

Deacidification of Vegetable Oils by Solvent Extraction

Christianne E. C. Rodrigues¹, Cintia B. Gonçalves¹, Eduardo Batista² and Antonio J. A. Meirelles^{2*}

¹Department of Food Engineering (ZEA - FZEA), University of São Paulo (USP), P.O. Box 23, Zip Code 13635-900, Pirassununga, São Paulo, Brazil, ²EXTRA-E, Department of Food Engineering (DEA), Faculty of Food Engineering (FEA), State University of Campinas (UNICAMP), P.O. Box 6121, Zip Code 13083-862, Campinas, São Paulo, Brazil

Received: October 3, 2006; Accepted: November 22, 2006; Revised: December 4, 2006

Abstract: The refining of edible oils requires a series of purification steps, with the most important being the decrease of the free fatty acid level of the crude oil. This step is very important for the quality of the final product and has a major impact on the economic feasibility of the whole process. Several techniques, alternative to the conventional caustic or steam distillation methods, are suggested in the literature, such as supercritical extraction, membrane technology and solvent extraction. In the present paper we discuss the main aspects related to the solvent extraction technique, coupled or not with the conventional methods. The reviewed patents indicate various advantages of a purification process based on the selective extraction of free fatty acids using short chain alcohols. Its technical feasibility is due to the differences in solubility of free fatty acids and neutral oil in the proposed solvents. This alternative technique does not generate waste products and can preserve nutraceutical compounds in the refined oil.

Keywords: Oil deacidification, free fatty acid extraction, ethanol, oil refining, vegetable oil or edible oil, oil extraction, short chain alcohols, isopropanol or n-propanol.

INTRODUCTION

Oilseeds are the major source for the production of edible oils that are regarded as an important component of the diet, an important source of energy, of essential fatty acids (such as linoleic acid), and of fat-soluble vitamins (such as vitamins A and E). The total world production of major oilseeds in 2004 was 380.3 million metric tons with a worldwide vegetable oil consumption of 105.6 million metric tons [1].

The crude oil that is extracted from the oilseeds is a mixture of triacylglycerols, partial acylglycerols, free fatty acids, phosphatides, pigments, sterols and tocopherols (compounds that present vitamin E activity) [2]. The complete steps of treatment to make the oil suitable for edible use is called refining and usually refers to the operations of pre-treatment, deacidification, bleaching and deodorization [2].

The removal of free fatty acids (deacidification) is the most difficult step of the oil purification process, mainly because it has the maximum economic impact on oil production. Deacidification of oils is industrially performed by chemical, physical or miscella methods. However, for oils with high acidity, chemical refining causes high losses of neutral oil due to saponification and emulsification. The physical method is also a feasible process for deacidification of highly acidic oils, since it results in a loss of neutral oil that is lower than the chemical method, but more energy is consumed. Moreover, in some cases, the refined oil is subject to undesirable alterations in color and to a reduction of stability to oxidation [3].

The refining of crude oil in the solvent extraction plant, prior to solvent stripping, is termed miscella refining. Turkey

and Civelekoglu [4,5] investigated the liquid-liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions. This method has been applied to a variety of oils but commercially it is used almost exclusively for the refining of cottonseed oil [6]. This technique makes possible the production of a light-colored cottonseed oil at a reduced cost, and with a low refining loss [7]. In spite of the advantages, the miscella refining requires high initial investments with explosion-proof equipments that limit the application of this deacidification method.

New approaches for deacidification of vegetable oils have been proposed in literature, such as biological deacidification, chemical reesterification, supercritical fluid extraction, membrane processing, and solvent (or liquid-liquid) extraction.

Biological deacidification or biorefining can be accomplished in two different ways: by the use of microorganisms or by enzymatic deacidification. According to Cho, Kwon and Yoon [8], microorganism system selectively assimilates free fatty acids (FFA) for its own growth. The disadvantage of this method is that linoleic acid and short-chain fatty acids (carbon number less than 12) are not utilized by the microorganism and sometimes these fatty acids even inhibit their growth. Studies about enzymatic deacidification have also gained importance over the years [9-14]; such process involves the unique ability of some microbial lipases to esterify FFA into triacylglycerols. Although this process results in low-energy consumption and high neutral oil yield, it presents as limitation, the high cost of the enzymes [15].

Chemical reesterification is also a deacidification method in which FFA is reesterified with the free hydroxyl groups remaining in the oil (or with added hydroxyl groups from glycerol) at a high temperature, and in an inert atmosphere, with or without a catalyst system [16]. Studies about chemical reesterification of FFA at high temperatures have been developed since the 19th Century [15], but in a work

*Address correspondence to this author at the Faculty of Food Engineering – State University of Campinas (UNICAMP) P.O. Box 6121 Zip Code 13083-862 Campinas – SP Brazil; Fax: +55-19-3521-4027; E-mail: tomze@fea.unicamp.br

published almost twenty years ago, its combination with the conventional alkali neutralization was also suggested [17]. Although it provides a high oil yield, this chemical reaction brings the disadvantage of being random, in contrast with the enzymatic method. Moreover, the high temperatures used in this process (until 270 °C) make chemical reesterification a costly process [18].

The use of carbon dioxide at temperatures and pressures above its critical point (supercritical fluid extraction, SCFE) has also been tested as an alternative deacidification process for oils with high acidity [19]. Such process presents high selectivity, minimum oil losses and can be accomplished at low temperatures. On the other hand, SCFE is an expensive process, and its use is only justified for deacidifying special oils and fats with high initial acidity, in which the quality and purity of the extracted components are of great importance [15].

In the membrane technology, components are separated by their molecular weight differences. Many works suggesting the use of membranes for deacidification of vegetable oils, with and without solvents, by using porous or nonporous membranes, have been found in the literature [20-24]. In fact, membrane process can be accomplished at room temperature, with low-energy consumption and without addition of chemicals, providing retention of nutrients and other desirable components. In contrast, studies have shown some limitations of this method, because of the small difference between triacylglycerols and FFA molecular weights that makes the separation process difficult, and because of the non-availability of membranes with high selectivity [15].

The aim of the present review is to discuss aspects related to deacidification of vegetable oils by the solvent extraction technology. This paper is based on the application of such technique to different fatty materials, reported in patents and articles and on the thermodynamic study, which guides the liquid-liquid extraction process.

THE SOLVENT EXTRACTION PROCESS

The difference of solubility of fatty acids and neutral triacylglycerols in an appropriate solvent is the basis of liquid-liquid extraction for oil deacidification [25,26]. This process has been receiving attention due to its advantages in comparison to the physical and chemical refining. As this process is normally carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments. Besides, the liquid-liquid extraction has the advantages of avoiding the formation of waste products and reducing the loss of neutral oil. Furthermore, solvent stripping from deacidified oil and solvent recovery from extract stream can be easily carried out, because of the high difference between the boiling points of the solvent, fatty acids and triacylglycerols. In fact, these operations can be accomplished by evaporation or distillation at relatively low temperatures, in most cases being lower than 80°C [27].

The use of solvent extraction for deacidification of vegetable oils was first proposed by Bollmann [28]. In this patent the author suggests the use of methyl alcohol, ethyl alcohol, amyl alcohol, acetone or acetic ester diluted or not

with water. The suggested process consists in contacting oil and solvent in successive stages. After each stage, the oil phase is separated from the solvent before flowing to the next stage. In every successive stage, the oil repeatedly encounters pure solvent, so that the process suggested by Bollmann [28] can be characterized as a crosscurrent one. The author tested the suggested process for deacidifying 3,000 kg of rape oil with 12 % of free fatty acids using 9,000 kg of 96% alcohol. In another test, 3,000 kg of coconut oil containing 15% free fatty acids were deacidified by extraction using 10,500 kg of 92 % methanol.

van Dijck [29] suggested a process combining liquid-liquid extraction and alkali refining. Free fatty acids from fat or oils were neutralized by adding a base such as ammonia, and subsequently the soaps were removed by countercurrent extraction with a suitable solvent such as ethanol. The free fatty acid content may be selectively neutralized and the resulting soaps removed with minimum loss of desirable triacylglycerols. In fact, the presence of the alcohol prevents the formation of emulsion and makes easier the separation of fatty acid salts and triacylglycerols.

Another invention based on liquid-liquid extraction associated with alkali refining was patented by Nestlé Co. [30]. The aim of the invention is to provide an industrially applicable process that selectively and quantitatively removes the free fatty acids without the disadvantages associated with alkali or physical refining. According to the inventors, free fatty acids are removed by controlled neutralization in an aqueous medium containing an alcohol or a polyol. Experimental tests were accomplished in batch reactors/extractors with controlled conditions of pH and temperature, leading to the partition of free fatty acids between a lipid phase and an alcoholic phase. A decisive advantage of the proposed invention, according to the authors, is that, in contrast to conventional refining processes, it is not necessary to add alkali in excess for the neutralization. This fact avoids the alkaline hydrolysis of the triacylglycerols and diminishes the losses of neutral oil. The experiments were conducted in a laboratory scale, for example using 100 g of coffee oil containing 4.85 % of free fatty acids and 100 mL of 94 % aqueous ethanol. In another case, 100 g of rice bran oil containing 9.14 % of free fatty acids and 150 mL of aqueous ethanol were used.

Swoboda [31] reported a process for refining palm oil and palm oil fractions. According to the invention of Swoboda [31], refining of palm oil or palm oil fraction can be accomplished subjecting the oil to solvent extraction with an alcohol, optionally in admixture with up to 25% by weight of water, and bleaching the raffinate of the said solvent extraction or oil derived therefrom. The extracting solvent should be mixtures of ethanol and water, or isopropanol and water, preferably with a composition near the azeotropic one. According to the author, azeotropic mixtures are preferred due to the advantages of recycling the solvent. In this invention, the experiments were carried out continuously in a countercurrent configuration. Crude palm oil subjected to solvent extraction may produce a raffinate containing a concentration of carotenoids similar to, or even larger than, the concentration of carotenoids in original source. The author suggests a subsequent alkali washing in

order to remove phosphorous compounds of non-polar nature and in order to remove color or color precursors. The solvent extracted palm oil may be of considerable value without further substantial refining by virtue of its high carotenoid content, absence of odor and flavor, and low free fatty acid level. Since the oil at this stage generally has a pronounced red color, it may be employed as a coloring material of natural origin. It may also be employed to provide a dietary source of vitamin A precursor [31].

A Japanese Patent application by Nippon Oils and Fats, cited by Hamm [32], suggested that it is possible to produce fish oil fractions enriched in eicosapentaenoic acid (EPA) by extraction with aqueous acetone. An increase of 85 % in eicosapentaenoic acid content was achieved by extracting the original oil, containing 12.88 % of this fatty compound with ten times its weight of a 9:1 acetone-water mixture.

According to the invention suggested by Plonis and Trujillo-Quijano [33], the deacidification of palm oil by liquid-liquid extraction may produce an olein (the fraction of the palm oil enriched in unsaturated fatty acids) with a carotene content of 750-1000 mg kg⁻¹. The proposed solvents are short chain alcohols or ketones, preferred ethanol, containing 1 to 25 % (in volume) of water and about 1% of citric acid. It was also mentioned that the suggested process may generate a deacidified oil with an enhanced flavor and aroma, and containing high levels of carotene and reduced amounts of diacylglycerols and free fatty acids.

Besserman *et al.* [34] reported a countercurrent liquid/liquid extraction process for fractionating complex mixtures of medium and long chain fatty acid triacylglycerol. Medium chain fatty acid, as used herein, is meant a saturated fatty acid, unsaturated fatty acid, or mixture thereof, having 6 to 10 carbon atoms and by long chain fatty acid is meant a saturated fatty acid, unsaturated fatty acid, or mixture thereof, having 18 to 24 carbon atoms. This application suggests the countercurrent liquid/liquid extraction for removing or separating out "light" and "heavy" impurities from such mixtures in order to provide preferred reduced calorie fats. The solvent stream used is a polar solvent, such as anhydrous methanol, aqueous ethanol and methanol/ ethanol mixtures.

A European Patent application by Matsumoto and co-workers (cited by Besserman *et al.* [34]) discloses a process for removing partial acylglycerols and/or free fatty acids from fats. The free fatty acids were removed by liquid-liquid extraction using solvents such as furfural, n-propyl alcohol, propionitrile, hexane, acetone, methanol and ethanol. This liquid-liquid extracted material is then subjected to fractional crystallization with acetone to remove the partial acylglycerols. This application points out that the liquid-liquid extraction and fractional crystallization do not cause a change in the triacylglycerols composition.

With the purpose of obtaining rice bran oil enriched with high levels of tocopherols - tocopherols and tocotrienols - and gamma-oryzanol, Cherukuri *et al.* [35] suggested a liquid-liquid extraction process using lower aliphatic alcohols (C1 to C6, preferably methanol, ethanol, or isopropanol). The process involves mixing rice bran oil and alcohol, separating the alcohol layer and subsequently distilling this layer in

order to recover enriched rice bran oil. The process was developed based on experimental runs performed in separation funnels in a laboratory scale.

In order to enhance the content of polyunsaturated fatty acids in the edible oil, Parson [36] developed an invention based on liquid-liquid extraction by selective solvents. The edible oil increases its polyunsaturated fatty acid content by a process comprising the contact of the oil with an organic polar solvent, such as amides containing two lower alkyl groups, each containing up to 4 carbon atoms attached to the nitrogen atom of the amide group, particularly N-lower alkyl pyrrolidones, or methyl derivatives and dimethyl formamide. This invention is based on the observation that triacylglycerols of highly unsaturated fatty acids, commonly found in natural oils, such as linoleic and linolenic acids, are more soluble in polar solvents than saturated and monounsaturated fatty acids. The two liquid phases formed consist of a fraction of oil rich in linoleic acid, which is preferably dissolved in the polar solvent, and a lean fraction comprising the residual oil. The two fractions are separated and the polar solvent removed from the rich fraction in order to recover oil enriched in linoleic acid.

PHASE EQUILIBRIUM

The extraction of free fatty acids from fatty materials using solvents has a long history and several studies had already shown that, in principle, this process is feasible using short-chain alcohols as solvent, especially ethanol [25,26, 37-47]. Ethanol has low toxicity, easy recovery in the process, good values of selectivity and distribution coefficient for free fatty acids [42, 48-52] and low losses of nutraceutical compounds [53-56].

Nevertheless, the development of such a deacidification process and its future use in an industrial scale requires a systematic study of the corresponding phase equilibrium involving several oils of commercial and nutritional interest, as well as studies of the continuous process in a pilot scale. For this reason our research group is engaged for a long time in the development of such a deacidification process. Some of our research works reported equilibrium data for systems composed by several vegetable oils (canola, corn, palm, rice bran, cottonseed, garlic, grape seed, sesame seed, Brazil nut and macadamia nut oils), and saturated, mono and diunsaturated free fatty acids, such as stearic, palmitic, oleic and linoleic acids [48-56]. Besides the acquisition of experimental equilibrium data, our investigations involve the thermodynamic modeling using group contribution methods (UNIFAC, ASOG) and molecular models (NRTL, UNIQUAC), the simulation of the deacidification process and experimental runs in the continuous equipments [27].

Batista *et al.* [48] reported liquid-liquid equilibrium data for the systems containing canola oil, oleic acid and short chain alcohols (such as methanol, anhydrous ethanol, isopropanol, n-propanol and aqueous ethanol) at different temperatures. Figure 1 presents the binodal curves for systems using solvents such as anhydrous methanol, anhydrous ethanol or anhydrous isopropanol, at 20°C. The information about mutual solubility of canola oil and solvent is contained in the base tie-line of each system. Figure 1 shows

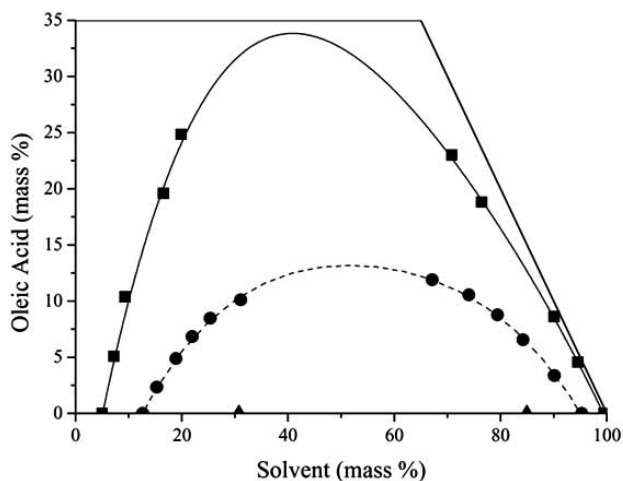


Fig. (1). Binodal curves for the systems refined canola oil + commercial oleic acid + solvents: (-■-) anhydrous methanol; (-●-) anhydrous ethanol; (▲) anhydrous isopropanol; at 20 °C.

that the mutual solubility increases and the two-phase region decreases with an increase in the length of carbon chain. For anhydrous isopropanol the region of two-phase coexistence is very small, so that only the mutual solubility oil-solvent was measured.

Figure 2 shows the heterogeneous regions and the tie-lines for the system composed by refined canola oil (1) + commercial oleic acid (2) + solvent (anhydrous ethanol) (3) at different temperatures (20°C and 30°C). The decrease in temperature from 30 to 20°C caused an increase in the two-phase region and only slight changes in the distribution coefficient.

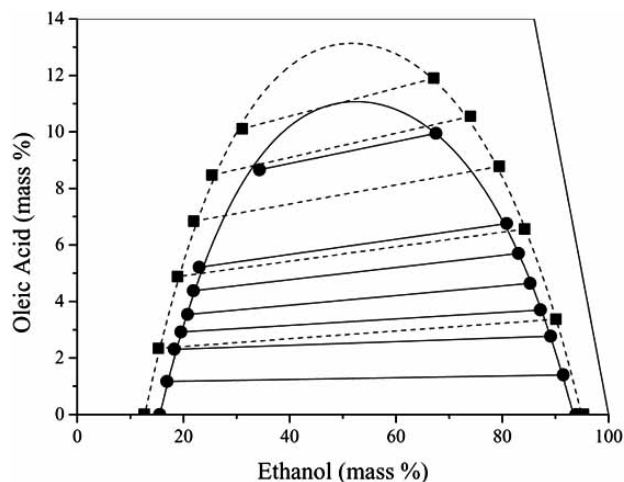


Fig. (2). Experimental tie-lines and binodal curves for the systems refined canola oil + commercial oleic acid + solvent (anhydrous ethanol) at 20 °C (-■-) and at 30°C (-●-).

All the experimental data obtained in this work were correlated by the NRTL and UNIQUAC models. Although this system was in fact a multicomponent and very complex

one, it was simplified, from the thermodynamical point of view, to a pseudo-ternary one, containing hypothetically a unique triacylglycerol equivalent to the edible oil. Despite this simplification, both models, NRTL and UNIQUAC, were able to describe reasonably well the liquid-liquid equilibrium data and the corresponding activity coefficients. Experimental data for systems containing canola oil, oleic acid, and anhydrous isopropanol at 20°C or anhydrous n-propanol at 10°C were also measured, but in these cases only a restricted range of concentrations generates a two-phase system, so that a solvent extraction process using such anhydrous solvents was not recommended. The addition of water to the solvent causes a high impact in the liquid-liquid equilibrium, mainly decreasing the mutual solubility oil-alcohol, enlarging the concentration range of phase splitting, but also decreasing the distribution coefficient of the fatty acids.

One feasible alternative that can extend the available liquid-liquid experimental data to other vegetable oils is the utilization of group contribution methods, such as UNIFAC and ASOG. Batista *et al.* [57] readjusted some group interaction parameters for both models using the experimental data available for systems composed by triolein, oleic acid or stearic acid and ethanol. Using the new parameters the predictions of liquid-liquid equilibrium systems composed by vegetable oils, fatty acids and ethanol were quite successful.

Gonçalves *et al.* [49] reported liquid-liquid equilibrium data for the system corn oil + oleic acid + ethanol + water at 25 °C and different water content (Fig. 3). The authors showed that a water content in the range of 4 to 6 mass %, added to the solvent, is appropriate for deacidification by solvent extraction, since it provides values of fatty acid distribution coefficient around unity, high values for the solvent selectivity and minimizes the loss of neutral oil. Such results were corroborated by Rodrigues *et al.* [51, 52] in the phase equilibrium investigations of systems composed by

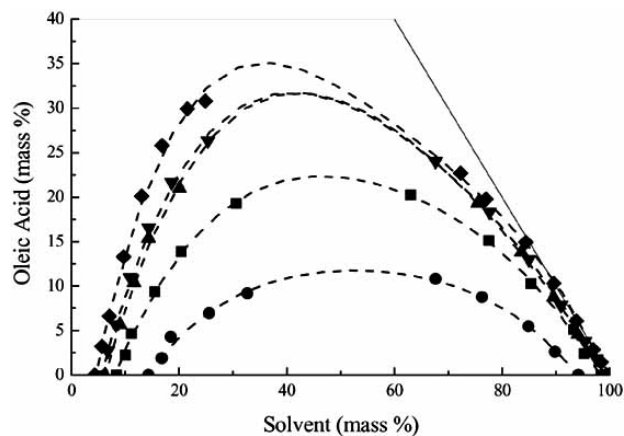


Fig. (3). Binodal curves for the systems refined corn oil + commercial oleic acid + solvent (ethanol + water): (●) anhydrous ethanol; (■) ethanol with 5 water mass %; (▲) ethanol with 8 water mass %; (▼) ethanol with 12 water mass %; (◆) ethanol with 18 water mass %, at 25 °C.

macadamia nut, Brazil nut, garlic, grape seed and sesame seed oils, fatty acids and hydrated ethanol. All the experimental data obtained in these works were correlated by the NRTL and UNIQUAC models, resulting always in a good description of the liquid-liquid equilibrium behavior.

Phase equilibrium data for the system refined rice bran oil + commercial oleic acid + ethanol + water were experimentally determined at 25 °C by Rodrigues *et al.* [53]. The data sets were correlated by the NRTL and UNIQUAC models, and the adjusted parameters were used in the prediction of liquid-liquid equilibrium for systems composed by crude rice bran oil + aqueous ethanol. Despite the difference in composition of the crude and refined rice bran oils, both molecular thermodynamic models allow a good prediction of phase equilibrium. The presence of water in the solvent minimizes the loss of neutral oil, making the extraction process more attractive from an economic point of view. Furthermore, the preliminary studies presented in this work on the minor component partition show that it is possible to refine rice bran oil by liquid-liquid extraction with a minimum loss of nutraceutical compounds, -oryzanol (Fig. 4) and tocols (tocopherols and tocotrienols). Fig. 4 shows that the distribution coefficient values for oryzanol are less than unity and as the water content in ethanol increases the distribution coefficient decreases, minimizing the loss of the nutraceutical component.

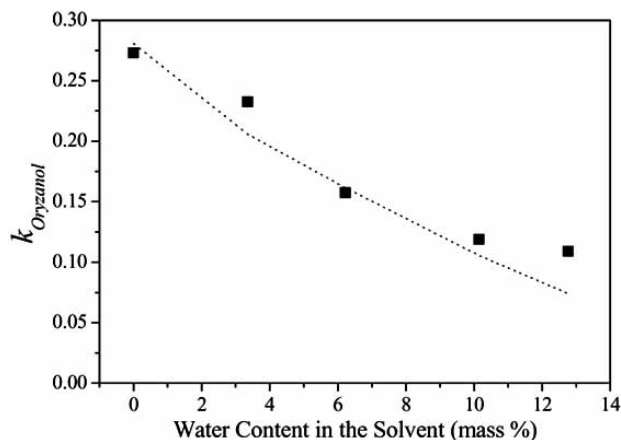


Fig. (4). Distribution coefficient of oryzanol (k) at 25°C for the systems degummed rice bran oil + free fatty acids + ethanol + water: (■) experimental; (.....) UNIQUAC model.

In a subsequent work, Rodrigues *et al.* [54] focused the behavior of -oryzanol and tocols in fatty systems containing crude or refined rice bran oil, free fatty acids, ethanol and water. Parameters for the NRTL and UNIQUAC models were adjusted and they describe with accuracy the phase compositions for the systems investigated. The interaction parameters between tocols and the others components of the system were adjusted for the UNIQUAC model using the approach of infinite dilution. The parameters obtained in this work, with the parameters published in a previous paper [53], were tested in the prediction of phase equilibrium for a system composed by crude rice bran oil from Thailand. Despite the differences in composition of rice bran oils from

different sources both thermodynamic models showed similar results for correlating as well as for predicting purposes, although the UNIQUAC equation slightly overestimates the extraction of free fatty acids and underestimates the extraction of nutraceutical compounds. These results confirm that the approach considering the fatty systems composed by pseudo-compounds may be successfully used in the correlation of complex multicomponent liquid-liquid equilibrium data. The adjusted parameters allow for the estimation of nutraceutical compound losses during the deacidification of rice bran oil by liquid-liquid extraction.

Gonçalves and Meirelles [50] reported liquid-liquid equilibrium data for model systems containing palm oil + palmitic acid + ethanol + water and palm oil + oleic acid + ethanol + water at 45°C, with different water contents. The experimental data set was used to adjust the parameters of the NRTL and UNIQUAC models. The adjusted interaction parameters were used to predict the liquid-liquid equilibrium of real systems composed by bleached palm oil (which contains free oleic and free palmitic acids, mainly) + aqueous ethanol. It was found that the main free fatty acids (palmitic and oleic) presented experimental distribution coefficients close to unity.

Liquid-liquid equilibrium data for the system refined cottonseed oil + commercial linoleic acid + ethanol + water, at 25°C, was published by Rodrigues *et al.* [55]. In this paper the influence of the solvent on the distribution coefficient of tocopherols was also studied (Fig. 5). Figure 5 shows that the distribution coefficient values for tocopherol are less than unity and as the water content in ethanol increases, the distribution coefficient decreases, minimizing the loss of the nutraceutical component. UNIQUAC and NRTL interaction parameters between tocopherols and the other pseudocomponents were determined assuming that the nutraceutical compound is present at infinite dilution in the liquid-liquid equilibrium system.

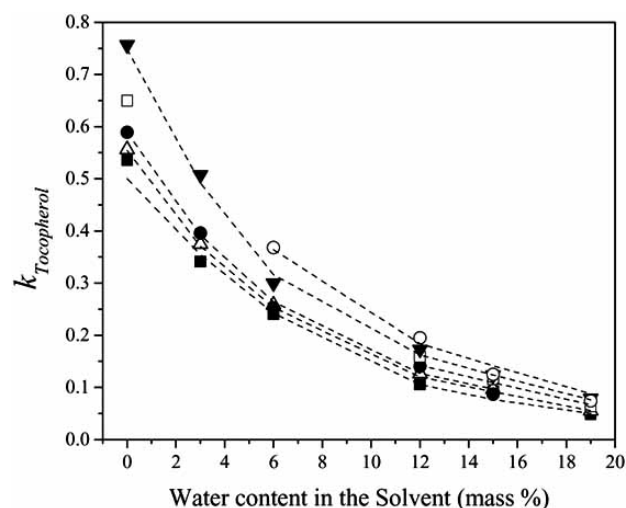


Fig. (5). Distribution coefficient of tocopherols (k) at 25°C for the systems cottonseed oil + commercial linoleic acid + ethanol + water. Free fatty acids content in the oil: (■) 0 mass %; (○) 2.5 mass %; (●) 5 mass %; (□) 10 mass %; (▼) 15 mass %; (○) 20 mass %; (- -) NRTL model

Gonçalves *et al.* [56] studied the partition of nutraceutical compounds in the deacidification of palm oil by solvent extraction. Figure 6 shows that the addition of water to the ethanolic solvent decreases the distribution coefficients of carotenoids. This means that increasing the concentration of water, the capacity of the solvent to extract this nutraceutical compound decreases. It can be also observed that for all aqueous ethanol solutions used, the distribution coefficient of carotenoids was less than unity, indicating their preference for the oil phase. This effect is benefic, since it demonstrates that most of the carotenoids remain in the deacidified oil.

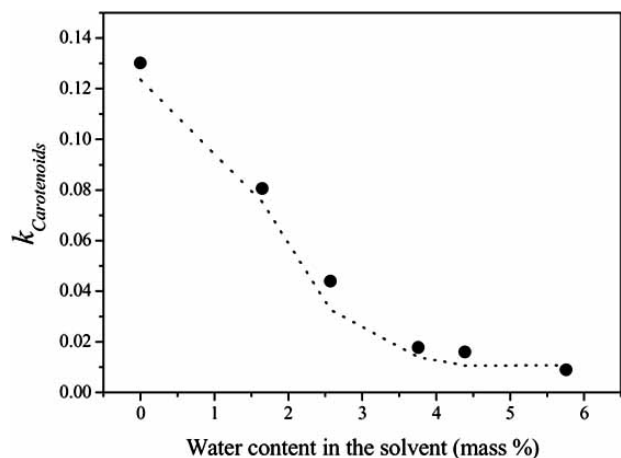


Fig. (6). Distribution coefficient of carotenoids (k) at 45°C for the systems palm oil + free fatty acids + ethanol + water: (●) experimental; (.....) UNIQUAC model.

Pina and Meirelles [27] investigated the deacidification of corn oil by continuous liquid-liquid extraction in a rotating disk column (RDC), using ethanol with approximately 6 mass % of water. The dispersed phase holdup observed in the equipment increased with the increase of the rotor speed and of the oil phase flow, suggesting that the mass transfer area also increases as a consequence of those changes in the operational conditions. Volumetric mass transfer coefficients were also measured, as a function of rotor speed and of oil/solvent ratio, so that a preliminary basis for designing continuous equipment for oil deacidification by solvent extractions is now available. The results proved that it was feasible to obtain deacidified oil with an oleic acid content lower than 0.3 mass % [58] using a column with a extraction zone of 1 m high and a feed oil with acidity not higher than 3.5 mass %. In these experiments, the loss of neutral oil dissolved in the solvent phase varied in the range of 2.0 to 5.9 % of the amount of neutral oil fed into the column. This loss of neutral oil is significantly lower than the results reported in the literature for alkali or physical refining of corn oil [3, 59].

Hamm [32] reported that a reduction of the free fatty acid content to a value of 1 % can easily be accomplished in a contactor having ten to fifteen theoretical stages, provided that solvent to crude oil flow ratio of at least 2 is used and

that the remaining free fatty acids is removed by neutralization with alkali after desolventization.

Batista *et al.* [60] simulated the deacidification of crude corn oil by liquid-liquid extraction using aqueous ethanol as solvent. The crude oil feed in the extractor was composed by 14 main triacylglycerols, 12 main diacylglycerols and 9 fatty acids. The solvent to crude oil flow ratio, the number of stages and the water percent in ethanol could be selected to guarantee minimum free fatty acid content in the refined oil with minimum loss of neutral oil in the solvent phase. The optimization study was carried out by surface response analysis based on the results from a factorial design and regression analysis of the simulation results. The best combination of operational and constructive conditions for guaranteeing a minimum loss of neutral oil and a concentration of free fatty acid lower than the required value of 0.3 mass % in the refined oil [58] was the following: a solvent to crude oil flow ratio of 1.27 in a column with ten theoretical stages and ethanol with 5.75 mass % of water as solvent. They selected a value for the solvent to oil flow ratio lower than that suggested by Hamm [32] and obtained a lower level of free fatty acids in the refined oil, so that a subsequent alkali deacidification step was not required. In the specified optimal conditions, the loss of neutral oil reported by Batista *et al.* [60] was equal to 2.4 %, much lower than the values presented in literature [3, 59], and 60.7 % of diacylglycerols feed in the extractor was transferred to the solvent phase.

A recent work published by Rodrigues *et al.* [61] reports the influence of process variables on the losses of γ -oryzanol, tocots and neutral oil, and on the transferred amount of free fatty acids during the deacidification process of rice bran oil by liquid-liquid extraction. The influence of variables such as acidity content in the oil, water content in the ethanolic solvent and oil to solvent ratio were analyzed using the response surface methodology. The main goal was to maximize the transfer of free fatty acids and minimize the losses of neutral oil and nutraceutical compounds. In general, the results showed that the total deacidification of rice bran oil by liquid-liquid extraction is possible, and the losses of neutral oil and nutraceutical compounds are controlled by the water concentration in the solvent.

The mentioned patents and research works confirm the technical feasibility of oil deacidification by solvent extraction. Furthermore, the experimental equilibrium data, the corresponding thermodynamic modeling for estimation of activity coefficients, and the mass transfer data obtained in continuous equipments will certainly help in designing industrial-scale equipments for oil deacidification by solvent extraction. Nevertheless, oil refining involves a series of purification steps, such as degumming, bleaching, dewaxing, deodorization that are interconnected with the deacidification step. Unfortunately, the influence of the deacidification by solvent extraction upon the whole sequence of purification steps was not investigated with the required depth. This aspect helps to explain the reason why this technique was not tested in an industrial scale until now, despite its technical feasibility.

Another aspect is its economic feasibility. The deacidification by solvent extraction involves at least three

equipments, a liquid-liquid extraction column, a stripper for desolventising the refined oil and a column for recovering the solvent of the extract stream. Besides the capital costs, the energy requirement for evaporating the solvent must be taken into account. Such capital and energy costs must be compared with the costs of a high vacuum and high temperature equipment used in the physical refining and with the costs of centrifuging and waste treatment required in the chemical refining.

CURRENT & FUTURE DEVELOPMENTS

The present review indicates that oil deacidification by solvent extraction is a feasible process from a technical point of view. The selection of an appropriate solvent, particularly ethanol, and the addition of low amounts of water to this solvent guarantee a low loss of neutral oil without compromising the solvent capacity of extracting free fatty acids. The loss of nutraceutical compounds is also minimized. Nevertheless, the use of such a process in an industrial scale requires further investigations. Aspects related to the combination of the deacidification step by solvent extraction and other steps of the whole refining process (degumming, bleaching, dewaxing, deodorization) should be considered. The quality of the final product must be investigated in depth and the recovery of the solvent from the raffinate and extract streams should also be evaluated. At last, an economic analysis is necessary in order to estimate the eventual cost benefits of replacing the conventional caustic or steam distillation methods by the alternative solvent extraction technique.

ACKNOWLEDGMENT

The authors are grateful to CNPq (303649/2004-6) and FAPESP (2005/53095-2; 2006/00565-4; 2006/00646-4) for financial support.

REFERENCES

- [1] <http://www.soystats.com/2005/Default-frames.htm> Accessed Aug 29th, 2006.
- [2] Cheryan M. Ultrafiltration and microfiltration handbook. Lancaster, Tecnomac, 1998.
- [3] Antoniassi R, Esteves W, Meirelles AJA. Pretreatment of corn oil for physical refining. *J Am Oil Chem Soc* 1998; 75: 1411-15.
- [4] Türkay S, Civelekoglu H. Deacidification of sulfur olive oil. I. single-stage liquid-liquid extraction of miscella with ethyl alcohol. *J Am Oil Chem Soc* 1991; 68: 83-86.
- [5] Türkay S, Civelekoglu H. Deacidification of sulfur olive oil. II. multi-stage liquid-liquid extraction of miscella with ethyl alcohol. *J Am Oil Chem Soc* 1991; 68: 818-821.
- [6] Hui YH. *Bailey's Industrial oil and fat products*. New York, John Wiley and Sons Inc. 1996.
- [7] Wan PJ, Pakarinen DR, Hron RJ. Miscella refining test method for the determination of cottonseed oil color. *J Am Oil Chem Soc* 1996; 73: 815-17.
- [8] Cho SY, Kwon TW, Yoon SH. Selective removal of free fatty acids in oils using a microorganism. *J Am Oil Chem Soc* 1990; 67: 558-60.
- [9] Sengupta R, Bhattacharyya DK. A comparative study between biorefining combined with other processes and physical. *J Am Oil Chem Soc* 1992; 69: 1146-49.
- [10] Bhattacharyya S, Bhattacharyya DK. Biorefining of high acid rice bran oil. *J Am Oil Chem Soc* 1989; 66: 1469-71.
- [11] Makasci A, Arisoy K, Telefoncu A. Deacidification of high acid olive oil by immobilized lipase. *Turk J Chem* 1996; 20: 258-64.
- [12] Sengupta R, Bhattacharyya DK. Enzymatic deacidification of rice bran oils of varying acidity. *J Oil Technol Assoc India* 1996; 28: 17-21.
- [13] Sengupta R, Bhattacharyya DK. Effect of monoglycerides on enzymatic deacidification of rice bran oil. *J Oil Technol Assoc India* 1996; 28: 125-30.
- [14] Buettgen, K., Lindemann, M., Prinz, D. US20067033803 (2006).
- [15] Bhosle BM, Subramanian R. New approaches in deacidification of edible oils-a review. *J Food Eng* 2005; 69: 481-94.
- [16] Anderson AJC. In Williams PN (Ed.), *Refining of oils and fats for edible purposes* (2nd ed., 92-103). London, UK, Pergamon Press 1962.
- [17] Bhattacharyya AC, Bhattacharyya DK. Deacidification of high FFA rice bran oil by reesterification and alkali neutralization. *J Am Oil Chem Soc* 1987; 64: 128-31.
- [18] Gingras L. Refining of rice bran oil. *Inform*, 2000; 11: 1196-203.
- [19] Brunetti L, Dagheta A, Fedeli E, Kikic I, Zanderighi L. Deacidification of olive oils by supercritical carbon dioxide. *J Am Oil Chem Soc* 1989; 66: 209-17.
- [20] Raman LP, Rajagopalan N, Cheryan M. Membrane technology (in vegetable oil processing). *Oils Fats Int* 1994; 10: 28-38.
- [21] Subramanian R, Nakajima M, Kimura T, Maekawa T. Membrane process for premium quality expeller-pressed vegetable oils. *Food Res Int* 1998; 31: 587-93.
- [22] Subramanian R, Raghavarao KSMS, Nabetani H, Nakajima M, Kimura T, Maekawa T. Differential permeation of oil constituents in nonporous denser polymeric membranes. *J Mem Sci* 2001; 187: 57-69.
- [23] Raman LP, Cheryan M, Rajagopalan N. Solvent recovery and partial deacidification of vegetable oils by membranetechnology. *Lipid* 1996; 98: 10-14.
- [24] Zwijnenberg HJ, Krosse AM, Ebert K, Peinemann K-V, Cuperus FP. Acetone-stable nanofiltration membranes in deacidifying vegetable oil. *J Am Oil Chem Soc* 1999; 76: 83-87.
- [25] Thomopoulos C. Méthode de desacidification des huiles par solvant sélectif. *Rev Fran Corps Gras* 1971; 18: 143-50.
- [26] Apelblat A, Zaharoskin T, Wisniak J, Korngold E. Extraction of oleic acid from soybean oil and jojoba oil - phase diagrams. *J Am Oil Chem Soc* 1996; 73: 239-44.
- [27] Pina, C. G.; Meirelles, A. J. A. Deacidification of corn oil by solvent extraction in a perforated rotating disc column. *J Am Oil Chem Soc* 2000; 77: 553-59.
- *[28] Bollmann, H.: US19211371342 (1921).
- [29] van Dijk, W.J.G.: US19422268786 (1942).
- *[30] Bertholet, R.: WO20009637 (2000).
- *[31] Swoboda, P.A.T.: GB19852144143 (1985).
- [32] Hamm W. In: Thornton JD Ed, *Science and practice of liquid-liquid extraction*. Oxford, Clarendon Press. 1992; 309-52.
- *[33] Plonis, G. F., Trujillo-Quijano J.: EP1995529107A (1995).
- *[34] Besserman, M.A., Morrison, Jr. L.R., Weber, V.L.: US19925104587 (1992).
- *[35] Cherukuri, R.S.V., Cheruvanky, R., Lynch, I., McPeak, D.L.: US19995985344 (1999).
- *[36] Parson, A.M.: GB19721444551 (1972).
- [37] Fachini S, Samazzi S. Behavior of alcohol in presence of olive oil which is acid. *Industr. Olii Grassi* 1925; 4: 31-3.
- [38] Schlenker E. Removal of fatty acids by means of alcohol. *Chem. Umschau Fette. Oele, Wachse Harse* 1931; 38: 108-10.
- [39] Kale V, Katikaneni SPR, Cheryan M. Deacidifying rice brain oil by solvent extraction and membrane technology. *J Am Oil Chem Soc* 1999; 76: 723-27.
- [40] Bhattacharyya AC, Majumdar S, Bhattacharyya DK. Refining of FFA rice bran oil by isopropanol extraction and alkali neutralization. *Oléagineux* 1987; 42: 431-33.
- [41] Shah KJ, Venkatesan TK. Aqueous isopropyl alcohol for extraction of free fatty acids from oils. *J Am Oil Chem Soc* 1989; 66: 783-87.
- [42] Sreenivasan K, Viswanath DS. Refining of cottonseed oil using solvents. *Indian J Technol* 1973; 11: 83-90.
- [43] Rius A, Martínez-Moreno JM. Diagramas de Solubilidad para la Desacidificación con Disolventes del Aceite de Oliva. *Anales Fis y Quim* 1947, 123-48.
- [44] Rius A, Gutiérrez-Jodra L. Diagramas de Solubilidad para la Eliminación de Ácidos Grasos Libres de los Aceites de Pescado por Extracción con Disolventes. *Anales Fis y Quim* 1947, 245-68.
- [45] Rius A, Crespi MA. Desacidificación de aceites vegetales por extracción con disolventes. *Anales Real Soc Esp Fis Y Quim* 1951, 4: 243-56.

- [46] Rigamonti R, Vaccarino C, Duzzi A. Sistemi Ternari tra Acido Oleico, Trioleina ed Alcoli. Applicazione alla Disacidazione degli Oli Vegetali Chim Ind 1951, 10: 619-23.
- [47] Rigamonti, R.; Botto, G. Équilibres de Solubilité entre Huile de Coton, Acétone et Eau. Oléagineux 1958, 1: 199-202.
- [48] Batista E, Monnerat S, Kato K, Stragevitch L, Meirelles AJA. Liquid-liquid equilibrium for systems of canola oil, oleic acid and short-chain alcohols. J Chem Eng Data 1999; 44: 1360-64.
- [49] Gonçalves CB, Batista E, Meirelles AJA. Liquid-liquid equilibrium data for the system corn oil + oleic acid + ethanol + water at 298.15K. J Chem Eng Data 2002; 47: 416-20.
- [50] Gonçalves C B, Meirelles AJA. Liquid-liquid equilibrium data for the system palm oil + fatty acids + ethanol + water at 318.2K. Fluid Phase Equilib 2004; 221: 139-50.
- [51] Rodrigues CEC, Silva FA, Marsaioli Jr. A, Meirelles, AJA, Deacidification of Brazil nut and macadamia nut oils by solvent extraction - liquid-liquid equilibrium data at 298.2 K. J Chem Eng Data 2005; 50: 517-23.
- [52] Rodrigues CEC, Filipini A, Meirelles AJA, Phase equilibrium for systems composed by high unsaturated vegetable oils + linoleic acid + ethanol + water at 298.2 K. J Chem Eng Data 2006; 51: 15-21.
- [53] Rodrigues CEC, Antoniassi R, Meirelles AJA, Equilibrium data for the system rice bran oil + fatty acids + ethanol + water at 298.2 K. J Chem Eng Data 2003; 48: 367-73.
- [54] Rodrigues CEC, Pessôa Filho PA, Meirelles AJA, Phase equilibrium for the system rice bran oil + fatty acids + ethanol + water + -oryzanol + tocopherols. Fluid Phase Equilib 2004; 216: 271-83.
- [55] Rodrigues CEC, Reipert ECCD, Souza AF, Pessôa Filho PA, Meirelles AJA, Equilibrium data for systems composed by cottonseed oil + commercial linoleic acid + ethanol + water + tocopherols at 298.2 K. Fluid Phase Equilibria 2005; 238: 193-203.
- [56] Gonçalves CB, Pessôa Filho, PA, Meirelles, AJA. Partition of Nutraceutical Compounds in Deacidification of Palm Oil by Solvent Extraction. J Food Eng (in press).
- [57] Batista E, Monnerat S, Stragevitch L, Pina CG, Gonçalves CB, Meirelles AJA. Prediction of liquid-liquid equilibrium for systems of vegetable oils, fatty acids, and ethanol. J Chem Eng Data 1999; 44: 1365-69.
- [58] Codex Alimentarius - Fats, oils and related products – volume eight - Joint FAO/WHO Food and Agriculture Organization of the United Nations and World Health Organization, Rome. 1993; 29-32.
- [59] Leibovitz Z, Ruckenstein C. Our Experiences in Processing Maize (Corn) Germ Oil. J Am Chem Soc 1983; 60: 347A-51A.
- [60] Batista E, Antoniassi R, Wolf Maciel MR, Meirelles AJA. Liquid-liquid extraction for deacidification of vegetable oils. Proceeding of International Solvent Extraction Conference. South Africa (2002).
- [61] Rodrigues CEC, Onoyama MM, Meirelles AJA, Optimization of the rice bran oil deacidification process by liquid-liquid extraction. J Food Eng 2006; 73: 370-78.