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EFFECT OF THE TEMPERATURE AND OXIDATION TIME ON SOME PHYSICOCHEMICAL CHARACTERISTICS OF THE RICE BRAN OIL

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ABSTRACT

Due to their excellent characteristics, vegetable oils are successfully used in various formulations of organic lubricants. In this context, the advanced biodegradability and excellent lubricity performance of rice oil leads to its being considered as a real potential for the lubricants industry. However, as with other vegetable oils, the stability of rice bran oil is strongly influenced by the oxidation process. Therefore, the aim of this work was the oxidation stability monitorization of rice bran oil by spectrophotometric techniques. For this purpose, oxidation tests of rice bran oil at elevated temperatures were performed.

In this paper, transmittance spectra were determined, and the trichromatic components and coordinates were calculated, as well as the colour differences for rice oils subjected to a forced oxidation treatment at temperatures of 100 °C and 120 °C for 4, 8 and 10 hours. The results obtained show that, although after the first 4 hours of forced oxidation significant changes appear on the physicochemical properties of rice bran oil, an increase in the test time from 8 to 10 hours does not lead to significant changes in the analysed parameters, the conclusion being valid for both test temperatures.

KEYWORDS: rice bran oil, oxidation, transmittance, eco-friendly lubricant

1. Introduction

Rice (Oryza Sativa L.) is considered the oldest cultivated plant; it began to be cultivated 8000 years ago in South Asia while in Europe it was first cultivated around the 8th century especially in Spain. In Romania, the first rice plantation dates to the 18th century and was cultivated in the Banat area [1].

Rice is the world's third most important cereal in terms of annual production, but the most important food crop in terms of caloric and nutritional value. In 2019, world's leading rice producers were: China - 148 million tons and India - 116 million tons, while in Romania rice production was 40,000 tons [2]. About two-thirds of the rice consumed by Europeans is grown in the EU, the rest is imported from India or Cambodia.

Rice bran oil is obtained by cold pressing the husk of the rice grain, followed by extraction and refining for dewaxing and deodorization. Rice bran oil contains saturated and unsaturated fatty acids as well as a number of bioactive compounds such as gamma-oryzanol, tocotrienols and tocopherols [3, 4].

Rice bran oil can also be used as an edible oil in recent times and as a raw material to produce bio-fuels and environmentally friendly lubricants [5-11]. Recently, a series of tribological and rheological studies have been conducted on rice bran oils [12-19]. The study of rice bran oil has been addressed by a number of researchers, among whom we can mention [20-23].

2. Experimental Details

In this paper, transmittance curves were determined for rice bran oils subjected to a forced oxidation treatment at temperatures of 100 °C and 120 °C, for 4, 8 and 10 hours, maintaining a constant flow of 29 L/min of air. The transmittances of the oxidized samples as well as the non-oxidized oil with the T60 spectrophotometer, produced by PG Instruments Limited (C.E.) were determined. The transmittance values in the wavelength range of 380 - 780 nm were determined.

Also, from spectral transmittance curves, the samples for colour in the x, y, z or L^*, a^*, b^* and

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C^*_{ab}, h_{ab} coordinates: CIEXYZ, CIE $L^*a^*b^*$ (CIELAB) and CIE $L^*C^*_{ab}{}^*h_{ab}$ (CIELCH) colour systems were measured. CIE $L^*a^*b^*$ scale is recommended by Commission Internationale de l'Eclairage [24]. Illumination was performed by D65/10°. Furthermore, the rice oil colour differences were calculated.

3. Experimental Results

Figures 1-5 show the transmittance curves of oxidized oils at temperatures of 100 ºC and 120 ºC for 4, 8 and 10 hours as well as for non-oxidized oil. Based on the experimental values of the transmittances determined at wavelengths of 445, 495, 550 and 625 nm, trichromatic components and coordinates were calculated (Tables 1 and 4), these being the calculation support for determining the chromatic coordinates (Tables 2 and 5) and colour differences (Tables 3 and 6) for the oxidized oils at temperatures of 100 ºC and 120 ºC for 4, 8 and 10 hours as well as for non-oxidized oil.

Figure 1 shows the transmittance curves of non-oxidized and oxidized oil for 4, 8 and 10 hours at 100 °C. Analysing the transmittance curves, it is observed that in the wavelength range between 380-470 nm there are no differences in the transmittance values between non-oxidized oil and oxidized oil for 4 hours. However, after 470 nm, due to oxidative degradation, under the action of O_2 from the bubbled air in the rice oil samples, through radical chain reactions [25], noticeable differences in transmittance spectra appear.

Increasing the exposure time to forced oxidation to 8 and 10 hours, respectively, over the entire wavelength range analysed, major differences in transmittance values appear compared to non-oxidized oil.

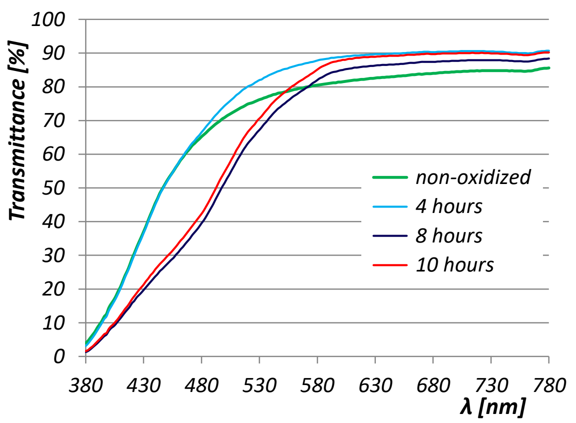

Fig. 1. *Spectral transmittance curves of oxidized rice oils at 100 °C for 4, 8 and 10 hours*

Comparing the oxidized oils for 8 and 10 hours, there are no major differences in the values of their transmittance. Both oils show, in the first half of the wavelength range, decreases in transmittances compared to non-oxidized oil, due to the oxidation of lipids present in the composition of rice oil, most likely caused by the presence of molecular oxygen. Subsequently, according to the results shown in figure 1, there are increases in transmittance in the last part of the studied interval. Moreover, performing the oxidation test at a higher temperature, respectively increasing the oxidation temperature to 120 °C, causes significant changes in the transmittance spectra of oxidized oils 4, 8 and 10 hours compared to non-oxidized oil (Fig. 2).

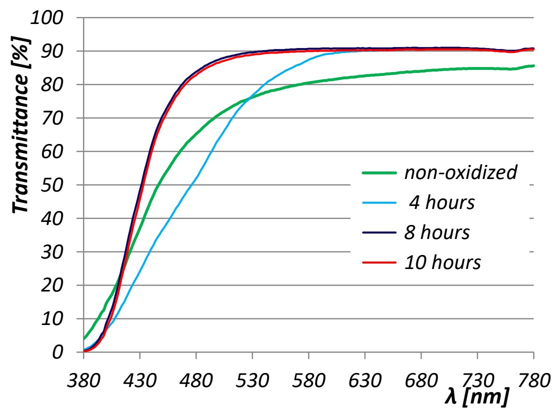

Fig. 2. *Spectral transmittance curves of oxidized rice oils at 120 °C for 4, 8 and 10 hours*

These changes have the probable cause that oxygen and the unsaturated substrate are potential generators of free radicals, a property that accentuates the temperature increase by 20 degrees. In this context, there is a decrease in the transmittance of the analysed sample to about 520 nm due to the increase in the degree of absorption. In addition, after this inflection point, due to the decomposition of hydroperoxides formed by excessive oxidation, there is a decrease in the degree of absorption. The same positive variation is also observed for the oxidation of rice oil samples for 8 hours and 10 hours. Between the latter, no noticeable differences in the variation of the transmittance spectra are found.

These results show that increasing the temperature to 120 °C for up to 8 hours leads to a maximum degree of oxidation of rice oil under the conditions of the experiment. It appears that after this time, the variation of the transmittance spectra is similar. All these findings presented above are also highlighted in Figures 3-5.

According to the obtained results, it is noted that at least in the second part of the transmittance spectra (after 580 nm) the oxidation of the oil samples at the highest temperature under the experimental conditions (120 °C) led to more accelerated transformations of monounsaturated fatty acids (C18: 1, over 41%) and polyunsaturated (C18: 2, over 30%) (the results not shown) in the composition of the studied oil. However, it is highlighted (Figure 3, Tables 2 and 5) the hypsochromic displacement in the first stage of oxidation of the oil samples, when there is also a colour change induced by the selective transmission of light.

All these changes in physicochemical properties due to the oxidation process can lead to a drastic change in lubrication performance, in the context of which this oil can be considered a potential eco-friendly lubricant.

Moreover, the oxidation of the oils was revealed by determining the chromatic parameters. Comparing the chromatic parameters calculated for each oxidized oil at a temperature of 100 ºC and the oxidation periods of 4, 8 and 10 hours, it is observed the increase of the brightness parameter (*L**) after 4 hours of oxidation by 2.93%. In addition, when the process of forced oxidation is continued, there is a decrease of about 3% of this parameter after 8 hours of oxidation. Although there is a slight increase after 10 hours of oxidation, this chromatic parameter still shows a decrease compared to the sample of non-oxidized oil (Table 2). Thus, after 10 hours of oxidation, the brightness decreases by 1.38% compared to non-oxidized oil.

On the other hand, if after the first 4 hours of oxidation at 120 ºC the increase in brightness is insignificant, our results show that the increase in oxidation temperature causes, after 8 hours of oxidation, an increase in the brightness parameter by 5.8% compared to the control sample.

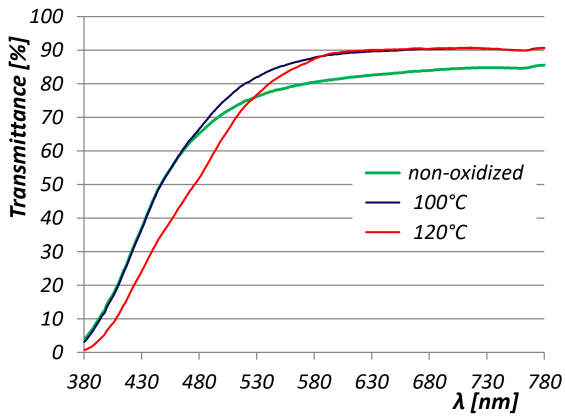

***Fig. 3.** Spectral transmittance curves of oxidized rice oils for 4 hours at 100 °C and 120 °C*

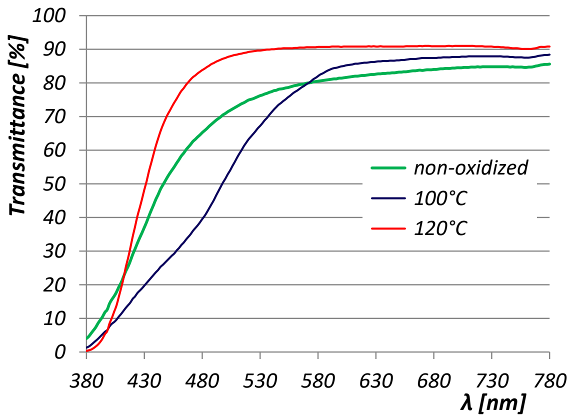

***Fig. 4.** Spectral transmittance curves of oxidized rice oils for 8 hours at 100 °C and 120 °C*

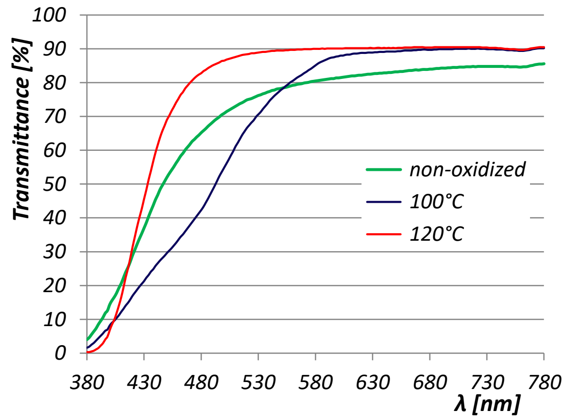

***Fig. 5.** Spectral transmittance curves of oxidized rice oils for 10 hours at 100 °C and 120 °C*

Likewise, the continuation of the forced oxidation up to 10 hours led to an increase in brightness by over 5%, although in this case there is a slight decrease compared to the previous stage of the study (Table 5).

The yellowness parameter (*b**) for oxidized oils at 100 ºC has a slight tendency to increase after 4 hours of oxidation, followed by a significant increase after 8 hours of oxidation, while after 10 hours of oxidation this parameter records an exceedingly small decrease compared to the previous oxidation (Table 2).

The increase in oxidation temperature from 100 °C to 120 °C causes a significant increase after 4 hours (approximately 125%), followed by a significant decrease after 8 hours of oxidation. There is then an insignificant increase in this parameter in the case of oxidized oil for 10 hours compared to oxidized oil for 8 hours (Table 5). This suggests that, after the first 4 hours of oxidation, the rice oil is much more exposed to the change in the CIE value *b**. The yellowness parameter was, however, the most noticeable change from a visual point of view. If in the case of oil samples subjected to oxidation at 100 °C the difference in yellow degree shows that they become yellower than the control sample regardless of the degree of oxidation (Tables 3 and 6), our results show that when oxidation is performed at 120 °C this has place only after oxidation for 4 hours.

In this case, after oxidation of the oil samples for 8 and 10 hours, respectively, it is found that they become less yellow (Table 6).

The results of this study indicated strong correlations of yellowness parameter with $C_{ab}*$ chroma, as well as with the angle of the shade, h_{ab}. Thus, from Table 2 and Table 5 the colour variation of the analysed oil can be noticed within the first quadrant of the chromatic circle, regardless of whether the study was performed at 100 °C or 120 °C. This means that although the other chromatic parameters confirm obvious colour changes depending on the oxidation conditions, however these changes do not pass from one dial to another in the chromatic circle.

In this respect, the degree of oxidation can also be highlighted by comparing the colour differences ($\Delta E*ab$) recorded between the oxidized samples and the non-oxidized reference samples (Fig. 6).

Oxidized oil at 100 ºC for 4 hours, although it produces or differs slightly, this is clearly seen. Increasing the oxidation time to 8 hours shows a sharp increase in colour differences, the oil undergoes an intense oxidation process, it is maintained after 10 hours of oxidation, the colour difference has a high value, but slightly less than that recorded in the case of oxidized oil 8 hours. In both cases, namely oxidation at 8 and 10 hours, the results obtained show distinct colours for the observer in the case of the analysed samples.

Increasing the test temperature to 120 ºC the highest value of colour differences is recorded after 4 hours of testing, this indicating an accentuated oxidation process, followed by lower values of this parameter for oxidized oils for 8 and 10 hours.

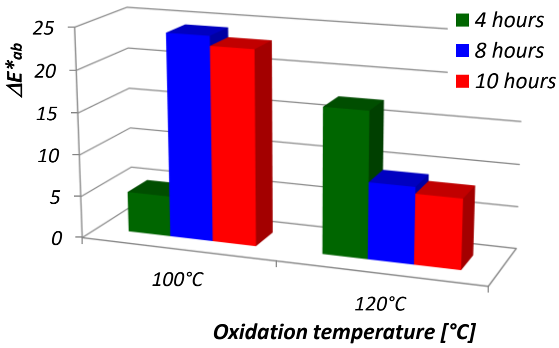

Fig. 6. *Colour differences ($\Delta E*_{ab}$) for oxidized rice oils*

Table 1. *Experimental results for rice oils oxidized at a temperature of 100 °C, obtained according to the colour system (x, y) CIE 1964 (CIEXYZ)/iluminant D65/10°*

Rice oils 100 °C	Trichromatic components			Trichromatic coordinates		
	X	Y	Z	x	y	z
Non-oxidized	72.324	74.149	62.775	0.346	0.354	0.300
4 hours oxidized	77.634	79.811	63.249	0.352	0.362	0.287
8 hours oxidized	67.669	68.580	35.692	0.394	0.399	0.208
10 hours oxidized	70.410	71.565	38.493	0.390	0.397	0.213

Table 2. *Chromatic coordinates (systems: CIELAB) for rice oils oxidized at 100 °C/ Iluminant D65/10°*

Rice oils 100 °C	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Non-oxidized	88.99	4.30	13.75	0.31	0.10	14.41	72.64
4 hours oxidized	91.60	3.98	17.83	0.22	0.05	18.26	77.42
8 hours oxidized	86.30	5.91	37.80	0.16	0.0244	38.26	81.13
10 hours oxidized	87.76	5.55	36.79	0.15	0.023	37.20	81.42

Table 3. *Experimental values of colour differences for rice oils oxidized at 100 °C*

Rice oils 100 °C	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
4 hours oxidized	2.61	-0.32	4.08	3.86	4.78	4.85
8 hours oxidized	-2.70	1.61	24.05	23.85	8.48	24.25
10 hours oxidized	-1.23	1.25	23.04	22.80	8.78	23.10

***Table 4**. Experimental results for rice oils oxidized at a temperature of 120 °C, obtained according to the colour system (x, y) CIE 1964 (CIEXYZ)/iluminant D65/10°*

Rice oils 120 °C	Trichromatic components			Trichromatic coordinates		
	X	Y	Z	x	y	z
Non-oxidized	72.324	74.149	62.776	0.346	0.354	0.300
4 hours oxidized	73.679	75.541	46.387	0.368	0.400	0.232
8 hours oxidized	83.727	86.364	83.330	0.330	0.341	0.329
10 hours oxidized	82.807	85.433	81.469	0.332	0.342	0.326

***Table 5.** Chromatic coordinates (systems: CIELAB) for rice oils oxidized at 120 °C/ Iluminant D65/10°*

Rice oils 120 °C	Chromatic coordinates			a^*/b^*	$(a^*/b^*)^2$	C^*_{ab}	h_{ab}
	L^*	a^*	b^*				
Non-oxidized	88.99	4.30	13.75	0.31	0.10	14.41	72.64
4 hours oxidized	89.65	4.32	30.92	0.14	0.02	31.22	82.05
8 hours oxidized	94.47	3.55	6.63	0.54	0.29	7.52	61.84
10 hours oxidized	94.07	3.50	7.32	0.48	0.23	8.11	64.43

***Table 6.** Experimental values of colour differences for rice oils oxidized at 120 °C*

Rice oils 120 °C	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	Δh_{ab}	ΔE^*_{ab}
4 hours oxidized	0.65	0.02	17.17	16.82	9.41	17.18
8 hours oxidized	5.47	-0.75	-7.12	-6.89	-10.80	9.01
10 hours oxidized	5.08	-0.80	-6.43	-6.29	-8.21	8.23

4. Conclusions

The rice bran oil was subjected to forced oxidation treatments at temperatures of 100 °C and 120 °C, the oxidation times being 4, 8 and 10 hours. The transmittance curves of the oxidized samples were determined and the trichromatic components and coordinates, chromatic coordinates and colour differences were calculated.

The present study showed that for oxidized oil for 10 hours at 100 °C, the brightness parameter (L^*) decreases by 1.4% compared to non-oxidized oil, while for oxidized oil at 120 °C this parameter increases by 5.7%. The yellowness parameter (yellow component b^*) was the most noticeable change visually. The yellowness parameter, in the case of oxidized oil for 10 hours at 100 °C, increases by 168% compared to non-oxidized oil, while for oxidized oils at 120 °C the increase occurs only in the first 4 oxidation hours. In the case of oxidation at 120 °C this parameter decreases throughout the oxidation set in this study by 76.7%.

The largest increases in colour differences were recorded in the case of oils tested at 100 °C for 8 to 10 hours. However, increasing the test temperature from 100 °C to 120 °C for oxidized oils for 4 hours results in a sharp increase in the colour difference. For oils tested at 120 °C, a significant increase in colour difference is observed after 4 hours of testing, followed by a significant decrease for both 8 and 10 hours.

Thus, the results obtained show that, although after the first 4 hours of forced oxidation there are significant changes in the physicochemical properties of rice oil, an increase in test time from 8 to 10 hours does not lead to significant changes in the analysed parameters, the conclusion being valid for both test temperatures.

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