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Physiochemical Characterization of Soybean Oil Deodorizer Distillate

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Increased use of industrial waste and byproducts fits the need of industry to comply with environmental rules. The substitution of natural products for artificial ingredients has gained worldwide attention in the food, pharmaceutical and other industries. These facts justify the study on the utilization of Soybean Oil Deodorizer Distillate (SODD) as tocopherol supplements. Tocopherol, which is physiologically active as vitamin E and a major natural antioxidant, is an especially important player in human and animal nutrition. SODD is a byproduct of the soybean oil refining process that is also rich in free fatty acids (FFA), sterols and hydrocarbons. It has been demonstrated that the use of SODD for vitamin E extraction is not economically viable. However, SODD in the semi-refined form (neutral) can be an alternative for animal and possibly human diet enrichment. The objective of the present study was to evaluate the SODD neutralizing process varying the type, concentration, and excess of alkali, as well as the process temperature and time for homogenization. To verify their potential like vitamin E supplement, SODD was semi-refined (neutral SODD) and characterized physical-chemically. The optimal conditions for the neutralizing process, i.e., in order to obtain the greatest reduction in free fatty acid content, the lowest leaching of tocopherols and the greatest yield, were defined experimentally. In the results FFA content was reduced from 53.4% to 6.1% after neutralization, requiring a second step of neutralization, thus obtaining a FFA content of 1.8% and 11.0% of total tocopherol (TT). Neutral SODD was statistically different from crude SODD regarding the following characteristics: FFA, unsaponifiable matter, saponification number and color. The composition of neutral SODD was 1.8% of FFA, 35.4% of unsaponifiable matter, 130.2 mg KOH/g sample of saponification number, 11% of total tocopherols, 114.8 mEq iodine/g sample of iodine index, 4.8 mEq/kg of peroxide value, 11 mg MDA/kg of TBA value, 0.8% of

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moisture, 9.7 kcal/g of energetic value and 0.906 g/mL of liter weight. These results suggest the potential use of SODD as a supplement.

1. Introduction

Deodorization is a step of soybean oil refine, that removes volatile compounds responsible for oil undesirable taste, producing Soybean Oil Deodorizer Distillate (SODD) like a byproduct. However, this process also removes tocopherols, making SODD a precious byproduct and its price depends on their tocopherol contents (Borher et al., 2002). Brazil is the second largest soybean producer and therefore has a big amount of byproduct, prevailing to tocopherols recovery (Martins et al., 2006a).

Chemically, SOOD is a complex mixture of free fatty acids (FFA), triglycerols, cetones, peroxides, hydrocarbons, oleins, sterols and tocopherols. A high concentration of FFA can be harmful to health, because its accumulation promotes apoptosis, i. e., leading to cellular death (Okoshi et al., 2007). Therefore, neutralization step is enough to use SODD like as a tocopherol supplement.

SODD has gained increased attention due to exportation, mainly to countries that obtain tocopherol concentrates to use in food and pharmaceuticals industries as natural antioxidants (De Greyt and Kellens, 2000). These concentrates require many techniques to be obtained, making the product expensive.

Tocopherols are compounds with vitamin E activity and are important antioxidants, protecting unsaturated lipids in cellular membranes against oxidation (Benites et al., 2005).

Nowadays there is a need to study alternative sources of tocopherols, such as from SODD, which could be used as a supplement without increasing final product costs. Vitamin E, present in SODD, was effective in protecting against lipids oxidation in rats liver, and showed no toxicity to animals. However, the results of lipid oxidation were higher than those obtained with supplementation of synthetic vitamin E (Moraes et al., 2004).

Therefore, given the importance of tocopherols, the use of SODD in the most crude form, non-toxic, can be a solution for a viable vitamin supplement. The use of this product as a nutrient in the diet also corroborates with the increase in the worldwide trend of using natural ingredients and compounds. Besides the economic aspect, researches with this product have been increasing, looking for methods to employ the SODD (Borher et al., 2002; Moraes et al., 2004), and studying possible SODD toxic effects in the body (Oliveira et al., 2005; Oliveira et al., 2006).

This work aims to characterize the crude and neutral SODD chemically, mainly as: composition of fatty acids, free fatty acids, levels of total tocopherols and their isomers, verifying its potential as a vitamin E supplement.

2. Materials and methods

SODD from the Cargill Agrícola S.A. industry (Mairinque, Brazil) was stequiometrically neutralized, considering an excess of 20% (Bhattacharyya & Bhattacharyya, 1987). Neutralization conditions were determined according methodology describes by Benites et al. (2005), with the parameters: Na_2CO_3 4.34N,

temperature 45.8°C and homogeneization time of 3'20". Both crude SODD and neutral SODD were characterized by:

- *Tocopherol content*: The analysis was carried out according to HPLC Ce 8-89 method (AOCS, 1998), using an isocratic pump Perkin Elmer 250 and fluorescence detector Shimadzu RF-10 AXL, which was set at: excitement - 290nm; emission - 330nm. The tocopherol separation was carried out on MERCK Li Chrosorb Si 60 column (250 x 4 mm) using as mobile phase 99:1 Hexane/Isopropanol at 1.1 mL/min and room temperature. The isomers were identified by retention time, co-chromatography and UV-Vis absorption spectrum as compared to standards (α, β, γ and δ-tocopherol, Calbiochem purity ≥ 95%) analyzed in the same conditions. The quantification was carried out by external calibration curves for α, β, γ and δ-tocopherol;
- *Fatty acid composition*: The FA were extracted according to the methylic esters method (Hartman & Lago, 1973), and were analyzed according to the Ce 1-62 injection method (AOCS, 1998). The gas-chromatograph used was a CGC AGILENT 6850 SERIES GC SYSTEM, with capillary column: DB-23 AGILENT (50% cyanopropyl – methylpolysiloxane, 60m x 0.25 mm internal diameter, 0.25 μm film thickness). The chromatographic conditions were: flow of 1.0 mL/minute; linear speed of 24 cm/seg; detector temperature of 280°C; injector temperature of 250°C; volume injected of 1μL; and Helium as carrier gas. The oven temperature programme was set as follows: 110°C (5 min), 110-215°C (5°C/min), 215°C (24 min). The fatty acids were identified by retention time as compared to a standard mixture analyzed in the same conditions;
- *Free Fatty Acids* (FFA): 940.28 (AOAC, 1995); *Peroxide value*: 965.33 (AOAC, 1995);
- *TBA value*: method described by Sinnhuber & Yu (1958);
- *Iodine index*: Hanus - 920.158 (AOAC, 1995);
- *Saponification number*: 920.160 (AOAC, 1995);
- *Moisture content*: Karl Fischer Tb 2-64 (AOCS, 1998);
- *Unsaponifiable matter*: Ca 6b-53 (AOCS, 1998);
- *Energetic value*: Measure made in automatic calorimeter (PARR 1261) with oxygen pump (PARR 1108);
- *Determination of mass per unit volume* (liter weight): Cc 10c-95 (AOCS, 1998);
- *Color*: the instrumental analysis was evaluated by total transmittance, through Hunter Lab colorimeter (Color Quest model), method CIELAB L*a*b* in universal program, using the parameters: 10° visual angle, lighting D 65, luminosity (L*, 100-white 0-black), red index (a* - red/green) and yellow index (b* - yellow/blue).

The data were collected and the averages compared by t student test ($P \leq 0.05$) using the software STATISTICA 7.0®.

3. Results and discussion

In relation to fatty acid (FA) composition, the main were palmitic (17.7,14.5,12.7 and 11.4%), oleic (23.3, 24.0, 26.4 and 24.2%) and linoleic (43.3, 47.5, 50.5 and 51.4%) for crude SODD, neutral SODD, synthetic vitamin E and soybean oil, respectively. According to Almeida et al (2003), crude SODD had 17.7% of palmitic, 23.3% of oleic and 43.3% of linoleic fatty acids. Augusto (1988) corroborates these data, obtaining as

main FA in the crude SODD: palmitic 23.1%, oleic 19.5% and linoleic 48.5%. For soybean oil, these values were 10.9, 21.8 and 57.1%, respectively.

The main physical and chemical characteristics of crude and neutral SODD samples are described in Table 1. Crude SODD had FFA of 53.8% (±0.5) and after neutralization, the FFA content was 1.8% (±0.1). So, the neutral SODD had its FFA content reduced in 96.7%. The SODD used by Martins et al. (2006b), had 57.8% of FFA content. According to Augusto (1988) the crude SODD characterization showed of FFA 37.1%.

In another work, Almeida et al. (2003) determined the mass per volume, saponification number and evaporation residue, being the first two analyses similar to the values found in the present work, but the moisture content was higher, possibly due to differences in method of analysis. The energetic value of SODD, measured by calorimetric pump, is coherent with oil products (9.5 and 9.7 kcal / g for crude and neutral SODD, respectively).

The oxidation rate of neutral SODD was reduced 36% for peroxides and 31.3% for TBA comparing to crude SODD, i.e., these oxidation products have been partially separated during the neutralization process. In literature, reference values for these rates have not been found, since depends on storage quality of the product.

As regards to the unsaponifiable matter content, Almeida et al. (2003) found a wide range of values (3.5 - 27.1%) for different SODD samples. In this work, this content was 20.1% (crude SODD), resulting in a higher tocopherols content (10.4%), since tocopherols are part of the unsaponifiable matter. Almeida et al. (2003) determined 8.6% of tocopherol for the sample with the highest unsaponifiable matter content (27.1%).

Table 1. Physiochemical characterization of crude and neutral

Analyses *		SODD	
		Crude	Neutral
FFA (%)		53.8 [a] (±0.5)	1.8 [b] (±0.1)
Mass per volume		0.906 (±0.002)	0.906 (±0.001)
Saponification number (mg KOH/g sample)		159.4 [a] (±3.7)	130.2 [b] (±4.6)
Moisture (%)		0.8 (±0.1)	0.8 (±0.1)
Energetic value (kcal/g)		9.5 (±0.01)	9.7 (±0.1)
Peroxide value (mEq/kg)		7.5 (±2.7)	4.8 (±0.9)
TBA value (mg MDA/kg)		16.0 (±4.2)	11.0 (±3.5)
Iodine Index (mEq Iodo/g sample)		109.6 (±1.8)	114.8 (±4.2)
Color	L*	52.46 [a] (±0.04)	18.65 [b] (±0.39)
	a*	31.10 [b] (±0.05)	33.94 [a] (±0.34)
	b*	77.43 [a] (±0.05)	29.67 [b] (±0.71)
Unsaponifiable matter (%)		20.1 b (±0.1)	35.4 a (±1.0)

* Mean values (± standard deviation)

Different letters in the same column indicate statistical difference (*t student* P<0.05)

Table 2 shows the tocopherol isomers content for crude and neutral SODD, synthetic tocopherol and soybean oil. The values for crude SODD were similar to the ones found by Augusto (1988) and Almeida et al. (2003). The SODD used by Martins et al.

(2006b), had lower total tocopherol content (9.0%), differing in the isomers ratio α-T (2.9%), β-T (0.1%), γ-T (4.7%) e δ-T (1.3%).

The tocopherols content is an important aspect to consider the use of SODD as supplement. Studying the application of intraruminal SODD in Nelore steer and evaluation of the absorption and incorporation of vitamin E in different tissues, Borher et al. (2002) found an increase in the vitamin E concentration in the liver, muscle and fat in their coverage, and better stability of the color of meat and increased oxidative stability of fat. Thus, the use of SODD *in nature* (crude) seems to be a low cost and efficient alternative for the incorporation of tocopherols in tissues and animals, bringing benefits to meat consumers.

Table 2. Mean values of tocopherol content (%) in crude and neutral SODD, synthetic vitamin E and soybean oil

Sample	Isomers (%)				Total
	α-T	β-T	γ-T	δ-T	Tocopherol (%)
Crude SODD	1.28 (± 0.02)	0.22 (± 0.01)	6.59 (± 0.03)	2.36 (± 0.04)	10.44
Neutral SODD	2.03 (± 0.04)	0.25 (± 0.01)	6.67 (± 0.28)	2.03 (± 0.08)	10.98
Synthetic vit. E	3.75 (± 0.05)	-	-	-	3.75
Soybean oil	0.02 (± 0.001)	0.002 (± 0.00)	0.07 (± 0.006)	0.01 (± 0.001)	0.10

Mean values (± standard deviation)

The neutralization process revealed to be an adequate method to allow the use of SODD, since FFA are harmful to cells and the tocopherols are difficult to extract.

In order to study an industrial by-product as a natural tocopherols source (vitamin E), the neutral SODD presented low cost, simple method of production and potential use as a supplement.

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