Effect of rape seeds microwave pretreatment on the composition and antioxidative properties of press rape oil

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Abstract

Introduction The influence of microwave pretreatment of rape seeds on the pressing oil yield, acid and peroxide values of oil, fatty acid composition of oil, phosphoruscontaining substances, tocopherols and carotene content in oil as well as oil oxidation stability were studied in this work.

Materials and methods Peroxide and acid values of oils were determined according to procedures given by IUPAC, total phosphorus and carotenes content – by spectrophotometric methods, fatty acid composition and tocopherols content of oils − by chromatographic methods. The induction periods of oil oxidation were calculated from the curve of oxidation in the presence of 2,2-azo-bis-isobutyronitrile.

Results and discussion The advantages of microwave heating are very high rates of temperature increase and as a consequence the high rates of the moisture decrease. We have shown that decreasing of rape seed moisture from 13.0 to 7.2 % had run during 10 and 30 min under microwave and conventional heating respectively. It was shown that pressing oil yield after microwave pretreatment of rape seeds increased by 16-90 %. The final seed moisture after pretreatment was the main factor that determines the pressing oil yield. The oil yield for the seeds with the same moisture after microwave and conventional pretreatment was higher in a case of microwave pretreatment by 16 %.

Data obtained have shown that used microwave heating had no effect on the fatty acid composition of rape oil. But oil from the rape seeds after microwave pretreatment had lower acid and peroxide values, higher phosphorus, tocopherols and carotenes content. Increasing of oxidative stability of oil sample after seed microwave pretreatment was confirmed by rising of induction period time of oil oxidation, initiated by 2,2-azo-bis-isobutyronitrile. Induction period of control sample oil was equal to 27 min. and for sample oil from microwave pretreated seeds it was three time longer and exceed 90 min.

Conclusions Microwave pretreatment of rape seeds can be used for increase of rape seeds pressing affectivity and improving of oil biological value and oxidation stability.

Introduction

The main advantage of microwave heating is its easy and quick penetration inside products and as result their temperature increases very rapidly. At the same time the energy of microwave frequency waves are strongly absorbed by water molecules. Thus the higher moisture of product the higher temperature increase under microwave heating. The high temperature of materials under microwave heating induces the high pressure inside the cells, rupture of cell wall and releasing the cell components [1].

Microwave heating is widely used for sterilization, pasteurization, cooking and drying the product. It is also used for intensification of extraction of different substances for food and other application.

The development of microwave assisted extractions was first reported by Ganzler *et al.* [2] and Ganzler and Salgo [3] as a sample preparation method for chromatography. Subsequently this method was proposed to use for extraction of different compounds from plant and animal materials, such as essential oil [4-7], phenolics with maximal antioxidant activities [8, 9] and other bioactive compounds from plant materials [10, 11].

Microwave pretreatment of raw material is predominately used for edible oil recovery from oil seed [12]. Valentova *et al.* [13] have shown that yield of cold-pressed rape oil increased with increasing doses of microwave irradiation up to about 40 % of seed mass (w/w) while the amount of oil, obtained from untreated flakes, was about 33% (w/w). The degree of lipid oxidation was significantly lower after microwave treatment, total phosphorus contents were higher in the oils from treated seeds. At the same time Terigar *et al*. [14] have not detected the effect of microwave on the phospholipid content in oil. Azadmard-Damirchi *et al.* [15] have shown that microwave pretreatment of rape seed can increase the oil yield (by 10%), phytosterols (by 15%), tocopherols (by 55%) of the pressing oil and increased oxidative stability to 8 h. In our previous study we have shown the influence of microwave pretreatment on the yield of press oil from soybean, sunflower, walnut and pumpkin seed [16].

Moreno *et al.* [17] have detected the increase of extraction efficiency in Soxhlet-hexane extraction coupled after microwave pretreatment of avocado. Terigar *et al*., [14] have proposed pilot-scale continuous microwave-assisted extraction system for soybean and rice bran oil.

On the other hand there are contrary data about influence of microwave roasting of sunflower seed on the oil quality [18]. Using extraction of oil by n-hexane the authors have revealed that microwave roasting decreased the oil content of the seeds significantly. Analysis of the extracted oils demonstrated a significant increase in free fatty acids (FFA) content, peroxide, p-Anizidine and saponification values, density, diene, conjugated triene and color values for roasting periods of 10 and 15 min. Such significant increase of saponification value is very doubtful on the basis of the fatty acids composition changes since the main changes concerned only the oleic and linoleic acids ratio but not the content of fatty acids of different molecular weight. The iodine values and the amounts of tocopherol constituents of the oils were remarkably decreased. Microwave heating resulted in increase of oleic acid content by 16–42% and decrease of linoleic acid content by 17–19%, but palmitic and stearic acid contents were not affected significantly.

It is obviously that such substantial changes of linoleic acid content could be only the result of its oxidation and these data indicate about acceleration of oil oxidation as a result of microwave roasting.

The influence of microwave roasting on fatty acid content was reported for other oils [19, 20].

However Yoshida *et al.* [21], have reported no significant ($P > 0.05$) changes in the FA composition within 12 min of roasting in sunflower seed oil. Yen [22], Yoshida and Kojimoto [19], Kim *et al.* [23] have not found differences in FA composition of sesame seed oils and of rice germ oil treared at different roasting temperatures and time.

Thus the question about the role of microwave heating in oil seed processing and its influence on the oil quality is still open. In our opinion parameters of microwave heating are very important for oil quality, notably the temperature of heating and seed moisture in the case of seed pretreatment. In this study we have investigated the influence of microwave pretreatment conditions on the yield of press rape oil and its composition.

Materials and methods

Materials. Seeds of the winter rape plant (*Brassica napus,* low content of glucosinolates and zero erucic acid), obtained from local market were used in this research. Moisture and oil content of seeds were 8.5 % and 46.4 % (of dry substances), respectively.

Proximate analysis. Moisture content was determined by drying of samples to stable mass. Determination of oil content in seeds and cakes was carried out by extraction in a Soxhlet extractor on a water bath (75–80 °C) for 16–18 h with *n*-hexane (b. p. 68 °C). The mass of extracted oil was calculated by weighing of seed residues after extraction.

Microwave pretreatment of rape seeds. 500 g of rape seed were moistened to moisture content 11-13 % by water vapour and then were heated in domestic microwave or in electric oven. Final seed moisture varied from 3 to 10 %. The frequency of microwave was 2450 MHz and capacity varied from 100 to 300 W. The temperature of microwave heating varied from 85 to 105 °C and conventional heating from 100 to 105 °C, respectively.

Seed pressings. Pressings of the seeds were performed after heating using the laboratory screw press at 55-60 °C operating temperature. Oil yield was calculated as difference between oil content in seeds and oil residuals in cake after pressing.

Quality parameters of pressed oils evaluation. Peroxide value (PV) and acid value were determined according to procedures given by IUPAC (2.501 and 2.201, respectively) [24]. Total phosphorus content was determined by a spectrophotometric method measuring absorbence of yellow molybdenumvanadiyphosphoric acid at λ= 400 nm using dry ashing and magnesium oxide as an ashing aid.

Tocopherols content determination. Content of tocopherol homologue was determined by high-performance liquid chromatography of unsaponifiable substances. For this purpose 5 g of oil was saponificated at 85-90 °C in the presence of 15 ml methanol, 10 ml of 10 % water solution of ascorbic acid and 4 ml of 50 % potassium hydroxide solution during 30 min. Unsaponfiable matters were extracted thrice by diethyl ether. Extract was properly washed by disstiled water and dried by incubation with sodium sulphate during 30 min. Ether was evaporated on rotor evaporater at 40…50˚C and residual was diluted in 10 ml of methanol. Obtained solutions were analyzed on Hewlett Packard liquid chromatograph model HP 1100 with reversed-phase column Hypersil MOS (200 mm x 2.1 mm). Detection was done with fluorescence (wave length of: excitation − 295 nm, absorbtion – 330 nm) and diode matrix detectors. The column was held at constant temperature by a water jacket at 40 °C. The eluant was composed of acetonitril/water (70:80), the eluation velocity was 0.4 ml/min. The standard solutions of α-tocopherolacetate (Supelco) were used for calibration.

Total carotenes content determination. Total carotenes content was determined by a spectrophotometric method. Solution of oil in hexane (1:9) was used for absorbance measurement at λ=451 nm. Total carotines content (g/100 ml) was calculated using the following equation:

$$C=10A/10\cdot256$$

where A correspond to the absorbance of oil solution at 451 nm and cuvette thickness equal to 10 mm and 256 is the specific absorption coefficient of β,β carotene at 451 nm [25].

Fatty acid composition of oils. Fatty acid composition was determined by gas-liquid chromatography of fatty acid methyl esters. They were prepared by IUPAC standard method 2.301 [24] and analyzed on Hewlett Packard gas chromatograph model HP 6890 with capillary column HP-88 (88%-cyanopropyl aryl-polysiloxane, 100m x 0.25 mm x 0.25 γm film thickness (Agilent Technologies). The temperature of injector was 280 °C, and pf detector − 290 °C. The column temperature program of heating rate was from 60 to 230 °C. The rate of carrier gas was 1.2 ml/min. Identification of the fatty acids was performed by comparison of the retention times with standards mixture of fatty acid methyl esters (37 Component FAME Mix, Supelco).

Oxidative stability of rape oil. The oxidative stability of rape oil was estimated as changes of peroxide value during 12 h exposition of oil in thermostat at 70 °C. The aliquots of oil were taken for PV determination every 2 h.

Induction periods of oil oxidation were calculated from the curve of oxidation, initiated by 2,2-azo-bis-isobutyronitrile (AIBN). Oxidation curves at 80 °C were measured as volume of absorbed oxygen. For oxidative reaction 2 g of oil mixed with 3 ml xylene and 0.3 ml of 0.1 mol/L solution of oxidation initiator 2,2-azo-bis-isobutyronitrile (AIBN) in xylene. Reaction mixture was oxygen purged during 1 min and thermostated at 80 °C during 10 min before measurements. Oxidation curves were plotted in coordinates: heating time (t, min) − height of absorbed oxygen column (H, mm).

Statistical analysis. Samples were analyzed in triplicate. Statistical analysis was performed using Microsoft Excel 2007 (Microsoft, City of Redmond, USA). The results were reported as mean±SD. Differences were considered to be significant at validity of α=0.95.

Results and discussion

Microwave heating effects on the yield of press oil

In our previous work [16] we have shown that microwave pretreatment of oil seeds had resulted in the increase of pressing oil yield. The main parameter affected pressing oil yield was moisture of seeds before pressing. Data, obtained in this work, had shown that highest oil yield was achieved when seed moisture was about 3.0 % (Table 1). About 92 % of oil was recovered from seeds. The advantages of microwave heating are very high rates of temperature increase and as a consequence the high rates of the moisture decrease. We have shown that decreasing of seed moisture from 13.0 to 7.2 % had run during 10 and 30 min under microwave and conventional heating respectively. The oil yield for the seeds with the same moisture after microwave and conventional pretreatment was higher in a case of microwave pretreatment by 16 %. Obviously in a case of microwave heating the changes of seeds microstructure are involved also as contributing factor to oil yield [26].

Table 1

Oil yield as a function of parameters of rape seed pretreatment and pressing

Seed moisture before heating, %	Microwave capacity, W/200 g of seeds	Temperature of seeds, °C	Time of treatment, min	Final moisture of seeds, %	Oil yield, % from seed mass
13.0±0.3	300	105±3	10	7.2±0.2	29±3
13.0±0.3	100	80±2	10	10.0±0.3	25±2
11.0±0.2	300	100±2	10	3.0±0.2	38±1
11.0±0.2	100	84±3	10	7.2±0.3	29±2
13.0±0.4	-	100±2	10	12.0±0.3	20±4
13.0±0.3	-	100±2	30	7.2±0.2	25±3

Chemical composition of press rape oil

According to our data, rape oil, obtained after microwave pretreatment, had lower content of free fatty acids and considerably lower mean of peroxide value (Table 2), possibly due to result of a short-time microwave heating, durations of heating in order to reach the same seeds moisture were 10 min and 30 min in microwave and electric oven respectively. On the other hand, it is possible that microwave heating inactivates lipases and of oxidative enzymes, such as peroxidases and lipoxygenases, more effectively comparing with conventional heating.

Table 2

Characteristics of Rapeseed Oil from Seeds after heat pretreatment

Characteristic	Pretreatment heating	
	conventional	microwave
Pressing oil yield, %	25±1.5	38±1.8
Peroxide value (meq O kg^{-1} of oil)	1.8±0.2	0.4±0.1
Acid value (mg KOH g^{-1} of oil)	2.2±0.1	1.5±0.05
Total phosphorus content (mg kg^{-1} of oil)	27.7±1.3	31.8±1.5
Tocopherol content (mg·100 g^{-1} of oil):		
α tocopherol	12.3±0.10	13.3±0.15
β tocopherol	20.5±0.2	21.1±0.15
Total carotines content, %	0.003±0.001	0.047±0.005

We have obtained very low total phosphorus content in all oil samples, but still it was higher (about 15 %) in oil after microwave heating. Since neutral lipid fractions are extracted from seeds under pressing at first and such as phospholipids are polar lipids, obviously the higher oil yield the more polar lipid fractions content in oil.

The tocopherol homologues content was somewhat higher in the sample of rape oil from microwave treated seeds. The α-tocopherol content increase was 8 % to control samples. It is known that this homologue has lowest optimum of antioxidative activity that

is10-25 mg/100 g of oil [27]. Thus it can cause the high oxidative stability of rape oil even at low concentration.

Analysis of fatty acid composition of obtained rape oil samples are shown in Table 3. We have not detected significant changes of fatty acid content in oil after microwave heating, neither decreasing linoleic acid content nor increasing oleic acid content as it was shown by [18-20]. We suppose that considerable changes in FA composition [18] could accompanying very strong destruction of oil, that is not evident from other oil characteristics (FFA content, PV value) shown in those works. Our data have shown that "soft" conditions of microwave heating do not cause nor considerable changes in FA composition nor creation of trans isomers of fatty acids.

Effect of microwave pretreatment on oxidative stability of rape oil

Changes of peroxide value of rape oil from seeds, treated in electric and microwave oven, under oxidation condition are given on Fig. 1. It is evident that oil from seeds after conventional heating had very poor oxidative stability, its oxidation have started from the very beginning of oil heating and the rate of peroxide accumulation was very high. At the same time the rate of peroxide formation in oil from seeds after microwave heating was increasing slowly during first 4 hours and then peroxide content was constant until 10 h. At the end of observation the rate of peroxide formation declined in both oil samples possibly as result of peroxide dissipation to second products of oxidation.

Increasing of oxidative stability of oil sample after microwave pretreatment was confirmed also by rising of induction period time of oil oxidation, initiated by 2,2-azo-bis-isobutyronitrile. Induction periods of oil oxidation were calculated from the curve of oxidation (Fig. 2). Induction period of control sample oil was equal to 27 min. and for sample oil from microwave pretreated seeds it was three time longer and exceed 90 min.

Table 3

Fatty acid composition of rape oils

Fatty acid	Fatty acid, % from the common content	
	Oil after microwave pretreatment	Oil after conventional heating
C 16:0	4,50 ± 0,15	4,49 ± 0,15
cis-9-C 16:1	0,23 ± 0,05	0,21 ± 0,05
C 18:0	1,66 ± 0,10	1,67 ± 0,10
cis-9-C 18:1	59,27 ± 0,20	59,63 ± 0,20
cis-11-C 18:1	4,94 ± 0,15	4,76 ± 0,15
cis, cis-9,12-C 18:2	19,29 ± 0,20	19,08 ± 0,20
C 20:0	0,55 ± 0,05	0,54± 0,05
cis,cis,cis-9,12,15-C 18:3	7,68 ± 0,20	7,80 ± 0,20
cis-11-C 20:1	1,19 ± 0,10	1,17 ± 0,10
cis-13-C 22:1	0,10 ± 0,05	0,09 ± 0,05
C 24:0	0,12 ± 0,05	0,11 ± 0,05
cis-15-C 24:1	0,13 ± 0,05	0,13 ± 0,05

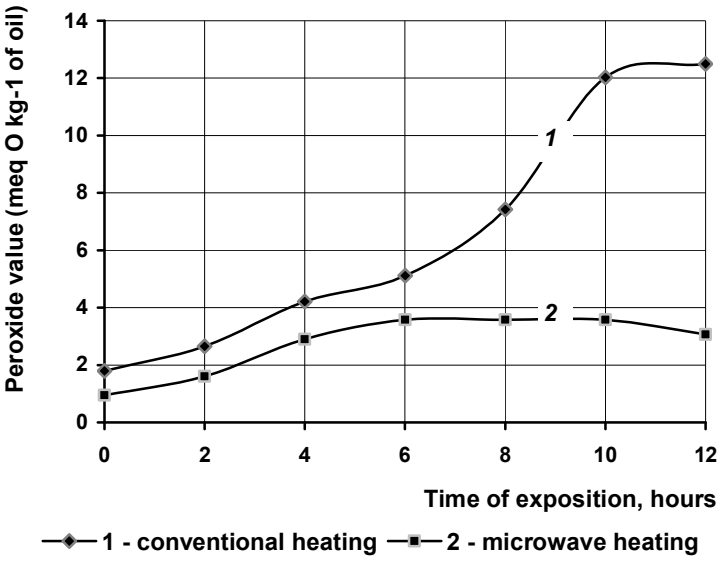

Fig. 1. Oxidation stability of rape oil after conventional and microwave pretreatment of seeds

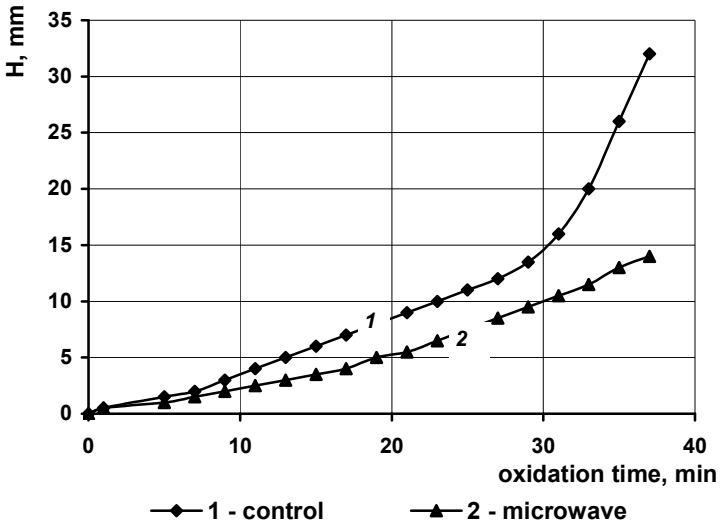

Fig. 2. Curves of rape oil oxidation, initiated by 2,2-azo-bis-isobutyronitrile

Conclusions

In this study we have shown that main parameters that influence the yield of press rape oil are seed moisture, which in turn depends on the temperature and the time of seed heating. The time which is necessary for achievement of proper seed moisture is considerably lower in case of microwave heating in comparison with conventional heating.

On the other hand since water has very high dielectric constant the higher initial seeds moisture the more effective heating.

Thus parameters that determine the effect of microwave heating on seed moisture are: microwave power, pretreatment duration as well as initial seed moisture. In addition, the influence of microwave heating on the oil yield is evidently the result of creation of proper inner microstructure of seed due to quick water heating and evaporation that results in creation of porous microstructure. Such microstructure is favorable for oil releasing.

Increasing of oil yield after microwave pretreatment is accompanied by increased content of polar lipids (phospholipids, carotines and tocopherols) in oil. Microwave pretreatment of seeds did not influence the fatty acid composition of rape oil. Rape oil from the seeds after microwave pretreatment had low peroxide value and considerably higher oxidative stability.

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