

The study of palm and rapeseed oil stability during frying

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(Submitted: December 12, 2017 Accepted: March 20, 2018)

Summary

Palm oil is characterized by high oxidation stability, high smoke point, low foam making properties, limited penetration into the product, what makes it ideal for processes requiring thermal treatment such as frying. The aim of the study was to investigate the chemical composition and thermooxidative stability of red palm olein, rapeseed oil and their mixtures during deep-frying of French fries. Analysis of fatty acids composition and basic parameters of fresh oils (acid number, peroxide value, polar compounds content, induction time) were performed. During frying, changes in acid number, polar compounds in oils as well as consumers' acceptance of the fries fried in these oils were investigated. During the 32-hour of frying, the lowest chemical changes occurred in palm olein, what was confirmed by low acid values (0.99 mg KOH/g) and low polar content (14.4%). At the end of the experiment, the oil mixture had the highest polar fraction value of 25.0%. In the opinion of consumers, fries fried in rapeseed oil were "the best", while French fries fried on palm oil were considered "artificial", "chemical" and "disgusting". The reason for this opinion was the addition of β -carotene to this oil. On the other hand β -carotene from palm olein had a great positive effect on the colour of the fries, but at the same time had a negative effect on the taste.

Introduction

The main components of edible oil are triacylglycerols (TAG) which are about 94-99%. They determine the physical properties of oil. In composition of palm oil there is almost equal the quantity of saturated (49.9%) and unsaturated (49.7%) fatty acids. Most of unsaturated fatty acids occur in 2nd position in a molecule of triacylglycerol (NAGENDRAN et al., 2000; SAMBANTHAMURTHI et al., 2000). Raw palm oil is a rich source of carotenoids which impart a deep orange-red colour (NAGENDRAN et al., 2000; ONG and GOH, 2002; MBA et al., 2017). Their contents vary between 700-800 mg/kg (of which 37% is *alfa*- and 50% is *beta*-carotene). This oil is also a rich source of tocopherols and tocotrienols (Vitamin E). Its contents vary between 600-1000 mg/kg (NAGENDRAN et al., 2000; SAMBANTHAMURTHI et al., 2000; ONG and GOH, 2002; MBA et al., 2017). Carotenoids and Vitamin E are natural antioxidants, however, because of the processing they are partly lost. They modify highly reactive radicals, mainly hydroxyl radical and peroxy radical, into less active forms. Thus they protect the oil from oxidation (NAGENDRAN et al., 2000; SAMBANTHAMURTHI et al., 2000; ONG and GOH, 2002; EDEM, 2002; BERGER, 2005). Palm oil is recommended for frying because of its high stability due to relatively high contents of oleic acid, high contents of saturated acids and large amounts of natural antioxidants. It slightly penetrates the fried product and it can be used repeatedly (ONG and GOH, 2002). It gives the products the colour of gold. Besides, there is no loss of nutritional value during frying in this fat (BERGER, 2005). However, according to NORIZZAH et al. (2004) the use of olein is limited, because of the excessive foaming during heating caused by the presence of short chain fatty acids.

In the rapeseed oil 25% of the TAG creates triolein. The saturated acids are mainly present in the molecule of TAG in 1st or 3rd positions, while unsaturated acids are present in 2nd position (PRZYBYLSKI, 1999; RICHARD and O'BRIEN, 2004). The rapeseed oil as opposed to palm oil contains small quantities of saturated acids (10 times). The dominant fatty acid is mono-unsaturated oleic acid (> 60%), and contains linoleic to α -linolenic essential fatty acids ratio of 2:1, making it nutritious. Moreover, rapeseed oil is rich source of natural antioxidants, including tocopherols, polyphenols and phytosterols (SCARTH and MCVETTY, 1999). Traditional rapeseed oil used for frying is characterized by the following properties: it does not transfer taste, it has a high smoke point of 204-230 °C, it almost completely filters, if it is not well hot it quickly absorbs into the product (PRZYBYLSKI, 1999; MATTHÄUS, 2006). The smoke point for palm olein is 195 °C (MATTHÄUS, 2006).

The aim of the study was to investigate the chemical and thermooxidative stability of palm oil, rapeseed oil and their mixtures during frying.

Materials and methods

Materials

The research material were: fractionated palm olein (Poland) (*beta*-carotene – 375 mg/kg of oil), refining rapeseed oil (Poland), palm olein and rapeseed oil mixture composed in the ratio of 1 to 1, pre-fried and frozen French fries (Poland). Fresh oils, oils during frying and oils after frying were tested.

Frying of potato fries

The oil was heated to a temperature of 175 °C. French fries were fried in 1 liter oil every one hour for about 6.5 min – starting from 100 g portions in fryer Tefal type FA 700 TE. In order to maintain the same share of the product in the ratio to oil, that is in the ratio of 1 to 10, the portions of fries were reduced every 2 h by about 5 g (in proportion to the loss of oil during frying). The study lasted 32 h, 8 h per day for 4 days. The samples for oil analysis were collected after 3, 12, 24 and 32 h of frying. In the samples taken, acid value and the contents of polar fraction were measured. Organoleptic characteristics of fries fried in fresh oils were also rated.

Determination of fatty acid composition

Fatty acid methyl esters (1 μ l), prepared by ISO 5509:2000 standard method, were separated on a GC-FID system (TRACE™ 1300, Thermo Scientific, Waltham, MA, USA) equipped with a BPX 70 capillary column (60 m length, 0.22 mm i.d., 0.25 mm film thickness). Helium was used as a carrier gas at a flow rate of 1.5 ml/min. A split/splitless injector was operated at a temperature of 230 °C with a split rate set to 100:1, and the detector was The GC-FID interface temperature was 220 °C, the ion source temperature was 200 °C. The GC's oven temperature was programmed as follows: 80 °C hold for 2 min, ramped to 230 °C at a rate of 2.5 °C/min, hold for 5 min. Fatty

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acids were identified by comparing their retention times with authentic standards, and the results were reported as weight percentages.

Oil quality analysis

Acid value was determined according to ISO 660:2005. The results were shown in mg KOH per gram (mg KOH/g). Peroxide value was determined according to ISO 3960:1996. The results were shown in miliequivalent O₂ per kg (m Eq O₂/kg).

Oxidative stability determined via accelerated stability test (Rancimat)

The Rancimat Test – oxidative stability of oils was determined according to ISO 6886:2006. The research was carried out by using Rancimat type 679 (a temperature of 120 °C, air circulation 20 l/h) produced by “Metrohm” company (Switzerland).

The contents of polar compounds

Polar compound was determined according to ISO 8420:2002. The contents of polar compounds (w) were calculated from the difference between the mass of oil sample and the mass of eluted non-polar compounds, according to the formula (Eq. 1):

$$\omega = 100 - m_1 - m_2 \times 100 m \quad (\text{Eq. 1})$$

where: m_1 : the mass of the flask and the mass of the non-polar compounds (g), m_2 : the mass of empty flask (g); m : the mass of oil sample (g).

Sensory analysis

Organoleptic assessment of French fries was determined according to ISO 5492:2008 and BARYŁKO-PIKIELNA and MATUSZEWSKA (2009) using a 0-10-point scale, where “0” implies the absence of a feature and “10” implies the greatest severity of characteristics. Sensory evaluation was performed in triplicate with a selected and trained panel consisting of 10 persons. Flavour attributes – colour, oil odour, off-odour, fatness, gumminess, tenderness, oil taste, potato taste, off-flavour, a general quality – were investigated. A quantitative

sensory description was conducted using a graded 10-point scale to measure the intensity of attributes, leading from zero (“not detectable”) to ten (“intense”).

Statistical analysis

All experiments were carried out in triplicate. Statistical analysis was performed using Statistica 10 software. Data were expressed as Mean \pm SD or as percentage. Variables were compared by T test, one-way Anova; post hoc Tukey Test and the significance of differences among means were determined at $p < 0.05$.

Results and discussion

The characteristics of the material

The oils used in the research have been chemically analysed. The acid value, peroxide value, the contents of polar fraction and induction time in the Rancimat test were determined (Tab. 1). Refined oils, according to CODEX STAN 210-1999 should not have an acid value more than 0.6 mg KOH/g and peroxide value more than 10 m Eq O₂/kg. All the oils and the mixtures prepared of them and used for the test fulfill the conditions of CODEX STAN 210-1999. Fatty acids composition (Tab. 1) in palm olein was as follows: palmitic acid – 43.3%, oleic acid – 38.9%, linoleic acid – 10.2%, and it followed observations of other authors [SAMBANTHAMURTHI et al., 2000; MBA et al., 2017; ANIOŁOWSKA and KITA, 2016; LI et al., 2017]. Rapeseed oil contained (Tab. 1): palmitic acid – 4.9%, oleic acid – 51.1%, linoleic acid – 24.0%, linolenic – 12.7% and it followed observations of CODEX STAN 210-1999, SCARTH and MCVETTY, 1999 and MBA et al., 2017.

Determination of oxidative stability of oils – the Rancimat test

The Rancimat test is one of the dynamic, fast methods used to determine oxidative stability of fats. Changes taking place in fats which are the cause of the formation of secondary products of its decomposition are the basis for the designation of kinetic curves based on which the induction time is determined. The induction time is the conventional measure of oxidative stability of fats, which is a measure of the rate of oxidation (LITWINIENKO, 2001). The shorter the

Tab. 1: Characteristics of used material

	Palm olein X \pm SD	Rapeseed oil X \pm SD	Mixed oil X \pm SD
Acid Value [mg KOH/g]	0.22 \pm 0.000	0.17 \pm 0.064	0.30 \pm 0.000
Peroxide Value [m Eq/kg]	0.76 \pm 0.005	2.01 \pm 0.047	3.33 \pm 0.000
Polar compounds [%]	6.200 \pm 0.378	3.024 \pm 0.382	5.610 \pm 1.338
Induction time [h]	5.17 ^a \pm 0.154	4.32 ^b \pm 0.066	4.45 ^b \pm 0.280
Fatty acid composition:			
C16:0	43.3	4.9	24.3
C16:1	0.3	0.05	0.16
C18:0	4.6	2.45	3.55
C18:1	38.9	51.1	49.7
C18:2	10.2	24.0	17.0
C18:3	0.3	12.7	6.4
C20:0	0.1	0.6	0.31
C20:1	ND	2.8	1.4

Values X represent mean \pm standard deviation SD ($n = 3$). Different small letters in superscript in a row indicate statistically significant differences at the level $p < 0.05$.

induction times the more unstable oil.

The induction time (in hours) of fats used in the study is shown in the table (Tab. 1). The shortest induction time was for liquid rapeseed oil (4.32 h), therefore this oil is the most unstable. This is due to its fatty acids composition, that is the presence of large quantities (10 times more in comparison to palm olein) unsaturated fatty acids which are easily oxidized due to the double chemical bonds. The longest induction time was for palm olein 5.17 h.

Acid value

Acid value which is a measure of free fatty acids which arise because of hydrolytic degradation of fat during frying. According to EU legislation the acid value must not exceed 2.5 or 5 mg KOH/g and it depends on a country. In Poland it must not exceed 2.5 mg KOH/g. Changes in acid value and the time of frying for each test of fresh oil, and after 3, 12, 24, 32 h of frying were shown in the Fig. 1. After statistical analysis on the significance level equal to 0.05 (p=0.05) it was found that frying time has statistically significant impact on the average value of acid value. While analyzing the changes in acid value during frying its growth in the case of any oil used for frying was observed (Fig. 1). However, acid value in any of the test fats did not exceed 2.5 mg KOH/g after the last hour, that is after 32nd h of frying, which otherwise would mean the withdrawal of oil from further use. Therefore, these oils can be used for frying for longer than 32 h. This is also confirmed by other authors (ANIOŁOWSKA and KITA, 2016). PUFA contents in refined palm olein after about 30 h of frying in 180 °C were labeled at the level of around 0.52% by JASWIR et al. (2000), in rapeseed oil after 7 days of frying in temperature of 160 °C were labeled at the level of around 5.2% by PAUL and MITTAL (1996), while acid value in rapeseed oil after 24 h of frying in temperature of 180 °C was labeled at the level of around 0.33 mg KOH/g by DANOWSKA-OZIEWICZ and KARPIŃSKA-TYMOSZCZUK (2005). Basing on Excel's Reglign function [Excel 2007], which predicts future value based on available values, the time after which the examined oils will be discarded when they reach AV = 2.5 mg KOH/g) were calculated. This was as follow:

- Palm olein – after 94 h
- Rapeseed oil – 47.4 h
- Mixed oil – 95.5 h

Graphical presentation of the increase in acid number with frying time up to AV = 2.5 is shown in the graph below (Fig. 2).

One-way ANOVA was performed in order to verify whether the type of oil affects the changes of acid value during frying. Based on that a statistically significant effect of the type of oil on acid value was found. On the basis of this analysis it is concluded that between palm olein and mixture there are no statistically significant differences which means that these two oils behave similarly during fry-

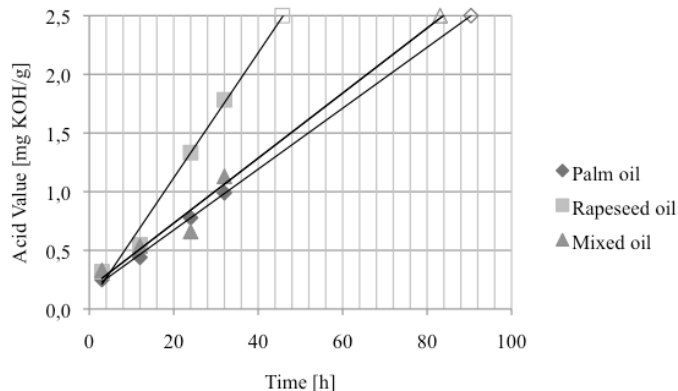


Fig. 2: The increase in acid number with frying time up to AV = 2.5

ing. A separate homogenous group constitutes rapeseed oil which is characterized by the lowest resistance to hydrolytic changes which means that the most free fatty acids arise from it during the frying. It may be associated with a more unsaturated fatty acid composition in comparison to palm olein.

The contents of polar compounds

The contents of polar compounds is currently considered to be the best indicator of the quality of frying fat (BERGER, 2005; ANIOŁOWSKA and KITA, 2016; HEIN et al., 1998; GERTZ, 2000), because it determines the degree of degradation of fat induced by thermo-oxidative changes. With the contents of polar fraction equal to 24% its further use is considered and limited and at 27% it is prohibited (BERGER, 2005; HEIN et al., 1998; GERTZ, 2000; GILL et al., 2004). However, in majority of countries the contents of polar compounds of 25% mean that the frying fats are not allowed be used (BERGER, 2005; LI et al., 2017; HEIN et al., 1998; GERTZ, 2000).

The changes in the contents of polar fraction and time of frying for different oils are presented in the Fig. 3. After statistical analysis on significance level equal to p=0.05 it was concluded that frying time has statistically significant influence on the content of polar compounds. For each oil, an increase of contents of polar compounds with frying time was observed. This is also confirmed by other authors (MATTHÄUS, 2006; LI et al., 2017; PAUL and MITTAL, 1996; GILL et al., 2004; LEDÓCHOWSKA and HAZUKA, 2006). After the final determination, that is after 32 h, the highest contents of this fraction was reached by mixed oil at 25.6% which means the withdrawal of the oil from further use. The lowest content of polar compounds was determined in rapeseed oil (11%). Each oil had its own characteristic initial contents of polar compounds. The largest quantity of

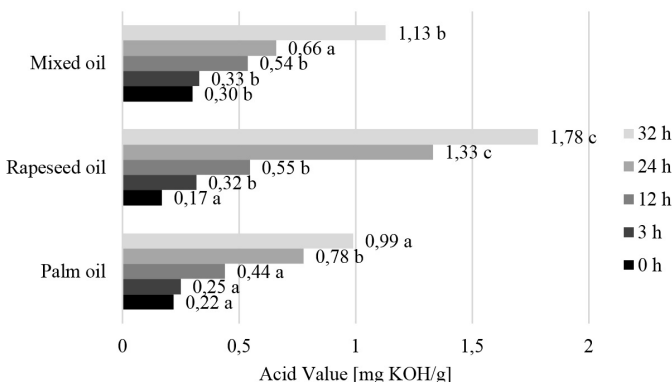


Fig. 1: AV changes in oil during frying.

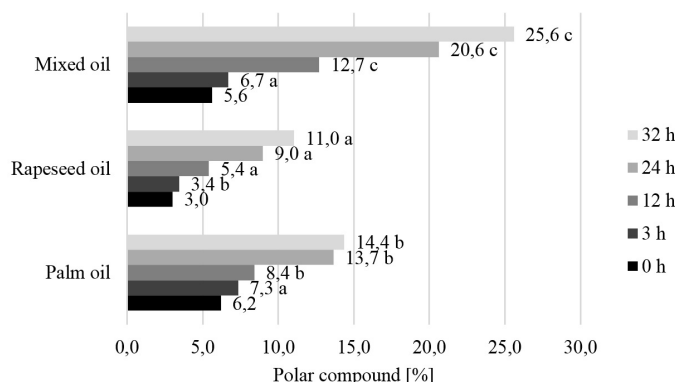


Fig. 3: Polar compounds changes in oil during frying.

this fraction contained palm olein, which is related to its chemical composition as it naturally contains 6-10% diacylglycerol, which in the chemical determination are the part of polar fraction. Referring the results of the determinations to the initial contents of polar compounds and comparing them to the final results it was noticed that after 32 h of frying its contents increase 2.3 times in palm olein, 3.6 times in the rapeseed oil, and 4.6 times in mixed oil. Similar dependencies between palm and rapeseed oil was observed by MATTHÄUS (2006) after 72 h of frying. As a result, it can be stated that the contents of polar fraction increased in the slightest degree in palm olein, which is tantamount to the fact that thermooxidative changes in it occur the slowest. PAUL and MITTAL (1996) marked the contents of polar compounds in rapeseed oil at 15% after 7 days of frying at 160 °C, while GILL et al. (2004) labeled in a double fractionated palm oil at 19% after frying about 32 h at 145 °C. Using Excel's Reglinx function a frying time after which palm olein and rapeseed oil exceed the illegal content of the polar fraction (polar fraction more than 25%) were provided, (Fig. 4).

This is as follows:

- Palm olein – after 70 h
- Rapeseed oil – after 87 h

The mixed oils were not considering because they reach 25% of polar fraction at 31 h.

Analyzing the results of one-way ANOVA for frying time of palm olein, no statistically significant differences were found in the contents of polar compounds between the fresh oil and after 3 h of use, between 3 and 12 h, and 24 and 32 h. In the case of rapeseed oil and mixed one, no statistically significant differences were found only between the contents of polar compounds in output oil and after 3 h of frying. One-way ANOVA was performed to check whether the type of oil is changing the contents of polar compounds with the time of frying. It has been found that the type of oil affects statistically significant changes in the contents of polar compounds during frying. It was also noticed that there were important differences between tested oils and, therefore, in each of these oils thermooxidative changes occur in varying degrees.

To examine whether there is a correlation between the value of acid value and the contents of polar compounds, simple correlation analysis was performed at the significance level $p=0.05$. It was found that for all tested oils, there is a statistically significant correlation between the contents of polar compounds and the acid value.

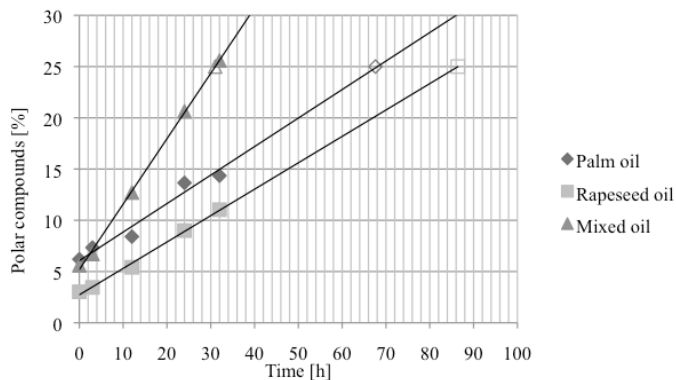


Fig. 4: Provides a frying time after which oils exceed the illegal content of the polar fraction 25%.

Interdependence is very high for each of the oils (oil mixed $r=95.1\%$, palm olein $r=98.2\%$, rapeseed oil $r=99.6\%$) and directly proportional, which means that the increase of acid value increases the contents of polar fraction and vice versa. And thus, with the increase in free fatty acids contents, the contents of polar compounds also increase. This is since free fatty acids belong to the polar fractions.

Organoleptic characteristic of French fries – profile method

In the organoleptic evaluation in consumers opinion the best fries were fried in rapeseed oil (9.4), similar results were obtained by RUTKOWSKA and JAWORSKA (2006) but other results have been obtained by MATTHÄUS (2006). The worst fries were fried in palm olein (4.6). Consumers issued an opinion that French fries in palm olein looked artificial and had off-flavour. The reason for that consumer sensation was probably the content of carotenoids, which gave an unpleasant aftertaste and a yellow colour of French fries. Based on these opinions we should not fry on the palm olein with of beta-carotene, because it might gives, after termal treatment, negative sensory characteristics of French fries (FRATIANNI et al., 2010; FRATIANNI et al., 2017; XIAO et al., 2018). It can be assumed that it would also have similar influence on other products. Graphic presentation of the organoleptic evaluation is illustrated in Fig. 5.

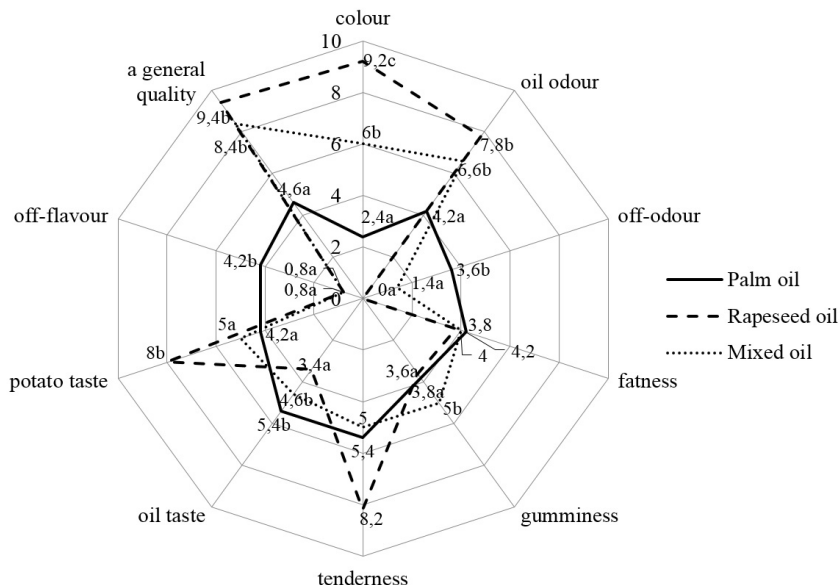


Fig. 5: Organoleptic characteristics of French fries fried in palm oil, rapeseed oil and mixed oil.

Generally, fries rating were determined by the type of oil, which was also proved by MATTHÄUS (2006) and RUTKOWSKA and JAWORSKA (2006). Fries fried in mixed oil and rapeseed oil did not show significant differences for such parameters as the smell of oil, strange smell, strange taste and general quality. Between the French fries in palm olein and mixed no significant differences were shown for the assessment of tenderness, taste of potato or oil. Among all the oils used, significant differences appeared in colour of the French fries, which means that each oil gave a characteristic colour of the fries depending on the content of carotenoids.

Correlation analysis was performed at the significance level $p=0.05$ to check whether there is a correlation between the assessed attributes and general rating. On that basis, it was found that there is a very strong and directly proportional correlation between colour and general assessment of French fries in palm olein ($r=91.9\%$) and mixed oil ($r=91.3\%$). This is due to the presence of carotenoids, which gives intense yellow colour of the fries, a bit softer in fries fried in mixed oil. Also, the existence of a very strong, directly proportional correlation was proved for the fragility – overall assessment ($r=91\%$) and taste of the potato – overall assessment ($r=91.3\%$) for the French fries in rapeseed oil. Very strong, but inversely proportional correlation emerged between the sensation of rubbery and the overall assessment ($r=-91.3\%$) for the French fries in mixed oil. This means that the more chips will be rubbery, the less desirable by consumers. In fries fried in palm olein the existence of very strong, direct proportional correlation was found between the strange taste and general assessment ($r=91.7\%$).

Conclusion

The tested oils and mixtures made of them in a 1:1 ratio were of good quality which was confirmed by chemical determinations. Because of a 32-hour frying the smallest thermooxidative changes occurred in palm olein, as evidenced by the value of acid value and the contents of polar compounds. At the end of the experiment mixed oil showed the highest contents of polar fraction more than 25.0%, which means the prohibition of further use of this oil. In the consumer rating French fries fried in rapeseed oil were the best assessed. French fries in palm olein have been recognized by consumers as “artificial”, “chemical”, and “distasteful”. The reason for such opinions was the content of *beta*-carotene to this oil. *Beta*-carotene had a significant influence on the colour of French fries. However, due to the rapid disintegration of *beta*-carotene such oil would not find application in industrial frying. Palm olein compared to rapeseed oil is characterized by greater thermooxidative stability. Mixtures composed of palm olein-based partly take over its properties.

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