Separation and Purification Technology 160 (2016) 106–111

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Deacidification of palm oil by solvent extraction

Cintia B. Gonçalves [a,*], Christianne E.C. Rodrigues [a], Elaine C. Marcon [b], Antonio J.A. Meirelles [b,*]

[a] LES, Separation Engineering Laboratory, Department of Food Engineering (ZEA-FZEA), University of São Paulo (USP), P.O. Box 23, Zip Code 13635-900, Pirassununga, São Paulo, Brazil
[b] EXTRAE, Department of Food Engineering (DEA-FEA), University of Campinas (UNICAMP), P.O. Box 6121, Zip Code 13083-862, Campinas, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form 12 January 2016
Accepted 13 January 2016
Available online 14 January 2016

Keywords:
Palm oil
Liquid–liquid extraction
Deacidification
Carotenoids
PRDC

ABSTRACT

The present work reports the influence of some process variables on the losses/transfer of fatty compounds during the deacidification of palm oil by liquid–liquid extraction. The response surface methodology (RSM) was used to analyze the effect of the mass ratio of oil to solvent and the water content in the solvent, aiming to minimize the losses of neutral oil and maximize the transfer of free fatty acids plus carotenoids preservation. By using appropriate conditions observed in RSM analysis (mass ratio of oil to solvent equal to 0.74 and water content around 6 mass%), the deacidification of palm oil by continuous liquid–liquid extraction was performed in a perforated rotating disc contactor (PRDC). The experimental results indicate that it is possible to obtain refined palm oil with a free acidity lower than 0.1 mass% by continuous liquid–liquid extraction.

1. Introduction

The rapid expansion in world production of palm oil over the last decades has attracted the attention of the oils and fat industry. Crude palm oil is extracted from the fresh mesocarp of the palm fruit and contains a small amount of undesirable components and impurities, such as mesocarp fibers, free fatty acids (FFA), phospholipids, trace metals, oxidation products, and odoriferous substances. Thus, as a consequence, palm oil is normally refined to obtain a stable product, which can be used for direct consumption or for formulation of edible products [1].

Two methods are available for refining crude palm oil: chemical and physical refining. They differ basically in the manner in which the free fatty acids are removed (deacidification step). Chemical refining, which involves neutralization of FFA with a solution of sodium hydroxide, is not recommended for oils with high acidity, such as palm oil, because it causes high losses of neutral oil by saponification and emulsification. Because of its efficiency and simple effluent treatment, physical refining is the major processing route for removing FFA from palm oil. However, the drastic conditions in which this process is carried out (temperature in the range 240–260 °C and pressure in the range 1–3 mmHg) led to the complete destruction of carotenoids [2] and to a significant reduction of tocopherols [3], both important components that confer to palm oil a high nutritional value, and promote several benefits to human health [4]. Nevertheless, some studies indicate that the use of alternative technologies [5] or optimized conditions in the deodorization step of refining [6] can lead to retention of significant amounts of these important nutraceutical compounds.

The deacidification of oils by liquid–liquid extraction using an appropriate solvent, such as ethanol, can be an alternative technique for refining palm oil. As this process is carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments, potentially preserving the nutraceutical compounds. This technique is based on the difference of solubility of FFA and triacylglycerols in an appropriate solvent [7]. Previous works indicate the decrease of FFA content in the oil submitted to solvent extraction, as well as, the losses of neutral oil and nutraceutical compounds during this process are also reported [7–15]. Literature also provides liquid–liquid equilibrium data for systems containing triacylglycerols (TAG), free fatty acids (FFA) and short chain alcohols, which are essential to planning and developing liquid–liquid extraction process [16–26]. In our prior works [20,21], liquid–liquid equilibrium data of systems containing palm oil, fatty acids (palmitic and oleic acids), aqueous ethanol and nutraceutical compounds were measured and correlated by thermodynamic models.

The present work reports the influence of process variables on the losses of neutral oil, the transfer of free fatty acids and the preservation of carotenoids during the deacidification of palm oil by liquid–liquid extraction. The response surface methodology (RMS) was used to analyze the effect of process variables, such as

* Corresponding authors.
E-mail addresses: cintiabg@usp.br (C.B. Gonçalves), tomze@unicamp.br (A.J.A. Meirelles).

http://dx.doi.org/10.1016/j.seppur.2016.01.016
1383-5866/

mass ratio of oil to solvent and water content in the solvent, aiming to minimize the losses of neutral oil and maximize the transfer of free fatty acids plus carotenoids preservation. By using appropriate conditions observed in RSM analysis, the deacidification of palm oil by continuous liquid–liquid extraction was performed in a perforated rotating disc contactor (PRDC).

2. Material and methods

In this study, two different samples of bleached palm oil (kindly supplied by the Agropalma, Pará, Brazil) were used. Both oils were analyzed by gas chromatography of fatty acid methyl esters, according to the official method Ce 1–62 [27], given that the samples were prepared in the form of fatty acid methyl esters according to the official method Ce 2–66 [27]. An HP 5890 gas chromatograph with a flame ionization detector and an integrator was used under the following experimental conditions: capillary fused silica column of cyanopropylsiloxane (60 m × 0.25 μm × 0.32 mm), hydrogen as the carrier gas at a rate of 2.5 ml min^{-1}, an injection temperature of 548.2 K, a column temperature of 448.2–498.2 K (1.3 K min^{-1}), and a detection temperature of 578.2 K. The fatty acid methyl esters were identified by comparison with the retention times of NU CHECK Inc. standards (Elysian, IL, USA) and the quantification was accomplished by internal normalization.

Fatty acid composition of the bleached palm oil used in the liquid–liquid equilibrium experiments (for composing the experimental design) has already been reported by Gonçalves and Meirelles [20]. Such sample presented 3.88 ± 0.01 mass% of free fatty acids, determined by titration (official method 2201 of IUPAC) [28] with an automatic burette (Metrohm, model Dosimat 215, Herisan, Switzerland) and 255 ± 0.01 mg kg^{-1} of total carotenoids, determined by spectrophotometry (model Lambda 40, Perkin Elmer, Waltham, MA, USA) at 450 nm, according to the method developed by the Palm Oil Research Institute of Malaysia (Porim Test Methods) [29], using hexane (Merck, Germany) as solvent and β-carotene 99% (Sigma) as standard. The solvents used were anhydrous ethanol (from Merck, Germany), with purity greater than 99.5%, and alcoholic solutions containing 1.91 ± 0.03, 5.76 ± 0.02, 10.00 ± 0.05 and 12.41 ± 0.01 mass% of water, prepared by the addition of deionized water (Milli-Q, Millipore) to anhydrous ethanol. The water concentration in the solvent was determined by Karl Fisher titration, according to the official method Ca 23–55 [27].

For the PRDC experiments, a bleached palm oil (BPO) containing 4.23 ± 0.01 mass% of free fatty acids and 225 ± 0.01 mg kg^{-1} of total carotenes was utilized. In addition, such sample was characterized in relation to mono-, di-, triacylglycerols and polymerized triacylglycerols by gel permeation HPLC according to the official method Cd 22-91 [27] (HPLC system Perkin Elmer model 250, refractive index detector Sicon Analytic, columns Jordi Gel DVB 300 mm × 7.8 mm id, 0.01 and 0.05 μm, mobile phase tetrahydrofurane, sample solution 1% (w/v) in tetrahydrofurane); peroxide value, according to the official method Cd 8b-90 [27]; iodine and saponification values calculated from fatty acid composition, following AOCS methods Cd 1c-85 and Cd 3a-94, respectively [27]; total tocopherols (tocopherols and tocotrienols) by HPLC (AOCS official method Ce 8-89 [27]; HPLC system Perkin Elmer model 250, fluorescence detector Shimadzu RF-10 AXL with excitation wavelength at 290 nm and emission wavelength at 330 nm, column Merck Li Chrosorb Si 60, 5 μm, 250 mm × 4 mm id, mobile phase isopropanol in hexane 1:99 (v/v)); total carotenoids, according to Porim Test Methods [29]; and Lovibond color read in a Lovibond Tintometer model E in a 5.25″ cell and expressed in units of yellow (Y), red (R) and blue (B). For the experiments in the PRDC, neutral ethanol (containing 5.8 mass% of water), food grade, purchased from Usina Ester (Cosmópolis, Brazil) was used as solvent.

Physical properties of the oils samples at 45 °C were also measured. The density measurements were performed using a DMA 58 Density Meter (Anton Paar, Graz, Austria). The dynamic viscosity data were obtained by an AMV 200 Viscometer (Anton Paar, Graz, Austria).

In order to compare the characteristics of oils submitted to different steps of refining process. the analysis described above were also performed in a crude palm oil (CPO), in a refined palm oil (RPO), both supplied by Agropalma (Pará, Brazil), and in the palm oil deacidified by liquid–liquid extraction (RPO-LLE) obtained in this work.

2.1. Response surface methodology

Liquid–liquid equilibrium experiments were accomplished by mixing bleached palm oil with ethanolic solvents (water content in solvent varying from 0 to 12 mass%) at different oil to solvent mass ratios (*O/S* varying from 0.36 to 2.77). The components were weighed on an analytical balance (Adam, model A250L, Milton Keynes, United Kingdom), accurate to 0.0001 g, and placed in polypropylene tubes (15 ml, Corning Inc., Lowell/MA, USA). The tubes were vigorously stirred for at least 15 min and left to rest for 24 h in a thermostatic bath (Cole-Parmer, model 12101-05, Chicago, IL) at 45 ± 0.1 °C, temperature in which the palm oil samples were completely in liquid state.

After phase equilibrium is established, samples of both phases were taken and analyzed. The concentration of free fatty acids was determined by titration according to IUPAC official method 2201 [28], using an automatic burette (Metrohm, model Dosimat 715, Herisan, Switzerland). The total solvent concentration was determined by evaporation at 65.0 °C in a vacuum oven (Napco, model 5831, New York, USA), with an inner absolute pressure equal to 126 mmHg. The water concentration was determined by Karl Fischer titration, according to AOCS official method Ca 23-55 [27], with a KF Titrino (Metrohm, model 701, Herisan, Switzerland). The quantification of total carotenoids was determined by spectroscopy at 450 nm, according to Porim Test Methods [29] [28]. The neutral oil (or triacylglycerol) concentration was determined by difference. All measures were performed at least in triplicate.

The response surface methodology was used to investigate the effect of the oil to solvent mass ratio (*O/S*) and the water content in solvent (*%Water*) on the carotenoids maintenance ($Carotene^{Oil}$), losses of neutral oil (L^{NO}) and on the free fatty acid transfer (T^{FFA}) during one equilibrium stage of the deacidification process by liquid–liquid extraction.

The T^{FFA} and the L^{NO} were calculated by Eq. (1).

$$T^{FFA} \text{ or } L^{NO}(\%) = 100 \cdot \frac{m^{AP} \cdot w_i^{AP}}{m^{Oil} \cdot w_i^{Oil}} \quad (1)$$

where *m* is mass, *w* is mass fraction, *AP* is alcohol phase and *i* is free fatty acid or neutral oil, given that m^{Oil} is the initial mass of palm oil and m^{AP} is calculated by mass balance.

The carotenoids maintenance was expressed as the respective content remaining in oil ($Carotene^{oil}$, in mg kg^{-1}) after one stage of equilibrium (Eq. (2)).

$$Carotene^{Oil}(\text{mg kg}^{-1}) = \left(1 - w_{solv}^{OP}\right) \cdot Carotene^{OP}(\text{mg kg}^{-1}) \quad (2)$$

where *solv* is the solvent (ethanol plus water) and *OP* is oil phase.

The experimental set was planned to obtain a quadratic model, consisting of 2^2 trials plus a star configuration with three repetitions in central point [30,31]. Response surfaces were built using the quadratic model for the statistically significant variables.