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# Deodorisation process variables for croaker (*M. furnieri*) oil

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ABSTRACT

Fish oil is the major food source of the long-chain omega-3 polyunsaturated fatty acids. Deodorisation represents a critical step of the refining process since it involves high temperature that could induce degradation reactions which affect oil integrity and quality. The present study evaluated the effect of the deodorisation variables (temperature, time and steam) on the croaker (*Micropogonias furnieri*) oil refining process. The evaluated parameters were Lovibond color (LC), free fatty acids (FFA), peroxide (PV), Iodine (IV) and Saponification (SV) values. The best deodorisation conditions were at 220 °C, 60 min and 5% of steam (based in oil mass), resulting in oil with LC of 0.4 red and 30 yellow, FFA of 0.09%, PV of 0.53 meq/kg. IV and SV were not significantly affected. The obtained fish oil presented high quality and oxidative stability, as well as EPA and DHA contents of approximately 12% of total fatty acids.



## 1. Introduction

Fish oil constitutes an important source of omega-3 polyunsaturated fatty acids (PUFA), mainly the eicosapentaenoic acid (EPA) and the docosahexaenoic acid (DHA). These fatty acids are beneficial to the human health, being essential for the development and functionality of certain organs and several physiological and biochemical responses of organisms (El-Badry, Graf, & Clavien, 2007; Fournier et al., 2007).

The croaker (*Micropogonias furnieri*) is a bottom-dwelling marine species, long-lived and with high adaptive capability to the variable conditions of its habitat. This marine specie is distributed from the Yucatan Peninsula (Gulf of Mexico, 20 N) to the Gulf of San Matias (Argentina, 41 S). It shows a high preference for estuarine areas, using them as nursery grounds; however, this behavior is apparently not strict. This species is considered economically important in Brazil, Uruguay and Argentina. Despite its wide distribution, it is commercially fished only from Cabo Frio (Brazil, 23 S) southward, where it is exploited because of its high abundance (Levy, Maggioni, & Conceição, 1998).

The refining operation is utilised for removing undesirable components and guaranteeing satisfactory purity and stability characteristics (acidity, color, oxidative and sensory). Particular attention has to be given to the quality of marine oil, considering that the refining process involves thermal treatment, which affect oil integrity. The chemical or alkaline refining includes the steps of degumming, neutralisation and washing, bleaching and deodorisation, in order to generate a product acceptable for human consumption These series of operations aim mainly towards removing phospholipids (PL), free fatty acids (FFA), pigments and hydroperoxides (Antoniassi, Esteves, & Meirelles, 1998; Azbar & Yonar, 2004; Berdeaux et al., 2007; Hafidi, Pioch, & Ajana, 2005; Wang, Wang, & Johnson, 2002).

Deodorisation is mass transfer purification process of the oil industry that aims towards vaporizing odoriferous compounds and free fatty acids from the oil by applying high temperatures and low pressures (Ceriane & Meirelless, 2007; Salas, Chavez, Cueto, & Ayala, 2003; Tubaileh, Garrido-Fernández, Ruiz-Méndez, León-Camacho, & Graciani-Constante, 2002). These extreme processing conditions lead to the occurrence of important chemical degradation reactions that influence the final oil quality (Berdeaux et al., 2007; Ceriane et al., 2007).

PUFAs are labile molecules which, when exposed to heat treatment, can be lost throughout different chemical transformations. Conditions used for the deodorisation of fish oils have been shown to induce oxidative deterioration involving the formation of hydroperoxides and reactions of polymerisation, geometrical isomerisation and intramolecular cyclisation (Berdeaux et al., 2007; Ceriane et al., 2007; Fournier et al., 2007).

For evaluation of oil quality and oxidative stability, commonly used methods include peroxide value (PV), free fatty acids (FFA), iodine value (IV), saponification value (SV) , color and total fatty acids (FA). The peroxide value (PV) is a parameter for evaluation of fat oils deterioration; increase of this parameter PV during deodorisation indicates formation of hydroperoxides due to oxidation. The amount of FFA in fats and oils can be used to indicate the extent of its deterioration due to hydrolysis of TAG and/or cleavage

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and oxidation of fatty acid double bonds. The iodine value (IV) is associated with the unsaturation degree of the fat acid and the average weight of fatty acids esterified to glycerol. A decrease in IV can be attributed to the destruction of double bonds by oxidation and polymerisation. The saponification value (SV) is a measure of molecular weight, and is defined as the amount of alkali required for fatty acid saponification in a given weight of oil (Abdulkarim, Long, Lai, Muhammad, & Ghazali, 2007).

The characteristic yellow–orange color of fish oil is the result of deposition of dietary carotenoids (Luterotti, Franko, & Bicanic, 1999). Color change in deodorisation oil is an indication of extent of oil deterioration caused by oxidation. Increase in color intensity is due to accumulation of nonvolatile decomposition products such as oxidised triacylglycerols and FFA (Abdulkarim et al., 2007). FA profile is used in order to determine composition of the fatty acids present in oil, verifying its nutritional quality (Montagner et al., 2005).

The aim of this work was to study the deodorisation of croaker (*M. furnieri*) oil, in order to obtain a final product with good quality and oxidative stability. The variables that influence this step were studied through a factorial experimental design, so as to obtain the best operating conditions.

## 2. Materials and methods

### 2.1. Raw material

Raw material used for the study of the deodorisation step was the crude oil of croaker (*M. furnieri*) fish residues, proceeding from fishmeal processes, obtained from local industries. The crude oil was stored in dark bottles in a refrigerator at 4 °C for one week.

### 2.2. Experimental methodology for deodorisation of fish oil

The process steps of the crude oil refining (degumming, neutralisation, washing, dehumidification and bleaching) were carried out using the operating conditions described below.

In the refine process, the degumming step was carried out for 30 min at a temperature of 80 °C and 500 rpm agitation, with addition of 1.0% of phosphoric acid (85% v/v) in relation to the oil mass. The neutralisation step occurred during 20 min, at a temperature of 40 °C and agitation of 500 rpm, with the addition of sodium hydroxide solution 20% w/w (using 4.0% of excess in relation to the certain acidity value after the degumming step). After each step, the material was centrifuged for 20 min at 7000*g* for oil separation.

The washing step consisted of the addition of 10% water in relation to the oil mass, at 95 °C for a contact time of 10 min, with 500 rpm agitation and oil temperature maintained at 50 °C. This step was repeated three times. The dehumidification step lasted for 20 min with temperature at 90–95 °C and 500 rpm agitation. The bleaching step was carried out at a temperature of 70 °C, 40 rpm agitation, with the addition of 5% of adsorbents (mixture of activated earth and activated coal at a 9:1 relationship), with contact time of 20 min. Filtration was carried out in Büchnner funnel with a pre-layer of diatomaceous earth. All of the steps of the refine process were carried out with manometric pressure in vacuum of approximately 700 mm Hg.

In deodorisation step, 1.5 kg of oil was loaded into a scale batch laboratory deodoriser; the oil was placed in vessel under vacuum (750 mm Hg), with an exit connected to a condenser, in order to remove the volatiles from the system. This vessel also possessed a steam entrance, provided by a steam boiler, with a valve controlling the outflow. The deodorisation of the bleached oil was carried out in conditions of temperature, time and amount of steam according to experimental design matrix.

The deodorisation experiments were performed through an experimental design, following a factorial experimental design matrix ($2^k$), where the study variables and their respective levels were indicated, as presented by Box, Hunter, and Hunter (1978).

Temperature ($X_1$), time ($X_2$) and steam percentage in relation to the oil mass ($X_3$) were chosen for independent variables. Lovibond color (LC), free fatty acid percentage (%FFA), peroxide value (PV), saponification value (SV) and iodine value (IV) were selected as the responses for the combination of independent variables.

Values of independent variables levels used in the deodorisation step were determined through preliminary tests and from bibliographical references (Ceriane et al., 2007; Erickson, 1995; Fournier et al., 2006; Fournier et al., 2007; Gancedo, Gonzáles, Bernat, Constante, & Camacho, 2002). Experiments were carried out in duplicate.

### 2.3. Analytical methodology

For the crude, bleached and deodorised oils, the following parameters were determined in duplicate: free fatty acids (FFA, Ca 5a-40), peroxide value (PV, Cd 8-53), iodine value (IV, Cd 1-25), saponification value (SV, Cd 36–76), according to the methodologies of the AOCS (1980).

Free fatty acids method was used, based on titration with a sodium hydroxide solution (phenolphthalein as indicator) of the oil, suitably diluted with an ethyl alcohol–ethyl ether mix. Results are expressed % oleic acid. Peroxide value method was used, based on titration with a sodium thiosulphate solution of the oil diluted with an acetic acid–chloroform mix and then treated with potassium iodide. Results are expressed as melliequivalents per kg of oil. Iodine value method was used, based on titration with a sodium thiosulphate solution (amid as indicator) of oil diluted with an chloroform and then treated with Wij's solution and potassium iodide. Results are expressed as cg $I_2$ per g. Saponification value method was used, based on titration with hydrochloride acid (phenolphthalein as indicator) of the oil diluted with a potassium hydroxide solution. Results are expressed as mg KOH per g.

Besides these parameters, the color of the oils was determined in duplicate, using the Lovibond method. Color was measured using the Lovibond (LOVIBOND COLOR STALER TINTOMETER, model F, ENGLAND) method described by Windsor and Barlow (1984), fixing the color yellow in 30 units and varying color red. Sample was taken in a cube and placed in the provided space in tintometer. The reflected color of the oil was matched by attempting different combinations of red and yellow slides until the reflected color matched the slide color combination. The yellow and red values of the slide color were taken and repeated three times for each sample.

For fatty acids identification and quantification, chromatographic analysis of fish oil obtained in the best deodorisation condition was performed.

Fatty acid profiles were determined by preparation of methyl esters as described by Ce 1-62 AOCS methodology (2002). The employed method detects from C6:0 to C22:6.

The fatty acid methyl esters (FAME) were identified by gas chromatography (model CGC AGILEN series 6850 GC SYTEM, USA) equipped with capillary column DB-23 AGILENT (50% cyanopropyl) methylpolysiloxane. Fatty acid esters analysis was performed, in duplicate, by injecting 1.0 μL; SPLIT ratio 1:50. A capillary column (60 m × 0.25 mm, 0.25 μm film in thickness). GC setting conditions were as follows: injection temperature 215 °C, flame ionisation detector temperature 215 °C, flow rate of helium gas carrier 1.0 mL/min and linear speed 24 cm/s, and oven temperature was held at 110 °C for 5 min, then increased to 215 °C at 5 °C/min and held at 215 °C for 24 min. The fatty acid methyl esters were identified by direct comparison of the retention times with standards

(NU-CHEK GLC-87), and were quantified as the percentage area of each FAME mixture.

### 2.4. Statistical methodology

Analysis of variance was used to compare means among treatments and mean separation tests were used to identify which treatment means were different. The values of characterisation for the croaker crude and bleached oils were compared using Tukey HSD test of differences of means (Box et al., 1978), with Statistic 6.0 (Statsoft, USA). Values were considered significant at a $P < 0.05$ level.

The experiments responses were treated statistically through an analysis of variance, in order to verify the significance of the factors (at 85% level) at the analyzed responses and the determination of the process operation region, through cube plots for the deodorisation step. (Box et al., 1978). The values of the independent variables levels used in the deodorisation step had already been determined through preliminary tests and by bibliographical references. In order to impede decrease in oil quality, small ranges of temperature, time and steam were chosen, therefore significance was considered at an 85% level ($P < 0.15$). Through regression analysis using the least square method, a theoretical statistical model in the codified form was obtained, considering the main effects and its interactions, for the responses Lovibond color (LC), free fatty acids percentage (%FFA), peroxide value (PV), saponification value (SV) and iodine value (IV), presented in Eq. (1) according Box et al.,1978.

$$Y_i = A_i + B_iX_1 + C_iX_2 + D_iX_3 + E_iX_1X_2 + F_iX_1X_3 + G_iX_2X_3 \quad (1)$$

where $A_i$, $B_i$, $C_i$, $D_i$, $F_i$, $E_i$, $F_i$, $G_i$ are the coefficients of the statistical model, $X_1$, $X_2$, $X_3$ are the study variables in codified form, −1 and +1, (temperature, time and percentage of steam, respectively) and $Y_i$ are the considered responses in their real values. Lack-of-fit test was performed in order to ensure that the model is adequate for this study.

**Table 1**
Characterisation of the crude and bleach oils of croaker

| | Crude oil[A] | Bleach oil[A] |
|---|---|---|
| Red color (30 yellow) | 3.1 ± 0.1[a] | 0.5 ± 0.1[b] |
| Free fatty acids (% oleic acid) | 3.02 ± 0.02[a] | 0.14 ± 0.01[b] |
| Peroxide value (meq peroxide/kg) | 0.92 ± 0.01[a] | 0.56 ± 0.01[b] |
| Iodine value (cg $I_2$/g) | 131 ± 2[a] | 133 ± 2[a] |
| Saponification value (mg KOH/g) | 188 ± 3[a] | 186 ± 2[a] |

Different superscript letters in the same line are significantly different ($P < 0.05$).
[A] Mean value ± standard error (in duplicate).

## 3. Results and discussion

Table 1 presents the values for color, free fatty acids content, peroxide, iodine and saponification values for the crude fish oil and for the bleached oil used in the deodorisation experiments.

Results indicated that the Lovibond color, peroxide value, and free fatty acid contents were reduced after bleaching of the crude oil (Table 1). There was a significance difference ($P < 0.05$) between the quality characteristic of crude oil and those of bleached oil as indicated by Tukey HSD tests. This was expected, given that the aim of the refining steps is to improve the fish oil characteristics, removing the components that cause color, free fatty acids and lipid oxidation products (Ceriani et al., 2007; Rossi, Gianazza, Alamprese, & Stanga, 2003).

Values found for the iodine and saponification values presented in Table 1 were not significantly affected ($P > 0.05$) after crude oil bleaching, with both values being within the determination analysis error. The bleaching of the crude oil does not affect the fatty acid composition of triacylglycerol; however, removal of impurities that affect the stability of the product occurs.

### 3.1. Analytical statistics of the results obtained from the deodorisation step

Table 2 presents the experimental design matrix used in fish oil deodorisation step, with the respective responses.

In Table 2, through Tukey HSD tests of differences of means, significant difference can be verified ($P < 0.05$) for experiments in the same column, for Lovibond color, peroxide value and free fatty acids percentage among the analyzed oils.

Also in Table 2, it can be verified that only in one condition of the deodorisation step (experiment n° 2) was there a peroxide value reduction of approximately 8.9%. In experiment n° 8 the peroxide values were drastically increased (higher than 100%), therefore it can be said that decomposition of hydroperoxides, with the formation of secondary products of oxidation such as aldehydes, ketones and alcohols, occurred. In the others experiments, it can be said that the increase of peroxide value was due the hydroperoxides formation, considering that pronounced increasing in the peroxide values did not occur, and also that the conditions used in the deodorisation experiments were less drastic than presented in literature for vegetal oil (Bernardini, 1986).

It can be verified in Table 2 that values found for iodine and saponification were not significantly affected ($P > 0.05$) after crude oil bleaching. These values are associated, respectively, to the unsaturated degree of the fatty acid and the average weight of the fatty acids esterified to glycerol. In this manner, peroxide values and free fatty acids were not significantly affected; however, iodine and saponification values are measures of low sensibility, not detecting small variations of these analyses and consequently among the experiments, with such variations being within the

**Table 2**
Responses of the experimental design matrix in fish oil deodorisation

| Experiment (n°) | Temperature (°C) | Time (min) | Steam[A] (%) | Color (red) | Free fatty acids (% oleic acid) | Peroxide value (meq peroxide/kg) | Iodine value (cg $I_2$/g) | Saponification value (mg KOH/g) |
|---|---|---|---|---|---|---|---|---|
| 1 | 180 | 60 | 5 | 2.0 ± 0.2[a] | 0.18 ± 0.03[a] | 0.77 ± 0.02[a] | 135 ± 1[a] | 187 ± 3[a] |
| 2 | 220 | 60 | 5 | 0.5 ± 0.1[b] | 0.08 ± 0.01[b] | 0.51 ± 0.01[a] | 136 ± 3[a] | 186 ± 1[a] |
| 3 | 180 | 120 | 5 | 1.0 ± 0.2[c] | 0.13 ± 0.02[ab] | 0.66 ± 0.02[a] | 136 ± 2[a] | 186 ± 2[a] |
| 4 | 220 | 120 | 5 | 0.8 ± 0.1[c] | 0.15 ± 0.03[a] | 0.87 ± 0.03[b] | 134 ± 1[a] | 187 ± 2[a] |
| 5 | 180 | 60 | 10 | 0.6 ± 0.1[b] | 0.16 ± 0.03[a] | 0.68 ± 0.02[a] | 136 ± 2[a] | 187 ± 3[a] |
| 6 | 220 | 60 | 10 | 1.2 ± 0.2[c] | 0.12 ± 0.02[ab] | 0.67 ± 0.02[a] | 135 ± 2[a] | 186 ± 2[a] |
| 7 | 180 | 120 | 10 | 1.0 ± 0.1[c] | 0.12 ± 0.02[ab] | 0.62 ± 0.02[a] | 135 ± 3[a] | 187 ± 2[a] |
| 8 | 220 | 120 | 10 | 2.0 ± 0.2[a] | 0.15 ± 0.03[a] | 1.3 ± 0.03[c] | 136 ± 3[a] | 186 ± 1[a] |

Different superscript letters in the same column are significantly different ($P < 0.05$).
[A] Amount of steam in relation to the oil mass. Mean value ± standard error (in duplicate).

analysis error. The iodine value (IV) and the saponification value (SV) for crude and bleached oils were within the range cited for Bernardini (1986), of 120–190 cg I/g and 160–190 mg KOH/g, respectively, for different fish species.

Analysis of variance of the studied factors for the three response of the model presented significant difference was determined. The responses (color, free fatty acids and peroxide value) were evaluated through the combination of the study factors and their interactions (temperature, time and steam).

Statistical analysis considered an 85% significance level by choosing small ranges of temperature, time and steam. In this manner, for the statistical analysis sensibility, an 85% ($P < 0.15$) significance level was considered in order to evidence significant changes in oil quality according to deodorisation conditions. It can be verified that the main effects of the studied factors were not significant ($P > 0.15$). However, the first order interaction between temperature and steam percentage ($T_{cod}$ $\%S_{cod}$) was important factor, because it significantly affected ($P = 0.14$) the Lovibond color (LC). In terms of free fatty acids percentage (%FFA) and peroxide value (PV) responses, in the analysis of variance it was verified that only the first order interaction between ($T_{cod}$ $t_{cod}$) was significant ($P = 0.14$ and $P = 0.12$, respectively).

The independent variables (temperature, time and percentage of steam) coefficients determined for the model (Eq. (1)) for three response variables are presented in Eqs. (2)–(4) (only the first order interaction that was significant was considered), with determination coefficients ($R^2$) of 87.5%, 91.8% and 89.2%, respectively, and no lack-of-fit.

$$LC = 1.08 - 0.01T_{cod} + 0.13t_{cod} + 0.06(\%S_{cod}) + 0.41T_{cod}\%S_{cod} \quad (2)$$

$$\%FFA = 0.14 - 0.04T_{cod} + 0.003t_{cod} + 0.0013(\%S_{cod}) + 0.048T_{cod}t_{cod} \quad (3)$$

$$PV = 0.66 - 0.07T_{cod} + 0.21t_{cod} + 0.06(\%S_{cod}) + 0.29T_{cod}t_{cod} \quad (4)$$

The adequate work conditions are defined through the cube plot analysis, Fig. 1a–c, where the study factors used in the deodorisation step are represented at the edges, in codified forms, and the responses determined by the theoretical model (Eqs. (2)–(4)) are placed at the vertices of the cubes.

It is verified through Fig. 1a that the lowest Lovibond color was obtained from the use of higher temperature (+1) and lower steam percentage (−1). This is explained by the fact that with higher temperature and lower amount of steam, larger removal of volatiles and pigment destruction occurred. On the other hand, with higher steam percentage, the increase of moisture content in the oil occurred at higher temperature (+1), favoring the hydrolysis reactions and the formation of oxidation by-products that react with pigments present in the oil causing an increase in color. The characteristic yellow–orange color of fish oil is the result of deposition of dietary carotenoids. Carotenoids are lipid–soluble antioxidants and their biological properties are related to their structures. The single and double bonds repeats in the polyenic chain determines to their chemical structures (Hidalgo, Brandolini, Pompei, & Piscozzi, 2006). The oil color depends on the temperature to which it is submitted. Therefore, with higher temperatures, occurs the formation of Schiff bases between protein traces and oxidation by-products due bonds carotenoids, it cause dark compounds. When extremely unsaturated oils, such as fish oil, are heated, isomerisation and migration of double bonds occurs, leading to the conjugation of the same ones. The conjugation of double bonds leads to the absorption of larger amounts of blue light, provoking an increase of orange and brown colors in oil. In this paper it was verified that Lovibond color (LC) in bleached and deodorised oils was equal at 0.5 red and 30 yellow, and at 0.4 red and 30 yellow, respectively. In this manner, it can be assumed that the conjugation of the double bonds did not occur in the deodorised oil (Abdulkarim et al., 2007; Manral, Pandey, Jayathilakan, Radhakrishna, & Bawa, 2008; Ceriani et al., 2007; Let, Jacobsen, & Meyer, 2004).

In Fig. 1b, a lower free fatty acids percentage was obtained with the use of higher temperature (+1) and lower time (−1). Consequently, in higher temperature and lower process time, a removal of the free fatty acids present in the oil occurred, avoiding more formation of free fatty acids due to a larger oil exposure to heating (Manralet al., 2008; Ceriani et al., 2007; Let et al., 2004).

In Fig. 1c, it can be verified that a lower peroxide value was obtained with the use of higher temperature (+1) and lower time (−1). With higher exposure time of the oil to the heating atmosphere, a higher susceptibility to the oxidation and peroxide formation occurs (Manral et al., 2008; Ceriani et al., 2007; Let et al., 2004).

The best work condition is defined for the deodorised oil as being 220 °C temperature, 60 min time and 5% steam in relation to the oil mass, where the Lovibond color is equal to 0.4 red and 30 yellow, the acidity percentage is equal to 0.09%, and peroxide value equal to 0.53 meq/kg (Fig. 1a–c). In this condition, a larger removal of free fatty acids, products of oxidation present in the oil, occurred, resulting in oil with quality and oxidative stability. Color

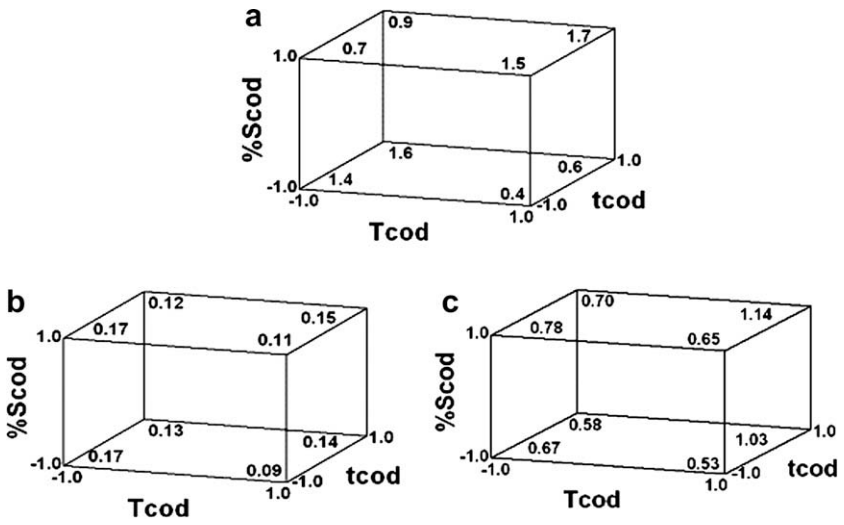


**Fig. 1.** Cube plots of the deodorised fish oil for the responses: (a) Lovibond color, (b) free fatty acids percentage and (c) peroxide value.

change in deodorisation is an indication of the extent of oil deterioration caused by oxidation. Increase in the color intensity is due to accumulation of nonvolatile decomposition products such as oxidised triacylglycerides and FFA. In this way, the color change not only reduced the carotenoids content (important in oil due to its antioxidant activity and vitamin A precursor), but also removed substances which affect the quality of the oil such as free fatty acids, thermal degradation products and traces of volatile. This is confirmed through the free fatty acids and peroxide value in Table 2, in the experiment where the largest color reduction was obtained. Deodorisation is an important step of the refining, which can produce fat and oils which are flavorless and odorless, and with reduced acidity.

The Lovibond color (0.4 red and 30 yellow) for the deodorised oil was below to value cited by Antoniassi et al. (1998) for deodorised corn oil , whose joined values had been 2.3 red and 30 yellow.

Wang et al. (2002) mentions free fatty acids percentage between 0.59% and 0.03% for soybean oil, Antoniassi et al. (1998) describe for deodorised corn oil the acidity percentage 0.26%. Gancedo et al. (2002) describe for olive oil and sunflower oil, after 6 h of deodorised 0.20% and 0.24%, respectively.

The peroxide value indicates oxidation of lipids; such oxidation is important for defining its deterioration state, mainly for the composite presence of low molecular weight proceeding from its degradation. The peroxide value for the presented oil deodorisation was below results cited for Ganga et al. (1998), who encountered for sardine oil 4.02 meq peroxide/kg ± 0.5 peroxide value. Wang et al. (2002) mention peroxide value from 0.86 to 0.04 meq peroxide/kg for soybean oil.

With the purpose of verifying quality of fish oil obtained in the best deodorisation conditions, a FAME assay was performed. Table 3 present the fatty acids profile of bleached and deodorised oils.

The bleached and deodorised fish oils presented as larger components: palmitic acid (C16:0), palmitoleic acid (C16:1) and oleic acid (C18:1), as present in Table 3, constituting approximately 54.1% of total fatty acids of bleached oil and 54.8% of total fatty acids of deodorised oil.

In Table 3 it can be observed that oleic acid, linoleic acid and linolenic acid contents in bleached and deodorised fish oils were superior than cited by Pozo, Pérez-Villarreal, and Saitua (1990) and Moffat, McGill, Hardy, and Anderson (1993) for albacore oil (*Thunnus obesus*), cavalla oil (*Scomberomorus cavalla*) and sardine oil (*Sardinella brasiliensis*). Their oils presented oleic acid contents of 19.1, 17.4, 17.1, linoleic acid contents of 1.1, 0.9, 1.1 and linolenic acid contents of 0.9, 1.2, 0.0, respectively.

It can also be seen in Table 3 that the unsaturated fatty acids contents present in bleached and deodorised oils represent around 61% of the total fatty acids, what makes it a rich source of unsaturated and polyunsaturated fatty acids. The PUFA content of the deodorised oil sample presented values superior to the ones of other fish oils cited by Pozo et al. (1990) and Moffat et al. (1993), with PUFA contents of around 50%, for cavalla oil and sardine oil.

The bleaching and deodorised fish oil samples shown in Table 3 presented EPA + DHA percentage around 12%, value smaller than cited by Cozzolino, Murray, Chree, and Scaife (2005) of approximately 20% of total fatty acids. However, this value was similar to the ones cited by Luzia, Sampaio, Castellucci, and Torres (2003) for crude oils of five commercially important species of Brazilian fish (sardine, croaker, tilápia, curimbatá and shrimp) in range 11.6–13.4%.

Conditions used for the deodorisation of fish oils have been shown to induce oxidative deterioration, involving the formation of hydroperoxides and reactions of polymerisation, geometrical isomerisation and intramolecular cyclisation. In relation to binomial time-temperature it can be concluded that the higher the exposition time of the oil to elevated temperatures, the higher is its degradation. According to Fournier et al. (2006), a longer reaction time favored the formation of highly isomerised EPA and DHA. These authors performed deodorisation of semi-refined fish oil with heating at 180, 220 or 250 °C for 3 h under a 1.5 mbar pressure and with 2% direct steam injection (based on oil). Deodorised oil at 180 °C showed only a small appearance of mono-trans form of DHA. In this paper, optimum deodorisation conditions were obtained at 220 °C for 60 min, with the utilisation of a lower process time when compared to condition utilised by Fournier et al. (2006). In this manner, reactions of oxidative deterioration and polymerisation cyclisation are less probable to occur.

**Table 3**
Percentage composition of fatty acids of deodorised fish oil

| Fatty acids[a] | Bleached oil sample (%)[b] | Deodorised oil sample (%)[b] |
|---|---|---|
| C14:0 | 3.7 ± 0.1 | 3.4 ± 0.3 |
| C15:0 | 0.7 ± 0.2 | 0.7 ± 0.1 |
| C16:0 | 20.0 ± 0.3 | 20.5 ± 0.2 |
| C16:1 | 14.2 ± 0.1 | 13.4 ± 0.2 |
| C17:0 | 1.7 ± 0.1 | 1.7 ± 0.1 |
| C18:0 | 5.3 ± 0.2 | 5.7 ± 0.1 |
| C18:1 | 19.9 ± 0.1 | 20.9 ± 0.1 |
| C18:2 | 3.6 ± 0.3 | 4.2 ± 0.2 |
| C18:3 | 1.9 ± 0.1 | 1.9 ± 0.1 |
| C20:0 | 0.7 ± 0.1 | 0.8 ± 0.1 |
| C20:1 | 3.5 ± 0.1 | 2.7 ± 0.2 |
| C20:4 | 2.0 ± 0.1 | 1.8 ± 0.3 |
| C20:5 | 5.8 ± 0.1 | 5.8 ± 0.2 |
| C22:0 | 0.3 ± 0.1 | 0.2 ± 0.1 |
| C22:1 | 1.8 ± 0.2 | 1.3 ± 0.1 |
| C22:6 | 5.6 ± 0.2 | 6.0 ± 0.2 |
| ∑u | 5.6 ± 0.1 | 5.9 ± 0.3 |
| ∑s | 32.4 ± 1.1 | 33.1 ± 0.9 |
| ∑uns | 62.0 ± 1.7 | 61.3 ± 1,8 |

[a] ∑u, sum of unidentified; ∑s, sum of saturated fatty acids; ∑uns, sum of unsaturated fatty acids.
[b] Mean value ± standard error ($n$ = 2 replicate).

## 4. Conclusions

Based on the data obtained in this study, it was established that the croaker (*M. furnieri*) oil deodorisation must be carried out at 220 °C for 60 min with 5% steam (w/w oil). Under these process conditions, fish oil with good quality and desirable oxidative stability was obtained, with Lovibond color at 0.4 red and 30 yellow, free fatty acids content at 0.09%, and peroxide value at 0.53 meq/kg. The deodorisation step had no significant effect on the iodine and saponification values.

The obtained refined croaker (*M. furnieri*) oil presented a high fatty polyunsaturated acid content of around 61%, being an important source of polyunsaturated fatty acids, from EPA and DHA groups, representing approximately 12 % of the total fatty acids.

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