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A Versatile Apparatus for the Bench Scale Bleaching and Deodorisation of Vegetable Oils

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Abstract

Filip V., Kyselka J., Hrádková I., Berčíková M., Cihelková M. (2015): **A versatile apparatus for the bench scale bleaching and deodorsation of vegetable oils**. Czech J. Food Sci., 33: 537–544.

A versatile isothermal glass apparatus provided with sintered glass on the bottom was designed for the bench scale adsorptive bleaching and deodorisation of vegetable oils. The stream of argon bubbles agitated the sample in both cases and protected the vegetable oil effectively against undesirable autoxidation and photooxygenation changes. However, a variable concentration of hexanal (27–30 μmol/kg) was always present in half-refined oils due to the heterolytic fragmentation of alkyl hydroperoxides. The colour on the Lovibond scale and the content of phosphorus (< 5 mg/kg) were efficiently decreased during the laboratory bleaching of rapeseed oil. It was found out that the adapted glass apparatus connected with a vacuum pump (1 hPa, a stream of argon gas instead of stripping steam) was able to reduce the content of carbonyl compounds below detectable concentration at 220–240°C. Furthermore, the extent of minor geometrical and positional isomerisation reactions was negligible (0.035–0.130 wt%). The results of the bench scale bleaching and deodorisation experiments were completely comparable with the industrial equipment under reduced pressure of the air.

Keywords: hexanal; alkyl hydroperoxides; heterolytic cleavage; rapeseed oil; bleaching

The usual arrangement of bench scale (laboratory) refining of vegetable oils includes degumming, alkali neutralisation, adsorptive bleaching, and deodorisation. Chemical deacidification by the addition of a caustic is suitable for the removal of free fatty acids from degummed oils with the content of free fatty acids lower than 1.5 wt%. Deacidification of edible oil with higher acid values has to be performed in miscella or during the physical refining stage. The reason is the excessive loss of "neutral" oil in a soapstock after the caustic treatment (Bhosle & Subramanian 2005). Degumming and alkali neutralisation are designed to decrease the content of phosphoglycerolipids below 0.0025 wt% (i.e. 25 mg P/kg) before adsorptive bleaching (Segers 1983). The output of bleaching process is bleached (half-refined) vegetable oil that usually contains < 0.10 wt% of free fatty acids and 5 mg/kg of phosphorus. Deodorisation, the last stage of bench scale vegetable oil refining, is a critical operation from the technical point of view. On a laboratory scale it can performed by a short path distillation unit, which enables also physical refining (physical deacidification) allowing the removal of free fatty acids, odour, and flavour components in one step (Lutišan & Cvengroš 1995; Martins *et al.* 2006). Therefore, caustic neutralisation can be omitted when free fatty acids and carbonyl compounds are eliminated during the last refining stage (Čmolík & Pokorný 2000).

Adsorptive bleaching of edible oils is a unit operation based on the principle of the physical and chemical adsorption of colorants onto the surface of a convenient bleaching agent (Bockisch 1998; Gomez de Oliveira & Porto 2005). Bleaching earths are

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generally activated by mineral acid treatment. The most common bleaching agents are aluminium hydrosilicates – montmorillonite and bentonite (Zschau 1985; Kirali & Lacin 2005), with slightly acid properties. They are also cation exchangers. The adsorption of chlorophyll, carotenes and glycerophospholipids (Čmolík & Pokorný 2000; Rossi *et al.* 2003) is accompanied by undesired side reactions, which should not be ignored. Bleaching earth effectively catalyses the lipid peroxidation (Kim *et al.* 2007) and fatty acid isomerisation reactions. Therefore, adsorptive bleaching is normally conducted under vacuum (50 hPa) at 90–110°C to avoid the above-mentioned side reactions (Bockisch 1998). However, secondary alcohols such as phytosterols undergo elimination reactions during the bleaching process that result in the formation of $\Delta^{3,5}$-steradienes. Dehydration of sterols is an evidence for the determination of edible oil refining in general (Gordon & Firman 2001; Crews *et al.* 2014). Bleaching of edible oils on a commercial scale is usually realised in a stirred adsorber under reduced pressure. This design is transferable into a laboratory scale (Bockisch 1998).

Half-refined vegetable oil does not meet the requirements of consumers because of its poor flavour and odour. The reason is the decomposition of alkyl hydroperoxides resulting in the formation of odoriferous volatile compounds (aldehydes, ketones, alcohols, and hydrocarbons). The deodorisation stage is responsible for the removal of compounds with relative molecular weight ≈ 300 g/mol by steam distillation (3–6 hPa, 200–240°C) in order to improve the quality of fully refined edible oil (Bockisch 1998). Carbonyl off-flavour compounds are usually accompanied by free fatty acids, squalene, tocopherols and phytosterols, which are ordered according to the relative vapour pressure. Thus, deodorisation condensate is a rich source of valuable sterols and vitamin E derivatives (Čmolík & Pokorný 2000; Xu *et al.* 2002). Isomerisation, oligomerisation, and numerous side reactions can occur during deodorisation. Heat induced geometrical and positional isomerisation of unsaturated fatty acids can result in the formation of all-*trans* conjugated diene system, the incoming reactants for consecutive oligomerisation according to the Diels-Alder reaction mechanism (Hénon *et al.* 1999; Cihelkova *et al.* 2013).

Process conditions used in the case of a deodorising apparatus operating on an industrial scale are highly difficult and their transfer to the bench scale apparatus is not easy. Therefore, our attention was primarily focused on the design of a versatile isothermal glass apparatus for the bench scale adsorptive bleaching and deodorisation of vegetable oils.

MATERIAL AND METHODS

Material. Standard deeply degummed rapeseed oil (low erucic rapeseed oil – LERO, the content of free fatty acids 0.28 wt%, peroxide value 0.4 mmol ½ O_2/kg, phosphorus content 15 mg/kg), which was purchased from the local producer Usti-Oils s.r.o. (Ústi n/L., Czech Republic), was the input feedstock of the bleaching process. Adsorption experiments were performed with commercial bleaching clay Tonsil Optimum 210 FF (Clariant, Munich, Germany). Deeply degummed, alkali neutralised and bleached rapeseed oil (LERO; Usti-Oils s.r.o.; the content of free fatty acids 0.25 wt%, peroxide value 0.6 mmol ½O_2/kg, phosphorus content 3 mg/kg) simulated half-refined edible oil entering the bench scale deodorisation experiments. Fatty acid composition of rapeseed oils was determined by capillary gas-liquid chromatography. Hexanal and nonanal standards were purchased from the Sigma Aldrich Company (Prague, Czech Republic). All other reagents and solvents were of analytical grade.

Testing and application of adapted bench scale apparatus. The bench scale apparatus provided with a sintered glass on the bottom has been previously applied to hydrogenation (Zajíc *et al.* 1984), isomerisation and polymerisation of fatty acids and their esters with high reaction yields (Cihelkova *et al.* 2013). Similar devices were designed for the laboratory bleaching and deodorisation of vegetable oils (Šmidrkal *et al.* 2014). Our improvement proposal (Figure 1) was based on the batch isothermal experiments performed in the glass apparatus equipped with porous frit (S4, pore diameter 5–15 μm) in the lower part and inert gas exhaust in the upper part, which was placed in an adapted oven of gas chromatograph (Chrom 4; Laboratorní přístoje, Prague, Czech Republic). Heat input of the air heating has to be extended to 4 kW. Adapted thermostat could operate in the range from 40°C to 300°C within experimental error (at 200°C the instrument error was approximately ± 0.5°C). Temperature was monitored by a digital thermometer F200 (Automatic Systems Laboratories, Croydon, UK). Glass apparatuses were developed in cooperation with glass making workshops of the University of Chemistry

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and Technology Prague, Czech Republic (UCT). Designed vessels were 500 mm high with different inner diameters 30–70 mm. They enable researchers to process 200–1000 ml of vegetable oil with a maximum height of the layer 300 mm. The stream of argon (Ar 4.8, purity 99.998%, oxygen content < 3 ppm), which passed through the sintered glass upwards into the sample of rapeseed oil, was regulated (20–100 dm^3/h). This system brought about a strong agitation and consequent effective distribution of argon bubbles. Therefore, the linear gas velocity was derived as 0.2–2.0 cm/s according to the flow control. Furthermore, described laboratory experiments could be transferred into a similar microapparatus in order to reduce the scale of processed batch (10^0–10^1 ml). An adapted bench scale apparatus could simulate the deodorisation process after connecting to a vacuum pump (under the vacuum < 2 hPa).

Rapeseed oil bleaching. Standard deeply degummed rapeseed oil (LERO, Usti-Oils s.r.o.) was pre-heated to 50°C and loaded into the glass apparatus (bleacher, Figure 1) through which a stream of argon passed upwards (0.2–1.0 ml Ar/ml of rapeseed oil per min) in order to remove the remaining air and to agitate the oil sample properly. The batch was subsequently heated up to a bleaching temperature of 90–110°C and the bleaching clay Tonsil Optimum 210 FF was added. The temperature range and bleaching clay content were variable parameters. The stream of argon was increased to 2.0–4.0 ml of Ar/ml of rapeseed oil per min during the adsorptive bleaching process. Laboratory bleaching was finished after 40 min and half-refined oil was filtrated after cooling down to 70°C. Three parameters were monitored: colour on the Lovibond scale (Lovibond 5.1/4", ISO 15305:1998 – Determination of Lovibond colour), content of phosphorus [ČSN EN 14107:2005 – Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry] and content of alkyl hydroperoxides [ČSN EN ISO 3960:2010 – Determination of peroxide value – Iodometric (visual) endpoint determination].

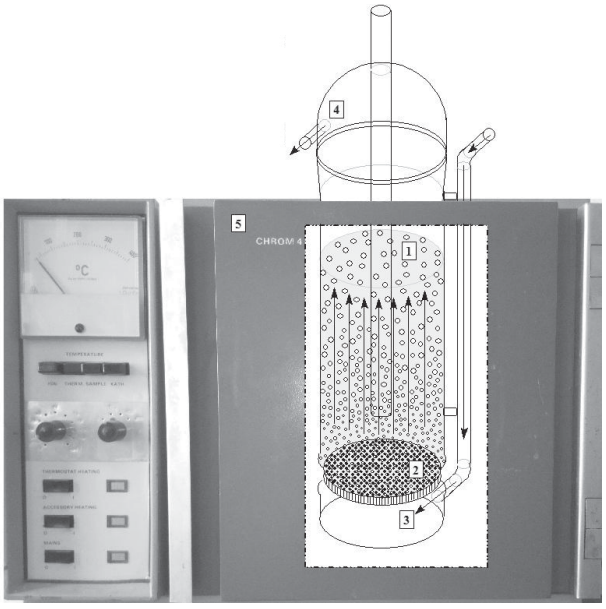

Figure 1. The design of versatile apparatus for bench scale bleaching and deodorisation

1 – Layer of vegetable oil with a stream of argon bubbles; 2 – Porous frit (S4); 3 – Inert gas inlet under the sintered glass; 4 – Inert gas exhaust in the upper part during bleaching/connection to a membrane pump with high vacuum performance during deodorisation; 5 – Adapted thermostat

Rapeseed oil deodorisation. Standard deeply degummed, alkali neutralised and bleached rapeseed oil (LERO, Usti-Oils s.r.o.) was pre-heated to 100°C and loaded into the glass apparatus (deodorisation apparatus, Figure 1) through which a stream of argon passed upwards (0.5–1.0 ml of Ar/ml of rapeseed oil per min). The batch was subsequently heated up to a deodorisation temperature of 200–240°C and the stream of the inert gas was increased to 2.0–4.0 ml of Ar/ml of rapeseed oil per minute. The duration of high temperature experiments at the atmospheric pressure was up to 4 hours. The temperature range and total pressure in the apparatus were variable parameters. Deodorisation operation time was 2 h under a vacuum lower than 2 hPa. The adapted apparatus (Figure 1) was connected to a vacuum pump with high vacuum performance. The stream of the inert gas (argon instead of stripping steam) passing through the layer of rapeseed oil was stabilised and it was observed that the argon bubbles increased in volume from 10 μm to 21 μm during the isothermal movement through the layer of rapeseed oil. At the given intervals, aliquots (5–10 g) were taken for the analysis. The impacts of high temperature experiments and the deodorisation process were monitored by a decrease in the content of carbonyl compounds (ČSN EN ISO 15303:2001 – Detection and identification of a volatile organic contaminant by GC/MS). Calibration curves of predominating hexanal and nonanal were constructed in the rapeseed oil matrix free of aldehydes (concentration range 0–70 μmol/kg). Other secondary oxidation products were monitored according to the changes of mass spectrometry detector (quadrupole mass

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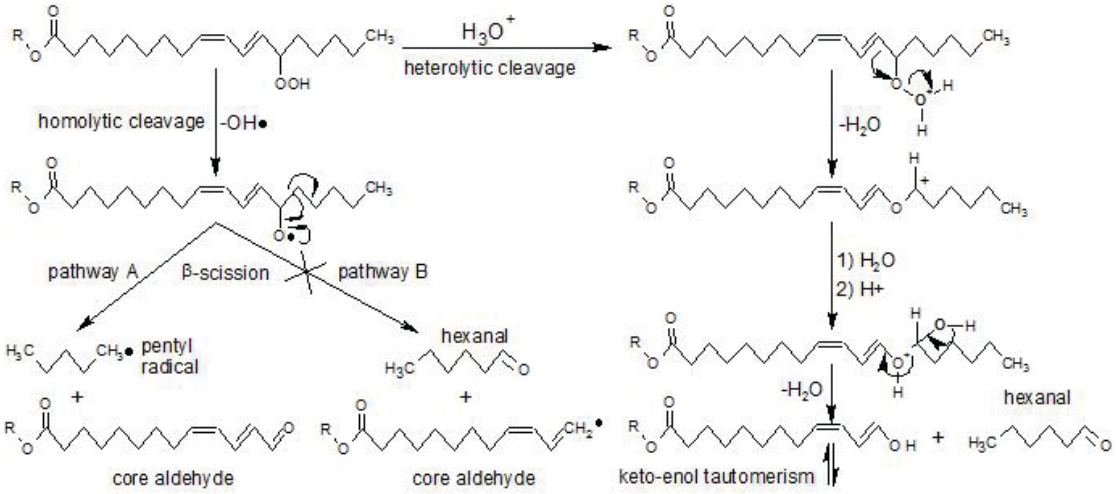

Figure 2. Mixed homolytic–heterolytic cleavage of alkyl hydroperoxides according to Frankel *et al.* (1984)

spectrometry detector Agilent Technologies 5975 MSD, 70 eV) response. Percentage content (m/m) of total conjugated dienes and trienes was determined according to IUPAC standard method (IUPAC 2.206:1987 – Determination of di- and triunsaturated fatty acids by UV spectrophotometry). Absorbance measurement was performed on a Varian Cary 50 UV-VIS spectrophotometer (Agilent Technologies, Inc., Santa Clara, USA).

RESULTS AND DISCUSSION

Bench scale apparatuses were developed and designed for the laboratory bleaching and deodorisation of edible oils. The improvement proposal was based on batch experiments performed in the apparatus provided with sintered glass on the bottom. Devices have been successfully applied to hydrogenation (Zajíc *et al.* 1984), isomerisation and polymerisation of fatty acids and their esters with high reaction yields (Cihelkova *et al.* 2013). A strong agitation was ensured by a stream of argon and the oil sample was fully under an inert argon atmosphere.

Industrially deeply degummed rapeseed oil (content of free fatty acids 0.28 wt%, phosphorus content 15 mg/kg) was the input feedstock for the bleaching process on a laboratory scale. The material was originally designed for the plant scale chemical refining, so the content of free fatty acids (0.28%) corresponded to the crude oil. The initial content of alkyl hydroperoxides was 0.4 mmol ½ O_2/kg before the bleaching. Two parameters were monitored: colour on the Lovibond scale and phosphorus content (Table 1). Temperature and the content of bleaching clay were variable parameters, whereas the bleaching time was constant – 40 minutes.

Results of the laboratory bleaching experiments were completely comparable with those achieved in industrial equipment under reduced pressure of the air (Bockisch 1998; Gomez De Oliveira *et al.* 2005). During the bleaching of rapeseed oil

Table 1. The impact of rapeseed oil bleaching process

Rapeseed oil	*t* (°C)	C_{BC} (wt%)	Rapeseed oil colour, Lovibond 5.1/4"				PV (meq O/kg)	Phoshorus content (mg/kg)
			red	yellow	blue	neutral		
Degummed			9.2	72.9	2.9	0.0	0.8	15.0
Bleached	90	1.5	1.2	15.0	0.0	0.3	0.7	4.5
	100	1.5	1.3	15.0	0.0	0.5	0.6	4.8
	110	1.5	1.1	14.0	0.0	0.4	0.6	4.4
	100	0.8	1.4	23.0	0.0	0.1	0.8	5.8
	110	1.2	1.4	19.0	0.0	0.1	0.7	4.3

c_{BC} – content of the bleaching earth; PV – peroxide value

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Table 2. The origin of odoriferous carbonyl compounds (Frankel *et al.* 1984; Velíšek 2014)

Fatty acyl moiety	Oxidation pathway	Secondary oxidation product precursors	β-Scission of alkyl hydroperoxides	Carbonyl compounds
Oleate	autoxidation by $^3O_2$	9-*trans*-11-OOH	homolytic, path. A	octanal
	photooxygenation by $^1O_2$/ autoxidation and resonance	8-*trans*-10-OOH	heterolytic, H^+ catalysed	nonanal
		10-*trans*-9-OOH	homolytic, path. A	*(2E)*-dec-2-enal
		10-*trans*-9-OOH	heterolytic, H^+ catalysed	nonanal
Linoleate	photooxygenation/autoxidation, resonance.	9-*cis*,11-*trans*-13-OOH	heterolytic, H^+ catalysed	hexanal
	photooxygenation by $^1O_2$	9-*cis*,13-*trans*-12-OOH	heterolytic, H^+ catalysed	*(2E)*-hept-2-enal
		9-*cis*,13-*trans*-12-OOH	heterolytic, H^+ catalysed.	hexanal
	autoxidation by $^3O_2$	9-*cis*,12-*cis*-11-OOH	heterolytic, H^+ catalysed	*(2E)*-okt-2-enal
		9-*cis*,12-*cis*-11-OOH	heterolytic, H^+ catalysed	heptanal
	photooxygenation by $^1O_2$	8-*trans*,12-*cis*-10-OOH	heterolytic, H^+ catalysed	*(3E)*-non-3-enal
		8-*trans*,12-*cis*-10-OOH	homolytic, path. B	*(2E)*-okt-2-enal
	autoxidation by $^3O_2$	10-*trans*,12-*cis*-9-OOH	homolytic, pathway A	*(2E,4E)*-deka-2,4-dienal
		10-*trans*,12-*cis*-9-OOH	heterolytic, H^+ catalysed	*(3E)*-non-3-enal
Linolenate	photooxygenation by $^1O_2$	9-*cis*,12-*cis*,14-*trans*-15-OOH	homolytic, pathway A	*(2E)*-but-2-enal
	photooxygenation by $^1O_2$/ autoxidation and resonance	9-*cis*,11-*trans*,15-*cis*-13-OOH	heterolytic, H^+ catalysed	*(3E)*-hex-3-enal
		9-*cis*,11-*trans*,15-*cis*-13-OOH	homolytic, pathway B	*(2E)*-pent-2-enal
	photooxygenation/autoxidation, resonance.	9-*cis*,13-*trans*,15-*cis*-12-OOH	homolytic, pathway A	*(2E,4E)*-hepta-2,4-dienal
	photooxygenation by $^1O_2$	9-*cis*,13-*trans*,15-*cis*-12-OOH	heterolytic, H^+ catalysed	*(3E)*-hex-3-enal

a decrease of the Lovibond coordinate (red) to the residual values 1.1–1.4 is practically independent of the temperature of bleaching in the temperature range of 90–110°C and of the content of bleaching clay in the range of 0.8–1.2%. The Lovibond yellow coordinate was more dependent on the temperature of bleaching process and on the content of the bleaching clay Tonsil Optimum 210 FF (c_{BC}, Table 1). The original content of phospholipids in the oil was reduced. The phosphorus content of 15 mg/kg was reduced to < 5 mg/kg during the process and thereby the input parameter for the oil deodorisation was accomplished (Bockisch 1998). Furthermore, the decomposition of the alkyl hydroperoxides occurred during bleaching (Table 1).

Industrially deeply degummed and bleached rapeseed oil (the content of free fatty acids 0.25 wt%, phosphorus content 3 mg/kg, peroxide value 0.6 mmol ½ O_2/kg) was the input material for the bench scale deodorisation. Variable parameters were temperature in the range of 200–240°C and the total pressure in the apparatus which corresponded to partial pressure of argon as the used inert gas (a) p_{Ar} < 1 hPa and (b) p_{Ar} = 990 hPa. Deodorisation operation time was 2 h under vacuum, whereas the duration of high temperature experiments at the atmospheric pressure was up to 4 hours. The impact of deodorisation was monitored by a decrease in the content of carbonyl compounds and other secondary oxidation products. They were formed after homolytic cleavage (decomposition) and subsequent stabilisation of alkyl hydroperoxides (PV = 0.6 mmol ½ O_2/kg), primary autoxidation products of the rapeseed oil fatty acyl moieties (oleic acid 58.2 wt%, linoleic acid 18.9 wt%, and linolenic acid 9.6 wt%). Predominating alkanals, minor secondary oxidation products and the precursors of listed volatile compounds are summarised in Table 2. Major aldehydes were arranged according to the fatty acyl moiety origin in Figures 3–5.

The bleaching earth treated with hydrochloric acid caused the decomposition of the first portion of alkyl hydroperoxides. The peroxide value decreased from 400 μmol ½ O_2/kg to 300–350 μmol ½ O_2/kg. It was an explanation of the high initial (zero time, Figure 4) content of hexanal (27–30 μmol/kg) and the same content of "core" (*9Z*)-dodec-9-enoate (27–30 μmol/kg)

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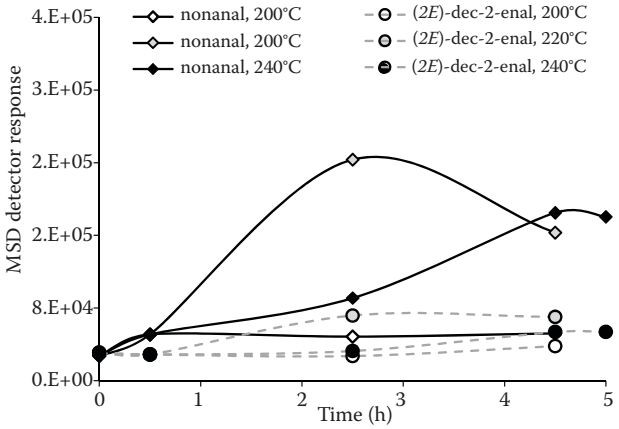

Figure 3. Major carbonyl compounds derived from the cleavage of oleic acid alkyl hydroperoxides during the high temperature experiments without vacuum

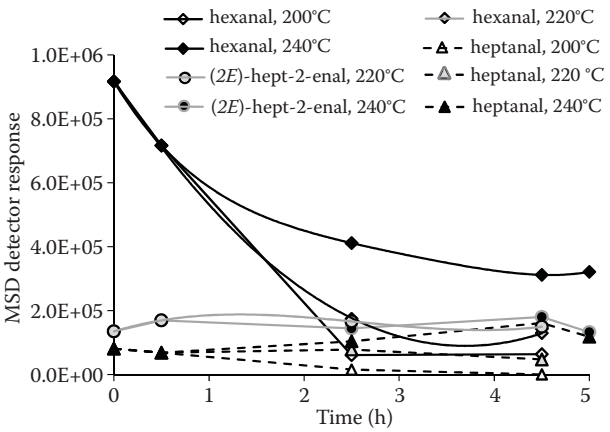

Figure 4. Major carbonyl compounds derived from the cleavage of linoleic acid alkyl hydroperoxides during the high temperature experiments without vacuum

before deodorisation experiments. The reaction mechanism was analogous to the Hock rearrangement of cumene hydroperoxide to phenol and acetone, which is catalysed by acidified bentonite clay. Treatment of organic hydroperoxides with bleaching agent (bleaching earth, celite, and Fuller's earth), acids (HCl, H_2SO_4), Lewis acids (BF_3), and metals have proved the same results (Frankel *et al.* 1984; Gardner & Plattner 1984). Residual alkyl hydroperoxides were completely decomposed during deodorisation and high temperature experiments. After homolytic cleavage, β-scission of alkoxyl radical into alkyl radical (pathway A) was preferred. Fragmentation pathway B was disfavoured because an unstable and rare vinyl radical had to be formed (Frankel *et al.* 1984; Gardner & Plattner 1984). It has too a high value of the heat of formation (298 kJ/mol) and bond dissociation energy (464 kJ/mol) compared to alkyl radicals ($\Delta_f H_{298}(R^\bullet)$ = 121 kJ/mol; $DH_{298}(R^\bullet)$ = 423 kJ/mol). The question was how hexanal could be formed (Figures 2 and 4) (Blanksby & Ellison 2003). The mechanism was probably "mixed" homolytic–heterolytic, when pathway A was included with the Hock rearrangement instead of pathway B (Frankel *et al.* 1984; Gardner & Plattner 1984). Relative percent values of predominating carbonyl compounds were plotted in Figures 3–5. Hexanal was formed during the bleaching of rapeseed oil (heterolytic pathway). Other carbonyl compounds were released by heat induced homolytic scission

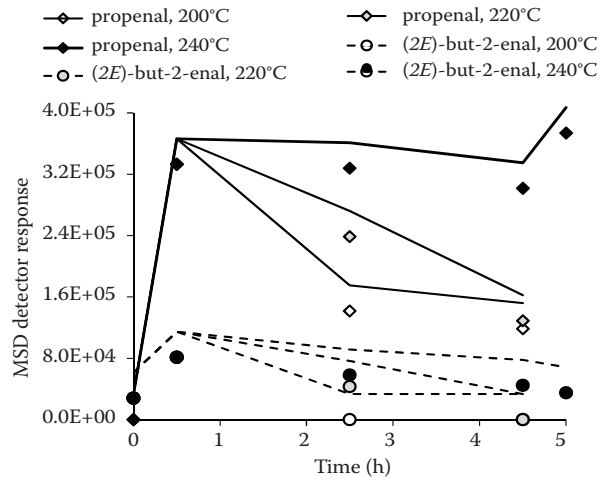

Figure 5. Removal of major carbonyl compounds derived from the cleavage of linolenic acid alkyl hydroperoxides and after the pyrolysis of acylglycerols during the high temperature experiments without vacuum

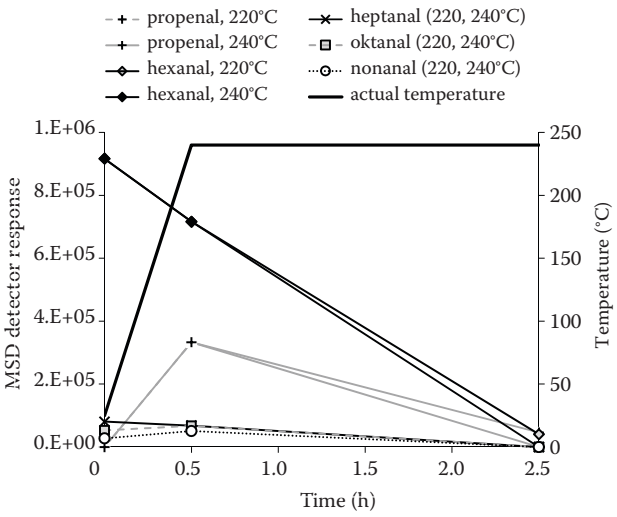

Figure 6. Removal of odoriferous carbonyl compounds during bench scale deodorisation

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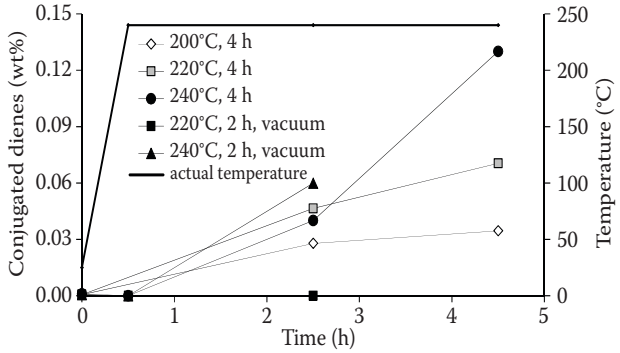

Figure 7. Formation of conjugated dienes by heat induced isomerisation during the deodorisation process

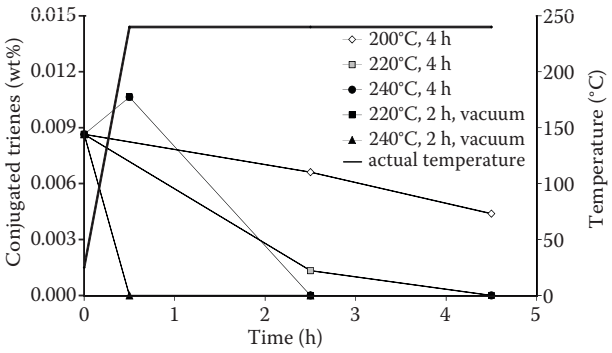

Figure 8. Formation of conjugated trienes by heat induced isomerisation during the deodorisation process

or acid catalysed (the content of free fatty acids is increasing) heterolytic cleavage. Pyrolytic changes were associated with the occurrence of propenal (Figures 5 and 6).

Geometrical and positional isomerisation and numerous consecutive side reactions can occur during deodorisation. Heat induced isomerisation can result in the formation of all-*trans* conjugated diene or triene system, the incoming reactants of cycloaddition reactions (Hénon *et al.* 1999; Cihelkova *et al.* 2013). These temperature dependent changes lead to the depreciation of oil from the nutritional point of view, especially due to the increasing content of *trans* isomers. Heat induced decomposition of the rest of fatty acid ester alkyl hydroperoxides RO-OH (BDE = 197 kJ/mol) produced unstable alkoxyl radicals, which were transferred into volatile alkanals, *(E)*-alk-2-enals, *(E,E)*-alka-2,4-dienals or core aldehydes by homolytic β-scission. Odoriferous volatile compounds influence negatively the taste and the smell of vegetable oil. High temperature isomerisation and decomposition of alkyl hydroperoxides contributed to the formation of conjugated dienes and trienes (Frankel *et al.* 1984; Gardner & Plattner 1984).

A versatile isothermal glass apparatus for high temperature experiments and deodorisation of vegetable oils was constructed. The results of the high temperature experiments (p_{Ar} = 990 hPa) showed that only the hexanal (based on a calibration curve) was reduced from 66–93% at 200–240°C. In the same conditions of Ar pressure there was not observed a decrease in the content of heptanal, oktanal and nonanal. Distillation with a stream of argon was efficient enough to completely remove odoriferous hydrocarbons, aldehydes and alcohols (Figure 6). The removal of predominating volatile carbonyl compounds shown in Figure 6 did not correlate with the increase of conjugated dienes in Figure 7. Thus, there was a close relation between the diene formation (0.035–0.130 wt%) and the sum of heat induced isomerisation changes and the formation of core aldehydes. Rising concentration of *n*-oxo fatty acid esters corresponded with increasing content of polar compounds. The conjugated trienes were completely removed during the high temperature experiments and deodorisation process above 220°C (Figure 8). Therefore, it was suggested that they were volatile enough to be inert gas distilled like *(E,E)*-alka-2,4-dienals with oxo group in conjugation with two double bonds.

CONCLUSION

We have confirmed that the isothermal glass apparatus provided with sintered glass on the bottom is a versatile tool for bench scale adsorptive bleaching and deodorisation of vegetable oils. Bleaching of edible oils on a commercial scale is usually realised in a stirred adsorber under reduced pressure. Our bench scale apparatus did not need any mechanical agitation, because the oil sample was sufficiently agitated by the stream of argon as an inert gas. Stirring, oxygen desorption and acid catalysed decomposition of alkyl hydroperoxides were performed in one step. Hexanal was a significant indicator of bleaching earth processing due to the heterolytic β-scission changes.

Special attention has been paid to deodorisation. It was confirmed that the application of argon instead of steam distillation was efficient enough to completely remove predominating aldehydes (96–100%). A simple design of the bench scale device indicated the robustness of the apparatus. Other volatile alkanals, *(E)*-alk-2-enals, *(E,E)*-alka-2,4-dienals or core aldehydes were indicators of heat-induced homolytic

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and acid catalysed heterolytic decomposition of alkyl hydroperoxides.

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