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Molecular Distillation

A Powerful Technology for Obtaining Tocopherols From Soya Sludge

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Abstract

Molecular distillation was studied for the separation of tocopherols from soya sludge, both experimentally and by simulation, under different operating conditions, with good agreement. Evaporator temperatures varied from 100°C to 160°C and feed flow rates ranged from 0.1 to 0.8 kg/h. The process pressure was maintained at 10^{-6} bar, the feed temperature at 50°C, the condenser temperature at 60°C, and the stirring at 350 rpm. For each process condition, samples of both streams (distillate and residue) were collected and stored at –18°C before tocopherols analyses. Owing to the differences between molecular weights and vapor pressures of free fatty acids and tocopherols, tocopherols preferentially remained in the residue at evaporator temperatures of 100°C and 120°C, whereas for higher temperatures (140°C and 160°C) and lower feed flow rate, tocopherols tended to migrate to the distillate stream.

Index Entries: Free fatty acids; molecular distillation; soya sludge; tocopherols.

Introduction

From a market perspective, the interest in natural substances to be used in food products is higher than for synthetic ones. Natural substances of commercial interest are present in complex mixtures made up of a number of different molecules. This is the case of tocopherols obtained from soya sludge. Most of the substances that are present in soya sludge are molecules of high molecular weight and are thermally sensitive. These properties hinder the separation or purification of substances through traditional methods, because they are decomposed when subjected to high temperatures.

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An alternative separation/purification of such products is the use of molecular distillation, which is a special evaporation technique, it operates under low pressure and at relatively low temperatures. Furthermore, this process has advantages over other techniques that use toxic or flammable solvents (as the separating agent, avoiding toxicity, and environmental problems). In fact, this process shows potential in the separation, purification and/or concentration of natural products which are often complex and thermal sensitivity molecules, such as vitamins, because it can minimize losses by thermal decomposition. In lipid chemistry, it has been used for the purification of monoacylglycerols *(1)*, recovery of carotenoids from palm oil *(2)*, fractionation of polyunsatured fatty acids from fish oils *(3)*, recovery of squalene *(4)*, and recovery of tocopherols *(5)*, among others.

As previously described by Lutisan et al. *(6)*, in a falling film molecular distillator apparatus, the distilled liquid continuously passes down the heated evaporating cylinder, evaporates partially and the vapors then condense on the internally cooled condenser placed close to the evaporating cylinder (Fig. 1). A sufficiently low pressure around 10^{-3} mmHg, is maintained in the evaporator. Therefore, evaporated molecules can pass through the distillation gap to the condenser freely. The evaporation of the liquid on the evaporating cylinder is a key step in the molecular distillation *(6)*.

Soya sludge, also known as deodorizer distillate of soya oil (DDSO), is an important byproduct from the refining process of soybean oil, because of the content of interesting products. It contains tocopherols (3–12%), mainly the γ-isomer, triglycerides (25–50%), free fatty acids (FFA) (25–85%), phytosterols (7–8%), hydrocarbon and other unsaponifiables in trace amounts. Owing to the high content of FFA, separation of these compounds from deodorizer distillate is an important step to concentrate tocopherols to high purity. The composition of soya sludge depends on the source and process conditions employed for the refining process of the soybean oil. The recovery of tocopherols, phytosterols, and other components is important from a commercial point of view for making value-added products *(7)*. Vitamin E, which includes four isomers (α, β, γ, and δ), is a major natural antioxidants used for protection of fats and oils against atmospheric oxidation. Phytosterols are used as starting materials for the synthesis of steroids for pharmaceutical purposes.

So, the aim of this work is to incorporate in the DISMOL (molecular distillation process simulator) the characteristics of some molecules present in the DDSO to simulate the molecular distillation process and then to validate the results with experimental data, in order to find out the range of operating conditions to obtain tocopherols from soya sludge. Complex systems must be well characterized in terms of physical–chemical properties of the components (e.g., critical pressure, critical temperature, critical volume, and acentric factor) to represent the system that will feed the molecular distillator. These properties are necessary to calculate other properties, for example, mean free path, enthalpy of vaporization, mass diffusivity, vapour

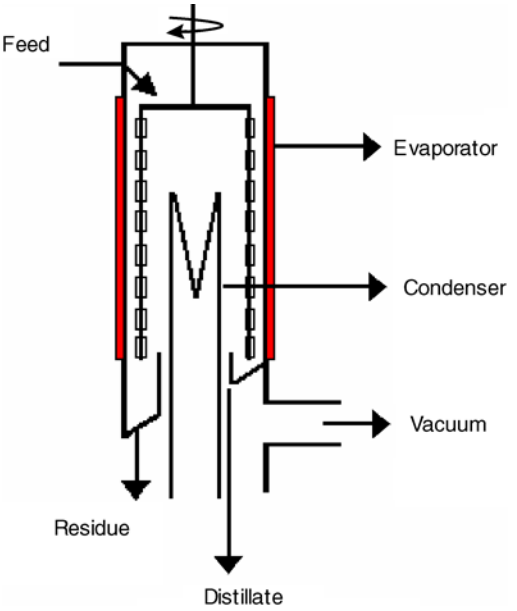

Fig. 1. Wiped Film Molecular Distillator.

pressure, liquid density, heat capacity, thermal conductivity, and viscosity of the system. Some properties are very difficult to find owing to the complexity of the involved components. Consequently, their determinations must be made through correlations and/or predictions, in order to be able to characterize the system and to simulate it. The simulation is very important to investigate the process viability as well as to establish the operating conditions, so that it is possible to improve the yield and purity of the final product. Therefore, in this work a comparison between simulated and experimental data is presented. The intention is to validate the simulation results for evaluating the tocopherols (vitamin E) recovery and, also, FFA elimination, using the DISMOL simulator. The equipment used in this study is the falling film molecular distillator. The problem may be stated as: for lower temperatures, FFA are eliminated from the residue stream along with a small amount of tocopherols; as the temperature increases, FFA concentrations in the distillate stream increase with an increasing amount of tocopherols as well. However, despite higher losses, operating at higher temperature has the advantage of minimizing the quantity of FFA in the desired product stream (tocopherols).

Methodology

Simulation

DDSO is a complex mixture owing to its large number of components. It includes thermal sensitive molecules such as tocopherols. Some physical

properties can not be experimentally determined without the decomposition of these molecules. Consequently, it is very hard to find their physical properties and they must be estimated and/or predicted before the simulation. Firstly, it was necessary to create hypothetical components using the UNIFAC group contribution method (a tool of the Commercial Simulator HYSYS™, Hyprotech Ltd.), to estimate some physical properties, for example, critical pressure, critical temperature, critical volume, and acentric factor. These properties will be necessary to calculate other properties, for example, mean free path, enthalpy of vaporization, mass diffusivity, vapor pressure, liquid density, heat capacity, thermal conductivity, and viscosity of the system to be studied (DDSO) to insert in the DISMOL simulator (which allows simulation of the molecular distillation process). The DISMOL simulator requires, besides the component and mixture properties, equipment, process, and system characteristics which are simulation inputs. Evaporation rate, temperature and concentration profiles, residence time, stream compositions, and flow rates are the outputs from the simulation. All explanations of the equations used, of the solution methods and of the routine of solution to represent the molecular distillation process have been described *(8)* as well as calculations of these properties for the studied system *(9)*. For molecular distillation there is no discussion about equilibrium, because this process is a nonequilibrium process.

In relation to the equipment, it is necessary to know its dimension, the feed flow rate, and its heating temperature. In this study, the equipment used was a falling film distillator and the DDSO composition, described in Table 1, was applied to the model. This results in concentrations and exit flow rates of the distilled and of the concentrated streams, the evaporation rate and the duration of distillation.

Experimental Procedure

Deodorizer distillate from industrial refining of soybean vegetable oil was obtained from Bunge Alimentos S. A. (São Paulo, Brazil). Solvents and reagents used for fatty acids analysis were of analytical grade. Hexane, isopropanol, acetonitrile, and water of high-performance liquid chromatography (HPLC) grade were used for the tocopherols and phytosterols analyses. Its composition is shown in Table 2. The DDSO composition was determined experimentally by the following methods.

Free Fatty Acid Analyses

The FFA were determined by titration with NaOH according to the Recommended Practice AOCS Ca 5a-40 using phenolphthalein as an indicator. The samples were dissolved in hot neutralized alcohol and the acids groups of FFA were neutralized with NaOH solution (1 *N*). The sample mass and the volume of alkali used in each determination were used to calculate the amount of free fatty acids. The percentage of FFA

Table 1
DDSO Composition Used in the Simulation

Components	Mass (%)
Palmitic acid	10.8
Stearic acid	2.4
Linoleic acid	26.2
Oleic acid	12.3
Lauric acid	1.9
Arachidic acid	4.2
Phytosterols	7.7
Tocopherols	8.9
Squalene	14.7
Glycerides	10.9
Total	100

Table 2
DDSO Composition Determined Experimentally (10)

Components	Mass (%)
Free fatty acids–oleic acid (FFA)	57.42
Tocopherols	8.97
Phytosterols	7.69
Triglyceride	8
Diglyceride	4.3
Monoglyceride	13.62
Total	100

in most types of fats and oils is calculated as oleic acid ($C_{18:1}$) using the formula:

$$\text{FFA (\%)} = \frac{\text{Alkali (mL)} \times N \times 28.2}{\text{Mass of sample (g)}}$$

where N corresponds to the normality of the sodium hydroxide solution.

Tocopherols Analysis

The composition of tocopherol was determined by normal phase HPLC (11) using a modular equipment composed by Waters 515 HPLC pump (Mildford, MA), equipped with a fluorescence detector (Waters model 2475 multi fluorescence). The separation was conducted in a microporasil column 125 Å, with particle size of 10 µ and 3.9 × 300 mm of dimension (Waters, Ireland). The mobile phase used was hexane:isopropanol (99:01). The feed flow rate of mobile phase was set at 1 mL/min. The data processing was done by the Millenium software 2010 Chromatography Manager Software

(Waters, Mildford, MA). The DDSO and samples of distillate and residue were dissolved in hexane (~1 mg/mL) and injected in the equipment. Each chromatografic run took about 10 min. This method determines α-, β-, γ-, and δ-tocopherol individually. The tocopherols detected in the chromatograms of DDSO were identified comparing the retention time of these compounds with the retention time of standards tocopherols.

Phytosterols Analyses

β-Sitosterol (24β-ethylcholesterol) standard with 98% of purity was purchased from Sigma (St. Louis, MO) to carry out phytosterols analyses by HPLC. This method determines the sitosterol content using UV detection with wavelength set at 206 nm. The mobile phase consisted of water: acetonitrile (78:22). Modular equipment consisted of HPLC (Waters, Milford, MA), equipped with a Waters 515 HPLC pump, Waters 2487 Dual Absorbance and an oven with a Waters temperature control module. Chromatographic separations were conducted in a Spherisorb S10 C8, 4.6 × 250 mm column (Waters, Ireland) under isocratic conditions, flow rate of 1 mL/min and temperature of 50°C. The samples were injected with no previous treatment into the 20 μL injection loop dissolved using ethanol before the analysis. Identification of compounds was achieved by comparing their retention times with the standards. For quantitative analysis, a calibration curve was used.

Triacylglycerols, Diacylglycerols, and Monoacylglycerols Analyses

Tri-, di-, and monoacylglycerols (Tg, DG, and MG, respectively) were determined according to literature procedure *(12)* using gel permeation chromatography (GPC). The samples were dissolved in tetrahydrofuran in the concentration of 1 mg/mL and injected into a modular equipment made up of an isocratic pump model Waters 515 HPLC (Mildford, MA), equipped with a differential refractometer detector model 2410 (Waters model, Mildford, MA) and an oven for columns. The samples were injected using a manual injector model Rheodyne 7725i with a 20-μL sample loop. The flow rate of the mobile phase was set at 1 mL/min. The separation was conducted using two GPC columns, Styragel HR1 and HR2 (Waters, Milford, MA), with dimensions of 7.8 × 300 mm, particle size of 5 μm and packed with styrenedivinylbenzene copolymer. The columns were connected in series using a U-shaped column joining tube. The acylglycerol content in the DDSO was based on the content of tocopherols, phytosterols, FFA, TG, DG, and MG, that are the main components present and their respective proportions were determined by GPC analysis.

Molecular Distillation

The distillation was performed using a laboratory wiped film molecular distillator model KDL 5, GmbH UIC (Alzenau, Germany) which is a variation from falling film molecular distillation with agitation. The major

Table 3
Molecular Weights and Vapor Pressures of FFA and Tocopherols (14)

Component	Molecular weight (g/gmol)	Vapor pressure at 200°C (mmHg)
FFA	180	4
Tocopherols	415	0.15

part of the equipment is made in glass. The heating of the evaporator was provided by a jacket circulating heated oil from an oil bath. The vacuum system included diffusion and mechanical pumps. The surface area of the evaporator is 0.048 m^2 and the surface area of the internal condenser was 0.065 m^2. The roller wiper speed inside the evaporator was fixed at 350 rpm.

The experiments were organized according to the following methodology: samples were melted to obtain a liquid and homogeneous mixture necessary to feed the equipment. The evaporator selected temperature was 100°C. Firstly, the evaporator temperature was fixed and, then, the feed flow rate was varied from 0.1 to 0.7 kg/h. For each process condition, samples of both streams (distillate and residue) were collected and submitted to tocopherols analyses. The process pressure was maintained at 10^{-6} bar, the feed temperature at 50°C, the condenser temperature at 60°C, and the stirring at 350 rpm. The collected samples of the distillate and residue streams were kept in a freezer at –18°C, for further analysis. The experiments were carried out in order to demonstrate that the FFA could be eliminated from the residue stream, facilitating the concentration of tocopherols through molecular distillation, manipulating operating conditions, such as evaporator temperature and feed flow rate, in order to remove from the residue stream a larger amount of FFA, and, increasing consequently, tocopherols concentration (13). It was a reasonable approach owing to the differences between molecular weights and vapor pressures of FFA and tocopherols (Table 3).

Owing to the values of molecular weights and vapor pressures, it was expected that FFA would be removed in the distillate stream and tocopherols preferentially concentrated in the residue stream. However, as discussed in the next section, depending on the level of temperature and feed flow rate, tocopherols may also be present in the distillate stream. Bearing this in mind, extensive evaluation was carried out to identify the temperature and feed flow rate conditions at which the tocopherol content would be maximized in the residue stream, while minimizing the amount of FFA.

Results and Discussion

The results of the analyses are presented in Figs. 2–5. It is observed that the simulated results agree with the experimental data. It is important to note that, although there are raw material differences as shown

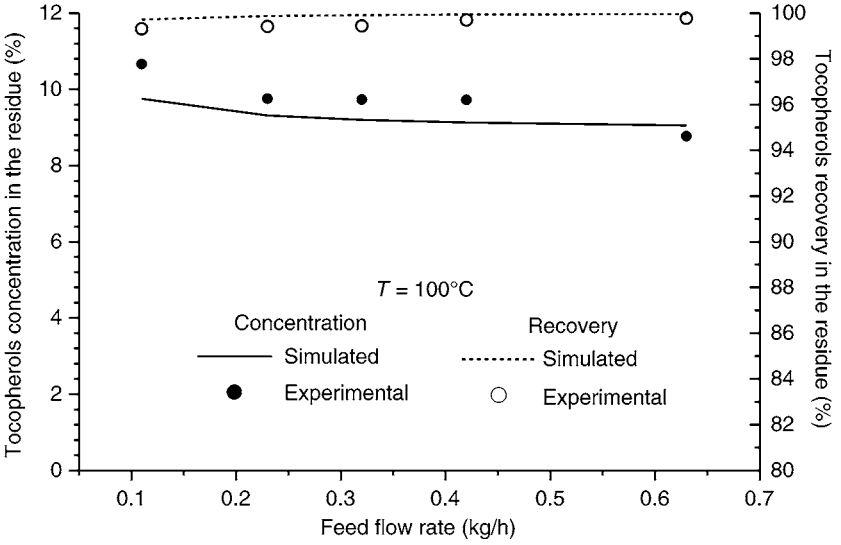

Fig. 2. Concentration of tocopherols in the residue (%) vs feed flow rate (kg/h) and recovery of tocopherols in the residue (%) vs feed flow rate (kg/h) at 100°C.

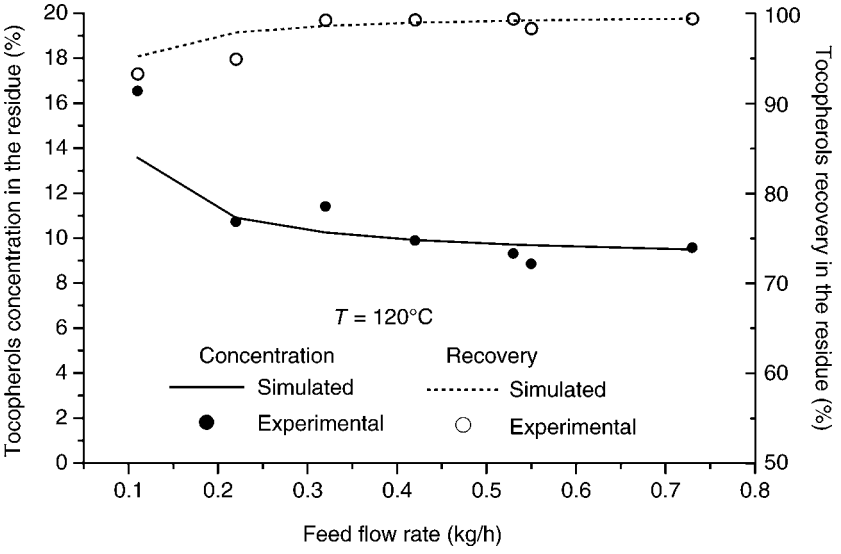

Fig. 3. Concentration of tocopherols in the residue (%) vs feed flow rate (kg/h) and recovery of tocopherols in the residue (%) vs feed flow rate (kg/h) at 120°C.

in Tables 1 and 2, a good agreement was reached between simulated concentration results and experimental data. Some of the deviations between experimental and simulated results occurred probably owing to (1) slight differences between real and simulated composition of the raw material and, (2) use of predicted properties of the components. Because the experimental curves follow a well defined behavior, although different for higher

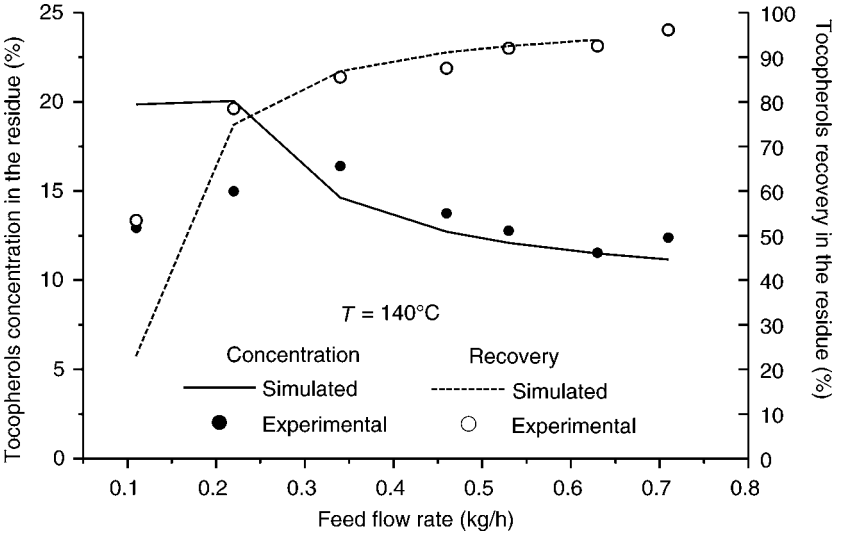

Fig. 4. Concentration of tocopherols in the residue (%) vs feed flow rate (kg/h) and recovery of tocopherols in the residue (%) vs feed flow rate (kg/h) at 140°C.

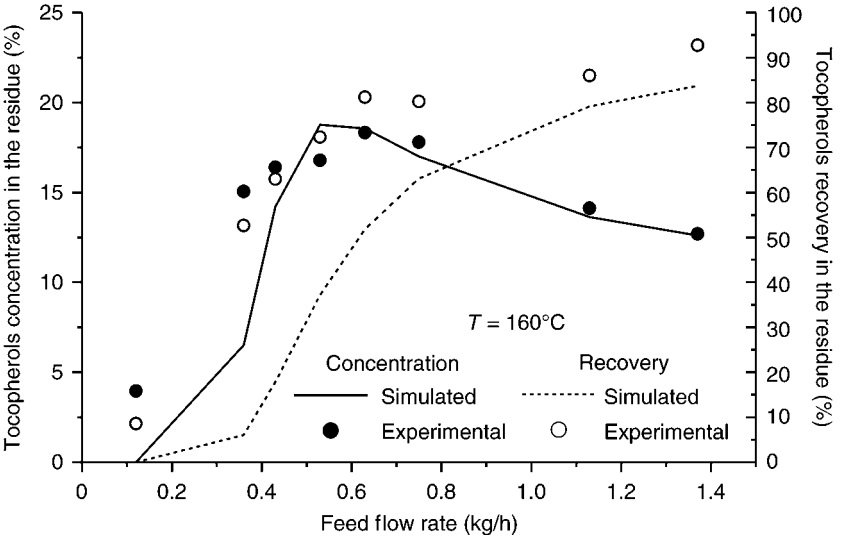

Fig. 5. Concentration of tocopherols in the residue (%) vs feed flow rate (kg/h) and recovery of tocopherols in the residue (%) vs feed flow rate (kg/h) at 160°C.

temperatures when compared with the lower ones (for higher operating temperatures, the tocopherols concentrations reach a maximum value), it can be said that there is no systematic experimental errors. So, probably, the deviations may be related to FFA and glyceride concentrations. Experimentally, FFA content was measured by titration and calculated as if FFA were made up of only oleic acid. The concentration of glycerides

was estimated as a total mixture of mono-, di-, and triglycerides. On the other hand, the simulated raw material considered each FFA, for example, palmitic, stearic, oleic, linoleic, lauric, and arachidic acids, as individual species and glycerides as only one group of substances, including mono-, di-, and triglycerides. Even so, larger deviations were observed at lower feed flow rates and higher temperatures.

Good quality properties are necessary for simulation and these data are very difficult to find in the literature, owing to the complexity of the components. The composition of the raw material and the estimated properties of individual substances influence the mixture properties used in the molecular distillation simulation. As the agreement of the experimental data and the predictions of the model is quite good, it can be said that property prediction procedures are suitable to be used for process simulation. In fact, the procedure is robust enough to allow for process condition definitions and operating strategy discrimination before doing experiments. Moreover, through molecular distillation simulation, it is possible to obtain important information on the equipment capacity, on the fractionating of each component as well as on what is needed for future process development.

Figures 2 and 3 show that tocopherols remain in the residue at the lower temperatures investigated (100°C and 120°C). For higher temperatures (140°C and 160°C), (Figs. 4 and 5), the results show that tocopherols tend to migrate to the distillate stream, as can be seen by the presence of a maximum of tocopherol concentration in the residue stream.

In the raw material, according to Table 2, the FFA composition is 57.4%. If all FFA (the most volatile component) were removed from the residue stream by the molecular distillation, the concentration of all other components including tocopherols would be 2.3 times higher than the original composition (this means around 42% of the original mass). Taking this into consideration, and analyzing Figs. 2–5, they show that in the region of tocopherols maximum concentration, the values of such concentrations increase with temperature (higher elimination of FFA). For temperature of 160°C, a maximum of 19% of tocopherols was obtained, which represent a concentration factor of about 2.2 times over its original value (i.e., nearly maximum efficiency). Analyzing the results of tocopherols recovery, it can be observed that for lower temperature and higher feed flow rate, practically 100% recovery is obtained. For higher temperatures, the recovery is smaller owing to carryover of tocopherols into the distillate stream.

Conclusions

This work showed that the Molecular Distillation is a powerful process to recover tocopherols from soya sludge, enabling a concentration of about 2.2 times their original value, at a temperature of 160°C, in which the maximum concentration was achieved. The results indicated good agreement between simulated results using the DISMOL simulator and experimental

results for tocopherols recovered from DDSO. This shows that the simulator can be used to evaluate new separations through molecular distillation, to define suitable operating conditions and to analyse different operating strategies, before carrying out experiments.

Acknowledgments

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References

1 Szelag, H. and Zwierzykowski, W. (1983), *Fette Seifen Anstrichmittel* **85,** 443–446.
2 Batistella, C. B. and Maciel, M. R.W. (1998), *Comput. Chem. Eng.* **22,** S53–S60.
3 Breivik, H., Haraldsson, G. G., and Kristinsson, B. (1997), *J. Am. Oil Chem. Soc.* **74,** 1425–1429.
4 Sun, H., Wiesenborn, D., Tostenson, K., Gillespie, J., and Rayas Duarte, P. (1997), *J. Am. Oil Chem. Soc.* **74,** 413–418.
5 Batistella, C. B., Moraes, E. B., Maciel Filho, R., and Maciel, M. R. W. (2002), *Appl. Biochem. Biotechnol.* **98,** 1187–1206.
6 Lutisan, J., Cvengros, J., and Micov, M. (2002), *Chem. Eng. J.* **85,** 225–234.
7 Nagesha, G. K., Manohar, B., and Udaya Sanar, K. (2004), *J. Supercritical Fluids* **32,** 137–145.
8 Batistella, C. B. and Maciel, M. R. W. (1996), *Comput. Chem. Eng.* **20(Suppl),** S19–S24.
9 Moraes, E. B., Batistella, C. B., Torres Alvarez, M. E., Maciel Filho, R., and Maciel, M. R. W. (2004), *Appl. Biochem. Biotechnol.* **113–116,** 689–711.
10 Martins, P. F. (2005), Master Thesis, Separation Process Development Laboratory (LDPS). Faculty of Chemical Engineering. State University of Campinas, (UNICAMP), Brazil.
11 AOCS, Ce 8-89, 1990, Official and Tentative Methods of the American Oil Chemist's Society, 4th ed., Champaign, IL.
12 Schoenfelder, W. (2003), *Eur. J. Lipid Sci. Techn.* **105,** 45.
13 Martins, P. F., Ito, V., Batistella, C. B., and Maciel, M. R. W. (2005), Separation and Purification Technology, vol 48/1, pp. 78–84.
14 Winters, R. L. (1986), In: *Proceedings World Conference on Emerging Technologies in the Fats and Oils Industry*, A. R. Baldwin, ed., American Oil Chemists' Society, Champaign, 184–188.