CONTAINER'S INFLUENCE ON THERMAL DEGRADATION OF VEGETABLE OIL

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ABSTRACT

The influence of the container on the thermal degradation of different vegetable oils were evaluated. Four oils, namely groundnut, rice bran, soybean and sunflower were heated in glass, copper and iron containers of identical shape, size and thickness at 180°C for 12 hours. The oils were evaluated for conjugated dienes, conjugated trienes and total phenolic content before and after heating. The findings revealed that the container surface had a discernible influence on the formation of conjugated diene and triene in vegetable oil. However, a general trend was not found and the results were dependent on the nature of the oil. Except for groundnut, all other oils showed maximum conjugated diene content when heated in glass. For groundnut oil, maximum conjugated diene was found in copper. However, except rice bran, all other oils showed maximum post-heating conjugated triene content when heated in a copper container. For rice bran oil, the maximum conjugated triene content was observed when heated in a glass container. Soybean oil heating in a glass and copper container produces statically identical values. Thus, it appears that copper containers are more efficient in converting the primary oxidation products into secondary products. The phenolic content of the oils, on the other hand, was found to be stable under the experimental condition and not particularly dependent on the container.

1. Introduction

Vegetable oils can be used for a variety of purposes. They are primarily the triesters of glycerol with saturated (SFA), monounsaturated (MUFA), and polyunsaturated (PUFA) fatty acids. These fatty acids play a key role in cellular metabolism by storing energy and providing it when needed. In addition to dietary applications, vegetable oils are utilized in industrial applications such as biofuels, soaps, paints, coatings, adhesives, lubricants, and so on(Kumar et al., 2016). Deep frying is a popular cooking technique, which involves emerging food in vegetable oils heated to extremely high temperatures (usually between 160 and 180°C) (Fauziah et al., 2000). Within a few minutes of immersion, several processes occur in food such as dehydration of the food surface, absorption of fat in food, production of flavour compounds, development of surface colour, and so on. The oil also degrades as a result of the harsh conditions used in deep-frying. It undergoes a number of processes, including pyrolysis, oxidation, hydrolysis, polymerization, isomerization, cyclization, and so on (Dobarganes et al., 2000). During this process, oxidation occurs resulting in large amounts of lipid peroxidation products such as conjugated diene hydroperoxides etc. Cleavage of these products generates aldehydes, such as malondialdehyde, which are toxic. To guarantee excellent oil quality, it is critical to check the oxidative condition of the oil on a regular basis. The thermal degradation of oil and fat is affected by a lot of factors. For example, numerous studies have revealed that unsaturated

fatty acids are more sensitive to oxidation during frying than saturated fatty acids (Kim et al., 2010; Liu et al., 2019; Normand et al., 2006; Warner et al., 1994). However, relatively little research was focused on the influence of the surfaces of the frying container on the thermal deterioration of vegetable oil. The topic is especially relevant when traditional cooking utensils made of copper or iron are used. Such metals are widely recognised for their ability to catalyze a wide range of organic reactions (Smith & Notheisz, 1999). Hence, the surface of these containers must influence numerous degradation processes in hot oil. According to one study, when sunflower, coconut, palm, and sesame oils were cooked at different temperatures, iron and copper containers produced much more malondialdehyde than aluminium and glass containers (Doureradjou & Koner, 2008). Another study found that using cast-iron containers increases the production of trans fatty acid 18:1 in groundnut and palm olein oil (Kala et al., 2012).

The conjugated diene and triene content are an effective indicator of the oxidation state of the vegetable oil (Chandran et al., 2017). For example, it was discovered that as microwave heating progressed, the amount of conjugated dienes and trienes steadily rose during heating. Also, it is noted that conjugated dienes were generated at somewhat greater levels than conjugated trienes (Hassanein et al., 2003). During the peroxidation of unsaturated fatty acids, substantial isomerization of double bonds occurs. This isomerization produces conjugated diene. Conjugated dienes can be detected by their strong absorption at 234 nm wavelength (White, 1991). Conjugated trienes are formed as the oxidation products of linolenate or by the dehydration of hydroxyl linoleate. They can be detected by their absorption at 268 nm wavelength (Houhoula et al., 2002). Phenolic antioxidants impart oxidative stability to the oil. Moreover, when consumed with oil they help in elevating oxidative stress in our body. A linear relationship was found between the total phenolic content of the oil and its oxidative stability by Rancimat (Salvador et al., 2001).

The purpose of this study was to determine the effect of containers on the stability of vegetable oils during heating. Four different commonly used oils; groundnut (GN), rice bran (RB), soybean (SO) and sunflower (SU) were chosen for this study. The total phenolic, conjugated diene and triene content of the oils were assessed before and after heating to evaluate the effect of containers on the thermal stability.

2. Materials and methods
2.1. Materials
Four vegetable oils - Groundnut, Rice bran, Soybean and Sunflower were purchased from the local market of Haryana, India. All the purchased oils had an expiry date exceeding the time period for this investigation. Three Containers made up of glass, copper and iron were also purchased, The containers have the same shape and size and thickness. All the chemicals and materials used were of analytical grade.

2.2. Sample Preparation
100 mL of different oils were placed in separate 500 mL containers of glass, copper and iron. The containers were then submerged in a silicone oil bath that was maintained at 180 ± 5 °C. For 12 hours, the oils were heated at this temperature. After that, the oils were allowed to cool to room temperature and kept in amber bottles to reduce oxidation. All of the assays were done within 12 hours of heating.

2.3. Statistical Analysis
All analyses were performed in triplicates. The findings were statistically evaluated by ANOVA and Duncan's multiple range tests using the R software programme (version 4.0.2). Statistical significance was defined as a p-value of < 0.05. The graphs were created in R using the ggplot package.

2.4. Methods
2.4.1. Conjugated dienes and trienes content

The oxidation products of oils and fats have distinct spectra in the UV region. Linoleic hydroperoxide and the conjugated dienes that may emerge from its breakdown exhibit an absorption band at around 232 nm, whereas subsequent products of oxidation, notably ethylenic diketones, have an absorption band at approximately 268 nm. Conjugated trienes exhibit a triple absorption band, with the primary peak at approximately 268nm, a secondary peak at about 278nm, and minima close to the primary peak at about 262 and 274 nm. As a result, determining the absorbance at 232 nm might possibly provide an indication of the oil's condition of oxidation. Furthermore, determining the absorbance at 268 nm would show the existence of subsequent oxidation products and conjugated trienes. Absorbance at 232 and 268 nm were used for determining conjugated dienes and trienes, respectively (Dieffenbacher & Pocklington, 1992). Conjugated dienes give an indication of primary oxidation products and conjugated trienes indicate secondary oxidation products. In brief, 0.2 g of oil sample was dissolved in 10 ml Isooctane. Further, this solution was diluted by adding 150 μL solution in 5 ml isooctane. Then, its spectra were taken against isooctane as a reference.

2.4.2. Total Phenol content

It was determined according to Folin–Ciocalteu's method (Singleton et al., 1999). The standard used was gallic acid, and the findings were expressed as gallic acid equivalents (GAE). The concentration of phenolics was expressed as micrograms of gallic acid equivalents per g of oil (μg GAE/ g) and was calculated using the following linear equation based on the calibration curve:

$$A = 0.41 \times C - 0.0799, R^2 = 0.99$$

where A is absorbance and C is concentration

Some modifications were made to the method (Karakaya & Şimşek, 2011). In 2 g oil, distilled water (3 ml), Folin–reagent Ciocalteu's solution(250μL), and 7 % Na_2CO_3 (750 μL) were added and incubated for 8 minutes at room temperature for TP analysis. After that, 950 μL of distilled water was added. The mixture was allowed to stand at room temperature for 2 hours. Similarly, a blank (without an oil sample) was made and allowed to stand for the same time. Then, the absorbance was determined at 765 nm against blank.

3. Results and discussions
3.1. Conjugated dienes (CD)

At the onset of thermal oxidation, the double bonds present in linoleate (18:2) and other higher polyunsaturated fatty acids (PUFA) change position. This occurs because generally oxidation starts with the loss of hydrogen from the methylene group sandwiched between two double bonds in the original configuration. The resultant pentadienyl radical reacts with oxygen to form conjugated hydroperoxides. These conjugated compounds are absorbed strongly at 232-234 nm. Hence, an increase in absorbance correlates with increased oxidation in these oils (White, 1995).

The results of the current study were shown in Table 1 and Figure 1. Dienes rose in metal containers and reduced in glass containers (GC) for groundnut oil (GN). Copper and iron were found to increase by 152.99% and 196.28% respectively compared to untreated. In the case of oil heated in glass, the value of CD reduced marginally (9.67%). Conjugated dienes were completely destroyed in Rice Bran oil heated in a copper container (99.86% decrease compared to untreated). A less severe decrease was observed in iron containers (30.38%). Glass on the other hand increased the value by 26.68%. The CD of soybean oil rises when it is heated irrespective of the container although the amount of increase depends on the container in which the oil is heated. Glass showed the most increase 422.40%, followed by iron, which caused an increase of 203.67%, while the increase in copper was only 129.50%. The relatively bigger changes in this oil compared to other oils may be

due to the presence of high amounts of PUFA in this oil. It is known that PUFA increases CD (Tekin et al., 2009). However, the sunflower oil shows very little change in CD. There is no statistically significant difference in CD between unheated oil and oil heated in iron. However, the value of glass and copper grew by 41.04% and 11.47%, respectively, with glass experiencing the greatest gain.

Table 1. Values of untreated and heated oils (mean ± standard deviation)

Oil	Treatment	Conjugated dienes by $E^{1\%}$(232 nm)	Conjugated trienes by $E^{1\%}$(268 nm)	Total Phenolic Content
GN	UT	3.153 ± 0.08	8.020 ± 0.22	20.116 ± 7.98
	GC	2.848 ± 0.06	1.209 ± 0.08	19.018 ± 6.58
	CC	7.978 ± 0.18	5.227 ± 0.16	14.079 ± 4.95
	IC	9.343 ± 0.22	2.008 ± 0.12	13.591 ± 4.34
RB	UT	7.683 ± 0.38	1.171 ± 0.28	57.25 ± 9.25
	GC	9.733 ± 0.28	4.513 ± 0.30	27.372 ± 4.05
	CC	0.01 ± 0.01	3.394 ± 0.16	27.372 ± 5.43
	IC	5.349 ± 0.21	2.600 ± 0.06	18.957 ± 3.83
SO	UT	4.340 ± 0.12	0.464 ± 0.07	20.116 ± 4.75
	GC	22.672 ± 0.43	5.647 ± 0.19	19.628 ± 6.00
	CC	9.96 ± 0.18	5.77 ± 0.27	10.908 ± 2.69
	IC	13.179 ± 0.24	3.532 ± 0.26	15.603 ± 3.31
SU	UT	13.242 ± 0.15	5.848 ± 0.15	13.591 ± 3.80
	GC	18.677 ± 0.31	3.137 ± 0.13	11.64 ± 2.80
	CC	14.762 ± 0.22	6.654 ± 0.22	10.786 ± 2.61
	IC	13.251 ± 0.21	3.744 ± 0.22	10.603 ± 4.25

The results show that the observed CDs after heating are dependent on the container for all four oils. However, the relative order among different containers depends on the oil type. Three of the four oils show maximum value in the glass container. When trying to understand these differences it must be kept in mind that CD represents the primary oxidation product. These

products are formed on heating but with time they are also decomposed to secondary oxidation. Thus, the observed values are results of the rate of formation of dienes subtracted by their rate of decomposition. So, a lower CD may be due to the slow formation of dienes but may also be because of the higher decomposition rate. If it is due to a lower rate of oxidation, then the values of CT are also expected to follow the same pattern, because conjugated trienes are formed from the degradation of dienes. However, if the rate of decomposition of dienes is the dominant factor, reversed trends are expected to be observed in CT. For most oils, maximum triene content post-heating was observed in GC. Thus, glass may be more effective in preventing the dienes from decomposing. The different behaviour of GN in GC needs further investigation.
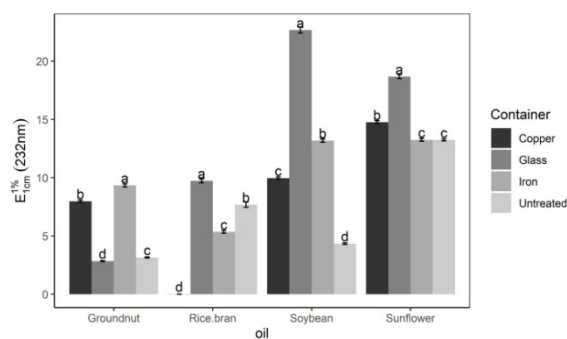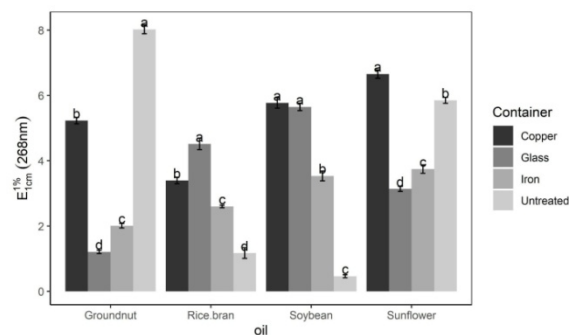

Figure 1. Conjugated dienes (CD) in untreated and heated oils. Data with the different superscript letters are significantly different (p<0.05)

3.2 Conjugated trienes (CT)

These hydroperoxides are unstable and under thermal treatment dehydrated from conjugated trienes which show a strong absorbance in the 268-270 nm region. Hence absorbance in this range is an indication of the formation of secondary products in oils (White, 1995).

The results were shown in Table 1 and Figure 2. The levels of CT in groundnut oil decrease when heated in various containers. The largest drop was 84.91% in the Glass

container, followed by 74.95% in the Iron container, and just 34.82% in the Copper container. The CT of Rice Bran and Soybean rises after heating in the order Glass > Copper > Iron. The greatest rise is seen in glass, at 285.41%, followed by copper at 189.89% and iron at 122.09%. Like CD increase in CT on heating in soybean substantially higher than the other oils. Glass and copper containers register around 1100% increase while the increase in the iron container is around 700%. This reflects the poor oxidative stability of the oil. The values in glass and copper are statistically identical and higher than that in the iron container. Copper > untreated > iron > glass is the sequence for sunflower oil. In the case of copper, there is a little rise of 13.78%, whereas CT falls by 35.96% and 46.35% in iron and glass, respectively. Again, it is observed that CTs are dependent on the container. Except for RB, all the other oils register maximum post-heating CT value in CC. So for GN, SO and SU the copper surface is most effective in producing CTs. RB behaves differently from the other 3 oils. Here the GC produces the highest degradation in terms of CD and CT. This observation warrants further investigation. One interesting observation is that it is also the only oil which registers a significant and substantial decrease in phenolic compounds on heating. At this point, it could be postulated that some unique minor ingredients in the oils such as γ-original may be responsible for this.
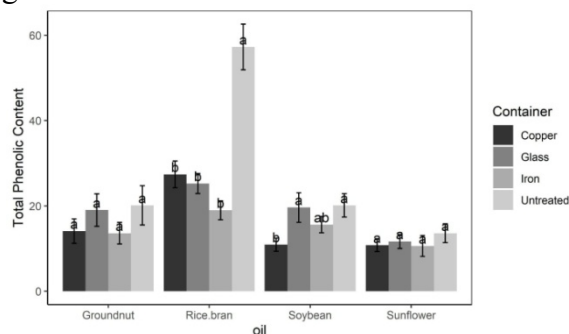

Figure 2. Conjugated trienes (CT) in untreated and heated oils. Data with the different superscript letters are significantly different (p<0.05)

3.3 Total Phenolic Content

Phenolic compounds serve as important antioxidants because of their ability to donate a hydrogen atom or an electron in order to form stable radical intermediates. Hence, they prevent oxidation and the antioxidant activity of oils varies due to changes in phenolic content (Nyam et al., 2009).

So, it was decided to study total phenolic content. The results were shown in Table 1 and Figure 3. Generally, it was observed that heating under the current protocol has little effect on total phenolic content. All of the values in groundnut and sunflower oil are statistically the same. The total phenolic content of Rice Bran oil drops when heated. However, containers do not have any effect on this decrease. Values are statically the same in all containers. In the case of soybeans, the values for untreated and glass containers were statically identical. However, there is a little decline of 45.77% in the case of copper. The value observed in iron is statically identical to both iron and glass containers.

Figure 3. Total Phenolic Content of untreated and heated oils. Data with the different superscript letters are significantly different (p<0.05)

4. Conclusions

The effect of containers on the thermal degradation of vegetable oil was investigated by conjugated dienes and trienes content. The phenolic content of the oils was also studied. The results of the experiments with glass, copper and iron container revealed that the container in which the oils were heated had an observable influence on the conjugated diene and triene content of the vegetable oils. Though which container caused the maximum degradation is dependent on the oil type. Except for GN, all other oils register maximum diene concentration when heated in a glass container. However, in general, maximum conjugated triene values were observed in the copper container. Thus it can be postulated that copper containers promote the decomposition of primary oxidation products into the secondary product. The current heating protocol does not produce appreciable changes in the phenolic content of the oil. Where there is some decrease in the concentration of phenolic compounds; the effect of containers is either nonexistent or minimal. There is a scope for further investigation of the topic with more parameters and oil types. The authors hope this study will initiate a discourse on the effect of the container on the thermal stability of vegetable oil. This is especially important in a time when popular opinion is turning against nonstick cookware.

5. References

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