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Dedicated to the memory of
Dr. Emilian GEORGESCU (1946-2020)

INFLUENCE OF EDIBLE OIL VARIETY ON TRANS FATTY ACIDS FORMATION DURING THE FRYING PROCESS

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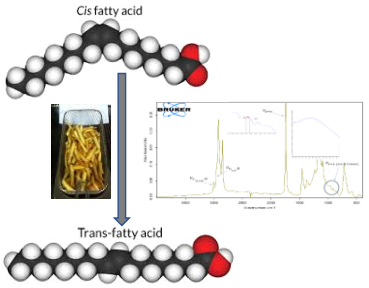
Trans fatty acids are formed during different processing phases to which vegetable oils are submitted to. Small amounts of trans fatty acids (TFA) could also produce into food products by natural processes. According to scientific studies, TFA can be very dangerous in time, by consumption of those processed foods. In this study we quantified the contribution of different edible oils, to the formation of TFA during the frying process. Four types of oils (sunflower, soybean, olive and corn oils) have been investigated during the frying process of potatoes. Results from ATR-FTIR analysis, have shown that, even after 14 frying cycles, the TFA content, for all four varieties of edible oils, was still under the admitted limit of 2g/100g.



INTRODUCTION

Ultimately, trans fatty acids (TFA), a class of unsaturated fatty acids that contain one or more unconjugated double bonds in *trans* configuration, have drawn scientists’ attention through the various harmful effects it produces into the human body. These acids are produced naturally, in the ruminant’s stomach after the anaerobic bacterial fermentation[1] or industrially, by hydrogenation of rich polyunsaturated fatty acids vegetable oils, by refining process or by different operations as frying or food irradiation.[2,3] Since the middle of 20th century, evidence regarding TFA’s negative impact on human organs, started to spread. Later on, other studies, Mensink and Katan,[4] revealed high percentages of trans fat in the body following deaths of heart diseases or Willett and collaborators[5] from Nurses’ Health Study, associated them with heart stroke risks, came to strengthen the direct connection between the intake of TFA and several diseases, especially, the coronary ones.[2] Recently, trans fatty acids, proved even more injurious being responsible for increasing the rate of diabetes, cognitive disorders, obesity or even cancer.[6] Shortly, following different experiments and clinical studies, results have revealed the direct connection between the intake of trans fatty acids and the development of Alzheimer disease, cognitive illnesses or tumors.[4]

Being popular, time-saver and enhancer of some unique sensorial (taste or texture) and nutritional properties (enrichment of food in vitamin E or essential fatty acids), the frying operation is the

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operation of choice for most industrial manufacturers as well as for most consumers. However, repeated frying cycles, at high temperature can promote different reactions of oxidation, polymerization, isomerization, affecting the final characteristics of fried products.[7] The degree of denaturation dependends on the fatty acids composition of the used frying oils, as well as on the conditions employed, time of exposure and temperature.

Given the result of studies performed on its actions, several countries perform a mandatory labelling of the TFA's content, and they have established a maximum level, depending on the products type. The targeted products were bakery products, vegetable fats and some fried foods. In 2003, Danmark was the first country to introduce the claim of 2g of TFA/100g of fat, followed by the majority of European countries.[8,9] In Roumania, although the regulation of EC 2019/649, imposing the same limit was drafted in 2019, it started to take effect only this year, in April 2021.

The need for fast, reliable and trustable method analysis therefore appeared. By using the chromatographic techniques an individual separation of compounds with a low detection limit can be assured. Meanwhile, ATR-FT-IR is a fast and cumulative analysis, quantifying the total TFA amount. In addition, M. Younis Talpur *et al.*, 2015 found a correlation coefficient between the two methods, the official (GC-MS) one and this newly developed (FT-IR) of 0.9963, further used for the data interpretation.[10-12]

During the performed experiments, ATR-FTIR method was used to quantify the TFA content into the four edible oil samples, collected after different frying cycles, in order to compare the samples and propose a healthy option for domestic or industrially frying. Moreover, the study aimed to establish the contribution of the edible oil variety to the formation of TFA during the frying process.

RESULTS AND DISCUSSION

The initial oil samples were characterized using the ^{1}H-NMR spectroscopy protocol in order to determine the composition in fatty acids, saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA), presented in Figure 1. These determined values can be easily compared and updated using the FoodData Central Database from the U.S. Department of Agriculture, https://fdc.nal.usda.gov/fdc-app.html#/food-details/1750349/nutrients.

FT-IR spectra of the vegetable oils offers a wide range of information. In Figure 2 is presented for example, the FT-IR spectra of sunflower oil highlighting areas used for TFA quantification.

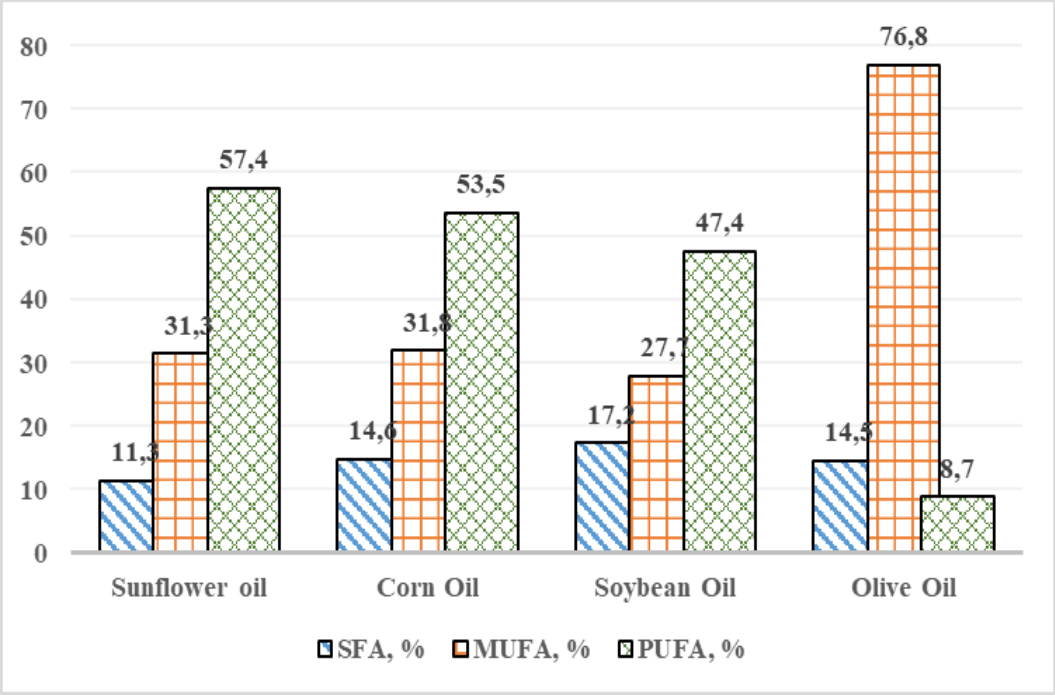


Fig. 1 – Composition in fatty acids of the studied vegetable oils.

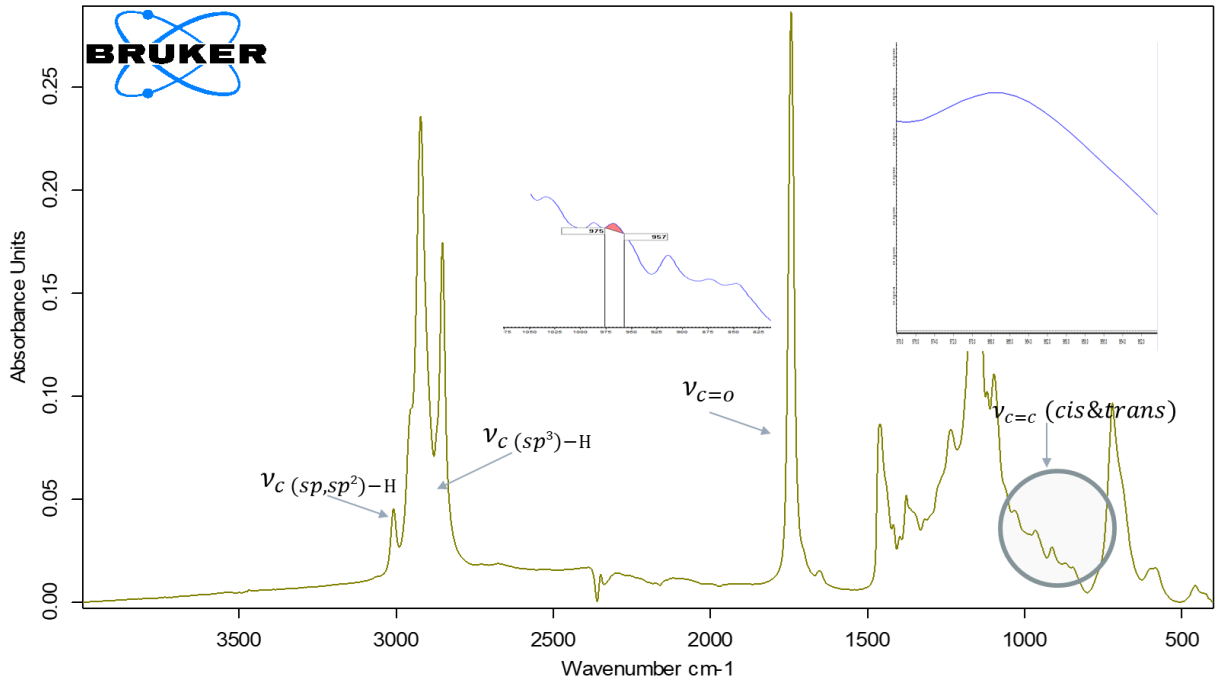


Fig. 2 – FT-IR ATR spectra for sunflower oil.

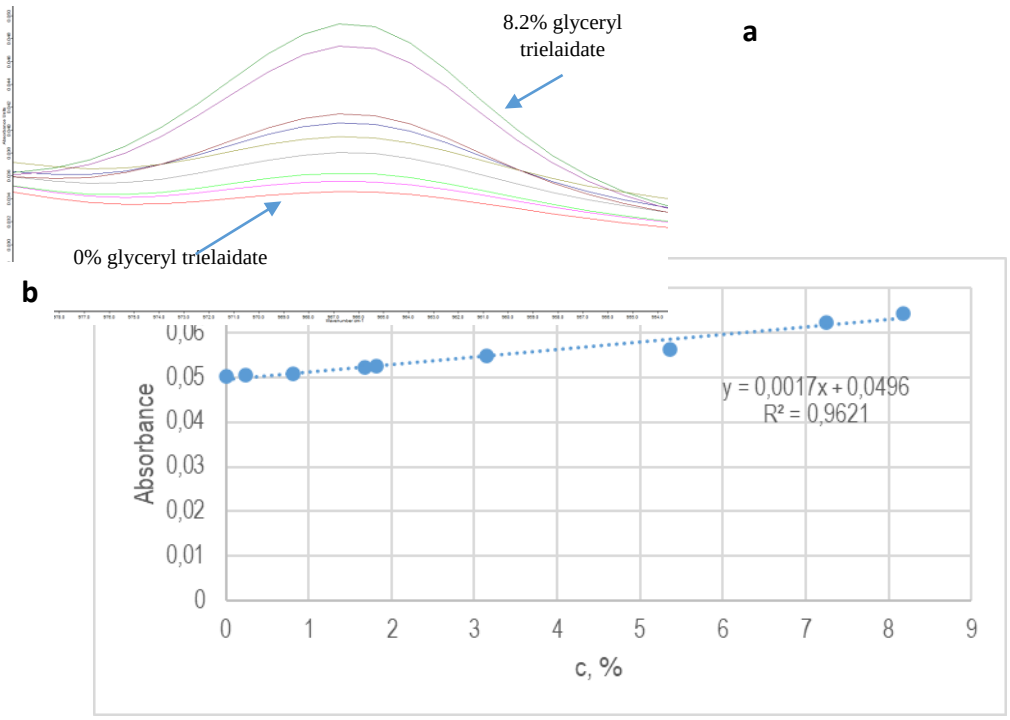


Fig. 3 – Trans Fatty Acids peak region selected for calibration (a) and calibration curve (b).

A calibrations curve was generated using mixtures of glyceryl trioleate and glyceryl trielaidate (reference standard) prepared at a concentration between 0–8.2%. The standards were homogenized before analysis, on a bath water and analyzed on the ATR accessory of the FT-IR equipment. Each sample was analyzed in triplicate, by reading the absorbance at 966 cm^{-1}. The calibration curve was plotted by the absorbance against TFA concentration in the standards. The regression coefficient obtained was presented in Figure 3, right side (R^2=0.9621).

TFA formation in edible oils

According to the variation of TFA in the four varieties of edible oils (corn, olive, sunflower, soybean), Figure 4, a clear difference can be noticed between them regarding the formation of TFA during frying process. The final TFA content after 14 frying cycles decreases from: sunflower > soybean > corn > olive oils. However, major changes occurred for sunflower and corn oil, in which the TFA concentration increased from 0.1 to almost 1.69 %, for corn oil as for sunflower oil, started from 0.09 % until, approximate 1.96 %. In addition, if we look close enough at the variation in TFA formation in olive oil we can see a very broad range of values, with ups and downs, far from a linear tendency, all the way till the fourteen-frying day. Therefore, for the olive oil the non-linear variation could be explained by the high number of sterols contained, especially β-sitosterol and highly unsaturated triterpenes, e.g. squalene which is proved to increase the frying stability of oils.

In Figure 5, a clear difference between the amount of TFA formed in the oils during frying could be noticed. Of a great importance is the Δc_{TFA} variation ratio, which means the amount of TFA formed in the process itself, without considering the initial TFA content of the oils. If we consider only the TFA concentration variation ratio ($\Delta c_{TFA} = c_{final\ TFA} - c_{initial\ TFA}$) the order of the oil's changes, and it is decreasing from: Δc_{TFA} sunflower > Δc_{TFA} corn > Δc_{TFA} soybean > Δc_{TFA} olive oils.

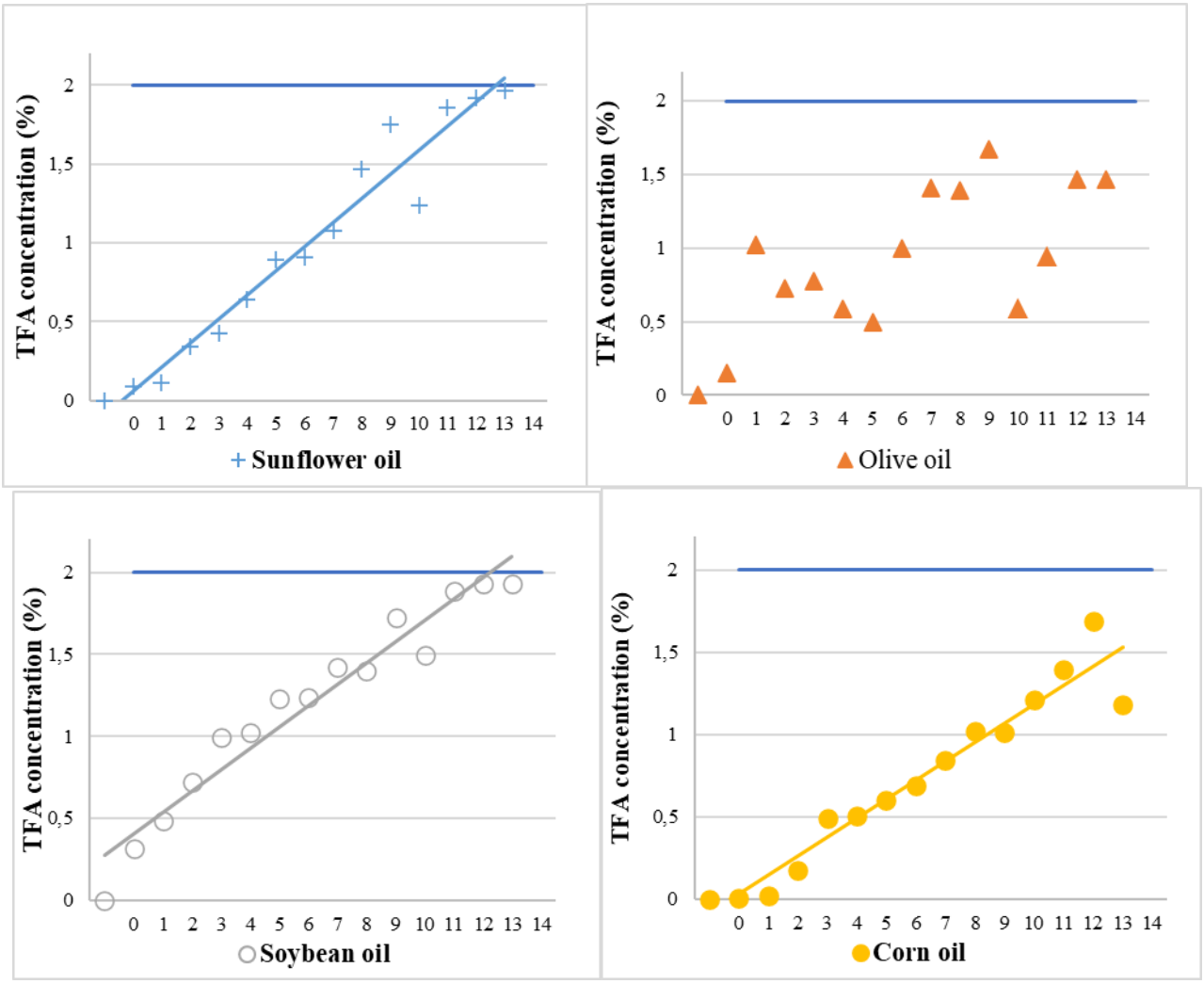
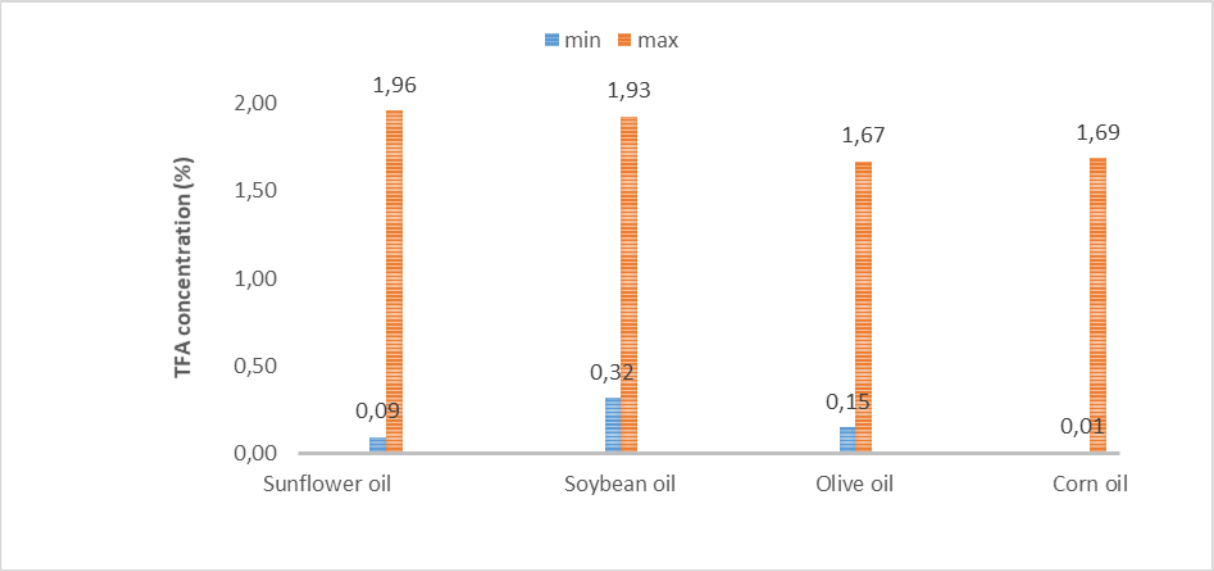


Fig. 4 – TFA variation in all four analyzed samples .



ΔCTFA:	**1.87**	**1.61**	**1.52**	**1.68**

Fig. 5 – TFA concentration level initial (in blue) and after 14th cycles of frying (in orange), and the TFA concentration variation ratio for all types of vegetable oils.

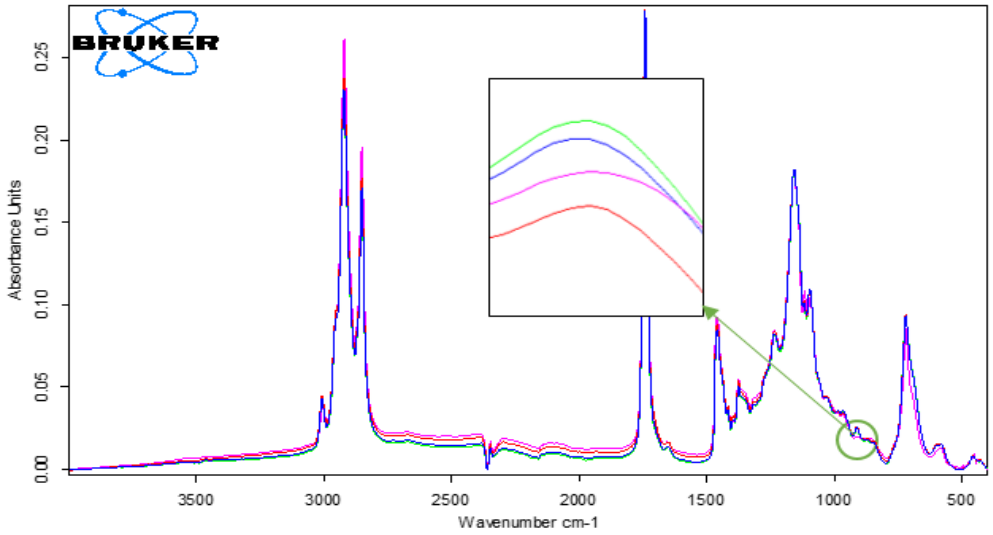


Fig. 6 – FTIR - ATR spectrum of vegetable oils used at 14th day of frying, red - corn, pink – pomace olive, green - sunflower, blue - soybean, emphasizing the interest area at 966 cm^{-1}.

Acidity variation in edible oils

As it can be seen in Figure 7, for all four samples of oils, the acidity increases in time, after each frying cycle. Soybean oil together with sunflower and olive oil, initially, have an acidity between 0.01 and 0.35%, while corn oil initially has more than 1% oleic acid. The acidity of olive oil shows an increase of approximatively three times compared to the initial value, meanwhile the acidity of soybean oil has an increase of approximatively six times from the initial value.

The acidity variation was investigated for all the samples during the fourteen frying cycles.

The sunflower oil has very low acidity values, so that on the last day of frying it reaches an acidity value equal to that of the olive oil from the initial moment, respectively 0.11% oleic acid.

Corn oil has the highest acidity, between 1.09% and 1.45% oleic acid, this is due to the higher amount of free fatty acids. However, corn oil also falls within the maximum imposed limit of the free fatty acids of 2% oleic acid.

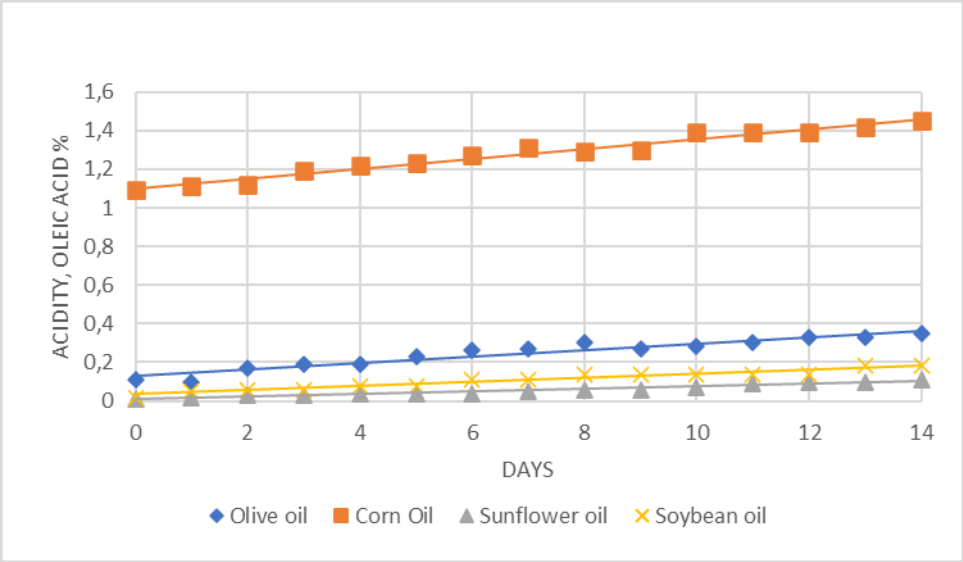


Fig. 7 – Variation of acidity expressed in oleic acid % in analysed samples.

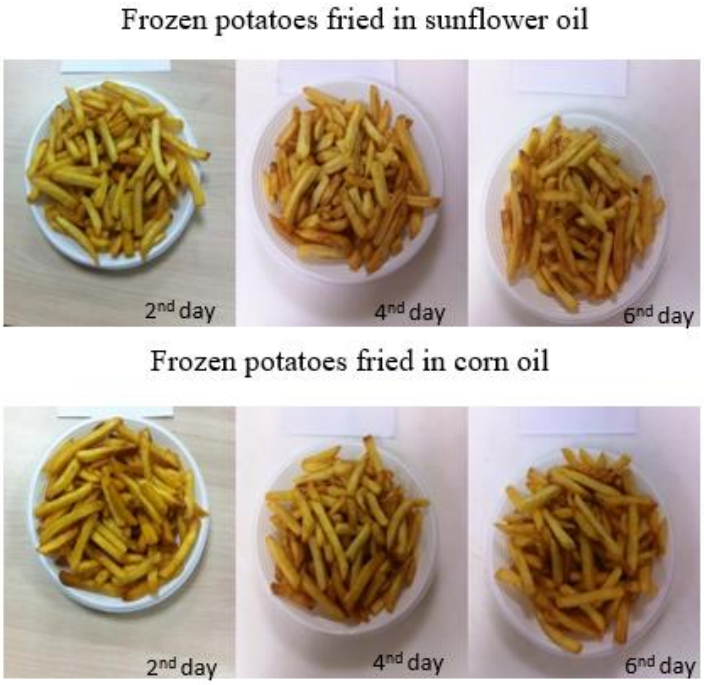


Fig. 8 – Potatoes fried in sunflower and corn oil in the 2nd,4th, 6th days.

EXPERIMENTAL

Materials and Methods

For the experiments French fries, frozen potatoes, and 4 different edible oils, sunflower, corn, olive and soybean were employed. Oil samples were purchased from Romanian market, being the ones habitually bought and used by the majority of population.

Ethyl alcohol absolute, acetic acid, analytical standard from Lachner, sodium hydroxide, ≥98%, pellets (anhydrous), sodium thiosulfate, 0.1M, phenolphthalein, 1%, were purchased from Merck, iso-octane, potassium iodine and starch were purchased from Chemycal, all with p.a.

Frying procedure. The research was carried out by successive frying of frozen, 10 mm straw potatoes, using electric fryer (Hendi Blue Line, 3300 W) with a capacity of 3.5 l oil, adjusted between 130-190ºC and stainless-steel tube and deep fry basket of 900g. Frying was performed daily for 14 days following the protocol: the oils were heated at 180ºC for 30 minutes, potatoes were introduced in the oil and were fried at 180ºC, for 10-15 minutes. The oils were allowed to cool at room temperature. Oil samples were collected and analysed daily. The frying process of potatoes was made without any renewal of oil.

Regarding the colour of the oils, it changed day by day, as well as the smell, these being finally transferred to the potatoes. In Figure 8 these is an example of frozen potato

samples fried in sunflower and corn oil, in the 2nd,4th and 6th days. It is observed that there is a significant change in their colour, although the frying process lasted 10 minutes, at the same temperature for each sample.

NMR Analysis. ^{1}H-NMR spectra were recorded on a Bruker Ascend III 400 MHz spectrometer, operating at 9.4 Tesla corresponding to the resonance frequency of 400.13 MHz for the ^{1}H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis. Typical parameters for ^{1}H-NMR spectra were: 45 pulse, 2.05 s acquisition time, 6.4 KHz spectral window, 16 scans, 26 K data points. The FID was not processed prior to Fourier transformation. The average acquisition time of the ^{1}H-NMR spectra was approximately 2 min. All spectra were processed with TopSpin 3.2 software. The chemical shift was measured based on a tetramethyl silane internal standard. Samples were analysed in 5 mm NMR tubes (Wilmad 507). The NMR samples were prepared by dissolving 0.2 mL oil in 0.8 mL $CDCl_3$.

ATR-FT-IR Analysis. FT- IR experiments were recorded on a Bruker Invenio S, spectrometer with a platinum ATR – accessory. 64 scans were performed for each sample, as for the background at a resolution of 4 cm^{-1} on a spectral window of [4000, 400] cm^{-1}. Samples were heated on a bath water, for 30 minutes, at 65°C, until complete melting and analysed on the ATR accessory of the equipment. After each measurement, the plate was carefully cleaned from any previous residues by wiping using isopropyl alcohol and dried with a soft tissue before performing in the next measurement. Data was collected and processed with OPUS, version 8.2, the spectroscopy software licensed.

Acidity assay. Acidity was determined based on SR EN ISO 3960/2010. 10g of oil were weighed. Separately, 50 mL of ethyl alcohol and 2-3 drops of 1% phenolphthalein were boiled and neutralized with sodium hydroxide. The oil sample was further added into the glass with the neutralized alcohol, re-boiled and titrated with the same base solution, 0,1%.

CONCLUSIONS

In all oil samples, TFA increased during the potato frying process. Despite the variation on TFA content along with the repeatedly frying cycles, at the end of the 14th frying cycles, all values for the studied vegetable oils (sunflower, soybean, olive and corn oils) were under the imposed limit, 2g/100g fat.

Although in absolute value the TFA content the oil varies decreasingly from sunflower > soybean > corn > olive oils, if we are taking into consideration the TFA concentration variation ratio, the denaturation order is changing to: sunflower > corn > soybean > olive oils.

Therefore, it is advisable to use edible oils for frying potatoes, but it is important to consider the influence of each type of oil on the total TFA content in case of oil mixtures used for cooking process. Using FT-IR spectroscopy a fast and responsible decision can be taken for the consumer health.

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