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ORIGINAL PAPER

The Effect of Operational Parameters of the Rancimat Method on the Determination of the Oxidative Stability Measures and Shelf-Life Prediction of Soybean Oil

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Abstract Operational parameters of the Rancimat method, including oil sample size, airflow rate, and temperature, were evaluated to determine their effects on the oxidative stability index (OSI), temperature coefficient, Q_{10} number, and shelf-life prediction for soybean oil. Operational parameters of the Rancimat method had statistically significant effects ($P < 0.05$) on the OSI. Whenever the oil sample size and airflow rate at a given temperature were such that the air-saturated condition could be established, the OSIs showed no statistically significant differences. As temperature increased, OSIs decreased, while their average coefficient of variation (CV) increased. In general, the conditions where the sample was saturated with air and had a relatively lower CV were an oil sample size of 6 g at all temperatures and airflow rates, then 3-g oil sample size at low temperatures (100 and 110 °C) and low airflow rates (10 and 15 L h^{-1}). The temperature coefficient and Q_{10} number were found to be independent of the oil sample size and airflow rate, and their mean values for soybean oil were calculated to be -3.12×10^{-2} °C^{-1} and 2.05, respectively. Oil sample size and airflow rate showed a significant effect on shelf-life prediction for soybean oil. Therefore, choosing the right levels of these operational parameters in the Rancimat method may produce the least possible difference between predictions from long-term storage studies and the OSI test.

Keywords Oxidative stability index · Q_{10} number · Rancimat · Shelf-life prediction · Soybean oil · Temperature coefficient

Introduction

Accelerated techniques most commonly used for assessment of the oxidative stability of edible fats and oils and fat-containing foods include the Rancimat method developed by Hadorn and Zurcher [1]. This test has gained acceptance owing to its ease of use and reproducibility: it is a continuous measurement requiring no periodic analytical determinations and uses no organic solvents for titrations [2, 3]. The Rancimat method is based on automatically determining the time elapsed for the maximum rate change of oxidation by measurement of the increase in the conductivity of deionized water caused by dry air bubbled through a heated sample carrying the volatile acids into a separate container with the deionized water [4–7]. This time, oxidative stability index (OSI), has correlated well with stability under various conditions of lipid oxidation and also with data obtained from independent sensory and/or analytical methods [6, 8–13].

The Rancimat method may also provide some other useful information regarding oxidative stability of edible fats and oils and fat-containing foods. By plotting the logarithms of OSIs versus elevated temperatures and extrapolating to room temperature, we can predict the shelf-life of the sample at ambient conditions. However, these predictions may result in overestimation or underestimation [14, 15], but sometimes acceptable results [16]. The slope of the

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curves represents the temperature coefficients for oil samples [3]. Also, a well-recognized temperature acceleration factor, known as the Q_{10} number, based on the increase in oxidation rate from a 10 °C increase in temperature, can be calculated from the data [17].

Oil sample size, airflow rate, and temperature are the operational parameters that can be adjusted easily in the Rancimat method and may affect the determination of the OSI, temperature coefficient and Q_{10} number (oxidative stability measures), and shelf-life prediction of edible fats and oils and fat-containing foods. Although a number of studies [1–3, 6, 18–20] have investigated the effect of these parameters independently and/or in a limited range, no comprehensive studies have been reported on the effect of these three parameters. The aim of the present work was to investigate the effect of the operational parameters of the Rancimat method on the determination of the oxidative stability measures and to predict the shelf-life of soybean oil.

Materials and Methods

Material

Refined, bleached, and deodorized soybean oil was supplied by a local factory and stored at –18 °C. The peroxide value was determined according to the thiocyanate method [21].

Apparatus

A Metrohm Rancimat model 743 (Herisau, Switzerland) capable of operating over a temperature range of 50–220 °C was used in this study. The glassware was rigorously cleaned between each run to avoid any contamination that would catalyze the peroxidation. The tubes were cleaned by boiling them with sodium hydroxide solution (2%) for 1h, followed by cooling and soaking in concentrated hydrochloric acid. The acid was washed off and the tubes were rinsed with distilled water [9]. Clean glassware was thoroughly dried in an oven. Measuring vessels, electrodes, and connecting tubes were cleaned several times with alcohol and distilled water, and were blown out with nitrogen before the experiment.

OSI Measurement

A stream of air was bubbled into oil samples (3.0, 6.0, and 12.0 g) contained in a reaction vessel placed in an electric heating block. Effluent air containing volatile organic acids from the oil sample were collected in a measuring vessel containing distilled water (60 mL). The conductivity of the water was measured automatically as oxidation proceeded. Filtered, cleaned, dried air was allowed to bubble through the hot oil at rates of 10, 15, and 20 L h^{-1}. The OSIs of the oil samples were automatically recorded at 100, 110, 120, and 130 °C. For each time studied, eight samples were accommodated in the equipment and analyzed simultaneously. Samples for all determinations were randomized on their position in the heating block.

Shelf-Life Prediction, and Temperature Coefficient and Q_{10} Number Calculation

The logarithms of OSIs versus elevated temperatures (100, 110, 120, and 130 °C) were plotted and lines were fitted to the data. The equation for each line was also determined. The slopes of the lines yielded temperature coefficients. The shelf-lives as the OSIs at 20 °C (OSI$_{20}$) were calculated from the corresponding equations. Q_{10} numbers were calculated as the OSI at T/OSI time at T + 10 °C [2, 3, 17, 18].

Statistical Analysis

All determinations were carried out in triplicate and data were subjected to analysis of variance. Analysis of variance was performed using the ANOVA procedure. Statistical analyses were performed according to the MSTATC software. Significant differences between means were determined by Duncan's multiple range tests. P values less than 0.05 were considered statistically significant.

Results and Discussion

The OSI and coefficient of variation (CV) results of treatment combinations (oil sample size × airflow rate) at the different temperatures are presented in Table 1. All soybean oil samples had peroxide values under 1.5 mequiv kg^{-1} prior to the start of the Rancimat test.

At 100 °C and an oil sample size of 3 g, the airflow rates of 10 and 15 L h^{-1} gave similar OSIs, but there was a significantly higher OSI at an airflow rate of 20 L h^{-1}. Jebe et al. [19] reported that an airflow rate of 9 L h^{-1} was sufficient to continuously saturate the oil sample with oxygen during the induction period. However, the results presented here indicate that airflow rates above 15 L h^{-1} affect the OSI. Hill and

Table 1 The oxidative stability index (*OSI*) and coefficient of variation (*CV*) results of the treatment combinations at different temperatures

Treatment	Oil sample size (g)	Airflow rate (L h^{-1})	Temperature (°C)							
			100		110		120		130	
			OSI	CV	OSI	CV	OSI	CV	OSI	CV
1	3	10	15.82 c ^{A}	0.71	7.58 d ^{B}	2.29	3.80 bc ^{C}	2.28	1.85 ab ^{D}	0.83
2	3	15	15.95 c ^{A}	1.61	7.64 d ^{B}	0.69	3.82 bc ^{C}	1.46	1.94 a ^{D}	1.57
3	3	20	16.79 ab ^{A}	0.79	8.25 b ^{B}	1.63	3.88 b ^{C}	1.27	1.94 a ^{D}	0.52
4	6	10	16.05 c ^{A}	0.22	7.36 d ^{B}	1.45	3.69 c ^{C}	0.95	1.74 b ^{D}	6.41
5	6	15	16.08 c ^{A}	1.55	7.69 cd ^{B}	2.02	3.72 c ^{C}	1.48	1.78 ab ^{D}	5.95
6	6	20	16.08 c ^{A}	0.40	8.08 bc ^{B}	1.05	3.82 bc ^{C}	2.76	1.83 ab ^{D}	4.14
7	12	10	16.65 b ^{A}	0.30	8.18 b ^{B}	2.76	4.04 a ^{C}	0.74	0.41 c ^{D}	6.29
8	12	15	16.79 ab ^{A}	1.20	8.35 ab ^{B}	1.72	4.08 a ^{C}	1.91	0.47 c ^{D}	8.60
9	12	20	17.17 a ^{A}	0.73	8.69 a ^{B}	1.43	4.14 a ^{C}	2.71	0.49 c ^{D}	3.12
Average CV				0.83		1.67		1.73		4.16

Means within a column with the same lowercase letters are not significantly different at $P < 0.05$. Means within a row with the same uppercase letters are not significantly different at $P < 0.05$. CV = (SD/average) × 100

SD standard deviation

Perkins [20] also reported significantly different OSIs for an oil sample size of 2.5 g at airflow rates of 12–20 L h^{-1}. It was interesting to find that the OSI of the oil sample at an airflow rate of 20 L h^{-1} was significantly higher than that of the sample at low airflow rates. Jebe et al. [19] reported that temperature stabilization at a sample size of 2.5 g was difficult when using the Rancimat method and thus recommended a 5-g sample. However, it seems that air-saturated conditions cannot be maintained for low oil sample sizes exposed to high airflow rates. The rigorously turbulent status of the oil sample results in more air escaping from the oil sample than is used for lipid oxidation. There is no significant difference among the three airflow rates for 6-g oil sample sizes and low airflow rates (10 and 15 L h–1) with a 3-g sample. This indicates that the air-saturated conditions have been reestablished, yielding a balance between airflow rate and oil sample size. Increasing the oil sample size to 12 g showed that the OSIs increase significantly. This suggests that the concentration of air in the oil is lower than necessary for the creation of air-saturated conditions. Therefore, treatment combinations 3, 7, 8, and 9 in Table 1 cannot create the air-saturated conditions. A relatively large CV for treatment combinations 2 and 5 suggests that the conditions under which oxidation occurs vary more than for the others. Hence, the preferred conditions at 100 °C are 6-g sample sizes with airflow rates of 10 or 20 L h^{-1}, then a sample size of 3 g with an airflow rate of 10 L h^{-1}.

As would be expected, OSIs significantly decreased with temperature (Table 1). As shown in Fig. 1, at 100–120 °C, a nearly similar trend for the OSIs occurred, but this was not observed at 130 °C. Also, the average CV of the treatment combinations increased with temperature. These observations indicate that the conditions under which the oil sample oxidizes vary with increasing temperature. In general, the conditions where the sample was saturated with air and had a relatively lower CV were an oil sample size of 6 g at all temperatures and airflow rates, then a 3-g oil sample size at low temperatures (100 and 110 °C) and low airflow rates (10 and 15 L h^{-1}).

The data calculated from the linear relationship between the natural logarithm of the OSI and the temperature for the treatment combinations in Table 1 are shown in Table 2. There was no statistically significant difference among the treatment combinations in terms of the temperature coefficients and Q_{10} numbers. This enables us to determine these two quantities for soybean oil independently from the oil sample size and airflow rate. According to the results, the temperature coefficient for soybean oil had a mean value of -3.12×10^{-2} °C^{-1}. Hasenhuettl and Wan [3] obtained temperature coefficients for vegetable oils between -2.78×10^{-2} and -3.15×10^{-2} °C^{-1} (mean value -3.01×10^{-2} °C^{-1}). A mean value of 2.05 calculated for the Q_{10} number means that an increase of 10 °C approximately halves the OSI of soybean oil.

The calculated OSIs for the treatment combinations at 20 °C (OSI$_{20}$) showed statistically significant differences. This indicates that the oil sample size and airflow rate have a definite effect on the shelf-life prediction for soybean oil. Frankel [17] stated that the extrapolation of the stability results obtained by the Rancimat test to ambient storage leads to either

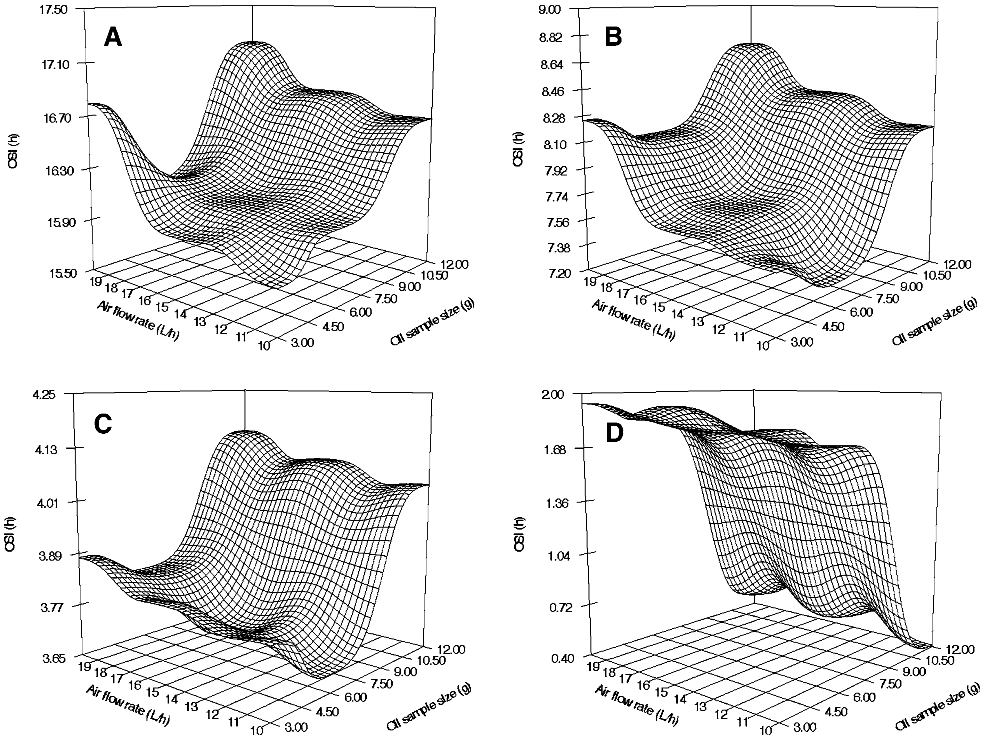

Fig. 1 The variation trend of the oxidative stability index (*OSI*) for different treatment combinations (oil sample size × airflow rate) at 100 °C (**a**), 110 °C (**b**), 120 °C (**c**), and 130 °C (**d**)

Table 2 The results calculated from the linear relationship between the natural logarithm of the OSI assessed by the Rancimat test and the temperature for the treatment combinations in Table 1

Treatment	Log OSI = $A(T) + B$			T_{coeff} ($\times 10^{-2}$)	OSI_{20} (h)	Q_{10}
	$A \pm$ SE	$B \pm$ SE	R^2			
1	–0.0310 ± 0.0006	4.2918 ± 0.0040	0.9999	–3.10 a	4,706 b	2.04 a
2	–0.0305 ± 0.0010	4.2417 ± 0.0035	0.9996	–3.05 a	4,291 c	2.08 a
3	–0.0314 ± 0.0003	4.3648 ± 0.0192	0.9998	–3.14 a	5,457 a	2.06 a
4	–0.0319 ± 0.0005	4.3938 ± 0.0178	0.9995	–3.19 a	5,687 a	2.09 a
5	–0.0318 ± 0.0001	4.3887 ± 0.0076	0.9999	–3.18 a	5,651 a	2.08 a
6	–0.0316 ± 0.0004	4.3699 ± 0.0213	0.9997	–3.16 a	5,477 a	2.07 a
7	–0.0308 ± 0.0007	4.2962 ± 0.0087	0.9999	–3.08 a	4,799 b	2.03 a
8	–0.0307 ± 0.0007	4.2983 ± 0.0092	0.9999	–3.07 a	4,829 b	2.03 a
9	–0.0309 ± 0.0008	4.3280 ± 0.0276	0.9994	–3.09 a	5,131 ab	1.99 a

Since the OSIs at 130 °C for 12-g oil samples severely decreased the curve linearity, the lines for these oil sample sizes were only fitted to the data at 100–120 °C. Means within a column with the same lowercase letters are not significantly different at $P < 0.05$

SE standard error T_{coeff} temperature coefficient, OSI_{20} OSI at 20 °C, Q_{10} OSI at T/OSI at T + 10 °C

overprediction or underprediction of the actual shelf-life depending on the type of oil. Mendez et al. [2] attributed this to the different mechanisms of peroxidation under accelerated conditions of the Rancimat test from the corresponding mechanisms at ambient storage conditions. Nevertheless, Presa-Owens et al. [16] showed that the shelf-life prediction of an infant formula based on such extrapolation provides reasonably acceptable results. Therefore, choosing the levels of these operational parameters in the Rancimat method depending on the type of the product may result in the least possible difference between predictions from long-term storage studies and the OSI test. This will lead to saving a lot of time, which is very precious in control laboratories as well as research and development laboratories.

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References

1. Hadorn H, Zurcher K (1974) Zur Bestimmung der Oxydations-stabilitat von Ölen und Fetten. Dtsch Lebensm Rundsch 70:57–65
2. Mendez E, Sanhueza J, Speisky H, Valenzuela A (1996) Validation of the Rancimat test for the assessment of the relative stability of fish oils. J Am Oil Chem Soc 73:1033–1037
3. Hasenhuettl GL, Wan PJ (1992) Temperature effects on the determination of oxidative stability with the Metrohm Rancimat. J Am Oil Chem Soc 69:525–527
4. Loury M (1972) Possible mechanisms of autoxidative rancidity. Lipids 7:671–675
5. deMan JM, Tie F, deMan L (1987) Formation of short chain volatile organic acids in the automated AOM method. J Am Oil Chem Soc 64:993–996
6. Matthaus BW (1996) Determination of the oxidative stability of vegetable oils by Rancimat and conductivity and chemiluminescence measurements. J Am Oil Chem Soc 73:1039–1043
7. Knothe G, Dunn RO (2003) Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. J Am Oil Chem Soc 80:1021–1026
8. Laubli MW, Bruttel PA (1986) Determination of the oxidative stability of fats and oils: comparison between the active oxygen method (AOCS Cd. 12–57) and the Rancimat method. J Am Oil Chem Soc 63:772–795
9. Gordon MH, Mursi E (1994) A comparison of oil stability based on the Metrohm Rancimat with storage at 20 °C. J Am Oil Chem Soc 71:649–651
10. Coppin EA, Pike OA (2001) Oil stability index correlated with sensory determination of oxidative stability in light-exposed soybean oil. J Am Oil Chem Soc 78:13–18
11. Anwar F, Bhanger MI, Kazi TG (2003) Relationship between Rancimat and active oxygen method values at varying temperatures for several oils and fats. J Am Oil Chem Soc 80:151–155
12. Kowalski B, Ratusz K, Kowalska D, Bekas W (2004) Determination of the oxidative stability of vegetable oils by differential scanning calorimetry and Rancimat measurements. Eur J Lipid Sci Technol 106:165–169
13. Velasco J, Andersen ML, Skibsted LH (2004) Evaluation of oxidative stability of vegetable oils by monitoring the tendency to radical formation. A comparison of electron spin resonance spectroscopy with the Rancimat method and differential scanning calorimetry. Food Chem 85:623–632
14. Kaya A, Tekin AR, Oner MD (1993) Oxidative stability of sunflower oil and olive oils: comparison between a modified oxygen method and long term storage. Food Sci Technol 26:464–468
15. Toro-Vazquez JF, Castillo AA, Hernandez-C R (1993) A multiple-variable approach to study corn oil oxidation. J Am Oil Chem Soc 70:261–267
16. Presa-Owens S, Lopez-Sabater MC, Rivero-Urgell M (1995) Shelf-life prediction of an infant formula using an accelerated stability test (Rancimat). J Agric Food Chem 43:2879–2882
17. Frankel EN (1998) Lipid oxidation. The Only Press, Dundee, pp 99–114
18. Reynhout G (1991) The effect of temperature on the induction time of a stabilized oil. J Am Oil Chem Soc 68:983–984
19. Jebe TA, Matlock MG, Sleeter RT (1993) Collaborative study of the oil stability index analysis. J Am Oil Chem Soc 70:1055–1061
20. Hill SE, Perkins EG (1995) Determination of oxidation stability of soybean oil with the oxidative stability instrument: operation parameter effects. J Am Oil Chem Soc 72:741–743
21. Shantha NC, Decker EA (1994) Rapid, sensitive, iron-based spectrophotometric methods for determination of peroxide values of food lipids. J AOAC Int 77:421–424