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Influence of rapeseed meal on lard stability

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Abstract: The experiment focused on the possibility to utilise the antioxidant potential of rapeseed meal to stabilize fats. The lard, which was used for this purpose, was characterized by gas chromatography. At first the non-sieved meal was added in lard. It is the least technologically difficult method of utilizing meal. Then, the meal was sieved to obtain five fractions, which were added to lard. The aim was to find a fraction of meal that would best stabilize the lard. The results of lard stability with added fractions were compared with the stability of lard enriched with non-sieved meal. Finally, we obtained ethanol and ethyl acetate extracts from non-sieved meal and from the fraction which was the best stabiliser of lard. The aim was to study the effect of these extracts on the stability of lard.

Rapeseed meal has stabilized the lard already at 0.5 wt. % content. The non-sieved meal addition of 1, 2 or 4 wt. % has improved the stability of lard by 1.2—2 times. Adding 8—15 wt. % of meal into lard has increased its stability by 3—8 times. The best lard stability has been determined in the fraction retained on the sieve with mesh size 0.15 mm. The lard with added sieved meal has gained a comparable stability the same as after addition of non-sieved meal. The lard with the same additions of extracts (ethanol and ethyl acetate) from non-sieved meal and from meal with sizes 0.15—0.315 mm was more stable than the lard with addition of meal alone. The lard containing ethanol extracts (0.5 wt. %) has a better stability than the lard containing butylated hydroxytoluene (0.02 wt. %).

Keywords: rapeseed meal, lard, sieving, extracts of meals, lard stability

Introduction

In the manufacture of rapeseed oil the rapeseed meal is a by-product used to produce feed for animals. It is a good source of antioxidant active substances that can be utilized to stabilise foods (Schmidt and Pokorný, 2005; Amarowicz et al., 2000). Crude post-expelled rapeseed oil had the highest phenolic content of the oils (Vuorela, 2005; Koski et al., 2003). In the production of rapeseed oil, most of these antioxidant active compounds remain in the rapeseed-cake and meal (Amarowicz et al., 2000). Rapeseed meal is formed by the extraction of rapeseeds with most commonly used technical hexane. According to Chen et al. (1996) and Naczk et al. (1998), the rapeseed meal contains significant amounts of protein, vitamins A, E, minerals, phenolic acids, polyphenols, flavonoids and condensed tannins. In the rapeseed meal the content of phenolic compounds is in the range 1—2 % which is 5 times greater content of phenolic compounds compared with soybean meal (Wanasundara and Shahidi, 1994). We have investigated how the addition of non-sieved rapeseed meal, sieved meals and their extracts increase the lard stability. For this purpose was used the method (automatized) of accelerated oxidation of fats with determination their induction period by apparatus Rancimat 743 (AOCS Cd 12b-92). The other applications of accelerated oxidation of fats are mainly Schaal and Swift test. There results have good correlation with real storage stability of oils, but these methods are not automatized (Schmidt, 2010).

According to Schmidt (2010), ethanol and methanol are suitable for extraction of polar antioxidants, such as flavonoids and phenolic acids from rapeseed meal. Antioxidants obtained with these solvents are suitable to be added, e.g. into meat products with higher fat content. According to Wanasundara and Shahidi (1994), ethanol extract of rapeseed meal was added to rapeseed oil in the concentration from 0.5 to 1 g kg^{-1} and that was more effective than 0.2 g kg^{-1} addition of butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and mixed antioxidant BHA/BHT/monoacylglycerol citrate.

Experimental

Materials and Methods

The following materials were used: the lard was prepared in laboratory from commercially available pork bacon; rapeseed meal was taken from oil industry, after the extraction of lipids by hexane (Palma Group, a.s., Bratislava)

Chloroform p.a., diethyl ether p.a., glacial acetic acid p.a., ethyl acetate (99.5 % v/v), methanol p.a., potassium iodide p.a., starch, sodium thiosulfate p.a (Mikrochem s.r.o., Slovakia), ethanol, (96 % v/v) (Leopoldov, Slovakia), *n*-hexane p.a., potassium hydroxide p.a., potassium chloride p.a., sodium sulphate p.a. (Lachema, Czech), butylated hydroxytoluene, *p*-anisidine (Sigma-Aldrich, USA), deionized water (prepared in the laboratory), nitrogen (Messer Tatragas, Slovakia).

Instruments and equipment

Analytical balance Mettler AJ 150 (Mettler – Toledo, Switzerland), Analytical balance AS 310/C/2 (Radwag, Poland), filter paper 390 (Filtrak, Germany), chromatographic station CSW 32 (DataApex, s.r.o., Czech), Rancimat 743 (Metrohm Ltd., Switzerland), rotary vacuum evaporator (Model Unipan 350, Poland), spectrophotometer Schimadzu 1601 (Schimadzu Corporation, Japan), magnetic stirrer MST basic (IKA Werke GmbH, Germany), heating mantle LTH 250 (Brnenska Druteva, Czech), sieving machine VP 200 and five sieve with mesh size: 0.75 mm, 0.63 mm; 0.315 mm; 0.15 mm a 0.05 mm (Construction engineering, Czech), drying-oven KWC 100 (Poland) and Simax laboratory glasses.

Analytical methods

The peroxide value was determined iodometrically and expressed in mmol 0.5 O_2 kg^{-1} of fat (AOCS Cd 8-53). The acid value was determined by alkalimetric titration and expressed in mg KOH g^{-1} of fat (AOCS Cd 3d-63). The iodine value was determined iodometrically according to Hanuš and expressed in g I_2 100 g^{-1} of fat (ČSN 58 0101). *p*-Anisidine value express the content of aldehydes in fats, especially 2-alkenals, by measuring the absorbance of the reaction product (IUPAC II.D.26.). Content of residual fats in rapeseed meal was determined using a Soxhlet apparatus. The extraction solvent petroleum was boiled 3.5 hours (IUPAC, I.B.2.).

The stability of fats was determined by the method of accelerated oxidation with the apparatus Rancimat 743 at a constant temperature of fat (110 °C) and air flow (20 dm^3 h^{-1}), which bubbled through the sample. The stability of lipids is expressed by induction period in hours (AOCS Cd 12b-92). The induction period is expression of the resistance of lipids to oxidation. It is exactly the time during which oxidation takes place at a constant and very slow speed (Velasco *et al.*, 2004). The antioxidant activity of the lard enriched with rapeseed meal and meal extracts is expressed as a protective factor (*PF*) calculated as a ratio of the induction period of lard with the addition of meal or extracts (IP_A) and without the addition of meal or extracts (IP_0):

$$PF = IP_A / IP_0 \quad (1)$$

Analysis of fatty acids content in lipids

Fatty acids were derived to methyl esters according the method of Christopherson and Glass (1969). To separate methyl esters the gas chromatograph Hewlett Packard 5890 series II (Palo Alto, USA) with a capillary column Supelcowax 10 (30 m × 0.53 mm; 1.0 μm film) was used. The sample was analyzed under the conditions: carrier gas – helium (7 cm^3 min^{-1}), the injection temperature was 250 °C, FID detector 260 °C.

Procedures

By rendering of 2 kg pork bacon 1.35 kg lard was obtained. This lard was dehydrated with sodium sulphate and filtered at melting temperature. Rapeseed meal contained on average 2.88 ± 0.13 % fat. Thus obtained lard and rapeseed meal were stored in a clear glass flask in a protective atmosphere, in a refrigerator at 5 °C (average temperature).

Preparation of rapeseed meal fractions: Rapeseed meal was sieved in a sieving machine (see Fig. 1) and divided into five fractions having different particle sizes. Fraction 1 contained particles longer than 0.75 mm (max. to 1 cm), which consisted mainly of hull conglomerates and rapeseed kernels (see Fig. 2). Fraction 2 and 3 contained rapeseed hulls with size 0.63–0.75 mm (see Fig. 3) and 0.315–0.63 mm (see Fig. 3). Fraction 4 was a mixture of hulls and rapeseed kernels with size 0.15–0.315 mm (see Fig. 4) and the fraction 5 contained dust of kernels with sizes 0.05–0.15 mm (see Fig. 4). The lard was enriched with 0.5, 1, 2, 4, 8 and 15 wt. % of sieved

Fig. 1. Sieving machine VP 200.

Fig. 2. Fraction 1 retained on a sieve with mesh size 0.75 mm.

rapeseed meal and non-sieved rapeseed meal. Ethanol A and ethyl acetate A extracts were obtained from the non-sieved meal. Ethanol B and ethyl acetate B extracts were obtained from the faction of meal with size 0.15—0.63 mm.

The extraction procedure: The meal weighing 20 g was mixed with 200 cm^3 of ethanol and at the second attempt with 200 cm^3 ethyl acetate on a magnetic stirrer (at 300 rpm) for one hour at 50 °C. After that time extraction continued even 24 hours at 25 °C without stirring. During extraction the Erlenmeyer flask were covered with aluminium foil. The extract of rapeseed meal (see Fig. 5) was filtered and the solvent was evaporated under reduced pressure in a rotary vacuum evaporator. The extract concentrations were adjusted by dissolving 1 g of residue (after evaporation) in 100 cm^3 solvent used in extraction.

Fig. 3. Fraction 2 retained on the sieve with a mesh size 0.63 mm (left), fraction 3 retained on a sieve with mesh size 0.315 mm (right).

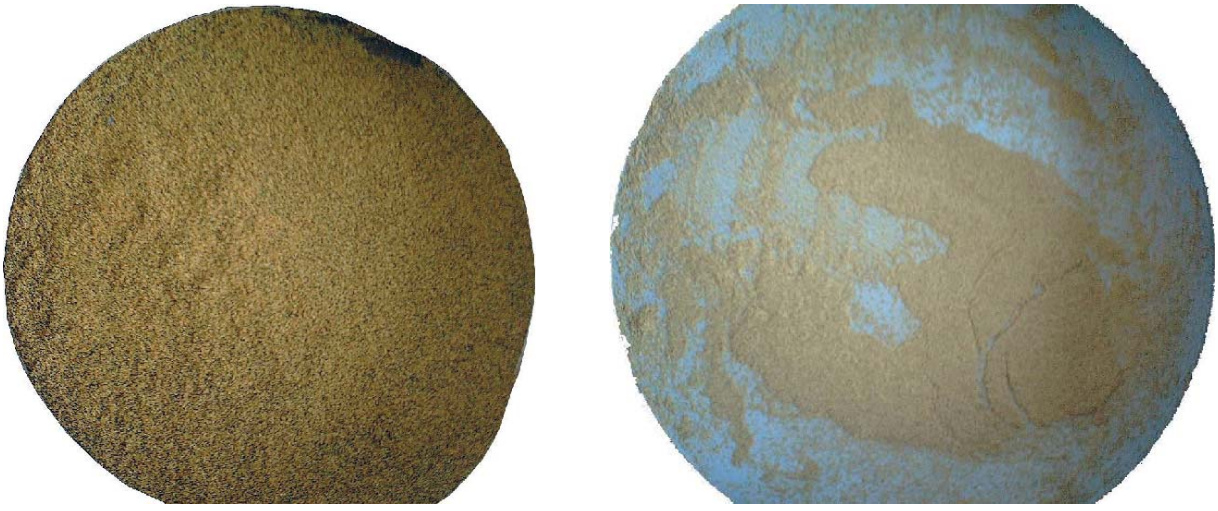

Fig. 4. Fraction 4 retained on the sieve with a mesh size 0.15 mm (left), fraction 5 retained on a sieve with mesh size 0.05 mm (right).

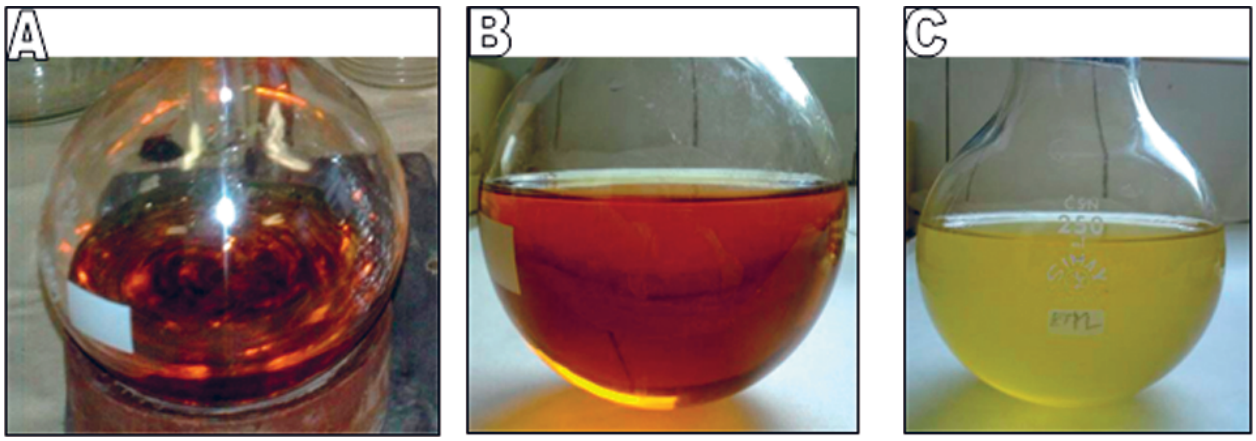

Fig. 5. Ethanol extract A from non-sieved rapeseed meal (A), ethanol extract B (B) and ethyl acetate extract B from sieved meal (C) (sieved meal-fraction 4).

Statistical analysis

A statistical analysis was carried out in the program Statgraphics Plus, version 3.0 for Windows (Manugistic Inc., USA). The chemical parameters were determined for every sample five times. The mean value of the measured data was determined with confidence interval (95.0 %), which was calculated with one-variable analysis of data. The figures were created in the program Origin, version 6.1 (Origin Lab Corporation, USA),

Results and discussion

Content of fatty acids and chemical properties of lard

From the fatty acids analysis of lard (Table 1.) is visible that the most abundant are oleic acid (39.6 %) and palmitic acid (24.3 %). Stearic acid also contributes a significant proportion (15.5 %) to the composition of fatty acids in lard. According to Ďuračková (1998), higher carboxylic acids with only one double bond, e.g. oleic acid, are almost not being damaged with lipoperoxidation. The higher saturated carboxylic acids are oxidized only under extreme conditions. From this fact results certain stability of lard and a disadvantage is the absence of natural antioxidants in the lard. The lard was obtained by rendering of pork bacon and served as fat without antioxidant. Therefore we analysed their chemical parameters and presence of fatty acids. The determined iodine value 57 g I_2 100 g^{-1} of fat is typical for lard. According to Ilavská *et al.* (1990) the iodine value of lard is in the range 53—77 I_2 100 g^{-1} of fat. Compared with the data of Shahidi *et al.* 2005, the presence of fatty acids in lard and their chemical parameters (Table 1.) are in good correlation.

Tab. 1. Chemical parameters and presence of fatty acids in lard.

Chemical parameters of lard		
Iodine value	[g I_2 100 g^{-1} of fat]	57.74 ± 0.41
Acid value	[mg KOH g^{-1} of fat]	1.29 ± 0.07
Peroxide value	[mmol 0.5 O_2 kg^{-1} of fat]	2.43 ± 0.16
p-Anisidine value		0.90 ± 0.03
Fatty acids content in lard		[area %]
14:0	Myristic acid	1.3
16:0	Palmitic acid	24.3
18:0	Stearic acid	15.5
20:0	Arachidic acid	0.2
16:1	Palmitoleic acid	2.1
18:1 *cis*-9	Oleic acid	39.6
18:1 *cis*-11	Vaccenic acid	3.0
20:1	Gadoleic acid	0.8
18:2	Linoleic acid	9.6
18:3 *cis*-9, 12, 15	α-Linolenic acid	0.9
Others		2.7

Sieving of rapeseed meal

The best method to fractionate the rapeseed meal was chosen after sieving the meal under three various conditions.

We were looking for a suitable relationship between time and vibration performance of meal sieving. First, the meal was sieved for 40 min. at sieving vibration performance 1.5. The second time the meal was sieved for 60 min. at vibration performance 3.5. The third time the meal was first fractionated for 40 min. at vibration performance 1.5 and then it continued to be fractionated for 60 min. at vibration performance 3.5. The using of third sieving method gave the best results. The rapeseed meal was retained better on the sieve 2, 3, 4 and 5, compare with other sieving method. The results on percentage compositions of fractions obtained by sieving are in Fig. 6.

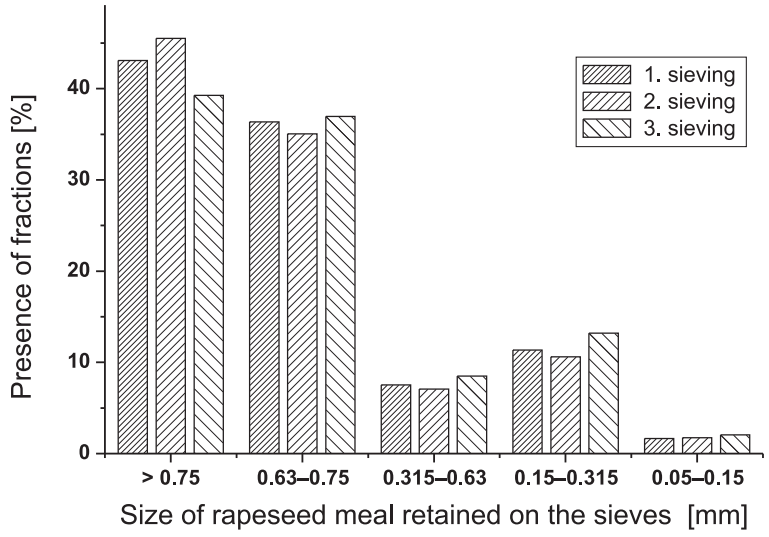

Fig. 6. Composition of fractions obtained by sieving of rapeseed meal.

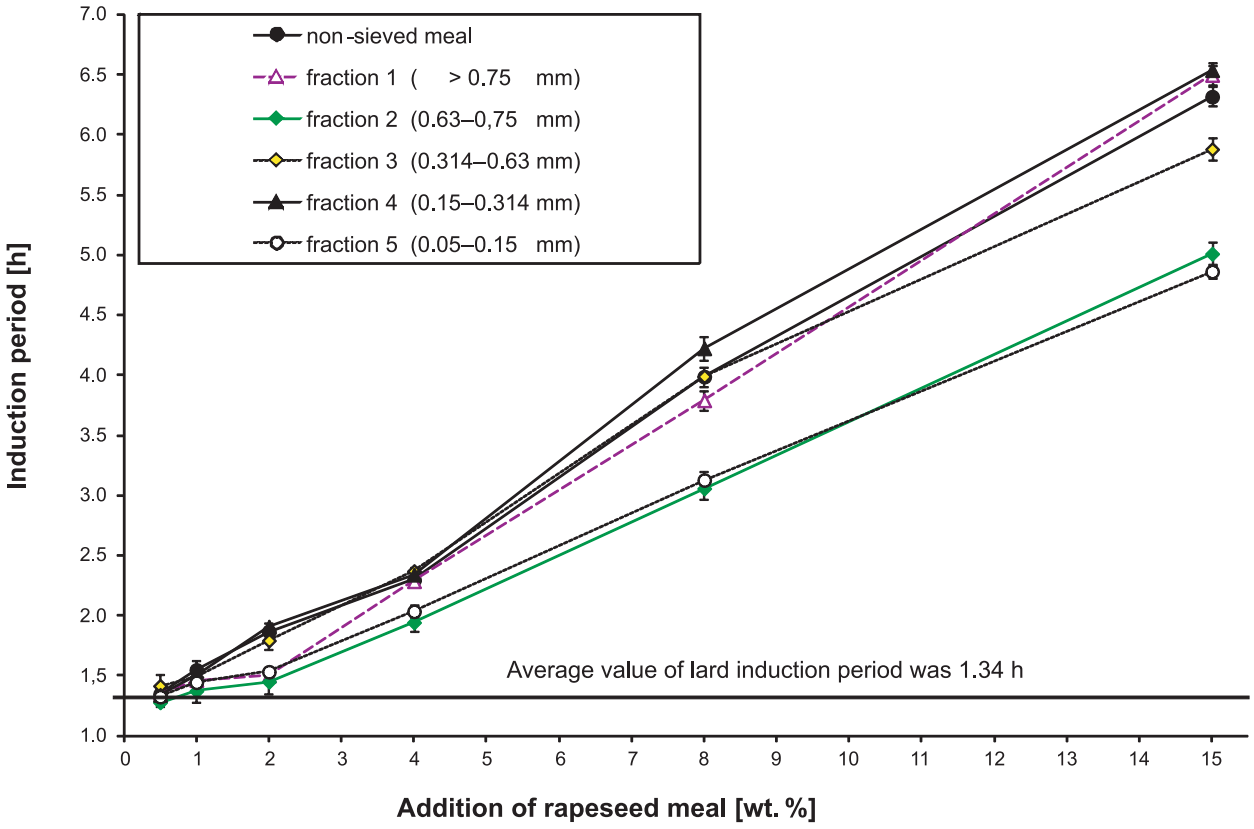

Fig. 7. Influence of rapeseed meal addition on the lard stability,

Lard stability affected by added rapeseed meal

A model system (lard/rapeseed meal) modelling lard with added rapeseed meal, containing a lot of phenolic compounds, was created. Lard does not contain natural antioxidants. That is why lard was used as a substrate to determine the stability and also the protective effect of rapeseed meal against oxidation of fats. An accelerated oxidation of lard was simulated with the apparatus Rancimat 743 at 110 °C.

Fig. 7 describe stability (induction period) of lard which depends on the addition of sieved and non-sieved rapeseed meal. The best lard stability was obtained by enriching lard with fraction 4. However, non-sieved meal added in lard had a similar stability effect as fraction 4. An acceptable stability of lard was found in mixtures of lard with fraction 1 and fraction 3. Compared with other fractions, adding fraction 5 and fraction 2 demonstrated the lowest lard stability.

Protective factor best refers to the protective effect of rapeseed meal in lard before self oxidation of lard. The best protective effect against oxidation of lard was found for fraction 4 and non-sieved meal (Fig. 8). We have seen in the microscope that the fraction 4 contained mainly kernels and lower rapeseed hulls. The non-sieved rapeseed meal consisted mainly of hull conglomerates and rapeseed kernels. According to Khattab *et al.* (2010), rapeseed meals have contained 15—18 g of total phenols on kg meals. The total phenolic content in dehulled rapeseed flour has been 11—13 g kg^{-1}. Based on these results, the non-sieved meal contained more phenols than the fraction 4. At the same addition of sieved and non-sieved meal into lard, the protection effect of non-sieved meal can be lowered owing to the presence of dust particles. It could be suitable to determine the content of total phenols in non-sieved rapeseed meal and its fractions. The 8 wt. % addition of fraction 4 and non-sieved meal protected lard better than 0.01 wt. % addition of BHT (100 mg kg^{-1} of lard). The non-sieved meal and fractions 1, 3 and 4, with 15 wt. % additions into lard had in average the protective effect 1.2 times greater than 0.02 wt. % addition of BHT into lard (200 mg kg^{-1} of lard). Comparing our results from the work of Kreps and Schmidt (2009), it was found that BHT has a better protective effect on lard than on vegetable oils.

Lard stability affected by added rapeseed meal extracts

We tried to get the antioxidants from rapeseed meal by using the method of extraction. Even a low amount of antioxidants added into the lard may markedly improve the lard stability.

Lard containing extract from non-sieved meal and the fraction 4 (0.15—0.314 mm), won by ethanol, had on average 1.2 times higher stability than lard enriched by extracts won by ethyl acetate. Fig. 9 describes that even small added amounts of extracts (0.01, 0.02, 0.05 wt. %) have stabilized the lard.

The stability of lard with added 0.5 wt. % extract B won by ethanol (obtained from fraction 4) was 4.2 times greater than the same amount of fraction 4 added to lard. The lard with added ethanol extract A had a comparable stability with the stability of the lard enriched with added ethanol extract B.

The protective effect of the extracts on lard was recognized already at 0.01 wt. %. The ethanol extract A from non-sieved meal and ethanol extract B from fraction 4 (Fig. 10) had the best protective effect against oxidation of lard. The protective factor of added (0.5 wt. %) ethanol extract A was 1.5 times greater than the protective factor of the same amount of added non-sieved meal. The 0.5 wt. % addition of ethanol extract had still greater protective effect on lard than 0.02 wt. % BHT (200 mg kg^{-1} of lard).

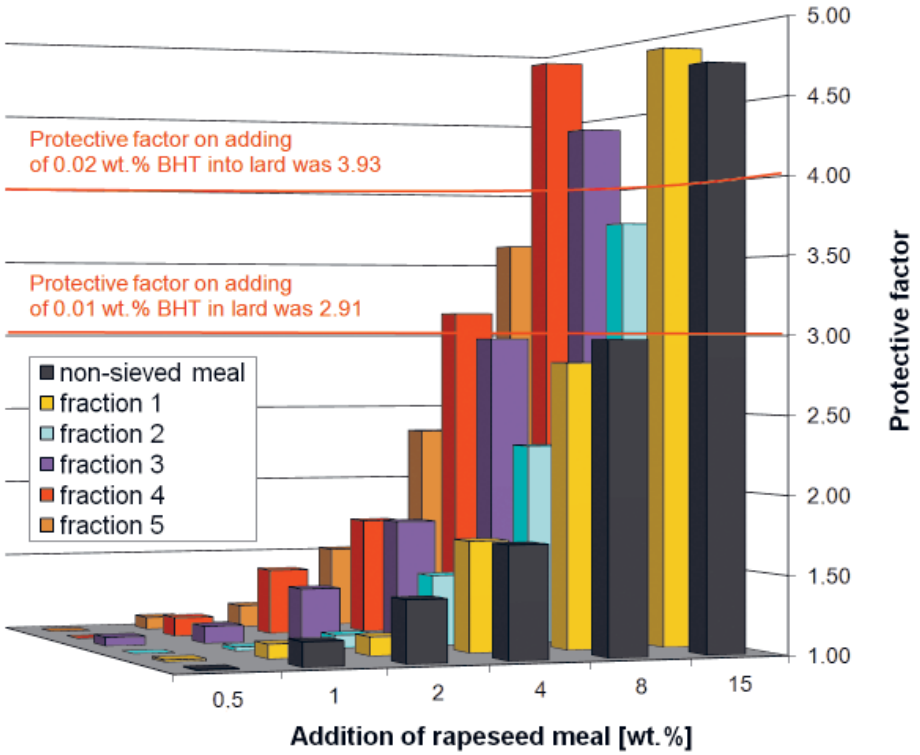

Fig. 8. Protective factor of rapeseed meal added into the lard.

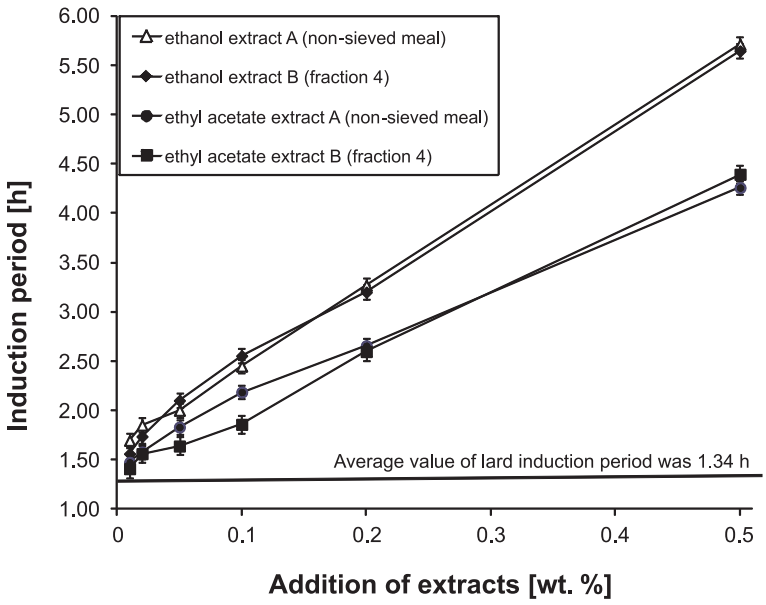

Fig. 9. Influence of rapeseed meal extracts on lard stability.

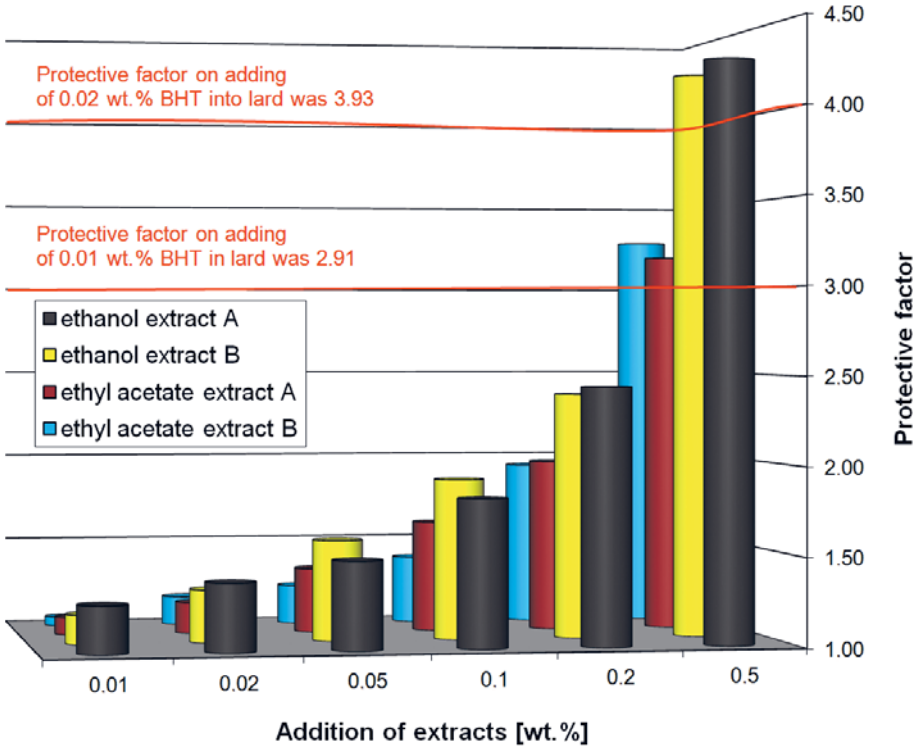

Fig. 10. Protective factor of extracts from rapeseed meal added into lard.

The protection effect of ethanol extracts was greater than the ethyl acetate extracts. The reason may be the better solubility of polar antioxidants from meal in ethanol than in ethyl acetate. According to Schmidt (2010), ethanol and methanol are suitable for extraction of polar antioxidants, such as flavonoids and phenolic acids from rapeseed meal. According to Khattab *et al.* (2010), rapeseed meal has contained mainly sinapine 9–10 g kg^{-1}, than sinapoyl glucose 1–2 g kg^{-1} and sinapic acids 0.3–0.4 g kg^{-1}. The content of flavonoids in rapeseed meal and oils has not been yet quantitatively determined.

Conclusions

From the experiments it can be concluded that the non-sieved rapeseed meal and extracts from it can stabilize fats well. The stability of lard and the protective effect of various combinations of

added non-sieved and sieved meal have been tested. The best results have been obtained by adding fraction 4 (0.15—0.315 mm) and non-sieved meal to lard. Their 8 wt. % addition protected the lard in a similar way as 0.01 wt. % addition of BHT (100 mg kg^{-1} of lard). Only in case of considerable enrichment of lard with rapeseed meal comparable protective effects, such as with BHT, have been obtained. The ethanol and ethyl acetate extracts were prepared from non-sieved meal and from fraction 4. The rather low addition of extracts to the lard (0.01 wt. %) markedly protects lard against oxidation. However, amazing protective effects on lard have been demonstrated by ethanol extracts of non-sieved meal. Their protective factor at 0.5 wt. % addition was 1.5 times greater than the protective factor of the same amount of non-sieved meal. It was even greater than 0.02 wt. % addition of BHT into lard (200 mg kg^{-1} of lard).

In our experiment we have proven that rapeseed meal may not only serve as feed for animals but is also suitable to increase stability and shelf-life of fats. The best protective effect against oxidation of fats has been found for ethanol extract from rapeseed meal.

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