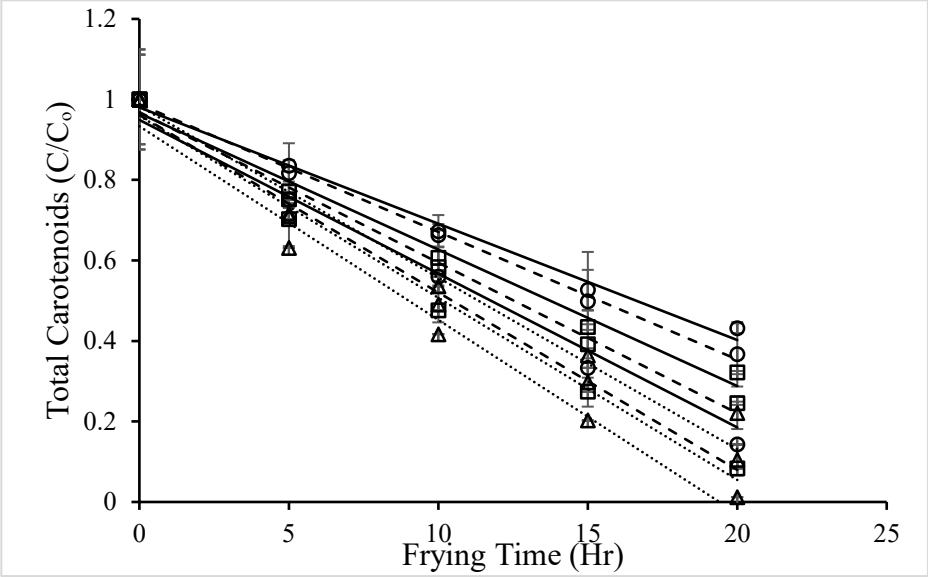

Figure 7.3: Plot of deterioration kinetics of carotenoids in oil samples used for deep-fat frying. 170 ºC (circle), 180 ºC (square) and 190 ºC (triangle). VPO (solid line), RCO (dotted line) and blend (broken line).

Different reaction orders were tested and the apparent order of the reaction was found to be 1.5 (Table 7.4). Kinetics of food quality changes mostly follow zero-, first- or second –order reactions. A number of reactions take place during thermal processing, either in series or in parallel and competing, thus fractional orders are also possible (Ling et al. 2014). Sampaio et al. (2013) when investigating the thermal degradation of carotenoids in palm oil at temperatures between 170 – 230 ºC reported that reaction order of 1.3 best describes the reaction order. Similarly, Achir et al. (2010) reported an order greater than 1 for β-carotene and lutein degradation at 120 – 180 ºC for palm olein and commercial frying oil heated on a hot-plate stirrer covered with a reaction block.

This reaction order could be due to the type and amount of other phytonutrients, additives and antioxidant synergism occurring in the oils (Wan Nik et al. 2005; Schrøder et al. 2006).

Even though the initial concentration of carotenoids in the RCO was very low 0.084±0.02 ppm (Table 7.2), the loss of carotenoids during frying was very rapid in this oil sample. On the other hand, VPO, the richest source of carotenoids lost only between 57 – 78%. This result is in agreement with literature reports. Early workers such as Budowski and Brondi (1960), determined that as the degree of oil unsaturation increases, carotene degradation increases. This is attributed to the rapid oxidation of unsaturated sites in the lipids that produce radicals that likely attacked carotenes. Beta-carotene has a highly unsaturated chain that can be attacked by radicals and oxygen, resulting in the production of carotenoid-peroxyl radical. This radical may, in turn, participate in further degradation and cleavage reactions of both unsaturated fatty acids and β-carotene. However, γ-tocotrienol (which is abundant in VPO) can rapidly regenerate carotenes (Schrøder et al. 2006). This may explain the similarity ($p>0.05$) in the deterioration rates of carotenoids in VPO and the blend.

The effect of temperature on the deterioration of carotenoids during deep-fat frying followed the Arrhenius model. The parameters of the regression estimate are shown in Table 7.4. The pseudo-R^2 was above 0.99 in the three oil samples and SEM ranged between 0.001 – 0.324. The E_a (kJ/mol) was calculated as 71±5 in VPO, 56±6 in RCO and 65±5 in the blend. These slightly differ from the previous E_a reports for carotene degradation in various foods. Activation energy E_a of 59.0 kJ/mol and 94.6 kJ/mol was reported for β-carotene degradation in soybean oil and peanut oil, respectively (Qiu et al. 2012), 86.0kJ/mol was reported for β-carotene degradation in palm olein (Achir et al. 2010), 109.4 kJ/mol for carotenoids degradation in heated palm oil (Sampaio et al. 2013), and 110 kJ/mol for β-carotene degradation in citrus juice (Dhuique-Mayer et al. 2007). The differences in the E_a could be due to differences in food matrix, heating *vs* real deep-fat frying, temperature ranges studied and the type of food that was fried.

7.5 Conclusion

This study showed that the thermo-stability of the phytonutrients found in VPO, RCO, and the blend during deep-fat frying was affected by the complex interplay of the fatty acid composition and oxidizability of the oils, the type and quantity of phytonutrients present, and their antioxidant activity. Each phytonutrient homolog deteriorated at a kinetics reaction rate greater than one. The

effect of temperature on the deterioration was adequately modeled by the Arrhenius equation with pseudo-R^2>0.99. The γ-tocotrienol was the least stable phytonutrient followed by the γ-tocopherol, while total carotenoids were relatively most stable in VPO. This could be due to higher antioxidant activity of γ-tocotrienol and its reported ability to protect carotenoids. In the RCO, α- and γ-tocopherols are the only endogenous antioxidants detected; the latter was less stable than the former during deep-fat frying. The pattern of deterioration of the tocopherol and tocotrienol homologs in the blend was similar to VPO but at a significantly lower rate. Overall, the fastest rate of deterioration was observed in γ-tocotrienol and γ-tocopherol irrespective of the oil sample. This was followed by the deterioration rates of α-tocopherol, α-tocotrienol and δ-tocopherol. The slowest rates of deterioration were observed in the carotenoids and δ-tocotrienol. The tocopherols and tocotrienols were comparatively most stable in the blend. The dilution effect of blending lowered the phytonutrients' concentrations. The stability and antioxidant efficacy of endogenous phytonutrients had been reported to depend on certain critical levels in the frying oil. The presence of other antioxidants such as phytosterols, phenolic compounds, and synthetic antioxidants can synergize with the tocochromanols and carotenoids to enhance stability and minimize loss.

CHAPTER 8

8. GENERAL SUMMARY AND CONCLUSION

The main objectives of this study were to monitor the behavior of VPO and its major phytonutrients during multiple deep-fat frying cycles. To modify the physicochemical properties of VPO and RCO by blending and comparing the frying characteristics of the blends with those of VPO and RCO alone. VPO is an oil with a unique fatty acid composition and very rich in endogenous bioactive phytonutrients such as carotenoids, tocopherols and tocotrienols. The ability of the phytonutrients to migrate into the fried foods produced using VPO and blends and the stability of the phytonutrients during extended deep-fat frying were investigated. Initial characterization of the oils using non-destructive Fourier transform near-infrared (FTNIR) technique and chemometric model was carried out. Gas chromatography (GC) technique was used to determine the fatty acid composition of the oils. The detector used was flame ionization detector (FID). The thermostability of the oils during frying was evaluated by monitoring the changes in the oil quality as frying time progressed. The quality indices used as evidence of thermal break down were free fatty acids, peroxide value, para-anisidine value, total polar compounds, and color index. Established kinetic models were used to determine the rate of evolution and accumulation of these breakdown compounds as frying temperature and time increased. Spectrophotometry and normal phase HPLC were used to track the changes in the amount of the bioactive phytonutrients present in fresh oil samples, fresh potato, French fries and used oil samples. Kinetic models were used to describe the stability of the phytonutrients. The specific objectives of the research described in this thesis are (i) non-destructive characterization and prediction of the basic chemical properties of crude palm oil (CPO), refined canola oil (RCO) and their binary blends using Fourier transform near-infrared (FTNIR) spectroscopy, (ii) Evaluation of the behavior and thermostability of CPO, RCO and blends as media for repeated deep-fat frying, (iii) To assess and model the degradation kinetics of CPO, RCO, blend at different frying temperatures and times, (iv) To determine the migration and retention of the carotenoids, tocopherols, and tocotrienols in the fried food and (v) To measure the thermostability and the degradation kinetics of the phytonutrients in the samples at different frying temperatures and times.

The following conclusions were drawn from this research:

1) The spectral reflectance response of VPO, RCO and the blend in the near infra-red (NIR) regions can be used to simultaneously characterize the iodine value (IV), free fatty acid (FFA) and peroxide value (PV) of the oil samples. The chemometric partial least square (PLS) prediction model equations for the IV was 1.062X - 3.011; for FFA it was 0.98X + 0.197 and for PV it was 0.939X + 0.115. The wavenumber ranges for the evaluation of IV, FFA and PV of oil samples were found to be 9,403.8 – 7,498.3 cm^{-1}; 7,502.2 – 6,098.2 cm^{-1} and 6,102 – 5,446.3 cm^{-1}, respectively. FTNIR is a fast method that reduces analysis time and reagent use as well as disposal problems associated with the wet chemical methods. It can reduce the cost of analyzing a large number of samples. It is a powerful technique for the routine characterization of vegetable oils before and after utilization.

2) Using VPO in frying plantain crisps resulted in significantly reduced oil uptake and more color changes when compared to using RCO. While the hardness and crispness values were higher in the crisps produced using VPO than the other oils, the values were not statistically significant. Overall, the quality characteristics of the plantain crisps produced using the 70:30 blend of VPO: RCO oil sample were not significantly different in quality from those produced using VPO alone. The moisture loss, oil uptake and color changes that took place during the frying process in each of the oil samples were satisfactorily described by the first order kinetic model. Good quality plantain crisps can be produced using VPO and other oils containing increased quantity of VPO in their blend ratio.

3) The first-order kinetic model adequately predicted changes in FFA and PV; while zero-order kinetic model fittingly predicted changes in *p*-AV, TPC, and color index, when these oils are used in deep-fat frying operations. The rate of changes in the quality indices of the oils and the activation energies were well described by the Arrhenius equation. The study showed that the activation energy E_a was least for PV and highest for FFA. The quality of the blend oil sample (VPO: RCO 1:1 w/w) was not just additive of the qualities of VPO and RCO. The blend assumed its own character and was more stable than VPO and RCO. This can be attributed to the dilution effect of blending which weakened any pro-oxidant

likely present in VPO and induced lag in the oxidation of the blend during frying. Also, reduction in double bond strength combined with synergistic radical scavenging activity of both natural and synthetic antioxidants could have made the blend oil sample most stable. TPC had a significant linear positive correlation with the other oil quality indices especially *p*-AV.

4) Deep-fat frying of French fries in VPO and VPO: RCO blend resulted in substantial enrichment of the fries with bioactive phytonutrients. The type and amount of phytonutrients present in French fries samples depend on the type of oil and the stability of the phytonutrient in the native oil. The order of magnitude found in the fries showed that carotenoids were the most absorbed, followed by the tocotrienols and tocopherols. The first order kinetic model with slight parameter modification adequately predicted the moisture loss, oil uptake and total change in color of the French fries samples. The oil uptake rate was 2 – 4 times lower than the moisture loss rate in the frying oils studied. The biphasic apparent first order model was successfully used to estimate the migration and concentration of the phytonutrients in the fried product. In all cases, the reaction rates of the fast phase were greater than the reaction rates of the slow phase. Even though blending resulted in a dilution and reduction in the initial amount of phytonutrients in the blend oil sample, the blend oil products had the greatest percentage migration of the original phytonutrients in the native oil. Despite differences in the amount of phytonutrients absorbed by the French fries, the potential of enriching French fries by frying in VPO and blend of oils containing VPO has been established.

5) Each phytonutrient homolog deteriorated at a kinetics reaction rate greater than one. The effect of temperature on the deterioration was adequately modeled by the Arrhenius equation with pseudo-R^2>0.99. The γ-tocotrienol was the least stable phytonutrient followed by the γ-tocopherol, while total carotenoids were relatively most stable in VPO. This could be due to higher antioxidant activity of γ-tocotrienol and its reported ability to protect carotenoids. In the RCO, α- and γ-tocopherols are the only endogenous antioxidants detected; the latter was less stable than the former during deep-fat frying. The pattern of deterioration of the tocopherol and tocotrienol homologs in the blend was similar to VPO

but at a significantly lower rate. Overall, the fastest rate of deterioration was observed in γ-tocotrienol and γ-tocopherol irrespective of the oil sample. This was followed by the deterioration rates of α-tocopherol, α-tocotrienol and δ-tocopherol. The slowest rates of deterioration were observed in the carotenoids and δ-tocotrienol. The tocopherols and tocotrienols were comparatively most stable in the blend. The dilution effect of blending lowered the phytonutrients' concentrations. The stability and antioxidant efficacy of endogenous phytonutrients had been reported to depend on certain critical levels in the frying oil. The presence of other antioxidants such as phytosterols, phenolic compounds, and synthetic antioxidants can synergize with the tocochromanols and carotenoids to enhance stability and minimize loss.

CHAPTER 9

9. CONTRIBUTIONS TO KNOWLEDGE AND RECOMMENDATIONS FOR FUTURE RESEARCH

9.1 Contributions to Knowledge

The utilization of unrefined vegetable oils (crude or virgin oils) in food preparations is not widely practiced except perhaps in the case of virgin olive oil. The general notion is that virgin oils in addition to their native triacylglycerol contain pro-oxidants and sometimes are high in free fatty acids (FFA). While many studies have been conducted on the auto- and thermal- oxidation of fats and oils, the mechanisms and by-products of oxidation, the kinetics of deterioration and/or accumulation of each breakdown products have not been well elucidated. The use of non-destructive analytical techniques to monitor food process unit operations and product performance is yet to be fully adopted by the food processing industry. Palm oil, a saturated tropical oil, has in the past been a victim of 'bad' press. Thus, palm oil has a negative image among consumers, especially in the western world. Therefore, this study aimed at addressing this wrong perception of virgin palm oil and addressing the limitations identified above. This thesis thus contributed to the knowledge on the utilization of virgin palm oil, explored oil blending as an optimizing procedure in deep-fat frying and production of fried products that can provide bioactive phytonutrients beside the traditional macronutrients and energy. These contributions include:

I. Fats and oil analysis is laborious and time consuming. Some of the wet methods give results that are highly subjective. A non-destructive technique, FTNIR, was adopted and suitable models were developed for the rapid characterization of fresh, stored and used vegetable oils.

II. This study clearly broadened the understanding of the behavior of virgin palm oil (VPO) as frying medium in deep-fat frying operations under atmospheric conditions.

III. It was demonstrated that blending VPO and refined canola oil (RCO) is a cost-effective way of enriching the frying medium, minimizing oil breakdown and optimize the stability of beneficial bioactive phytonutrients.

IV. Fried foods typically described as “junk foods” became highly enriched with health beneficial bioactive phytonutrients and natural antioxidants through careful selection of frying oil and frying process.

V. The kinetic evaluations and results gave a better understanding of the reaction rates of individual quality parameters of vegetable oil and individual homologs of the phytonutrients especially tocotrienols that have been less studied.

9.2 Recommendations for further research

From this work the following areas of further research were identified:

i. The use of other non-destructive techniques, such as Raman spectroscopy, fluorescence spectroscopy, electron spin resonance spectroscopy and hyperspectral imaging, for rapid characterization and authentication of oil quality parameters should be explored. This will make techniques comparison possible and broaden the horizon for the rapid assessment of the quality of the oil samples.

ii. To investigate and validate the influence of blending VPO and RCO on the triacylglycerol (TAG) composition of the new oil medium. The TAG type and level can have a strong effect on the foaming and stability of the oils during frying.

iii. Examine if the addition of synthetic antioxidants to a natural antioxidant rich matrix such as VPO forms new products at the frying temperatures and to examine the safety thresholds of both the natural antioxidants and the new products formed.

iv. To study the effects of adding other oils rich in other phytonutrients, especially phenolic compounds and phytosterols, on the stability of binary or ternary oil blends.

v. Further investigate the potentials of under-exploited and lesser known sources of natural phytonutrients that are thermostable and can be used to further improve oxidative stability at the elevated frying temperature and time as well as enrich the fried products.

CHAPTER 10

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