Factors Affecting Thermal Stability of Vegetable Oil

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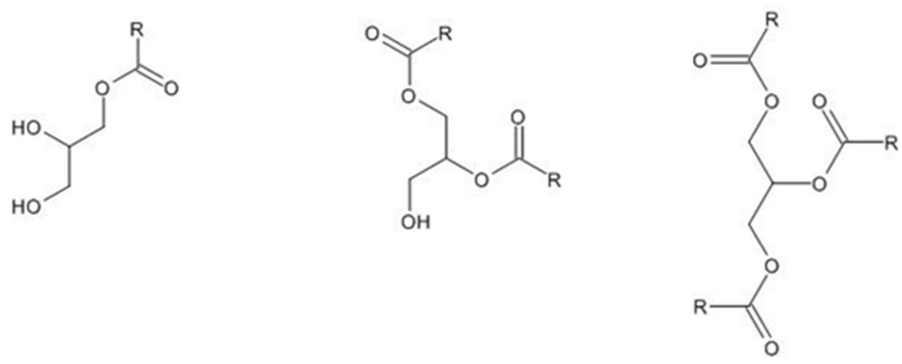
Abstract

The thermal degradation of vegetable oils presents considerable challenges for the food processing sector and public health. This paper explores the complexities of the thermal degradation of vegetable oil, highlighting the interdependent interactions among its various factors. The heterogeneity in oil composition and external factors such as temperature, frying time, and frying cycles, adds to the difficulty in understanding the degradation process. Research efforts have focused on internal factors like fatty acid composition and antioxidants and external factors such as heating temperature and time. Antioxidants from natural sources have shown promise in stabilizing vegetable oils, yet further research is needed to make them effective in elevated temperatures. Additionally, the role of metal surfaces in the degradation process remains underexplored, This review aims to summaries current knowledge and identify gaps for future research in improving vegetable oil stability and safety. The review is also relevant to the biodiesel application.

Keywords: *Thermal degradation, Fatty acid composition, Heating time, Heating cooling cycle, Effect of metal*

1. Introduction

Vegetable oils primarily consist of glycerides, which are esters of glycerol and fatty acids. Triglycerides are the principal component of any oil and fat. Along with them, they also contain diglycerides, monoglycerides (Figure 1) and free fatty acids. Some traces of phosphatides, sterols, fatty alcohols and fat-soluble vitamins are also found in oil and fat. The relative amounts of different fatty acids esterified with glycerol vary in different oil types (Chemat, 2017).



Monoglyceride Diglyceride Triglyceride

Figure 1. Different types of glycerides

Oil carries water-insoluble essential elements vital for growth and metabolism, protects brain cells and reduces the risk of heart diseases. It provides essential fatty acids for the human body (O'Brien, 2008). However, the fundamental reason for their use in cooking is that they contribute to the flavour and texture of the food, making dishes tasty and giving them a good, smooth mouthfeel (Bockisch, 2015). They make baked products crispier and conduct heat while cooking. Thus, oil is an integral part of food preparation. In addition to their culinary applications, oils are utilised for various purposes such as fuel, medical treatments, lubrication, and in the manufacturing of various paints and plastics (Samarth & Mahanwar, 2015). They are also used as purifying agents (Yara-Varón et al., 2017). Lipid-based nanocarriers for pharmaceuticals demonstrate enhanced efficacy compared to conventional drug formulations (Fagionato Masiero et al., 2021).

Vegetable oils are prone to oxidation during heating and deep-frying. When these oxidations reach a critical point, essential fatty acids are destroyed and a plethora of toxic compounds and polymers are formed. These oxidative products harm flavour and human health. So, to determine the quality of any oil, it is essential to evaluate its oxidative stability. This review aims to summarize the key factors effecting the thermal stability of vegetable oil.

2. Degradation of oil during heating/frying

Deep frying is one of the most common culinary techniques. A series of complex reactions occur in oil during deep frying due to the presence of air, moisture and high temperature (Stevenson et al., 1984). The reaction of oxygen with unsaturated fatty acids is similar to the autoxidation of the oil but occurs much more rapidly due to elevated temperature (Tian, 2013). These reactions produce several toxic breakdown products including aldehydes, ketones, peroxides, and esters, which are absorbed in food (Bansal et al., 2010) and affect the quality of the oil and food by giving them rancid flavours and odours and also shorten their shelf-life (Chung et al., 2006). *trans*,*trans*-2,4-decadienal (*tt*-DDE) is detected in cooking oil fumes. It is an oxidation product of vegetable oil and is identified as the main causative agent of respiratory diseases and lung cancer (C.-K. Wang et al., 2010)**.**

2.1. Effect of different factors on the degradation of vegetable oil

Various factors associated with the process of frying, as well as the molecular makeup of the oil, play a role in its degradation. Some major factors reported to affect oil degradation during frying are summarised in Table 1.

Table 1. Some major factors affecting the stability of vegetable oil during heating/frying

S. No	Factor	Oil	Frying protocol	Result	Reference
1	Nature of the oil	Sunflower, extra virgin olive and high-oleic acid sunflower oil	300 g potatoes were fried in 3L oil in a domestic fryer at 160 °C	Sunflower oil was found to be less stable than the other two oils	(Martínez-Pineda et al., 2011)
2	Nature of the oil + heating time	Soybean, palmolein, groundnut and palm kernel oil	Oils were heated at 185 ± 5 °C for varying times of 1 to 7 hour	The effect of heating time was not observed. The stability order of oils was as follows: soybean > palmolein > groundnut > palm kernel oil	(Nduka et al., 2021)
3	Nature of the oil	Refined, bleached, deodorised (RBD) palm olein, canola, RBD palm olein / sesame (1:1 w/w), RBD palm olein/canola (1:1, w/w), sesame / canola (1:1, w/w),	100 g potatoes were fried in a batch fryer using 3.5 Kg of oil for 20 minutes at 180 °C	RBD palm olein/canola oil (1:1, w/w) was found to be the most stable and canola oil was the most unstable	(Alireza et al., 2010)

		and RBD palm olein / sesame / canola oil (1:1:1, w/w/w)			
4	Nature of the oil	Sunflower, canola and olive oils.	Oils were heated at 160 ℃ for a total of 5 hours and samples were analysed every 3 hour	The order of oxidative degradation observed in oils was sunflower oils > canola oils > olive oils.	(Vaskova & Buckova, 2015)
5	Nature of the oil	High-quality extra virgin olive (EVOO), virgin olive, olive, canola, rice bran, grapeseed, coconut (CoO), high oleic peanut, sunflower and avocado oil	3 L oil was heated to 180 ℃ for 60, 180 and 360 minutes	EVOO and CoO were found to be the most stable	(Guillaume et al., 2018)
6	Nature of the oil	Corn and mustard oils	Repeated frying with potato at boiling temperature	IR spectral data indicates that the oxidation products produced in the two oils were different	(Zahir et al., 2017)
7	Nature of the oil	Palm, peanut, rapeseed and sunflower oil.	5 L of oil was heated at 180 ± 5 ℃ for 12 hours per day for 9 continuous days in an electrical fryer	The order of thermal stability of the oils was found to be: palm > rapeseed > sunflower > peanut	(Yuan et al., 2021)

8	Unsaturated fatty acid	Olive, Safflower, rapeseed, rice bran, natural sesame, natural perilla, corn, soybean, sesame, and Perilla	4 L oil was taken in a stainless steel electric fryer. French fries were fried at 180 °C for 3 minutes. After 27 minutes the possess was repeated. This was done 5 hours per day for 5 days	It was found that unsaturated fatty acid like linoleic acid has a strong effect on the thermal degradation of oil	(X. Liu et al., 2021)
9	Antioxidant	Refined rapeseed oil mixed with lecithin or rosemary extract (1 g Kg^{-1}) or TBHQ or ascorbyl palmitate or BHT, or BHA or D-δ-tocopherol (0.2 g Kg^{-1})	350 g potato slices were fried in 1.5 L oil at 162 °C in a domestic frye. Frying time was 10 min and 12 baches were fried in 6 days with 2 baches daily	The effectiveness of antioxidants was found to be: TBHQ > lecithin > ascorbyl palmitate > rosemary extract > BHT ≈ BHA ≈ D-δ-tocopherol	(Gordon & Kourkimskå, 1995)
10	Antioxidant	Soybean oil, soybean oil with antioxidants removed, soybean oil with 1 g kg^{-1} rosemary extract	30 mL of oils were heated at 180 °C continuously for 10 hours	Rosemary extract improved the oxidation stability of oil	(Ramalho & Jorge, 2008)
11	Antioxidant	Soybean, rice bran and cottonseed oil mixed with 0.4 g kg^{-1} rosemary extract or 50% BHA and 50% BHT at 0.2 g kg^{-1} concentration	Oils were heated at 120 °C with a 20 $L.h^{-1}$ airflow rate	Rosemary extract was found to be more effective than the BHA and BHT mixture in decreasing oxidative degradation	(Yang et al., 2016)

12	Antioxidant	0.20 g of TBHQ was added to 999.80 g of fractionated palm oil	500 g of oil were heated at varying temperatures of 80 to 180 ℃ and 0 to 96 hours	It was found that the antioxidant effect of TBHQ significantly decreased above 135 ℃	(C. Liu et al., 2016)
13	Antioxidant	Canola oil	The oil was heated with antioxidants TBHQ, BHT, BHA, PG, phytic acid and SAIB at 180 °C for 10 consecutive days (8 hours daily)	It was found that SAIB has the most protective effect	(Reda, 2011)
14	Antioxidant	Hazelnut, corn, soybean and riviera type olive oil	Potato chips were fried in the oils at 190 ± 2 °C	After 50 minutes of frying in hazelnut oil and corn oil, it was found that the antioxidant activity was significantly reduced. It took 75 and 25 minutes to decrease in soybean oil and olive oil respectively	(Karakaya & Şimşek, 2011)
15	Metal ions + antioxidant	Cu(II)-cyclohexanebutyrate and Fe(III)-cyclohexanebutyrate were added to olive	Rancimat study at a temperature of 110 °C with an airflow of 20 L h^{-1}	Copper was a more effective catalyst for oil degradation than iron. Caffeic acid	(De Leonardis & Macciola, 2002)

		oil with varying concentrations of 0 to 0.96×10^{-3} g kg^{-1}. Caffeic acid was added as an antioxidant in concentrations ranging from 0 to 0.02 g kg^{-1}		showed a significant protective effect	
16	Metal (elemental)	Olive oil in the presence of iron, copper, tin, and lead	Oils were heated in a Thermoanalyzer up to a temperature of 325 °C	It was observed that iron and tin increase the oxidation of oil, while the effect of other metals was not observed	(Paz & Molero, 2000)
17	Container of heating	Groundnut, palmolein, partially hydrogenated vegetable fat and hydrogenated vegetable fat	Oils and fats were heated for 12 h at 175–185 °C in glass, cast iron, stainless steel and hindalium container	Oils and fats heated in different containers showed the following order of oxidation iron > Hindalium > stainless steel > glass	(Kala et al., 2012)
18	Container of	Coconut, canola,	100 mL oils were	Oils and fats	(Randhawa

	heating	soybean, sunflower, groundnut and rice bran oils	heated in 500 mL glass, copper and iron containers at 180 ± 5 °C	heated in different containers showed the following order of oxidation iron > copper > glass	& Mukherjee, 2023a)
19	Heating temperature + heating time + water	Sunflower oil	Oil was heated at 120, 150 and 190 °C for 65 hours at a rate of 8 hours/day or between 90 to 190 °C for 7 minutes 8 times per day for 9 days. For the water effect, 1.2 g water /min was supplied	The results showed oil degradation is more at higher temperatures and for intermittent heating. It was further found that water increases the degradation	(Achir et al., 2006)
20	Heating temperature + heating time + food to oil ratio	Palm olein oil	Marinated chicken drumsticks were fried at 170, 180 and 190 °C for 15, 18 and 21 min. Oil to chicken ratio varied from 10:0.5 to 10:3.0	Oxidation of oil increases with an increase in temperature and time. A low food-to-oil ratio (10:0.5) is more beneficial for the oxidative stability of the oil	(Sunisa et al., 2011)
21	Heating temperature+ heating time	Canola oi	Oil was heated at 185 ± 5 and 215 ± 5 °C for 7 days (7 hours/day).	Oxidation of oil increases with an increase in temperature and	(Aladedunye & Przybylski, 2009)

			Frozen French fries fried for 5 minutes in 8 batches per day	time	
22	Heating temperature + heating time	Corn oil	200 g clam meat was fried at 160 and 180 °C for 5, 10 and 15 min in 3 L oil	Most of the aldehyde species displayed a temperature-dependent accumulation. However, some aldehyde species showed a slight decrease at higher temperatures	(Z.-Y. Liu et al., 2020)
23	Heating temperature + heating time	Palm oil	Potato chips were fried at 150, 165 and 180 °C. Fring was conducted in 30 minutes cycle for 8 hours per day for 5 days	Oxidation of oil increases with an increase in temperature and time	(Aniołowska & Kita, 2016)
24	Heating temperature + heating time	Refined sunflower, soybean and olive oil	Oils were heated at 170, 180 and 190 °C for 0, 2, 4, 6 and 8 h	Furan formation in oils increased with an increase in time and heating temperature.	(Emektar et al., 2022)

25	Heating time	Soybean-oil	Tortilla chips were fried at 190 °C for 10 min at hourly intervals for a total of 60 hours	Degradation of oil increased with an increase in frying time	(Tseng et al., 1996)
26	Heating time +oil type	Cottonseed and groundnut oil	Oils were heated at 180 °C	Degradation of oil increased with the increase in heating time. More degradation was observed in cottonseed oil	(Andrew et al., 2012)
27	Heating time	Palm, cottonseed and groundnut oil	Potato chips were fried at 170 °C	Degradation of oil increases with the increase in heating time.	(Daoud & Mirghani, 2020)
28	Heating time	Soybean and palm olein oil	French fries, chicken leg fillets and pork chops were fried at 180 °C for 3, 6 and 9 min,	A liner correlation was found between oil detonation and heating time	(Chen et al., 2013)

			respectively. The food to oil ratio was 1:20 (kg/L)		
29	Food type + antioxidant	Refined olive, corn and soybean oils	French fries and chicken drumsticks (500 g) were fried in 2.5 L oil at 180 °C. For the antioxidant effect 0.5 g caffeic, ferulic and vanillic acid was dissolved in ethanol and added to 2.5 L oil. Similarly, 25 ml tea extract was added to 2.5 L oils. These modified oils were also used for frying	Frying chicken drumsticks produce a higher deterioration than frying french fries. The antioxidants were effective in the order caffeic acid > vanillic acid > ferulic acid > tea extract	(Naz et al., 2005)

2.1.1. Nature of oil

The nature of the oil is one of the most important factors determining the degree of degradation. M. Martı´nez-Pineda *et. al.* studied the degradation of three oils: extra virgin olive oil, sunflower oil and high-oleic acid sunflower oil under deep-frying conditions at 160 $^{\circ}$C. They tried various parameters to understand the condition of the oils. The study concluded that peroxide value is a poor diagnostic of oil degradation during frying. In contrast, iodine value, conjugated diene content, and viscosity accurately reflect the oil deterioration. This may be attributed to the fact that peroxides experience enhanced decomposition rates when subjected to increased temperatures. Based on the results of their study, it was found that extra virgin olive oil and high-oleic acid sunflower oil demonstrated superior performance as frying oils when compared to regular olive oil (Martínez-Pineda et al., 2011). The poor performance of the regular oil may be due to the removal of antioxidants during refining. Though M. Mart'nez-Pineda *et al.* do not believe that peroxide value is a good indicator of oil degradation during frying, J. K. C. Nduka *et al.* ranked oils based on the change in peroxide value after prolonged heating. They found that soybean oil is the most stable, followed by palm olein and groundnut oil, while, palm kernel oil is the least stable (Nduka et al., 2021). These results are interesting because soybean oil has higher PUFA (~60%) (Zambiazi et al., 2007) than palm kernel oil (~15%) (Mancini et al., 2015) and it is documented that oxidative stability of the oil decreases with increase in PUFA content (Srivastava & Semwal, 2015). Thus the results of this paper are contrary to the expectation. A possible differentiating factor may be the presence of antioxidants. However, the paper did not report the antioxidant content of the oils. In a separate study when refined, bleached, deodorised (RBD) palm olein, canola oil, RBD palm olein/sesame oil (1:1 w/w), RBD palm olein/canola oil (1:1, w/w), sesame oil/canola oil (1:1, w/w), and RBD palm olein/sesame oil/canola oil (1:1:1, w/w/w) were heated at 180ºC for five consecutive days; it was discovered that canola oil had the least stability in terms of C18:2/C16:0 ratio and the iodine value. Conversely, the RBD palm olein/canola oil (1:1, w/w) blend shows the best stability (Alireza et al., 2010). This difference may be due to the difference in the amount of unsaturated fatty acids. The greater the unsaturation in oils, the quicker the oxidation. The rate and amount of primary product formation increase with the increasing levels of unsaturation in oils (Choe & Min, 2006). This hypothesis was supported by a study on the mono-alkyl esters of different fatty acids, where it was found that even modest amounts of highly unsaturated fatty acid had an inordinately large effect on oxidative stability. The same study also claimed that free acids are less stable than their esters (Knothe & Dunn, 2003). The negative effect of unsaturation was also supported in a Raman spectroscopic study of the oxidative degradation of edible oils. In this study, sunflower oil exhibited the most significant degradation due to its elevated polyunsaturated fatty acid concentration (Vaskova & Buckova, 2015). Guillaume *et.al.* also believed that the total concentration of PUFA determines the oil's performance when heated. According to their research, extra virgin olive oil had the highest thermal stability, followed by coconut oil and other virgin oils including avocado and high oleic acid seed oils (Guillaume et al., 2018). In one infrared study, it was found that the spectra of corn oil after boiling or multiple frying with potato produce bands in frequencies range of 2852.7 to 2926.0 cm^{-1} but for mustard oil, a new peak appears at 3633.8 cm^{-1}. This difference was possibly due to the formation of different secondary oxidation products (Zahir et al., 2017). To understand the effect of fatty acid composition on degradation; Wang, T. and Briggs, J.L. artificially modified the fatty acid composition of soybean oils and studied their degradation behaviour by measuring the viscosity and differential scanning calorimetry profile of the oils. The oils investigated include (i) oil with unmodified fatty acid composition, (ii) oil with high-oleic acid, (iii) oil with low saturated fatty acid, (iv) oil with low-linolenic acid and (v) oil from lipoxygenase-free soybean. They found that oil modified to have a high-oleic acid content shows the highest viscosity and viscosity change. Furthermore, the high-oleic acid oil and the oil with low-saturated fatty acid content had distinct DSC profiles than the other oils (T. Wang & Briggs, 2002). Similarly, it was reported by Yuan,

L. et.al. that oil with higher saturated fatty acid content has a longer thermal oxidation time. This conclusion was based on the analysis of the total polar compound. The amount of polymers and oxidised products in oil grows linearly as the thermal oxidation time rises, according to this study. At the first stage of heat oxidation, their canonical correspondence analysis revealed substantial positive connections between oleic acid and oxidised triglyceride monomer (Yuan et al., 2021). Using multiple linear regression data, it was concluded that the effects of unsaturated fatty acids (mostly linoleic acid) were stronger than the effect of tocopherols (mainly γ-Tocopherol) (X. Liu et al., 2021). Furthermore, it has been discovered that radical reactions occur slowly in saturated fatty acid-rich dietary oils. Oil with a high amount of unsaturated fatty acids can quickly create additional free radicals (Yuan et al., 2021).

Against these prevailing reports Warner *et al.* found that canola oil with the highest oleic acid level (78%) had the lowest total polar compound and total volatile chemical content. This study compares the stability of six canola oil samples including unmodified canola oil and oils with fatty acid compositions modified by mutation breeding or hydrogenation. Potato chips were fried in these oils for a 2-day, 18-hour cycle (Warner et al., 1994).

2.1.2. Antioxidant

Antioxidants inhibit the process of oxidation through various mechanisms and at varying rates. The effectiveness of the antioxidant is influenced by its amount and structural characteristics, impurities of the bulk oil system, storage conditions, temperature, fatty acid profile and presence of prooxidants and other antioxidants (Shahidi & Zhong, 2010).

Research on the degradation of antioxidants during heating has garnered significant attention. It was reported that there was no significant variation in phytosterol concentration when vegetable oils were heated at 50°C for several weeks or at 100°C for 1 hour. However, Subjecting the oils to a temperature of 200°C for a duration of one hour led to a decrease in phytosterol content by approximately 50-60% (Thanh et al., 2006). Many other antioxidant molecules break down at the elevated temperature of frying. The effect of antioxidants; ascorbic acid, sorbic acid, citric acid, sodium erythorbate, TBHQ(tertiary butyl hydroquinone), BHT (3,5-di-tert-butyl-4-hydroxytoluene), BHA (butylated hydroxyanisole), PG (propyl gallate), phytic acid and the SAIB (sucrose acetate isobutyrate) on the thermal stability of canola oil were studied by subjecting canola oil to a temperature of 180ºC for 8 hours over 10 days. The following antioxidants were found to be less protective - citric acid, sodium erythorbate, BHA, BHT, TBHQ and sorbic acid as they decompose at temperatures below 180ºC. However, the antioxidants - phytic acid, ascorbic acid and propyl gallate (PG), are the most resistant as their decomposition processes start at temperatures between 180-200 ºC. Thermal analysis revealed that the SAIB antioxidant exhibits superior protective properties and demonstrates high resistance to oxidation (Reda, 2011). Another research discovered that TBHQ has stronger antioxidant effects in palm oil when heated to 135°C. However, increasing the heating temperature and duration resulted in a considerable loss of TBHQ. They further found that when heated to the same temperature, the acid values of palm oil with and without TBHQ were almost identical (C. Liu et al., 2016).

The change in antioxidant activity after frying was also dependent on the nature of the oil. In one study it was found that after 50 minutes of frying in hazelnut oil and corn oil, the antioxidant activity was significantly reduced. However, it took 75 and 25 minutes of frying to register a significant decrease in the antioxidant activity of soybean oil and olive oil respectively (Karakaya & Şimşek, 2011). However, this study used the DPPH assay to measure antioxidant activity and it is known that oxidation products can contribute positively to this assy(Randhawa

& Mukherjee, 2023b). Due to the high PUFA content soybean oil is expected to generate more oxidation products. This may be the reason why the DPPH inhibition activity of soybean oil decreases more slowly.

Because of the low cost and excellent antioxidant activity, synthetic antioxidants are commonly used in the edible oil sector to prevent oxidation. The addition of small amounts of artificial antioxidants can increase the thermal stability of lipids. Some of the artificial antioxidants are butylated hydroxy anisole (BHA), butylated hydroxytoluene (BHT), tertiary butylated hydroxy quinone (TBHQ) and propyl gallate (PG). However, there are questions about their long-term health effect (Blasi & Cossignani, 2020). For example, it is found in an animal model that BHA and BHT can cause liver damage and carcinogenesis (Williams et al., 1999). Natural antioxidants are safer. It was observed for example that beta-carotene provides a strong protective effect (Gordon & Kourkimskå, 1995; Ullah et al., 2003). However, the limited stability of natural antioxidants and the loss of activity after heat processing limit their use in edible oils. The encapsulation of natural antioxidants in nanoemulsions is an effective approach for enhancing their antioxidant activity, dispersibility, stability, and solubility (Sharma et al., 2019). Natural extracts from diverse plant parts (e.g., peel, fruit, leaf, flower, and root) belonging to various herbs, agri-food residues, and by-products were studied for their antioxidant capacity as well as their application for enriching edible oils. Natural extracts were found to include a wide spectrum of bioactive chemicals, the majority of which were identified as carotenoids and phenols (Blasi & Cossignani, 2020). By-products of fruit and vegetable processing are rich in bioactive compounds, which can be used to increase the oxidative stability of oil. Indeed, plant parts such as leaves, kernels, peels, flowers, and roots, which are considered waste or by-products, are high in antioxidant compounds that have been shown to benefit human health.

Anthocyanidins, phenolics, carotenoids, flavonols, flavanones, and glycosides are the most common antioxidant molecules found in plants and vegetable waste material (Blasi & Cossignani, 2020). Herbs, spices, seeds, fruits, and vegetables are all recognised as natural sources of antioxidants. The interest in these natural antioxidants is driven not only by their biological significance but also by their economic effect, as the majority of them may be harvested from food byproducts and underutilised plant species (Lourenço et al., 2019).

Phenolic compounds, tocopherols and carotenoids are known to exhibit antioxidative properties. These compounds are the best natural antioxidants due to their biological activity. They can protect oil to a good extent without decreasing the sensory properties of fried food. However, these antioxidants are more effective at storage conditions than frying (Wu et al., 2019). The order of effectiveness found for antioxidants in heated oil was TBHQ > lecithin > ascorbyl palmitate > rosemary extract > BHT, BHA, D-**δ**-tocopherol, although this order can show some variations according to the condition of heating (Gordon & Kourkimskå, 1995). Refined sunflower oil was fortified with 1000 ppm of rosemary extract, followed by exposure to thermal oxidation conditions at a temperature of 180 °C. It was reported that rosemary extract extends the oxidative stability from 7.52 to 13.5 hours (Ramalho & Jorge, 2008).

2.1.3. Metal

In general, metal ions are known to increase the oxidation of vegetable oil. The presence of metal ions was reported to increase the formation of formaldehyde, acetaldehyde, propanal, and heptenal in the heated oil. The effect is highest for copper ions followed by iron and aluminium(Bastos & Pereira, 2010). Both copper and iron ions showed prooxidative catalytic effects in olive oil, though the impact of copper was again more pronounced. This was found by a Rancimat experiment at 110 °C on olive oil spiked with Cu(II)- and Fe(III)-

cyclohexanebutyrates (De Leonardis & Macciola, 2002). The addition of ferric stearate in partially hydrogenated soybean oil was reported to decrease its thermoxidative stability. These results were obtained by heating the oil at various temperatures between 120 to 200 ℃. The amount of iron added to the oil ranges between 0.5 and 1.2 mg iron per kg of oil (Coscione & Artz, 2005). In a comparable study, heme iron was incorporated into partially hydrogenated soybean oil at a concentration of 2.7 ppm. The modified oil also showed poor stability when subjected to heating within the temperature range of 160 to 200 °C over a duration of 72 hours. The oil was tested for multiple oxidation parameters such as acid values, colour, food oil sensor readings, and TAG polymer content (Artz et al., 2005). It was further observed that heating rice bran oil that has been adulterated with ferric chloride at a temperature of 180 °C for a duration of 5 hours resulted in an increase in lipid peroxidation, as well as accelerated degradation of γ-oryzanol(Khuwijitjaru et al., 2011).

The detrimental effect of metallic iron on the oxidative stability of olive oil was reported by Paz, I. and Molero, M. They further found that tin had a similar negative effect. However, their thermogravimetry and derivative thermogravimetry studies do not show any significant change in the degradation rate due to the presence of copper and lead (Paz & Molero, 2000). The formation of trans fats in heated vegetable oil is also affected by the nature of the metal container in which it is heated. In one paper, it was reported that the formation of trans fat in vegetable oils heated in the three metal containers has the following order: cast iron > Hindalium (an aluminium alloy) > stainless steel. In comparison to these metal containers, glass containers have the least amount of trans fat accumulation (Kala et al., 2012). One report from our lab investigates the impact of container material on the thermal degradation of various vegetable oils (coconut, canola, soybean, sunflower, groundnut, and rice bran). Oils were heated in glass, copper, and iron containers. The findings indicated that the container surface significantly influenced the thermal degradation process. Metal surfaces, particularly iron, exhibited higher pro-oxidizing properties compared to glass. Re-esterification was favoured on copper surfaces. The container surface also impacted the changes in iodine value. Leaching of copper was noted in many oils. Additionally, the metal surface accelerated the degradation of antioxidants in oils, with iron showing the most pronounced effect in this regard (Randhawa & Mukherjee, 2023a).

2.1.4. Temperature

When compared to the values before frying, the acid and peroxide levels of edible oil increased after frying. This could be attributed to the high frying temperatures inducing the breakdown of glycerides (Alajtal et al., 2018). The findings of N. Achira *et.al.* demonstrated that the highest deterioration was seen at 190 °C in discontinuous mode when sunflower oil was heated at 120, 150, and 190 °C in both continuous and discontinuous mode (Achir et al., 2006). At higher temperatures, the thermal and oxidative destruction rate of PUFA increased dramatically. Frying temperature above 195 °C can promote intense PUFA isomerization, thereby increasing the amount of trans isomers. The peroxide value, free fatty acid value and p-anisidine (Sunisa et al., 2011), as well as the colour-changing phenomena (Krokida et al., 2001), escalate with an increase in temperature. Similarly, Aladedunye, F.A. and Przybylski, R. found that an increase in total polar contains, *p*-anisidine value, colour components and trans fatty acid are a function of temperature. Furthermore, it is reported in this paper that the decrease in polyunsaturated fatty acid concentration is directly proportional to the frying temperature (Aladedunye & Przybylski, 2009). In another study using HPLC-ESI-MS/MS, 16 reactive aldehydes were identified in oil after frying clam (*Ruditapes philippinarum*). Some aldehydes such as acrolein and trans-2-pentenal showed a slight decrease at higher temperatures possibly due to evaporation. However, the concentration of other aldehyde species increases with an increase in heating temperature (Z.-Y. Liu et al., 2020). To investigate the impact of high temperatures on the concentration of glycidyl esters in palm oil; potato chips were cooked periodically in palm oil that was heated for 8 hours every day for five days. Frying was done at three different temperatures: 150, 165, and 180 °C. Acid and *p*-anisidine values, alterations in fatty acid profile, total polar contents, polar fraction composition, and colour component development were used to assess the oil's thermo-oxidative changes. Liquid chromatography-mass spectrometry was used to determine the amount of glycidyl esters in the sample. The quantity of hydrolysis, oxidation, and polymerisation products (excluding reduction in the degree of unsaturation) increased sharply as the frying temperature and duration increased. The content of glycidyl esters reduced when the temperature and frying time were increased. The degree of oil deterioration was shown to be associated with the extent of glycidyl esters decline (Aniołowska & Kita, 2016). Furan formation was investigated in several vegetable oils after heat treatments. Temperature and time were noted to have a substantial influence on furan formation. Additionally, more furan was produced in oils with high polyunsaturated fatty acids (Emektar et al., 2022).

2.1.5. Frying Time

It is known that increasing frying time increases the peroxide value, free fatty acid value and *p*-anisidine value of the oil (Sunisa et al., 2011). According to one study, when refined soybean oil was used to fry tortilla chips at 190 °C for 60 hours, variations in colour readings became more visible after 30 hours of frying. Between 20 and 30 hours, foam and off-flavour formed. After 30 hours of frying, the convective heat transfer coefficient changed more quickly (Tseng et al., 1996). C. Andrew *et al.* backed this up with an experiment in which they heated oil to 180 °C without adding food. they monitor the refractive index of the oil, which they discovered increases with heating time (Andrew et al., 2012). Daoud, J. I. and Mirghani, M. E. S. used multivariate analysis of variance (MANOVA) to show that there is a significant correlation between frying time and tocopherol content, iodine value, peroxide value, free fatty acids and polymer content of oil. They fry potato chips in palm oil, cottonseed oil and groundnut oil at 170 °C and found that peroxide value, free fatty acids and polymer content increase with heating time; while tocopherol content, and iodine value decrease (Daoud & Mirghani, 2020). A linear correlation was reported between frying time and both total polar compounds and acid value in soybean and palm olein oil (Chen et al., 2013). Similarly, it was found mutagenic 4-hydroxy-2-trans-nonenal formed in soybean oil and its concentration increased with increased heating time up to 6 hours. After 6 hours the concentration started to drop, possibly due to further oxidation of the compound (Seppanen & Saari Csallany, 2002). The frying temperature and time not only affect the oil's major component triglyceride but also change its minor components. For example, in a study, it was found that heating at 180 °C reduced the hydroxytyrosol derivatives of olive oil by 60% in 30 minutes; after 60 minutes only 10% of the original hydroxytyrosol derivatives were found to be left in the oil. Compared to this, tyrosol derivatives degrade only to a smaller extent while the lignans content of the oil remains unchanged. If the heating temperature is lowered to 100 °C, it was reported that only 20% deterioration of the phenolic compound was observed even after 2 hours of heating (Daskalaki et al., 2009).

Against the popular view, J. K. C. Nduka *et al.* found that heating the oils at varying times had no significant effect on their physicochemical qualities. They based their findings on the study of the effects of heating for 1–7 hours on specific gravity, viscosity, saponification value, iodine value, free fatty acid, and peroxide value of the oils (Nduka et al., 2021).

Not only frying time, but the duration and the number of heating-cooling cycles also have a significant effect on the amount of deterioration in oil. For example, in a report on marinated chicken drumsticks frying, it was found that the quality of oil after three consecutive days of frying at a rate of ten batches per day was superior to the oil used to fry 30 batches in a day (Sunisa et al., 2011). Contradicting results were observed in a 2013 publication by Das, A.K., *et al.* They investigated the impact of frying pooris on the quality of groundnut oil in two scenarios: one in which poories were fried for 8 hours continuously, and the other in which poories were fried for four consecutive days, two hours each day. The oils were evaluated by multiple parameters such as peroxide value, anisidine value, diene value, oxidised fatty acid, viscosity, unsaturated fatty acids, saponification value and smoke point. All of these factors show that intermittent frying degrades oil more than continuous frying (Das et al., 2013).

2.1.6. Food type and food-to-oil ratio

In an experiment with marinated chicken drumsticks, it was found that the lower the oil-to-chicken ratio, the slower the changes in used oil (Sunisa et al., 2011). Another study found that when the oil-to-potato ratio was lower, potatoes had a statistically significant influence on the rate of development of total polymerisation products (Kalogianni et al., 2010). Chen, W.A. *et. al.* fried french fries, chicken leg fillets and pork chops with soybean and palm olein oil. They failed to identify any significant effect of food type on the quality of the used oil (Chen et al., 2013). On the other hand, Koh, E. and Surh, J. found that food type does influence the degradation profile of vegetable oil. They collected 200 samples of soybean oil used in deep frying for the preparation of meals from 6 schools. The samples were divided into four groups based on the food type. These groups were vegetables, fish, meat and carbohydrate-rich foods. The carbohydrate-rich group showed the lowest sign of lipid oxidation. Though the vegetable group showed low hydroperoxides and malondialdehyde content, they reportedly had higher conjugated dienes and triene. The fish group showed the highest malondialdehyde content and p-anisidine value (Koh & Surh, 2015). In a similar study Naz, S. *et. al.* reported that frying chicken drumsticks produces a higher amount of free fatty acid in corn oil than frying french fries (Naz et al., 2005). However, the effect of fried food on the change of polar compounds such as triglyceride dimer, oxidised triglyceride monomer, and diglyceride was less pronounced than the effect of the type of oil (Li et al., 2019).

3. Conclusion

The degradation of vegetable oils is a matter of concern for the vegetable oil and food processing industries, as well as for public health. Numerous degradation products have been identified as detrimental to human health, making it crucial to comprehend the underlying process. However, understanding this process is challenging due to the complex nature of vegetable oil, which consists of a multitude of compounds. These compounds interact with each other in a complex and interdependent manner, further complicating the degradation process. Additionally, the relative proportions of these compounds vary among different types of oils, and even within the same type of oil, the compositions are not consistent. Furthermore, external factors such as temperature, frying time, and frying cycle, also influence the degradation process.

Considerable effort was being made to comprehend the process. The thrust areas in this field were summarized in the previous section. Among the internal factors, the effects of fatty acid compositions were most researched followed by the effects of antioxidants. In external factors, the effect of heating temperature and heating time are best understood.

Antioxidants from different natural sources already showed promising stabilizing activity for vegetable oil. Though this is still an open research field. Many common food ingredients still needed to be tested. This is important for the development of more effective and sustainable antioxidants for vegetable oil and also for understanding how these ingredients affect the stability of the oil.

The influence of metal surfaces remains relatively unexplored. Nevertheless, it is known that metals can function as catalysts in the degradation process and may also have a more direct involvement in the process.

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