The Correlation Between Color and Oxidation Status in High Oleic Deep-Frying Oils: Impact of Antioxidants

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ABSTRACT

Frying oil is a heat and mass transfer medium, which affects the quality of food. The reaction mechanisms in deep-frying oils are mainly thermal oxidation, hydrolysis, and polymerization, which result in lipid deterioration. Addition of synthetic or natural antioxidants can effectively slow down lipid deterioration during deep-frying. Total polar components, polymerized triglycerides, *p*-anisidine value, acid value and iodine value are reliable indicators for assessing oil degradation during frying. Color darkening of deep-frying oils is one of the apparent changes during deep-frying and is closely associated with the levels of decomposition compounds in the frying oils. However, the evidence of the relationship between color and deep-frying oil quality indicators are scanty. The main objective of this thesis is to develop a model for rapid assessment of oil quality during 30-hour deep-frying processes using oil color and quality as indicators. Significant color changes ($p < 0.05$) were observed in soybean oil as compared to canola and sunflower oil during 30-hour deep-frying trials. Canolol-enriched frying oils showed the highest color values before deep-frying, but the final results showed the least color changes ($p < 0.05$) during the 30-hour deep-frying trials. The highest percentage of total polar components (15.55 %), polymeric triglycerides (9.3 %), and *p*-Anisidine value (62.34) were found in TBHQ-enriched deep-frying oil samples in soybean oil. The highest acid value (3.06 mg KOH/100g) was found in canolol-enriched frying oil samples in canola oil. Rosemary and canolol-enriched deep-frying oil samples showed significant effect ($p < 0.05$) on color changes while reducing formation of total polar components, polymeric triglycerides, and aldehydes

during the 30-hour deep-frying study. Significant correlations ($p < 0.05$) were found between color and oil quality indicators in all of the deep-frying oil samples; significant regression ($p < 0.05$) models are expressing the level of oil deterioration from color (light-dark, red-green, yellow-blue) in deep-frying oils. Overall, this study established several models using color as an indicator aiming to rapidly assess deep-frying oil quality.

Keywords: high oleic vegetable oils, deep frying, antioxidants, color, correlations

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LIST OF ABBREVIATIONS

AOCS	**American Oil Chemists' Society**
ASE	**Accelerated Solvent Extraction**
AV	**Acid Value**
CAL	**Canolol-Enriched Deep-Frying Oil**
CON	**Control**
DGF	**German Society for Fat Science**
FFA	**Free Fatty Acids**
HOCAN	**High Oleic Canola Oil**
HOSUN	**High Oleic Sunflower Oil**
HOSOY	**High Oleic Soybean Oil**
IV	**Iodine Value**
***p*-AnV**	***p*-Anisidine Value**
PTG	**Polymeric Triglycerides**
RM	**Rosemary-Enriched Deep-Frying Oil**
TBHQ	***tert*-Butylhydroquinone**
TPC	**Total Polar Components**

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Deep-frying refers to the process of preparing food by immersing in hot oil at high temperature of 150 °C to 200 °C (Pedreschi et al., 2005; Serjouie et al., 2010). During frying, the most common chemical reactions taking place are thermo-oxidation, hydrolysis, and polymerization (Chung et al., 2004; Li et al., 2008). Oil quality will deteriorate with a significant amount of oxidized products in the oils formed during long-term successive deep-frying. Aldehydes, ketones, non-volatile compounds, polymeric, and polar compounds are oxidation products formed in the deep-frying oils, which could impact human health negatively through DNA mutations, gastrointestinal irritations, or oxidation stress (Bansal et al., 2014). As well, these oxidized products change the food flavor, affect food color and texture, shorten the shelf life of deep-fried products, and decrease nutritional quality of foods (Ahromrit & Nema, 2010; Li et al, 2008).

A high oleic vegetable oil could be used to extend the shelf life of frying oils and fried food products (Merrill et al., 2008). Deep-frying studies indicated oleic acid levels should not be too low nor linoleic acid too high because the frying oil and fried food can have lower stability (Warner & Gupta, 2005). In general, linoleate was 40 times more reactive than oleate of the oxygen uptake, and linolenate was 2.4 times more reactive than linoleate (Holman & Elmer, 1947; Min & Bradley, 1992). Linolenic acid needs to be even lower than 5% for frying oils

because linolenic acid–containing vegetable oils such as canola and soybean are well known to produce off-flavors and odors such as "fishy" when they are exposed to deep-frying temperatures (Warner & Gupta, 2005). High oleic canola oil and soybean oil are good for frying because they contain large amounts of oleic acid and lower levels of linoleic fatty acids and linolenic fatty acids than conventional oils. They are high in tocopherols, which enhance the ability to resist polymerization, and have a higher smoking point than the conventional liquid oils (Warner & Gupta, 2005; Syed 2013; Merrill et al., 2008). The oxidative stability of high oleic sunflower oil showed greater results than regular sunflower and soybean oil (Smith, et al., 2007). Thus, it is imperative to understand the action of antioxidants in high oleic oils that are used extensively in North America for commercial frying. Further evaluation and applications of the antioxidants to improve color stability in deep-frying oils is lacking until now.

Additional antioxidants are used by food industries to increase the stability and performance of deep-frying. Recent studies showed strong evidence that additional synthetic antioxidants or natural antioxidants reduced the formation of secondary oxidation products in deep-frying oils. A synthetic antioxidant such as *tert*-butylhydroquinone (TBHQ) is widely used in highly unsaturated oils due to low cost without changing the color and odor of the oils (Wanasundara & Shahidi, 2005; Li et al., 2006). Natural antioxidants such as rosemary extract are used for protecting edible oils against oxidative deterioration, but its cost depends on the concentration, types of formulation and solubility in the frying oils (Cordeiro et al., 2013). Another example of a natural antioxidant not applied commercially, but protective in deep-frying

experiments is Canolol, which is derived in rapeseed via roasting treatments (Aachary et al., 2014; Matthaus et al., 2014).

The factors that influence the stability of frying oils depend on the types of deep-frying oils (internal factor) or operation methods (external factor) (Aladedunye et al., 2016). The external factors that can affect oil quality are: oxygen, frying temperature, frying management, and food preparation. The internal factors are endogenous antioxidants in the oils and fatty acids composition. Quality assessment is used extensively for monitoring the quality of oils in frying processes (Aladedunye & Przybylski, 2009). The level of total polar components (TPC), polymeric triglycerides (PTG), *p*-anisidine value (*p*-AnV), iodine value (IV), and free fatty acids (FFA) are reliable parameters to assess frying-oil quality (Li et al., 2008; Arias-Mendez et al., 2013). Furthermore, color is another important criteria for discarding the deep-frying oils as per regulations of the Manufacturing Process Inspection because darkening of oil is evidence of the unsuitability and requires rejection (Bansal et al., 2010). Recently, our laboratory focused on studies to consider color as a criteria of deep-frying oils as a rapid assessment to monitor the oil quality. One of the main advantages of this approach is that color parameters (Hunter L, a*, b* or Lovibond RYBN) can be obtained rapidly without any solvents (Moyano, et al., 2010). However, limited data is available on oil color changes for high oleic vegetable oils during deep-frying. Data is also limited on the effects of using additional natural antioxidants on the color in high oleic oils during deep-frying. Moreover, the correlation between color and other oil quality indicators in deep-frying tests needs more investigation.

1.2 Hypothesis & Objectives

Hypothesis: Color correlates with oxidative status of deep fried oils.

Objectives: The long-term objective of the study is to assess the oil quality during frying, and establishes a model between color and several quality indicators of deep-frying oils with different additional antioxidants treatments. The specific objectives of the study are indicated below:

1. To assess the color of deep-frying oils using Hunter Lab, Lovibond RYBN.
2. To determine the level of total polar components, acid value, polymeric triglycerides *p*-anisidine value, acid value, and iodine value of deep-frying oil.

3. To develop a multiple linear regression model between color and oil-quality indicators of deep-frying oils.

1.3 Thesis overview

PART 1: GENERAL INTRODUCTION

Chapter 1: This chapter consists of the introduction, objectives and thesis overview.

PART 2: LITERATURE REVIEW

Chapter 2: This chapter summarizes recent literature regarding the oxidation processes in deep-frying oils; the criteria to assess the oil quality; synthetic antioxidants and natural extracts were applied in frying oils to improve the stability of frying oils.

PART 3: MANUSCRIPTS

Chapter 3 (Manuscript 1): Antioxidants during deep-frying stabilization of high oleic

vegetable oils: effect on color parameters

Chapter 4 (Manuscript 2): The relationship between color and oxidation status in high oleic vegetable oils: impact of antioxidants

PART 4: GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES

Chapter 5: General conclusions based on the results obtained from the studies are drawn, the limitations of this study, as well as future perspectives are discussed.

CHAPTER 2

2. LITERATURE REVIEW

This chapter will review the chemical changes such as thermal oxidation, hydrolysis, and polymerization induced during the frying of high oleic oils and in general vegetable oils. This chapter will also evaluate the internal and external factors affecting the quality and the frying stability of deep-fried oils. The antioxidants that are applied to improve the frying stability will be discussed. This chapter will also discuss the antioxidants found in canola meal and canola oil.

2.1 Oxidation Products in Vegetable Oil During Frying

2.1.1 Thermal oxidation

The oxidation mechanism in deep-fried oils is mainly thermal oxidation, which results in the formation of off-flavor, foaming, color darkness and an increase in viscosity of frying oils (Choe & Min, 2007). Both volatile and nonvolatile compounds are identified in the series of chemical reactions that occur during deep-frying (Aladedunye & Przybylski, 2009; Petersen, et al., 2005). Free radical mechanism is a significant reaction leading to thermal oxidation during deep-frying as shown in Figure 2.1 (Marquez-Ruiz et al., 2007; Warner, 2007). The reaction speed of free radical mechanism increases with the oil's temperature (Marquez-Ruiz, et al., 2007; Choe & Min, 2007; Achir, et al., 2007). The mechanism of thermal oxidation involves three stages (Figure 2.2): the initiation stage, propagation stage, and termination stage (Marquez-Ruiz, et al., 2007; Choe & Min, 2007; Chung, et al., 2004).

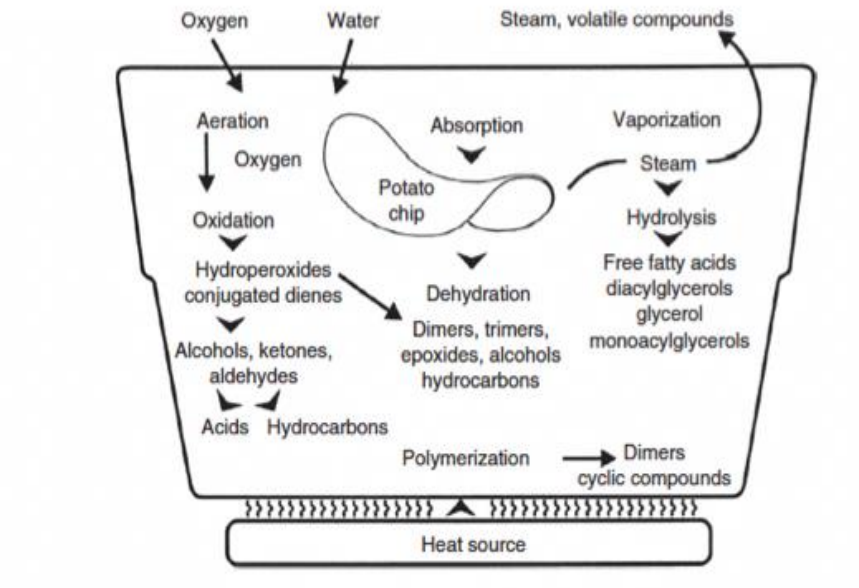

Figure 2.1 Physical and chemical reactions that occur during frying (Warner, 2007)

The initiation stage in the oxidation reaction of oil is the formation of an alkyl radical from an oil molecule by oxidation-reduction mechanism (Marquez-Ruiz, et al., 2007; Chung, et al., 2004; Choe & Min, 2007). A more detailed explanation is that the oil oxidation reaction requires the oil in a radical state to react with radical oxygen. In order to become radical, the hydrogen with the weakest bond on the carbon of oil should be removed first. The radical carbon is rearranged to form a conjugated pentadienyl radical carbon with a trans double bond (Marquez-Ruiz, et al., 2007; Chung, et al., 2004; Choe & Min, 2007). In addition, some factors such as heat, light, metals, and reactive oxygen species facilitate the radical formation in the oil (Ahromrit & Nema, 2010; Achir, et al., 2006).

A free radical chain reaction is induced in the propagation stage of lipid oxidation. The lipid radicals with a reduction potential react rapidly with oxygen to produce peroxyl radicals.

The peroxyl radical with a reduction potential abstracts hydrogen from the fatty acid and produces hydroperoxide and another lipid radical (Marquez-Ruiz, et al., 2007; Chung, et al., 2004; Choe & Min, 2007). Peroxy radicals also react with other radicals to form dimers or polymers. The chain reactions of free lipid radicals and peroxy radicals accelerate the free radical mechanism in the frying oil (Choe & Min 2007; Velasco, et al., 2005).

The formation of non-radical volatile and nonvolatile compounds at the end of oxidation is called the termination stage (Marquez-Ruiz, et al., 2007; Chung, et al., 2004; Choe & Min, 2007). Particularly, hydroperoxides are not generally stable during deep-frying because the oxygen-oxygen bond strength is a relatively weak covalent bond (Nawar, 1984). Hydroperoxides are decomposed to alkoxyradicals and hydroxy radicals by homolysis of the peroxide bond. The alkoxy radical reacts with other alkoxy radicals or is decomposed to form non-radical products (Nawar, 1984). The initiation stage, propagation stage, and termination stage are the chemical mechanisms that contribute to the frying of oils leading to its deterioration.

Initiation	RH	$\longrightarrow R\cdot + H\cdot$
Propagation	$R\cdot + {}^3O_2$	$\longrightarrow ROO\cdot$
	$ROO\cdot + RH$	$\longrightarrow ROOH + R\cdot$
Termination	$ROO\cdot + R\cdot$	$\longrightarrow ROOR$
	$R\cdot + R\cdot$	$\longrightarrow RR$

(R : lipid alkyl)

Figure 2.2 Thermo oxidation in deep-frying oils (Choe & Min, 2006)

2.1.2 Hydrolysis

Water, steam, and oxygen mix together when food is immersed in the hot frying oil, and chemical reactions are started (Figure 2.3) (Choe & Min, 2007; Petersen, et al., 2013). Water is a

weak nucleophile, and it attacks the ester linkage of triacylglycerols producing monoacylglycerol, diacylglycerols, glycerol, and free fatty acids (Velasco, et al, 2005). They accelerate the further hydrolysis reaction of the frying oil (Velasco, et al, 2005). Glycerol evaporates at the frying temperature and the remaining glycerol in oil promotes the production of free fatty acids by hydrolysis (Choe & Min, 2007; Petersen, et al., 2013; Velasco, et al, 2005). Hydrolysis is more likely induced in the oil with more short and unsaturated fatty acids, which are more soluble in water than long and saturated fatty acids (Nawar, 1986). In other words, water from foods is easily accessible to short-chain fats and oils for hydrolysis, and large contact between the oil and the water phase of food increases hydrolysis of frying oil (Choe & Min, 2007; Petersen, et al., 2013). Hydrolysis can produce large amounts of free fatty acids, which makes the oil less acceptable for deep-frying.

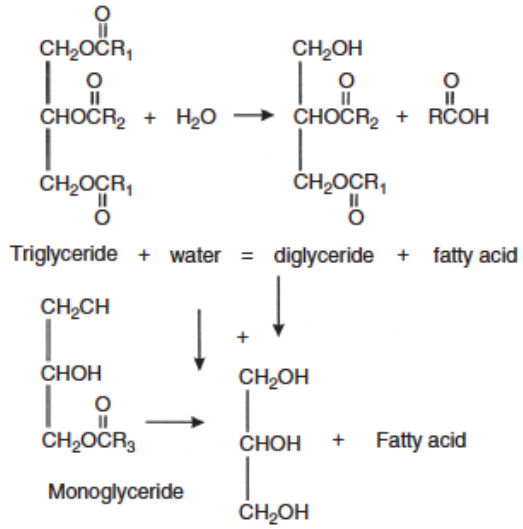

Figure 2.3 Hydrolysis in deep-frying oils (Warner, 2007)

2.1.3 Polymerization

The main decomposition products of oils subjected to frying are nonvolatile polar compounds and triacylglycerol dimers and polymers (Steel et al., 2006; Choe & Min, 2007). As the frying temperature and the numbers of frying increase, the amounts of dimers and polymers are increased (Steel et al., 2006; Choe & Min, 2007). Dimers or polymers are either acyclic or cyclic depending on the reaction process and kinds of fatty acids in the oil. Dimers and polymers can be polar or nonpolar depending on whether the monomers are connected by a carbon-carbon, carbon-oxygen-carbon, or a carbon-oxygen-oxygen-carbon linkage, and the presence or absence of hydroperoxy, epoxy, hydroxy or carbonyl functional groups (Steel et al., 2006; Choe & Min, 2007). The formation of dimers and polymers will be discussed in detail later.

Dimerization and polymerization in deep-frying oils can occur via radical and non-radical reaction routes (Steel et al., 2006; Choe & Min, 2007). The two kinds of dimers, oxydimers and peroxydimers, are formed through dimerization of two radicals at the termination stage. Also, as earlier mentioned, triacylglycerols react with oxygen and produce alkyl hydroperoxides or dialkyl peroxides in the oil, and they are readily decomposed to alkoxy and peroxy radicals by homolytic scission. Alkoxy radicals can abstract hydrogen from oil molecule to produce hydroxy compounds, or combine with other alkyl radicals to produce oxydimers. Peroxy radicals can combine with alkyl radicals and produce peroxy dimers (Steel, et al., 2006; Choe & Min, 2007). A non-radical, cation-initiated reaction mechanism for the dimerization of unsaturated fatty acids has also been proposed and suggested to be more important than the radical mechanism under frying conditions (Kochhar & Gertz, 2004; Gertz, 2004).

Diels-Alder reaction, the combination reaction between conjugated diolefinic and olefinic structures have also been proposed to be involved in the dimerization process of frying oil (Steel et al., 2006). However, in a recent NMR study, no evidence of Diels-Alder reaction products were found in soybean oil oxidized at the frying temperature (Hwang et al., 2013). The formation of cyclic compounds in frying oil depends on the degree of unsaturated fatty acids and the frying temperature (Steel et al., 2006; Choe & Min, 2007). From the same study, cyclic polymers increased as the amount of linolenic acid increased. Furthermore, the cyclic compounds are not reached to a significant level until the oil temperature reaches 200 °C to 300 °C (Steel et al., 2006; Choe & Min, 2007).

2.2 Synthetic Antioxidants vs. Natural Antioxidants

Frying temperature and heating duration can affect the antioxidant content in vegetable oils (Houhoula, et al., 2003; Arias-Mendez, 2013). Most frying operations are conducted at temperatures of 175 °C to 195 °C, while German regulations allow maximal frying temperatures of up to 165 °C to limit formation of acrylamides (Rojas, et al., 2013). The prolonged heating at high temperature in the presence of moisture and oxygen causes an interrelated series of chemical reactions in the oils (Petersen, et al., 2013; Choe, & Min, 2007). As a result, a number of harmful compounds are produced that degrade the quality of vegetable oils and fried foods. Although frying oils remain susceptible to the deteriorating effects of oxygen and high temperatures during frying, the addition of synthetic or natural antioxidants to the oils is

commonly used for reducing lipid thermo-oxidation (Shahabadi et al., 2009; Lalas & Dourtoglou et al., 2003). Recent studies showed that synthetic antioxidants, notably, butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT) and *tert*-butylhydroquinone (TBHQ) are concerning to consumers; however, natural antioxidants and their blends have been effective in food products containing fats and oils (Li et al., 2006).

2.2.1 *tert*-Butylhydroquinone (TBHQ)

tert-butylhydroquinone (TBHQ) is a oil soluble antioxidant widely used in a variety of fats and oils, particularly highly unsaturated vegetable oils and edible animal fats, because of its low cost; as well, it does not change the color, flavor or odor of the oil initially (Wanasundara & Shahidi 2005; Shahabadi et al., 2009; Li et al., 2006). TBHQ has a similar structure to butylatedhydroxyanisole (BHA), as it contains a tert-butyl moiety. It can be made from hydroquinone by alkylation with t-butanol (Domingos et al., 2007). The antioxidant activity of TBHQ is superior compared with other commonly used synthetic antioxidants such as butylatedhydroxytoluene (BHT) or butylatedhydroxyanisole (BHA) in frying tests (Li, et al., 2006; Reda, 2009; Sharayei, 2011). TBHQ exhibited significant antioxidant activity especially at high temperatures in both frying and emulsion systems (Domingos, 2007). According to Li, et al. (2006), in deep-frying experiments TBHQ was readily distributed into the oil phase and in emulsions acted as effectively as an antioxidant. Compared to BHT and BHA, TBHQ is more hydrophilic; thus, it is easier to congregate at the interface of air–lipid, and protect oils and fats from the autoxidation (Domingos, 2007; Shahabadi, 2009).

TBHQ indicated its efficacy as an antioxidant by production of conjugated dienes, peroxides and aldehydes under the frying process conditions (Wanasundara & Shahidi, 2005; Ou et al., 2010). The level of conjugated dienes throughout the frying process was lowest in the canola oil containing 100 ppm TBHQ compared with the same concentration of BHT and BHA during a 5-day deep-frying study of potatoes at 190 °C (Ou et al., 2010). Another important result observed for TBHQ was reducing the levels of peroxides after 16 hours of heating (Ou et al., 2010; Li et al., 2006). According to Ou et al., (2010), TBHQ showed a remarkable antioxidant potential on secondary decomposition products such as aldehydes and ketones, which contribute to rancid and unpleasant flavors and reduce the nutritional value of fried foods (Ou et al., 2010). TBHQ has significant benefits in protecting deep-frying oils, but it became less efficient due to degradation through volatilization or decomposition, which have negative effects on human health (Li et al., 2006; Reda, 2009; Shahbadi, 2009; Sharayei, 2011). Although synthetic antioxidants are low-cost and effective, the commercial use of synthetic antioxidants is strictly controlled (Okubo, 2003). The toxicity and carcinogenic effects, and growing consumer concerns about their safety have directed attention toward the use of natural antioxidants as alternatives to synthetic compounds (Okubo, 2003).

2.2.2 Rosemary extracts (*Rosmarinus officinalis L.*)

Natural antioxidants are a proven alternative to synthetic antioxidants. Natural antioxidants derived from fruits, herbs, and cereals, have been utilized by the food industry (Yanishlieva, et al., 2006) for many years. Rosemary extract (*Rosmarinus officinalis* L.) has been shown to be an

excellent protection factor in the oxidative stability of frying oils (Cordeiro, et al., 2013; Gertz, 2004; Lalas & Dourtoglou, 2003). The compounds in rosemary extract that are active against thermal oxidation were carnosol, rosmarinic acid, carnosic acid, caffeic acid, and rosmanol (Carvalho, et al., 2005; Caldera, et al., 2012).

The methods for extracting the antioxidant compounds from rosemary include hydrodistillation, soxhlet extraction, microwave-accelerated hydrodistillation (MAHD) and supercritical fluid extraction (SFE) (Boutekedjiret, et al., 2003; Caldera, et al., 2012). Rosemary extract obtained through supercritical fluid extraction showed good antioxidant profile in frying tests (Carvalho, et al., 2005; Boutekedjiret, et al., 2003; Caldera, et al., 2012). One of the advantages of SFE is the extraction can be obtained without toxic solvent used; further, supercritical extracts are often recognized for superior quality when compared with those produced by hydro-distillation or liquid-solid extraction (Caldera, et al., 2012; Boutekedjiret, et al., 2003). The chemical composition of rosemary extract varies widely depending on agricultural conditions of cultivation as well as the extraction technique used (Carvalho, et al., 2005). It has been reported that rosemary extracts from SFE have the highest antioxidant activity compared to that obtained by extraction with organic solvent, as the ratios between carnosic acid and carnosol in SFE extracts are greater than those from other methods (Carvalho, et al., 2005).

According to Cordeiro, et al., (2013), both rosemary extract and TBHQ in vegetable oils showed remarkable antioxidant activity at storage temperatures as well as frying temperatures. Rosemary displayed a more effective protective action compared to TBHQ (Cordeiro, et al.,

2013). Based on studies by Cordeiro, et al. (2013) and Lalas & Dourtoglou (2013), rosemary extract proved an effective antioxidant during frying in canola oil. However, both synthetic antioxidants or natural antioxidants decompose during deep-frying, with the loss attributed to the volatilization or decomposition of bioactive constituents, such as carnosic acid (Lalas & Dourtoglou, 2013). Furthermore, Lalas & Dourtoglou (2003) mentioned that fried foods such as potato chips oxidize easily, thus losing commercial value and health properties. Rosemary extract exhibited its remarkable activity by increasing the resistance to oxidative rancidity not only of the frying oils, but also oils absorbed in potato chips, thereby improving the storage stability of the chips (Lalas & Dourtoglou, 2003).

2.2.3 Tocopherols

Tocopherols and tocotrienols belong to the family of vitamin E active substances (Gliszczynska-Swiglo, et al., 2007). They are a group of naturally occurring compounds in plants, and are the endogenous antioxidants widely distributed in oilseeds (Aladedunye & Przybylski, 2011). Tocopherols are major lipophilic antioxidants, and efficient scavengers of alkoxyl and peroxyl radicals (Gliszczynska-Swiglo, et al., 2007). The efficacy of α-, β-, γ-, δ-tocopherols, and tocotrienols are differentiated by the number and location of methyl substituents in the chromane ring (Gliszczynska-Swiglo, et al., 2007). The antioxidant ability of tocopherol isomers is different, γ-tocopherol has the highest radical-scavenging capacity (Gliszczynska-Swiglo, et al., 2007; Aladedunye & Przybylski, 2011). Also, the contents of tocopherols (Table 2.2) are associated with the types of oilseeds. Tocopherols have been reported to increase the oxidative

stability of vegetable oils rich in polyunsaturated fatty acids during frying (Al-Khusaibi, et al., 2012). The most abundant nonpolar phenolic compounds in rapeseed are tocopherols but their content decreases as the oil refining increases (Al-Khusaibi, et al., 2012).

Table 2.1 The Range of Tocopherols Content in oilseeds (μg / mg)

Oil type	α-tocopherol	β-tocopherol	γ-tocopherol	δ-tocopherol	Total tocopherol
Rapeseed oil	280-320	ND	410-420	10-13	710-740
Canola	197-290	ND	246-603	ND	594-893
Sunflower	671-883	14-23	4-13	ND	698-898
Soybean	59-116	4-17	578-1247	263-352	974-1739
Olive	96-188	1-6	10-12	ND	114-200

Reference: Al-Khusaibi, et al., 2012; Aladedunye & Przybylski, 2011; Aladedunye & Przybylski, 2009.
ND: Not Detected

2.2.4 Phenolic compounds in canola meal

Canola is one of the most important oil-seed crops in the North American (Serjouie, et al., 2010). The fatty acid composition of canola oil offers important health benefits as well as improved nutritional value carried by fried foods (Serjouie, et al., 2010; Matthaus, 2006). Canola oil is high in oleic acid, and low in saturated fatty acids; it has moderate levels of polyunsaturated fatty acids, of which most are linoleic and linolenic acids (Serjouie, et al., 2010; Matthaus, 2006). However, due to its high levels of linoleic and linolenic acids, this oil is not optimal for frying which has been documented in some studies (Serjouie, et al., 2010). For

example, 4-hydroxynonenal (HNE), a secondary oxidation product formed by oxidative degradation of linoleic acid, which is related to pathogenesis of several human diseases (Serjouie, et al., 2010). Large amounts of phenolic compounds however are found in canola meal including phenolic acids, flavonoids and tannins (Sun-Waterhouse, et al., 2012; Catel, et al., 2012). They exhibit antioxidant activity that improves frying performance and oxidative stability in frying oils (Sun-Waterhouse, et al., 2012; Catel, et al., 2012. The application of rapeseed antioxidants for improving frying stability and thermo-oxidation is discussed later (Ch 4).

Phenolics vary in the carbon skeleton and hydroxylation of the phenolic rings (Balasundram, et al., 2006). Phenolic compounds can suppress lipid oxidation by donating hydrogen atoms to lipid peroxyl radicals and interfere with the initiation or propagation of primary oxidation (Balasundram, et al., 2006). Canola meal contains large amounts of phenolic compounds. The amount of phenolic compounds in dried canola meal is about ten times higher than soybean meal (Spielmeyer, et al., 2009; Thiyam, et al., 2003; Aladedunye & Przybylski, 2011). Phenolic compounds in canola or rapeseed include sinapic acid, phenolic acids, flavonoids, and condensed tannins, with sinapic acid the main phenolic compound present. The post-expelled crude rapeseed oil contains the greatest amount of phenolics, but an increasing degree of oil refining will decrease the content of phenolics (Spielmeyer, et al., 2009; Thiyam, et al., 2003). In order to maintain a high content of phenolic compounds in the oil after the refining process, phenolic compounds extracted from the rapeseed meal can be added after the refining process to the oil (Sun-Waterhouse, et al., 2012).

Phenolic compounds are readily extracted from canola by the solvents such as methanol or ethanol using conventional extraction techniques (Balasundram, et al., 2006). Methanol was the most efficient solvent for extracting phenolic compounds from canola seed as it gave the highest total phenolic content, as well as the highest contents for the major phenolics, including sinapine, sinapoyl glucose and sinapic acid (Balasundram, et al., 2006). Canola oil supplemented with a fraction rich in phenolic acids isolated from canola meal, and the addition of sinapic acid showed higher oxidative stability and inhibits the formation of 4-hydroxynonenal (HNE) in frying tests (Aladedunye & Przybylski, 2011; Sun-Waterhouse, et al., 2012).

Canolol is a highly active antioxidant and potent lipid peroxyl radical scavenger found in rapeseed (Wakamatsu, et al., 2005). It has been reported to show greater antioxidant power than other rapeseed phenolic compounds (Spielmeyer, et al., 2009; Thiyam, et al., 2003; Wakamatsu, et al., 2005). The chemical structure of canolol is 4-vinyl-2,6-dimethoxyphenol, which can be formed by decarboxylation of sinapic acid (Wakamatsu, et al., 2005). Canolol can be produced by decarboxylation of sinapic acid during the cold press process or roasting of the seeds (Wakamatsu, et al., 2005). Thus, the food value of the rapeseed and rapeseed oil may be enhanced by elevating the canolol content through heat related processing or by roasting of rapeseed before pressing. Different roasting conditions were tested and compared with the optimum roasting temperature for canolol formation being 160 °C (Spielmeyer, et al., 2009). The canolol content of the rapeseed samples with optimal roasting was recorded as 720 μg/g, which is a 120-fold increase compare to the unroasted sample (Spielmeyer, et al., 2009). However, the

canolol content decreases when the roasting temperature was over 170 °C (Spielmeyer, et al., 2009). This decrease of canolol content must result from potential side reactions of canolol with other rapeseed components such as lipid peroxyl radicals that accumulate during the heat treatment (Spielmeyer, et al., 2009). Thermal decomposition of canolol can also occur during the prolonged roasting of rapeseed.

To test the antioxidant activity of phenolic compounds during frying conditions, individual phenolic compounds were added to the stripped Canola oil after removing endogenous tocopherols (Aladedunye & Przybylski, 2011; Catel, et al., 2012; Sun-Waterhouse, et al., 2012). This purification step was necessary to assess the accurate antioxidative potential of the added individual phenolic compounds; otherwise, the endogenous antioxidants present in the oil may interfere with the test results (Catel, et al., 2012; Sun-Waterhouse, et al., 2012). The formation of conjugated dienes, a measure of primary oxidation products, and hexanal, which is a secondary oxidation product, were monitored during the period of frying and the antioxidant activity of the phenolic acids was established (Aladedunye & Przybylski, 2011; Sun-Waterhouse, et al., 2012). The addition of sinapic acid inhibited hydroperoxide formation as compared to alpha-tocopherol (Catel, et al., 2012; Sun-Waterhouse, et al., 2012). Phenolic acids, including sinapic acid, have also been shown to be potent radical scavengers and antioxidants in several lipid-containing systems (Catel, et al., 2012; Sun-Waterhouse, et al., 2012; Thiyam et al., 2007).

2.3. The Criteria Used to Assess Quality of Deep-Frying Oils

Generally, frying temperature, frying frequency, frying time, oil replenishments, fatty acid profile of frying oils, and food ingredients are main factors which could affect oil and deep-fried food quality. Deteriorations of oils used in frying are generally followed by changes in the chemical components of the oil (Figure 2.4) (Aladedunye & Przybylski, 2009; Warner, 2007). During the frying process, oil quality decreases due to the formation of undesirable compounds that are human health hazards (Aladedunye & Przybylski, 2009). Therefore, various criteria have been developed to judge the quality of frying oils (Aladedunye & Przybylski, 2009; Li et al., 2008; Bansal et al. 2010). Quality assessment of high oleic oils in frying processes are usually conducted by the analysis of total polar components (TPC), peroxide value (PV), *p*-Anisidine value (*p*-AnV), level of free fatty acids, color and viscosity.

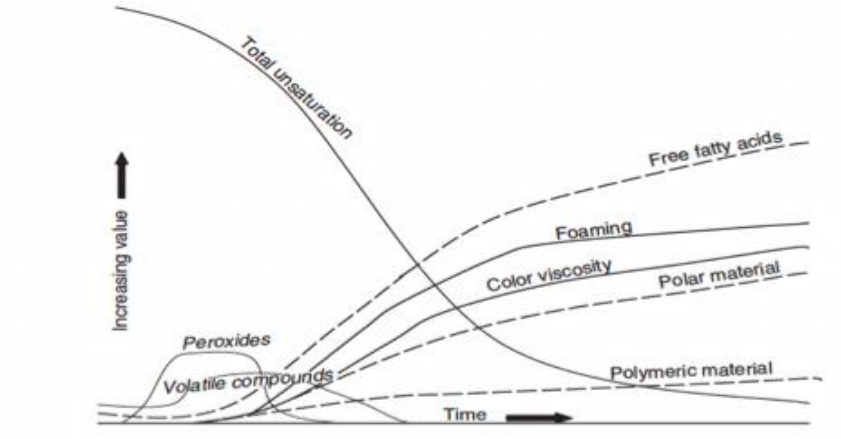

Figure 2.4 Formation and degradation of compounds during frying (Warner, 2007)

2.3.1 Total Polar Components

Analysis of total polar components (TPC), also referred to as total polar materials (TPM), is one of the most reliable criteria for assessing the quality of deep-frying oils (Aladedunye &

Przybylski, 2009; Houhoula et al., 2003; Li et al., 2008). Total polar components include all newly formed compounds that have higher polarity, which can be summarized as mono- and diglycerides and free fatty acids, dimeric and polymeric triglycerides and fatty acids, and oxidized triglyceride monomers (Warner, 2007). The maximum levels for polar compounds of frying or cooking fats and oils is 25–27 g per 100 g oil (Aladedunye & Przybylski, 2009; Houhoula et al., 2003; Li et al., 2008). Total polar components can be measured with AOCS Official Method Cd 20-91 or Fourier-Transform-Near Infrared (FT-NIR) with standard methods C-I 1 to C-I 5 from DGF; NIR spectroscopy analyzes organic materials with respect to their tendency to absorb light in a certain area of the electromagnetic spectrum. This DGF standard method specifies a procedure for the rapid analysis of four important parameters of oxidative degradation in used frying fats and oils with pre-calibrated Fourier-transform-NIR (FT-NIR) spectroscopy (Gertz, et al., 2013). According to Gertz (2001), the method is applicable to all fats and oils used for frying food, and other bakery products.

2.3.2 Polymeric Compounds

The content of polymerized triglycerides in deep-frying oils is defined as the sum of all di- and oligomer triglycerides, and is expressed as a percent (Gertz, 2001). The contribution of polymers in total polar components increases consistently with frying time and frying temperature (Aladedunye & Przybylski, 2009; Houhoula et al., 2003; Li, et al., 2008). Large amounts of polymers are generated in palm oil at 185 °C at the end of 7 days of frying compared with the polymer content after the first day. There is a 16-fold increase in polymers when

increasing the frying temperature up to 215 °C (Houhoula et al., 2003). As the polymers increases, the quality of the frying oil is reduced and degraded. The predominant group of non-volatile compounds formed during frying of unsaturated fats includes dimers and oligomers. These high molecular weight compounds are mostly formed in the termination stages of free radical oxidation. According to the type of fatty acid precursors, these carbon-carbon dimers include monoene, diene, and tetraene structures. Polar dimers are oxygenated and form ether by combing alkyl and alkoxyl radicals and are linked by ether bonds C-O-C, or by combing radical containing oxygenated functions (hydroxyl, keto, epoxy). Polar dimers linked by peroxy bonds (C-OO-C) are only formed at low temperatures and decompose at elevated temperatures above 100 °C. Even though there is no information on the intake of oxidized fats, it is known that fried foods are important contributors to the ingestion of oxidized fatty acids in normal diets (Marmesat et al., 2012). The polymeric compounds are easily absorbed and have been associated with the development of cardiovascular diseases and certain types of cancer (Márquez-Ruíz et al, 2007). In most of Europe, the frying fats are recognized as objectionable and to be rejected if the level of the polar materials exceeds 25-30%. This range of polar materials corresponds to 13-15 % polymeric triglycerides. Normally, the rejection point was set up to 10 % of polymeric triglycerides by most food industries (Frankel, 2014).

2.3.3 *p*-Anisidine Value

p-Anisidine value (*p*-AnV) is defined by converting as 100 times the optical density measured at 350 nm in a 1 cm cuvette of a solution containing 1.00 g of the oil in 100 mL of a

mixture of solvent and reagent. It has been adapted to measure the level of aldehydes under certain frying conditions in vegetable oils with the reject level of *p*-AnV being 30 (Chung et al., 2004; Firestone, 2009; Kim et al., 2013; Bansal et al., 2010). During frying, aldehydes are formed, and although some of the aldehydes produced are volatile and lost by evaporation during frying, a significant amount remains and is assessed by *p*-AnV (Kim et al., 2013). *p*-AnV reached the maximum value in the middle of a 7-day frying period, and then decreased consistently until the end of frying period (Kim et al., 2013). *p*-AnV increases because the decomposition of hydroperoxides increases with elevating frying temperature (Kim et al., 2013; Li et al., 2008); aldehydes are the secondary oxidation products of the decomposition of lipid hydroperoxides. Furthermore, *p*-AnV is influenced by the level of polyunsaturated fatty acids, linoleic and linolenic acids (Aladedunye & Przybylski, 2009). The higher the content of polyunsaturated fatty acids, the higher the *p*-AnV in the frying oils (Aladedunye & Przybylski, 2009). Thus, *p*-anisidine value is not only influenced by the frying temperature, but also by the amount of polyunsaturated fatty acids in the oil.

2.3.4 Acid Value

Elevated levels of free fatty acids (FFAs) contribute to smoke and off-flavors of vegetable oils (Kim et al., 2013). Glycerol partially evaporates because it volatilizes above 150 °C, and the reaction equilibrium is shifted in favor of other hydrolysis products. The extent of hydrolysis depends on oil temperature, interface area between the oil and the free fatty acids and low molecular weight acidic products arising from fat oxidation enhance the hydrolysis in the

presence of steam during frying. Hydrolytic products, such a free fatty acid, decrease the stability of frying oils and can be used as a measure of oil fry life (Warner, 2007). The increase in acid value content during frying is due mainly to hydrolysis and partly due to the carboxylic groups present in polymeric products of frying (Kim et al., 2013; Li, et al., 2008; Aladedunye & Przybylski, 2009). The acid value is determined by the number of milligrams of KOH necessary to neutralize 1 g of the oil sample. Frying oils and fats must be rejected when the acid value reach to 2.0 – 2.5 mg KOH/100g. Although FFA content is not a particularly good parameter for comparing different frying processes or oil stability, it can still be used as an indicator of oil quality (Li, et al., 2008). This is because FFA has a significant effect on the organoleptic quality of fried foods, due to the extensive mass exchange between the frying oil and the fried food.

2.3.5 Iodine Value

Measuring levels of polyunsaturated fatty acids, such as linoleic acid, can help determine extent of thermal oxidation (Choudhary, et al., 2014). Iodine value is a measure of the number of double bonds in the oil. Canola oil has iodine value of about 188–193, while sunflower oil ranges from 110–143, soybean oil has iodine value from 120–143, high oleic safflower oil has iodine value from 90–100 (Knothe, 2002). In general, deep-frying processes decrease the content of unsaturated fatty acids in frying fat and oil due to oxidation and polymerization. During deep-frying at 160 °C, a progressive decrease in unsaturation was observed in all of the oil samples (Lalas, 2009). This decrease shows the consumption of double bonds by oil oxidation. While the decrease in iodine value results from complex physicochemical changes, it is

indicative of the oxidation rate (Lalas, 2009) and could be a useful quality parameter to control oil quality during frying. Choudhary et al., (2014), found that the relative loss of the C 18:2 fatty acid and a decrease in the iodine value of oil after heating was due to more intensive thermo-oxidative transformations occurring as compared to heated oil containing food. The decrease in the iodine value can be attributed to the destruction of double bonds by oxidation, scission, and polymerization. Heat treatment causes oxidative rancidity resulting in an increase in the free fatty acids. This is why heated and unheated fats and oils should be monitored by analysis of the fatty acid composition and iodine value to indicate the degradation of the fatty acids (Choudhary et al., 2014).

2.3.6 Color

Color changes in deep frying oil not only represents physical changes towards a darker color, but also indicates possible alterations in the stability and nutritional composition as well as health-related effects of deep frying food products and oils (Zhang et al., 2015; Siger et al., 2015). Food contains carbohydrates, fats, proteins and other nutrients and undergo complex reactions during deep-frying, with the formation of numerous polymeric and degradation products are associated with color darkening in deep-frying oils (Zhang et al., 2015). As well, the pigments from food can be exchanged into deep-frying oils during deep-frying processing. Browning such as caramelization and Maillard reaction is one of the most important chemical processes, which is occurring in food during the deep-frying (Quintas et al., 2007; Siger et al., 2015). Leaching of pigments from the food into the frying oil, and the presence of Maillard reaction products,

formed during frying by the reaction of carbohydrates and some lipid oxidation products with amines, amino acids, and proteins also affects color development (Corzo-Martinez et al., 2012; Mah & Brannan 2009; Delgado-Andrade et al., 2010). Furthermore, particles from food being fried can become caramelized and release some fat-soluble pigments into the oil (Vijayan et al., 1996). Products with a molecular weight of 300–551 Daltons and containing double bonds, carboxyl, ester, peroxide or hydroxyl functions contribute to the darkening of oil during frying (Aladedunye, 2011). The previous deep-frying studies indicated darkening of oil is evidence of the unsuitability of frying oils and requires rejection，therefore color should be one of the criteria for discarding the frying oils (Bansal, et al, 2010). One of the main advantages of the objective measurement of color is that accumulative effects of several parameters can be in a matter of seconds, color assessment therefore can be very appropriate to obtaining a rapid estimation of the quality of frying oils (Moyano, et al., 2010).

The principle of color measurement is that matching the color of the light transmitted through a specific depth of liquid fat or oil to the color of the light originating from the same source, transmitted through glass color standards (AOCS Official method Cc 13e-92). Wesson (AOCS method Cc 13b-45), Lovibond (AOCS method Cc 13e-92) and spectrophotometric (AOCS method Cc-13c-50) procedures are official methods recognized for the measurement of color in frying oils (Firestone, 2009). The Wesson and Lovibond methods are colorimetric methods used to determine the color of the oil by comparison with colored glasses of known characteristics. In the spectrophotometric method, the absorbance of the oil is measured at 460,

550, 620, and 670 nm, and the photometric color index (PCI) is computed according to the equation: $PCI = 1.29(A_{460}) + 69.7(A_{550}) + 41.2(A_{620}) – 56.4(A_{670})$. Where A_{460}, A_{550}, A_{620}, and A_{670}, are absorbance at 460, 550, 620, and 670 nm, respectively. The spectrophotometric method at 490 nm was used widely for oil color assessment during frying processes (Umbreit & Russell 2013; Xu, 2003; Aladedunye & Przybylski, 2009). The Lovibond color scale is an internationally accepted uniform color measurement. The 3-dimensional color scale of Lovibond Hunter Lab was developed according to human perception, the chromatic coordinate L indicates the lightness of color (L = 0 yields black and L = 100 means diffuse white); a* characterizes the position between red and green, which negative values indicate green and positive values indicate red; b* suggests the position between yellow and blue, which means negative values indicate blue and positive values indicate yellow (Zhang, et al., 2014).

Results from previous studies suggested that colorants in deep-frying oils include secondary oxidation products, sugar fragments and proteins (Quintas, et al., 2007). A red color may correlate with the oxidized fatty acids and pyrolytic condensation products in the oil, while a yellow color may relate to the combined peroxides and aldehydes in the oil (Maskan, 2003; Pedreschi, et al., 2005). According to Aladedunye & Przybylski, (2009), an increase in the optical density of frying oil was recognized with the 30 °C increase in frying temperature in all vegetable oil samples examined. A study on the spectrophotometric method for the rapid assessment of frying oils by Xu, (2000), reported that the highest correlation was observed between absorbance measured at 490 nm and the TPC value (r = 0.953). The results of a recent

study by Bansal et al. (2010), however, showed that any wavelength in the range of 400–500 nm could be utilized to provide a good correlation between TPC and the spectrophotometric absorbance. Irrespective of the methods used, results obtained on color formation during frying must be interpreted with caution as the rate of color development differs from oil to oil and also depends on the initial color of the oil and the type of the food fried in it (Gertz 2001).

Generally, the colors of vegetable oils depend on the seeds, harvest, or soil conditions. Vegetable oil has its own color; factories monitor each stage of the refining process to reach their standard range (O'Brien, 2009). The color of high oleic oil varies depended on the oils, for example, sunflower oil has lighter color than canola oil and soybean oil, because soybeans contain more pigments than sunflower and canola, which cannot be removed completely during oil processing (Gupta & Warner, 2005). The color of deep-frying oils and deep-fried foods are important to consumers; as well, higher absorbance at 490 nm with spectrophotometric approach in deep-frying oils is associated with total polar materials during deep-frying (Xu, 1999; Xu, 2003; Aladedunye & Przybylski, 2009). Thus, color darkening in deep-frying oils is associated with the quality of deep-frying oils and deep-fried foods. Thus, researchers are looking for rapid methods to assess oil quality during deep-frying, and color measurement is particularly interesting to the food industries because of the numbers of advantages; for example, color analysis of deep-frying oils is a simple, fast procedure without the use of toxic solvents. However, evidence is lacking on the relationship between color (light-dark, red-green, yellow-blue) and reliable oil quality indicators in high oleic oils. The majority of deep-frying

studies showed oil color darkening was positively correlated with frying time and frying temperatures, but they did not indicate how the oxidation products effect on color changes during deep-frying (Xu, 2003; Aladedunye & Przybylski, 2009). Antioxidants significantly inhibited lipid deterioration, but there is no evidence that additional antioxidants affected color changes during deep-frying in high oleic oils. Consequently, there a need for a systemic study of color changes during deep-frying processes.

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CHAPTER 3

MANUSCRIPT 1

The Impact of Antioxidants in Improving Deep-Frying Stability of High Oleic Oils: Effect on Color Parameters

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Short version of title: Improving color by antioxidants in high oleic deep-frying oils

3.1 Abstract

Color darkening of vegetable oils during deep-frying is a complicated process, involving the thermo-oxidation of the oil during frying the food. This study compared the effect of three antioxidants (200 ppm *tert*-butylhydroquinone (TBHQ), 200 ppm rosemary extracts (RM), 200 ppm canolol-enriched extracts (CAL) on the color of high oleic canola oil, high oleic sunflower oil, and high oleic soybean oil during frying. Six batches of straight-cut potatoes (100 g each) were fried each day at 185 ± 5 °C for 4 minutes, 60 minutes apart for a total of 6 hours per day of frying for 5 days. Two color measurements: Hunter L a* b*, and Lovibond RYBN were used for color analysis of the fried oils. After 5 days of frying (30 hours), the largest total color change was found with the oil samples containing RM, and the smallest color change was observed in the oil samples supplemented with CAL. Control samples and TBHQ samples did not show significant ($p < 0.05$) changes in oil darkening. CAL had the greatest efficacy in controlling the total color change during the 5-day frying period.

Key words: *high oleic vegetable oils, deep-frying, quality assessment, antioxidants, color analysis*

3.2 Introduction

The color of deep-frying oils is the most obvious change observed during deep-frying. The color of deep-fried foods is one of the most important attributions to consumers, who may be influenced by the color of deep-frying oils. Researchers tend to overlook the important influence of color while investigating chemical indicators such as total polar components, aldehydes or hydroperoxides, and free fatty acids of the oils. The oxidation products of lipid oxidation have been associated with oil color darkening, which has an adverse effect on food color, odor, flavor, and nutritional value. Thus, color measurement is a rapid assessment that has commonly been used as an index for determining the quality of used oils (Maskan 2003; Totani et al., 2012, Smith et al., 2007). Various scales for color measurement of edible oils during frying have been introduced for assessment of color, including Hunter Lab, Lovibond RYBN, and spectrophotometric methods (Umbreit & Russell 2013; Xu, 2003; Aladedunye & Przybylski, 2009).

To enhance the quality of frying, a high-stability vegetable oil is used to extend the shelf life of frying oils and fried food products (Merrill et al., 2008). Deep-frying studies showed oleic acid levels should not be too low or linoleic acid too high because the frying oil and fried food would have lower stability (Warner & Gupta, 2005). Linolenic acid should be less than 5% in frying oils because linolenic acid-containing vegetable oils such as canola and soybean are well known to produce off-flavors and odors such as “fishy” when exposed to deep frying temperatures (Warner & Gupta, 2005). High oleic canola and soybean oils, however, are good

for frying because they contain large amounts of oleic acid and lower levels of linoleic fatty acids and linolenic fatty acids compared to conventional oils. As a result, they have better ability to resist polymerization, and a higher smoking point than conventional liquid oils (Warner & Gupta, 2005; Syed, 2013; Merrill et al., 2008). The oxidative stability of high oleic sunflower oil showed greater stability than regular sunflower and soybean oil (Smith, et al., 2007). Thus, it is important to understand the potential of antioxidants in high oleic vegetable oils that are used commonly for frying foods, especially in relation to the stability of color darkening of frying oil (Matthaus, 2006).

Synthetic and natural antioxidant extracts used to increase frying stability and extend the performance of deep-frying. They decrease the formation of polar compounds, diacylglycerols, and free fatty acids and increase the frying life and quality of oils (Wanasundara & Shahidi 2005; Li et al., 2006). TBHQ, RM are often used in highly unsaturated vegetable oils to protect edible vegetable oils against oxidative deterioration during frying (Cordeiro et al., 2013). Previous studies showed the effectiveness of canolol enriched extracts at elevated temperature to slow down peroxides formation in high oleic canola oil; however, they have not established that antioxidants retard the development of oil darkness (Aachary, 2014). The present study focuses on: 1) evaluating the oil color changes during a 30-hour deep-frying trial; 2) comparing the color changes in three high oleic frying oils with different antioxidants (200 ppm TBHQ, 200 ppm rosemary extract, 200 ppm canolol-enriched extracts) during 30-hour deep-frying; 3) the effectiveness of supplementation of antioxidants (200 ppm TBHQ, 200 ppm rosemary extracts, 200 ppm canolol)

on improving the stability of deep frying in high oleic canola oil during a 30-hour deep-frying study.

3.3 Materials and Methods

3.3.1 Materials

Three different high oleic vegetable oils were used for deep frying trials. High oleic canola oil and soybean oils were provided by Bunge Canada. High oleic sunflower oil was purchased from Jedwards International, Inc. (Braintree, MA, USA). The fatty acid composition of the high oleic deep-frying oils is shown in Table 3.1. Canola seeds were provided by Bunge Canada. Commercial straight-cut potatoes (Brand McCain) with uniform size (7-10 cm length of 1 cm × 1 cm) were purchased from a local Superstore, in Winnipeg, Canada. All chemicals were of analytical grade. Diatomaceous earth, *tert*-butylhydroquinone (TBHQ) and *n*-hexane, methanol, were purchased from Sigma–Aldrich, Canada. Rosemary extract, namely INOLENS 4 (a solution of natural rosemary extract in vegetable oil containing 4% carnosic acid) was purchased from Vitiva d.d., Slovenia.

Table 3.1 Fatty acids composition (%) of high oleic oils

Fatty Acids Composition (%)	HOCAN	HOSUN	HOSOY
C:16 Palmitic Acid	4.41	3.7	6.39
C:18 Stearic Acid	2.24	3.7	4.08
C:18:1 Oleic Acid	74.53	81.3	74.04
C:18:2 Linoleic Acid	13.72	10.1	9.03
C:18:3 Linolenic Acid	1.74	0.1	2.87

3.3.2 Canolol-enriched Extracts

Canolol-enriched extracts were obtained from canola seeds using an Accelerated Solvent

Extractor (ASE 300, Dionex, Sunnyvale, CA, USA). Canola seeds were ground for 30 seconds in a coffee grinder with 15 g of grounded samples mixed carefully with 15 g of Ottawa sand using a spatula (1:1 ratio wt/wt). Two filter papers were placed at the bottom of each of the sample cells followed by filling it with samples up to the top level of cell. Cell caps were securing hand tightened for both sides and then placed in an ASE cell holder. The phenolic compounds were then extracted using analytical grade *n*-hexanes at 160 ºC for 5 minutes static time and 60% flush volume for 2 cycles extraction. A rotary evaporator was used to eliminate *n*-hexane to get the concentrated canolol-enriched extract.

3.3.3 Quantification of Canolol-enriched Extracts

To determine the content of canolol, 2 g of the concentrated extracts were extracted with 70% analytical grade of methanol twice. The phenolic profiling of canolol extract was established following a reversed-phase HPLC–DAD analysis using an HPLC system (Ultimate 3000; Dionex, Sunnyvale, CA, USA), consisting of a diode array detector Synergi 4μ Fusion-RP 80 Å; 150 Å~ 4.0 mm − 4 μm (Phenomenex, Canada) column for peak separation. Peaks were identified by comparing their relative retention times and spectrum with those of the authentic standards of sinapic acid. Solvent A was made by 90% methanol acidified with 1.25% of o-phosphoric acid; solvent B was made by 100% methanol acidified with 0.1% o-phosphoric acid. Both of solvent A and B were used as mobile phases in a gradient elution, where in the concentration of mobile phase B changed in the following sequences at specified time periods (minutes) 0 (10), 7 (20), 20 (45), 25 (70), 28 (100), 31 (100) and 40 (10) (Khattab, et al., 2010).

Other conditions of analysis were strictly maintained: flow rate (0.8 ml/min), column compartment temperature (25 °C) and wavelengths of analysis (270 nm).

3.3.4 Antioxidants enrichment of deep-frying oils

Three high oleic vegetable oils—canola oil (HOCAL), sunflower oil (HOSUN), and soybean oil (HOSOB)—were used as frying media. The four treatments were: (i) high oleic frying oils without any additional antioxidant or extracts (control), (ii) high oleic frying oils with 200 ppm *tert*-butylhydroquinone (TBHQ), (iii) high oleic frying oils with 200 ppm rosemary extract (RM), and (iv) high oleic frying oils with 200 ppm canolol-enriched extract (CAL). All treatments were conducted in duplicates at the Richardson Center for Functional Food and Nutraceuticals (RCFFN), University of Manitoba, Winnipeg, Canada. TBHQ was added to the oil by dissolving it in a minimum quantity of methanol and then mixing with oil under N_2. Rosemary extract and canolol-enriched extracts were added to the oils directly.

3.3.5 Frying Protocol

Frying experiments were conducted in 3-L stainless steel deep fryers (Hamilton Beach Company, Picton, Canada). The protocol include intermittent frying at 185 ± 5 °C with total heating/frying time of 30 hours (5-day period). Three liters of high oleic oils were used for each frying. Over a period of 6 hours per day for 5 consecutive days, batches of straight-cut potatoes were deep fried in oils continuously heated at 185 ± 5 °C. Each day fresh oil was added to make up oil to the initial level in the fryer, to replenish the used oil before frying commenced. Oil

samples were collected from each fryer on every day after the oils had cooled at room temperature, flush them with nitrogen, and stored them at -22ºC until further analysis.

3.3.6 Color Analysis

The color of deep-frying oils was assessed according to AOCS Official method Cc 13e-92: Lovibond Hunter Lab; Lovibond RYBN color scale using a Lovibond PFx 995Tintometer, a PFX*i* series of spectrophotometric colorimeter. Frozen oil samples were brought to room temperature, mixed with diatomaceous earth (0.16% w/w), and agitated for 2.5 minutes at 250 rpm using a rotator mixture at room temperature. It was then filtered using Whatman qualitative circles and then transferred to the cuvettes (1 inch optical cell). Lovibond PFx 995Tintometer, a PFX*i* series of spectrophotometric colorimeter, was used to measure oil color. The color scale was set as Lovibond Hunter L a* b* and RYBN color scale, the heater was preheated to 30 °C for color analysis. L value represents Lightness-darkness dimension; a* value represents red-green dimension; b* value represents yellow-blue dimension. R represents red, Y represents yellow, B represents blue, and N represents neutral. The color difference was calculated using the equation: $\Delta E = [(L_t - L_0)^2 + (a_t - a_0)^2 + (b_t - b_0)^2]^{1/2}$, where, L_0, a_0 and b_0 were the L, a, b values of fresh oil and L_t, a_t, b_t referred to the color values of oil at final / various frying cycles.

3.4 Statistical Analysis

All analyses were carried out in triplicates with results expressed as experimental means ± SD. Univariate analysis of variance, two-tailed Pearson correlation, and multiple linear regression were done using SPSS software version 23 (IBM Corp., USA). Statistical significance

was determined using the least significant difference t-test. Statistical significance was accepted at $p < 0.05$.

3.5 Results and Discussion

3.5.1 Color Results

Lovibond color scales were used in color analysis. The data were expressed as the mean ± standard deviations from all oil samples over the whole frying period respectively (Table 3.2-3.4). In Hunter L a* b* color scale, L value represents lightness-darkness dimension; the higher L value, the more lightness the oil was (Bansal et al., 2010). L values did not show the significant differences ($p > 0.05$) in all oil samples from day 0 to day 5, and decreased gradually over the frying period. CAL showed lower L value among all frying oil samples. The changes in a* values for frying oils during 30 hours of frying are shown in Table 9- 11. All oil samples were initially in the green region with a* values decreasing after 18 hours of frying. All three frying oils with added canolol showed significant differences ($p < 0.05$) in a* before frying. RM showed significant difference at the last day of frying ($p < 0.05$) in high oleic canola oil and sunflower oil while CAL showed significant difference in oleic soybean oil. TBHQ and control samples did not show any significant difference in all three types of frying oils. All of the samples were in the yellow region at the initial level. With b* values increasing gradually during 5 days frying, b* value for CAL showed significant ($p < 0.05$) difference after 6 hours in all three types of frying oils. CAL had higher b* among all of oil samples, but decreased after 6 hours of frying, and then increased after 12 hours of frying. b* values were different after the first day of

frying, it changed fastest when compared with L and a* values in all samples. Control, RM and TBHQ samples did not show significant difference after 30 hours in high oleic canola oil and soybean oil.

Lovibond RYBN color scale is used widely in the food industry for the quality monitoring of fat, oil and derivatives. B and N were eliminated because deep-frying oils did not contain blue and neutral color (Hendry & Houghton, 1996). R and Y are shown in Table 3.5-3.7. All of the oil samples showed increasing R and Y with increase in the frying period. CAL oils showed high R and Y values during 5 days frying. While control, TBHQ and RM oils did not show significant difference in R values during 5 days frying. CAL and RM oils had similar R and Y values in high oleic canola oil and sunflower oil after 6 hours of frying; but did not show any significant difference in high oleic soybean oil.

The total color difference in L, a*, b* values (ΔE) are shown in Figure 3.1-3.3. These show the differences between the initial color values (before frying) and after 6, 18, 30 hours deep-frying. Total color changes increased with frying time with having the RM highest ΔE than control oils in all high oleic deep-frying oils. CAL containing oil, however, showed the highest color stability on minimized total color difference among all frying oil samples during 30-hour frying period. In control samples, significant total color difference was found in high oleic soybean oil followed by high oleic canola oil, while high oleic sunflower oil exhibited the highest stability for ΔE in control oils. The frying oils enriched with TBHQ had higher values for ΔE than control, but these values were lower than the oils containing RM. Overall, CAL

containing oils showed the highest stability by lowing the total color changes in all high oleic frying oils. High oleic sunflower oils had the lowest values in total color changes compared to canola oil and soybean oil during 30 hours deep-frying.

Table 3.2 L, a*, b* values of high oleic canola oil during 30-hour deep-frying

	L*				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	94.68 ± 0.27	94.96 ± 3.34	93.12 ± 0.22	91.79 ± 0.65	-4.40 ± 0.03	-4.35 ± 0.11	-4.22 ± 0.11	-6.23 ± 0.08	10.63 ± 0.07	10.61 ± 0.17	12.72 ± 0.06	22.64 ± 0.17
6	93.36 ± 0.06	93.12 ± 0.10	92.40 ± 1.29	89.70 ± 0.15	-4.81 ± 0.02	-4.88 ± 0.04	-6.30 ± 0.03	-4.68 ± 0.07	13.73 ± 0.17	14.41 ± 0.38	18.42 ± 0.16	19.36 ± 0.37
18	91.16 ± 0.04	83.61 ± 0.51	89.71 ± 0.12	87.37 ± 0.26	-5.46 ± 0.10	-4.85 ± 0.02	-6.79 ± 0.07	-4.33 ± 0.07	18.77 ± 0.54	18.52 ± 0.12	25.24 ± 0.32	23.98 ± 0.28
30	90.12 ± 0.47	88.47 ± 0.31	88.13 ± 0.07	84.19 ± 0.35	-5.99 ± 002	-5.67 ± 0.15	-6.76 ± 0.16	-4.34 ± 0.07	23.61 ± 0.66	25.38 ± 0.34	29.61 ± 0.43	29.26 ± 0.19

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.

Table 3.3 L, a*, b* values of high oleic sunflower oil during 30-hour deep-frying

	L*				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	95.01 ± 0.14	94.52 ± 0.74	94.73 ± 0.50	92.40 ± 0.50	-3.51 ± 0.03	-3.43 ± 0.08	-3.82 ± 0.03	-5.86 ± 0.28	8.60 ± 0.03	8.70 ± 0.28	9.50 ±0.11	20.88 ±1.70
6	94.30 ± 0.49	94.61 ± 0.13	93.97 ± 0.83	91.52 ± 0.83	-4.08 ± 0.11	-3.95 ± 0.01	-5.90 ± 0.03	-4.66 ± 0.11	9.05 ± 0.06	9.05 ± 0.05	15.91 ± 0.03	15.95 ± 0.99
18	93.70 ± 0.57	93.26 ± 0.67	92.58 ± 1.22	89.62 ± 1.22	-4.60 ± 0.33	-4.62 ± 0.21	-7.05 ± 0.03	-4.94 ± 0.18	11.40 ± 0.76	12.61 ± 0.89	20.71 ± 0.37	19.92 ±1.17
30	93.27 ± 0.07	92.43 ± 0.34	91.81 ± 0.17	87.93 ± 0.88	-5.55 ± 0.25	-5.62 ± 0.15	-7.49 ± 0.02	-5.39 ± 0.32	14.70 ± 0.21	16.46 ± 0.41	23.62 ± 0.29	25.07 ±1.58

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.

Table 3.4 L, a*, b* values of high oleic soybean oil during 30-hour deep-frying

	L				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	95.71± 0.05	95.31± 0.52	95.43± 0.16	94.17± 0.03	-3.44± 0.19	-3.22± 0.32	-3.28± 0.05	-5.18± 0.04	6.76± 0.57	6.74± 0.70	6.59± 0.31	15.67± 0.07
6	92.58± 1.48	91.61± 0.95	92.93± 0.16	92.11± 0.22	-5.55± 0.17	-5.50± 0.27	-7.22± 0.10	-5.20± 0.10	16.04± 0.56	17.64±0.41	23.12± 0.14	17.26± 0.45
18	92.24± 0.46	91.87± 0.25	91.77± 0.06	91.18± 0.47	-8.08± 0.18	-8.31± 0.02	-8.91± 0.04	-5.83± 0.24	24.37± 1.40	26.52± 0.05	29.57± 0.31	21.57± 0.48
30	90.65± 0.73	89.80± 0.09	89.77± 0.38	88.68± 0.24	-8.61± 0.08	-8.51± 0.04	-8.90± 0.08	-6.15± 0.15	29.88± 2.64	32.28± 0.58	33.98± 0.50	27.59± 0.22

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.

Table 3.5 R, Y values of high oleic canola oil during 30-hour frying

	R				Y			
Frying hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	0.10 ± 0.00	0.10 ± 0.00	0.20 ± 0.00	0.35 ± 0.05	0.60 ± 0.00	0.60 ± 0.00	0.80 ± 0.00	2.00 ± 0.11
6	0.20 ± 0.00	0.25 ± 0.05	0.20 ± 0.00	0.50 ± 0.00	0.90 ± 0.00	0.95 ± 0.05	1.40 ± 0.00	1.65 ± 0.05
18	0.32 ± 0.08	0.45 ± 0.05	0.50 ± 0.00	0.75 ± 0.05	1.55 ± 0.05	1.65 ± 0.05	2.45 ± 0.05	2.45 ± 0.05
30	0.55 ± 0.05	0.80 ± 0.11	0.80 ± 0.11	1.00 ± 0.00	2.20 ± 0.11	2.55 ± 0.05	3.30 ± 0.11	3.45 ± 0.05

R, Y values are representing red and yellow.

Table 3.6 R, Y values of high oleic sunflower oil during 30-hour deep-frying

	R				Y			
Frying hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	0.10 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.30 ± 0.00	0.50 ± 0.00	0.50 ± 0.00	0.60 ± 0.00	1.75 ± 0.16
6	0.00 ± 0.00	0.00 ± 0.00	0.20 ± 0.00	0.25 ± 0.05	0.60 ± 0.00	0.60 ± 0.05	1.10 ± 0.00	1.15 ± 0.16
18	0.10 ± 0.00	0.10 ± 0.00	0.30 ± 0.11	0.50 ± 0.11	0.60 ± 0.00	0.75 ± 0.05	1.65 ± 0.05	1.73 ± 0.15
30	0.10 ± 0.00	0.30 ± 0.00	0.30 ± 0.00	0.75 ± 0.16	0.90 ± 0.00	1.30 ± 0.00	2.10 ± 0.00	2.50 ± 0.22

R, Y values are representing red and yellow.

Table 3.7 R, Y values of high oleic soybean oil during 30-hour deep-frying

	R				Y			
Frying hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.20 ± 0.00	0.40 ± 0.11	0.40 ± 0.11	0.40 ± 0.11	1.10 ± 0.00
6	0.20 ± 0.00	0.20 ± 0.00	0.30 ± 0.00	0.30 ± 0.00	1.33 ± 0.05	1.30 ± 0.00	1.90 ± 0.00	1.35 ± 0.05
18	0.30 ± 0.11	0.40 ± 0.00	0.40 ± 0.00	0.40 ± 0.00	2.10 ± 0.33	2.50 ± 0.00	2.90 ± 0.11	1.75 ± 0.05
30	0.45 ± 0.16	0.65 ± 0.05	0.65 ± 0.05	0.70 ± 0.00	3.05 ± 0.50	3.65 ± 0.16	4.00 ± 0.11	2.80 ± 0.00

R, Y values are representing red and yellow.

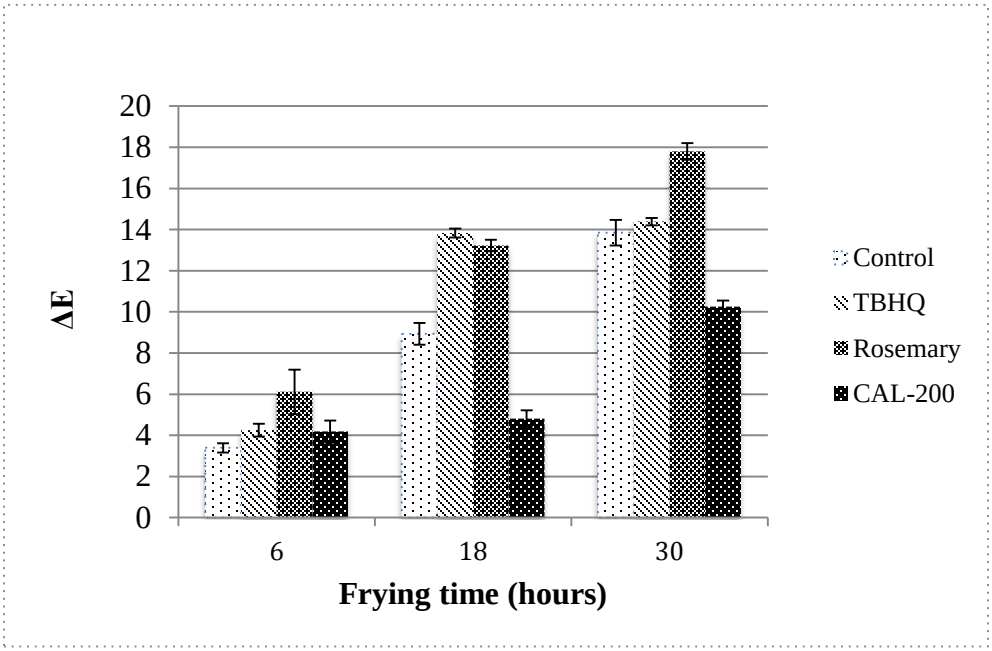

Figure 3.1 ΔE in high oleic canola oil at 6, 18, and 30 hours deep-frying: 600 g of straight-cut potatoes (100 g/batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days.

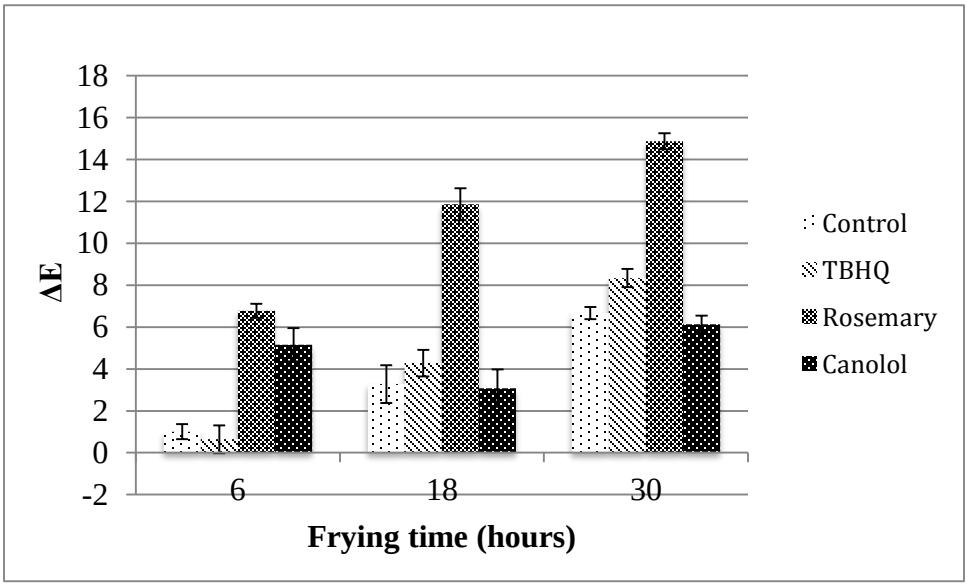

Figure 3.2 ΔE in high oleic sunflower oil at 6, 18, and 30 hours deep-frying: 600 g straight-cut potatoes (100 g/batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days.

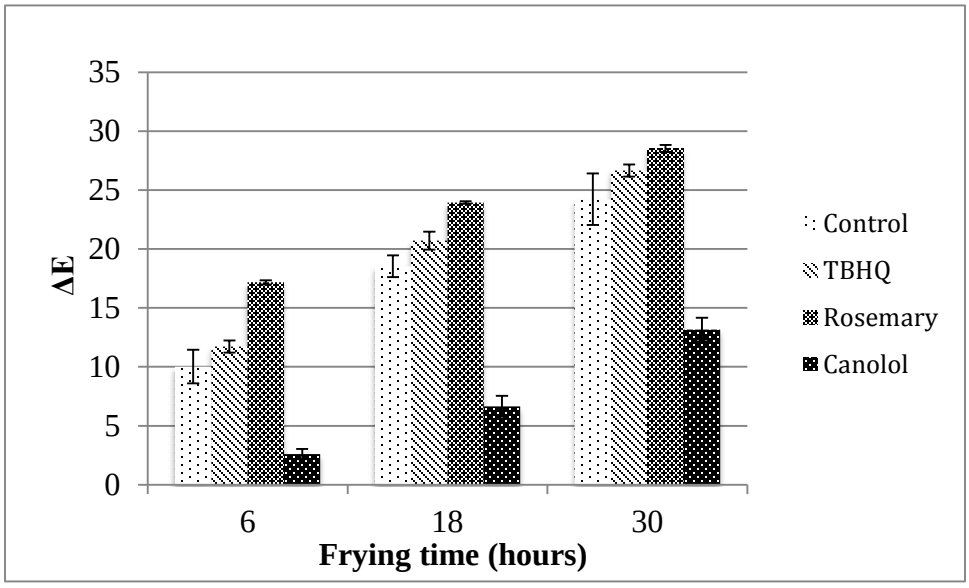

Figure 3.3 ΔE in high oleic soybean oil at 6, 18, and 30 hours deep-frying: 600 g of straight-cut potatoes (100 g/batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days.

3.5.2 Canolol Degradation in High Oleic Deep-Frying Oils During 30 Hours Frying

Antioxidants are added to frying oils to improve thermal stability, but they can also improve the storage stability of food after frying if taken up by the food. The amount of antioxidant coming into the food depends on the type of antioxidant and on the level of antioxidant in the frying medium at the time of each frying operation. The canolol chromatogram is shown Figure 3.4; Figure 3.5 summarizes the degradation of CAL through the 30-hour frying process. The highest degradation of CAL was observed within 12 hours of frying, which resulted in a more than 50% reduction of CAL. High oleic sunflower oil fortified with 200 ppm CAL showed significant higher ($p < 0.05$) canolol levels compared to canola oil and soybean oil after 6 hours of frying. The canolol content in all high oleic vegetable oils did not show significant

difference ($p > 0.05$) between them after 12 hours of deep-frying. Only trace amounts of canolol remained after 30 hours of frying.

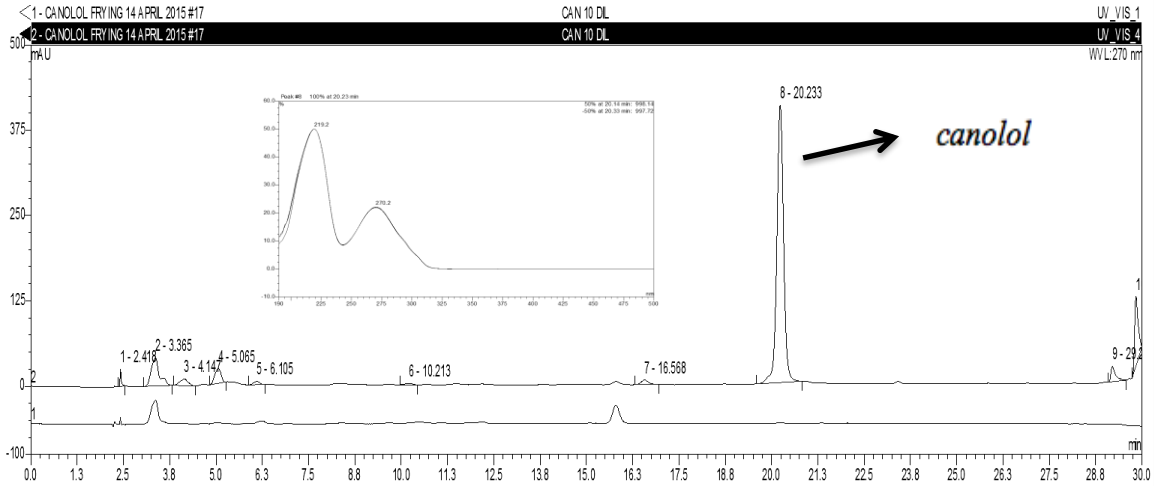

Figure 3.4 Quantification of canolol using HPLC

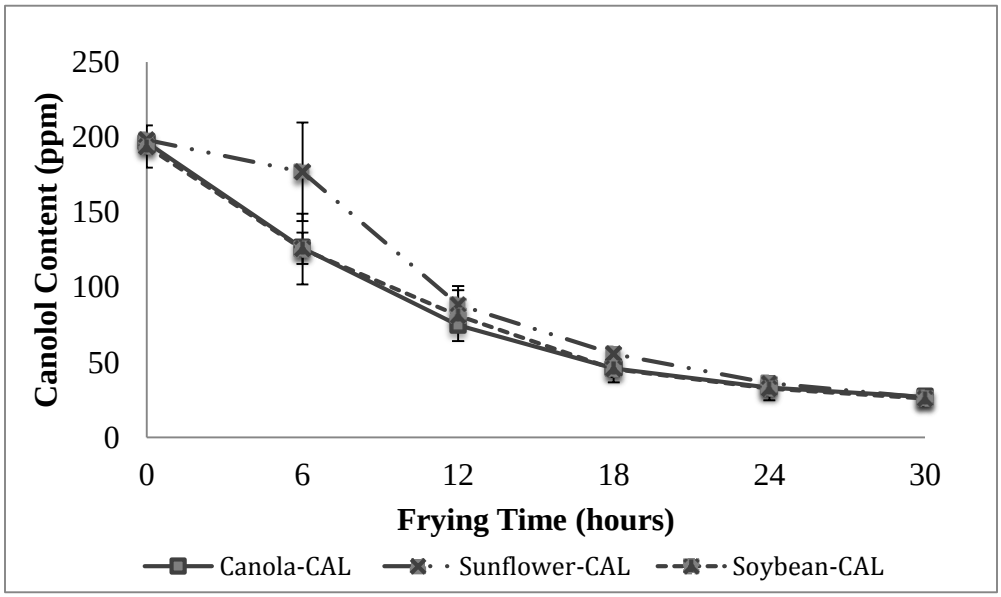

Figure 3.5 Canolol degradation in high oleic oils during 30-hour deep-frying

3.5.3 Deep-Frying Observations

Significant increases in the optical density and color darkness were observed in all frying oil samples after 18 hours frying. There was not significant visual observation on color changes

in canola, sunflower and soybean oils during the first 12 hours of frying. Specifically, all of the frying oils with 200 ppm CAL treated oils showed more dark color than the others. High oleic canola oil containing 200 ppm TBHQ was identified with more redness after three days (18 hours) frying. In general, high oleic sunflower oil was lighter in color with all of treatments while the high oleic soybean oil developed a darker color during 30-hour frying. Smoking was observed in all the frying oils after 18 hours of frying. Among all three frying oils, control and TBHQ treated oils generated more smoking after three days of frying (18 hours), while the oil with rosemary extract had less smoking during the 30-hour frying experiment. Overall, control and TBHQ treated oils did not produce any distinct odor during 30-hour frying. Rosemary extract and canolol containing oils had a strong distinct odor in first two days of frying, which decreased significantly after 18 hours deep-frying.

3.5.4 Discussion

Many products arising from thermo-oxidative alteration of oil components contribute to color change during frying. The red and dark color of a frying oil increases as the amount of polymeric materials increases, while yellow color may be related to the combined peroxides and aldehydes in oil (Maskan 2003; Totani et al., 2012). In the present study, the lightness decreased in all of deep-fried oils with increase in total polar components and polymeric triglycerides. This confirmed with Aladedunye & Przybylski, (2009), a deep-frying study in which potatoes were fried in canola oil, and an increase in the optical density of the frying oil was recognized with the 30 °C increase in deep-frying temperature. In the present study, only potatoes were deep-fried

during 30 hours so that carbohydrates were the main food ingredients. The results showed lightness values were lower when compared to the previous studies, in which conventional canola oils were fried with fish or meatballs. Leaching of pigments from the food into the frying oil, and the presence of Maillard reaction products, formed during frying by the reaction of carbohydrates and some lipid oxidation products with amines, amino acids, and proteins also promote color development (Mah & Brannan, 2009, Lalas et al., 2003; Delgado-Andrade et al., 2010). Furthermore, particles from food being fried can become caramelized and release some fat-soluble pigments into the oil (Vijayan et al., 1996).

Natural antioxidants such as rosemary extract (*Rosmarinus officinalis L.*) and canolol could provide positive protection in the stability of frying oils (Cordeiro et al., 2013; Matthaus et al., 2014). The effects of the oxidative stability tests demonstrated that *Rosmarinus officinalis L.* displayed a more effective protective action, compared with the synthetic antioxidant TBHQ (Cordeiro et al., 2013). In the present study, RM and CAL oils showed significant differences in the initial color before frying, and protected from color darkening during 30-hour frying. CAL oils had a significant effect on the color stabilization in all of high oleic oils during 30 hours of frying. While the canolol content decreased significantly after 18 hours of frying, the total color difference (ΔE) for CAL containing oil was much lower than control and other antioxidants treatment. In a previous study, a grape seed extract added prior to bread baking induced visual colorimetric changes by reducing lightness but promoting redness and yellowness. This resulted in a lower color index value inversely correlated to the levels of grape seed extract addition

(Peng, et al., 2010, Siger, et al., 2015). A similar study showed when rosmarinic acid was added to cookie pastries, it decreased the redness and increased the yellowness of cookies (Zhang, et al., 2014). The potential alteration in color induced by natural dietary polyphenols could be both physical, upon food product appearance, and chemical, related to the stability and compatibility of the color in a certain food category.

3.6 Conclusion

In conclusion, deep-frying oils darken with increasing frying time. High oleic oil is popular for frying. Synthetic antioxidants, extracts and natural antioxidants were added to increase frying stability and performance of three high oleic oils during deep-frying. After 30 hours, significant total color differences were found in RM samples, while the minimal color changes were exhibited in CAL samples in all of high oleic oil samples. The oil samples with TBHQ treated were less effective toward oil darkening when compared to the canolol treated oils. In contrast, CAL-containing samples exhibited a stronger ability to control and minimize color difference (ΔE) during 30 hours frying. This study proved the efficacy of canolol-enriched extracts to stabilize the color in frying oil when compared to other antioxidants, RM and TBHQ. Future studies will focus on the potential in extended time of frying beyond 30 hours.

Acknowledgement

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CHAPTER 4

MANUSCRIPT 2

Correlation between Color and Oxidation Status in High Oleic Deep-Frying Oils: Impact of Antioxidants

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Running title: Correlations between color and oxidation status in high oleic deep-frying oils

4.1 Abstract

Color darkening of frying oils is closely associated with the levels of oxidation status in the frying oils. Three high oleic vegetable oils (canola oil, sunflower oil, soybean oil) with added antioxidants (200 ppm) *tert*-butylhydroquinone (TBHQ), rosemary extracts (RM), and canolol-enriched extracts (CAL) were supplied to 30-hour deep-frying with straight-cut potatoes. Total polar components (TPC), polymerized triglycerides (PTG), *p*-anisidine value (*p*-AnV) were estimated with Fourier Transform (FT) – Near Infrared (NIR) spectroscopy following German Society for Fat Science (DGF). Hunter L (lightness – darkness), a* (redness – greenness), b* (yellowness – blueness) values were measured by the official methods of the American Oil Chemists' Society (AOCS). The results showed oils with TBHQ were not significantly different ($p > 0.05$) from control samples with present to TPC, PTG, *p*-AnV and AV during 30-hour deep-frying. CAL significantly ($p < 0.05$) slowed down color darkening during 30-hour deep-frying in high oleic oils when compared to control, TBHQ, and RM in oils. RM and CAL both significantly ($p < 0.05$) reduced the formation of TPC, PTG, and *p*-AnV in deep-frying oils after 18-hour frying. Correlations between color and these oil quality indicators were generated. The study established models for color evaluation of deep-frying oils, leading to a simple and rapid method for monitoring oil quality during deep-frying.

Key Words: *high oleic oils, deep-frying, antioxidants, color, oil quality assessment, correlations, regression models*

4.2 Introduction

Total polar components, polymeric triglycerides and aldehydes that are from lipid oxidation and degradation at elevated temperature have adverse effects on shelf life of deep-frying oils, nutritional value and overall quality of foods (Maskan 2003; Totani et al., 2012, Simth et al., 2007). Prolonged heating at high temperature in the presence of the oxygen, carbohydrates, protein, fats and the minerals, as well as the water from the food causes an interrelated series of complex chemical reactions in the oils, mainly thermo-oxidation, hydrolysis, and polymerization (Gertz, 2014). As a result, a number of harmful compounds are produced that degrade the quality of deep-frying oils and fried foods. Frying oils remain susceptible to the deteriorating effects of oxygen and high temperatures thus, many strategies are used to maintain the quality of oil. A high content of oleic fatty acids and/or addition of antioxidants is considered to slow down lipid deterioration (Shahabadi, et al., 2009; Lalas & Dourtoglou, et al., 2003) and mainatian the quality of the oils.

Quality assessments of oils in frying processes are usually conducted by the analysis of total polar components (TPC), polymeric triglycerides (PTG), *p*-anisidine value (*p*-AnV), acid value (AV), and iodine value (IV). Deep-frying oils should be rejected when TPC exceeded to 25 - 30 %; PTG exceeded to 13 % - 15 %; *p*-AnV exceeded to 30; AV exceeded to 2.5 – 3.0 KOH/g (Frankel, 2014). Moreover, in the 7th International Symposium on Deep-Fat Frying (San Francisco (USA), recommended that TPC and PTG are the best deep-frying oil quality indicators, however, peroxide value, AV, and *p*-AnV should not be used to monitor the degree of

degradation of different oils (Gertz & Stier, 2013). Determining the level of polar compounds and oxidized products from deep-frying oils are important, which are suspected of impairing the nutritional and physiological properties of the oils. These oxidized compounds such as acrylamide and 4-hydroxynonenal (HNE) that from the deep-fried food, and oxidized monomeric triacylglycerols that from the deep-frying oils have been associated with cardiovascular diseases and certain types of cancer (Gertz & Stier, 2013; Aladedunye, et al., 2011). However, the analysis procedures of these oil quality indicators, need advanced laboratory equipment and skilled technicians; are often tedious and thus, a rapid assessment of the oil quality indicators is needed (Xu, 2000; Aladedunye & Przybylski, 2011).

High oleic deep-frying oils are used to extend the shelf life of frying oils and fried food products. Studies indicated that high oleic acid present in the frying oil and fried food, slow down the formation of polar materials, off-flavors and fishy odors during frying (Merrill et al., 2008，Warner & Gupta, 2005). Thus, higher level of oleic fatty acids and lower linolenic fatty acids has been shown to improve the stability of deep-frying oils, leading to a wide adoption of high oleic oils such as high oleic canola, sunflower oil and soybean oils. But these oils need to be tested in deep-frying studies for their stability with respect to color and other quality parameters. In addition to the use of high oleic oils, natural antioxidants – enriched oils are used to enhance the stability during deep-frying.

The endogenous components in vegetable oils like tocopherols are the main lipophilic antioxidants, and efficient scavengers of alkoxyl and peroxyl radicals (Gliszczynska-Swiglo, et

al., 2007). Tocopherols have been reported to increase the oxidative stability of vegetable oils rich in polyunsaturated fatty acids during frying (Al-Khusaibi, et al., 2012). On the other hand, synthetic antioxidants, such as butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT) or *tert*-butylhydroquinone (TBHQ), are widely used for extending shelf life of both the deep-fried oils and deep-fried foods, but many reports raise issues about their safety. Moreover, the toxicity and carcinogenicity effects of these synthetic antioxidants, and the growing consumer concerns about their safety have directed attentions toward the use of natural antioxidants as alternatives to synthetic ones (Okubo, 2013). Several natural antioxidants derived from fruits, herbs, and cereals have been utilized by the food industry (Yanishlieva, et al., 2006). Extract of rosemary (*Rosmarinus officinalis* L.) and canolol, a lipid peroxyl radical scavenger found in rapeseed, has been shown to provide excellent protection against oxidation for frying oils (Matthaus, et al., 2014) and improving the storage stability of the deep-fried potato chips (Cordeiro, et al., 2013; Lalas & Dourtoglou, 2003). However, these deep-frying studies demonstrating efficacy of the antioxidants in slowing down the oil deterioration, did not explain the impact of these antioxidants on reducing oil color. Thus, it is necessary to investigate the effectiveness of antioxidants and the impact on oil color change during deep-frying studies.

Color changes in deep-frying oils reflects formation of Maillard reaction and products related to other thermo oxidation reactions. Thus color not only represents physical changes, but also indicates possible alterations in the stability, nutritional composition as well as health-related effects of deep-frying food products and oils (Zhang, et al., 2015; Siger, et al.,

2015). Color intensity of frying oil increases as the amount of polymeric materials increases (Paul & Mittal, 1996), and has been commonly used as an index to determine the quality of used oils (Maskan, 2003). Regulations in many countries stipulate that color is one of the criteria for discarding frying oils (Bansal et al., 2010). For instance, the Manufacturing Process Inspection document, published by the U.S. Department of Agriculture, stipulates that the darkening of oil is evidence of unsuitability of frying oils and requires rejection of the oil (USDA, 1985). In the previous studies, a strong correlation has been shown between the oil color absorbance using a spectrophotometric method and the content of total polar components in deep-frying oils. However, the correlation between reliable oil quality indicators, such as total polar materials, polymeric triglycerides, *p*-anisidine value and color parameters such as lightness-darkness, yellowness-blueness, redness-greenness is not established. Moreover, most of the previous deep-frying studies focused on the conventional oils, and not high oleic oils. Since higher level of high oleic fatty acids and lower linolenic fatty acids are commonly used currently, high oleic canola, high oleic sunflower oil and high oleic soybean oil needs to be tested in deep-frying studies with these objectives. The main objective of this paper was to evaluate the efficiency of antioxidants in three high oleic vegetable oils during 30-hour continuous frying; and to establish a model using color as a rapid assessment to determine the oxidation status of high oleic oils during 30-hours deep-frying.

4.3 Materials and Methods

4.3.1 Materials

Three different high oleic vegetable oils were used for deep frying trials. Canola oil and soybean oil were provided by Bunge Canada. Sunflower oil was purchased from Jedwards International, Inc. (Braintree, MA, USA). The fatty acid composition of high oleic deep-frying oils is shown in Table 4.1. Canola seeds for canolol extraction were also provided by Bunge Canada. Commercial straight-cut potatoes (Brand MCain) of uniform size (7-10 cm length of 1 cm × 1 cm) were purchased from a local store (Winnipeg, Canada). All chemicals were of analytical grade. Diatomaceous earth, *tert*-butylhydroquinone (TBHQ) and *n*-hexanes, methanol, were purchased from Sigma–Aldrich (Canada). Sinapic acid standard was procured from Sigma–Aldrich (St. Louis, MO, USA). Rosemary extract, INOLENS 4, a solution of natural rosemary extract in vegetable oil containing 4% carnosic acid, was purchased from Vitiva d.d. (Slovenia).

Table 4.1 Fatty acids composition (%) of high oleic oils

Fatty Acids Composition (%)		HOCAN	HOSUN	HOSOY
C:16	Palmitic Acid	4.41	3.7	6.39
C:18	Stearic Acid	2.24	3.7	4.08
C:18:1	Oleic Acid	74.53	81.3	74.04
C:18:2	Linoleic Acid	13.72	10.1	9.03
C:18:3	Linolenic Acid	1.74	0.1	2.87

4.3.2 Methods

Canolol-Enriched Extraction

Canolol enriched extracts were obtained from canola seeds using an Accelerated Solvent Extractor (ASE 300, Dionex, Sunnyvale, CA, USA). Canola seeds were ground for 30 seconds in a coffee grinder. Then, 15 g of grounded samples was mixed carefully with 15 g of Ottawa sand

using a spatula (1:1 ratio w/w). Two filter papers were placed at the bottom of each sample cells, which was then filled with the seed mixture up to top level of cell. Cell caps were hand tightened securely for both sides and placed in ASE cell holder. Canolol was extracted using analytical grade *n*-hexanes at 160 ^{o}C by a 5-minute static extraction time, followed by a 60% flush volume repeated for 2 extraction cycles. *n*-Hexane was removed from the extract using a rotary evaporator.

Quantification of Canolol-Enriched Extracts

Canolol content was determined using 2 g of the concentrated extracts extracted with 70 % analytical grade of methanol twice. The analysis was done using a reversed-phase HPLC analysis (Ultimate 3000; Dionex, Sunnyvale, CA, USA), with a diode array detector. Elution was done with solvent A (90 % aqueous methanol acidified with 1.2% o-phosphoric acid) and solvent B (100% methanol acidified with 0.1% o -phosphoric acid0.1 %) using a gradient elution, where the concentration of mobile phase B (%, indicated in brackets) changed in the following sequences at specified time periods (minutes) 0 (10), 7 (20), 20 (45), 25 (70), 28 (100), 31 (100) and 40 (10) (Khattak, et al., 2010). The column was a Synergi 4µ Fusion-RP 80 Å; 150 Å~ 4.0 mm − 4 µm (Phenomenex, Canada). Both the mobile phases and phenolic extracts were passed through syringe filters (0.45 µm). Other conditions of analysis were strictly maintained, which included: flow rate (1 ml/min), column compartment temperature (25 °C) and wavelengths of analysis (270 nm). Peaks were identified by comparing their relative retention times and spectrum with those of the authentic standards of sinapic acid.

Extraction of Tocopherols

The deep-frying oil samples were extracted directly with absolute methanol twice followed by methanol / 2-propanol (1:1, v/v) mixture twice (Tasioula-Margari, & Okogeri, 2001) as described. Two grams of oil sample were first extracted with 10 mL of absolute methanol for 3 min. The residue was extracted with 10 mL of methanol/2-propanol mixture (1:1, v/v) three times. The supernatants were pooled and made up to 40 mL, filtered using a Whatman No. 1 filter paper, and evaporated to dryness under N_2, and the residue was re-dissolved in 5 mL of the methanol/2-propanol (1:1, v/v) mixture.

Quantification of Tocopherols

The chromatographic separation of tocopherols was performed on a 250 mm Å~ 4.6 mm i.d., 5 μm, C18 Prodigy ODS-2 column (Phenomenex, Torrance, Canada) as described previously (Tasioula-Margari, & Okogeri, 2001) with slight modifications. The elution solvents used were1% acetic acid/water (1:99), which is solvent A; and 1% acetic acid/methanol (1:99), which is solvent B. Elution for α-tocopherol was done with 100% of solvent B, and γ-tocopherol was done with 1% of solvent A and 99% of solvent B. An isocratic elution was performed with 1% A and 99% B for 30 min. The column was maintained at 25 °C with a flow rate of 1.0 mL/min. The injection volume was 20μL. Chromatograms were acquired at 294 nm; identification of tocopherols was achieved by comparing the relative retention times and spectrum with the standards of α- and γ-tocopherols. Triplicate samples were analyzed with duplicate injections of each sample for statistical validation of results.

Antioxidants Enriched Deep-Frying Oils

Three high oleic vegetable oils—canola oil (HOCAL), sunflower oil (HOSUN), and soybean oil (HOSOB) —were used as frying media. Four treatments used were: (i) oil without any additional antioxidant or extracts (control), (ii) oil with 200 ppm *tert*-Butylhydroquinone (TBHQ), (iii) oil with 200 ppm rosemary extract, and (iv) oil with 200 ppm canolol-enriched extract. All treatments were conducted in duplicate at Richardson Center for Functional Food and Nutraceuticals (RCFFN), University of Manitoba, Winnipeg, Canada. TBHQ was added to the oil by dissolving it in a minimum quantity of methanol and then mixed with oil under N2. CAL- and RM-enriched oils were mixed uniformly with the canola oil under inert conditions.

Deep-Frying Protocol

Frying experiments were conducted in 3-L stainless steel deep fryers (Hamilton Beach Company, Picton, Canada). The protocol includes intermittent frying at 185 ± 5 °C with total heating/frying time of 30 hours (5-day period). Three liters of oil were used for the frying. Over a period of 6 hours per day for 5 consecutive days, batches of straight-cut potatoes were deep fried in oils which were continuously maintained at 185 ± 5 °C. Every day, fresh oil was added to replenish the used oil and maintain the initial oil volume in the fryer. Every day, oil samples were collected from each fryer after the oils had cooled down to room temperature. The oil samples were flushed with nitrogen, and stored at -22 ºC until further analysis.

Analyses of Quality Indicators

Total polar components (TPC), polymeric triglycerides (PTG), *p*-Anisidine value (*p*-AnV), acid value (AV), iodine value (IV) were determined by FT-NIR transmission measurement in MaxFry (Hagen, Germany) (Gertz, et al., 2013). The measurement was done according to DGF method. C- III 3b (06) – Polar compounds. DGF C- III 3c (10) – Polymerized TAGs. Determination in severely heat-stressed fats and oils (deep- frying fats) by high performance size- exclusion chromatography (HPSEC). DGF C- VI 6e (05) – *p*-Anisidine value - VI 6e (05); DGF C- V 2 (06) – Acid value and free fatty acid content (Acidity); iodine value – C-V 11a (02). In brief, oil samples were put into 8 mm disposable vials. All spectra were recorded in triplicate at 50 ± 1°C after a thermal preconditioning for 10 min in a separate thermo block to avoid turbid solutions. Spectra were obtained in transmission mode from 12,500 to 4,000 cm $^{-1}$. Each spectrum was time-averaged based on 32 scans at a resolution of 8 cm^{-1} using Bruker MPA FT-NIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany), equipped with validated calibration models developed by multivariate analysis using partial least squares (PLS2) algorithms. The color of deep-frying oils was assessed according to AOCS Official method Cc 13e-92: Lovibond Hunter L a* b* color scale using a Lovibond PFx 995Tintometer, a PFX*i* series of spectrophotometric colorimeter.

4.4 Statistical Analysis

All analyses were carried out at least in triplicate and results were presented as experimental means ± SD. Univariate analysis of variance, two-tailed Pearson correlation, and multiple linear regression were done using SPSS software version 23(IBM Corp., USA).

Statistical significance was determined using least significant difference t test. Statistical significance was accepted at $p < 0.05$.

4.5 Results and Discussion

4.5.1 Total Polar Components

The percentage of TPC in canola, sunflower and soybean oils showed in Figure 4.1-4.3. Antioxidants, types of deep-frying oils and frying time are factors, which had significant effect ($p < 0.05$) on the TPC formation. In high oleic canola oil, RM showed statistically significant ($p < 0.05$) effects on formation of TPC from 6 hours to 30 hours when compared to CAL. The percentage of TPC in high oleic sunflower oil among all deep-frying oil samples was below 1.5%, RM significantly ($p < 0.05$) reduced the formation of TPC in the oils compared to other treatments after 6 hours frying. CON, TBHQ and CAL treated sunflower oil were not show to be significantly different ($p > 0.05$) from 6 hours to 30-hour deep-frying. In high oleic soybean oil, RM and CAL exhibited significant effects ($p < 0.05$) on formation of TPC after 6 hours of frying. Control and TBHQ did not exhibit significant difference ($p > 0.05$) when compared to RM and CAL during 30-hour deep-frying. CAL showed the strongest effect ($p < 0.05$) on reduction the formation of TPC formation during 30-hour deep-frying in high oleic soybean oil. In conclusion, high oleic canola oil and sunflower oil had lower TPC when compared to soybean oil during 30 hours of deep-frying. RM showed significantly reduced TPC formation in canola oil and sunflower oil, CAL showed significantly reduced TPC formation in soybean oil during 30-hour deep-frying.

TPC is the best indicator to all degraded products other than the initial triglycerides present in the fresh oil (Bansal, et al., 2010). The maximum levels for polar compounds in frying or cooking fats and oils at 25 – 27 g per 100 g oil (Aladedunye & Przybylski, 2009; Houhoula, et al., 2003; Li, et al., 2008). None of oil samples exceeded their limitation of TPC during 30-hour deep-frying in the current study. The lowest TPC content was found in RM treated canola oil (4.99 %), while the highest TPC content was found in TBHQ treated soybean oil (15.55 %) after 30-hour frying. The lower TPC formation in this deep-frying study is because of high oleic vegetable oils in frying. The current results agreed with previous literature suggesting that high oleic sunflower oil and high oleic low linolenic canola oil are the most stable vegetable oils for limiting TPC level during deep-frying (Matthaus, 2007). Previous studies using high oleic sunflower oil that fried French fries, which showed TPC did not exceed 15 % after 28 hours deep-frying (Aladedunye & Przybylski, 2013).

The current study showed that natural antioxidants at 200 ppm RM in high oleic canola oil and 200 ppm CAL in high oleic soybean oil significantly reduced the TPC formation after 30-hour frying. The result was confirmed by the study by Matthaus, et al. (2014), who also showed with high oleic canola oil treated with canolol, which reduced the formation of polar compounds during frying. Canola oil treated with 200 ppm CAL reached a value of 13.2 % TPC, while CON and RM exceeded 25 % of TPC after 30-hour deep-frying (Matthaus, et al., 2014). RM and CAL treated in canola oils showed different results when comparing the current study and previous deep-frying studies, which have been done by Matthaus et al. (2014), which may be

due to the different techniques used to obtain canolol-enriched extracts and differences in oil types with respect to the level of unsaturation. The content of polar material increased faster in oils treated with canolol-enriched extracts despite their higher oxidative stability and phenolic contents, but it is possible that significantly high amounts of oligomer precursors such as free fatty acids, mono- and di- acylglycerols, and other oxidized compounds in the antioxidative phenolic compounds were present during the extraction process (Taha et al., 2014).

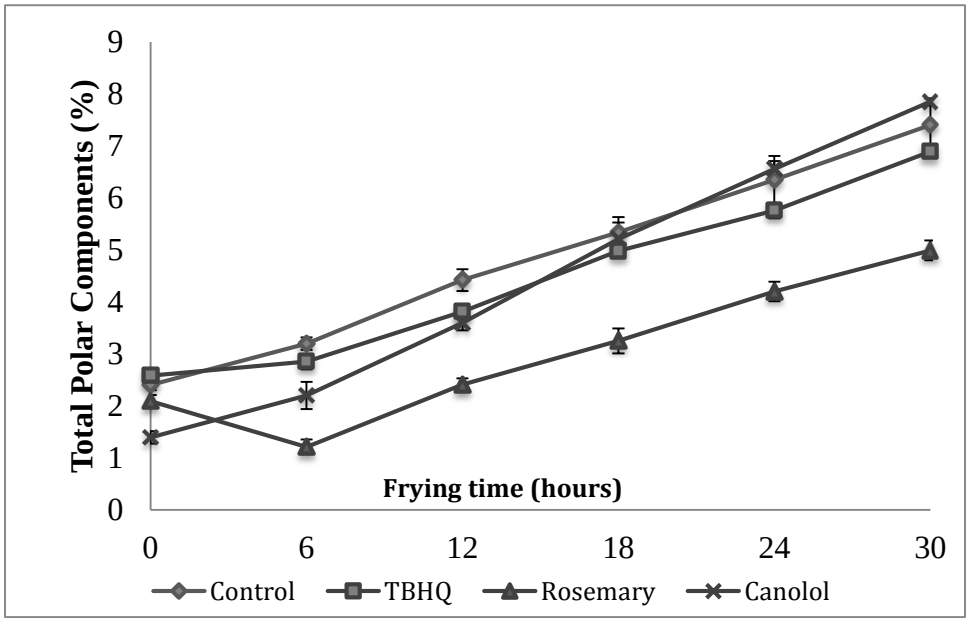

Figure 4.1 Formation of total polar components in high oleic canola oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were at 200 ppm concentration.

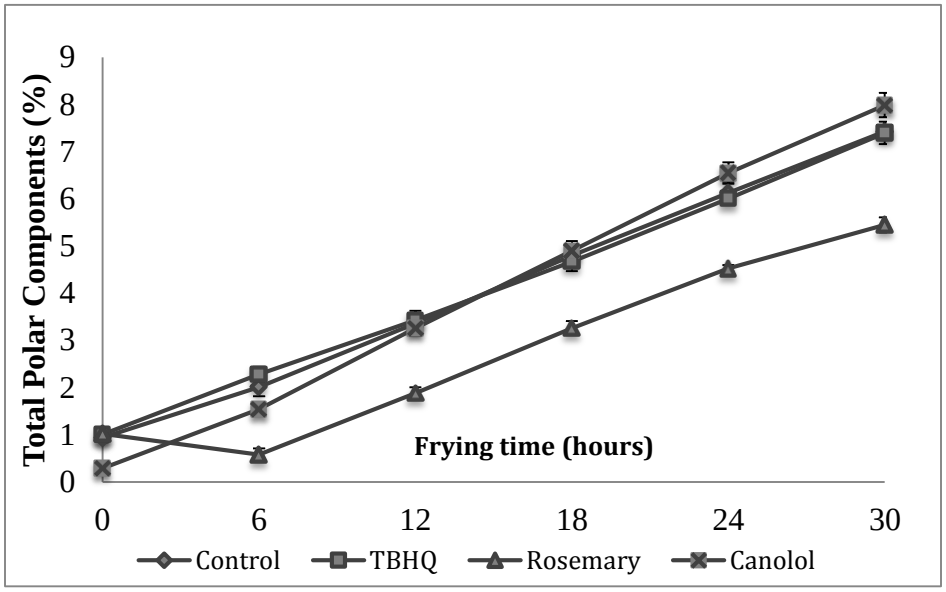

Figure 4.2 Formation of total polar components in high oleic sunflower oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were at 200 ppm concentration.

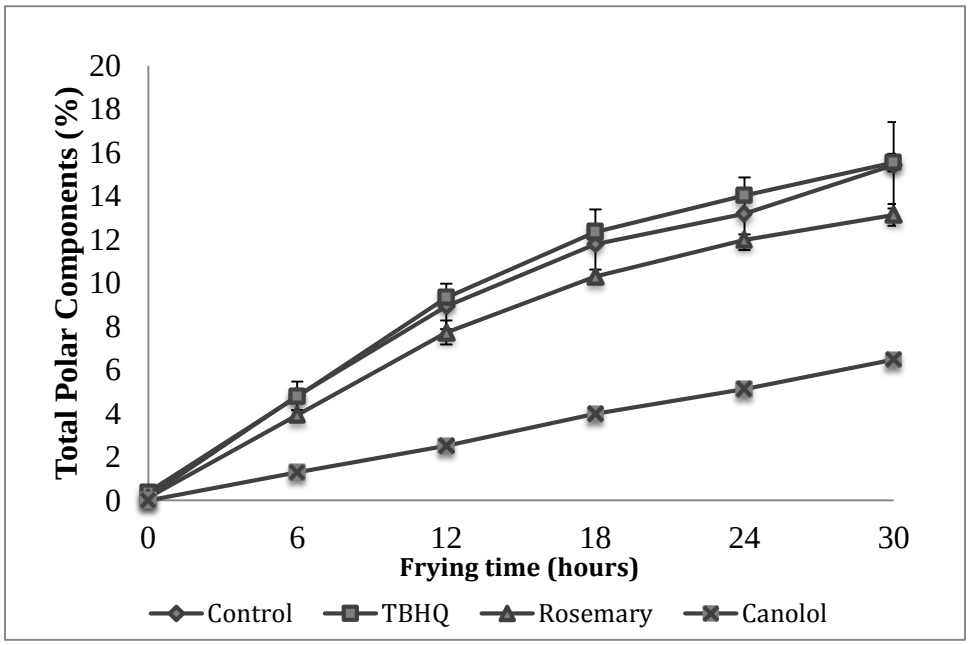

Figure 4.3 Formation of total polar components in high oleic soybean oil during 30-hour

deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were at 200 ppm concentration.

4.5.2 Polymeric Triglycerides (PTG)

The percentage of PTG in all of oil samples showed a linear increase during 30-hour deep-frying (Figure 4.4-4.6). The CAL supplemented canola oil was significantly lower ($p < 0.05$) in PTG content compared to TBHQ treated canola oil before frying. After 30-hour frying, the lowest PTG content was found in canola oil containing RM (2.9 %), compared highest PTG content was found in CON (3.85 %). The PTG content in control, TBHQ, RM and CAL treated in high oleic sunflower oil was below 1% before frying. RM containing sunflower oil showed significant low PTG content when compared to other treatments during 30-hour deep-frying. CAL treated in sunflower oil had a lower PTG content compared to TBHQ treated sunflower oil after 12 hours of frying, but was not significant different ($p > 0.05$) than CON. RM and CAL treated sunflower oils showed significantly lower in PTG content compared to CON and TBHQ treated sunflower oil from 12 hours to 30 hours. The PTG content increased significantly ($p < 0.05$) in all of deep-frying oil samples during 30-hour frying in high oleic soybean oil when compared to canola oil and sunflower oil samples. CAL treated soybean oil showed significant effects ($p < 0.05$) by controlling PTG formation during 30-hour frying. CON, TBHQ, and RM treated soybean oil samples were significantly different ($p > 0.05$) with reducing the PTG formation during 18 hours of frying. RM treated soybean oil sample exhibited significantly lower

on PTG content from 18 hours to 30 hours frying when compared to CON and TBHQ treated oil samples.

The content of polymerized triglycerides in deep-frying oils is defined as the sum of all di- and oligomer triglycerides, which is expressed in percent (Gertz, 2001). In most of Europe, the frying fats are recognized as objectionable and to be rejected if the level of polymeric triglycerides exceeded 13-15 %. Normally, the rejection point was at 10% of polymeric triglycerides in most food industries (Frankel, 2014). In the current study, PTG showed a linear increase with deep-frying time increasing. None of the deep-frying oil samples, however, exceeded the limitation of PTG. RM treated canola and sunflower oils showed stronger effects on slowing down the formation of PTG during 30-hour frying. This results confirmed to Petersen, et al., (2013), who deep-fried French fries for a 32-hour with several vegetable oils. The PTG value of 12% only slightly exceeded by the sunflower oil sample, while the lowest PTG value of 4.8 % was found in palm olein after 32 hours of heating. Natural antioxidants RM and CAL both showed strong effects in minimizing the formation of PTG during 30-hour deep-frying, and this result matches previous studies (Taha, et al., 2014; Mattaus et al, 2014).

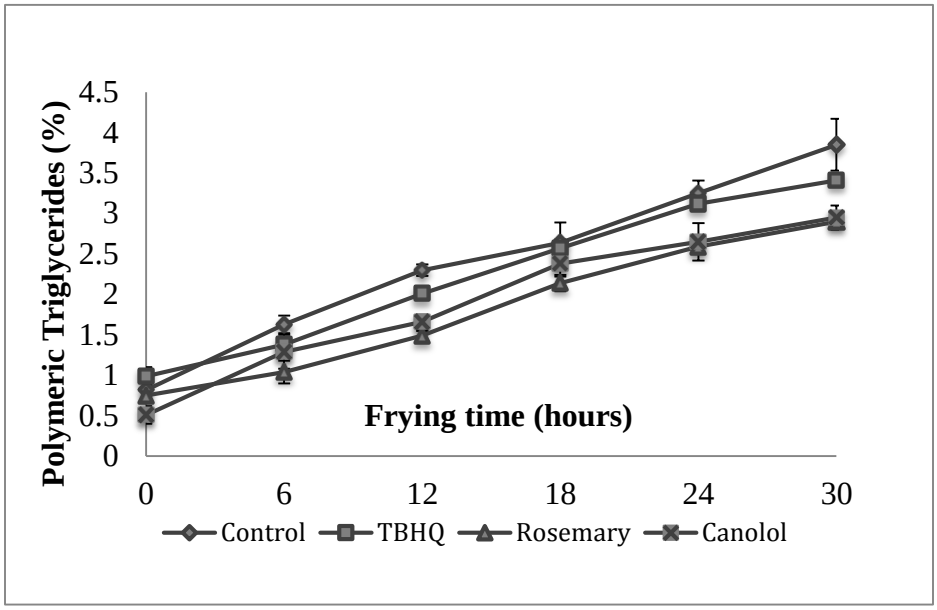

Figure 4.4 Formation of polymeric triglycerides in high oleic canola oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

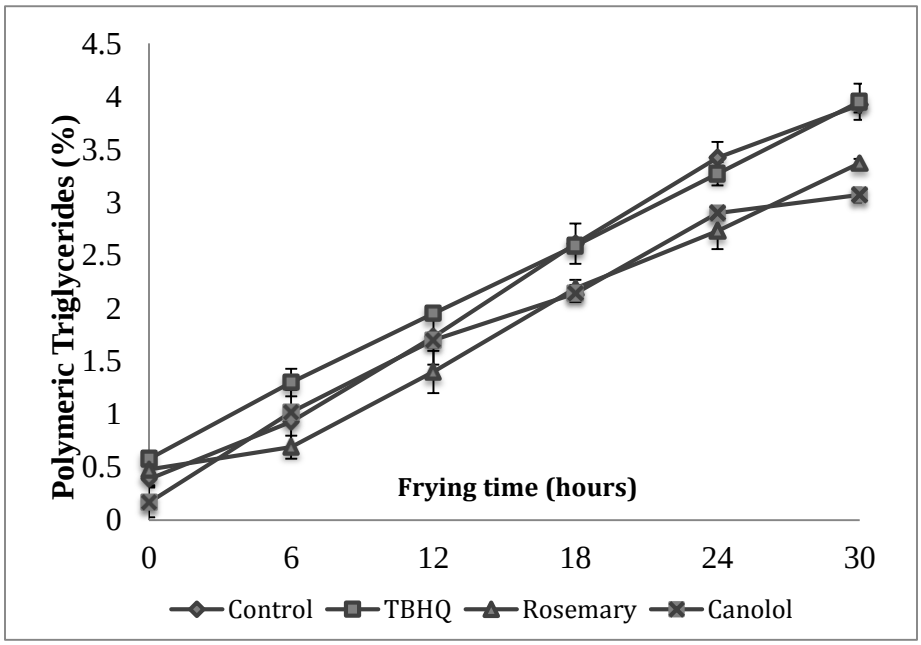

Figure 4.5 Formation of polymeric triglycerides in high oleic sunflower oil during 30-hour

deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

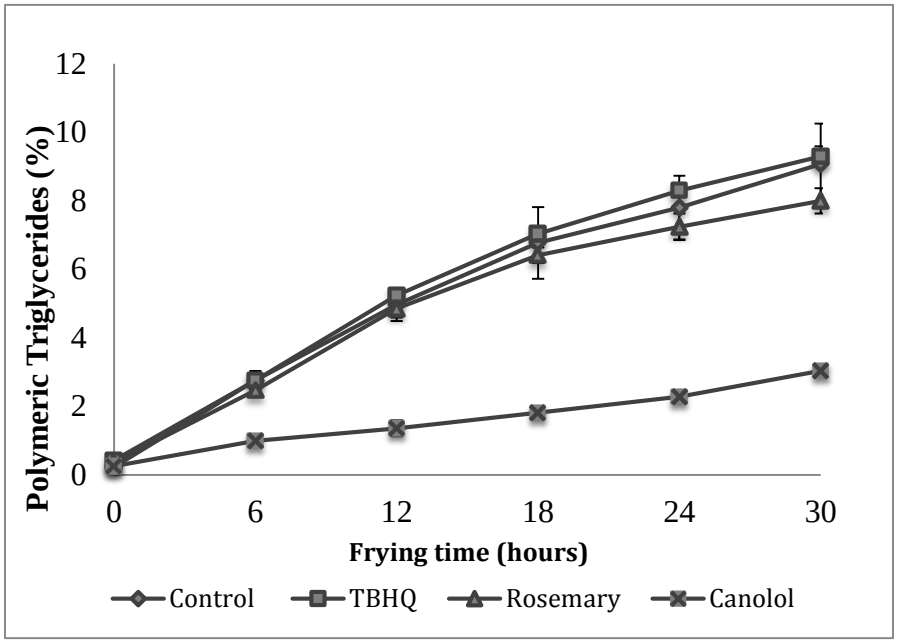

Figure 4.6 Formation of percentage of polymeric triglycerides in high oleic soybean oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

4.5.3 *p*-Ansidine Value (*p*-AnV)

p-Ansidine value for all deep-frying oil samples increased gradually during 30-hour frying (Figure 4.7-4.9). CON of canola oil showed significantly higher *p*-AnV ($p < 0.05$) compared to other treatments in canola oil during 30-hour frying. CAL and TBHQ treated canola oils were not significantly ($p > 0.05$) different during 30-hour frying; RM treated canola oil showed significant

effects by limiting *p*-AnV during 30-hour frying. In high oleic sunflower oil, *p*-AnV showed relatively higher values before frying when compared to canola oils. TBHQ, CAL and CON sunflower oils were not significantly ($p > 0.05$) different during 30-hour deep-frying. RM treated sunflower oil exhibited significant lower ($p < 0.05$) *p*-AnV from 6 to 18 hours frying; CAL and RM treated sunflower oils were not significantly different ($p > 0.05$) from 18 to 30 hours frying. In high oleic soybean oil, all of frying oil samples did not show significant difference ($p > 0.05$) before frying. CAL treated soybean oil sample were significantly ($p < 0.05$) lower *p*-AnV compared to TBHQ, RM and CON soybean oils during 30-hour deep-frying, while TBHQ, RM and CON soybean oils were not significantly different ($p > 0.05$) during 30-hour deep-frying in high oleic soybean oil.

p-Anisidine value (*p*-AnV), is defined by convention as 100 times the optical density measured at 350 nm in a 1 cm cuvette of a solution containing 1.00 g of the oil in 100 mL of a mixture of solvent and reagent. The method has been adapted to measure the level of aldehydes under certain frying conditions in vegetable oils, in which the rejection level of *p*-AnV is 30 (Chung, et al., 2004; Firestone, 2009; Kim, et al., 2013; Bansal, et al., 2010). *p*-AnV increases because of increasing aldehydes, which is the decomposition of hydroperoxides in elevating frying temperature (Kim, et al., 2013; Li, et al., 2008). According to Kim et al., 2013, *p*-AnV reached the maximum value in the middle of a 7-day frying period, and then decreased consistently until the end of frying period. The previous studies showed the *p*-AnV reached to 100 after 7 to10 hours deep-frying with canola oil or rapeseed oil (Aladedunye & Przybylski,

2009; Petersen, et al., 2013). However, in the current study, *p*-AnV showed a linear increasing trend during 30-hour frying, and the oil samples did not exceed the limitation of *p*-AnV in high oleic canola oil and sunflower oil, this is because the differences of deep-frying oils were used in deep-frying studies, and the study durations. Furthermore, *p*-AnV is influenced by the content of polyunsaturated fatty acids like linoleic and linolenic acids (Aladedunye & Przybylski, 2009). The higher the content of polyunsaturated fatty acids, the higher the *p*-AnV in the frying oils (Aladedunye & Przybylski, 2009). High oleic soybean oil showed higher *p*-AnV during 30-hour frying, CON, TBHQ, and RM treated soybean oils exceed the maximum level of *p*-AnV after 6 hours frying, only CAL treated soybean oil showed significant effects on slowing down the increasing of *p*-AnV; moreover, it did not exceed the limitation of *p*-AnV after 30-hour frying. It is because of the different fatty acids composition in high oleic soybean oil, which contains higher linolenic fatty acids. Overall, high oleic vegetable oils have been used for the current deep-frying study explaining the different values in *p*-AnV.

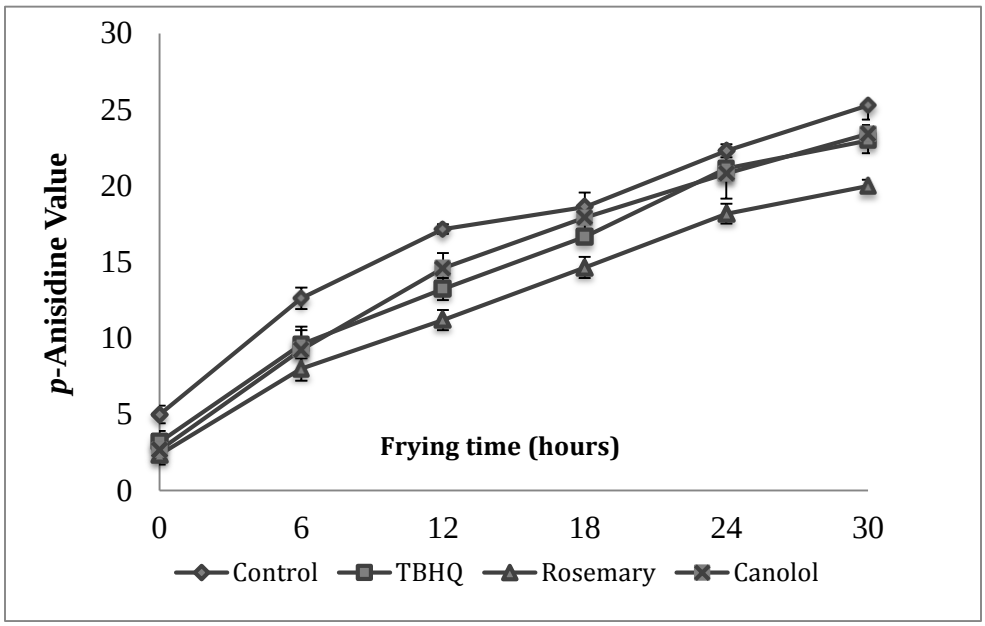

Figure 4.7 Formation of *p*-Ansidine value in high oleic canola oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

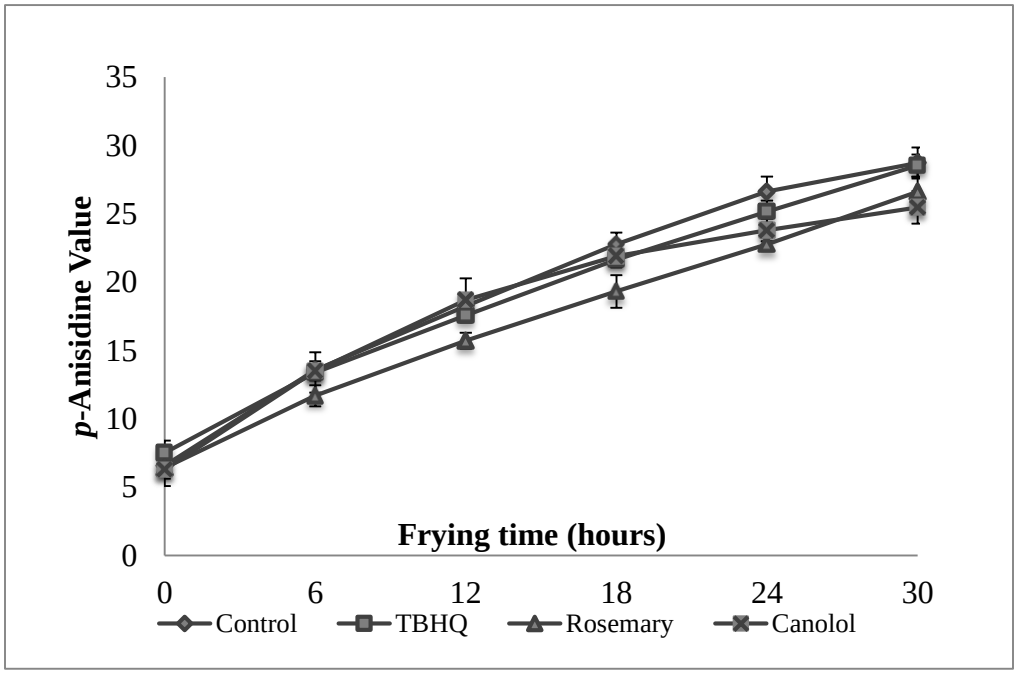

Figure 4.8 Formation of *p*-Ansidine value in high oleic sunflower oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

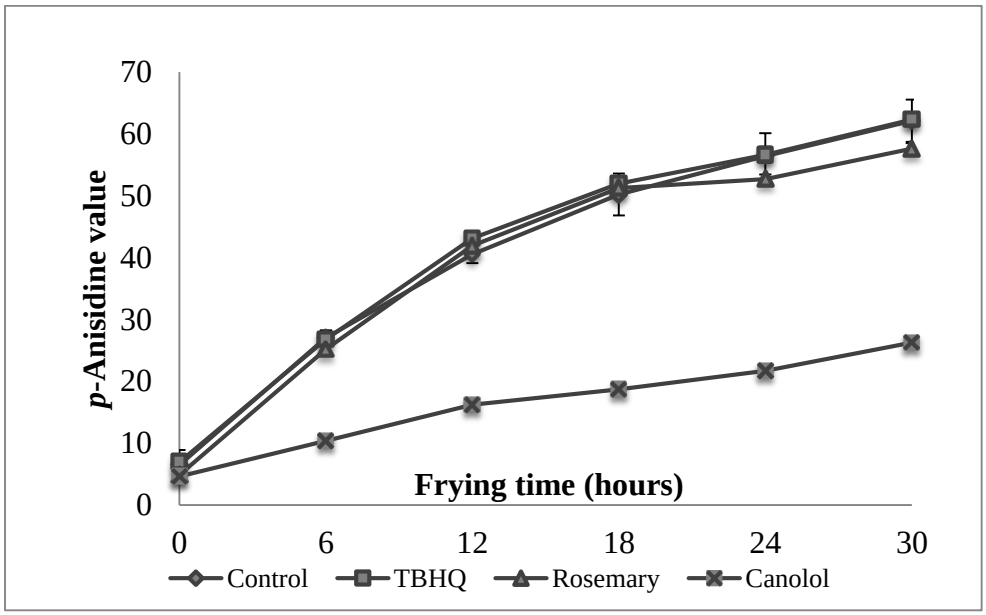

Figure 4.9 Formation of *p*-Ansidine value in high oleic soybean oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

4.5.4 Acid Value (AV)

The acid value of all deep-frying oil samples showed similar trend for all of high oleic deep-frying oils (Figure 4.10-4.12). CAL treated canola and sunflower oils showed the highest ($p < 0.05$) acid value during 30-hour deep-frying when compared to CON, RM and TBHQ in canola oil and sunflower oil. The acid value of CON, RM and TBHQ treated canola, sunflower

and soybean oil increased gradually in, but they were not significantly different ($p > 0.05$) during 30-hour frying. Overall, the AV in canola oil was the highest across all treatments during 30-hour deep-frying when compared to sunflower and soybean oils. After 30-hour deep-frying, the highest AV was found in CAL treated canola, sunflower and soybean oils with 3.06 mg KOH/g, 2.74 mg KOH/g, and 1.62 mg KOH/g respectively.

Acid value is determined by the numbers of milligrams of KOH necessary to neutralize 1 g of the oil sample. Frying oils and fats need to be rejected when the acid value reaches 2.0 – 2.5 mg KOH/100g. On the other hand, the recommendations of the 7th Symposium on Deep-Fat Frying (2014) do not consider the content of free fatty acids as a regulatory index to monitor and compare the degree of degradation of frying oils. Although FFA content is not a particularly good parameter for comparing different frying processes or oil stability, it could still be used as an indicator to evaluate oil quality (Li, et al., 2008). This is because FFA has a significant effect on the quality of fried foods, and there is an extensive mass exchange between the frying oil and the fried food. In the current study, CON, TBHQ, RM treated canola, sunflower, and soybean oil showed very strong effects on slowing down the presence of free fatty acids in deep-frying oils, however, CAL treated oils had the opposite effect on AV. It elevated AV significantly ($p < 0.05$) during deep-frying, which exceeded the limitation of AV after 18 hours deep-frying in high oleic canola oil and sunflower oil. CAL treated soybean oils showed significant increasing of AV, but it did not exceed 2 KOH/g after 30-hour deep-frying. The results was similar to the previous deep-frying study by Matthaus et al., (2014), but this could be partially explained by the

influence of free fatty acids perhaps formed during the short heating of the grounded canola seeds at 160 °C during extraction using ASE. The presence of moisture might come from the canola seeds during the extraction processing.

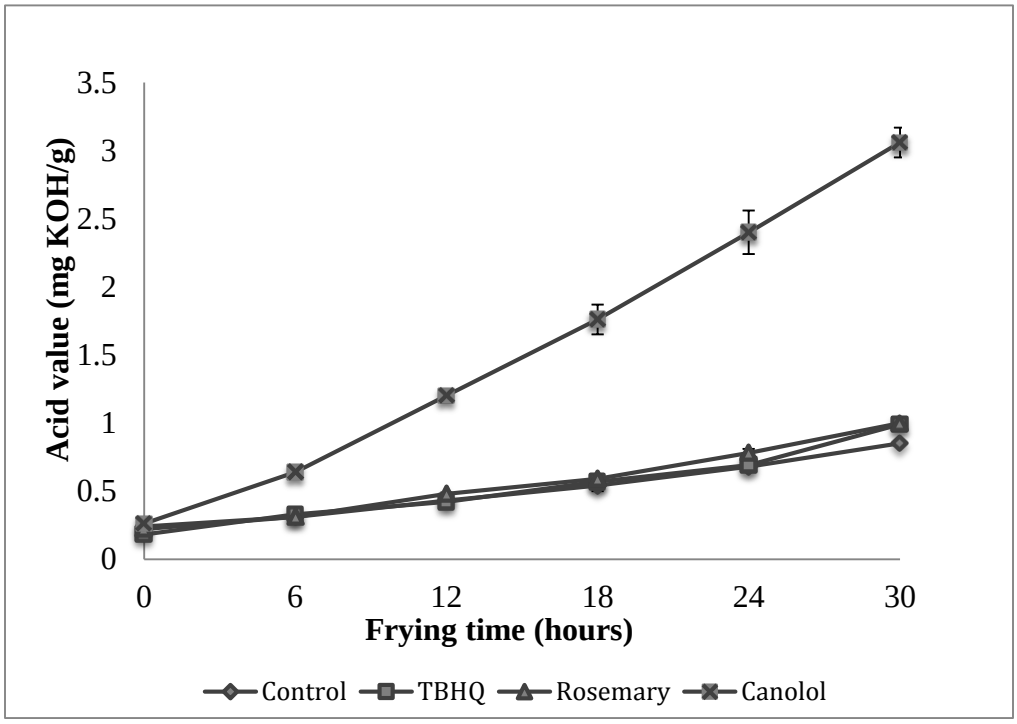

Figure 4.10 Formation of acid value in high oleic canola oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

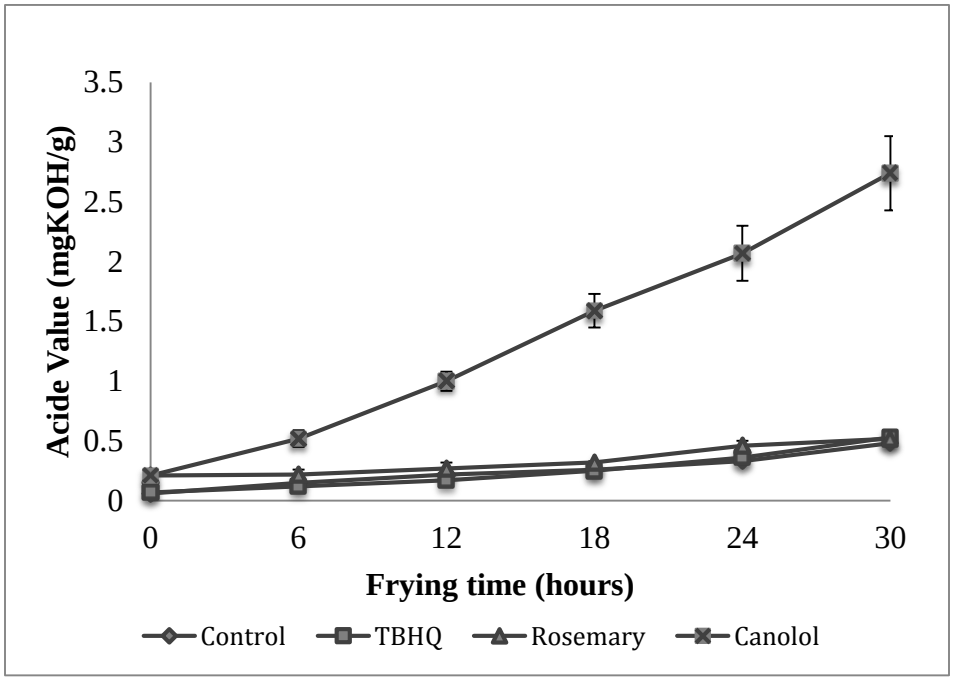

Figure 4.11 Formation of acid value in high oleic sunflower oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

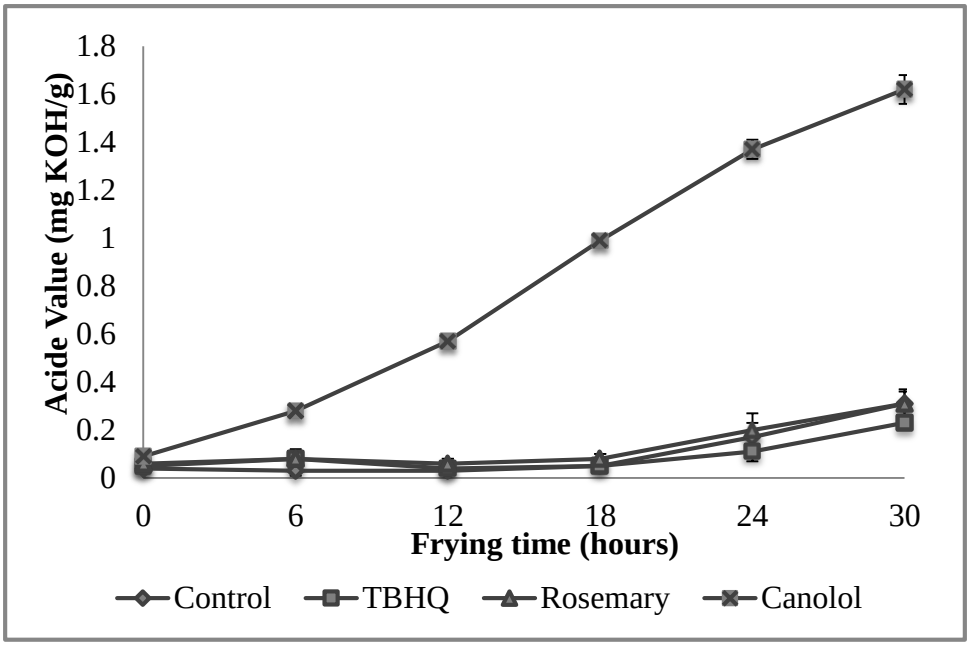

Figure 4.12 Formation of acid value in high oleic soybean oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

4.5.5 Iodine Value (IV)

Generally, IV decreased gradually in canola, sunflower and soybean oil samples during 30-hour frying (Figure 4.13-4.15). CON, TBHQ, RM and CAL treated sunflower and soybean oil and were not significantly difference ($p > 0.05$) of IV before frying started, while CAL treated canola oil showed significant difference ($p < 0.05$) of IV compared to CON, TBHQ and RM treated canola oil before deep-frying. CAL treated canola oil showed significantly ($p < 0.05$) higher iodine value when compared to RM treated canola oils after 6-hour deep-frying. CON, TBHQ, RM and CAL treated canola oil were not significantly different from 12-hour to 24-hour deep-frying. RM and CAL treated sunflower oil were significantly ($p < 0.05$) higher on IV from 6-hour to 12-hour frying, while CAL treated canola and sunflower oils dropped IV very significantly ($p < 0.05$) after 12-hour deep-frying. RM treated canola and sunflower oils showed significant higher IV when compared to CON, TBHQ, and CAL treated canola and sunflower oils during 18 hours of frying. CON, TBHQ and RM treated high oleic soybean oil were not significantly different ($p > 0.05$) during 30 hours of frying. CAL treated soybean oil showed significant higher iodine value than CON of soybean oil after 12-hour deep-frying, and CAL treated soybean oil did not decrease significantly ($p > 0.05$) during 30-hour deep-frying. Overall,

CAL showed significant effect on slowing down the drop in iodine value during 30-hour deep-frying in high oleic soybean oil.

Measuring levels of polyunsaturated fatty acids, such as linoleic acid, can help determine extent of thermal oxidation (Choudhary, et al., 2014). Iodine value is a measure of the number of double bonds in the oil. Canola oil has iodine value about 188–193, sunflower oil ranges from 110–143, soybean oil has iodine value from 120–143, and high oleic safflower oil has iodine value from 90–100 (Knothe, 2002). In general, the deep-frying process decreases the content of unsaturated fatty acids in frying fat and oil because of oxidation and polymerization. During deep-frying at 160 °C, a progressive decrease in unsaturation was observed in all oil samples. This decrease shows the consumption of double bonds by oil oxidation. Although the decrease in iodine value is a result of complex physicochemical changes, this decrease is indicative of the oxidation rate (Lalas, 2009) and could be a useful quality parameter to control oil quality during frying. Choudhary et al., 2014, have found a relative loss of the C18: 2 fatty acid and a decrease in the iodine value of oil after heating due to more intensive thermo-oxidative transformations that occur as compared to heated oil containing food. The decrease in the iodine value can be attributed to the destruction of double bonds by oxidation, scission, and polymerization. According to previous studies, the heat treatment causes the oxidative rancidity resulting in an increase in free fatty acids. This is why heated and unheated fats and oils should be monitored by means of analysis of the fatty acid composition and iodine value indicating the degradation of the fatty acids.

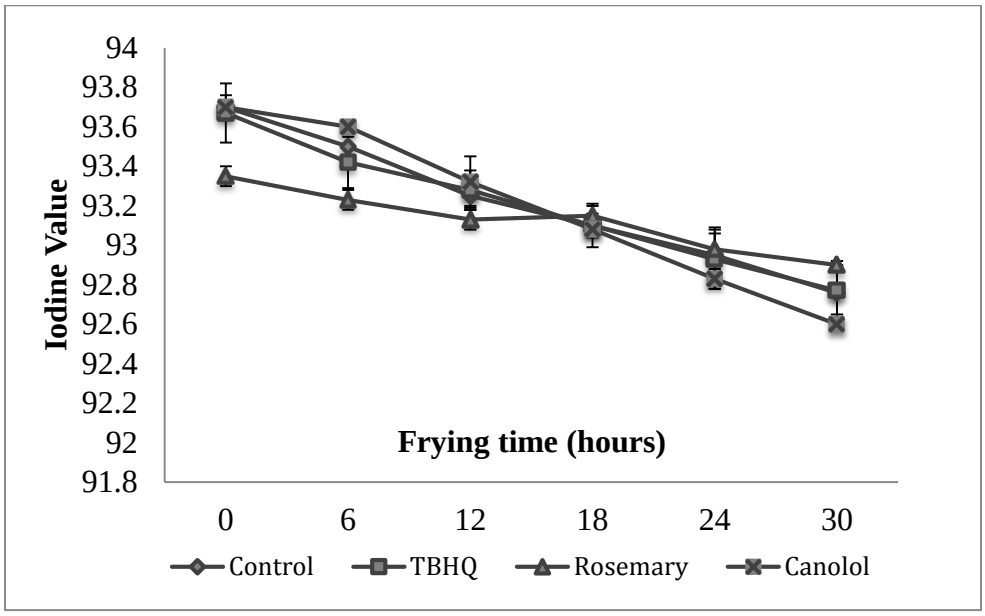

Figure 4.13 Formation of iodine value in high oleic canola oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

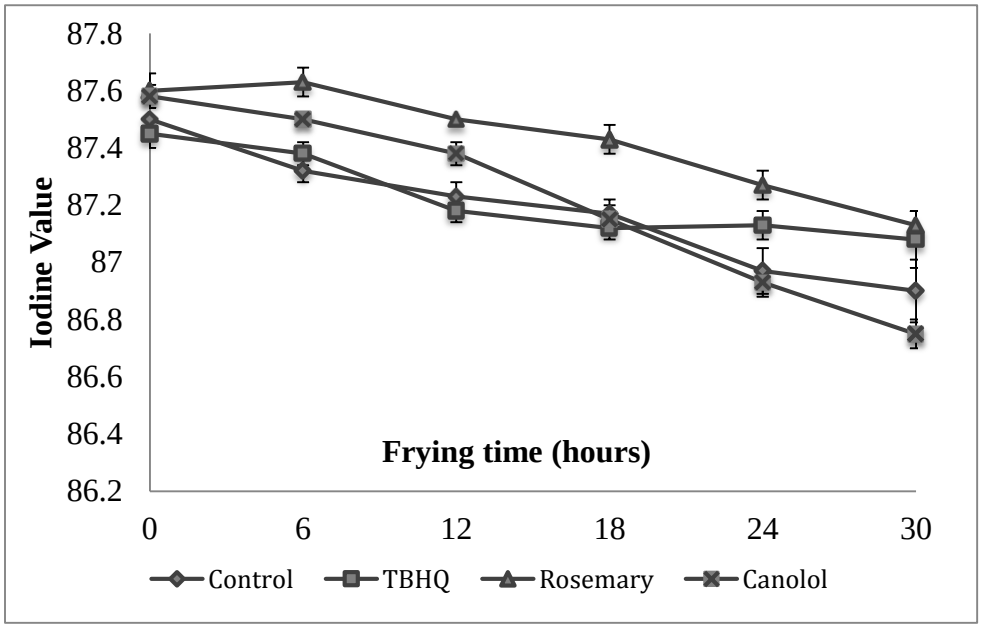

Figure 4.14 Formation of iodine value in high oleic sunflower oil during 30-hour deep-frying.

Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

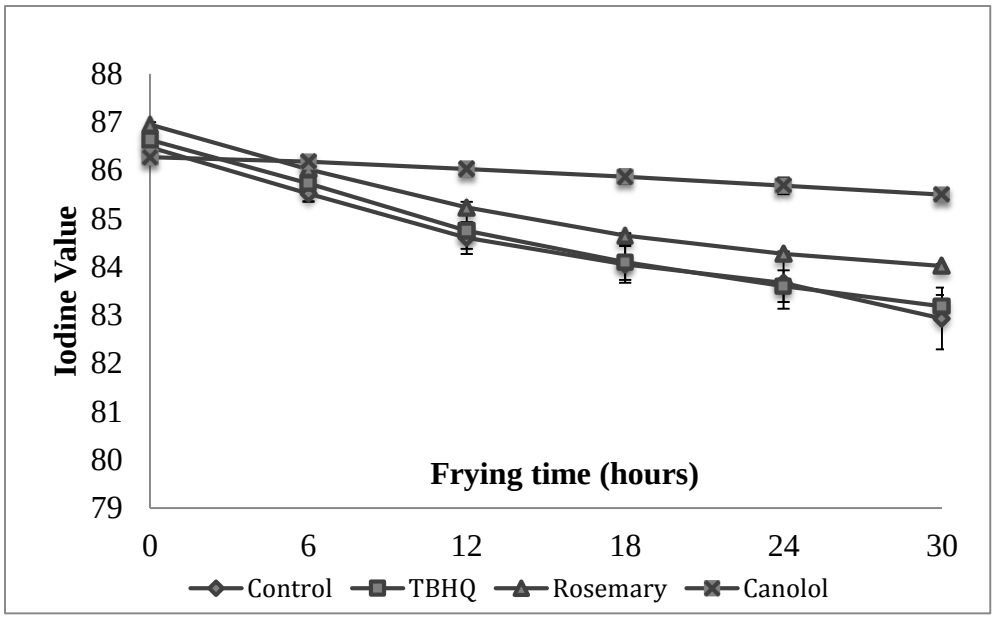

Figure 4.15 Formation of iodine value in high oleic soybean oil during 30-hour deep-frying. Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the antioxidant treatments were treated at 200 ppm concentration.

4.5.6 Degradation of tocopherols after 30-hour deep-frying

High oleic vegetable oils mainly contain α-tocopherol and γ-tocopherol; canola oil and sunflower oil has higher α-tocopherol content, while soybean oil has higher level of γ-tocopherol. Both α- and γ-tocopherols were significant ($p < 0.05$) degraded after 30-hour deep-frying (Table 4.2). Deep-frying oils fortified with CAN and RM were significant amounts of α- and

γ-tocopherol found after 30 hours of frying. The degradation rate of α- and γ-tocopherol was lower for oil fortified with antioxidants during deep-frying. γ-tocopherol showed faster degradation rate in comparison to α-tocopherol in which agreement with the finding of Aggelousis & Lalas (1997) who described the relative decomposition rates after 5 days of frying as δ > γ > α-tocopherol. Also Carlson and Tabach (1997) showed that the decomposition rates of tocopherols in fried soybean oils were γ- > α-tocopherol. The results of present study showed the addition of natural antioxidants can slow down the tocopherols degradation during deep-frying. This result is in agreement with findings of Reblova and Okrouhla (2010), who showed that different phenolic compounds were able to protect α-tocopherol significantly.

Table 4.2 The degradation of α- and γ-tocopherols in high oleic oils after 30 hours deep-frying

α-tocopherol (mg/kg)												
Frying	CON			TBHQ			RM			CAL		
Hours	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil
0	163.43 ± 3.55	581.10 ± 2.96	60.61 ± 2.80	258.28 ± 2.46	565.90 ± 11.15	120.52 ± 12.11	158.20 ± 11.38	671.92 ± 1.4	53.71 ± 11.12	186.32 ± 0.42	534.49 ± 0.83	121.99 ± 4.64
30	43.62 ± 13.36	409.70 ± 2.85	0.00 ± 0.00	166.64 ± 7.03	475.94 ± 8.97	12.58 ± 7.34	143.87 ± 2.08	442.06 ± 11.23	0.00 ± 0.00	173.48 ± 7.99	465.59 ± 10.68	71.98 ± 12.16
γ-tocopherol (mg/kg)												
Frying	CON			TBHQ			RM			CAL		
Hours	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil	Canola oil	Sunflower oil	Soybean oil
0	291.12 ± 3.68	60.48 ± 5.56	584.60 ± 5.58	376.34 ± 5.62	54.97 ± 5.10	750.83 ± 11.10	305.13 ± 6.85	61.09 ± 6.26	562.01 ± 3.91	334.74 ± 16.48	67.59 ± 6.04	587.48 ± 4.95
30	191.84 ± 16.14	54.39 ± 8.66	49.24 ± 7.41	209.70 ± 4.27	52.26 ± 3.66	77.78 ± 5.40	213.39 ± 7.35	43.00 ± 4.31	76.30 ± 4.71	182.06 ± 6.00	39.66 ± 5.74	336.96 ± 6.08

All data are expressed as mean ± standard deviation (Experiment replications n=2)

4.5.7 Color

Lovibond color scales Hunter L a*b* were used in color analysis. The data were expressed as the average values and standard deviations for all oil samples in the whole frying period respectively (Table 4.3-4.5). In Hunter L a* b* color scale, L value represents lightness-darkness dimension; the higher L value, the more lightness the oil was displaying (Bansal et al., 2010). L values did not show significant differences ($p > 0.05$) in all oil samples from day 0 to day 5, and it decreased gradually with increasing the frying time in all frying oil samples. CAL treated oils showed significant effects on lowering L value among all frying oil samples. All of the samples were in greenness dimension at the initial level, a* values in all frying oil samples decreased after 18 hours of frying. CAL treated oils showed significant difference of a* before frying started ($p < 0.05$) in canola, sunflower and soybean oils. CON, TBHQ and RM treated oils had a similar tendency during 5-day frying, while CAL treated oils had opposite tendency of a* values compared to others, which means a* was increasing during 5-day frying in three type of frying oils. All of the samples were in yellowness dimension at the initial level. b* values in all the samples increased gradually during 5-day frying. The b* value of CAL treated oils showed significant difference on day 0 and day 1 ($p < 0.05$) in all three types of frying oils. CAL treated oil had higher b* among all of oil samples, but it decreased after 6 hours of frying, and then increased after 12 hours of frying.

Color formation is one of the most noticeable degradation reactions that occur in deep frying oils. Physical and chemical reactions in response to frying temperature, frying time, and

food ingredients The lightness decreased with increasing frying cycles, the brown color could from caramelization and Millard reaction from the fried food (Bansal et al., 2010; Choe & Min 2007; Petersen et al., 2013). RM and CAL treated oils were significantly ($p < 0.05$) different on the initial color before frying due to the dark color in the extractions (Bansal et al., 2010; Li et al., 2008). There is a positive correlation between color and antioxidant properties in extractions where the formation of antioxidant is prevalent during processing (Siger et al., 2015). The potential alteration in color induced by natural dietary polyphenols could be both physical, upon food product appearance, and chemical, related to the stability and compatibility of the color in a certain food category.

The color change may be attributed to the diffusion of food pigments into the oil during frying (Maskan 2003). The formation and accumulation of high-molecular-weight compounds such as polar materials in deep-frying oils may also have contributed to the increase in total color darkness (Maskan 2003; Totani et al., 2012). Redness may be due to the formation of polymers, which promote the darkening of oil; the yellow color may be related to the combined peroxides and aldehydes in oil (Maskan 2003; Totani et al., 2012). Leaching of pigments from the food into the frying oil, and the presence of Maillard reaction products, formed during frying by the reaction of carbohydrates and some lipid oxidation products with amines, amino acids, and proteins also affects the color development (Lalas et al., 2006; Delgado-Andrade et al., 2010). Furthermore, particles from food being fried can become caramelized and release some fat-soluble pigments into the oil (Vijayan et al., 1996).

Table 4.3 L, a*, b* values of high oleic canola oil during five days of frying

	L				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	94.68 ± 0.27	94.96 ± 3.34	93.12 ± 0.22	91.79 ± 0.65	-4.40 ± 0.03	-4.35 ± 0.11	-4.22 ± 0.11	-6.23 ± 0.08	10.63 ± 0.07	10.61 ± 0.17	12.72 ± 0.06	22.64 ± 0.17
6	93.36 ± 0.06	93.12 ± 0.10	92.40 ± 1.29	89.70 ± 0.15	-4.81 ± 0.02	-4.88 ± 0.04	-6.30 ± 0.03	-4.68 ± 0.07	13.73 ± 0.17	14.41 ± 0.38	18.42 ± 0.16	19.36 ± 0.37
18	91.16 ± 0.04	83.61 ± 0.51	89.71 ± 0.12	87.37 ± 0.26	-5.46 ± 0.10	-4.85 ± 0.02	-6.79 ± 0.07	-4.33 ± 0.07	18.77 ± 0.54	18.52 ± 0.12	25.24 ± 0.32	23.98 ± 0.28
30	90.12 ± 0.47	88.47 ± 0.31	88.13 ± 0.07	84.19 ± 0.35	-5.99 ± 002	-5.67 ± 0.15	-6.76 ± 0.16	-4.34 ± 0.07	23.61 ± 0.66	25.38 ± 0.34	29.61 ± 0.43	29.26 ± 0.19

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.
All data are expressed as mean ± standard deviation

Table 4.4 L, a*, b* values of high oleic sunflower oil during five days of frying

	L				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	95.01 ± 0.14	94.52 ± 0.74	94.73 ± 0.50	92.40 ± 0.50	-3.51 ± 0.03	-3.43 ± 0.08	-3.82 ± 0.03	-5.86 ± 0.28	8.60 ± 0.03	8.70 ± 0.28	9.50 ±0.11	20.88 ±1.70
6	94.30 ± 0.49	94.61 ± 0.13	93.97 ± 0.83	91.52 ± 0.83	-4.08 ± 0.11	-3.95 ± 0.01	-5.90 ± 0.03	-4.66 ± 0.11	9.05 ± 0.06	9.05 ± 0.05	15.91 ± 0.03	15.95 ± 0.99
18	93.70 ± 0.57	93.26 ± 0.67	92.58 ± 1.22	89.62 ± 1.22	-4.60 ± 0.33	-4.62 ± 0.21	-7.05 ± 0.03	-4.94 ± 0.18	11.40 ± 0.76	12.61 ± 0.89	20.71 ± 0.37	19.92 ±1.17
30	93.27 ± 0.07	92.43 ± 0.34	91.81 ± 0.17	87.93 ± 0.88	-5.55 ± 0.25	-5.62 ± 0.15	-7.49 ± 0.02	-5.39 ± 0.32	14.70 ± 0.21	16.46 ± 0.41	23.62 ± 0.29	25.07 ± 1.58

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.

All data are expressed as mean ± standard deviation

Table 4.5 L, a*, b* values of high oleic soybean oil during five days of frying

	L				a*				b*			
Hours	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL	Control	TBHQ	RM	CAL
0	95.71± 0.05	95.31± 0.52	95.43± 0.16	94.17± 0.03	-3.44± 0.19	-3.22± 0.32	-3.28± 0.05	-5.18± 0.04	6.76± 0.57	6.74± 0.70	6.59± 0.31	15.67± 0.07
6	92.58± 1.48	91.61± 0.95	92.93± 0.16	92.11± 0.22	-5.55± 0.17	-5.50± 0.27	-7.22± 0.10	-5.20± 0.10	16.04± 0.56	17.64±0.41	23.12± 0.14	17.26± 0.45
18	92.24± 0.46	91.87± 0.25	91.77± 0.06	91.18± 0.47	-8.08± 0.18	-8.31± 0.02	-8.91± 0.04	-5.83± 0.24	24.37± 1.40	26.52± 0.05	29.57± 0.31	21.57± 0.48
30	90.65± 0.73	89.80± 0.09	89.77± 0.38	88.68± 0.24	-8.61± 0.08	-8.51± 0.04	-8.90± 0.08	-6.15± 0.15	29.88± 2.64	32.28± 0.58	33.98± 0.50	27.59± 0.22

L a* b* values are representing lightness – darkness, redness – greenness, yellowness – blueness, respectively.

All data are expressed as mean ± standard deviation

4.6 Evaluating the Relationship between Color and Quality Indicators of Deep-frying Oils

The correlation between color scales: Hunter L, a*, b* and oil quality indicators: total polar components, polymeric triglycerides, *p*-anisidine value, acid value and iodine value are indicated in Table 4.6 - 4.8. From a general perspective, high oleic soybean oil got a stronger correlation between color scales and oil quality parameters, followed by high oleic canola oil, while high oleic sunflower oil did not show many correlation. CON showed negative correlation between color parameters and the quality parameters, Lightness in CON of canola oil highly correlated with TPC, PTG, *p*-AnV, AV and IV (r = -0.98, -0.98, -0.99, -0.95 and 0.99 respectively). The redness-greenness dimension a* had a negative correlation (r = -0.95) with AV in TBHQ of canola oil. Lightness in RM of canola oil negatively correlated *p*-AnV and AV (r = -0.98 and -0.99 respectively). Lightness in CAL of canola oil showed negative correlation with TPC PTG and AV (r = -0.99, -0.98 and -0.99), while L positively correlated with *p*-AnV and IV (r = 0.98). CON and TBHQ showed higher correlations between all of color parameters, but RM and CAL did not show any significant correlations between color parameters and TPC ($p > 0.05$). Lightness in CON and TBHQ did not show any significant correlations ($p > 0.05$) with all of quality parameters in high oleic soybean oil, while RM and CAL showed significant negative correlations between lightness and PTC, PTG, *p*-AnV, and IV. CON, TBHQ, and CAL showed significant negative correlations between a* and TPC, PTG.

The linear regression models were generated using color parameters as explained in material and methods section to express TPC, *p*-AnV and PTG, which are acceptable oil quality

indicators (Table 4.9 - 4.11). There is about 65% of variances that could follow in the regression model when mixing the data from three types of deep-frying oil and additional antioxidants treatments together. If the data were separated from three types of high oleic vegetable oils, and mixed with antioxidants treatments only, less than 60% variables fitted with the model in high oleic canola oil; only half of the variances could fit into the model in high oleic sunflower oil; over 80% variables could fit the models in high oleic soybean oil. The regression models were sensitive with oil categories and treatments, which means the color of different deep-frying oils and different antioxidants treatments showed significant effects on the regression model. About 80% to 90% variables could fall in those models. However, AV did not show any significant in the regression model for CON, TBHQ and RM treated oils. Overall, the regression model that was generated with different antioxidants treatments could fit for larger amount of variances.

Color changes can be observed in deep-frying oils much earlier than the flavor and odor of the oil becomes unacceptable (Paul and Mittal, 1997). Color measurement has become a particular measurement in food industries and their advantages are being discussed. Color evaluation of deep-frying oils is the easiest way to judge the oil quality but the rate of oil darkening varies from oils and it also depends upon the initial color before frying (Gertz, 2000). According to Xu, (2003), a deep-frying study showed a strong correlation ($r = 0.96$, $p < 0.001$) was found between the polar compound contents and color indices of palm olein, monola oil and canola oil samples. If the color index of frying oils exceeds 45, it means the total polar compounds are over 27% which is the maximum level permitted in a frying oil (Xu, 2003).

Another study mentioned polymers, total polar compounds and free fatty acids in deep-fried canola oil were highly correlated with color at r = -0.965, -0.984, -0.993 respectively. Furthermore, spectrophotometric method is another rapid assessment of colors for deep-frying oils. The most significant changes in frying oil samples were observed between 470 and 500 nm. The researchers found the highest correlation of spectrophotometric absorbance at 490 nm with total polar content ($r = 0.953$, $P < 0.001$). According to Baixauli et al (2002), an equation for the conversion of spectrophotometric absorbance to TPC was developed as $y = -2.7865\ x^2 + 23.782\ x + 1.0309$. It means if 27 % TPC is used as the maximum level allowed in the frying oil, the spectrophotometric absorbance of frying oil at 490 nm should be ≤ 1.3. Comparing the previous study to the current study, the equations are generated by the reliable indicators for used oils. The rapid assessment could be done by measuring the color parameters (L, a*, b*) as the indicators of deep-frying oils. If the outcomes of the equations were over 27 % TPC, or 30 of *p*-AnV, the used oil needs to be rejected.

Table 4.6 The correlation between color parameters (L, a*, b*) and total polar components, polymeric triglycerides, *p*-anisidine value, acid value and iodine value in high oleic canola oil with control, TBHQ, rosemary, and canolol treatment.

		TPC (%)	**PTG** (%)	**p-AnV**	**AV** (mg KOH/100g)	**IV**
CON	L	-0.98	-0.98	-0.99	-0.95	0.99
	a*	NS	NS	NS	-0.98	NS
	b*	NS	NS	0.99	0.99	NS
TBHQ[a]	L	NS	NS	NS	NS	NS
	a*	NS	NS	NS	-0.95	NS
	b*	NS	NS	NS	NS	NS
RM[a]	L	NS	NS	-0.98	-0.99	NS
	a*	NS	NS	NS	NS	NS
	b*	NS	0.98	NS	NS	NS
CAL[a]	L	-0.99	-0.98	0.98	-0.99	0.98
	a*	NS	NS	NS	NS	NS
	b*	NS	NS	NS	NS	NS

[a] TBHQ, RM, CAL at 200 ppm
NS: Not Significant ($p>0.05$)

Table 4.7 The correlation between color parameters (L, a*, b*) and total polar components, polymeric triglycerides, *p*-anisidine value, acid value and iodine value in high oleic sunflower oil with control, TBHQ, rosemary, and canolol treatment.

		TPC (%)	**PTG** (%)	**p-AnV**	**AV** (mg KOH/100g)	**IV**
CON	L	-0.96	-0.96	NS	NS	NS
	a*	-0.99	-0.98	-0.98	NS	NS
	b*	0.99	0.98	0.99	NS	0.98
TBHQ[a]	L	-0.97	-0.97	-0.96	-0.96	-0.99
	a*	-0.98	NS	NS	NS	-0.97
	b*	0.99	0.99	0.97	0.99	NS
RM[a]	L	NS	-0.98	NS	NS	-0.96
	a*	NS	NS	NS	NS	NS
	b*	NS	NS	NS	0.97	NS
CAL[a]	L	NS	NS	-0.97	NS	NS
	a*	NS	NS	NS	NS	NS
	b*	NS	NS	NS	NS	NS

[a] TBHQ, RM, CAL at 200 ppm

NS: Not Significant ($p > 0.05$)

Table 4.8 The correlation between color parameters (L, a*, b*) and total polar components, polymeric triglycerides, *p*-anisidine value, acid value and iodine value in high oleic sunflower oil with control, TBHQ, rosemary, and canolol treatment.

		TPC (%)	**PTG** (%)	**p-AnV**	**AV** (mg KOH/100g)	**IV**
CON	L	NS	NS	NS	NS	NS
	a*	-0.99	-0.98	NS	NS	0.97
	b*	NS	NS	NS	NS	-0.99
TBHQ[a]	L	NS	NS	NS	NS	NS
	a*	-0.98	-0.97	-0.99	NS	0.97
	b*	0.99	0.99	NS	NS	-0.99
RM[a]	L	-0.97	-0.96	-0.96	NS	0.97
	a*	NS	NS	NS	NS	NS
	b*	NS	NS	0.97	NS	-0.95
CAL[a]	L	-0.97	-0.99	-0.98	-0.96	0.96
	a*	-0.98	-0.96	-0.97	NS	0.98
	b*	NS	NS	0.98	NS	NS

[a] TBHQ, RM, CAL at 200 ppm

NS: Not Significant ($p > 0.05$)

Table 4.9 Regression models[a] of total polar components, acid value, *p*-anisidine value, and polymeric triglycerides in three high oleic oils during 30-hour deep-frying[b]

	P value	R^2	Linear Regression Model
TPC	0.00	0.61	TPC = 95.94 – 1.08 L – 1.87 a* - 0.10 b*
AV	p >0.05	NS[c]	NS[c]
p-AnV	0.00	0.65	*p*-AnV = 59.36 – 0.90 L – 8.73 a* - 0.25 b*
PTG	0.00	0.65	PTG = 11.61 – 0.17 L – 1.25 a* - 0.036 b*

[a] The regression model was made by mixing all of three high oleic oils and all of the treatments together.
[b] 30-hour deep-frying: Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the treatments were at 200 ppm concentration.
[c] NS: Not Significant

Table 4.10 Regression models[a] of total polar components, acid value, *p*-anisidine value, and polymeric triglycerides in high oleic canola oil, high oleic sunflower oil and high oleic soybean oil during 30-hour deep-frying[b]

Oils	Indicators	R^2	Linear Regression Model
HOCAN	TPC	0.50	TPC = 81.01 – 0.96 L – 1.93 a* - 0.10 b*
	AV	NS	NS[c]
	p-AnV	0.55	*p*-AnV = 70.65 – 0.75 L + 0.45 a* + 0.65 b*
	PTG	0.47	PTG = 10.64 – 0.11 L – 0.02 a* - 0.07 b*
HOSUN	TPC	0.51	TPC = 231.64 – 2.46 L – 3.25 a* - 1.08b*
	AV	0.42	AV = 57.96 – 0.60 L – 0.13 a* - 0.16 b*
	p-AnV	0.68	*p*-AnV = 789.89 – 8.39 L – 13.64 a* - 4.14 b*
	PTG	0.58	PTG = 115.07 – 1.23 L – 2.01 a* - 0.63 b*
HOSOYB	TPC	0.82	TPC = 85.57 – 1.01 L – 3.39 a* - 0.38 b*
	AV	0.20	AV = 125.22 – 1.31 L – 1.35 a* - 0.57 b*
	p-AnV	0.87	*p*-AnV = 318.35 – 3.74 L – 15.44 a* - 1.96 b*
	PTG	0.81	PTG = 29.59 – 0.37 L – 1.93 a* - 0.17 b*

[a] The regression model was depending on the types of high oleic oils.
[b] 30-hour deep-frying: Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the treatments were at 200 ppm concentration.
[c] NS: Not Significant

Table 4.11 Regression models[a] of total polar components, acid value, *p*-anisidine value, and polymeric triglycerides on control, TBHQ, rosemary and canolol treatments during 30-hour deep-frying[b]

Treatments	Indicators	R^2	Linear Regression Model
CON	TPC	0.91	TPC = 104.51 – 1.12 L + 0.53 a* - 0.10 b*
	AV	NS[c]	NS
	p-AnV	0.91	*p*-AnV = -8.31 – 0.30 L – 13.38 a* - 0.77 b*
	PTG	0.92	PTG = -13.19 + 0.08 L – 1.38 a* + 0.07 b*
TBHQ	TPC	0.94	TPC = 41.73 – 0.46 L + 0.80 a* + 0.71 b*
	AV	NS	NS
	p-AnV	0.89	*p*-AnV = -48.24 + 0.18 L – 10.38 a* + 0b*
	PTG	0.92	PTG = -6.69 + 0.02 L – 1.31 a* + 0.06 b*
RM	TPC	0.91	TPC = 4.95 – 0.06 L + 2.18 a* + 0.97 b*
	AV	NS	NS
	p-AnV	0.90	*p*-AnV = -1157.03 + 12.01L + 9.20a* + 6.23b*
	PTG	0.83	PTG = -130.42 + 1.35 L + 1.31 a* + 0.81 b*
CAL	TPC	0.80	TPC = 35.80 – 0.38 L + 1.73 a* + 0.54 b*
	AV	0.85	AV = 64.84 – 0.68 L – 0.65 a* - 0.24 b*
	p-AnV	0.56	*p*-AnV = 537.94 – 5.94 L – 10.65 a* - 2.06 b*
	PTG	0.75	PTG = 65.55 – 0.73 L – 1.23 a* - 0.22 b*

[a] The regression model was depending on additional antioxidant treatments.
[b] 30-hour deep-frying: Six batches of straight-cut potatoes (100 g / batch) were fried each day, one hour apart for a total of 6 hours of frying for 5 days. All of the treatments were at 200 ppm concentration.
[c] NS: Not Significant

4.7 Conclusion

This study evaluated the effects of 200 ppm antioxidants (TBHQ, RM, CAL) on the stability of high oleic vegetable oils during 30 hours of deep-frying, and regression models were generated by oil color parameters L, a*, b* and TPC, PTG, *p*-AnV. The addition of CAL in soybean oil showed strong effectiveness on slowing down the formation of TPC, PTG, and aldehydes during 30 hours frying; however increased the acid value of canola, sunflower and soybean oil in compared to other additional antioxidants. RM treated canola and sunflower oil showed significant effect on slowing down the formation TPC and PTG during 30 hours frying. CAL treated canola, sunflower and soybean oils showed significant effects by slowing down oil darkening during 30 hours of frying, even though the oil was initially darker when fortified with CAL before frying. RM and TBHQ treated canola, sunflower and soybean oils showed adverse effects on ΔE during frying. This study showed significant correlations between color parameters and TPC, PTG, and *p*-AnV during 30-hour frying. The linear regression models were generated by color parameters (L, a*, b*), there is over 80% of variables falling into the models to predict the content of TPC, PTG or *p*-AnV. Further investigations need to be done for the effects of ingredients of fried foods on color changes using high oleic canola oils in small scale deep-frying. More linear regression models will be generated using different fried foods. Furthermore, more investigation needs to be done on the composition of canolol-enriched extracts and contribution of the individual compounds on the antioxidant activity of the extracts.

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CHAPTER 5

GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES

5.1 General Conclusion

High oleic vegetable oils contain higher amount of oleic fatty acids and lower amount of unsaturated fatty acids, which could affect frying performances in deep-frying oils. The volatile and nonvolatile compounds generated by oxidation in the frying oil will degrade the quality and stability; also, increase viscosity, and contribute to darkness of color. The color of used oils is the most apparent change during deep-frying. Antioxidants were applied to increase frying stability and performance of deep-frying. After 30 hours, the highest total color change has been observed in RM samples, and the lowest color change was in CAL samples in all of oil samples. Control and TBHQ did not show significant difference in oil darkening. CAL showed significant effects on slow down oil darkening during 30 hours of frying, even though the oil was darker when fortified with CAL before frying. CAL samples showed the highest ability to control the total color change during the 30-hour frying period. It provides baseline data on the color stabilizing effects of canolol-enriched extracts in frying oil in comparison with other antioxidants.

The addition of CAL in soybean oil showed strong effectiveness on slowing down the formation of TPC, PTG, and aldehydes during 30 hours frying; however, it increased the acid value of all three types of high oleic oils in comparison to other additional antioxidants. This study also established a linear regression model to rapid assessment of used oils. This study

showed significant correlations ($p<0.05$) between color parameters and TPC, PTG, and *p*-AnV during 30-hour frying. The linear regression models were generated by color parameters (L, a*, b*), there is over 80% of variables falling into the models to predict the content of TPC, PTG or *p*-AnV. The models are based on the straight-cut potatoes were fried in to high oleic canola oil, high oleic sunflower oil and high oleic soybean oil, which have been fortified with TBHQ, rosemary extracts and canolol-enriched extracts at 200 ppm.

5.2 Limitations & Future Perspectives

There are several limitations in the present study. The current deep-frying trials were conducted using small fryers more suitable for a laboratory setting rather than a deep-frying setting used in restaurants or food industries. The frying frequency of the current study is lower than the restaurants or cafeterias. Moreover, the food component used in the current study is potato only, thus more types of foods need to be assessed. Further investigations need to be done on the efficiency of additional natural antioxidants such as canolol on different types of fried foods using high oleic canola oil. Furthermore, linear regression models for rapid assessment of frying oil quality need to be generated using different types of fried foods.