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EVALUATION OF CHANGES IN PHYSICOCHEMICAL PARAMETERS OF RAPE AND SOYBEAN OILS DURING THE FRYING PROCESS OF FRENCH FRIES

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Abstract: Fats, including vegetable oils, are an important component of the diet. They not only have a high energy value, but also contain nutrients that are essential for the proper functioning of the human body. The increasing consumption of fried products affects the consumption of the oils used for a long time in the deep frying processes. Vegetable oils contain large amounts of unsaturated fatty acids, which are subject to oxidative and hydrolytic processes, while thermal polymerization can also occur in them. The aim of the study was to compare the oxidative stability of rapeseed and soybean oils while frying potato chips in them at 180°C. The study presents changes in the acid and peroxide values, as well as changes in the sensory characteristics of the oils under the influence of heating. The studies showed that rapeseed oil was characterized by greater sensitivity to oxidation compared to soybean oil. Soybean oil contained more hydrolysis products, but during the frying process their increase was similar to the products formed in rapeseed oil.

Keywords: vegetable oils, physicochemical changes, quality, sensory characteristics.

1. INTRODUCTION

Fats, including vegetable oils, are an important component of the diet and are important for health reasons. They are characterized by a high content of unsaturated fatty acids and the absence of cholesterol [Maniak, Zdybel and Bogdanowicz 2012]. Animal fats, which contain vegetable fats, form a source and decomposer of fatty acids [Gertz, Klostermann and Kochhar 2000; Kondratowicz-Pietruszka 2010]. Fats perform various functions in the body and determine many processes. When consuming products containing fat, important ingredients are delivered to the body, primarily vitamins A, D, E and K [Lacband, Frauen and Friedt 2000; Lesiak and Ostasz 2006]. In the human diet, fats occur in a visible form (e.g. vegetable oils) or invisible, as an ingredient of food products. The content and quality of fat in food also affects its sensory properties (fat is a carrier of flavor and determines the texture and appearance) and physicochemical oxidations: auto-oxidation, photosensitized oxidation and enzymatic oxidation involving lipoxygenase [Wąsowicz et al. 2004; Drozdowski 2007; Szponar, Mojska and Ołtarzewski 2012; Zielińska, Rutkowska and Antoniewska 2017].

The consumption of oils is systematically increasing, but more often in a form changed by thermal treatment, through the consumption of fried products, rather than raw. The ever-increasing consumption of fried products influences the consumption of long-term oils used in the deep-frying processes. Due to the fact that vegetable oils contain large amounts of unsaturated fatty acids, they are subject to oxidative and hydrolytic processes, as well as thermal polymerization. These processes are very complex and ultimately lead to deterioration of the quality of the oil and the fried products [Ostasz 2004; Lesiak and Ostasz 2006; Zielińska, Rutkowska and Antoniewska 2017]. High temperatures during frying intensifies lipid oxidation processes, with the heated oil and fried raw material producing a number of harmful chemical compounds [Buczek and Leśniak 2007]. For nutritional reasons, frying oil should not have a high content of unsaturated acids, especially polyene acids, and should not contain significant amounts of saturated acids [Buczek and Leśniak 2007; Maniak, Zdybel and Bogdanowicz 2012; Zielińska, Rutkowska and Antoniewska 2017]. Frying fat should contain features that cause slight changes during heating, as well as being characterized by favorable sensory properties, suitable for the fried product [Ostasz and Kondratowicz-Pietruszka 2005; Martin-Torres et al. 2023]. The commonness of unfavorable changes in fats, caused mainly by oxidation processes, makes the control of their degree of oxidation or hydrolysis a generally accepted practice when assessing the quality of fat products [Ratusz et al. 2005; Fadda et al. 2022].

The aim of the research was to assess the changes in the acid and the peroxide number, as well as the changes in the sensory characteristics of the tested oils under the influence of heating.

2. RESEARCH METHODOLOGY

The research process was carried out in 2021 and involved material that included rapeseed oil from Kujawski Bunge Polska and Basso soybean oil from Global Mirex Italy. The rapeseed oil was straw-colored and had a typical rapeseed smell, while the soybean oil was golden-yellow and had a characteristic smell, typical for this specific oil.

A total of 4 kg of the oils were heated in a CLATRONIC fryer, model FR 3195, to 180°C for 30 minutes, then the potatoes, cut into strips, were placed in the fryer and fried for 5-6 minutes. Before frying, the potatoes were washed and then peeled using a hand peeler. The raw material was washed again, cut into sticks, rinsed and dried on a paper towel. The size of a single serving of potatoes was 220 g. After this time, the French fries were taken out and the oil was drained. The entire process of heating the oil and frying the French fries was repeated 8 times.

Oil samples were collected in test tubes (Ependorfs) with a capacity of 50 cm^3, and protected from light. A total of 5 samples of each oil were obtained. The first sample was heated oil, the second was oil after an hour of frying, the third, fourth and fifth samples were taken after each subsequent hour of frying. The interval between taking each sample was 1 hour.

The following parameters were determined in the rapeseed and soybean oil samples: acid value, peroxide value, and color using the spectrophotometric method, while a simplified sensory evaluation was also carried out. The tests were carried out in three repetitions. The acid value of oils was determined according to PN-ISO 660:1998, the peroxide value of oils was determined according to PN-ISO 3960:1996, and the color was determined by the spectrophotometric method of oils according to PN-A86934:1995. The color parameter was read at two wavelengths in the visible range: λ = 442 nm for the group of carotenoid dyes, λ = 668 nm for the group of chlorophyll dyes, with the absorbance value being read from the spectrophotometer scale.

The read absorbance values were summed and expressed as a color as an integer.

This formula was used: $B = 1000 \times (A442 + A668)$ where:

A442 – measured average absorbance value of the oil sample at a wavelength of λ = 442 nm,

A668 – measured average absorbance value of the oil sample at a wavelength of λ = 668 nm,

1000 – conversion factor.

A simplified sensory assessment of the oils (visual assessment) is presented in the form of a description. The assessment was carried out at room temperature, approximately 20°C, and included: color, consistency, clarity, smell and taste. The evaluation panel consisted of 2 professional technicians and 12 students of Food Technology and Human Nutrition (7 women and 5 men) in the age range of 22–24 years. The student evaluators were selected by technicians and had passed a test enabling sensory evaluation.

The statistical analysis of the test results was carried out using the ANW program (Analysis of Variance of Experiences). The analysis of variance was performed for two factors. The first factor was the type of oil, as two types were used (soybean, rapeseed). The second factor was the frying time of the French fries in the tested oils, which was assessed on 4 levels (0 – unheated oil, 1 – oil heated for 1 hour, 2 – oil heated for 2 hours, 3 – oil heated for 3 hours, 4 – oil heated for 4 hours).

The analysis of the results led to the assessment whether the time of heating the oil and the frying of the French fries had a significant impact on the changes occurring in the tested vegetable fats.

5. RESULTS

The acid number determines the amount of free fatty acids formed as a result of lipid metabolizm, given in mg KOH/g fat.

Table 1 shows the changes in the acid number in the soybean and rapeseed oil during the frying process.

Table 1. Changes in the acid number in rapeseed and soybean oil during frying

Frying time (h)	**Acid number (LK) mg KOH/g fat**	
	Rapeseed oil	**Soybean oil**
0	0.11	0.38
1	0.20	0.43
2	0.20	0.46
3	0.21	0.46
4	0.24	0.49
$NIR_{\text{heat treatment}}$ 0.008	$NIR_{\text{type of oil}}$ 0.005	$NIR_{\text{heat treatment of oil}}$ 0.011

Source: own work.

The fresh, unheated oils had an acid number (LK) of 0.11 mg KOH/g of oil for the rapeseed oil and 0.38 mg KOH/g of oil for the soybean oil. It was found that the tested oils differed significantly in this parameter. After 1 hour of frying at 180°C, an increase in LK in the rapeseed oil to 0.20 mg KOH/g of oil and in the soybean oil to 0.43 mg KOH/g of oil was observed. In the following hours, the increase in this parameter in the rapeseed oil was smaller than in the soybean oil. After the frying process, the rapeseed oil had LK = 0.24 mg KOH/g of oil, while the soybean oil had LK = 0.49 mg KOH/g of oil.

A greater increase in LV was observed in the rapeseed oil than in the soybean oil only after 1 hour of frying, and amounted to 0.09 mg KOH/g of oil. In the following hours of frying, the soybean oil showed greater increases in LV, which means that it was more susceptible to the breakdown of triacylglycerols. Statistical analysis showed that the heating time and frying of the potato chips in both oils had a significant impact on the rate of changes occurring in them. Changes in the acid number varied both with the type of oil and the thermal treatment used. Research by Lesiak and Ostasz [2006] showed that heating rapeseed oil at 180°C with a tolerance of 1°C for 230 minutes increases LK from 0.142 mg KOH/g of oil to 0.215 mg KOH/g of oil. They showed that a greater increase in this parameter occurred when frying burgers from 0.18 mg KOH/g of oil to 0.41 mg KOH/g of oil, which means that the product intensified the fat hydrolysis process.

Also in studies by Ostasz [2007], an increase in the acid number was shown during frying, this time of French fries for 6 hours at a temperature of 180°C. The acid number in the rapeseed oil increased from 0.082 mg KOH/g of oil to 0.195 mg KOH/g of oil, in the soybean oil from 0.069 mg KOH/g of oil to 0.195 mg KOH/g of oil, while the smallest increase was recorded in the sunflower oil from 0.065 mg KOH/g of oil to 0.158 mg KOH/g of oil.

Research by Mitrea et al.[2022], who analyzed sunflower, rapeseed, corn, palm and coconut oils, showed an increase in values above the recommended limits (0.6 mg KOH/g of oil and 10 mEqO2/kg of oil) for the tested oils, except for the rapeseed oil, which was within the acidic limits (0.26 mg KOH/g rapeseed oil). Their research is consistent with the research by Ostasz and Kondratowicz-Pietruszka [2005], in which they also subjected the oil to the same temperature and fried the French fries in it for approximately 5 hours (330 min). They presented an initial LK value of 0.132 mg KOH/g of oil, while after frying it was 0.292 mg KOH/g of oil for the rapeseed oil.

In turn, Robak and Gogolewski [2000] heated rapeseed oil for 30 hours at different temperatures (140°C, 160°C and 180°C). They showed the greatest increase in LK at 180°C after 30 hours, when the acid number increased from 0.11 mg KOH/g of oil to 0.59 mg KOH/g of oil. Heating the oil for an hour also causes an increase in LV, as observed by Stec et al. [2009] in their research. They reported that in the soybean oil heated at 178°C with a tolerance of 2°C for 1 hour, there was a slight increase in LK from 0.20 mg KOH/g of oil to 0.22 mg KOH/g of oil.

Research by Ghafoor et al. [2020] showed that frying French fries in palm oil with the addition of thyme and rosemary were characterized by greater oxidative stability, and the sensory evaluation showed that this product became more acceptable among consumers. Zelenakova et al. [2022] showed that at the beginning of frying the French fries in rapeseed oil, the acid number was 0.374 mg KOH.g-1 and 1.271 mg KOH.g-1 on the fourth day of frying.

Peroxide value (LOO) is a measure of the amount of peroxides produced as a result of the transformations taking place in the fats, mainly as a result of the oxidation process, and is treated as an indicator of the degree of rancidity of the fat, given in milliequivalents of active oxygen in 1 kg of fat [Kędzior 2012].

Table 2 shows changes in the peroxide value in rapeseed and soybean oil during the frying of the French fries.

Table 2. Changes in the peroxide value in rapeseed and soybean oil during frying

Frying time (h)	Peroxide value (LOO) mEqO2/kg	
	Rapeseed oil	Soybean oil
0	0.63	0.33
1	0.84	0.35
2	0.91	0.46
3	1.07	0.52
4	1.14	0.73
$NIR_{heat\ treatment}$ 0.027	$NIR_{type\ of\ oil}$ 0.017	$NIR_{heat\ treatment\ of\ oil}$ 0.039

Source: own work.

The peroxide value (LOO) was determined in the fresh oils tested and was 0.33 mEqO2/kg and 0.63 mEqO2/kg, respectively. It was found that the tested oils differed significantly in the content of this parameter. During frying, fat oxidation reactions occurred, which resulted in an increase in LOO. After 1 hour of frying, the peroxide value in the soybean oil increased to 0.35 mEqO2/kg, while a much greater increase in this number was observed in the rapeseed oil, to 0.84 mEqO2/kg. After frying for 4 hours, the peroxide value for the soybean oil was 0.73 mEqO2/kg and for the rapeseed oil 1.14 mEqO2/kg. After the fourth hour of frying the French fries in the soybean oil, a significant increase in the peroxide value was observed from 0.52 mEqO2/kg to 0.73 mEqO2/kg (approx. 30%). In the rapeseed oil, this parameter increased by 45% after 4 hours, which is more than in the case of soybean oil. Statistical analysis showed that the time of frying potato chips in both oils significantly differentiates the peroxide value.

In the research by Ostasz [2007], who fried French fries at a temperature of 180°C for 360 minutes, an increase in the peroxide value was found with the passage of frying time. The greatest increase in LOO was observed in the sunflower oil, from 1.67 mEqO2/kg to 5.1 mEqO2/kg, and in the rapeseed oil, from 0.35 mEqO2/kg to 3.33 mEqO2/kg. The smallest increase in this parameter was observed in the soybean oil, from 1.17 mEqO2/kg to 2.06 mEqO2/kg. A much greater increase in LOO compared to the research was noted by Ostasz and Kondratowicz-Pietruszka [2005]. They fried the French fries in rapeseed oil at 180°C for 330 minutes. The increase in the peroxide value was as much as 4.12 mEqO2/kg (from 2.3 mEqO2/kg to 6.42 mEqO2/kg).

In turn, the study by Stec et al. [2009] showed a significant increase in LOO in soybean oil. The fried product was egg whites, and the frying time was 1 hour at a temperature of 178°C with a tolerance of 2°C. The authors showed that within 60 minutes the peroxide value increased from 0.333 mEq O2/kg to 3.86 mEq O2/kg (approx. 91%). The research by Zula and Teferra [2022], who fried fish in palm oil, showed that the quality of the oil and the quality of the fried fish deteriorated as a result of long-term deep frying in subsequent cycles. This was related to an increased amount of oxides produced and a decrease in the content of healthy fats.

Robak and Gogolewski [2000] heated rapeseed oil for the longest time, as much as 30 hours, at three different temperatures: 140°C, 160°C and 180°C, and showed that at 140°C the maximum LOO after 18 hours of frying with rapeseed oil was 2.67 mEq O2/kg. They observed that frying for longer than 18 hours at this temperature caused the peroxide value to decrease, while at 160°C, the peroxide value constantly increased, and after 30 hours of frying it amounted to 3.24 mEq O2/kg. The smallest increase was observed in oil heated to 180°C, when they found that the maximum LOO value was 1 mEq O2/kg from the initial 0.43 mEq O2/kg and also decreased, but only in the 30th hour. The peroxide value then dropped to 0.89 mEq O2/kg. Research by Zelenakova et al. [2020], who assessed changes in the TPC, acid value and peroxide value as well as the composition of the fatty acids in the edible oils during the production of French fries, showing that a lower TPC content was found in rapeseed oil (3.3%), while the threshold (24%) was achieved on the fourth day. The total spoilage time for deep frying rapeseed oil was 23½ hours. On the contrary, in fresh sunflower oil, the TPC content was 5.5% on the first day and the limit of 24% was reached on the third day. The total spoilage time for the sunflower oil for deep frying was 17.5 hours. The measured peroxide value at the beginning of frying was 4.3 mEq O2.kg-1 and at the end 10.5 mEq O2.kg-1. The initial values of peroxides and acids were correspondingly higher in the sunflower oil compared to the rapeseed oil. Perkins [1976] suggests that this is the result of the decomposition of peroxides predominating over their formation.

Our own research is inconsistent with the results of the research by Leśniak and Ostasz [2006], who heated rapeseed oil at 180°C with a tolerance of 1°C for 230 minutes. The result of their research was a decrease in the peroxide value, which before frying was 1.36 mEq O2/kg, and after frying it had decreased to 1.33 mEq O2/kg.

The color was assessed using the spectrophotometric method and the content of carotenoid and chlorophyll pigments was assessed, the amount of which in the oils depends on the species and maturity of the raw materials as well as the extraction and refining technology [Rotkiewicz, Konopka and Tańska 2002].

Table 3 shows the color changes depending on the time of frying the French fries in rapeseed oil and the content of carotenoid and chlorophyll pigments.

Table 3. Evaluation of the color spectrophotometric method of rapeseed oil

No	Carotene pigments	Chlorophyll pigments	Color
0	0.030	0.003	33
1	0.038	0.009	47
2	0.038	0.009	47
3	0.051	0.012	63
4	0.047	0.019	66

Source: own work.

The studies have shown that rapeseed oil contains mainly carotenoid pigments, in the amount of 0.030, while chlorophyll pigments are 10 times less (0.003). The amount of chlorophyll pigments increased with the extension of the frying time, and after 4 hours it was 0.019. On the other hand, the content of carotenoid pigments increased to the level of 0.051 in the 3rd hour of frying. Prior, Vadke and Sosulski [1993] report that fresh canola oil contains 126–216 ppm of carotenoids, while Płatek and Węgrowski [2001] assessed rapeseed oil samples, determining the amount of chlorophyll pigments, showed that their amount was on average 49 ppm.

Table 4. Evaluation of the color spectrophotometric method of soybean oil

No	Carotene pigments	Chlorophyll pigments	Color
0	0.033	0.035	71
1	0.040	0.042	82
2	0.038	0.044	82
3	0.043	0.044	87
4	0.049	0.044	93

Source: own work.

Fresh soybean oil was characterized by an almost identical content of chlorophyll pigments (0.035) and carotenoid pigments (0.036). During one hour of frying the oil, the content of both pigments increased - carotenoids to 0.040 and chlorophylls to 0.042. The maximum content of chlorophyll pigments (0.044) was obtained in the 2nd hour of frying in soybean oil and this value was maintained until the end of the frying process. In the case of rapeseed oil, the highest carotenoid pigment content was determined after frying, when it was 0.049.

Rotkiewicz, Konopka and Tańska [2002] report that the content of carotenoid pigments in such oils as soybean, corn and cottonseed is in the wide range of 16–128 ppm. Color evaluation using the spectrophotometric method showed that unheated rapeseed oil was characterized by the lightest color and its value was determined at 33. After subsequent hours of frying, a slight change in color was observed: after 1 and 2 hours of frying to a value of 47, after 3 hours to 63, and after four hours to 67. The color of the unheated soybean oil was darker in comparison to rapeseed oil by about 100%. After the next hours of frying, a slight change in colour was observed: after 1 and 2 hours of frying to the value of 82, after 3 hours to 87, and after four hours to 93.

The results of our own research are similar to the research of Lesiak and Ostasz [2006], who determined the colour of rapeseed oil using the spectrophotometric method, before and after frying (at 180°C with a tolerance of 1°C for 230 minutes). Fresh rapeseed oil had a colour value of 28, while the oil after frying had a colour value of 33.

Sensory evaluation of the analyzed vegetable oils.

Cold-pressed rapeseed oil is characterized by a yellow, greenish to brown color, while refined oil is light yellow, has a mild and pleasant smell [Ostasz and Kondratowicz-Pietruszka 2006].

Table 5 presents the sensory evaluation of rapeseed and soybean oil, taking into account the time of frying French fries in it.

Table 5. Sensory evaluation of rapeseed and soybean oil

Type of oil	Frying time [h]	Consistency	Clarity	Smell	Taste
Rapeseed oil	0	Liquid	Clear	Specific	Specific
	1	Liquid	Clear	Slightly noticeable smell of French fries	Specific
	2	Liquid	Clear	Clearly noticeable smell of French fries	Slightly noticeable foreign aftertaste
	3	Liquid	Clear	Clearly noticeable smell of French fries	Slightly noticeable foreign aftertaste
	4	Liquid	Clear	Clearly noticeable smell of French fries	Slightly noticeable foreign aftertaste
Soybean oil	0	Liquid	Clear	Specific	Specific
	1	Liquid	Clear	Slightly noticeable smell of French fries	Slightly noticeable foreign aftertaste
	2	Liquid	Clear	Clearly noticeable smell of French fries	Slightly noticeable foreign aftertaste
	3	Liquid	Clear	Clearly noticeable smell of French fries	A clearly noticeable foreign aftertaste
	4	Liquid	Clear	Clearly noticeable smell of French fries	A clearly noticeable foreign aftertaste

Source: own work.

The fresh rapeseed oil was characterized by a liquid consistency, a specific taste and smell, a straw color and the fact that it was clear. During the entire frying process in rapeseed oil, the consistency and clarity did not change. The smell of the oil changed first, after 1 hour the smell of French fries was slightly noticeable, in the following hours of frying the smell was already clearly noticeable. The color changed after 2 hours of frying, from straw to gold. The taste of the oil also changed only after 2 hours of frying, the samples fried for 2 and 3 hours were characterized by a slight foreign aftertaste, and the sample after 4 hours had a distinct foreign aftertaste. Fresh, unheated soybean oil was liquid, clear, golden-yellow in color, with a characteristic taste and smell. Heat treatment, similarly to rapeseed oil, did not affect the consistency and clarity, but the taste and smell changed slightly after 1 hour of frying. The smell of the oil was clearly changed after 2 hours of frying, while the taste only after 3 hours. The color of the oil changed after 2 hours from golden yellow to yellow and remained that way until the end of the process.

4. CONCLUSIONS

One of the effects of lipid oxidation in food is a reduction in the content of PUFA and bioactive compounds [Wąsowicz, Gramza and Hęś 2004]. Fatty acid losses correlate with the degree of their unsaturation and depend on the storage conditions of the food products. However, they can be so small that they do not affect the deterioration of the nutritional value of the product. Oxidation processes are reactions that commonly occur in food containing lipids. Their course is complex and dependent on many factors, with the resulting oxidation products reducing the nutritional value of the food products, the consumption of which can have serious health consequences.

The studies conducted showed that the oils tested showed similar sensitivity to high temperature. Rapeseed oil was found to be more resistant to hydrolytic decomposition, which was confirmed by a lower acid value than soybean oil. Soybean oil was more resistant to the oxidation process, which was confirmed by the peroxide value. Frying time also had a significant effect on the deepening of changes associated with the increase in fat values in the oils tested. Sensory studies have shown that frying significantly affected the color change of rapeseed and soybean oil, while the frying process lasting 4 hours slightly affected the change in taste and smell of the oils tested. However, no changes in consistency and clarity were observed.

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