ORIGINAL ARTICLE



Thermal oxidation of rice bran oil during oven test and microwave heating

Richa Mishra • Harish K. Sharma • Bhavesh C. Sarkar • Charanjiv Singh

Revised: 21 May 2010/Accepted: 6 July 2010/Published online: 12 February 2011 © Association of Food Scientists & Technologists (India) 2011

Abstract The purpose of the present study was to evaluate the oxidative stability of physically refined rice bran oil (RBO) under oven heating at 63 °C and microwave heating conditions by absorptivity. Oil samples with tertiarybutylhydroquinone (TBHQ) (100 ppm and 200 ppm), citric acid (CA), butylhydroxyanisole/butylhydroxytoluene (BHA/ BHT) and in other combination, BHA/BHT+CA were submitted to oven test for 6 days, and the linear coefficient of correlation between peroxide value and absorptivity at 232 nm was determined. The gradual increase in peroxide value and absorptivity at 232 nm was observed in all the RBO samples, control and antioxidant added. RBO samples added with tertiary-butylhydroquinone (TBHQ) had shown the least peroxide value and absorptivity as 6.10 and 5.8 respectively, when added at a concentration of 200 ppm whereas; the control RBO samples had shown the maximum values. The peroxide values obtained from the correlations during the oven test were found closely correlated with the peroxide values obtained during the microwave oven heating experimentally. The effect of microwave heating on the oryzanol content and p-anisidine value was also observed and the correlation to the oven test was established. The oryzanol content and p-anisidine values obtained after oven heating when correlated to the microwave heating data showed the oryzanol content 13,371, 13,267 and 13,188 ppm after 1 day, 4 days and 5 days respectively which were closely correlated with the experimental value.

Keywords Rice bran oil · Absorptivity · Oryzanol value · Oven heating · Microwave heating · Antioxidants

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Longowal 148 106 Sangrur, India e-mail: h_sharma27@rediffimail.com The high-quality rice bran oil has a very neutral, delicate flavour and high smoke point therefore is considered good cooking oil. Beside this, the oil is known for its significant nutritional attributes due to the naturally occurring antioxidants. The light viscosity of the oil allows less oil to be absorbed during cooking therefore provides economic viability to the industry. The deterioration by autooxidation in rice bran oil and other edible oils is the cause of concern with respect to the shelf life of the product.

Antioxidants either in combination or singly are commonly added to oils and fats to retard oxidation changes (Omura 1995). Among the commonly used antioxidants, tertiary-butylhydroquinone (TBHQ) gave adequate protection, whereas butylhydroxyanisole (BHA) and butylhydroxytoluene (BHT) were relatively ineffective (Asap and Augustine 1986; Augustin and Berry 1983). Storage tests, like the oven test can be used to indicate the effect of an antioxidant, but it requires time to give the result. The oxidative stability of refined, bleached and deodorised canola oil was evaluated under oven test (Vieira TMFS, Regitano-D'Arce MAB 2001). A good correlation between peroxide value (PV) and absorptivity at 232 nm during oven test (65 °C, 17 days) was observed with canola oil that had BHA, BHT, TBHQ or a canola extract added (Wanasundara and Shahidi 1994). Results of PV and absorptivity at 232 nm during oven test (62.8 °C) and ambient storage for Brazil nut crude oil suggested a linear correlation coefficient over than 0.9 (Regitano-d'Arce and Vieira 1996). Natural antioxidants extracted from olive oil mill waste water are highly effective for oxidative stabilization of lard (De Leonardis et al. 2007).

Various studies have been conducted on microwave heating of fats and oils. Peanut oil was heated in a microwave oven and the fatty acid composition was determined (Mai et al. 1980). Linseed, soybean, corn, olive and palm oil were heated by microwave and after 10 min of exposure the amount of tocopherols decreased and the occurrence of oxidation were determined by the increase in peroxide, p-anisidine, TBA and carbonyl values (Yoshida et al. 1990). The results obtained for PV of olive, sunflower (Albi et al. 1997) and soybean oils (Vieira TMFS, Regitano-D'Arce MAB 1998) heated in microwave oven did not increase in a clear way, due to the instability of hydroperoxides at high temperatures. Ruiz-Lopez et al. (1995) observed a small increase in PV of extra virgin olive oil after 8 min of microwave heating. The oxidative stability of canola oil was evaluated under oven test and microwave heating conditions by absorptivity (Vieira and Regitano-d'Arce 2001). The present study was undertaken to explore the oxidative stability of physically refined rice bran oil in an oven test (630 C) and the microwave heating in the different dosages of antioxidants.

Materials and methods

Physically refined rice bran oil, without addition of any antioxidant was obtained directly from A. P. Solvex Ltd., Dhuri, Punjab. TBHQ, BHA, BHT and CA all antioxidants used in the study were of Milestone Preservatives Pvt. Ltd., Vadodara (India). Oryzanol was procured from Sigma Aldrich, Saint Louis, US. All the solvents used in the study were of HPLC grade and the reagents were of analytical grade.

Sample preparation The antioxidant tertiarybutylhydroquinone (TBHQ), butylhydroxy-anisole/butyl hydroxytoluene (BHA/BHT), citric acid (CA) and BHA/ BHT + CA were prepared as: BHA/BHT- 200 mg/kg, BHA/ BHT(200 mg/kg) + CA(100 mg/kg), CA(100 mg/kg), TBHQ (100 mg/kg and 200 mg/kg) and pure rice bran oil for control sample. Requisite amount of antioxidants were added in a small amount of the oil sample at elevated temperature and then the sample was added directly to the oil which was homogenized mechanically at ambient temperature for 10 min.

Oven test Samples (50 ml) of each oil treatment were placed in separate 100 ml open beakers, without stirring and held in an oven at 63 °C temperature during 1, 2, 3, 4, 5 and 6 days. Immediately after each storage period, oil samples were analyzed.

Microwave heating Samples (50 ml) of each treatment were placed in 100 ml beakers and covered with PVC film. Samples were heated in Onida power-grill 25, microwave oven (900 W effective power) for 0, 2, 4, 6, 8, 10, 12, 16, 20, 24, 28 and 32 min. After each heating period, the oil temperature was determined with a thermocouple, and all the samples were withdrawn and analyzed.

Analytical procedures Free fatty acids, Iodine value, Peroxide value (PV) and p-anisidine value were determined as per the standard analytical methods, Ca5a-40 Cd1-25 Cd8-53 and Cd18-90 (AOCS 2004). Colour of the oil samples was determined by Tintometer (Model F, Effem Technologies Pvt. Ltd, New Delhi, India). Oryzanol content (IICT 2008) was determined by spectrophotometric (UV- SHI-MAZDU) method. Absorptivity at the wavelength of 232 and 270 nm were determined by using spectrophotometric method, II.D.23 (IUPAC 1979).

Statistical analysis Each value is the mean of three repetitions. The ANOVA and Tukey's test were applied. The Microsoft office excel software was used for analysis.

Results and discussion

Oven test The initial quality of rice bran oil (RBO) sample is shown in Table 1. The oil sample had colour, oryzanol and p-anisidine value in the proportion of 17 units, 13,324 ppm and 51.07 respectively while the free fatty acids (ffa), peroxide value (PV) and iodine value(I.V.) were found in the range as per the regulatory standards. The absorptivity at the wavelength of 232 and 270 nm were 3.231 and 0.808 respectively.

Figure 1 shows the I.V. and ffa content of the RBO samples, exposed at a temperature of 63 °C for 6 days in presence of different proportions of antioxidants. No significant difference was observed (P<0.05) in the iodine value and free fatty acids. The changes in oryzanol content and p-anisidine value during oven test at 63 °C with respect to time are given in Fig. 1. The results indicate that the oryzanol content was decreased and the p-anisidine value was increased. The oryzanol content was 13,324 ppm in the control sample and 12,894 ppm in the RBO sample stored at 63 °C after 6 days. The oryzanol content was

Table 1 Initial quality of rice bran oil

| Parameter | Rice Bran Oil | | |
|---------------------------|---------------|--|--|
| Iodine value ^a | 101.03 | | |
| Colour(y+5r unit) | 17.0 | | |
| Oryzanol(ppm) | 13,324 | | |
| Free fatty acid (%) | 0.06 | | |
| Peroxide value (meq/kg) | 0.56 | | |
| p -anisidine value (AnV) | 51.07 | | |
| Absorptivity at 232 nm | 3.231 | | |
| Absorptivity at 270 nm | 0.808 | | |
| | | | |

^aRepresents grams of iodine absorbed per 100 g

Results are average of three individual experiments

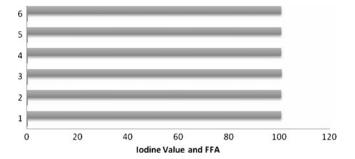


Fig. 1 Iodine values and free fatty acid values after 6 days of oven heating at 63°C temperatures. Pure RBO- 1(control sample), TBHQ (100 ppm)-2, TBHQ(200 ppm)-3, CA(100 mg/kg)-4, BHA/BHT (200 mg/kg)-5, BHA/BHT(200 mg/kg)+CA(100 mg/kg)-6

significantly different after 5 days (P < 0.05). The similar trend was observed for the p- anisidine value.

Tables 2 and 3 shows the effect of antioxidants during oven test on the changes in peroxide value and absorptivities at 63 °C. The formation of hydroperoxides is coincidental with conjugation of double bonds in polyunsaturated fatty acids, measured by absorptivity in the UV spectrum (Shahidi and Wanasundara 1997). The gradual increase in peroxide value and absorptivity at 232 nm was observed in all the rice bran oil samples, control and antioxidant treated. Rice bran oil samples treated with tertiary-butylhydroquinone had shown the least peroxide value and absorptivity as 6.10 and 5.8 respectively after 6 days, when added at a concentration of 200 ppm whereas, the control RBO samples had shown the maximum values. The change in the concentration of TBHO as 100 and 200 ppm brought significant changes in the peroxide value and absorptivity. The results are in agreement with the findings of Vieira TMFS, Regitano-D'Arce MAB (2001) on the canola oil. However, the RBO samples treated with citric acid had shown the comparatively higher peroxide value and absorptivity among all the antioxidants treated samples.

The correlation between oryzanol content and panisidine value was plotted (Fig. 2). The uniformity and (2)

(4)

(5)

homogeneity of the points along with the curve indicates that the results are highly correlated. The correlation model coefficient for oryzanol content and p-anisidine value was found as 0.939 indicating the suitability of the model. The derived equation is given as follows:

Oryzanol content =
$$-68.61 \times p$$
 - anisidine value + 168.7
(1)

Conjugated dienes values can be used as a stability index for lipid containing foods (ST. Angelo et al. 1975). The correlation was also observed between PV and absorptivity at 232 nm. The results were found to be highly correlated between these two indices in all the treated samples except the sample treated with the citric acid. The correlation coefficients between PV and absorptivity were found to be greater than 0.9 for all the antioxidants treated samples except the sample treated with citric acid. The citric acid treated sample showed the correlation coefficient of 0.712. The results of absorptivity at 232 nm and peroxide value of the cold pressed oil of brazil nuts stored for 120 days at ambient temperature showed a good correlation coefficient, greater than 0.9 (Regitano-d'Arce 1998). The linear equations and the coefficients obtained are given as follows:

Rice Bran Oil,

$$PV = 2.345 Xabsorptivity - 8.779 (R2 = 0.963)$$

Rice Bran Oil + 100 ppm TBHQ,

$$PV = 1.661Xabsorptivity - 6.164 (R2 = 0.980)$$
(3)

$$PV = 2.145 Xabsorptivity - 7.648 (R2 = 0.952)$$

Rice Bran Oil + CA,

$$PV = 2.252Xabsorptivity - 7.976 (R2 = 0.712)$$

Table 2 Peroxide Value (meq/kg) during oven test at 63 °C temperature

| Time (Days) | RBO | RBO+TBHQ (100 ppm) | RBO+TBHQ (200 ppm) | RBO+CA | RBO+BHA/BHT | RBO+BHA/BHT+CA |
|-------------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 1 | 1.19 ^a | 1.08 ^a | 1.03 ^a | 1.06 ^a | 1.05 ^a | 1.07 ^a |
| 2 | 1.88 ^{ac} | 1.51 ^{ac} | 1.47 ^{ac} | 1.49 ^{ac} | 1.50 ^{ac} | 1.52 ^{ac} |
| 3 | 2.96 ^{ace} | 2.79 ^{ace} | 2.68 ^{acf} | 2.81 ^{ace} | 2.85 ^{acf} | 2.87 ^{acg} |
| 4 | 4.61 ^{aceg} | 3.80 ^{ace} | 3.41 ^{acf} | 3.93 ^{ace} | 3.99 ^{acf} | 4.01 ^{acg} |
| 5 | 6.63 ^{bceg} | 6.01 ^{bce} | 5.35 ^{bdf} | 6.13 ^{bce} | 6.09 ^{bcf} | 6.12 ^{bcg} |
| 6 | 8.13^{bdfg} | 7.36 ^{bde} | 6.10 ^{bdf} | 7.47 ^{bde} | 7.32 ^{bdf} | 7.38 ^{bdg} |

*Means within the same column sharing a common small letter are not significantly different at P < 0.05

RBO rice bran oil; *TBHQ* tertiary butylated hydro quinone; *CA* citric acid; *BHA* butylated hydroxy anisole; *BHT* butylated hydroxy toluene Results are average of three individual experiments

| Time (Days) | RBO | RBO+TBHQ (100 ppm) | RBO+TBHQ (200 ppm) | RBO+CA | RBO+BHA/BHT | RBO+BHA/BHT+CA |
|-------------|------------------------|---------------------|---------------------|-----------------------|---------------------|---------------------|
| 1 | 4.33 ^a | 4.05 ^a | 4.03 ^a | 4.06 ^a | 4.07 ^a | 4.05 ^a |
| 2 | 4.89 ^{ac} | 4.35 ^{ac} | 4.18 ^{ac} | 4.48 ^{ac} | 4.50 ^{ac} | 4.32 ^{ac} |
| 3 | 5.41 ^{ace} | 5.24 ^{ace} | 5.64 ^{acf} | 5.70^{acg} | 6.00 ^{ach} | 5.20 ^{ace} |
| 4 | 6.92 ^{aceg} | 4.93 ^{ace} | 4.97 ^{acf} | 6.24 ^{acg} | 6.10 ^{ach} | 5.67 ^{ace} |
| 5 | 7.48 ^{bceg} | 6.41 ^{bce} | 5.53 ^{bcf} | 7.58 ^{bcg} | 7.32 ^{bch} | 6.40 ^{bde} |
| 6 | 8.51^{bdfg} | 6.92 ^{bde} | 5.80 ^{bdf} | 8.36 ^{bdg} | 8.34 ^{bdh} | 6.61 ^{bde} |

Table 3 Absorptivity at 232 nm during oven test at 63 °C temperature

*Means within the same column sharing a common small letter are not significantly different at P < 0.05

RBO rice bran oil; *TBHQ* tertiary butylated hydro quinone; *CA* citric acid; *BHA* butylated hydroxy anisole; *BHT* butylated hydroxy toluene Results are average of three individual experiments

Rice Bran Oil + BHA/BHT,

$$PV = 1.507Xabsorptivity - 5.334 (R2 = 0.989)$$
(6)

Rice Bran Oil + BHA/BHT + CA,

PV = 1.519Xabsorptivity - 5.401 (R2 = 0.968) (7)

No difference in the absorptivity at 270 nm was found (data not shown) w the control and antioxidant treated rice bran oil samples during the oven test at 630 C with respect to time. This indicates that secondary oxidation compounds (including trienes) could not be detected in the rice bran oil samples during oven test.

Microwave heating Microwave heating may promote oxidation of rice bran oil and the Absorptivity has been proven to be a good analytical indice to measure oxidative changes. The temperature achieved during microwave heating at different time periods is given in Fig. 3. The absorptivity and peroxide value data from Tables 4, 5 and 6 indicate that citric acid was not effective in the protection of oxidation of

rice bran oil whereas TBHO was the most effective among all the antioxidants. Phenolic antioxidants are frequently added to the edible oils to minimize oxidative deterioration and tertiary-butylhydroquinone has been shown to be the most effective antioxidants for stabilizing the edible oils (Icenhour and Vandolah 1991). The data from Table 5 indicate that TBHQ in the proportion of 200 ppm showed better protection to the oxidation. The absorptivity at 232 nm was 5.452 and 5.963 when TBHQ was added in the proportion of 200 and 100 ppm respectively compared to control sample, 6.889 after 32 min of microwave heating. However, no significant changes were observed in the control and antioxidant added sample after heating them in microwave for 10 min, however the value increased from 5.211 after 12 min of heating to 6.453 after 28 min of heating due to the larger formation of conjugated dienes.

The value of the absorptivity at 270 nm for the rice bran oil and heated rice bran oil in microwave for different period of time is shown in Table 5. The absorptivity was increased from 0.808 to 2.016 for control and microwave heated sample for 32 min respectively. No significant difference in the absorptivity was found in the rice bran oil samples for 12 min of heating. After 16 minutes,

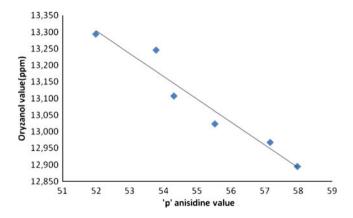


Fig. 2 Correlation between oryzanol value and p-anisidine value of rice bran oil at 63°C temperatures

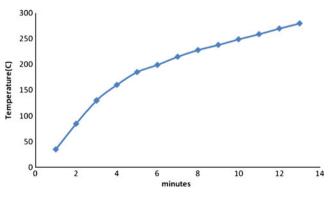


Fig. 3 Rice bran oil temperature (°C) reached during microwave heating time (min)

| Time (min) | Pure RBO | RBO+TBHQ(100 ppm) | RBO+TBHQ(200 ppm) | RBO+CA | RBO+BHA/BHT | RBO+BHA/BHT+CA |
|------------|---------------------------|----------------------|-------------------------|--------------------------|-------------------------|------------------------|
| 0 | 3.231 ^a | 3.231 ^a | 3.230 ^a | 3.231 ^a | 3.231 ^a | 3.231 ^a |
| 2 | 3.449 ^{ac} | 3.321 ^{ac} | 3.288 ^a | 3.328 ^{ac} | 3.327 ^a | 3.327 ^a |
| 4 | 3.612 ^{ace} | 3.405 ^{ac} | 3.101 ^{ac} | 3.409 ^{ace} | 3.404 ^{ac} | 3.407 ^{ac} |
| 6 | 3.781 ^{aceg} | 3.688 ^{ac} | 3.516 ^{ace} | 3.682 ^{aceg} | 3.675 ^{ace} | 3.667 ^{ace} |
| 8 | 4.562 ^{acegi} | 3.885 ^{ac} | 3.791 ^{aceg} | 3.954 ^{acegi} | 3.879 ^{aceg} | 3.932 ^{aceg} |
| 10 | 4.763 ^{acegik} | 4.271 ^{ac} | 3.991 ^{acegi} | 4.369 ^{acegik} | 4.358 ^{acegi} | 4.361 ^{acegi} |
| 12 | 5.211 ^{bdfhikm} | 4.564 ^{bce} | 4.306 ^{bcegik} | 4.614 ^{bcegikm} | 4.588 ^{bcegik} | 4.562 ^{bcegi} |
| 16 | 5.569 ^{bdfhikmo} | 4.925 ^{bce} | 4.683 ^{bdegik} | 5.013 ^{bdfgikm} | 4.969 ^{bdegik} | 4.876 ^{bdegi} |
| 20 | 5.991 ^{bdfhjkmo} | 5.325 ^{bce} | 4.874 ^{bdfgik} | 5.482 ^{bdfhjkm} | 5.352 ^{bdfgik} | 5.312 ^{bdfgi} |
| 24 | 6.238 ^{bdfhjkmo} | 5.561 ^{bde} | 5.003 ^{bdfgik} | 5.614 ^{bdfhjkm} | 5.605 ^{bdfhik} | 5.598 ^{bdfhi} |
| 28 | 6.453 ^{bdfhjkmo} | 5.752 ^{bde} | 5.191 ^{bdfhik} | 5.853 ^{bdfhjkm} | 5.754 ^{bdfhik} | 5.662 ^{bdfhi} |
| 32 | 6.889 ^{bdfhjlno} | 5.963 ^{bdf} | 5.452 ^{bdfhjk} | 6.108 ^{bdfhjlm} | 6.021 ^{bdfhjk} | 5.989 ^{bdfhi} |

Table 4 Absorptivity at 232 nm of RBO heated in microwave oven

*Means within the same column sharing a common small letter are not significantly different at P<0.05

RBO rice bran oil; *TBHQ* tertiary butylated hydro quinone; *CA* citric acid; *BHA* butylated hydroxy anisole; *BHT* butylated hydroxy toluene Results are average of three individual experiments

significant differences were observed in the absorptivity for the control sample and the sample consisted of citric acid whereas the samples consisted of the other antioxidant showed significant difference after 20 min. The least value of absorptivity at 270 nm was observed in the sample consisted of TBHQ in the proportion of 200 ppm, in the similar line as for absorptivity at 232 nm.

The changes in the peroxide value are shown in Table 6. The peroxide value also showed significant changes but did not increase gradually. Rice bran oil sample showed a maximum peroxide value after microwave heating of 20 min and thereafter the peroxide value decreased. The changes in peroxide value may be due to the occurrence of oxidised compounds such as ketones, acids etc. Farag et al. (1992) reported an increase of cottonseed oil oxidation during microwave heating observed by increase in peroxide value due to the presence of reactive radicals that might be formed by exposure to the microwaves. A small increase in peroxide value of olive and sunflower oil heated in microwave oven has also been reported (Albi et al. 1997).

| Time (min) | Pure RBO | RBO+TBHQ (100 ppm) | RBO+TBHQ (200 ppm) | RBO+CA | RBO+BHA/BHT | RBO+BHA/ BHT+CA |
|------------|------------------------------|------------------------------|-------------------------------|----------------------------|---------------------------|----------------------------|
| 0 | 0.808^{a} | 0.803 ^a | $0.805^{\rm a}$ | 0.807^{a} | $0.807^{\rm a}$ | 0.806 ^a |
| 2 | 0.869 ^{ac} | 0.864 ^{ac} | 0.861 ^{ac} | 0.867 ^{ac} | 0.865 ^{ac} | 0.863 ^{ac} |
| 4 | 0.897^{acg} | 0.881 ^{ace} | 0.876 ^{ace} | 0.886 ^{ace} | 0.884 ^{ace} | 0.883 ^{ace} |
| 6 | 0.946 ^{acgi} | 0.921 ^{aceg} | 0.915 ^{aceg} | 0.931 ^{aceg} | 0.928 ^{aceg} | 0.926 ^{aceg} |
| 8 | 0.992 ^{acgik} | 0.957 ^{acegi} | 0.944 ^{acegi} | 0.961 ^{acegi} | 0.959 ^{acegi} | 0.957 ^{acegi} |
| 10 | 1.063 ^{acgikm} | 0.985 ^{acegik} | 0.979 ^{acegik} | 0.991 ^{acegik} | 0.989 ^{acegik} | 0.987 ^{acegik} |
| 12 | 1.209 ^{acgikmo} | 1.189 ^{acegikm} | 1.023 ^{acegikm} | 1.198 ^{acegikm} | 1.195 ^{acegikm} | 1.192 ^{acegikm} |
| 16 | 1.455 ^{bcgikmoq} | 1.353 ^{acegikmo} | 1.341 ^{acegikmo} | 1.399 ^{bcegikmo} | 1.374 ^{acegikmo} | 1.368 ^{acegikmo} |
| 20 | 1.528 ^{bdhikmoqs} | 1.485 ^{bcfhikmoq} | 1.411 ^{bcegikmoq} | 1.457 ^{bdegikmoq} | 1.452 ^{bdegikmo} | 1.449 ^{bdegikmoq} |
| 24 | 1.771 ^{bdhjlnoqst} | 1.689 ^{bdfhjlnoqs} | 1.676 ^{bcfhjlnpqr} | 1.697 ^{bdfhjlnoq} | 1.693 ^{bdfhjlmo} | 1.691 ^{bdfhjlnoq} |
| 28 | 1.839 ^{bdhjlnprstu} | 1.746 ^{bdfhjlnoqst} | 1.731 ^{bdfhjlnpqrs} | 1.751 ^{bdfhjlnoq} | 1.749 ^{bdfhjlmo} | 1.748 ^{bdfhjlnoq} |
| 32 | 2.016 ^{bdhjInprstu} | 1.932 ^{bdfhjlnprst} | 1.905 ^{bdfhjlnpqrst} | 1.938 ^{bdfhjlnpq} | 1.937 ^{bdfhjlno} | 1.935 ^{bdfhjlnpq} |

Table 5 Absorptivity at 270 nm of RBO heated in microwave oven

*Means within the same column sharing a common small letter are not significantly different at P < 0.05

RBO rice bran oil; *TBHQ* tertiary butylated hydro quinone; *CA* citric acid; *BHA* butylated hydroxy anisole; *BHT* butylated hydroxy toluene Results are average of three individual experiments

| Time (min) | Pure RBO | RBO+TBHQ (100 ppm) | RBO+TBHQ (200 ppm) | RBO+CA | RBO+BHA/BHT | RBO+BHA/ BHT+CA |
|------------|--------------------------|--------------------------|---------------------------|-----------------------|------------------------|------------------------|
| 0 | 0.54 ^a | 0.53 ^a | 0.53 ^a | 0.54 ^a | 0.54 ^a | 0.53 ^a |
| 2 | 1.32 ^{ac} | 1.15 ^{ac} | 1.12 ^{ac} | 1.23 ^{ac} | 1.24 ^{ac} | 1.22 ^{ac} |
| 4 | 1.6 ^{ace} | 1.3 ^{ace} | 1.21 ^{ace} | 1.36 ^{ac} | 1.35 ^{ace} | 1.34 ^{ace} |
| 6 | 1.27 ^{aceg} | 1.03 ^{aceg} | 0.99 ^{aceg} | 1.11 ^{ac} | 1.15 ^{aceg} | 1.09 ^{aceg} |
| 8 | 1.01 ^{acegi} | 0.99 ^{acegi} | 0.96 ^{acegi} | 1.08 ^{ac} | 1.12 ^{aceg} | 1.08 ^{aceg} |
| 10 | 0.98 ^{acegik} | 0.99 ^{acegik} | 0.95 ^{acegim} | 0.97^{ac} | 0.96 ^{aceg} | 0.94 ^{aceg} |
| 12 | 0.99 ^{acegikm} | 0.87 ^{acegikm} | 0.82^{acegim} | 0.91 ^{ace} | 0.92 ^{aceg} | 0.89 ^{aceg} |
| 16 | 2 ^{bcegikmo} | 1.8 ^{bcegikmo} | 1.5 ^{acegilmo} | 1.84 ^{aceg} | 1.81 ^{bcegi} | 1.79 ^{bcegi} |
| 20 | 2.9 ^{bdfhjlno} | 2.91 ^{bdfhjlno} | 2.6 ^{bdfhjknpq} | 2.96 ^{bdfhi} | 2.98^{bdfhjk} | 2.9^{bdfhi} |
| 24 | 2.6 ^{bdehjlno} | 2.4 ^{bdehjlno} | 2.1 ^{bcehjlnoq} | 2.42 ^{bdfgi} | 2.45 ^{bdehik} | 2.4 ^{bdehi} |
| 28 | 2.71 ^{bdehjlno} | 2.47 ^{bdfhjlno} | 2.34 ^{bdfhjlnoq} | 2.55 ^{bdfgi} | 2.48 ^{bdfhik} | 2.82 ^{bdfhi} |
| 32 | 2.68 ^{bdehjlno} | 2.39 ^{bdehjlno} | 2.16 ^{bdehjlnoq} | 2.02 ^{bcfgi} | 2.39 ^{bdehik} | 2.26 ^{bcehi} |

Table 6 Peroxide value (meq/kg) of Rice Bran Oil heated in microwave oven

*Means within the same column sharing a common small letter are not significantly different at P < 0.05

RBO rice bran oil; *TBHQ* tertiary butylated hydro quinone; *CA* citric acid; *BHA* butylated hydroxy anisole; *BHT* butylated hydroxy toluene Results are average of three individual experiments.

This trend was observed in all the oil samples, containing different antioxidants. The maximum peroxide value was observed after 20 min of microwave heating but the significant changes in the peroxide value were observed after 16 min compared to the control sample (P < 0.05). However, the least peroxide value of 2.6 meg/kg was observed in the rice bran oil consisting of 200 ppm of TBHO among all the samples. The equations which were established during oven heating for different period of time were held for microwave heating, the absorptivity at 232 nm values showed peroxide value 5.26 for the control rice bran oil sample and 2.81 for the rice bran oil sample consisting of 200 ppm of TBHO respectively after 20 min of microwave heating. The values were found closely correlated with the peroxide values obtained during the microwave oven heating experimentally, indicating the suitability of the oven test to predict the auto-oxidation during the microwave heating. The similar trend was also reported by Vieira TMFS, Regitano-D'Arce MAB (2001) for the canola oil thermal oxidation.

The effect of microwave heating on the oryzanol content and p-anisidine value was also observed and the correlation to the oven test was established. The oryzanol content was gradually decreased with respect to time of heating in microwave. The changes were significantly different in the oryzanol content after 5 days. The data when applied during the oven test in Eq. 1 showed the oryzanol content was 13,371, 13,267 and 13,188 ppm whereas the p-anisidine values were found as 51.90, 54.93 and 56.60 respectively after 1 day, 4 days and 5 days respectively. The values were found closely correlated

with the experimental value obtained during the microwave hating (Table 7) indicating the suitability of the oven test during microwave heating.

The study concluded that microwave heating time is associated with the absorptivity and this analysis may be adopted to compare the oxidative analysis of oils under microwave heating. The peroxide values obtained from the correlations during the oven test were found closely correlated with the peroxide values obtained during the microwave oven heating experimentally, indicating the suitability of the oven test to predict the auto-oxidation during the microwave heating. The oryzanol content and panisidine values obtained after oven heating when correlated to the microwave heating, data showed the oryzanol content 13,371, 13,267 and 13,188 ppm after 1 day, 4 days

 Table 7 Oryzanol and p-anisidine values of rice bran oil during microwave heating

| Time(Days) | Oryzanol Value (ppm) | p-anisidine values |
|------------|-----------------------|-----------------------|
| 1 | 13,310 ^a | 51.01 ^a |
| 2 | 13,276 ^{ac} | 51.48 ^{ac} |
| 3 | 13,190 ^{ace} | 51.71 ^{ace} |
| 4 | 13,102 ^{ace} | 52.53 ^{bceg} |
| 5 | 13,065 ^{bce} | 52.87 ^{bceg} |
| 6 | 12,988 ^{bde} | 53.68 ^{bdfg} |

*Means within the same column sharing a common small letter are not significantly different at P < 0.05

Results are average of three individual experiments

and 5 days respectively which were closely correlated with the experimental value.

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