

Physicochemical changes of post-frying sunflower oil

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Abstract. Composition of higher fatty acids, peroxide value (PV), acidic value (AV), as well as colour of raw, commercial rape oil and oil fraction formed after each of seven heating cycles of the oil conducted in two ways – with and without frying potato chips, were compared. After each heating of the oil, the duration of which corresponded with time required to fry potato chips, it was cooled down to room temperature and stored in conditions simulating those of a small gastronomy restaurant. The goal of undertaken research was evaluation of physicochemical properties and usability of post-frying sunflower oil as a substrate for biofuel production. Utilization of post-frying sunflower oil as a fuel seems to be justifiable when the beneficial ratio of saturated and unsaturated fatty acids in oil fraction, a property that stabilizes as a result of surface contact with potato chips, as well as ecological (utilization of waste) and economic (partial substitution of crude oil derived fuels) benefits are taken into consideration.

Key words: sunflower oil, post-frying oil, fatty acids composition, acidic value, peroxide value, fuel biocomponent

INTRODUCTION

Waste vegetable oils come mainly from gastronomy points: bars, restaurants, canteens, households, and are called post-frying oils. The most commonly used for frying is rape oil, but another popular one in Poland is sunflower oil. Producers of sunflower oil recommend it not only for salads but also for frying. It is characterized with high linolic and oleinic acid content – 75 and 35%, respectively. It also contains a significant amount of vitamin E, hence should not be heated to temperatures exceeding 100°C, so its usability for baking and long frying is limited (Valdés and Garcia, 2006).

Plant oils undergo numerous transformations during frying, causing destruction of fat. They take place during reactions of autooxidation, hydrolysis and polymerization.

There are a few directions in which degradation of post-frying plant oils runs. The kinetics of transformations are related with the structure and chemical properties of oil used, high temperature and access of sunlight, as well as numerous precursors (Normand *et al.*, 2006; Romero *et al.*, 2006; Sikorski and Kołakowska, 2003; Valdés and Garcia, 2006). The most important among them are atmospheric oxygen with oxidation catalysts like heavy metals, and water which is a component of raw material and interacts hydrolytically with some substances added to food and residues of substances used for frying equipment cleaning (Choe and Min, 2006).

The main reactions of fat transformations are related with either carboxyl group (ester) or carbohydrate chain (mainly unsaturated fatty acids) (Sikorski and Kołakowska, 2003). The rate of frying oil degradation depends on the type of product fried, oil chemical composition, and conditions in which the process takes place. As a result of repetitive heating, and interactions between frying oil and the product fried in it, volatile and nonvolatile compounds are formed. The first group includes compounds with molecular mass lower than 1 800 Da, such as hydrocarbons, aldehydes, furans, carbocyclic acids. It must be noted that triacylglycerol, whose mass is between 900 and 1 000 Da, is not included into this group as it is not volatile in temperatures observed during frying. Nonvolatile substances, with molecular mass exceeding 1 800 Da, to which group cyclic and acyclic monomers, dimers, and trimers are included, accumulate in a fryer and their presence testifies to advanced processes of fat degradation (Hoffman, 2004; Normand *et al.*, 2006; Romero *et al.*, 2006; Sikorski and Kołakowska 2003; Valdés and Garcia, 2006).

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High content of oxygen diluted in oil is propitious to its reactions with double bonds of fatty acids and to the formation of hydroperoxides (precursors of series of changes generating substrates of free radical oxidation transformations), and (as a result of particle splitting) alcohols, aldehydes and short-chain fatty acids, and as a result of dehydration also the formation of ketones is possible (Normand *et al.*, 2006; Romero *et al.*, 2006; Sikorski and Kołakowska, 2003; Valdés and Garcia, 2006). The basis for fat oxidation is the formation of free radicals which is affected by, having catalytic effect, ions of metals like copper, cobalt, chromium, and divalent and trivalent iron (Hoffman, 2004). In deeper layers of oil, where access of oxygen is limited, transformations leading to the creation of free radicals dominate. They are precursors of polymerization transformations of oil. Formation of these polymers results in changes of density and consistency of fat (Valdés and Garcia, 2006). Another result of polymerization is increase of viscosity of heated oil, the effect of which, among other things, is the formation of dark residue on fryer walls (Hoffman, 2004). Water, which gets into oil with detergents, emulsifiers, and caustic soda, is an environment for hydrolytic transformations of oil favouring increase of its acidic value, secondary oxidation transformations of fatty acids, and transesterification of fat (Valdés and Garcia, 2006). Fatty acids released as a result of hydrolysis may undergo secondary oxidation transformations (Hoffman, 2004). Reactions of hydrolysis are caused by agents used in frying equipment cleaning, such as caustic soda and other alkalis, and chemical substances present in food, like baking powder (Blumenthal, 1991). Also polymers, formed in frying oil as a result of oxidation and thermal changes, indirectly contribute to intensification of hydrolytic changes, because they cause foaming of fat, which favours holding steam in frying oil. Foaming of frying oil is also favoured by reactions of free fatty acids with sodium and potassium cations present in fried product (Hoffman, 2004).

Prolonged heating of fat leads to change of its colour, the degree of which is related to the time of oil frying applied. The main cause for colour changes is oxidation reactions, leading to accumulation of nonvolatile substances, mainly polymers, in a fryer. Other factors affecting changes of colour are hydrocarbons, phosphatides, sulphur compounds and trace amounts of heavy metals present in fried food. These compounds may react with fat, and products of its degradation, creating colourful substances. The reason for frying oil darkening is also Maillard's compounds, formed of the product which remained in the frying oil. They contain water, simple and compound carbohydrates and amino acids, which are substrates of non-enzymatic browning reactions. All fried products may affect the colour of fat by releasing colourful substances and lipids into frying oil (Hoffman, 2004; Mehta and Swinburn, 2001).

Knowledge of physicochemical properties of oils enables determination of areas of their potential utilization. There are three main possible directions of waste oil and fat utilization: processing into biofuel (biodiesel), hydrolysis of oils – obtaining fatty acids, and composting. In many countries post-frying oils from food processing sites are collected in separate containers and used to feed livestock, while oil used in households is poured into the sewage system, thus becoming an additional pollutant in waste waters. Fat getting to a waste water treatment plant affixes to apparatuses, causes corrosion of equipment and concrete, increases work level of fans and energy input, disturbs work of activated sludge. All of these result in lowering the effectiveness of waste water treatment plant operation.

Selective collection of post-frying fat yields material which can be utilised for biofuel production. Annually, 5 kg of oil per person (which adds up to 37 000 t when the whole country is taken into consideration) is reclaimed in Austria. Biofuel obtained this way can cover 1.5% of Austria's fuel demand. In the town of Mureck, the first plant producing MEFA (Methyl Esters of Fatty Acids), the production of which is based on post-frying oil, was opened in 1994. Its construction was based on an already operating installation processing rape oil, and currently it can process about 3 000 t year⁻¹ (http://mif.duo.netstrefa.pl/paliwa_files/PrezentEMKT.pdf).

Effective utilization of restaurant-derived fat was suggested by Lee *et al.* (2002) who proposed fractioning, by means of filtration and column chromatography, prior to esterification.

According to Tsai *et al.* (2007) local consumption of edible oil in Taiwan reaches about 700 000 t year⁻¹ and 200 000 t of waste post-frying oil is disposed of every year. In Japan, consumption reached about 2 mln t of edible oil and, respectively, 70 000 t became waste. In the past, there was no effective method of utilising this waste. It was simply dumped into the sewage system, causing many environmental problems like odour and possibility of spontaneous combustion. Recently, recycling of post-frying oil has been taken into consideration.

Complying with the provisions of the European Union's programme, Poland is planning to reduce the amount of waste disposed of in landfills. Accepted in Poland 'National Programme of Waste Management' projects intensification of actions promoting recycling of inorganic wastes, composting, and various high-temperature forms of organic wastes utilization. It is expected that approximately 1 400 000 t of municipal organic wastes will have been burned by the end of 2010. This shows that approximately 10 GJ t⁻¹ may be used as energy (Nilsson *et al.*, 2006).

The goal of undertaken research was evaluation of chosen physicochemical properties and usability for production of engine biofuel of fresh trade sunflower oil compared to oil action obtained after each of seven cycles of heating of oil used for chips frying.

MATERIALS AND METHODS

This research was focused on sunflower oil. Five litres of oil from a batch available on the market trade was used. It was purchased in 5 containers of 1 litre each, the contents of which were then poured into one container and mixed. The obtained mixture was called raw sunflower oil. The oil was heated in the container to temperature enabling proper frying of chips made of raw potatoes. They had shape and size similar to frozen potato chips which can be found in trade. After frying and separation of potato chips, the oil was left in the container at room temperature for 24 h, following which a sample was collected and marked as frying I. After 24 h the remaining oil was heated again and all actions described above were repeated – yielding another sample marked as frying II. The whole process of heating, cooling and sampling was repeated until it yielded samples marked with numbers III, IV, V, VI and VII. In order to investigate the effect of frying on properties of sunflower oil, similar cycles of heating and cooling, but without frying chips, were conducted yielding samples marked as heating I-VII.

Each collected sample was subjected to laboratory testing and the following properties were determined: peroxide value (PN-ISO 3960-1996), acidic value (PN-ISO 660-1998), colour of oil (Paul and Mittal, 1996) and composition of higher fatty acids (Krełowska-Kułas, 1993).

Oil colour was determined by means of spectrophotometric method, measuring absorbency for four light wavelengths of 460, 550, 620, and 670 nm. Photometric colour index (PCI) was calculated as follows:

$$PCI = 1.29(Ab_{460}) + 69.7(Ab_{550}) + 41.2(Ab_{620}) - 56.4(Ab_{670})$$

where: $Ab_{(460)}$, $Ab_{(550)}$, $Ab_{(620)}$, $Ab_{(670)}$ are values of absorbency measured for four light wavelengths of 460, 550, 620, and 670 nm, respectively (Paul and Mittal, 1996).

Each oil sample (with and without chips, after each heating) was analysed in six repetitions. Determination of fatty acids composition was conducted by means of gas chromatography. Extracted fat was subjected to alkaline analysis with sodium hydroxide solution in anhydrous methanol, and then released fatty acids were transformed into methyl esters with hydrogen chloride in methanol. Obtained esters were separated in chromatographic column and then their participation in the sum of fatty acids was determined (Krełowska-Kułas, 1993).

RESULTS AND DISCUSSION

This paper presents characteristics of chosen physicochemical changes of sunflower oil after each of its seven heating cycles. Analysed changes of acidic value, peroxide value, photometric colour index (PCI) and participation of particular fatty acids in the sum of fatty acids are presented in graphic and tabular forms in Figs 1, 2 and Table 1. Characteristics of post-frying oil properties might be a basis for elaboration of a model of these changes in oils subjected to long-term periodical gastronomic use.

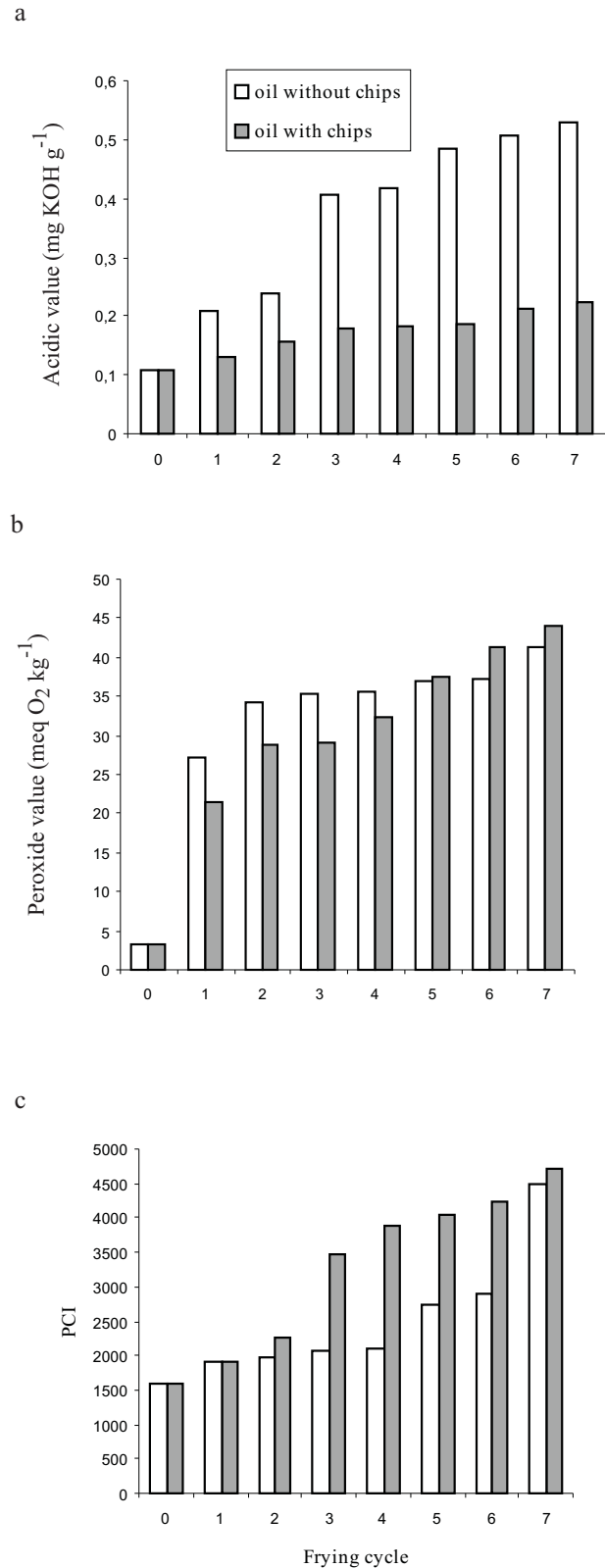


Fig. 1. Changes of: a – acidic, b – peroxide, c – PCI value in sunflower oil heated with and without potato chips.

Table 1. Participation of fatty acids in the sum of fatty acids of post-frying sunflower oil

Symbol of acid	Name of acid	Raw sunflower oil	Frying cycle															
			I		II		III		IV		V		VI		VII			
			without chips	with chips	without chips	with chips	without chips	with chips	without chips	with chips	without chips	with chips	without chips	with chips	without chips	with chips		
C14 : 0	Myristic acid	0.07	0.06	0.06	0.03	0.07	0.03	0.03	0.05	0.03	0.04	0.03	0.03	0.05	0.04	0.05	0.02	0.02
C16 : 0	Palmitic acid	6.06	5.64	5.76	3.06	5.31	3.05	3.09	5.10	3.69	3.69	3.38	3.09	4.24	3.94	4.67	2.00	2.31
C18 : 0	Stearic acid	3.58	3.33	3.40	1.81	3.14	1.80	1.83	3.01	2.18	2.18	1.99	1.83	2.50	2.32	2.76	1.18	1.36
C20 : 0	Arachidic acid	0.23	0.21	0.19	0.11	0.20	0.11	0.11	0.19	0.14	0.14	0.12	0.11	0.16	0.14	0.17	0.07	0.08
	Sum of saturated	9.94	9.24	9.41	5.01	8.72	4.99	5.06	8.37	6.05	6.05	5.52	5.06	6.96	6.44	7.65	3.27	3.77
C16 : 1	Palmitoleic acid	0.21	0.19	0.19	0.09	0.18	0.10	0.10	0.17	0.12	0.12	0.11	0.10	0.14	0.13	0.16	0.06	0.07
C18 : 1	Oleic acid	25.45	23.69	24.21	12.88	22.32	12.83	13.01	21.43	15.50	15.50	14.42	13.01	17.81	16.54	19.64	8.43	9.71
C18 : 2	Linolic acid	62.83	58.48	59.78	31.81	55.10	31.67	32.13	52.92	38.26	38.26	35.09	32.13	43.98	40.83	48.49	20.83	23.97
C18 : 3	Linolenic acid	0.94	0.87	0.89	0.47	0.82	0.47	0.48	0.79	0.57	0.57	0.52	0.48	0.64	0.61	0.72	0.31	0.35
C20 : 1	Eicosenoic acid	0.31	0.28	0.29	0.15	0.27	0.15	0.15	0.26	0.18	0.18	0.17	0.15	0.21	0.20	0.23	0.11	0.12
	Sum of unsaturated	89.74	83.51	85.36	45.40	78.69	45.22	45.88	75.57	54.63	54.63	50.31	45.88	62.78	58.31	69.24	29.74	34.22
	Oxidation products	–	6.91	4.85	49.36	12.29	49.58	48.85	15.76	39.09	39.09	44.14	48.85	30.09	35.08	22.81	66.84	61.84
	Analysis sum	99.68	99.66	99.62	99.77	99.70	99.80	99.79	99.65	99.79	99.79	99.97	99.79	99.87	99.83	99.70	99.85	99.83

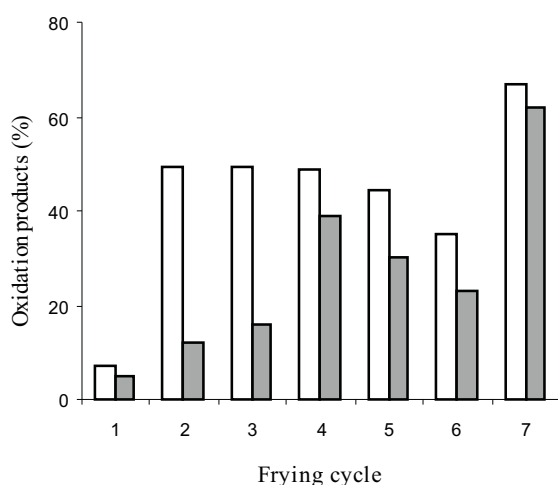


Fig. 2. Changes of oxidation products content in post-frying sunflower oil. Explanations as in Fig. 1.

Raw sunflower oil characterized by typical properties meeting quality standards (PN-A-86908, 2000) of product being a subject to business trade – $PV=3.3 \text{ meq O}_2 \text{ kg}^{-1}$ and $AV=0.108 \text{ mg KOH g}^{-1}$ of fat. The oil was lucid, clear – no residue was noted. Similar results were obtained by Maszewska and Krygier (2005), determining, for fresh sunflower oil, AV ranging from 0.1 to $0.21 \text{ mg KOH g}^{-1}$ of fat. In samples of oil heated without potato chips, acidic number (AV) increased systematically, reaching finally a level 390% higher than that for the initial raw oil. In the analogical trail for oil heated with potato chips, increase of AV reached only 107% (Fig. 1a). A similar tendency for property changes of rape oil was also noted earlier in a similar research, by Szmigielski *et al.* (2008). The data indicate a similar profile of changes of rape and sunflower oils subjected to gastronomic exploitation in model conditions. Both in the research conducted by Szmigielski *et al.* (2008) and in this one, oxidation transformations seem to be the key profile of investigated oil changes.

Since samples of oil heated and used for frying chips, characterized with lower AV values than samples of oil in which no frying was conducted (when samples having same numbers of frying cycle were considered), which may result from small influence of hydrolytic transformations (related mainly to water fraction introduced into oil with potato chips) and from absorption of hydrolysis products on porous surface of potatoes, a statement that the key factor affecting changes of investigated oil are oxidation transformations seems to be justified and confirmed by results obtained both in the research presented by Szmigielski *et al.* (2008) and in this one.

Peroxide value of oil subjected to the first heating increased rapidly, reaching levels about seven and nine times higher, in samples heated with and without potato chips, respectively, than the value determined in raw oil (Fig. 1b). A similar tendency concerning changes of properties of rape oil subjected to gastronomic use was observed by Szmigielski *et al.* (2008).

An instrumental and visible effect of changes taking place in oils heated seven times was darkening, intensified by prolonged time of oil exploitation. The main reason for colour changes, leading to accumulation of nonvolatile compounds in a fryer, are oxidation reactions. These compounds have a capacity of reacting with fat, or products of its degradation, forming colourful substances. Another reason for darkening of oil are Maillard compounds, substrates of which are simple and compound sugars, proteins and amino acids, products of peroxides degradation (Sikorski and Kolakowska, 2003; Medeni, 2003; Hoffman, 2004).

The value of PCI of investigated oils ranged from 1599 to 4729 for oil in which chips were fried, while for oil without chips from 1599 to 4488. PCI value for raw sunflower oil was 1599. Increase of PCI noted in post-frying oil reached 180 and 195% for sunflower oil with and without chips, respectively (Fig. 1c). Heating of sunflower oil in laboratory conditions (small size of the container in which the experiment was conducted and good access of air) caused significant changes of higher fatty acids composition which was characteristic mainly for oxidation processes (Table 1). Characteristic property of such changes is high initial decrease of unsaturated fatty acids content with simultaneous increase of fat partial oxidation products content and increase of PV value. Products of fatty acids oxidation observed in the investigated oils made up from 6.91 to 66.84% in oil heated without chips, and from 4.85 to 61.84% in oil heated with potato chips. In this process, catalytic influence of potato chips (Fig. 2) and sorption of oxidation products by chips are possible.

Utilization of such oil as substrate for biofuel production may be difficult. Sunflower oil after seven heating cycles is characterized with increased acidic number, which may cause encumbrance in the process of biofuel production based on such oil. However, it should not be an obstacle when such fuel was to be combusted in an engine, for the process of biofuel production embraces a stage of alkaline hydrolysis nature during which such oil would be neutralized (Alonso *et al.*, 2002; Staat and Vallet, 1994).

CONCLUSIONS

1. Sunflower oil used for gastronomic purposes shows different physicochemical properties than fresh oil.
2. Increase of acidic value and peroxide value as well as changes of fatty acids composition of sunflower oil suggest presence of oxidation-type transformations.

3. Occurrence of new compounds, products of oxidation and polymerization of unsaturated fatty acids, were noted in post-frying oil.

4. Each heating cycle brought sunflower oil change. Increase of photometric colour index was noted. Darkening of oil colour after frying chips was caused by oxidation-type reactions and by Maillard reactions.

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