Effects of Moisture and Extrusion Temperatures on the Oxidative Stability of Milling Oat Products with Granularity Below 532 μm

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ABSTRACT

The present research had as objective to study the effects of moisture and extrusion temperatures on the oxidative stability of oat fine (< 532 mm) milling products. The oat caryopsis were ground in a Brabender mill and separated in two fractions, coarse over 532 mm and fine less than 532 mm. The fine fraction, with higher amount of starch and low amount of crude protein, lipids and dietary fiber content when compared to oat coarse milling products was conditioned to moisture levels (15.5-25.5 %) and extruded in a simple one-screw Brabender laboratory extruder (C/D= 20:1). The conditions of extrusion were compression ratio 3:1, screw speed of 100 rpm, a die of 6 mm in diameter and temperatures between 77.6 and 162.4 °C in the 2nd and 3rd zones while the 1st zone was maintained at 80 °C. The extruded material was dried, ground, conditioned in plastic bag and periodically determined the peroxide value and n-hexanal. The unsaturated fatty acids content of the oil fraction was higher (79.20 %). Independent of moisture level, all extruded products in temperatures less than 120 °C showed low oxidative rancidity.

Key words: Avena sativa; lipids; peroxide; n-hexanal.

INTRODUCTION

The industrial processing of oat is unique due to the anatomic structure and chemical composition of the grain (Fulcher, 1986). The husk is waxy, fibery and totally indigestible to the human system, being necessary its elimination in the grain processing. The caryopsis lipid content ranges from 6 to 11% and is well distributed in the grain, with higher levels in the germ and bran. The external layers have active enzymes that transform the lipids into free fatty acids. The protein content is high, ranging from 14 to 18%, and the balance of amino acids is adequate. However, such proteins do not form gluten when mixed with water. The oat bran is relatively fine, bright, and usually not separated from the endosperm.

In the industrial processing of oat grains, the enzymes are inactivated through treatment with steam (Deane & Commers, 1986). The intensity of such treatment is monitored by determining the activity of residual enzymes, such as tyrosinase and peroxidase (Webster, 1986). In addition to the steam treatment, other process for enzymatic stabilization have been tested at both laboratory and industry levels. Frey & Hammond (1975) used a wet milling process, either in 95% ethanol or in hot water, followed by vacuum drying. Liukkonen et al. (1995) dispersed oat flour in weak alkaline solution. Additional methods for enzymatic inactivation through microwaves or thermoplastic extrusion were proposed by Vetrimani et al. (1992) and Fretzdorff & Seiler (1987), respectively.

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The extrusion technique is a promising tool in the processing of cereal grains, not only for human consumption but also for the industrial purposes. Although this technique has shown to be efficient in processing grains (El-Dash, 1982), its use in oats is still not well investigated.

The objective of this research was to study the effects of initial moisture levels and extrusion temperatures on the oxidative stability of its extruded oat products of milling fraction with granularity lower than 532 μm. This was attempted through determining the peroxide value and n-hexanal.

MATERIALS AND METHODS

Oat grains of the UPF 16 cultivate, from the University of Passo Fundo breeding program, were used in this research. The grains were cleaned by airing and sieving. The husks were removed by impact milling machine. The caryopsis were dried to 10% moisture and milled in an experimental roll mill (Brabender Quadrumat Senior) using the break section and the sieving system. The oat fraction of granularity below 532 μm, with an extraction yield of 50%, was collected separately. The oil was extracted according to the method proposed by Bligh & Dyer (1959) and the fatty acids composition was determined through the Ce 1-62 method by the American Oil Chemists' Society (1990).
The samples were dried to varying moistures (15.5 - 25.5%) and processed in a Brabender extruder (model 20D/N-GNF 1014/2, Brabender OHG, Duisburg, Germany) of single screw type, operated at a 3:1 compression rate, 100 rpm, 6 mm-diameter matrix, and a 70 g/min-constant input. The temperature was 80 °C in the first zone and between 77.6 and 162.4 °C in the second e third zones, respectively. The extruded products were dried in a laboratory oven with air circulation, at 45-50 °C for 15 hours, milled in a mill of knives and rolls (< 500 μm) and packaged in plastic bags of low density polyethylene (70 μm thick). After being identified and sealed, the bags were stored at room temperatures (25°C±2), protected from light, and periodically used to determine the peroxide value and n-hexanal.

The peroxide value was determined according to the Cd 8-53 method of the American Oil Chemists' Society (1990). The oil extraction was done a low temperatures using petroleum ether; traces of water were removed by adding anhydrous sodium sulfate and the petroleum ether was separated from the oil by means of a rotary evaporator at 35-40°C, under vacuum. The peroxides were quantified by reaction with 0.005 N sodium thiosulfate.

The n-hexanal was determined according to the method proposed by Fritsch & Gale (1977), using 15 g of sample in 250 mL erlenmeyer; 4-heptanona internal pattern completed with boiling distilled water to 150 mL. The erlenmeyer were sealed and kept under shaking. After one minute, an 1 mL sample was collected and injected into a Varian gas chromatograph (model 3 400), connected to a Varian integrator (model 4 400). The chromatograph characteristics were: still packed column measuring 2 m length × 1/8" diameter, 4% OV101/6%OV210 CWHP; flame ionization detector; on column type injector; attenuation of 2×10^{-12}; temperatures of 100 °C (column), 150 °C (injector), and 200 °C (detector). The n-hexanal concentration in the samples was expressed as mg/kg.

To study the combined effect of the independent variables a statistical design of rotational composed central type, of 2^{nd} degree, applied to a surface response methodology (Box & Draper, 1987) was used. The independent variables and the variation levels studied are presented in Table 1. In this experiment 11 treatments

were tested, being four factorial (combining the levels -1 and +1), four axial (one variable at $\pm\infty$ and the other one at zero), and three central (two variables at zero).

Statistical data were analyzed in SAS (Sas Institute, 1985). The model significance was tested using ANOVA while the individual effects of the response variables were adjusted through the stepwise procedure at the 10% significance level ($p \leq 0.10$). The non-significant elements were dropped off the model and this was subjected to new analyses.

Table 1. Variables and levels of variation of the extrusion experiment

Independent variables	Levels of variation[1]				
	$-\infty$	-1	0	+1	$+\infty$
Extrusion temperature(%)	77.5	90	120	150	162
Moisture raw material (%)	15.5	17	20.5	24	25.5

1. ∞= 1.4141 for k = 2 (two independent variables).

RESULTS AND DISCUSSION

The composition of fatty acids in the caryopsis oil and in the fraction of milled oat grains studied is shown in Table 2. The variations found were relatively small. The lowest levels of unsaturated fatty acids were found in the caryopsis.

Of the total amount of fatty acids present in the oil extracted of the fraction with granularity below 532 μm, 20.80% were saturated fatty acids and 79.20% were unsaturated. The linoleic, oleic, and palmitic acids had levels of 39.49%, 38.35%, and 18.32%, respectively, and represented 96.16% of the total fatty acids. The miristic, estearic, arachidic, and linoleic totaled only 3.84%. Such levels are in agreement with results obtained by Kahlon (1989) and Peterson (1992).

The composition of lipids in oat grains is favored by the high content of unsaturated fatty acids. Among these, the linoleic, which is considered essential to human nutrition, is the most common. On the other hand, such composition of fatty acids is responsible for the weak stability of oat products and the formation of undesirable compounds (Galliard, 1983). To monitor the extension of oxidative rancidity, one can determine the individual or total volatile carbonilic compounds formed by degradation of hydroperoxides (Shahidi, 1995). The n-hexanal, one of the main secondary products formed during the linoleic acid oxidation (Frankel et al., 1981) has been used to monitor the oxidative rancidity in cereal grain products.

The oxidative stability of products extruded from the oat grain fraction with granularity below 532 μm was determined at zero (t = 48 hours), 21, 42, 63, 84, and 126 days of storage, taking into account the presence and levels of primary and secondary rancidness products. Based on experimental data, regressions models for the times zero, 42, 84, and 126 days were established. The models were significant at $p \leq 0.05$. Using the complete model as a starting point, the non-significant coefficients ($p \geq 0.10$) were eliminated by means of stepwise analysis. The adjusted models that resulted from the analysis are shown in Table 3.

In the assessment of peroxides during storage of products extruded from oat fine milling products, it was observed a convex quadratic relationship, that is, the peroxide value increased as the temperature of extrusion was higher. This increase was due to lipid degradation as higher extrusion temperatures were used. The peroxide value also increased proportionally to the storage time of zero, 42, 84, and 126 days (Fig. 1).

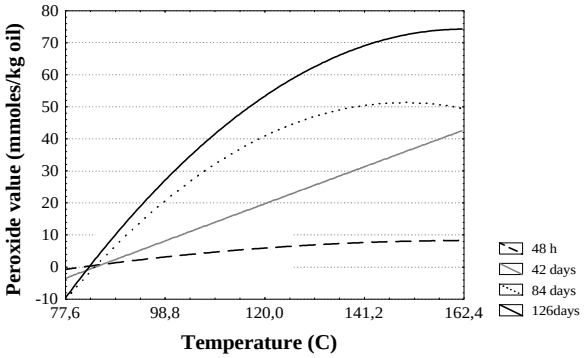

Fig. 1. Effect of temperature of extrusion on peroxide value for extruded oat products, fraction with granularity below 532 μm, as a function of time of storage (t = 48 horas, 42 days, 84 days, and 126 days).

Table 2. - Composition of fatty acids in oat oil extracted from the caryopsis and from the fraction of granularity below 532 μm

Fatty acid	Caryopsis (%)	< 532 μm (%)
Miristic C14:0	0.11	0.08
Palmitic C16:0	18.21	18.32
Estearic C18:0	1.9	1.48
Arachidic C20:0	0.94	0.92
Total for saturated acids	20.65	20.80
Oleic C18:1	38.99	38.35
Linoleic C18:2	39.16	39.49
Linolenic C18:3	1.20	1.36
Total for unsaturated acids	79.35	79.20

In treatments one and five, as well as in non-processed oats, only trace levels of peroxides were found, even after 126 days of storage. In extruded products, however, the peroxide value (mmoles per kg of oil) increased from 6.05, at time zero, to 85.60 at 126 days of storage. According to Mustakas et al. (1970), the minimum of peroxide value limit required to stabilize the extruded products is 20 mmoles. If this value is taken into account to analyze the results obtained, then the extruded 3 is acceptable, in addition to numbers one and five already cited. All other treatments reached values higher than 20 mmoles, which means that the oxidative rancidity has occurred, therefore, altering the flavor and quality of the extruded products.

Poskocilova et al. (1988) verified that extruded from oats can be stored for 1.5 months without loss of quality. However, when the extruded was subjected to milling and toasting, the product quality was significantly reduced. In work done by Oda et al. (1988), the peroxide value was only traces for non-processed oats. In the oat flour extruded at 177 °C, the level was 9.6 mmoles at 10 days and 32.8 mmoles at 12 months.

Regarding the evaluation of n-hexanal levels in extruded oat products, granularity below 532 μm, after zero, 21, 42, 63, 84, and 126 days of storage, significant ($p \leq 0.05$) regression models were obtained. Such models, their coefficients of determination, and their significance levels are presented in Table 4. Both the linear and quadratic terms of the variable temperature of extrusion interfered significantly on the adjusted models.

At the evaluation of the extrusion temperature effect on the stability of stored extruded oats, at zero, 21, 42, 84, and 126 days (Fig. 2), the n-hexanal presented a convex, quadratic relationship, increasing as the extrusion temperature was elevated. The n-hexanal concentration increased proportionally as the storage time of the extruded products was lengthened. Bruechert et al. (1988) had already verified that volatile components increased as the extrusion temperatures were higher. Ekstrand et al. (1993) observed that the formation of n-hexanal in oat products depended on the processing conditions, but they did not obtained any correlation with the amount of free fatty acids. Similar results were achieved in this research.

Similarly to what happened to the peroxide levels, the treatments one and five, as well as the non-processed oats, presented low levels of n-hexanal, even after 126 days of storage.

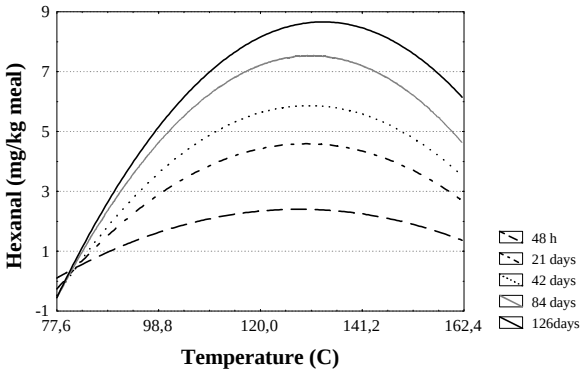

Fig. 2. Effect of the extrusion temperature on the level of n-hexanal in extruded oat products, fraction with granularity below 532 μm, along storage (48 hours, 42 days, 84 days, and 126 days).

Fritsch & Gale (1977), studying the oxidative rancidity in processed cereal products, verified that a rancid smell developed when the level of n-hexanal reached something between 5 and 10 mg/kg. In oat products, the same authors observed good relationship between the sensorial evaluation and levels of n-hexanal in the range of 0.3 and 5 mg/kg. In cereal products with substantial amounts of linoleic acid, the level of n-hexanal is lower than 1 mg/kg soon after grain processing, but it increases up to 5 mg/kg, or even more, during storage. This results in oxidation of lipids and lack of stability of the stored products. If the deterioration process continues after this point, the n-hexanal increases and other peaks show up. According to the authors, the deterioration is affected by the chemical composition and moisture level of the product, processing conditions, superficial area, and some unknown factors. The increment in n-hexanal levels and their peaks on extruded oat products are shown through the chromatograph charts presented in Fig. 3.

If a concentration of n-hexanal equal to 5 mg/kg of sample is considered the cutting value to analyze the products, after 126 days of storage, the treatments 1, 3, 5, and 7 are acceptable. All other treatments had values higher than those established by Fritsch & Gale (1977), which shows that the oxidative rancidity developed and altered both the flavor and quality of the extruded products. The treatments conducted at temperatures equal or higher than 120 °C were eliminated, regardless of the initial moisture level of raw material.

Therefore, to define the ideal extrusion conditions for fractions of oats with granularity below 532 μm, assessed through the level of n-hexanal after 126 days of storage, temperatures lower than 120 °C were adequate for processing, regardless the initial moisture level of the prime matter. To conduct the extrusion at higher temperatures it is necessary to control other factors, such as the water activity in the processed products, their superficial area, and packing conditions (Fritsch & Gale, 1977), or to add anti-oxidant components to the products (Percheron & Löliger, 1990). Utilization of lower compression rates and higher screw speeds at the processing may also help to keep the stability of extruded oat products during storage.

Under the conditions this experiment was conducted, the results allow to conclude that the oil present in the oat fraction with granularity below 532 μm has high amounts of unsaturated fatty acids (79.20%), among which the linoleic acid is the major component. Regarding the oxidative stability of the extruded products, the extrusion temperature is the processing factor that limits the storage time. The processing of oat grains through extrusion can be conducted at temperatures lower than 120 °C, regardless of the initial moisture level of raw material (15.5-25.5%). It is possible to evaluate primary and secondary alterations in oxidative rancidity of extruded oat products by monitoring indicators such as peroxide value and n-hexanal concentration.

Table 3. Regression model, coefficient of determination (R^2), and significance level for the peroxide value during storage of extruded oat products of the fraction with granularity below 532 μm as a function of the extrusion temperature

Response	Model[1]	R^2	Prob > F
t = 48 h	$y = -86.10+0.9852T+3.023U-0.0012T^2-0.0288TU$	0.8953	0.0042
42 days	$y = -46.72+0.5627T-0.00007T^2$	0.9439	0.0001
84 days	$y = -213.30+3.5341T-0.0118T^2$	0.8469	0.0005
126 days	$y = -233.80+3.7970T-0.0117T^2$	0.8101	0.0013

1. T = extrusion temperature (°C)

Table 4. Regression models, coefficients of determination (R^2), and significance levels for the level of n-hexanal during storage of extruded oat products, fraction with granularity below 532 μm, as a function of the extrusion temperature

Response	Model[1]	R^2	Prob > F
t = 48 h	$y = -12.37+0.2306T-0.0009T^2$	0.7099	0.0071
21 days	$y = -25.61+0.4663T-0.0018T^2$	0.6943	0.0087
42 days	$y = -33.06+0.5984T-0.0023T^2$	0.6823	0.0102
63 days	$y = -34.33+0.6172T-0.0024T^2$	0.6940	0.0088
84 days	$y = -41.78+0.7563T-0.0029T^2$	0.6690	0.0120
126 days	$y = -44.42+0.7981T-0.0030T^2$	0.6432	0.0162

1. T = extrusion temperature (°C).

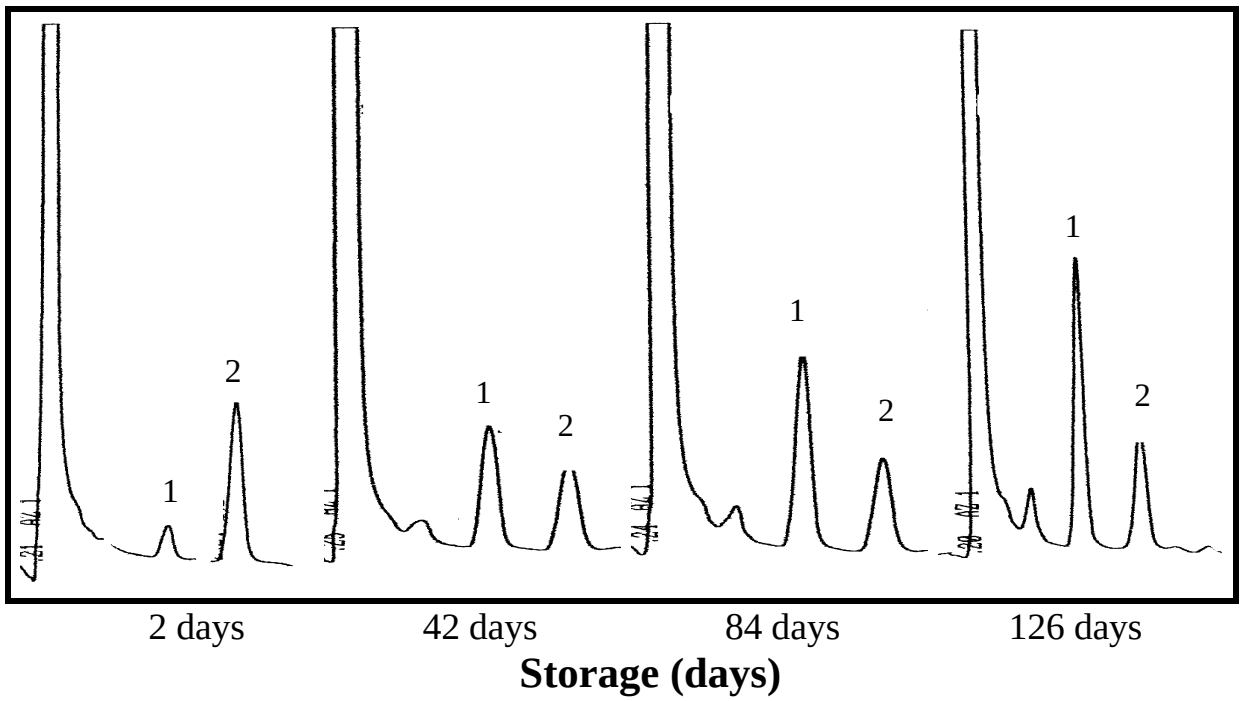

Fig. 3. Chromatograph charts representing the formation of n-hexanal in oat products, fraction with granularity below 532 μm, extruded at the temperature of 120 °C and moisture level of 20.5% in the raw material, along storage (48 hours, 42 days, 84 days, and 126 days). 1= n-hexanal; 2= 4-heptanona (internal pattern).

AKNOWLEDGEMENTS

The authors are thankful to FAPESP (State of São Paulo Foundation for Research) for providing funds to this research; to the Instrumental Laboratory of the Department of Food Technology of the FEA/UNICAMP for lending of a gas chromatograph.

RESUMO

Estudos foram realizados com o objetivo avaliar os efeitos de umidade inicial da matéria-prima e da temperatura de extrusão na estabilidade oxidativa de produtos de aveia (*Avena sativa* L). Cariopses de aveia foram moídas em moinho de rolos Brabender e obtidas frações de granulometrias superior e inferior a 532 μm. A fração de granulometria inferior a 532 μm, de alto teor de a,mido e baixos teores de proteínas, lipídios e fibra alimentar, foi condicionada na umidade desejada (15,5-25,5%) e extrusada em extrusor de laboratório Brabender monorosca. As condições usadas na extrusão foram taxa de compressão de 3:1, rotação de 100 rpm, matriz de 6 mm de diâmetro e temperaturas entre 77,6 e 162,4°C nas 2ª e 3ª zonas e de 80°C na 1ª zona. O material extrusado foi seco em estufa, moído, acondicionado em sacos plásticos e utilizado periodicamente nas determinações de peróxidos e de n-hexanal. O conteúdo de ácidos graxos insaturados no óleo da fração de aveia estudada foi elevado (79,20%). Independentemente do teor de umidade inicial da matéria-prima, todos os produtos extrusados em temperaturas inferiores a 120 °C apresentaram baixa rancidez oxidativa.

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Received: February 13, 1998;
Revised: April 06, 1998;
Accepted: August 19, 1998;