

Polar Compounds in Frying Oils: A Review

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Abstract Quality of oil is not only limited to the composition of fatty acids present therein but it also encompasses the effect/ impact of storage and usage conditions such as the environment, temperature and moisture as well as the food cooked in it. The deterioration can usually be attributed to processes such as hydrolysis, oxidation, and polymerization reported to occur during the process of heating fat at high temperature such as during frying. These processes result in the formation of several by-products such as polar compounds. Total polar compound (TPC) is an established quality index for assessing the degradation status of oils used for frying because they strongly relate with primary and secondary level processes associated with hydrolysis, oxidation and polymerization of heated oils. TPC levels above 20-25% are considered to be indicator for rejection or replenishment of the frying oil as they are negatively associated with its quality such as viscosity, flavor and also the nutritive value of the foods fried therein. Studies on polar compounds need impetus as animal trials have found them to be associated with retarded growth, irregular intestinal activities, enlarged liver and kidney, anemia as well as cancer.

Keywords: Total Polar Compound (TPC), deep-fat frying, hydrolysis, oxidation, polymerization

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1. Introduction

India is the largest importer and the third largest consumer of edible oils in the world [1]. According to the Ministry of Food Processing Industries [2], in year 2007, the annual and per capita consumption of edible oils was 11 million tones and 11.5kg, respectively. According to reference [3] the most common applications of edible oils are in deep-frying, salad dressings and as food emulsions. Deep-fat frying is one of the oldest and most common methods used for preparation of food. Fried foods are popular around the globe because they have desirable flavor, color and crisp texture [4]. Frying is a process of cooking food in fat at a high temperature 150°C - 190°C. However, heating of fat at such high temperatures particularly for prolonged duration can bring about undesirable changes. According to reference [5,6] deep-fat frying results in foam formation, darkening of color, viscosity, density, specific heat as well as increase in the content of free fatty acids (FFAs), polar material, and polymeric compounds in oils. It also results in decrease in the level of unsaturated fatty acids in oil.

The above mentioned deteriorative changes are the result of hydrolysis, oxidation, and polymerization of oil - the common chemical reactions observed during frying are shown in Figure 1. These reactions result in the production of several volatile and non-volatile compounds such as hydroperoxides, conjugated dienes, oxidized triacylglycerol monomer, trans configuration

compounds, polymers, sterol derivatives, nitrogen and sulphur containing compounds, acrylamide to name a few [5,7]. They also lead to the formation of decomposition products with high molecular weights such as polar compounds. Polar compounds are hydrocarbon compounds containing nitrogen, sulphur or oxygen [8]. The polar compounds such as dimeric and higher polymeric triglycerides are formed through thermal polymerization of triglycerides (diacylglycerides, oxidized triacylglycerides, dimers and polymers), monomeric oxidized products, mono- and diglycerides as well as FFAs formed through hydrolytic cleavage of triglycerides [9].

The quantity of total polar compound (TPC) is considered to be an established quality index for frying oils with 20-25 percent as the upper limit for rejection or replenishment of the cooking oil because it is negatively associated with the quality of frying oil, flavor and nutritional value of the fried food. Polar compounds are formed principally due to the action and interaction of atmospheric oxygen, water content of the food stuff and the high temperature at which frying takes place [10].

2. Chemical Reactions in Oil during Deep-Fat Frying

2.1. Hydrolysis of Oil

Heat induced hydrolysis has been found to take place primarily with in the oil phase rather than the water-oil interface [11]. When food is fried in heated oil, the

moisture present in air and food forms a blanket of steam which gradually subsides as the foods are fried. Air get entrapped in the steam blankets as a result of which chemical reactions such as oxidation, hydrolysis and polymerization get initiated and accelerated as shown in Figure 1. Water breaks the ester linkage of triacylglycerols which results in the production of di and mono acylglycerols and FFAs. Free fatty acid (FFA) content in frying oil increases with the number of frying cycles [12]. It is therefore used to assess and monitor the quality of frying oils. The salient volatile compounds formed include hydrocarbons, ketones, aldehydes, alcohols, esters, lactones while the major non-volatile compounds formed are monoacylglycerols, diacylglycerols, oxidized triacylglycerols, triacylglycerol dimers, triacylglycerol trimers, triacylglycerol polymers, FFAs are formed when oil is heated repeatedly during frying [13]. The amount of volatile compounds formed in oil during frying varies widely depending on the composition of oil, food and the environment in and around frying [14]. The disappearance or decrease in the content of volatile compounds in frying oil is related to a number of factors such as evaporation in air during frying, decomposition and involvement in further reactions within the oil and with the oil as well as the food [15]. The parent triacylglycerol get hydrolyzed to monoacylglycerol, diacylglycerol and glycerol. They further undergo oxidized polymerization and thermal polymerization to result in the formation of TAG polymers such as dimers, trimers and oligomers. Presence of oxygen results in the formation of polar polymers. It is important to note that the degradation products of triacylglycerols have lower molecular weight than their parent TAGs [7].

Hydrolysis occurs more frequently in oils with greater

amount of short and unsaturated fatty acid chains as compared to in oils with long and saturated fatty acid chains because short and unsaturated fatty acids are more soluble in water as compared to long and saturated fatty acids [11,16]. Frequent replacement of used oil with fresh oil; but not the duration of frying; retards the process of hydrolysis hence delays the formation of polar compounds [17]. Sodium hydroxide and other alkalis which are often used for cleaning a fryer/ utensil accelerate the process of oil hydrolysis.

2.2. Oxidation of Oil

Thermal ($\approx 180^\circ\text{C}$) oxidation of vegetable oils during frying deteriorates sensory and nutritional properties of the oil and results in the production of volatile compounds such as relatively short chain aldehydes and alcohols and nonvolatile products such as dimers and polymers. Some of these compounds may be toxic. Their presence results in physical changes in oil such as darkening of color and in increase in viscosity. Formation of polar compounds is strongly and linearly associated with the primary and secondary oxidation processes that take place during heating of oil and frying [10]. For example, the development of secondary monoacylglycerols and diacylglycerols occurs due to combination of oxidative and hydrolytic reactions which in turn leads to the accumulation of polar compounds in oils subjected to heating and /or frying. Oxidized TAG monomers with keto, epoxy, hydroxyl, aldehyde and epoxy groups and subsequently certain TAG polymerized products such as dimers, trimers and oligomers are formed through oxidation, epoxidation and free radical reaction [7,13].

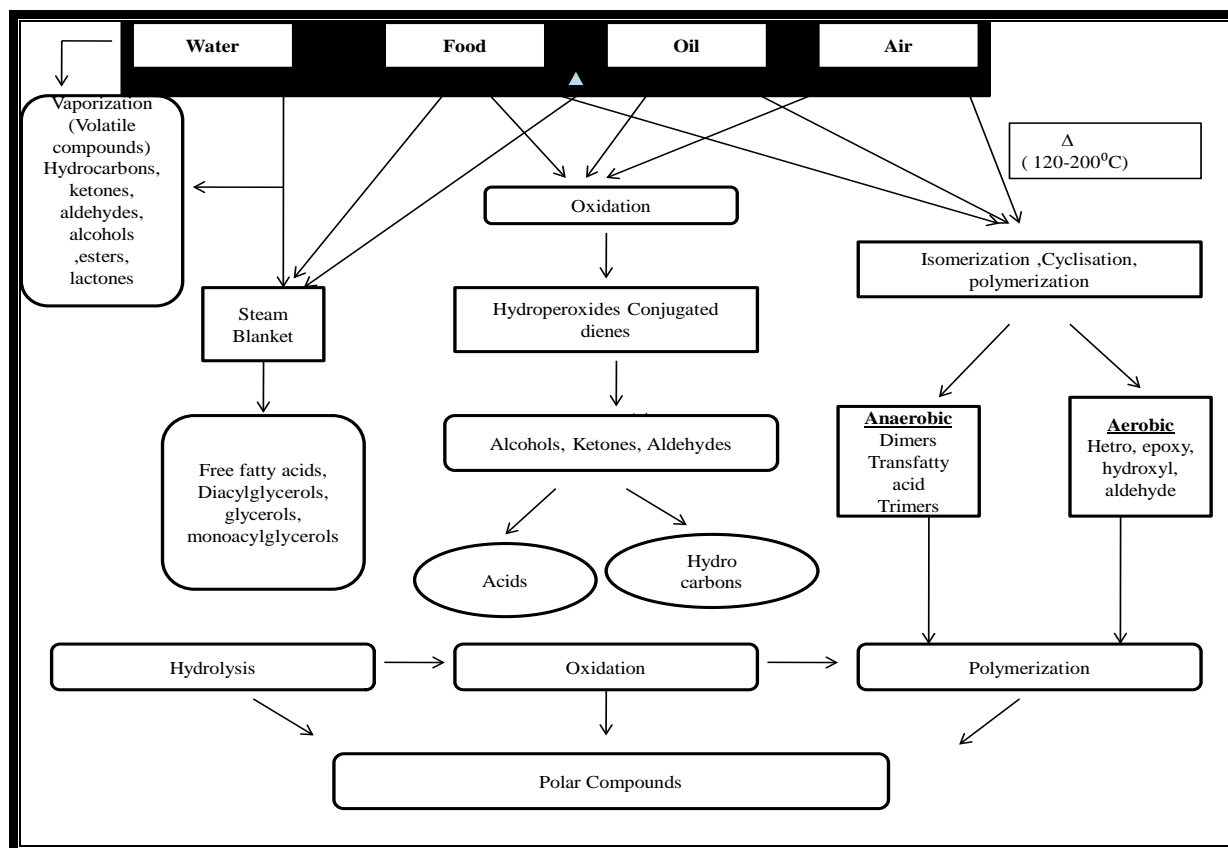


Figure 1. Physical and chemical reactions that occur during frying

It has been observed that most of the mono- and di-acylglycerols are formed during the initial stages of frying as compared to the latter stages. This is so because the high interfacial tension in the frying system breaks steam bubbles and forms a steam blanket over the oil surface. This reduces the contact between the oil and oxygen, and retards the rate of oxidation in oils during frying [18,19]. However, as frying continues the steam blanket reduces and the oxidation process gets accelerated.

2.3. Polymerization of Oil

Polymers are highly conjugated dienes. Their presence in the frying system over a period of time results in the production of a brown, resin-like residue which can be seen along the sides of the fryer where the oil along with metals of the utensils or mineral ions in the food come in contact with oxygen from the air. Polymers are formed when the moisture and air get entrapped within the oil during the frying process such as due to the formation of steam blanket when food is introduced into the oil. High temperature frying results in the formation of oxidative and non oxidative polymers such as oxidized TAG with keto, epoxy, hydroxyl, aldehyde [20,21]. Polymers accelerate further degradation of the oil, resulting in increased viscosity, foam formation as well as development of undesirable color in the food [22,23]. They are also associated with reduced heat transfer and hence increased absorption of oil by foods [5].

During frying the polymerization process results in production of compounds with higher molecular weight and polarity. Majority of the polymers get formed from free radicals. During the formation of polymers, triacylglycerols and cyclic fatty acids form within one fatty acid while dimeric fatty acids form between two fatty acids or within/ between the triglycerides. Subsequent cross-linking of dimers with other cyclic fatty acids and triacylglycerols results in the formation of greater amount of polymers [13]. It has been reported that the formation of cyclic compounds depends on the degree of un-saturation and the frying temperature. The formation of cyclic monomers and polymers is linearly associated with the amount of linolenic acid and temperature. If the linolenic acid content is lower than 20 percent, the formation of cyclic monomers is negligible; the formation being significantly greater at 200°C and above [5].

The role of Diel- Alder reaction in the development of polymers in heated oils has been extensively studied. While certain studies indicate its role in the formation of polymers [5,13] others have refuted this mechanism [6,24]. Recent, evidence indicates that Diel- Alder reaction may not be a major contributor to the formation of polymers during frying. It has been reported that if <5 mol percent of Diel- Alder products are formed, they may not get detected by the currently used nuclear magnetic resonance (NMR) technique [6].

Thus, the hydrolytic, oxidative and thermal alterations in oils being used for frying are interrelated as well as superimposed. The effects of various factors on the formation of polar compounds are discussed below.

3. Factors Influencing Formation of Polar Compounds during Frying

The oil turnover rate, duration and temperature of frying, composition of oil, initial (pre-use/fresh) oil quality, composition of food to be fried, type of fryer, antioxidants as well as oxygen content are some of the common factors which affect the formation of polar compounds and hence the deterioration of oil during deep frying.

3.1. Replenishment of Fresh Oil

If used oil is frequently replenished with fresh oil during the process of frying, there is decreased formation of polar compounds, di-acylglycerols and FFAs. It therefore helps to maintain quality of oil longer and increases frying life of the oil [17,25]. Frying in commercial food service establishments such as restaurants and road side kiosks is typically conducted on consumer demand and, as a result, heating of oil tends to tide-up and down throughout the day. Frying oil turnover is therefore an indicator of how much stress (oxidation, hydrolysis, polymerization) the oil has been subjected to in a daily operation. According to reference [26], oil turnover (in hours) for a food service operation can be calculated by the following formula:

$$\text{Oil turnover} = \frac{\text{Total pounds of oil in the fryer}}{\text{Average pounds of oil used per hour}}$$

To calculate the oil turnover (in hours) for a food service operation, oil usage is based on the total time the fryer is 'on'. If the fryer is turned off during idle periods, the 'ebb or latent period' need not be counted. However, if the fryer remains 'on', even if it is set to a lower temperature, the time should be counted for oil turnover calculation.

The frequent turnover of oil causes more oxidative reactions rather than hydrolytic reactions such as observed during deep-fat frying of potatoes [27]. The recommended daily oil turnover rate is 15 per cent to 25 per cent of the capacity (volume) of the fryer. High turnover can decrease the use of antifoaming agents such as silicones [5].

3.2. Types of Fryer

Deterioration of oil used during frying is to a great extent influenced by the type of fryer. Even and rapid transfer of heat from the walls and bottom of the fryer to the oil can prevent formation of hot spots on the food as well as burning of oil. Uneven heating of oil results in deposition of polymers around the walls of the fryer and this in due course of time results in further deterioration of fat. A physical sign of such deterioration of oil can be observed through its gradual darkening in color. It is therefore recommended that fryer-oil ratio should be low i.e. small surface area fryers should be preferred over large wide bottom fryers [5]. The fryer size, shape and volume of the fryer should be selected according to the shape of the food being fried. For example shallow fryers

are suitable for doughnuts, poories, vadas etc. whereas narrow and deep fryers are suitable for products such as French fries, cheese sticks etc. Small fryers are associated with reduced oil turnover, slower deterioration and reduced expenditure on fuel. It has been reported that most batch fryers involved in frying of French fries have average turnover rates in the 5 to 12 hours range. Usually a 5 hour turnover helps to maintain satisfactory quality of oil under most frying conditions. A longer, such as 12 hour turnover, results in significant deterioration in the quality of oil [26].

3.3. Composition of Frying Oil

The degree of unsaturation of fatty acids influences the oxidation any hydrolytic deterioration of fats. Higher the level of unsaturation greater is the speed and extent of deterioration [28]. According to reference [29] a pro-oxidant effect of FFAs is observed in all refined oils, independently of lipidic substrate and of its state of hydrolytic and oxidative alteration. They concluded that avoidance of oil filtration during processing can extend shelf life of oil (olive oil). Oils with lesser unsaturated fatty acids such as corn oil are more suitable for frying as compared to soybean oil or canola oil [30,31,32]. According to reference [33] oils with low linolenic fatty acid content could be better alternatives to hydrogenated fats for the purpose of frying. In several under-developed and developing regions frequent change in the choice of oil by small street food vendors/ kiosks results in unrecognized blending of oils. Such blending of oils can result in change in the fatty acid composition of oil present in the fryer. The variations in fatty acid composition can either decrease or increase the rate of oxidation depending upon the composition of resultant oil in the fryer at the time of heating/ frying [34,35]. Therefore, the correct selection of the oil for frying plays an important role in maintaining quality of oil being used for frying [28].

According to reference [26] the inherent stability of a fat to oxidation helps to determine its suitability for frying. Inherent stability can be calculated and its numbers refer to the relative rate of reaction of unsaturated fatty acids with oxygen when oil is heated or used for frying. The inherent oxidation stability uses the relative oxidation

rates to calculate stability of heated fats and oils. It is defined as the weighted sum of relative oxidation rates multiplied by the percentage content of each constituent fatty acid, in such a way that the lower the inherent stability value, the more stable a fat or oil is [36]. Thus, an oil with a low inherent stability number is lesser susceptible to oxidation during frying as compared to an oil with high inherent stability number. The fatty acid composition and the calculated inherent stabilities of common fats and oils are given in Table 1.

In a study conducted by [10] four oils viz hazelnut oil, corn oil, soyabean oil and Riviera type olive oil (mixture of virgin plus refined olive oil) were used to fry potato chips over two replicates of 125 minute trails each at $190 \pm 2^\circ\text{C}$ in separate fryers. Potato chips (75g) were fried in each of the oils for 8 minutes. After each frying process, the oils were allowed to cool for 7 minutes and then frying and cooling steps were repeated 15 times. Oil samples were taken every 25 minutes (25, 50, 75, 100 and 125) and analyzed or stored at -40°C . The TPC content in all oils were found to be lower than 5 per cent, indicating that the oils were suitable for frying up to 125 minutes of use.

3.4. Temperature and Duration

The changes in oils subjected to frying of food are different as compared to when they are heated without the presence of food. It has been found that the concentration or the amount of polar compounds and dimer triglycerides in oil increases linearly with process time while the polymeric triglycerides increase exponentially as observed during frying. Dimeric and polymerized triglycerides are formed in greater amount when fat is heated as compared to when used for frying at the same temperature. The rate of increase in the amount of oxidized triglycerides is lower as compared to that of polymerized triglycerides during heating as compared to that during frying. Thus, polar compounds are formed in greater amount during heating as compared to during frying operation. This is important from the perspective that in several road side kiosks and commercial establishments, the heat is usually reduced and not stopped during intermittent frying operations which could lead to development of higher amounts of certain polar compounds.

Table 1. Fatty acid composition and Inherent stabilities of commonly used fats and oils [26,37,38]

Oil	Fatty acid content			Inherent stability
	Saturated fatty acid	MUFA	PUFA	
Safflower	9.19± 0.58	14.04±0.60	76.78±1.15	7.6
Soyabean	15.96±0.37	24.06±1.75	59.98±1.57	7.0
Sunflower	11.39±0.10	25.96±1.54	62.65±1.56	6.8
Corn	16.60	33.67	49.74	6.2
Cottonseed	28.17	19.66	52.16	5.4
Rapeseed (46.5%)**	10.7	56.0	32.6	***
High Erucic Acid	***	***	***	4.1
Low Erucic Acid	***	***	***	5.5
Peanut	18.94±1.26	53.89±1.08	29.17±0.99	3.7
Lard	46.2*	45.2	11.0	1.7
Olive	14.8	74.5	10.0	1.5
Palm	44.98±0.67	43.53±0.40	11.49±0.29	1.3
Tallow	54.9*	40.9	4.2	0.86
Palm kernel	47.7	41.4	10.6	0.27
Coconut	90.86±0.33	7.24±0.25	1.90±0.14	0.24

The normal temperature range for frying is usually from 160 to 190°C. The products fried between 170-250°C absorb about 8-25 percent oil. Frying at lower temperatures takes longer time to cook food, lighter development of color and flavor, increased absorption of oil as well as increased formation of FFAs, polar compounds (TAG dimers and oxidized triacylglycerols) and polymers [39,40,41]. High temperature frying leads to formation of thinner crusts, lesser absorption of oil, accelerated oxidation and polymerization of oils which leads to polar compound formation. The amount and type of polar compounds formed during deep-fat frying is influenced by several factors. For example, the temperature and duration of frying not only influence the amount but also the types of TPCs. Studies indicate that with increase in temperature the amount of polymers formed also increase linearly. However, in case of dimers the content increases initially and later on decreases slightly due to the conversion of dimer into polymers. The contribution of oxidized triacylglycerides to the total polar content also reduces with increase in temperature due to faster degradation at higher temperature [42].

In a study conducted by [43] the effect of frying potatoes on the formation of polar compounds was studied. Ten batches of Potatoes were deep-fried in virgin olive oil at 170°C for 120 minutes. At the end of process, TPC remained within the 25-27 percent limit. The amount of TPC increased linearly with the frying cycle; however, the increase was faster in high oleic sunflower oil as compared to in olive, corn and soyabean oil. After 60 frying cycles, the amount of TPC for both oils reached approximately 20- 23percent. The number of TPC in all oils increased significantly with the increased duration of frying [10].

Intermittent heating and cooling of oils has been found to cause higher deterioration of oils than continuous heating. This can be attributed to the fact that the solubility of oxygen increases when the oil cools down from a higher to a lower temperature [44]. In yet another study conducted by [42] the content of total polar compound (TPC) was found to reach 19.8% at 185°C and 38% at 215°C when 8 batches of food (Frozen par-fried French fries) were fried in canola oil for 7 hour duration for 7 days. The TPC level reached the discard level (24%) at the end of 4th day thus the extent of oxidative deterioration in context to TPC content was found to be 2.6 times faster when the oil was heated at 185°C. Polar content has been found to increase with the duration of frying, number of frying operations in repeated discontinuous frying. According to reference [19], as the temperature increases, a larger number of possible combinations of polar dimers, oligomers and other compounds are formed and they have the potential of generating higher polymer of triglycerides. Reference [19] has reported that variations occur in the type and content of various polar fractions as the duration of frying increases. According to their study the average molecular weight of various polar fractions such as polymerised triglycerides, dimeric triglycerides, oxidized triglycerides, mono and diglycerides as well as free fatty acids is 3700, 2500, 1200, 370-600 and 298.5 respectively. Their retention period is also different for example the retention period of polymerised triglycerides, dimeric triglycerides,

oxidized triglycerides, mono and diglycerides as well as free fatty acids is 14.7, 15.4, 16.5, 17.0 and 18.0 respectively.

3.5. Composition of Foods

Moisture in foods initiates and promotes oxidative reactions with the hydrolytic compounds in oils being used for frying. Foods with high water content like potato and foods covered with breading or battering materials accelerate hydrolysis of oils when heated at high temperature for frying because presence of bread crumbs and other food particles which get detached from food during frying tend to get burnt over a period of time and cause thermal deterioration of fat [45]. Presence of water enhances the process of hydrolysis i.e. the acid-value. However, water can also serve as a physical barrier generating a steam “blanket” over the oil and preventing contact between oxygen and oil. It can play a role as a physical agent for “steaming out” the volatile oxidative products from the oil and enhancing their evaporation. Hence, water can both accelerate hydrolysis and furnish protection against oxidation [46,47].

According to reference [48] has reported that frying of chicken strips coated with hydroxyl propylmethyl cellulose films decreases formation of free fatty acids in groundnut oil during deep-fat frying. In studies conducted by reference [49,50] it was found that addition of spinach powder at 5, 15 or 25 percent to flour based dough decreased the formation of polar compounds in soybean oil. However, addition of carrot powder to flour based dough at 10, 20 or 30 percent decreased the oxidative stability of soybean oil during frying. Addition of red ginseng extract in flour dough at 1 and 3 percent has been found to decrease the formation of free fatty acids, conjugated dienoic acids, and aldehydes when deep-fat fried in palm oil at 160°C [51]. Deep-frying of lecithin added foods accelerates foam formation during the initial stages of frying [30]. Transition metals such as iron present in animal food, get accumulated in the oil during frying [52] and result in enhanced rate of oxidation and thermal degradation of oil [53] which may in turn increase the risk of formation of TPC.

3.6. Oxygen Content in Oil

According to reference [54] the oxygen content of oil increases at temperatures between 25-120°C. The oxygen content of oils gets reduced when they are heated at 180°C and above. However, when such oils are subsequently allowed to cool under aerobic conditions, they gradually absorb oxygen. This results in increased formation of polar compounds. Aerobic conditions favour formation of polar polymers while anaerobic conditions favour formation of non polar polymers [7,55]. Carbon dioxide renders greater protection against oxidation of oils as compared to nitrogen. This can be attributed to higher solubility and density of carbon dioxide as compared to that of nitrogen. Carbon dioxide has been found to suppress oxidation of oils to a greater extent as compared to nitrogen. According to reference [55] have suggested that a minimum of 15 minutes of nitrogen or 5 minutes of carbon dioxide flushing prior to heating is sufficient to

significantly reduce the oxidative reactions in oil during the process of frying.

3.7. Antioxidants

Presence of antioxidants (natural and synthetic) such as tocopherol, butylated hydroxyl toluene (BHT) and butylated hydroxyl anisole (BHA) is associated with reduced formation of polar compounds [56]. Both natural and synthetic antioxidant such as tocopherols, BHA, BHT, propyl gallate (PG), and tertiary-butyl hydroquinone (TBHQ) reduce the speed of oxidation of oil at room temperature. However, antioxidants (natural/ synthetic) become less effective at frying temperature as they get lost from the oil due to volatilization or decomposition [57,58] especially above 200°C thereby increasing risk of TPC formation. The effectiveness of antioxidants varies with the composition of fat and is influenced to a great extent by the processing and handling conditions. For example TBHQ has been found to exhibit antioxidant activity in fried food similar to that of BHA. Like TBHQ, BHA also has good stability and is an effective antioxidant in fried foods. BHT has been found to be more effective in animal fats as compared to vegetable oils and gets lost through steam [59].

Tocopherols and phenolic compounds are important natural antioxidant present inherently in vegetables oils or are added to oils for improving their stability. According to reference [60] α -tocopherol captures peroxy radicals. Which are associated with the formation of TPC. During frying thermal oxidation, polymerization, and hydrolysis lead to a decrease in tocopherols and total phenols [10]. According to reference [61] carotenes are not able to protect the oil from thermal -oxidative stress in the absence of other antioxidants. Although carotenes are major compounds which react with oil radicals such as in case of red palm olein, they decrease linearly in red palm olein with increasing number of frying cycles, apparently yielding overall protection of the phenols. Since laboratory trials with laser flash photolysis have found that tocopherols/tocotrienols regenerate carotenes from carotene radicals, it is being hypothesized that carotenes rather than phenols are the primary substrate for lipid- derived radicals in red plamolein. Tocotrienols and carotenes exhibit a synergistic effect to delay oxidation of oil more effectively as compared to when used alone. Rosemary and sage extracts have also been found to be effective in delaying the deterioration of oil such as that observed during a 30 hour intermittent deep- fat frying of potato chips at 180°C \pm 5°C [62]. According to reference [63] has also reported the synergistic antioxidant effect of rosemary, sage extract and citric acid in palm olein oil during deep- fat frying of potato chips.

4. Determination of Polar Compounds

The analysis of polar fractions can be carried out by high-performance size exclusion chromatography (HPSEC) which facilitates separation and quantification of triglyceride polymers, triglyceride dimers, oxidized triglyceride monomers, diglycerides, and FFA. These components differ not only in polarity or molecular weight but also in nutritional

significance [9]. According to reference [64] has compared four methods to assess polar compounds in frying oils viz; gel permeation chromatography (GPC), liquid chromatography (LC) on a silica gel column, polar and non-polar components by column chromatography (CC) on silica gel and petroleum ether-insoluble oxidized fatty acids. Each of these four methods have unique characteristics with respect to assessment of polar compounds. Assessment of petroleum ether- insoluble oxidized fatty acids is a time consuming process and does not give accurate results. The GPC method can be used to determine dimeric and oligomeric triacylglycerols in frying oil. However, the LC method has the advantage of assessing the total amount of polar as well as oxidized compounds. Separation of polar and non-polar compounds by CC method is most simple and quick.

Now-a-days quantitative analysis of polar compounds is being carried out by the method prescribed by AOAC or by the method given by the International Union of Physical and Applied Chemistry IUPAC standard method 2.507 based on adsorption chromatography on silica gel [65]. The name of the method given by Association of official agricultural chemists (AOAC) is “982.27 Polar compounds in polar components in frying fats- chromatographic Method- first Action 1982, final action 1984” (IUPAC-AOAC Method). It is the same as IUPAC method. It is the most accurate and widely used method for assessing the content of total polar compounds in frying oils. This method helps to assess deterioration of used frying fats, and is applicable to all fats and oils. According to AOAC (1997) “*polar components are the components of fats determined by column chromatography under conditions specified, and include polar substances such as monoglycerides, diglycerides and FFAs found in unused fats, as well as polar transformation products formed during frying of foodstuffs and/ or during heating. Nonpolar components are mostly unaltered triglycerides*”. In this method the non-polar and polar components present in the oil/fat are separated by using a column chromatography on silica gel. The amount of polar components is calculated by subtracting the concentration of non-polar components. The thin layer chromatography is used to assess the quality of separation of polar and non-polar compounds. Several European countries have established regulatory limits for TPCs in frying oils and are given in Table 2.

Table 2. Cut off values for Total polar compounds [66].

S.No	Country	TPC Cutoff value
1	Austria	Not more than 27%
2	Belgium	Not more than 25%
3	France	Not more than 25%
4	Germany	Not more than 27%
5	Italy	Not more than 25g/100g
6	Spain	Not more than 25 %
7	Hungary	Between 25-30%

The main drawback with the use of polar compounds as a quality standard in regulatory and quality controls especially in countries with limited resources is that the standard chemical/laboratory method is time consuming [18]. It may take about 3.5 hours to run one sample and the analysis is chemical intensive as well as expensive.

To reduce the experiment time and expenses several quick tests have been developed to measure the degradation state of oils through the assessment of TPC. For example, the Food Oil Monitor 310 (FOM 310) and the Testo 270 deep- frying oil tester are frequently used for rapid measurement of the content of TPCs in oils or oils used for deep fat frying. Before taking any measurement, the test mode (liquid, semiliquid or solid) of FOM 310 is selected which depends upon the state of the sample, and the sensor needs to be calibrated using the fresh oil at 100°C or above. FOM 310 is useful to check the quality of oils between 160-200°C. The sensor of FOM 310 need to be submerged into oil sample and reading of the content of polar compounds (per cent) is provided by the monitor in less than one minute. The testing procedure of Testo 270 is very similar to FOM 310, except that there is no test mode selection or calibration. The rapid oil quality or TPC testing kits are based on the principle of dielectric constant of oil. The dielectric constant is converted into the quantity of total polar compounds which is expressed in percentage. The rapid detection kits are useful for field based studies and also for easy monitoring of oil quality by small manufacturers [45].

5. Health Concerns

Compromised quality of frying oils has been considered as an important risk factor for the development of chronic diseases, such as diabetes and liver disorders [67]. Frequent consumption of foods (i.e., four or more times per week) fried in abused oil has been found to be associated with a higher risk of cancer, type2diabetes, obesity, hypertension, asthma, damage to the mucosal lining of eyes, throat and lungs [68,69,70]. Regular consumption of over-cooked edible oils has also been found to be associated with impaired vaso-relaxation, endothelium dysfunction and prostate cancer [71].

Some volatile oxidation products inhaled during frying have been found to be mutagenic [46]. The study conducted by [72,73] in China and Taiwan indicates that lung cancer in women is linked to inhalation of vapors released during frying of fish. According to a study conducted by [46] a fraction of polar compounds separated from frying oils obtained from restaurants have been found to exhibit mutagenic activity as assessed through the Ames test in salmonella. Thiobarbituric acid reaction substance (TBARS) which is formed from fatty acids with three or more double bonds in thermally abused oils, has been found to be positively associated with cancer. Melondialdehyde (MDA) has been found to be mutagenic in several studies. MDA has been found to be associated with skin cancer, retarded growth, irregular intestinal activities, enlarged liver and kidney, anemia as well as low serum and liver vitamin E levels [74,75]. Oxidized products in frying oils have been found to cause adverse effects on health. Feeding experiment with albino rats produced diarrhea and rapid death and slower growth rate when oil with <10 per cent polymerized products were fed. However, when 10 per cent of the polymers from auto-oxidized cottonseed oil was included in the diet, only of the half of the rats were able to survive for four weeks; at the 20 per cent polymeric residue in the diet all rats died

within a week [76]. When polar fractions were fed to rats at 20 percent by weight in the diet for 1.5 year period, a 20 percent increase in the activity of serum enzymes glutamic pyruvic transaminase and serum glutamic oxaloacetic transaminase was observed when compared with control group [77].

6. Conclusion

This review provides an outline related to the formation, assessment and health issues associated with repeatedly heated frying oils with special reference to polar compounds. While literature is available pertaining to the oxidative and hydrolytic deteriorative changes taking place in cooking/frying oils, not much information is available specifically with reference to polar compounds. It has been felt through this exercise that there is need for developing data- base regarding the levels of polar compounds in frying oils in small/ micro food service units especially those situated on the roadside. Since, the conventional methods prescribed by IUPAC/ AOAC may not be viable for assessing the quality of oils in the field, there appears to be vast scope of the quick- test kits to develop data base regarding polar compounds. Such data- base on total polar content would be a valuable indicator of oil quality and can be utilized for developing information- education and communication (IEC). IEC material can help to generate awareness among food operators which would help to maintain quality of oil. Such information would also be useful in developing policy framework pertaining to maintenance of oil quality by small food business operators. It shall also facilitate in strengthening the existing surveillance system of the food laws especially in developing and under developed nations particularly in the unorganized food- sector.

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