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COMPARATIVE STUDY ON SOME VEGETABLE OILS PRODUCTION TECHNOLOGIES AND THE IMPACT ON THEIR PHYSICO-CHEMICAL INDICES

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Abstract

Vegetable oils are a good source of high quality lipids, ω-3 and ω-6 acids, vitamin E and other biologic active components recommended to be included in a healthy diet. Based on the type of oil seeds and processing technology, the composition and physico-chemical proprieties of oils differs. For the research, we used samples of sunflower oil (pressed and refined), soybean oil, olive oils and nuts oil, which were characterized accordingly to standards, based on certain characteristics (phosphatides level, acidity index, peroxide index, saponification index, refraction index, neutralization index). The results have shown the influence of processing on the final characteristics of oils and also helped to draft and understand the recommendation regarding their storage.

Key words*: fatty acids, oils, physico-chemical characteristics, quality, technology.*

INTRODUCTION

Most vegetable oils are obtained from beans or seeds, which generally furnish two valuable commodities: a fatty oil and a protein-rich meal. Seed extraction is achieved by pressing and/or by extraction with hexane. Oils such as palm and olive, on the other hand, are pressed out of the soft fruit (endosperm).

Some oils, such as virgin olive oil, are used without further treatment other than filtering, but most are refined in some measure before use. The refining processes remove undesirable materials (phospholipids, monoacylglycerols, diacylglycerols, free acids, colour and pigments, oxidised materials, flavour components, trace metals, sulphur compounds and pollutants), but may also remove valuable minor components, including antioxidants and vitamins such as carotenes and tocopherols. The refining processes must therefore be designed to maximise the removal of undesirable components and minimise the removal of the valuable minor components. Some of the latter are recovered from side streams of the refining process to give commercial products such as phospholipids, free acids, tocopherols, carotenes, sterols and squalene. Because of changes that occur during refining, it is important to know whether compositional data refer to crude or refined oil (Gunstone, 2002).

Vegetable oils and fats are also used in the confectionery products; their market is increasing and evolving into a diverse range of products, which are highly appreciated by consumers (Bahaciu, 2019).

Aging represents a great concern in developed countries because of the number of people involved and the pathologies related to it, like atherosclerosis, Parkinson, Alzheimer's disease, vascular dementia, cognitive decline, diabetes and cancer.

The Mediterranean diet, rich in virgin olive oil, improves the major risk factors for cardiovascular disease, such as the lipoprotein profile, blood pressure, glucose metabolism, and antithrombotic profile. Endothelial function, inflammation, and oxidative stress are also positively modulated. Some of these effects are at attributed to minor components of virgin olive oil (Boskou, 2006).

MATERIALS AND METHODS

Materials

We have analyzed five types of vegetable oils: refined sunflower, canola oil, soybean oil, olive oil and nuts oil. The samples were bought from the market, they were packed and ready to consume.

In order to analyze the exposure to oxidation, we have investigated samples of cold pressed filtered sunflower oils stored in cold dry place for 4, 24, 52, 72 and 110 weeks. The samples were obtained from a local producer based in Vrancea county.

Table 1. Codes used for samples analysis

Sample	Code
Refined sunflower oil	RSF
Cold pressed filtered sunflower oil 4 weeks	FSF-4
Cold pressed filtered sunflower oil 24 weeks	FSF-24
Cold pressed filtered sunflower oil 52 weeks	FSF-52
Cold pressed filtered sunflower oil 72 weeks	FSF-72
Cold pressed filtered sunflower oil 110 weeks	FSF-110
Canola oil	Can-O
Soybean oil	Soy-O
Olive oil	Olive-O
Nuts oil	Nut-O

Methods

The official methods used in order to characterize the chemistry of analyzed oils were:

- the acid value (free fatty acids) accordingly with EN ISO 660 standard methodology;
- the saponification value - accordingly with EN ISO 3657;
- the peroxide value - accordingly with EN ISO 27107;
- the iodine value - accordingly with EN ISO 3961;
- the refractive index - accordingly with ISO 6320: 2000.

RESULTS AND DISCUSSIONS

1. Comparison of the main quality parameters of analyzed samples

1.1. The acid value (free fatty acids)

Oils degradation during processing and storage is determined by a range of hydrolysis and oxidation reactions due to oxigen exposure and water content of oils. This has an important effect on oils nutritional and sensorial quality, safety and acceptability.

By enzymatic hydrolysis of triglycerides, free fatty acids level is increasing thus the risk of double bonds oxidation is also increased.

The acid value is determined as the quantity of free fatty acids hydrolyzed by KOH added to titration. It is expresses as % of oil acid.

The higher the acid value is, the higher the free fatty acid in oils.

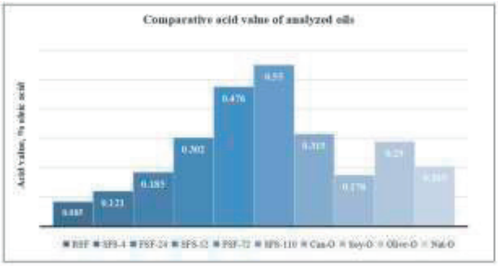

Figure 1. Comparative acid value of analyzed oils

In Figure 1 it is shown that the highest acid value was observed for cold press filtered sunflower oil stored for 110 weeks. This was expected first of all because the cold press filtered sunflower oil (not refined) had an increased water content which facilitated the hydrolysis and secondly, during such a long period of storage time, the lipolysis process is intense and determine the accumulation of free fatty acids in oil.

Among the varieties of oils, the higher acid value was observed for canola oil (0.315% oleic acid) and olive oils (0.29% oleic acid). The smaller acid value was determined for refined sunflower oil (0.085% oleic acid).

1.2. The saponification value

Saponification value represents the number of KOH milligrams required for the saponification of 1g oil. It depends on the molecular mass of the oil. The higher the molecular mass is, there will be less molecules of triglycerides/g, so, the smaller the saponification value will be. High molecular mass lipids will have low saponification value.

In Figure 2 it is represented the comparison among oils regarding the saponification value.

It can be observed that the values are quite similar, with the exception of canola oil which has the saponification value of 181.14 mg KOH/g oil.

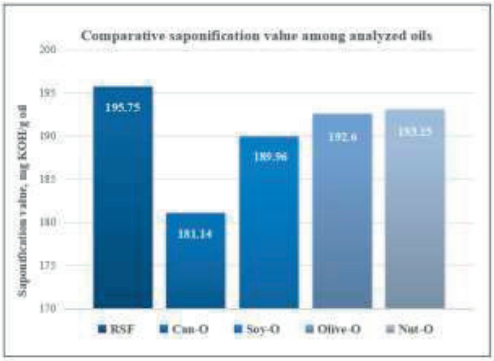

Figure 2. Comparative saponification value among analyzed oils

1.3. The peroxide value

The peroxide value is determined in order to establish the freshness of oils, by showing the incipient phase of oil oxidation, taking into consideration that peroxides are the first components of oil oxidation.

The increasing rate of the peroxide value of an oil depends on the storage conditions (temperature, time, light exposure and humidity) and it is used to evaluate the stability of an oil.

The purpose of peroxide value determination was to establish the oxidative alteration status in analyzed oils. A sensorial analysis was not conducted in this experimental plan, but when preparation of samples was done it was observed an increased rancid scent for samples that were registered the higher peroxide value.

In Figure 3, the comparative peroxide value among analyzed oils are shown.

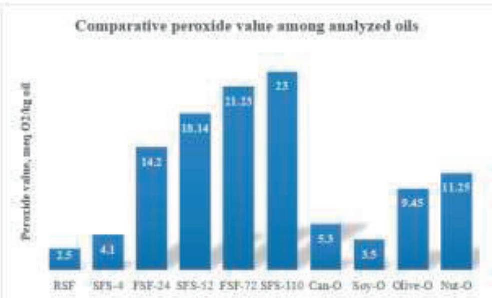

Figure 3. Comparative value among analyzed oils

The highest number for peroxide values were obtained for samples of cold pressed filtered sunflower oils. The more they are stored, the higher the peroxide value rise.

Regarding the other oils, the highest score for peroxide value was observed for nuts oil (11.25 mEq O_2/kg oil), followed by olive oil (9.45 mEq O_2/kg oil). The smaller peroxide value was for refined sunflower oil (2.5 mEq O_2/kg oil).

A detailed analysis on the influence of the storage time on the peroxide value for cold pressed filtered sunflower oil will be presented below, at point 2.

1.4. The iodine value

The iodine value indicates the degree of unsaturation of oils and it represents the amount of Iodine (grams) added to 100g oil. The higher the Iodine value is, the more unsaturated the oil is (more double bonds, more Iodine needed to addition to them, higher Iodine value).

It was expected that the oils with high level of unsaturated fatty acids content to have an increased value of the Iodine value.

In figure 4, it can be observed that nuts oil has the highest Iodine value (153.12 g I_2/100 g oil), followed by canola oil (146.10 g I_2/100 g oil) and refined sunflower oil (141.15 g I_2/100 g oil).

It also can be observed that the Iodine value for stored cold pressed filtered sunflower oils decreased up to 118.15 g I_2/100 g oil after 110 weeks of storage. This can be explained by the decrease of the number of double bonds due to oxidation.

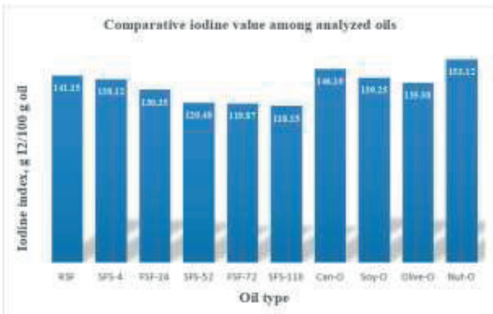

Figure 4. Comparative iodine value among analyzed oils

1.5. The refractive index

The refractive index is a parameter which is correlated with molecular mass, fatty acids constituents, length of their chain, unsaturation degree and also the degree of conjugation of double bonds.

On the other hand, the refractive index increases with the size of the carbon bond chain in fatty acids and with the number of double bonds present in fatty acids (O'Brien, 2009).

This index is a measure of the angle at which the light falls when refracted by changing direction at the boundary between two media.

For the analyzed oils, the values of the refractive index are shown in Figure 5.

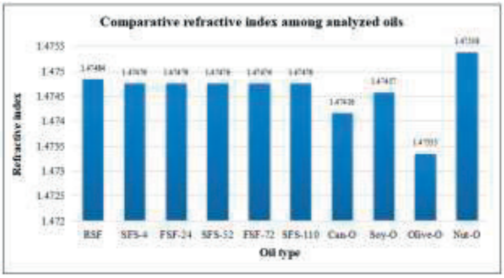

Figure 5. Comparative refractive index among analyzed oils

Although it is not a uniform correlation, it can be seen that nut oil (with a large number of fatty acid double bonds) has the highest refractive index, respectively 1.75375.

The next should be the refractive index of olive and rapeseed oil, but probably due to their high peroxide index, the value of the refractive index was also influenced (Oycan, 2009).

2. Evaluation of exposure to oxidation

Vegetable oils and fats are rich in unsaturated fatty acids, ω-3 and ω-6, which are recommended by nutritionist to be consumed for a good health of the heart and artery.

Unsaturated fatty acids are involved in prostaglandine synthesis, modulation of some essential functions like smooth muscle tone, inflammatory response, renal function, nervous system functions (Segal, 2002).

During storage, due to time, temperature, light exposure, oxidation is initialized and unsaturated fatty acids are involved. This determines changes in sensorial (rancid smell and taste) and chemical characteristics (Gunstone, 2008).

The main parameters that change are acid value (Figure 6) and peroxide value (Figure 7).

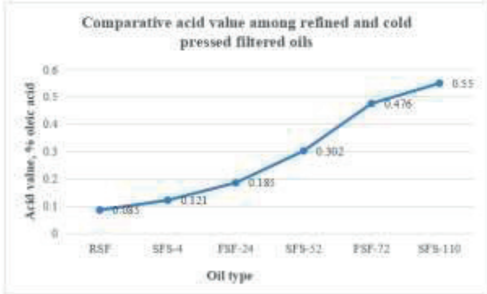

Figure 6. Comparative acid value among refined and cold pressed filtered oils

As regarding the acid value of cold pressed filtered sunflower oil, it can be observed that this was starting to increase in the first 4 weeks of storage and reaches 0.55% oleic acid after 110 weeks of storage, which means 6.47 times higher than refined sunflower oil and 4.55 times higher than cold pressed filtered sunflower oil stored for 4 weeks.

Furthermore, the processing technology, which not include refining, influence the composition of oils: cold pressed oils contain an increased amount of free fatty acids, waxes, odors, colour compounds, enzymes, which can also influence the oxidation process. (Hamilton, 2002).

Figure 7. Comparative peroxide value among refined and cold pressed filtered oils

A separate analysis of the four types of sunflower oil, shown in Figure 7, shows that as the oil storage time increases, the peroxide index increases.

It is very clear that by storing sunflower oil for a very long time, the peroxide index increases, reaching values of 23 meq O_2/kg oil.

It is also interesting that, although packaged in brown glass packaging, olive and walnut oils, which are valid, recorded quite high values of peroxide indices: 9.45 and 11.25 meq O_2/kg, respectively. This can only be explained by the possible storage of these oils at high temperatures.

From the above information, but also from the study of the literature (Gurr, 2009; Nawal-A-Al Badr, 2014), the acidity index and the peroxide index are both indicators of the degradation status of vegetable oils: the acidity index, the hydrolytic and oxidative degradation.

We thought it would be interesting to follow the evolution of these two parameters in the same graph, to see if they correlate.

As a result, in figure 8 it can be observed the correlation of peroxide and acid values for all analyzed oils.

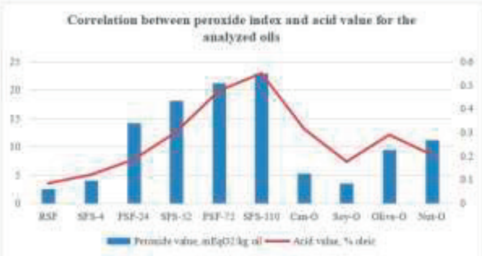

Figure 8. Correlation between peroxide index and acid value for the analyzed oils

Figure 9 shows the acidity and peroxide indices for the sunflower oils analyzed.

We observed what was intuitive: both indices increase with the exposure of sunflower oil to the action of hydrolases or factors that increase the degree of oxidation.

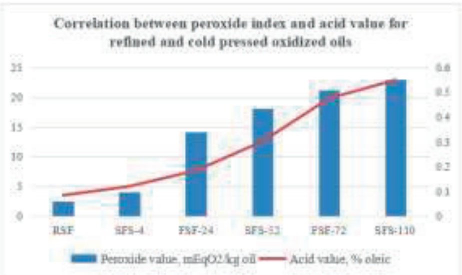

Figure 9. Correlation between peroxide index and acid value for refined and cold pressed filtered oils

CONCLUSIONS

1. Depending on the technological process adopted, the chemical composition of the oils is different.

2. The initial processing method, the oil extraction method (by pressing or extraction, or both) also influences the compositional qualities of the vegetable oils taken into analysis.

3. The type of oil processing, the existence or not of the refining process, influences the nutritional qualities of the oil, on the one hand, but also their stability, on the other hand.

- ✓ In the case of cold-pressed oils, they retain all the vitamins and nutrients from the raw material, but at the same time its stability over time is reduced, mainly due to the high water content.
- ✓ Refined oils have the advantage of obtaining uniform batches, eliminating differences in color, taste and smell between batches, but at the same time the oil may contain traces of chemicals (hexane) and saturated fatty acids (trans fats) (Bahaciu, 2007).

4. The evaluation of some biochemical parameters of essential oils established the dependence of the parameters investigated by each other, but also on the methods of oil manufacture.

5. The use of empirical mathematical formulas can give indicative indications on some indices, but for concrete and correct values laboratory analyzes specified in the specific standards on the product must be performed.

Using antioxidants in oils could improve their stability to peroxidation during cooking and home processing.

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***EN ISO 3961. Iodine value

***EN ISO 27107. Peroxide value

***ISO 3657.Saponification value

***EN ISO 660. Acid value, free fatty acids (FFA).