Chemical resistance of sunflower oil enriched with cumin oil

**Olena Podobii, Svitlana Kovalyova,
Ihor Zhytnetskyi, Olena Mayboroda**

National University of Food Technologies, Kyiv, Ukraine

Keywords:

Oil
Cumin
Sunflower
Antioxidant
Frying
Polyphenol

Article history:

Received
14.10.2020
Received in revised form 20.12.2020
Accepted
25.12.2020

Corresponding author:

SvitlanaKovalyova
E-mail:
sval_kov@ukr.net

DOI:
10.24263/2310-1008-2020-8-2-10

Abstract

Introduction. The antioxidant properties of cumin oil are used to inhibit destructive processes in sunflower oil. The chemical resistanse of sunflower oil and f mixtures of sunflower oil and cumin seed oil was studied.

Materials and methods. The chemical values for samples for vegetable oils and their binary mixtures during long-term heating at 180-195 °C were monitored. The content of free acids and unsaturated compounds was determined by titrometric method, the content of polyphenols and carbonyl compounds – by spectrophotometric analysis..

Results and discussion. The most change of acid value from the start of the frying experiment to the end of the 20 hour frying was shown for sunflower oil. The least change of the acid value during frying was found for mixture of sunflower oil and black cumin oil, especially for a mixture with a higher content of cumin oil. The higher oxidative resistance of black cumin oil compared to sunflower oil is due to the higher content of saturated acids and oleic acid (monounsaturated) and the low content of polyunsaturated fatty acids in triacylglycerols.

As expected, the iodine value of oils decreases during frying, that means a destruction double C-C bonds of fatty acids residue in triglyceride molecules. The most significant relative decrease in iodine value was noticed for sunflower oil, and the percentage of iodine value decrease was 6.62% at the end of the frying terms. However, the decrease in the iodine value of the mixtures of cumin oil and sunflower oil in the ratio of 10:90 and 20:80 was less.

An increase in thiobarbituric acid value (TBA) during frying was observed for all oil samples. The highest TBA was shown for sunflower oil at the end of the frying terms. At the same time, for oil mixture with most content of cumin oil the TBA was lowest at the end of the frying terms. The less changes in TBA of oils indicates that natural antioxidants in cumin oil have an inhibitory effect on the formation of secondary oxidation products during frying terms.

Conclusions. Blending sunflower oil with cumin oil leads to a positive effect on the chemical resistance of oil compositions under heating conditions.

Introduction

Sunflower oil is widely used in food, cosmetic and pharmaceutical industries. This vegetable oil is a suitable medium for fat-soluble vitamins – important components in the human diet.

Like most vegetable oils known for a high content of triglycerides of unsaturated fatty acids, sunflower oil tends to oxidize during contact with atmospheric oxygen, that leads to a deterioration of the organoleptic characteristics for the oil, a decrease in its nutritional value, as well as the formation and accumulation carbonyl and carboxyl compounds of various length carbon chain. Oxidation processes in oils accelerate significantly with increasing temperatures and especially under deep-fat frying conditions, where the temperature reaches 190 °C [1]. Chemical transformations of triglycerides are influenced by different components, for instance, moisture, that contained in food immersed in hot oil[2]. Oxidative reactions of lipids are inhibited in various ways, for example, by inactivation of enzymes that catalyze oxidation, the addition of chelating agents, or the addition of antioxidants of both synthetic and natural origin.

Among antioxidants, substances of natural origin are of particular interest, since, unlike synthetic analogues, they are ecologically safe. As nature antioxidants, some extracts from various herbal plants, such as rosemary, Chinese green tea, and cumin containing substances with antioxidant activity that can inhibit radical oxidation processes and thereby extend the shelf life of the oil, are used.

Blending has long been used to modify oils and fats in order to improve their functional properties and therefore better use them in food. Blending oils with other oils influences their physicochemical properties not changing their chemical composition [3]. Blending oils is used to obtain compositions with good resistance to oxidation under frying conditions through some substances in one of the oils providing protective effect. Such oil compositions can be safely reused for frying foods [4].

Phenol derivatives are important components of vegetable oils, the amount of them correlates with the resistance of triglycerides of the oil to the action of oxidants [5, 6]. Sunflower oil has a good nutritional profile and low oxidation stability. Oxidative degradation of unsaturated fatty acids is one of the main reasons for the deterioration of the organoleptic properties of the oil and a decrease in its nutritional value [7].

Black cumin seeds contain 36% oil, and the fatty acid profile of cumin oil is similar to sunflower oil. Black cumin has unique nutritional profile, its oil, used in both cooking and medicine, is enriched with phytochemicals. Due to the content of tocopherols, carotenes and, especially, various polyphenols in cumin oil, it can be considered as a source of natural antioxidants.

The aim of this study was to evaluate the chemical parameters of binary mixtures of sunflower and cumin oils subjected to prolonged high-temperature exposure by determining the acid value, iodine value and thiobarbituric acid value (TBA).

Materials and methods

Black cumin seeds and refined sunflower oil were purchased from a local supermarket. All reagents and chemicals used in the work were of analytical grade.

Extraction of black cumin seed oil

The seeds were crushed and pressed on a hydraulic laboratory press. The resulting oil was dried over anhydrous sodium sulfate. Filtered dry oil was stored at 4 ± 0.5 °C in a brown glass bottle.

Preparation of binary mixtures. Black cold pressed cumin oil was mixed with sunflower oil in proportions (% vol.); 0: 100, 10:90, 20:80. The initial analysis of binary mixtures was carried out after preliminary homogenization of the samples at 60 °C.

Frying process. about 500 ml of refined sunflower oil and its binary mixtures with black cumin seed oil were placed in a stainless steel food container and heated to 185-190 °C with 10-15 g of frozen mushrooms were immersed in the heated oil. Oil samples were taken every 5 hours with continuous frying for 20 hours, cooled and stored at −10 °C until chemical analysis.

Determination of fatty acid composition of black cumin seed oil and refined sunflower oil

The fatty acid composition of the individual oil samples was determined by gas chromatography (GC) [15]. The triglycerides of the studied oils were subjected to hydrolysis and subsequent methylation. The obtained methyl esters of carboxylic acids were analysed on an automatic gas chromatograph with a flame ionization detector to identify the composition and determine the mass fraction of individual fatty acids.

Determination of thiobarbituric acid value

For samples of sunflower oil and binary oil mixtures subjected to heat treatment, the thiobarbituric acid value was additionally determined. The 2-thiobarbituric acid (TBA) value is a frequently used measure of the oxidation degree of oils, fats, and fatty foods and characterizes the accumulation of carbonyl compounds in oil that are intermediate products being resulted by oxidized destruction triglycerids and do not influence acid value of oil. The method for determining the thiobarbituric value is based on the reaction of thiobarbituric acid with different aldehydes [16], formed during the oxidation of unsaturated fatty acids, among them malondialdehyde [17] (Figure 1).

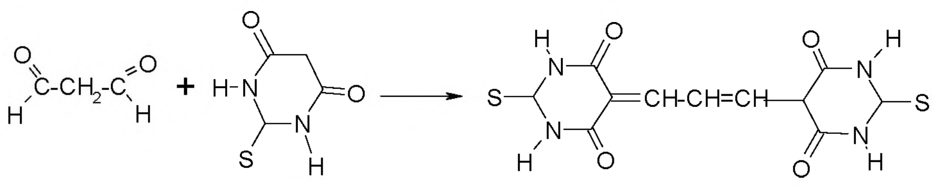

Figure 1

Therefore, the TBA-value is often expressed in mg of malondialdehyde per 1000 g of vegetable oil [2]. Carbonyl compounds react with thiobarbituric acid to form colored compounds, the content of which can be determined photometrically at a wavelength of 532 nm [16, 17]

1000 mg of each oil sample is dissolved in propan-1-ol, and the solution of thiobarbituric acid (TBA) is made up with the same solvent by dissolving 400 mg TBA in 100 ml propan-1-ol. A volume of 3 ml each sample solution and 3 ml TBA-reagent are mixed, stoppered, the content placed into a silicon oil bath and stirred at 95 °C for 2 h. Then the mixture is cooled by running tap water for about 10 min, and the absorbance is measured (within 30 min) at 530 nm using the blank solution in the reference cell (the molar extinction coefficient is $1.56 \cdot 10^5$ $cm^{-1} \cdot M^{-1}$). A blank is carried out in the same way using 3 ml of propan-1-ol instead of the oil sample solution.

Results and discussion

Chemical analysis of black cumin seed oil and refined sunflower oil

Based on the results obtained, it can be argued that the oils used have a similar composition according dominant fatty acids – linoleic and oleic. It should also be noted the presence of ~ 10% polyunsaturated acids (Omega-3) in the cumin seed oil and a higher content of saturated carboxylic acids than in sunflower oil.

Table 1

Fatty acid composition of Black Cumin seed oil and refined Sunflower oil

Fatty acid type	Cumin oil	Sunflower oil
Total unsaturated fatty acids, including;	79.85	83.64
Oleic acid	16.59	28.47
Linoleic acid	42.76	56.71
Total saturated fatty acids	15.13	9.75
Total fatty acids	94.98	93.39

Chemical indicators of the quality of the studied oils: acid value, iodine value, as well as the total content of phenolic compounds in black cumin seed oil and in sunflower oil are shown in Table 2 [8].

Table 2

Chemical indicators for Black Cumin seed oil and refined Sunflower oil

Value	Black Cumin seed oil	Refined Sunflower oil
Acid value (as mg KOH/g oil)	2.8 (up to14)	0.4
Iodine value	112	123
Content of polyphenols (in terms of gallic acid, mg / 100 g)	135	-

Changes in acid value

The acid value was used to assess the degree of hydrolysis of oil triglycerides during frying and the dynamics of change them influenced by the product subjected to heat treatment [9, 10]. Changes in the acid value of sunflower mixed with various portions of black cumin oil during deep-frying at 185-190 °C are shown in Figure 2.

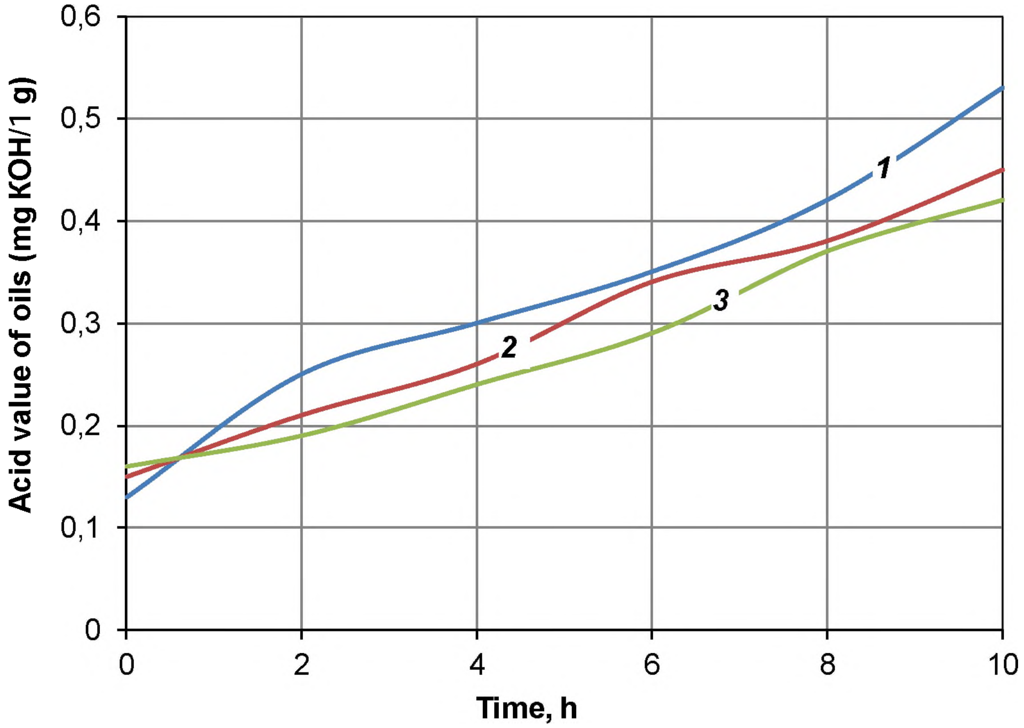

Figure 2. Changes in acid value for oils during deep-frying:
1 – sunflower oil;
2 – cumin and sunflower oil as 10:90;
3 – cumin and sunflower oil as 20:80

The most initial acid value of the oil as 0.16 mg KOH/g oil is determined for binary oil mixture containing cumin and sunflower oil as 20:80. The least acid value as 0.13 mg KOH/g oil is characterized for refined sunflower oil.

Frying of the studied oils at 185–190 °C for 20 hours led to a gradual increase in the acid value that indicates the formation of free fatty acids with an increase in the frying time as a result of the oxidation and hydrolysis of oil triglycerides [11, 12]. The most change of acid value from 0.13 at the start of the frying experiment up to 0.53 (relative change is as 307 %) at the end of the frying period was shown for sunflower oil. The least change of the acid value is found for mixture of sunflower oil and black cumin oil with a higher content of cumin oil. The increase in the acid value of the mixtures of cumin oil and sunflower oil in the ratio of 10:90 and 20:80 was less and amounted to 200 % and 163 % at the end of frying, respectively.

The higher oxidative resistance of black cumin oil compared to sunflower oil is due to the high content of saturated acids and oleic acid (monounsaturated) and the low content of polyunsaturated fatty acids in triacylglycerides and by content of a large amount of phenolic compounds with antioxidant and anti-hydrolysis properties [8]. The data obtained on the relative increase in the acid number of the samples indirectly confirm the formation of free acids not only as a result of hydrolysis of triglycerides, but as a result of oxidative destruction of double C-C bonds of unsaturated fatty acid residues.

Changes in iodine value

The iodine value is one of the parameters used to assess the quality of oil [13] that correlates with the degree of unsaturation in oils. The most initial iodine value is found for sunflower oil, the least one – for mixture of cumin and sunflower oils in ratio as 20:80. The lower initial values of the iodine value of the obtained binary oil mixtures in comparison with sunflower oil one are explained by the higher content of monounsaturated fatty acids in cumin oil.

As expected, the iodine value of oils decreases during frying, that means a destruction double C-C bonds of fatty acids residue in triglyceride molecules [14]. The most significant relative decrease in iodine value was noticed for sunflower oil, and the percentage of iodine value decrease is 6.62 % at the end of the frying terms. However, the decrease in the iodine value of the mixtures of cumin oil and sunflower oil in the ratio of 10:90 and 20:80 is less and amounted to 6.29 % and 5.88 % at the end of frying, respectively. Auto-oxidation of triglycerides of sunflower oil proceeds faster, since it contains about 65% polyunsaturated linoleic acid [15]. The phenolic compounds contained in caraway oil largely suppress the course of radical oxidation processes. Therefore, the addition of cumin oil with a higher content of monounsaturated acids and natural antioxidants to sunflower oil reduces the oxidation rate, as evidenced by the relatively low decrease in the iodine value (Figure 3).

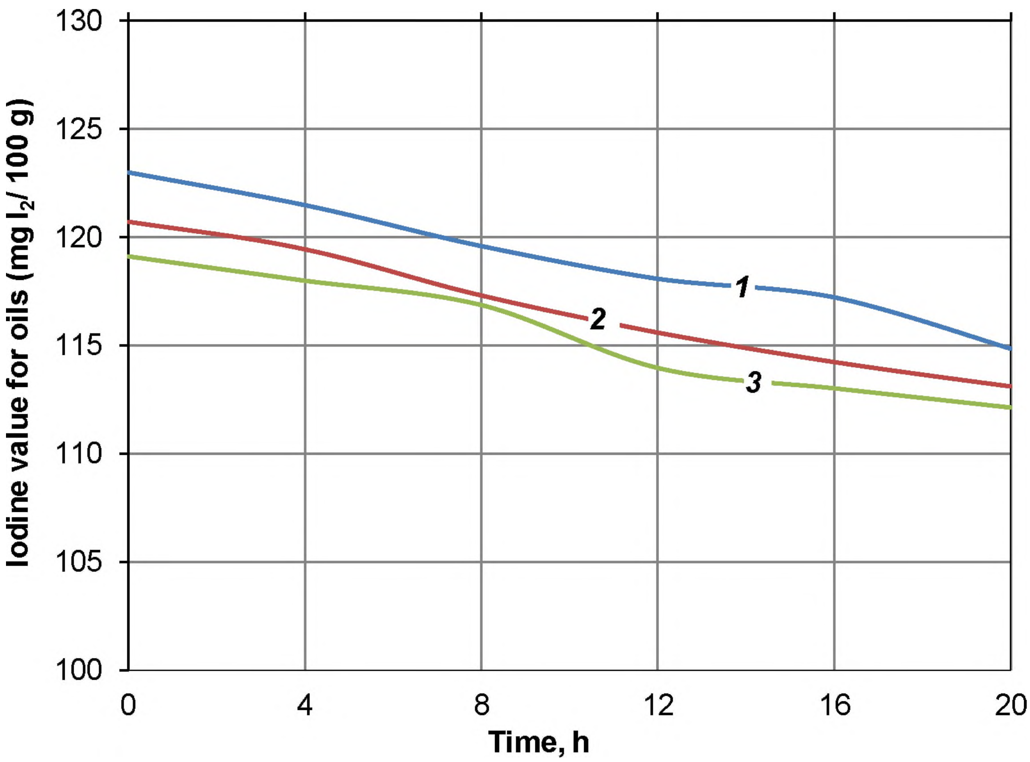

Figure 3. Changes in iodine value for oils during deep-frying:
1 – sunflower oil;
2 – cumin and sunflower oil as 10:90;
3 – cumin and sunflower oil as 20:80

Changes in thiobarbituric acid value (TBA)

Changes in the thiobarbituric value (absorbance at 532 nm) for sunflower oil and binary mixtures of oils during deep-frying at 185-190 °C are shown in Figure 4. An increase in TBA during frying was observed for all three oil samples. The most change of thiobarbituric acid value from 0.07 at the start of the frying experiment up to 0.92 was shown for sunflower oil (0.97 as absorbance at 532 nm) at the end of the frying terms. At the same time, the TBA of mixture consisted of cumin oil and sunflower oil in ratio 20:80 was lowest at the end of the frying terms.

The relative change in thiobarbituric acid values for all samples was found to be approximately the same, which can be explained by the higher content of polyunsaturated fatty acids in cumin oil. Linoleate hydroperoxides are known to decompose faster than oleate ones [18]. The ratio of oxidated oleate: linoleate: linolenate has been reported to be on the order of 1:12:25 [18]. These literature data are consistent with the discussed results of carried out experiment.

However, it may be concluded, the less changes in TBA of oils indicates that the presence of natural antioxidants in cumin oil has an inhibitory effect on the formation of these secondary oxidation products during frying terms.

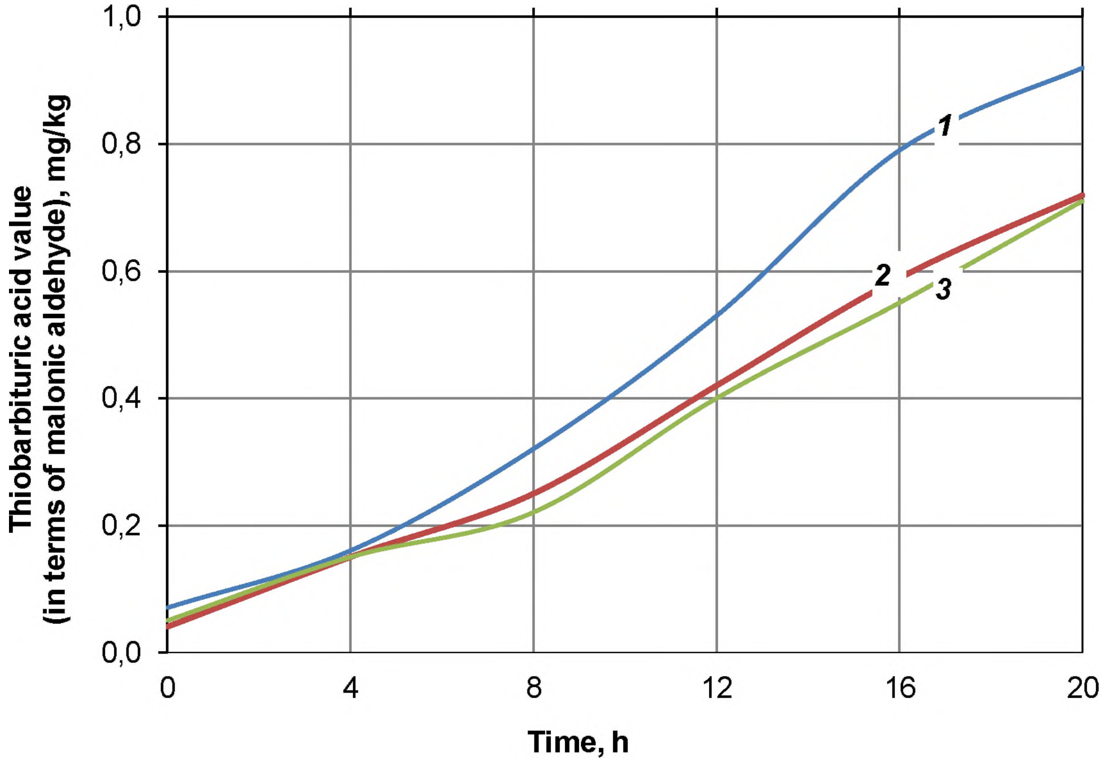

Figure 3. Changes in thiobarbituric value for oils during deep-frying:
1 – sunflower oil;
2 – cumin and sunflower oil as 10:90;
3 – cumin and sunflower oil as 20:80

Conclusions

Cumin oil contains a significant amount of polyphenolic compounds and is therefore a promising source of natural antioxidants to create oil compositions.

It is shown that the blending sunflower oil with cumin oil has a positive effect on the resistance of triglycerides under deep-heating conditions and to hydrolysis.

Comparative analysis of the chemical parameters of the studied oil compositions shows that the greater resistance of triglycerides to thermal destruction correlates with a higher concentration of cumin oil in the mixture.

Thus, mixtures of cumin and sunflower oil are more suitable for deep frying than just sunflower oil.

References

1. Yamsaengsung R., Moreira R.G. (2002), Modeling the transport phenomena and structural changes during deep fat frying. Part II: Model solution and validation, *Journal of Food Engineering*, 53(1), pp. 11–25.
2. Andrikopoulos N.K., Dedoussis G.V., Falirea A., Kalogeropoulos N., Hatzinikola H.S. (2002), Deterioration of natural antioxidant species of vegetable edible oils during the domestic deep-frying and pan-frying of potatoes, *International Journal of Food Sciences and Nutrition*, 53(4), pp. 351–363.
3. Abdelbaset Salama M. etc. (2020), Erratum to: Oxidative stability of Opuntiaficus–indica seeds oil blending with Moringaoleifera seeds oil, *Oilseeds and fats, Crops and Lipids*, 27, DOI: 10.1051/ocl/2020045
4. Toliwal S.D., Tiwari M.R., Verma S. (2005), Studies on Thermal stability of Palm Corn Oil Blends. Oil Technologists' Association of India, *J Oil TechnolAssoc India*, 37, pp. 18–20.
5. Henna Lu F.S., Tan P.P. (2009), A Comparative study of storage stability in virgin coconut oil and extra virgin Olive oil upon thermal treatment, *International Food Research Journal*, 16, pp. 343–354.
6. Cheikh–Rouhou S., Hentati B., Besbes S., Blecker C., Deroanne C., et al. (2006), Chemical Composition and Lipid Fraction Characteristics of Aleppo Pine (*Pinushalepensis* Mill.), Seeds Cultivated in Tunisia, *Food Science and Technology International*, 12, pp. 407–415.
7. Hemalatha G., Ghafoorunissa (2007), Sesame lignans enhance the thermal stability of edible vegetable oils, *Food Chemistry*, 105, pp. 1076–1085.
8. Topcagic A., Zeljkovic S.C., Karalija E., Galijasevic S., Sofic E. (2017), Evaluation of phenolic profile, enzyme inhibitory and antimicrobial activities of *Nigella sativa* L. seed extracts, *Bosnian Journal of Basic Medical Sciences*, 17(4), pp. 286–294.
9. Melton S.L., Jafar S., Sykes D., Trigiano M.K. (1994), Review of stability measurements for frying oils and fried food flavor, Journal of the American Oil Chemists' Society, 71, pp. 1301–1308.
10. Jung-Min Park, Jin-Man Kim (2016), Monitoring of Used Frying Oils and Frying Times for Frying Chicken Nuggets Using Peroxide Value and Acid Value, *Korean Society for Food Science of Animal Resources*, 36(5), pp. 612–616.
11. Ruixue M.A., Tian G.A.O. etc. (2016), Effects of oil-water mixed frying and pure-oil frying on the quality characteristics of soybean oil and chicken chop, *Food Science and Technology*, 36(2), pp. 329–336.
12. Choe E., Min D.B. (2007), Chemistry of Deep-Fat Frying Oils, *Journal of food science*, 72(5), pp. 77–85.

13. Azmil Haizam Ahmad Tarmizi, Siew Wai Lin, Ainie Kuntom (2008), Palm–Based Standard Reference Materials for Iodine Value and Slip Melting Point, *Analytical Chemistry Insights*, 3, pp. 127–133.
14. Ayodeji Osmund Falade, Ganiyu Oboh (2015),Thermal Oxidation Induces Lipid Peroxidation and Changes in the Physicochemical Properties and β–Carotene Content of Arachis Oil, *International Journal of Food Science*, DOI: 10.1155/2015/806524.
15. Murat Reis Akkaya (2018), Prediction of fatty acid composition of sunflower seeds by near–infrared reflectance spectroscopy, *Journal of Food Science and Technology*, 55(6), pp. 2318–2325.
16. Alam Zeb, Fareed Ullah (2016), A Simple Spectrophotometric Method for the Determination of Thiobarbituric Acid Reactive Substances in Fried Fast Foods, *Journal of Analytical Methods in Chemistry*, 2016, pp. 1–5.
17. Teruo Matsushita, Shin‐ichi Inoue, Ryusuke Tanaka (2010), An Assay Method for Determining the Total Lipid Content of Fish Meat Using a 2‐Thiobarbituric Acid Reaction, Journal of the American Oil Chemists' Society, 87, pp. 963–972.
18. Aparicio R., Roda L., Albi M.A., Gutiérrez F. (1999), Effect of various compounds on virgin olive oil stability measured by Rancimat, *Journal of Agricultural and Food Chemistry*, 47, pp. 4150–4155.