ACTA SCIENTIARUM POLONORUM
Acta Sci. Pol. Technol. Aliment. 18(3) 2019, 293–303
www.food.actapol.net pISSN 1644-0730 eISSN 1898-9594 http://dx.doi.org/10.17306/J.AFS.2019.0675

ORIGINAL PAPER

Received: 16.06.2019
Accepted: 26.07.2019

THE DYNAMICS OF OXIDATIVE CHANGES IN SELECTED FATS DURING THE FRYING OF FRENCH FRIES

Elżbieta Kondratowicz-Pietruszka✉, Lidia Ostasz, Kinga Tataruch

Department of Chemistry, Cracow University of Economics
Rakowicka 27, 31-510 Cracow, **Poland**

ABSTRACT

Background. An analysis of the changes in the quality of edible fats used in the process of frying food products is a crucial issue for both food safety and consumer health. The purpose of this paper is to compare the dynamics of oxidation of selected fats during the frying of French fries at a temperature of 180°C, in an open and closed vessel.

Materials and methods. The subject of the study was the following frying media: rapeseed oil, coconut oil, frying fat and lard, for which characteristic numbers, fatty acid profile and oxidisability were determined. The fats were fried with 20 portions of French fries. The total frying time was 5 hours. In order to determine the oxidative stability of the fats, changes in the Totox index during frying were examined. The results of the research were elaborated by applying kinetic analysis methods. Orders, constant speeds and the speeds of fat oxidation processes were determined.

Results. The dynamics of fat oxidation during frying varied, which was proven by the values of the orders of processes, ranging from 0.2 to 0.7. The rates of oxidation processes were compared on the basis of velocity constants and it was found that rapeseed oil oxidised 1.35 times faster than frying fat, 1.55 times faster than lard and 1.72 times faster than coconut oil. The order of fat oxidisability calculated on the basis of fatty acid profiles was confirmed by the results of the kinetic analysis.

Conclusion. The methods of kinetic analysis applied in this study are well-suited for determining the dynamics of fat oxidation processes during frying. Thus, they can be used as a criterion for selecting an appropriate frying medium.

Keywords: frying fats, oxidation dynamics, Totox index, kinetic analysis

INTRODUCTION

Frying is one of the oldest and most popular forms of food processing. It owes its popularity both to the short period of heat treatment when compared to boiling or baking and to the specific sensory characteristics of fried products, such as colour, flavour, texture and tastiness (Andrikopoulos et al., 2003; Banks and Lusas, 2002; Dobarganes et al., 2000; Gertz, 2014; Rossel, 2001).

It is not only the product that changes in the frying process, but also the frying medium, which is exposed to high temperatures for an extended period of time. When adding food products, atmospheric oxygen is

Funding Source Declaration. The project was financed by the Ministry of Science and Higher Education granted pursuant to Decision No 044/WTiZP-KChO/01/2018/S/8044.

✉kondrate@uek.krakow.pl, https://orcid.org/0000-0003-4684-7496, phone +48 12 293 7858, fax +48 12 293 7800

released into the frying fat, which leads to fat oxidation and its gradual degradation. Water, organic compounds, enzymes and metals are transferred from fried food to a frying medium (Grootveld et al., 2014; Romero et al., 2000). Each of these components affects the properties of the frying medium, leading to mostly negative changes in its quality. The type of fat and foodstuff, as well as the conditions in which it is fried, determine the rate of degradation of the frying fat (Banks and Lusas, 2002; Saguy and Dana, 2003; Stier, 2004). The most important chemical reactions occurring in fat in the process of frying include oxidation, hydrolysis and polymerisation (Choe and Min, 2007; Gertz et al., 2000). The quality of a fat medium, which changes during frying, influences the characteristics of the resulting products (Kita et al., 2005). An analysis of the changes in the quality of edible fats used in the process of frying food products is crucial for both food safety and consumer health (Paul and Mittal, 1996; Weisshaar, 2014). Peroxide and anisidine values, as well as Totox index values, are selected to assess the quality of fats (Ahmadi et al., 2018; Mohammadi et al., 2013; Sebastian et al., 2014).

Fats used in heat treatment are of vegetable and animal origin. The first group includes refined vegetable oils, such as rapeseed oil, olive oil, soya bean oil, sunflower oil, peanut oil, coconut oil, palm seed oil and palm oil fractions. This group also comprises hardened vegetable oils, i.e. frying fat containing fully or partially hydrogenated polyunsaturated fatty acids. The group of animal fats includes lard and clarified butter. A wide selection of frying fats is commercially available, including mixtures of hydrogenated vegetable fat and vegetable oils (Kristott, 2003). When selecting a proper frying medium, special attention should be paid to its oxidative and thermal stability, which unambiguously determine the quality of frying fat.

Frying fat should be refined and have a suitable fatty acid profile: a high proportion of saturated fatty acids (SFA), a low content of polyunsaturated fatty acids (PUFA; less than 2%) and a low content of trans-fatty acids (less than 5%). The compliance with these criteria determines its high resistance to oxidation processes and a high smoke point, i.e. the temperature at which heated fat begins to decompose and toxic substances become released (Brinkmann, 2000; Mehta and Swinburn, 2001).

The frying fat most commonly used in Poland is rapeseed oil. The products fried in this medium absorb less fat than those fried in either palm oil or a mixture of rapeseed oil and palm oil (Kmiecik and Korczak, 2010). Rapeseed oil contains a valuable nutritional composition of fatty acids. It contains a low amount of saturated acids (7%), and a high amount of monoenic acids (58%) and polyenic acids (30%). One consequence of a high content of oleic acid is the high oxidation stability of rapeseed oil. Edible oils with a high oleic acid content (up to 70%) store very well and are resistant to high temperatures. Due to its relatively high α-linolenic acid content (up to 10%), rapeseed oil is often referred to as 'the olive oil of the north' (Dubois et al., 2007; Onacik-Gür et al., 2014).

Coconut oil is obtained mechanically by pressing the hard flesh of coconuts from a coconut palm tree (*Cocos nucifera*). In the commodity trade, it usually occurs in a refined form. At room temperature, it is solid, stable and resistant to rancidification. Coconut oil belongs to the group of lauric oils and contains over 90% saturated fatty acids, which causes its high oxidative stability (Dubois et al., 2007, Lu and Tan, 2009). Coconut oil is becoming more and more popular in the food industry in Poland and with consumers.

Frying fat is pure, refined palm oil or a mixture of palm oil and animal fats (e.g. beef tallow). It is resistant to long heating and it can be used repeatedly for frying successive dishes. The optimal frying temperature amounts to approx. 180–190°C. The smoke point is above 200°C and the smoking temperature is around 350°C. Frying fat has a high resistance to oxidation and does not affect the taste and smell of fried dishes, which is a desirable feature of frying fats. Solid frying fat contains about 50% unsaturated fatty acids. It is a commonly used frying medium in eateries in Poland.

Lard is a fat of animal origin obtained from the fatty tissue of pigs, cattle or poultry. Its high smoke point makes it excellent for heat treatment, as it does not change its properties even over a long period of heating (Love, 1996; Rohman et al., 2012). Lard is a popular frying medium with consumers in Poland, as it has been traditionally used in Polish households for centuries.

The aim of the research was to compare the rate of oxidation of the most popular frying fats in Poland by applying kinetic analysis methods.

MATERIALS AND METHODS

The subjects of the research were the following frying media, in the paper designated with the symbols:

- RO – "Wielkopolski" rapeseed oil – refined oil, pressed once from Polish rapeseed, producer: EOL POLSKA Sp. z o.o. Szamotuły
- CO – "KOKOSOLIE" coconut oil, the country of origin: Thailand
- FF – frying fat, vegetable fat consisting of palm fat and rapeseed oil, producer: Butella-Werk, Germany
- L – selected lard, pork fat, melted, edible fat, producer: Sokołów S.A. Poland.

The aforementioned fats were used to fry frozen French fries – AVIKO Original, by a Dutch producer. Nutrients per 100 g of product: fat – 4.9 g, including saturated fatty acids 2 g, carbohydrates 26.4 g, including sugars 0.5 g and fibre 2.8 g, protein 2.5 g and salt 0.8 g.

French fries were fried in an open and closed vessel at a temperature of 180°C. The open vessel was an enamel pot (P) with a diameter of 24 cm and a capacity of 3 liters, and the closed vessel was a fryer (F). The temperature of the frying process was controlled in the fryer by means of a built-in electronic thermostat, while in the open vessel by means of an electronic thermometer. The volume (mass) of fat samples was – 2 L of rapeseed and 2 kg of coconut oil, lard and frying fat. The subsequent portions of French fries were fried in a 15-minute cycle, one portion of French fries, weighing 200 ±1 g, was fried for about 5 minutes. The total frying time of the French fries in the frying media amounted to 300 minutes. Within this time, 20 portions of French fries were fried.

The initial values of the characteristic numbers, determined on the basis of the International Standards ISO:

- AcV acid, expressed in mg KOH/g of fat, was determined in accordance with ISO 660:2009 (EN) standard (±0.03 mg KOH/g)
- iodine IV expressed in mg I_2/100 g, was determined according to ISO 3961:2018 (EN) (±2 mg I_2/100 g for IV <50–100>, ±3.5 mg I_2/100 g for IV <100–135)
- peroxide PV, expressed in milliequivalents of active oxygen per kilogramme of fat, was determined in accordance with ISO 3960:2017 (EN) standard (±0.2 mEq O_2/kg)
- anisidine value AV was determined in accordance with ISO 6885:2016 (EN) norm, on the Meterek SP830 spectrophotometer (±0.2).

During the frying of French fries, samples were taken to determine changes in the values of characteristic numbers at the following intervals:

- acid value AcV initial values
- iodine value IV – initial values and after the frying process
- peroxide value PV every 30 min
- anisidine value AV every 60 min.

The experiments were conducted in triplicate, and the mean values and standard deviations are reported.

The value of the Totox index, i.e. the total degree of oil oxidation, was calculated on the basis of the determined peroxide and anisidine values from the formula (Madawala et al., 2012):

$$Totox = 2PV + AV.$$

The fatty acid profile was determined in accordance with ISO 12966-4:2015 (EN), BF3 version. Fatty acids were analysed in the form of methyl esters in the manner described in the standard. The analysis was performed on an SRI 8610C gas chromatograph with a *Restek* RTX-2330 l column = 105 m, Ø = 0.25 mm with an FID detector, using hydrogen as the carrier gas. The H_2 pressure at the column inlet was 3.8 bar resulting in a linear flow rate of 30 m/min. The analyses were carried out in a temperature program that started heating the column from 80°C with a temperature increase of 4°C/min to 170°C and then at a rate of 2.5°C/min to 220°C. The program ended with the bending of the column at 240°C. This procedure allows a good separation of peak C4 from strong solvent signal (isooctane), an isolation of signals from trans isomers (C18:1, C18:2) and an analysis of the sample in a reasonable time (55 min). Restek's *Food Industry FAME Mix*, catalogue number 35077, was used as a model. It is a mixture of 37 fatty acid methyl esters.

Table 1. Initial values of characteristic numbers of frying media

Parameters	Fats			
	RO	CO	FF	L
AcV_0, mg KOH/g	0.071 ±0.05	0.424 ±0.05	0.311 ±0.05	0.431 ±0.05
IV_0, g I_2/100 g	114.02 ±0.4	10.88 ±0.6	55.44 ±0.5	57.68 ±0.5
PV_0, mEq O_2/kg	1.073 ±0.04	0.399 ±0.05	0.682 ±0.04	1.092 ±0.04
AV_0	1.266 ±0.06	0.582 ±0.05	2.004 ±0.06	0.221 ±0.05
Totox, mEq O_2/kg	3.412	1.380	3.368	2.405

RESULTS AND DISCUSSION

Table 1 presents the initial values of the characteristic numbers, determined on the basis of ISO standards. The presented results are an arithmetic mean of min. 3 repetitions.

The obtained values of characteristic numbers in the frying media do not exceed the recommended values (Codex Alimentarius, 1999; Sebastian et al., 2014). The value of the peroxide in rapeseed oil should not exceed 5 mEq O_2/kg. The anisidine value in refined oils should not exceed 6 units. The acid value for refined oils should not exceed 0.6 [mg KOH/g]. The iodine value for rapeseed oil should range between 94 and 120 (Codex Alimentarius, 1999). The values of characteristic numbers given in Table 1 correspond to those set out and described by other authors. In the paper by Kita et al. (2007), the characteristics of fresh rapeseed and palm oils were determined, taking into account fatty acid composition, and iodine and peroxide values (IV_0 – fresh rapeseed oil 105, fresh palm oil 55; PV_0 – rapeseed oil 2.08, palm oil 1.43). Similar values were determined for lard, rapeseed oil, coconut oil and palm oil. The initial values of these parameters were as follows: IV_0 – coconut oil 11.9 g I_2/100 g, lard 57.6 g I_2/100 g, rapeseed oil 113.4 g I_2/100 g, palm oil 50.8 g I_2/100 g; AV_0 – lard 0.36, rapeseed oil 0.3 and palm oil 1.35 (Chebet et al., 2016; Park and Kim, 1996).

Analysis of fatty acid composition

Table 2 shows the fatty acid profile of the tested fats before frying. No trans isomers were found in the fats. The composition of fatty acids changes during frying, which is one of the most important factors determining the oxidation stability of oils. This is the result of reactions between the medium and the fried products taking place over a long period of frying. The acid profiles of the frying media were varied and corresponded to the acceptable ranges of fatty acid composition variations for selected vegetable and animal fats described in the applicable food standards (Codex Alimentarius, 1999).

Table 2 shows the content of saturated fatty acids SFA, including palmitic acid C16:0. This acid is dominant in the group of SFA acids in the tested fats. The exception is coconut oil, which contains the highest amount of lauric acid C12:0. This oil contains only about 9% unsaturated fatty acids, while in rapeseed oil the share of these acids amounts to over 93%. Lard and frying fat contain 55% and 48% UFA acids respectively. The highest content of C18:1 (cis-9) oleic acid was recorded in the monoene-fatty acid fraction. Similar results of the fatty acid analysis were obtained by other authors (Kim et al., 2013; Kita et al., 2007; Li et al., 2017; Lu and Tan, 2009; Roman et al., 2013). Table 2 shows the content of unsaturated acids divided into mono- and polyenes.

On the basis of the profile of fatty acids, the oxidizability (Ox) of the tested oils was calculated using the formula (Cosgrove et al., 1987):

$$Ox = (0.02 \cdot C18{:}1 + 1 \cdot C18{:}2 + 2 \cdot C18{:}3) / 100$$

where:

C18:1 – the percentage of oleic acid,
C18:2 – the percentage of linoleic acid,
C18:3 – the percentage of linolenic acid.

The highest oxidizability in the group of the analysed frying fats, calculated on the basis of the data

Table 2. Profile of fatty acids in frying media

FA, % m/m	RO 0	CO 0	FF 0	L 0
C6:0	–	0.72	–	–
C8:0	–	7.68	0.36	–
C10:0	–	6.06	0.32	0.11
C12:0	–	45.92	4.18	0.15
C14:0	–	18.17	2.4	1.9
C16:0	5.22	9.36	41.12	29.09
C18:0	1.64	2.84	3.8	14.09
C20:0	–	–	–	–
SFA	6.86	90.75	46.92	45.34
C16:1 (cis-9)	0.31	–	0.2	3.07
C18:1 (cis-9)	62.47	7.16	34.54	39.78
C20:1 (cis-11)	1.07	–	0.25	0.7
MUFA	63.85	7.16	40.25	43.55
C18:2 (cis-9, 12)	18.86	2.09	10.71	9.52
C18:3 (cis-6, 9, 12)	0.72	–	0.4	0.16
C18:3 (cis-9, 12, 15)	9.22	–	1.72	0.75
C20:2 (cis-11, 14)	0.25	–	–	0.37
C20:3 (cis-8, 11, 14)	0.24	–	–	0.31
PUFA	29.29	2.09	12.83	11.11
UFA	93.14	9.25	47.82	54.66
Oxidizability	0.40	0.02	0.16	0.12
C18:2/C16:0	3.62	0.22	0.26	0.33

from Table 2, was found in rapeseed oil. Its oxidisation is on average 2.6 times higher than that of frying fat, 3.3 times higher than that of lard and more than 19 times higher than that of coconut oil.

Figure 1 exemplifies the total content of saturated, monoenoic and polyenoic acids for rapeseed oil, before frying RO, after frying in the pot RO (P) and in the deep fryer RO (F).

After frying the French fries, changes in individual fatty acid fractions could be observed in all frying media. As regards saturated fatty acids, the highest increase in the content of this fraction (an increase

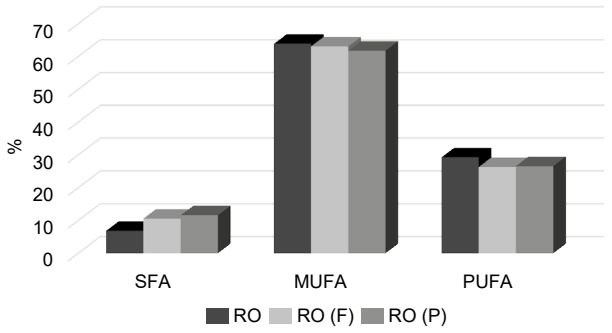

Fig. 1. Contents of saturated, mono- and polyenoic fatty acids in rapeseed oil, before frying (RO), after frying of French fries in the pot RO (P) and in the deep fryer RO (F) at 180°C

from 6.85% before frying up to 10.60% after frying in a fryer, and 11.57% after frying in a pot) was recorded in rapeseed oil, at the expense of unsaturated MUFA and PUFA fatty acids.

For the remaining fats, the changes in the SFA fraction contents were much lower and were in the range 1–2% in relation to the initial value. Other authors (Li et al., 2017; Lu and Tan, 2009) also observed slight changes in the fatty acid profile within several hours of heat treatment, for coconut and palm oils.

Linoleic acid (C18:2) is more susceptible to oxidation than palmitic acid (C16:0), therefore, the ratio C18:2/C16:0 is calculated on the basis of the percentage of these acids in fresh fats and after the heat treatment process. The value of this ratio determines the susceptibility to fat oxidation and is an indicator of quality deterioration in the frying process (Li et al., 2017; Zribi et al., 2014). Table 2 shows the values of this ratio for fats before frying.

For rapeseed oil, the percentage decrease in the value of the tested parameter was the highest (44.5%), which indicates the greatest susceptibility to oxidation in the process of deep frying. The highest oxidative stability on the basis of the value of this ratio was a characteristic of frying fat (3.9%). The percentage decrease of this indicator for coconut oil amounted to 27.3%, which does not confirm that this oil is the most resistant to oxidation, despite it having the highest content of saturated acids. In the fractions of these acids, lauric acid is dominant, while in the C18:2/C16:0 ratio, which determines the susceptibility to oxidation, palmitic acid occurs.

The values of this coefficient after frying in an open (P) and closed (F) vessel decreased for rapeseed oil (from 3.62 to 1.82) and coconut oil (from 0.22 to 0.15), while for lard and for frying fat no significant differences were observed.

Analysis of changes in the values of the characteristic numbers of frying media

The iodine value indicates the degree of fat saturation, including the average number of double bonds. As a result of frying products in oils, their quality deteriorates, thus reducing the value of this parameter and indicating a decrease in the number of unsaturated bonds (Chebet et al., 2016). The iodine value was determined for tested fats before and after the frying of French fries in a deep fryer and in a pot.

The biggest changes in the iodine value after frying in an open vessel (P) were found in rapeseed oil (from 114.0 to 106.8 g I_2/100 g). A smaller decrease in the value of this parameter was observed in the case of frying fat (from 55.44 g I_2/100 g for fresh fat to 50.08 I_2/100 g after frying) where palm oil is a dominant component. For the other examined fats, changes in the iodine value after frying were smaller (for lard from 57.46 to 56.98 g I_2/100 g and for coconut oil from 10.88 to 9.35 g I_2/100 g). Changes in the parameters of the analyses proceeded similarly in both open and closed vessels. The iodine value for fresh oils and the character of the changes in the iodine value during the frying processes were directly related to the fatty acid profile of the examined edible oils.

In the analysed literature, the influence of frying processes and various storage conditions on the change, or, to be more specific, on the decrease of the iodine value in vegetable oils were demonstrated. In the work by Lu and Tan (2009), changes in the iodine value were determined for fresh coconut oil and that after the frying of French fries at 190°C (6 chip-frying cycles, 5 minutes for each portion, total frying time – 75 min). The iodine value varied from 11.09 g I_2/100 g for fresh oil to 3.26 I_2/100 g after frying and after 40-day storage at room temperature. The results obtained in the conducted research confirm that the frying process reduces the iodine value.

The peroxide PV is a parameter commonly used for assessing the degree of fat oxidation and determines the content of primary oxidation products. Fats used for frying must have the initial value of $PV_0 < 2$ mEq O_2/kg (Sebastian et al., 2014). The initial values of the peroxide value of the tested media determined in the tests are lower than the given value (Table 1).

During the process of frying French fries in a deep fryer and in a pot, the changes in the peroxide PV value in the fats were observed. The changes to this parameter over time proceeded similarly in both closed (Fig. 2) and open vessels (Fig. 3).

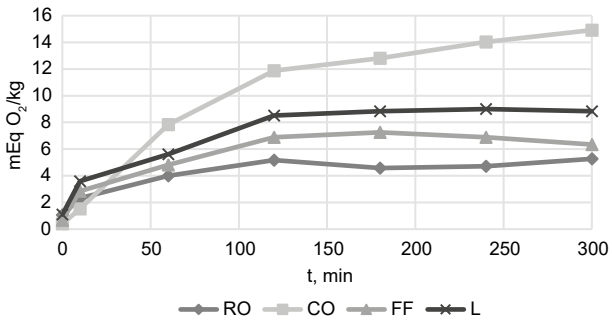

Fig. 2. Changes in the peroxide value in frying media during frying of French fries in a deep fryer at 180°C

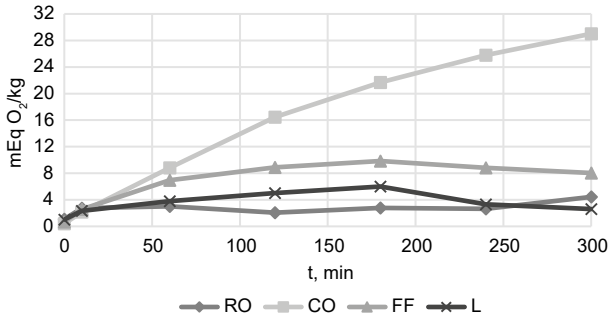

Fig. 3. Changes in the peroxide value in frying media during frying of French fries in a pot at 180°C

For coconut oil, the changes in the peroxide value were the greatest when compared to other frying media. The values of this parameter changed in the range of 0.40–14.92 mEq O_2/kg during the frying of French fries in a deep fryer and 0.4–29.01 mEq O_2/kg in a pot. For rapeseed oil and lard, bigger changes in this parameter were observed during frying in a deep fat

fryer. The exception was frying fat, for which a greater number of original oxidation products was produced during frying in a pot. In rapeseed oil, the changes of the peroxide value were the lowest and did not exceed 5.5 mEq O_2/kg.

The anisidine value AV determines the content of secondary lipid oxidation products, including aldehydes and ketones. The value of this parameter is considered to be the most reliable indicator of fat oxidation in heat treatment. Secondary oxidation products are more stable than hydroxides and peroxides, which are formed in the first stage of oxidation (Sebastian et al., 2014). While frying French fries in a pot, the biggest changes were found in the anisidine value for rapeseed oil (from 1.27 to 106.31), and the smallest for coconut oil (from 0.58 to 32.84). Smaller values of this parameter were observed for each medium during frying in a deep fryer. For example, for rapeseed oil the values ranged from 1.27 to 68.11, and for coconut oil from 0.58 to 23.39. The character of the changes in the anisidine value while frying French fries in open and closed vessels was analogous and, additionally, was similar to the changes in the peroxide value over time (Fig. 2, 3).

On the basis of the changes in the peroxide values, no significant differences resulting from the type of frying vessel used – open (pot) or closed (fryer) – were observed. This means that the direct access to oxygen of an open vessel under the conditions of the frying process (fat volume 2l, time 300 min) did not affect the formation of primary oxidation products, i.e. hydroperoxides. However, when analyzing changes in the anisidine value, it was found that the more oxygen available (open vessel) the more secondary oxidation products were formed. Research on the influence of oxidation was also conducted by Roman et al. (2013).

The value of the Totox index, i.e. the total degree of oil oxidation, was calculated on the basis of the determined peroxide and anisidine values. While frying French fries in a pot, the biggest changes in the Totox index were found for rapeseed oil (from 3.41 to 115.18 mEq O_2/kg), and the smallest for lard (from 2.28 to 60.38 mEq O_2/kg). Smaller values of this parameter were observed for each medium while frying in a deep fryer. For example, for rapeseed oil the values ranged from 3.41 to 78.65 mEq O_2/kg. For other media, the values of the Totox index after frying reached similar values of about 53 to 58 mEq O_2/kg. The character of the changes in the value of the analysed index while frying French fries in a deep fat fryer and in a pot is shown in Figures 4 and 5.

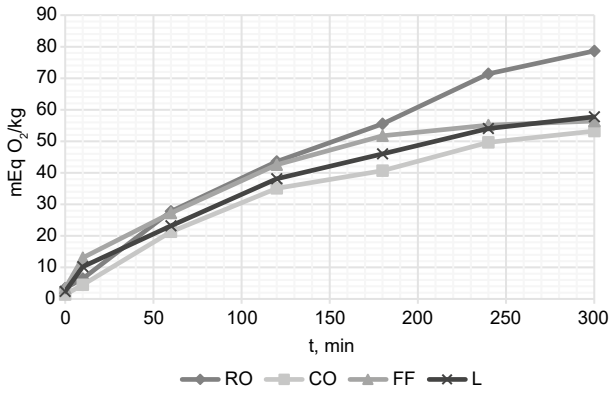

Fig. 4. Changes in the Totox index while frying French fries in a deep-fat fryer at 180°C

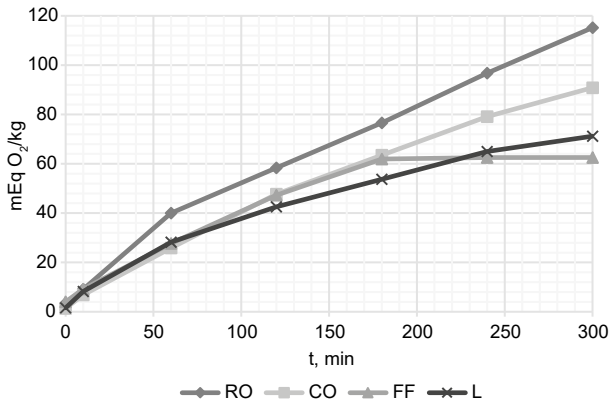

Fig. 5. Changes in the Totox index while frying French fries in a pot at 180°C

Kinetic analysis of empirical curves

The diagrams of changes in the Totox index relation as a function of time (Fig. 4, 5) are concave in form. These forms of curves, marked in this paper with the *dw* symbol, are characterised by an increase in the parameter over time and a decrease in the rate of increase of the indicator value. The obtained sets of experimental data were subjected to kinetic analysis in order to

determine models describing changes of the Totox index in the used fats and to compare the dynamics of their oxidation processes.

The following kinetic parameters were calculated over the course of the analysis presented (Kondratowicz-Pietruszka and Ostasz, 2000):

- the process order n, i.e. the dimensionless order of the descriptive function and the k_n speed constant – by the method of substitution for the formula, for $n > 0$

$$k_n = \frac{\text{Totox}_t^{1+n} - \text{Totox}_0^{1+n}}{(1+n)\cdot t}, \text{ mEq } O_2/\text{kg}^{1+n}\cdot\text{h}^{-1} \quad (1)$$

- theoretical values of the Totox index by descriptive function for a specific order n:

$$\hat{\text{Totox}}_t = [\text{Totox}_0^{1+n} + k_n\cdot(1+n)\cdot t]^{1/1+n}, \text{ mEq } O_2/\text{kg} \quad (2)$$

- constant speed ratio, two processes, A and B, called the affinity ratio:

$$K_B^A = \frac{k_{n.A}}{k_{n.B}} \quad (3)$$

where:

$k_n \geq 0$, $n \geq 0$,

Totox_0 – initial value of the Totox index,

Totox_t – value of the Totox index at time t.

For all the analysed processes, the parameter e_m [%] was calculated, which is an average deviation of the experimental values of the Totox index from the theoretical values, that is the accuracy of fitting to kinetic function, according to the formula:

$$e_m = \frac{|\text{Totox}_t - \hat{\text{Totox}}_t|}{\hat{\text{Totox}}_t}\cdot 100\% \quad (4)$$

To describe the process of fat oxidation in the process of frying French fries, the changes of the Totox coefficient values were selected, taking into account the formation of both hydroxides and secondary oxidation products.

The experimental data were described with kinetic models of type *dw.* The initial value of the Totox index was estimated for a time of t = 10 min. This is the time when the frying media reached the temperature of 180°C.

Table 3 presents the calculated kinetic parameters of descriptive functions: orders of models n, constant growth rates of the Totox k_n index, and the e_m parameter [%].

The orders of oxidation processes of the analysed fats used for frying French fries in an open vessel (P) were different (0.2–0.7 *dw*), while in a closed vessel (F) they were identical and amounted to 0.7 *dw*. The values of affinity coefficients are used to compare the dynamics of the processes, provided that the compared processes are of the same order. This condition is fulfilled only for frying media in a deep fryer. The dynamics of oxidation of frying media during frying in a deep fryer varies. Rapeseed oil was the fastest to

Table 3. Kinetic parameters of descriptive functions

Sample symbol	n (*dw*)	k_n, (mEq O_2/kg)$^{1+n}\cdot$h^{-1}	Totox t = 10 min	Descriptive function (mEq O_2/kg)$^{1+n}$h^{-1}	e_m, %
RO (P)	0.2	0.7927	9.14	$[14.2277 + 0.9512\ t]^{0.8333}$	3.75
CO (P)	0.4	1.2745	6.88	$[14.8807 + 1.7843\ t]^{0.7143}$	4.06
L (P)	0.7	2.0204	7.79	$[32.7804 + 3.4347\ t]^{0.5882}$	3.89
FF (P)	0.6	2.6248	9.67	$[37.7296 + 4.1997\ t]^{0.6250}$	7.64
RO (F)	0.7	3.1166	6.42	$[23.5944 + 5.2982\ t]^{0.5882}$	5.05
CO (F)	0.7	1.8132	4.47	$[12.7504 + 3.0824\ t]^{0.5882}$	3.88
L (F)	0.7	2.0082	10.19	$[51.7483 + 3.4139\ t]^{0.5882}$	4.14
FF (F)	0.7	2.3177	13.08	$[79.1103 + 3.9401\ t]^{0.5882}$	7.15

oxidise – 1.35 times faster than frying fat, 1.52 times faster than lard, and 1.72 times faster than coconut oil.

CONCLUSIONS

The analysis of the fatty acid composition in the studied frying media showed large differences in the SFA content as well as in the group of MUFA and PUFA acids.

Frying media showed different values of calculated oxidizability. The coefficient of deterioration of the quality of a frying medium was the ratio of percentage of fatty acids C18:2/C16:0. The values of this ratio before and after frying were the highest for rapeseed oil (44.5%), which means that this oil was most prone to oxidation. The highest oxidative stability on the basis of this ratio was found for frying fat (3.9%). The oxidizability of rapeseed oil was on average 2.6 times higher than that of frying fat, 3.3 times higher than that of lard and more than 19 times higher than that of coconut oil.

The Totox index value is the most reliable indicator of fat oxidation in heat treatment. While frying French fries in a pot, the biggest changes in the Totox index were found for rapeseed oil (from 3.41 to 115.18 mEq O_2/kg), and the smallest for lard (from 2.28 to 60.38 mEq O_2/kg). The changes in the value of this index while frying French fries in an open and closed vessel, were characterised by different dynamics of the oxidation process. The curves obtained of the change in this parameter as a function of time were of an upward and downward nature. They were described by kinetic functions with orders ranging from 0.2 to 0.7. The fitting error of the kinetic models to the experimental data was 3.75–7.64%.

On the basis of the calculated values of affinity coefficients for the processes of frying French fries in a deep fryer, it was found that the dynamics of oxidation of frying media varied. Rapeseed oil oxidised most rapidly, 1.35 times faster than frying fat, 1.55 times faster than lard, and 1.72 times faster than coconut oil.

REFERENCES

Ahmadi, E., Mosaferi, M., Nikniaz, L., Tabrizi, J. S., Jafarabadi, M. A., Safari, G., Bargar, M. (2018). Frying oils quality control: Necessity for new approach of supervision. Brit. Food J., 120, 490–498. https://doi.org/10.1108/BFJ-04-2017-0202

Andrikopoulos, N. K., Boskou, G., Dedoussis, G. V. Z., Chiou, A., Tzamtzis, V. A., Papathanasiou, A. (2003). Quality assessment of frying oils and fats from 63 restaurant in Athens, Greece. Food Serv. Technol., 3, 49–59. https://doi.org/10.1046/j.1471-5740.2003.00064.x

Banks, D. E., Lusas, E. W. (2002). Snack food processing. London, New York, Washington: CRC Press.

Brinkmann, B. (2000). Quality criteria of industrial frying oils and fats. Eur. J. Lipid Sci. Tech., 102, 539–541. https://doi.org/10.1002/1438-9312(200009)102:8/9<539::AID-EJLT539>3.0.CO;2-B

Chebet, J., Kinyanjui, T., Cheplogoi, P. K. (2016). Impact of frying on iodine value of vegetable oils before and after deep frying in different types of food in Kenya. J. Sci. Innov. Res., 5, 193–196.

Choe, E., Min, D. B. (2007). Chemistry of deep-fat frying oils and fats. J. Food Sci., 7, 77–86. https://doi.org/10.1111/j.1750-3841.2007.00352.x

Codex Alimentarius International Food Standards (1999). Standard for named vegetable oils, 210-1999.

Cosgrove, J. P., Church, D. F., Pryor, W. A. (1987). The kinetics of the autoxidation of polyunsaturated fatty acids. Lipids, 22, 299–304. https://doi.org/10.1007/BF02533996

Dobarganes, M. C., Perez-Camini, M. C., Marquez-Ruiz, G., Velasco, J. (2000). Interactions between fat and food during deep-frying. Eur. J. Lipid Sci. Tech., 102, 521–528. https://doi.org/10.1002/1438-9312(200009)102:8/9<521::AID-EJLT521>3.0.CO;2-A

Dubois, V., Breton, S., Linder, M., Faanni, J., Parmentier, M. (2007). Fatty acid profiles of 80 vegetable oils with regard to their nutritional potential. Eur. J. Lipid Sci. Tech., 109, 710–732. https://doi.org/10.1002/ejlt.200700040

Gertz, C. (2014). Fundamentals of the frying process. Eur. J. Lipid Sci. Tech., 116, 669–674. https://doi.org/10.1002/ejlt.201400015

Gertz, C., Klostermann, S., Kochhar, S. P. (2000). Testing and comparing oxidative stability of vegetable oils and fats at frying temperature. Eur. J. Lipid Sci. Tech., 102, 543–551. https://doi.org/10.1002/1438-9312(200009)102:8/9%3C543::AID-EJLT543%3E3.0.CO;2-V

Grootveld, M., Rodado, V. R., Silwood, C. J. L. (2014). Detection, monitoring, and deleterious health effects of lipid oxidation products generated in culinary oils during thermal stressing episodes. Am. Oil Chem. Soc., 25 (10), 614–624.

ISO 12966-4:2015 (EN) (2015). Animal and vegetable fats and – Gas chromatography of fatty acid methyl esters. Part 4: Determination by capillary gas chromatography", pp. 1–21.

ISO 660:2009 (EN) (2009). Animal and vegetable fats and oils – Determination of the acid value and acidity", pp. 1–9.

ISO 3960:2017 (EN) (2017). Animal and vegetable fats and oils – Determination of peroxide value – Iodometric (visual) endpoint determination", pp. 1–10.

ISO 3961:2018 (EN) (2018). Animal and vegetable fats and oils – Determination of the iodine value", pp. 1–12.

ISO 6885:2016 (EN) (2016). Animal and vegetable fats and oils – Determination of the anisidine value", pp. 1–7.

Kim, T. S., Yeo, J. D., Kim, J. Y., Kim, M.-J., Lee, J. H. (2013). Determination of the degree of oxidation in high-oxidised lipids using profile changes of fatty acids. Food Chem., 138, 1792–1799. https://doi.org/10.1016/j.foodchem.2012.11.119

Kita, A., Lisińska, G., Powolny, M. (2005). The influence of frying medium degradation on fat uptake and texture of French fries. J. Sci. Food Agric., 85, 1113–1118. https://doi.org/10.1002/jsfa.2076

Kita, A., Lisińska, G., Gołubowska, G. (2007). The effect of oils and frying temperatures on the texture and fat contents of potato crisps. Food Chem., 102, 1–5. https://doi.org/10.1016/j.foodchem.2005.08.038

Kmiecik, D., Korczak, J. (2010). Tłuszcze smażalnicze – jakość, degradacja termiczna i ochrona [Frying fats – quality, thermal degradation and protection]. Nauka Przyr. Technol. 4, 2, #23 [in Polish]. https://www.npt.up-poznan.net/pub/art_4_23.pdf

Kondratowicz-Pietruszka, E., Ostasz, L. (2000). Quality changes in edible oils at high temperature. Kinetic analysis. Eur. J. Lipid Sci. Tech., 102, 276–281. https://doi.org/10.1002/(SICI)1438-9312(200004)102:4%3C276::AID-EJLT276%3E3.0.CO;2-Y

Kristott, J. (2003). High-oleic oils – how good are they for frying? Lipid Technol., 3, 29–32.

Li, X., Li, J., Wang, Y., Cao, P., Liu, Y. (2017). Effects of frying oils' fatty acids profile on the formation of polar lipids components and their retention in French fries over deep-frying process. Food Chem., 237, 98–105. https://doi.org/10.1016/j.foodchem.2017.05.100

Love, J. A. (1996). Animal fats. In F. Shahidi (Ed.), Bauley's industrial oil and fat products. Edible oil and fat products. New York: John Wiley.

Lu, H. F. S., Tan, P. P. (2009). Comparative study of storage stability in virgin coconut oil and extra virgin Olive oil upon thermal treatment. Int. Food Res. J., 16, 343–354. http://www.ifrj.upm.edu.my/16%20(3)%202009/7[1]%20Henna%20Lu.pdf

Madawala, S. R. P., Kochhar, S. P., Dutta, P. C. (2012). Lipid components and oxidative status of selected specialty oils. Int. J. Fats Oils, 63, 143–151. http://dx.doi.org/10.3989/gya.083811

Mehta, U., Swinburn, B. (2001). A review of factors affecting fat absorption in hot chips. Crit. Rev. Food Sci. Nutr., 41, 133–154. https://doi.org/10.1080/20014091091788

Mohammadi, M., Hajeb, P., Seyyedian, R., Mohebbi, G.H., Barmak, A. (2013). Evaluation of oxidative quality parameters in imported edible oils in Iran. Brit. Food J., 115, 789–795. https://doi.org/10.1108/BFJ-Feb-2011-0035

Park, J.-M., Kim, J.-M. (1996). Monitoring of used frying oils and frying times for frying chicken nuggets using peroxide value and acid value. Korean J. Food Sci. Anim. Resour., 36, 612–616.

Paul, S., Mittal, G. (1996). Dynamics of fat/oil degradation during frying based on physical properties. J. Food Process Eng., 19, 201–221. https://doi.org/10.1111/j.1745-4530.1996.tb00390.x

Rohman, A., Triyana, K., Sismindari, S., Erwanto, Y. (2012). Differentiation of lard and other animal fats based on triacylglycerols composition and principal component analysis. Int. Food Res. J., 19, 475–479. http://www.ifrj.upm.edu.my/19%20(02)%202012/(14)IFRJ-2012%20Rohman.pdf

Roman, O., Heyd, B., Broyart, B., Castillo, R., Maillard, M.-N. (2013). Oxidative reactivity of unsaturated fatty acids from sunflower, high oleic sunflower and rapeseed oils subjected to heat treatment, under controlled conditions. LWT – Food Sci. Technol., 52, 49–59. https://doi.org/10.1016/j.lwt.2012.12.011

Romero, A., Cuesta, C., Schnez-Muniz, F.J. (2000). Cyclic fatty acid monomers and thermoxidative alteration compounds formed during frying oil. J. Am. Oil Chem. Soc., 77, 1169–1175. https://doi.org/10.1007/s11746-000-0183-5

Rossel, J. B. (2001). Frying. Improving quality. Cambridge England: Woodhead Publ.

Saguy, I. S., Dana, D. (2003). Integrated approach to deep fat frying: engineering, nutrition, health and consumer aspects. J. Food Eng., 56, 143–152. https://doi.org/10.1016/S0260-8774(02)00243-1

Sebastian, A., Ghazani, S. M., Marangoni, A. G. (2014). Quality and safety of frying oils used in restaurants. Food Res. Int., 64, 420–423. http://dx.doi.org/10.1016/j.foodres.2014.07.033

Onacik-Gür, S., Żbikowska, A., Marciniak-Łukasiak, K. (2014). Pochodzenie, metody otrzymywania i trwałość oksydacyjna tłuszczów wysokooleinowych [Source,

methods of obtaining and oxidative stability of high-oleic fats]. Żywn. Nauka Technol. Jakość, 6(97), 18–28 [in Polish]. http://dx.doi.org/10.15193/zntj/2014/97/018-028

Stier, R. F. (2004) Frying as a science – An introduction. Eur. J. Lipid Sci. Tech., 106, 715–721. https://doi.org/10.1002/ejlt.200401065

Weisshaar, R. (2014). Quality control of used deep-frying oils. Eur. J. Lipid Sci. Tech., 116, 716–722. https://doi.org/10.1002/ejlt.201300269

Zribi, A., Jabeur, H., Aladedunye, F., Rebai, A., Matthaus, B., Bouaziz, M. (2014). Monitoring of quality and stability characteristics of fatty acid compositions of refined olive and seed oils during repeated pan– and deep frying using GC, FT-NIRS, and chemometrics. J. Agric. Food Chem., 62, 10357–10367. https://doi.org/10.1021/jf503146f