0273-2289/06/129–132/716–726/$30.00

Natural Compounds Obtained Through Centrifugal Molecular Distillation

Vanessa Mayumi Ito, Patricia Fazzio Martins, César Benedito Batistella, Rubens Maciel Filho, and Maria Regina Wolf Maciel*

Separation Process Development Laboratory, School of Chemical Engineering, State University of Campinas, PO Box 6066, 13081-970, Campinas, Brazil, E-mail: wolf@feq.unicamp.br and vanessa@lopca.feq.unicamp.br

Abstract

Soybean oil deodorized distillate (SODD) is a byproduct from refining edible soybean oil; however, the deodorization process removes unsaponifiable materials, such as sterols and tocopherols. Tocopherols are highly added value materials. Molecular distillation has large potential to be used in order to concentrate tocopherols, because it uses very low levels of temperatures because of the high vacuum and short operating time for separation and, also, it does not use solvents. However, nowadays, the conventional way to recover tocopherols is carrying out chemical reactions prior to molecular distillation, making the process not so suitable to deal with natural products. The purpose of this work is to use only molecular distillation in order to recover tocopherols from SODD. Experiments were performed in the range of 140–220°C. The feed flow rate varied from 5 to 15 g/min. The objective of this study was to remove the maximum amount of free fatty acids (FFA) and, so, to increase the tocopherol concentration without add any extra component to the system. The percentage of FFA in the distillate stream of the molecular still is larger at low feed flow rates and low evaporator temperatures, avoiding thermal decomposition effects.

Index Entries: Centrifugal distillation; molecular distillation; natural products; tocopherol.

Introduction

Soybean oil is the most consumed vegetable oil in the world, representing 54% of the total world production *(1)*. Brazil is the second largest producer of soybeans. The refining process has several steps: degumming, refining, bleaching, hydrogenation, and deodorization. Deodorization removes compounds that give odor and flavor to the oil. Soybean oil deodorized distillate (SODD) is produced in the deodorization step of the

*Author to whom all correspondence and reprint requests should be addressed.

oil refining *(2)*, corresponding from 0.1 to 0.4 wt% of the crude oil weight, and contains between 0.8 and 10 wt% of tocopherols *(3)*. SODD is a complex mixture made up of free fatty acids (FFA), sterols, tocopherols, sterol esters, hydrocarbons, breakdown products of fatty acids, aldehydes, ketones, and acylglycerol species *(4)*, and, therefore, it can be a good raw material for producing vitamin E and sterols *(5)*. Tocopherols are natural antioxidants and have vitaminic activity. Sterols are important in the production of hormones and in the artificial production of other vitamins *(6)*, for instance, vitamin D.

FFA are different according to the number of carbons and saturations. SODD contains high levels of FFA (25–75%) and acylglycerols (3–56%), *(7)*, depending on the raw material and on the type (physical or chemical way) and conditions of the refining process *(4)*. FFA have molecular weights in the range 180–300 g/gmol, and higher vapor pressure than tocopherols.

Tocopherols, which are substances physiologically active as vitamin E, are important natural antioxidants and find extensive applications in food, cosmetic, and pharmaceutical industries *(7)*. Preparing high-purity concentrates of tocopherols normally involves a series of physical and chemical treatment steps in conventional processes *(8)*. Because deodorized distillate is a complex mixture and the properties of its components are very similar, it is difficult to recover high-quality concentrates of tocopherols with good yield *(9)*.

Several processes can be used in order to separate FFA from tocopherols and phytosterols. Some of them use molecular distillation together chemical reactions, what mischaracterizes them as natural processes.

Ramamurthi et al. *(10)* studied the lipase-catalyzed esterification of FFA. This process used methanol to esterify the FFA from canola oil deodorized distillate.

Chang et al. *(11)* recovered tocopherols and FFA, investigating a supercritical fluid CO_2 extraction process of SODD. Good recovery is achievable, but it is necessary to employ high pressure. Lee et al. *(12)* studied the lipase-catalyzed esterification, transesterification to form methyl esters, followed by supercritical fluid CO_2.

Buczenko et al. *(13)* performed the separation of tocopherols from sterols using a liquefied petroleum gas extraction. First, saponification step is used to separate fatty acids from the raw material. Then, the separation was carried out in the liquefied petroleum gas extractor.

Chu et al. *(14,15)* recovered tocopherols from palm distillate by batch adsorption using an orbital shaker. The raw material was preconcentrated through neutralization and so, extracted with hexane, centrifuged, and dried. Then, the preconcentrate mixture is carried out at batch adsorption equipment.

Chu et al. *(16)* studied the enzymatic hydrolysis using a commercial immobilized *Candida antarctica* lipase, followed by hydrolysis and washing to remove FFA salts. Hirota et al. *(2)* distillated the SODD by molecular

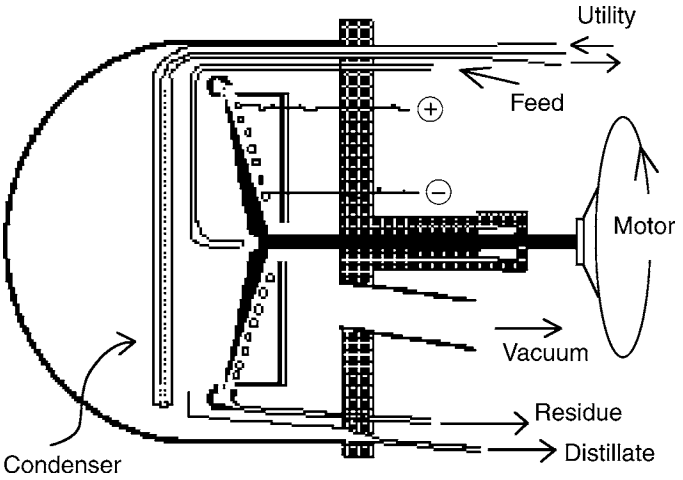

Fig. 1. Centrifugal molecular still schematic.

distillation, followed by a lipase-catalyzed hydrolysis and another molecular distillation step to separate FFA from steryl esters.

Ghosh and Bhattacharyya *(17)* recovered tocopherol by lipase-catalyzed hydrolysis and esterification reactions, followed by fractional distillation of the derived ester product. Owing to the similar volatility of sterols, tocopherols, and fatty acids, it is quite difficult to separate tocopherols and sterols from FFA using fractional distillation. Exposure to high temperatures may degrade tocopherols.

The processes above have various operating steps and are laborious. They need attention to prevent decomposition of tocopherols because of the exposure to molecular oxygen, to light, and to high temperatures.

Molecular or short-path distillation is, generally, accepted as the most suitable distillation method to separate and to purify both thermosensitive and high-molecular-weight compounds *(18)*. Two main types of molecular stills are available: falling film and centrifugal *(19)*. The centrifugal molecular still scheme, used in this work, is shown in Fig. 1. Figure 2 shows the material stream throughout the molecular distillator *(20)*. The feed stream is introduced in the center of the equipment. The liquid flows, by centrifugal force, uniformly around the evaporator until the border of the rotor in a thin film *(21)*. The light compounds are volatilized and condensed (distillate stream) and the heavy compounds are collected as residue stream. The process is characterized by high vacuum in the distillation space, and a small distance between the evaporator and the condenser, resulting in a short exposure of the distilled liquid to the operating temperature, on the order of a few seconds, which is guaranteed by distributing the liquid in the form of a thin film *(22)*. Under these conditions, i.e., short residence time and low temperature, distillation of heat-sensitive materials is accompanied by only negligible thermal decomposition *(21)*.

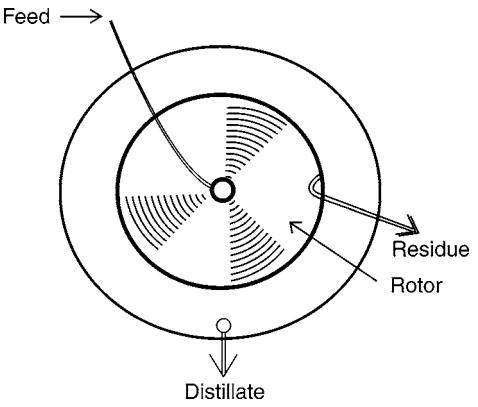

Fig. 2. Centrifugal molecular still material streams.

Molecular distillation is applied at several areas, such as monoglycerides concentration *(23)*, carotenoids recovery from palm oil *(24)*, heavy petroleum characterization *(25)*, and herbicides. The present study aims the recovery of tocopherols and FFA from SODD just using molecular distillation.

Materials and Methods

Materials

SODD was provided by Bunge Ltda., São Paulo, Brazil. All samples were stored in the refrigerator at 4°C until analysis. All solvents and reactants for the analyses were of analytical grade. A tocopherol kit consisting of α-, β-, γ-, and δ-tocopherol (purity ≥95%) was purchased from Calbiochem (San Diego, CA) and used as reference standards for tocopherols analysis. The reactants used for the free fatty acid analysis were ethyl alcohol, phenolphetalein and sodium hydroxide. The solvents, hexane, and isopropanol for tocopherol analysis were of high-performance liquid chromatography (HPLC) grade from Tedia Company, Inc. (Fairfield, OH).

Methods

Centrifugal Molecular Distillation

The FFA distillation was performed using a centrifugal molecular still. The process conditions were maintained at 13.3 Pa, the feed temperature at 50°C, and the condenser temperature at 50°C. The molecular distillation experiments were conducted according to the following procedure: a sample of SODD was homogenized before feeding the equipment. The distillation was performed at 140–220°C. The feed flow rate varied in the range 5–15 g/min. For each molecular distillation run, samples of both streams (distillate and residue) were collected and submitted to FFA and tocopherols analyses.

Table 1
Raw Material Characteristics

Analysis	SODD
FFA (wt% as oleic acid)	53.04 ± 1.1
α-tocopherol	1.41 ± 0.25
β-tocopherol	0.12 ± 0.05
γ-tocopherol	1.95 ± 0.15
δ-tocopherol	0.58 ± 0.09
Tocopherol total	4.06 ± 0.54

Analytical Methods

The FFA analysis: FFA content were determined according to Method AOCS Ca 5 a-40 *(26)*. This method used titration with a standard alkali, NaOH. The FFA concentration is expressed as percentage of oleic acid ($C_{18:1}$). The expression is:

$$\%\text{FFA as oleic acid} = \frac{\text{alkali volume (mL)} \cdot \text{alkali normality} \cdot 28.2}{\text{sample weight (g)}}$$

Tocopherols analysis: the method AOCS Ce 8-89 *(26)* was used to determine the α-, β-, γ-, and δ-tocopherol contents. A known amount of the sample was dissolved in hexane (approx 1 mg/mL) and 20 μL of the solution was injected into a HPLC modular equipment composed by Waters 515 HPLC pump (Mildford, MA), equipped with a fluorescence detector (Waters model 2475 multifluorescence, Mildford, MA). The flow rate of the mobile phase (hexane:isopropanol, 99:1 v/v) was set at 1 mL/min. The separation was conducted in a μporasil column 125 Å, with particle size of 10 μm and 3.9 × 300 mm of dimension (Waters, Ireland). The tocopherols detected in the chromatograms were identified comparing the retention time of the compounds with the retention time of standard solutions. Quantification of each type of tocopherols was done using calibration curves. The data processing was carried out through the Millennium software (Waters, Mildford, MA).

Results and Discussion

The SODD was analyzed in relation to the FFA and tocopherols contents. Table 1 shows the characteristics of the soybean oil deodorizer distillate. The SODD used is brownish and semisolid at room temperature.

The feed flow rate and the evaporator temperature are the main variables in the molecular distillation process *(23,24)*, so the experiments were performed from 140 to 220°C and the feed flow rate varied from 5 to 15 g/min. The procedure consists of keeping the evaporator temperature fixed and the feed flow rate is varied. For all distillation runs, the condenser temperature was maintained at 50°C (to avoid solidification of distillate stream on the condenser) and the feed temperate at 50°C.

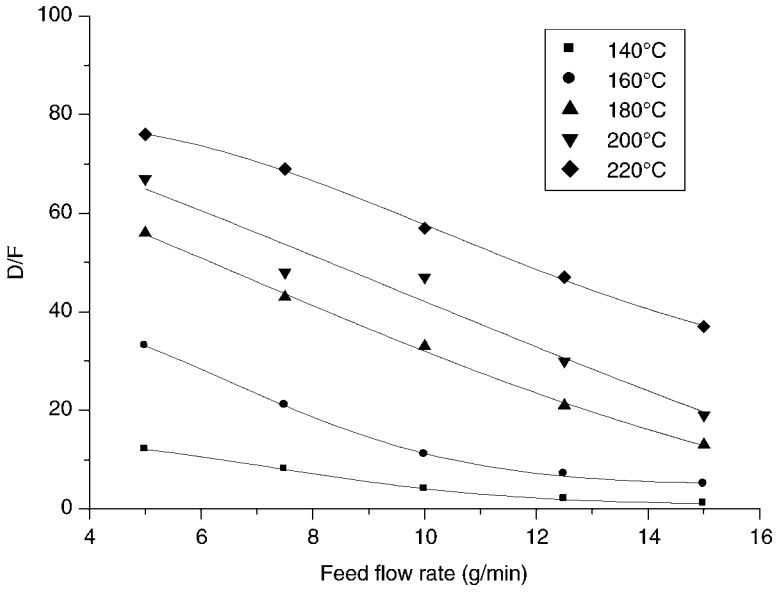

Fig. 3. Distillation profile for the ratio D/F in function of feed flow rate at different values of evaporator temperature.

The evaporation ratio D/F (mass of distillate/mass of feed) is a useful parameter to evaluate the molecular distillation process. Figure 3 shows the profile of evaporation ratio D/F as a function of feed flow rate (F) at different evaporator temperatures. The results show that the feed flow rate affects significantly the evaporation ratio D/F. Increasing the feed flow rate, the material, that it will be distillate, increases. The evaporator efficiency is lower because of the poor contact between the material and the heated surface, so the ratio D/F declines. At constant temperature, the ratio D/F decreases increasing the feed flow rate. On the other hand, increasing the evaporator temperature and maintaining the same feed flow rate, the evaporation ratio D/F increases. At feed flow rate of 5 g/min and 220°C is obtained the maximum distillate amount. Figure 4 shows the profile of residue flow rate of the centrifugal molecular still. The residue flow rate is directly proportional to the feed flow rate and inversely to the evaporator temperature. As the vaporization rate was constant at one temperature; the residue percentage rose with increased feed flow rate.

The percentage of FFA of SODD (before the centrifugal molecular distillation) was 53.04%. FFA tends to concentrate in the distillate stream because they are lighter molecules than tocopherols. As it is known, the split ratio D/R (mass of distillate/mass of residue) is another important parameter to evaluate the molecular distillation process *(27)*. Figure 5 shows the free fatty acid recovery in the distillate stream in function of the split ratio D/R. It can be obtained a recovery higher than 90% using a split ratio higher than 2.

Figure 6 shows the FFA content in the residue streams. The loss of FFA occurs in the residue stream of the centrifugal molecular still with the

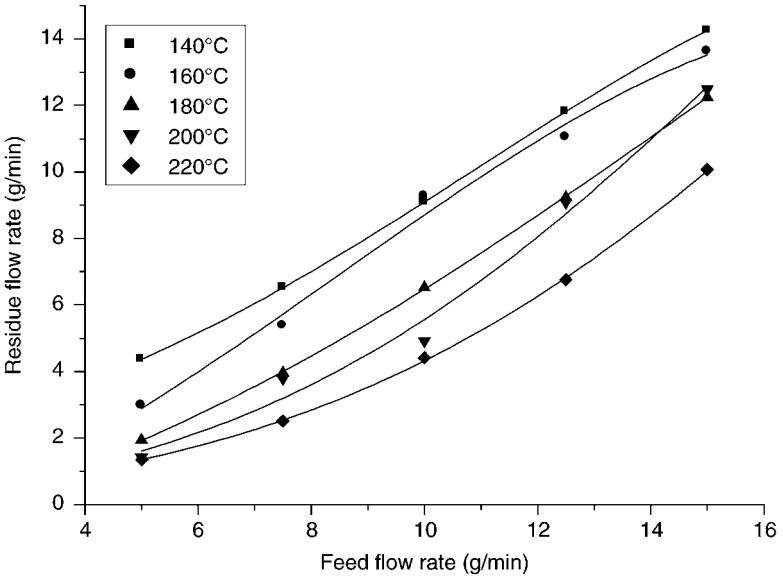

Fig. 4. Residue stream from centrifugal molecular still.

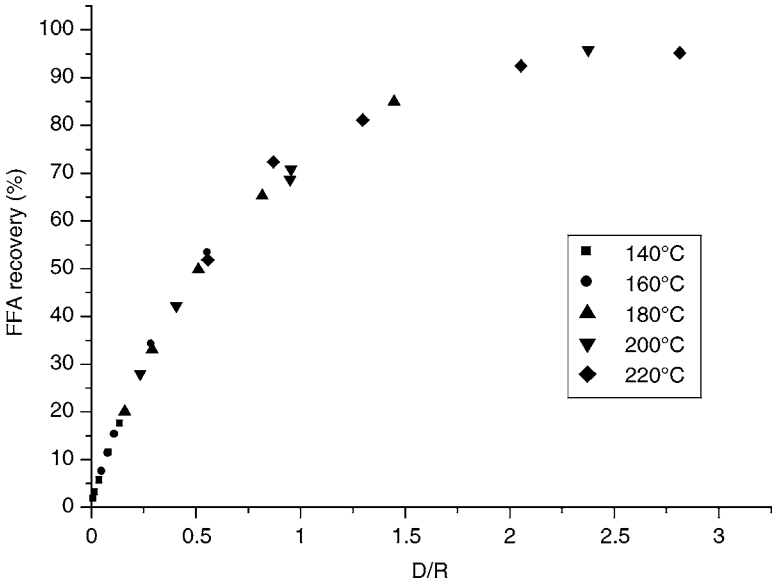

Fig. 5. Percentage of FFA recovery in the distillate stream.

increase of feed flow rate and the decrease of the evaporator temperature. It is important to note that the percentage of FFA in the residue stream depends on the evaporator temperature and feed flow rate. At temperatures of 140°C and 160°C, there is a great loss of FFA in the residue stream. Then, it is necessary to operate the molecular distillation conditions at 5 g/min and evaporator temperature greater than 180°C.

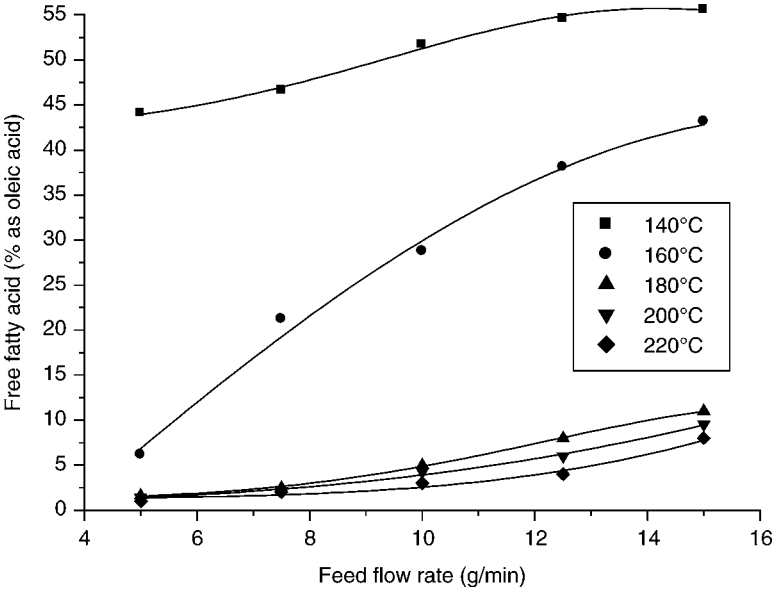

Fig. 6. Free Fatty Acid content in the residue stream.

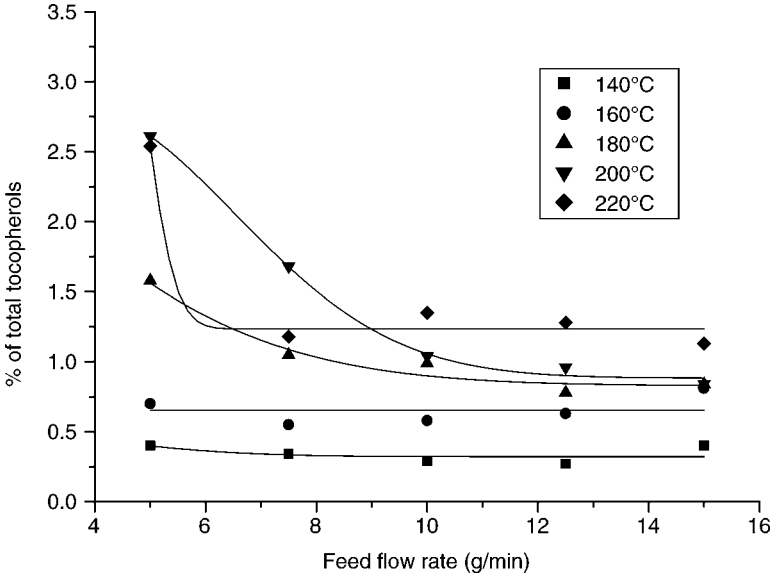

Fig. 7. Total tocopherols content vs feed flow rate in the distillate stream.

Figure 7 shows the total tocopherols content in the distillate stream (loss of tocopherols, they are to be recovered in the residue stream). At 140°C, the percentage of total tocopherols was lower than 0.5% for all the feed flow rates. At higher temperatures, the loss of tocopherols increases.

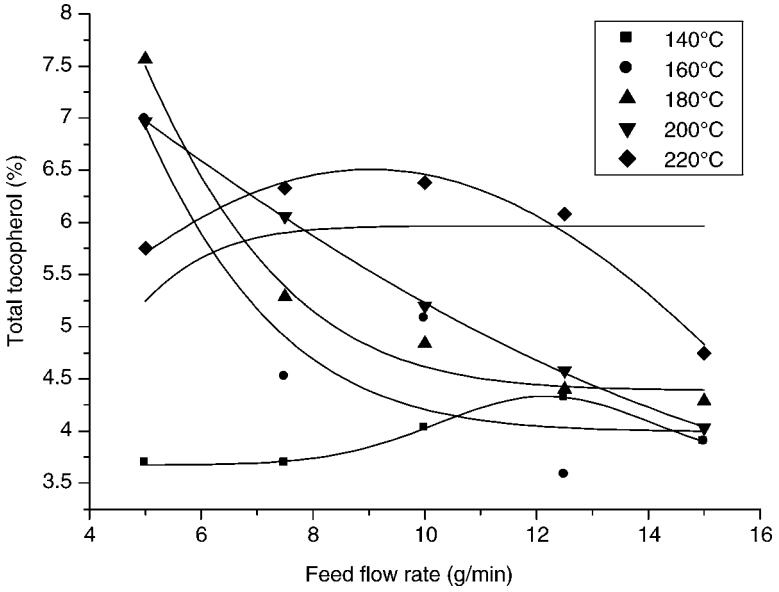

Fig. 8. Total tocopherols content vs feed flow rate in the residue stream.

The increase of feed flow rate decreases the loss of tocopherols. The optimum operating conditions are low evaporator temperatures (140°C) and high feed flow rate (12.5 g/min).

The tocopherols content in the residue stream is affected by the evaporator temperature and feed flow rate. It was observed in Fig. 8 that at 180°C and 5 g/min the product reached 7.7% of total tocopherols. In this case, the tocopherol enrichment was 1.9 for just one molecular distillation step.

The profile of tocopherol recovery evaluating the split ratio was observed in Fig. 9. It is possible to obtain a recovery higher than 90% using a split ratio lower than 0.25. The increase of tocopherols recovery implies a loss of FFA in the residue stream. The FFA loss decreases with increasing the split ratio D/R.

It can be seen in Fig. 10 that the intersection of the tocopherol and FFA recovery curves is the optimum ratio D/R. The optimum ratio D/R value is 0.96. In this operating condition, 73% of total tocopherol and FFA are recovered in its respective streams.

Concluding Remarks

In this work, the elimination of FFA and concentration of tocopherols present in SODD through the centrifugal molecular distillation was studied. The initial composition of FFA in SODD was around 53%. The percentages of distillate and residue compositions depend on operating variables (evaporator temperature and feed flow rate). High concentration of FFA is obtained using a split ratio higher than 2. It can be

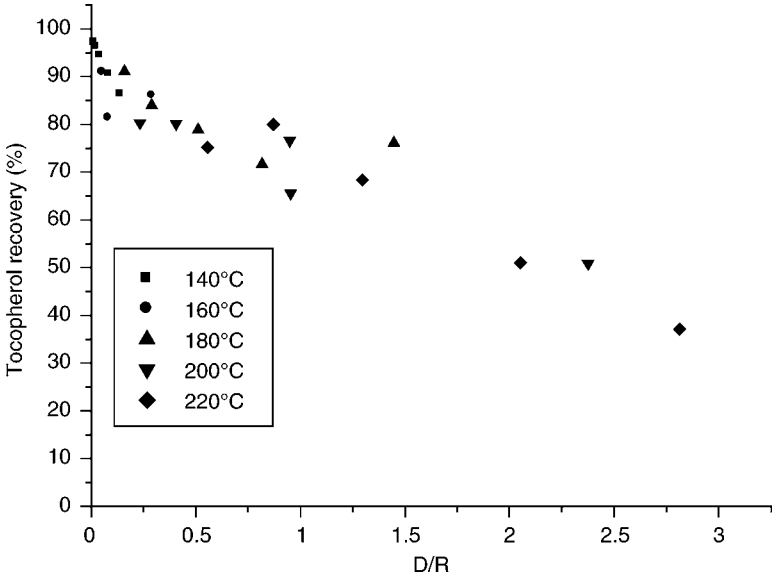

Fig. 9. Tocopherol recovery in the residue stream.

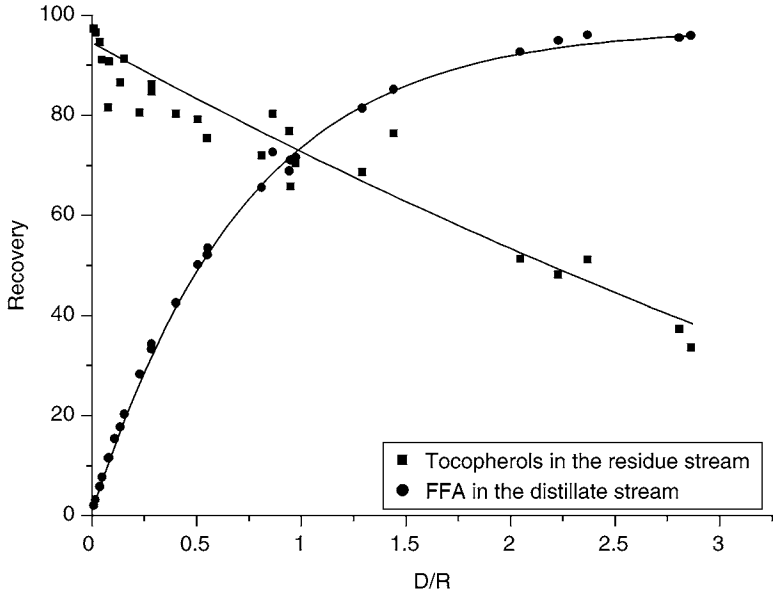

Fig. 10. Optimized conditions for tocopherols and FFA recovery.

used different evaporator temperature and feed flow rate to reach the same split ratio. To concentrate tocopherols, it is necessary to work at a low evaporator temperature and feed flow rate. Tocopherols were concentrated twice in relation to the raw material. Then, the split ratio used to reach high recovery of tocopherols is low. At D/R split ratio of 0.96, it is obtained a recovery of 73% of tocopherols and FFA.

Acknowledgments

The authors are grateful to Fapesp (Fundação de Amparo à Pesquisa do Estado de São Paulo), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support.

References

1 Mendes, M. F., Pessoa, F. L. P., and Uller, A. M. C. (2002), *J. Supercritical Fluids* **23,** 257–262.
2 Hirota, Y., Nagao, T., Watanabe, Y., et al. (2003), *J. Am. Oil Chem. Soc.* **80,** 341–346.
3 Augusto, M. M. M. (1988), M. Sc. Thesis, State University of Campinas, Brazil.
4 Ramamurthi, S., and McCurdy, A. R. (1993), *J. Am. Oil Chem. Soc.* **70(3),** 287–295.
5 Moraes, E. B., Batistella, C. B., Torres Alvarez, M. E., Maciel Filho, R., and Wolf Maciel, M. R. (2004), *Appl. Biochem. Biotechnol.* **113,** 689–711.
6 Bondioli, P., Mariani, C., Lanzani, A., Fedeli, E., and Muller, A. (1993), *J. Am. Oil Chem. Soc.* **70(8),** 763.
7 Chu, B. S., Baharin, B. S., and Quek, S. Y. (2002), *Food Chem.* **79(1),** 55–59.
8 Nagesha, G. K., Subramanian, R., and Sankar, K. U. (2003), *J. Am. Oil Chem. Soc.* **80,** 397.
9 Lin, K. M. (2002), National Chung Hsing University, M.S., Texas A & M University.
10 Ramamurthi, S., Bhirud, P. R., and McCurdy, A. R. (1991), *J. Am. Oil Chem. Soc.* **68(12),** 970–975.
11 Chang, C. J., Chang, Y., Lee, H., Lin, J., and Yang, P. (2000), *Ind. Eng. Chem. Res.* **39,** 4521–4525.
12 Lee, H., Chung, B. H., and Park, Y. H. (1991), Concentration of tocopherols from soybean sludge by supercritical carbon-dioxide, *J. Am. Oil Chem. Soc.* **68(8),** 571–573.
13 Buczenko, G. M., Oliveira, J. S., and von Meien, O. F. (2003), *Eur. J. Lipid Sci. Technol.* **105,** 668–671.
14 Chu, B. S., Baharin, B. S., Che Man Y. B., and Quek, S. Y. (2004), *J. Food Eng.* **62(1),** 97.
15 Chu, B. S., Baharin, B. S., Che Man Y. B., and Quek, S. Y. (2004), *J. Food Eng.* **62(1),** 105.
16 Chu, B. S., Quek, S. Y., and Baharin, B. S. (2003), *Food Chem.* **80(3),** 295–302.
17 Ghosh, S., and Bhattacharyya, D. K. (1996), *J. Am. Oil Chem. Soc.* **73(10),** 1271–1274.
18 Cvengros, J., Mrazik, M., and Kmetty, G. (1999), *Chemical papers-chemicke Zvesti*, **53(2),** 102–106.
19 Batistella, C. B. and Maciel, M. R. W. (1996), *Comp. Chem. Eng.* **20,** S-19–S-24.
20 Batistella, C. B., Moraes, E. B., Maciel Filho, R., and Wolf Maciel, M. R. (2002), *Appl. Biochem. Biotechnol.* **98–100,** 1187–1206.
21 Batistella, C. B. and Wolf Maciel, M. R. (1998), *Com. Chem. Eng.* **22,** S53–S60.
22 Batistella, C. B., Maciel, M. R. W., and Maciel Filho, R. (2000), *Comput. Chem. Eng.* **24,** 1309–1315.
23 Fregolente, L. V., Batistella, C. B., Maciel Filho, R., and Wolf Maciel, M. R. (2005), *J. Am. Oil Chem. Soc.* **82(9),** 673–678.
24 Batistella, C. B., Moraes, E. B., Maciel Filho, R., and Wolf Maciel, M. R. (2002), *Appl. Biochem. Biotechnol.* **98–100,** 1149–1159.
25 Sbaite, P., Vasconcelos, C. J. G., and Martins, P. F., et al. (2003), 4th European Congress in Chemical Engineering (ECCE4), Granada, Spain.
26 AOCS (1997), *Official Methods and Recommended Practices of the American Oil Chemists Society*. 5th ed., Champaign, IL.
27 Martins, P. F., Ito, V. M., Batistella, C. B., and Maciel, M. R. W. (2006), *Sep. Purification Technol.* **48,** 78–84.
28 Cvengros, J., Lutisan, J., and Micov, M. (2000), *Chem. Eng. J.* **78**, 61.