

Evaluation of Tocopherol Recovery Through Simulation of Molecular Distillation Process

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Abstract

DISMOL simulator was used to determine the best possible operating conditions to guide, in future studies, experimental works. This simulator needs several physical-chemical properties and often it is very difficult to determine them because of the complexity of the involved components. Their determinations must be made through correlations and/or predictions, in order to characterize the system and calculate it. The first try is to have simulation results of a system that later can be validated with experimental data. To implement, in the simulator, the necessary parameters of complex systems is a difficult task. In this work, we aimed to determine these properties in order to evaluate the tocopherol (vitamin E) recovery using a DISMOL simulator. The raw material used was the crude deodorizer distillate of soya oil. With this procedure, it is possible to determine the best operating conditions for experimental works and to evaluate the process in the separation of new systems, analyzing the profiles obtained from these simulations for the falling film molecular distillator.

Index Entries: Molecular distillation; vitamin E; deodorizer distillate of soya oil; DISMOL; property estimation.

Introduction

Molecular distillation is characterized by short exposure of the distilled liquid to elevated temperatures, high vacuum in the distillation space, and a small distance between the evaporator and the condenser. The short residence time of the liquid on the evaporating cylinder, in the order of a

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few seconds to 1 min, is guaranteed by distributing the liquid in the form of a uniform thin film (1). By reducing the pressure of noncondensable gas in the evaporator to lower than 10^{-1} mbar, a reduction in distillation temperature can be obtained. A molecular distillation process is useful in the separation and purification of materials of high molecular weight, as well as for those that are thermally sensitive, such as the vitamins (2–4), by minimizing losses through thermal decomposition. The combination of a small distance between the evaporator and the condenser (about 2 cm) and a high vacuum in the distillation gap results in a specific mass transfer mechanism with evaporation outputs as high as $20\text{--}40\text{ g}/(\text{m}^2\cdot\text{s})$. Under these conditions (e.g., short residence time and low temperature), distillation of heat-sensitive materials is accompanied by only negligible, thermal decomposition and at flow rates that make the process technologically viable (1). This means that in relation to conventional or even vacuum distillation, in the case of molecular distillation, the materials in some cases remain unaltered but in others small decomposition can occur (e.g., 3% in the case of tocopherols). The decomposition is a direct function of the residence time and an exponential function of the temperature. On the other hand, the productivity of the process is high, considering the treatment of high-added-value compounds.

During molecular distillation, small variations in process conditions can lead to considerable changes in the characteristics of product streams (5–7). Thus, it is very important to have robust simulation results in order to evaluate the process and even to guide the experimental work. The objective of the present work was to incorporate in the Dismol simulator the data to simulate the process. The complex systems typical of the application of molecular distillation must be well characterized.

Molecular distillation shows promise in the separation, purification, and/or concentration of natural products, usually constituted by complex and thermally sensitive molecules. Furthermore, this process has advantages over other techniques that use solvents as the separating agent, avoiding problems with toxicity. Molecular distillation has also been used for heavy petroleum characterization, demonstrating the potential of this separation process in other situations (8).

Tocopherols are extensively used as antioxidants in a growing trend of consumer preference for natural antioxidants. Natural tocopherols are recovered from vegetable oil deodorizer distillate, a byproduct of the vegetable oil-refining process. Deodorizer distillate is composed of fatty acids, sterols, tocopherols, sterol esters, hydrocarbons, breakdown products of fatty acids, aldehydes, ketones, and acyl glycerol species. This byproduct is sold on the basis of tocopherol content, which is valued for both its vitamin E activity and antioxidant property (9). Sterols are used as starting materials or as intermediates for the manufacture of pharmaceutical drugs, and steroids are used for medicinal purposes. Fatty acids constitute 25–75% of the distillate depending on the raw material being refined, the type of refining process, and the conditions employed. Deodorizer distillate can

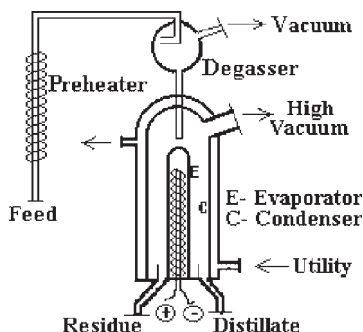


Fig. 1. Falling film molecular distillation.

have significantly different characteristics, uses, and values. When derived from soybean or other unsaturated vegetable oils, it can be a good raw material for the production of vitamin E and sterols. From other fats and oils, the distillate may be useful only for fatty acid production (10). Deodorizer distillates are used in nonfood and low-cost applications, because they are contaminated with fatty acids (11).

Taking all of these concerns into consideration, in the present work, we propose a molecular distillation process for tocopherol (vitamin E) recovery using as a raw material the crude deodorizer distillate of soya oil (DDSO). The determination of several physical-chemical properties must be made through correlations and/or predictions, in order to have a better characterization of the system that will be studied. Then, the DISMOL simulator can be used to evaluate tocopherol recovery from crude DDSO, in order to determine the feasibility of the process and the best experimental conditions for the falling film molecular distillation. The simulator used was a DISMOL, which was developed by Batistella (12). Tocopherols need to present a low acidity level (< 2%) and purity according to their application (from 30 to 90%). The price varies according to this concentration. Squalene is tolerable in tocopherol concentration, but fatty acids must be eliminated during the process.

DISMOL Simulator: Falling Film Distillation

A schematic of the falling film molecular distillator is shown in Fig. 1. The main part of the installation consists of a cylindrical evaporator surrounded by a condenser jacket. The liquid to be distilled is transported from a storage tank through a preheater to the surface of the unheated evaporator. It is also possible to heat the evaporator internally. In the case of a heated evaporator, the distillation rate is faster, but the separation factor decreases at higher temperatures. The velocity is that of a laminar and isothermal film with a smooth surface. In the first stage, tocopherols are recovered in the residue stream (according to Fig. 1) and in the second processing stage in the distillate stream.

The simulator used was a DISMOL, described previously by Batistella and Maciel (2). All explanations of the equations used, the solution methods, and the routine of solution are described in Batistella and Maciel (5). DISMOL is a simulator that permits changes in feed composition, feed temperature, the evaporation rate, as well as feed flow rate. The effective rate of surface evaporation is obtained from the kinetic theory of gases. The liquid film thickness is obtained by mass balance and geometry of the evaporator. The temperature in the liquid obeys the Fourier-Kirchhoff equation. The solution of the velocity profile requires knowledge of the viscosity and the liquid film thickness over the evaporator. The solution for the temperature and the concentration profiles requires knowledge of the velocity profiles, which determine the convective heat and mass fluxes.

The solution is accomplished by a numerical technique using a finite-difference method. The procedure involves the following steps:

1. Solution of the rate equation of the distillation components.
2. Solution of the thickness equation of the liquid film over the evaporator.
3. Solution of the velocity profile equation in the liquid film flowing over the evaporator.
4. Solution of the temperature profile equation in the liquid film.
5. Solution of the concentration profile equation in the liquid film.

These equations are solved in each segment of the evaporator, from the feed point to the exit points of the components, and depend on the process conditions and the properties of the system to be studied including the vapor pressure, vaporization enthalpy, molecular weight, mass diffusivity, mean free path, and composition of the involved components; and the density, thermal conductivity, heat capacity, and viscosity of the mixture. Regarding the equipment, it is necessary to know the dimensions (evaporator diameter and length), and as characteristic of the process, the feed flow rate, feed temperature, and heating temperature. The simulator also allows comparative analyses between the centrifugal and falling-film processes (2).

Calculation and Estimation of Physical, Thermodynamic, and Transport Properties

Table 1 gives the components present in the crude DDSO and their properties: critical pressure (P_c), critical temperature (T_c), critical volume (V_c) and acentric factor (ω). These properties were obtained from hypothetical components (a tool of the commercial simulator HYSYS) that are created through the UNIFAC group contribution. The developed DISMOL simulator requires these properties (mean free path; enthalpy of vaporization; mass diffusivity; vapor pressure; liquid density; heat capacity; thermal conductivity; viscosity; and equipment, process, and system characteristics that are simulation inputs) in calculating other properties of the system, such as evaporation rate, temperature and concentration profiles, residence time, stream compositions, and flow rates (output from the simulation). Furthermore, film thickness and liquid velocity profile on the evaporator are also calculated.

Table 1
Properties Obtained from HYSYS Commercial Simulator

Components	X_i	P_c (bar)	T_c (K)	V_c (cm ³ /mol)	ω	M (g/mol)
Palmitic acid	0.1271	14.0801	887.34	955.50	0.9744	256.43
Stearic acid	0.0283	12.2512	935.12	1067.50	0.9678	284.48
Linoleic acid	0.3295	13.1943	950.98	1027.50	0.9656	280.45
Oleic acid	0.1438	12.7097	942.86	1047.50	0.9683	282.47
Lauric acid	0.0221	19.2198	797.43	731.50	0.9047	200.31
Araquidic acid	0.0496	10.7569	985.41	1179.50	0.9290	312.52
Campesterol	0.0417	9.1661	1128.81	1461.50	0.8130	400.69
β -Sitosterol	0.0933	8.6556	1159.21	1517.50	0.7465	414.72
Stigmasterol	0.0355	8.9267	1162.70	1497.50	0.7850	412.70
α -Tocopherol	0.0114	2.9222	1075.61	5355.74	1.8001	430.71
γ -Tocopherol	0.0462	3.3819	1058.62	4624.61	1.7325	416.69
Δ -Tocopherol	0.0275	3.9136	1041.13	3994.35	1.6621	402.66
Squalene	0.0440	6.3845	978.38	2447.09	1.4036	410.70

We do not discuss equilibrium because the molecular distillation is a nonequilibrium process. Molecular distillation belongs to the class of processes that uses the technique of separation under high vacuum, operation at reduced temperatures, and low exposition of the material at the operating temperature. It is a process in which vapor molecules escape from the evaporator in the direction of the condenser, where condensation occurs. Then, it is necessary that the vapor molecules generated find a free path between the evaporator and the condenser, the pressure be low, and the condenser be separated from the evaporator by a smaller distance than the mean free path of the evaporating molecules. In these conditions, theoretically, the return of the molecules of the vapor phase to the liquid phase should not occur, and the evaporation rate should only be governed by the rate of molecules that escape from the liquid surface; therefore, phase equilibrium does not exist.

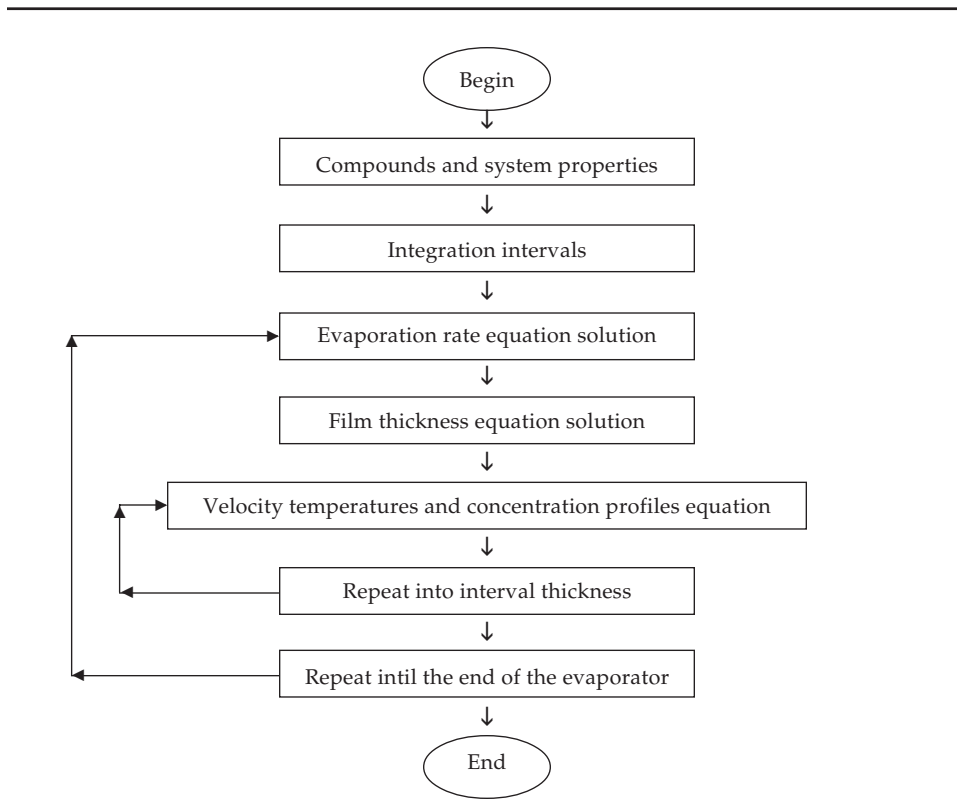
Equipment, Process, and System Characteristics

The equipment, process, and system characteristics are as follows:

1. Equipment characteristics: evaporator diameter = 10 cm; evaporator length = 0.25 m.
2. Process characteristics: feed temperature = 60°C; heat temperature = 120–180°C (evaporator); feed flow rate = 0.5–1.0 kg/h.
3. System characteristics—crude DDSO (13): properties of the components and of the mixture calculated from the properties obtained from HYSYS (see Table 1) through the equations presented. Note that all errors mentioned, one for correlation, were suggested by the authors of the equations.

Table 2 illustrates the simulation procedure.

Table 2
Simulation Procedure



Component System Characteristics

MEAN FREE PATH

The Clausius equation (14) gives the value of the mean free path, L , of a component at ideal conditions, i.e., path without collisions with residual gases:

$$L = \frac{1}{\sqrt{2} \pi \sigma^2 N} \quad (1)$$

in which

$$N = 9.66 \times 10^{18} \frac{P}{T}$$

(expression developed from the equation of state of an ideal gas);

$$\sigma = 8.09 \times 10^{-9} V_c^{1/3}$$

(15); L is the mean free path (cm); N is the number of molecules per volume unit (mol/cm³); P is the pressure (mmHg); T is the temperature (K); V_c is the critical volume (cm³/mol); and σ is the diameter of the molecule (cm).

ENTHALPY OF VAPORIZATION

A pure component constant that is occasionally used in property correlations is the enthalpy of vaporization at the normal boiling point, ΔH_b^{vap} . In addition, several special estimation methods are suggested. The Chen equation (15) gives a relation among the enthalpy of vaporization, the reduced vapor pressure, and the reduced temperature. When applied to the normal boiling point, Eq. 2 is obtained, with an average error of 2%:

$$\Delta H_b^{vap} = \frac{RT_c T_{br} (3.978 T_{br} - 3.958 + 1.555 \ln P_c)}{1.07 - T_{br}} \quad (2)$$

For different temperatures, a widely used correlation between the enthalpy of vaporization and temperature is the Watson equation (14), with an average error of 2%:

$$\Delta H^{vap} = \Delta H_b^{vap} \left(\frac{T_c - T}{T_c - T_{br}} \right)^{0.38} \quad (3)$$

in which P_c is the critical pressure (bar); T_b is the normal boiling temperature (K); T_c is the critical temperature (K); T_{br} is equal to T_b/T_c (reduced normal boiling temperature); ΔH^{vap} is the enthalpy of vaporization (J/mol); and ΔH_b^{vap} is the enthalpy of vaporization at normal boiling temperature (J/mol).

MASS DIFFUSIVITY

For a binary mixture of solute A in solvent B , the diffusion coefficient D_{AB}^o of A diffusing in an infinitely dilute solution of A in B implies that each molecule A is in an environment of essentially pure B . In engineering work, however, D_{AB}^o is assumed to be a representative diffusion coefficient even for concentrations of A up to 5 and, perhaps, 10 mol%.

An older, but still widely used, correlation for D_{AB}^o , the Wilke-Chang technique, is, in essence, an empirical modification of the Stokes-Einstein relation (Eq. 4). Several systems were studied by these investigators, and an average error of about 10% was noted:

$$D_{AB}^o = \frac{7.4 \times 10^{-8} (\phi M_B)^{0.5} T}{\eta_B V_{bA}^{0.6}} \quad (4)$$

in which D_{AB}^o is the mutual diffusion coefficient of solute A at very low concentrations in solvent B (cm^2/s); M_B is the molecular weight of solvent B (g/mol); T is the temperature (K); η_B is the viscosity of solvent B (cP); V_{bA} is the molar volume of solute A at its normal boiling temperature (cm^3/mol), and ϕ is the association factor of solvent B (dimensionless). Wilke and Chang recommend that ϕ be chosen as 2.6 if the solvent is water, 1.9 if it is methanol, 1.5 if it is ethanol, and 1.0 if it is unassociated.

In a binary liquid mixture, as already noted, a single diffusion coefficient was sufficient to express the proportionality between the flux and the concentration gradient. In multicomponent systems, the situation is considerably more complex, and the flux of a given component depends on the gradient of $n - 1$ components in the mixture. One important case of multicomponent diffusion results when a solute diffuses through a homogeneous solution of mixed solvents. When the solute is diluted, there are no concentration gradients for the solvent species and one can consider a single solute diffusivity with respect to the mixture D_{Am}^o . Perkins and Geankoplis evaluated several methods and suggested Eq. 5 (15):

$$D_{Am}^o \eta_m^{0.8} = \sum_{j=1 \neq A}^n x_j D_{Aj}^o \eta_j^{0.8} \quad (5)$$

in which D_{Am}^o is the effective diffusion coefficient for a diluted solute A into the mixture (cm^2/s); D_{Aj}^o is the infinite dilution binary diffusion of solute A into the solvent j (cm^2/s); x_j is the mole fraction of j ; η_m is the mixture viscosity (cP); and η_j is the pure component viscosity (cP). When tested with data for ternary systems, errors were normally $<20\%$. Perkins and Geankoplis also suggested that the Wilke-Chang equation might be modified to include the mixed solvent case, i.e., Eq. 6:

$$D_{Am}^o = \frac{7.4 \times 10^{-8} (\phi M)^{0.5} T}{\eta_m V_A^{0.6}} \quad (6)$$

in which

$$\phi M = \sum_{j=1 \neq A}^n x_j \phi_j M_j$$

Although not extensively tested, Eq. 6 provides a rapid, reasonably accurate estimation method.

VAPOR PRESSURE

Antoine Vapor Pressure correlations have been widely used over limited temperature ranges (15):

$$\text{Log } P^{vap} = A - B/(T + C) \quad (7)$$

in which A is a characteristic constant of a substance, to be adjusted; B is a characteristic constant of a substance, to be adjusted; C is a characteristic constant of a substance, to be adjusted; P^{vap} is the vapor pressure (bar); and T is the temperature (K).

Values of A , B , and C are tabulated for a number of materials. The applicable temperature range is not large and in most situations corresponds to a pressure interval of about 0.001–2 bar. The Antoine equation should never be used outside the stated temperature limits, since extrapolations beyond these limits may lead to absurd results. The constants A , B , and C form a set. It is recommended never to use one constant from one tabulation and other constants from different tabulation. Usually, in the

range of 0.01–2 bar, the Antoine equation provides an excellent correlating equation for vapor pressures (15). When Antoine parameters are determined from data in this pressure range (as they usually are), the equation underpredicts vapor pressure at higher pressures.

For the systems studied in the present work, these constants are not available. However, a graphic is available that depicts the vapor pressure curve of fitosterols and tocopherols (16). From this graphic, the constants A , B , and C of the Antoine equation were obtained. These values were introduced in the DISMOL simulator.

Characteristics of Mixture

LIQUID DENSITY

Even if no data are available, there are a number of techniques for estimating specific volumes or densities of pure liquid. An equation to estimate saturated volumes that was developed by Rackett and later modified by Spencer and Danner (15) is as follows:

$$V_S = \frac{RT_c}{P_c} \left\{ Z_{RA} \left[1 + (1 - T_r)^{2\eta} \right] \right\} \quad (8)$$

in which Z_{RA} is a unique constant for each component. If a value of Z_{RA} is not available, it may be estimated by $Z_{RA} = 0.29056 - 0.08775\omega$.

Since $\rho = m/v$, Eq. 9 can be written as follows:

$$\rho_{eb} = \frac{MP_c}{RT_c \left\{ Z_{RA} \left[1 + (1 - T_r)^{2\eta} \right] \right\}} \quad (9)$$

It is possible to correlate the density of a pure compound at any temperature through the Mathias' equation, with a maximum error of 2% (14):

$$\rho = \rho_{eb} \left(\frac{2T_c - T}{2T_c - T_{br}} \right) \quad (10)$$

Mixing rules for both the modified Rackett and Hankinson equations have been published and are given below. The modified Rackett equation (15) for mixtures at their bubble points is

$$V_m = R \left(\sum_i \frac{x_i T_{ci}}{P_{ci}} \right) Z_{RA_m} \left[1 + (1 - T_r)^{2\eta} \right] \quad (11)$$

or, as shown in Perry and Green (17)

$$\rho_{eb} = \frac{P_{c,m}}{RT_{c,m} \left\{ Z_{RA,m} \left[1 + (1 - T_{r,m})^{2\eta} \right] \right\}}$$

in which

$$Z_{RA,m} = \sum_i x_i Z_{RA_i}; P_{c,m} = \sum_i x_i P_{c_i}; T_{c,m} = \sum_i x_i T_{c_i}; T_r = T/T_{cm};$$

M is the molecular weight (g/gmol); P_c is the critical pressure (bar); $P_{c,m}$ is the mixture critical pressure (bar); V_c is the critical volume (cm³/mol); R is the universal gas constant (bar·cm³/mol·K); T_c is the critical temperature (K); $T_{c,m}$ is the mixture critical temperature (K); T_b is the liquid temperature at its boiling point (K); Z_{RA} is the Rackett compressibility factor; T_r is the reduced temperature; x_i is the mole fraction of the component i ; ρ is the liquid density (g/mL); ρ_{eb} is the liquid density at its boiling point (g/mL); ρ_i is the density of the component i (g/mL); ρ_m is the density of the liquid mixture (g/mL); and ω is the acentric factor.

HEAT CAPACITY

Estimation methods applicable for liquid heat capacities fall into four general categories: theoretical, group contribution, corresponding states, and Watson's thermodynamic cycle. An assumption is made that various groups in a molecule contribute with a value to the total molar heat capacity, which is independent of other groups present.

Chueh and Swanson (15) have proposed values for different molecular groups to estimate molar liquid heat capacity, C_p , at room temperature ($T = 293$ K). This method is accurate and more general. Errors for the Chueh-Swanson method rarely exceed 2 to 3%:

$$C_p = \sum \Delta_{Cp} \quad (12)$$

in which Δ_{Cp} is the group contribution for the Chueh-Swanson method (J/mol·K).

For temperatures other than 20°C, the equation of Watson must be used (14):

$$\frac{C_{p2}}{C_{p1}} = \left(\frac{W_1}{W_2} \right)^{2.8} \quad (13)$$

in which $W = 0.1745 - 0.0838T_r$.

For calculating the heat capacity of a liquid mixture, the following expression can be used (14):

$$C_{p,m} = \sum (X_i C_{p_i}) \quad (14)$$

in which C_p is the heat capacity (J/mol·K); C_{p_i} is the heat capacity of the component i (J/mol·K); $C_{p,m}$ is the heat capacity of the mixture (J/mol·K); T_r is the reduced temperature; W is the expansion factor of the liquid phase; X_i is the mass fraction of component i ; 1 is temperature 1 (normally 20°C, reference temperature); and 2 is temperature 2 (operation temperature).

THERMAL CONDUCTIVITY

All estimation techniques for the thermal conductivity of pure liquids are empirical, and with only limited examination, they often appear rather accurate. Below the normal boiling point, the thermal conductivities of most organic, nonpolar liquids lie between 0.10 and 0.17 W/(m·K). With this fact in mind, it is not too difficult to devise various schemes for estimating λ_L within this limited domain. Sato (15) suggested that at the normal boiling point (Eq. 15)

$$\lambda_L(T_b) = \frac{1.11}{M^{1/2}} \quad (15)$$

in which $\lambda_L(T_b)$ is the thermal conductivity of the liquid at the normal boiling point (at 1 atm) (W/[m·K]) and M is the molecular weight (g/mol).

To estimate λ_L at other temperatures, the Riedel (15) equation may be used:

$$\lambda_L = B \left[3 + 20 (1 - T_r)^{2/3} \right] \quad (16)$$

Thus, by combining Eqs. 15 and 16, the thermal conductivity of a pure liquid can be estimated, with a maximum mean error of 20%, as described in Eq. 17:

$$\lambda_L = \frac{\left(\frac{1.11}{M^{1/2}} \right) \left[3 + 20 (1 - T_r)^{2/3} \right]}{3 + 20 (1 - T_{b,r})^{2/3}} \quad (17)$$

The thermal conductivities of most mixtures of organic liquids are usually less than those predicted by either a mole or weight fraction average, although the deviations are often small (15). Then, it can be calculated through the following expression (14), with errors of about 4%:

$$\lambda_m = \sum (x_i \lambda_i) \quad (18)$$

in which M is the molecular weight (g/gmol); $T_{b,r}$ is equal to T_b/T_c (reduced normal boiling temperature); T_r is the reduced temperature; x_i is the mole fraction of the component i ; λ_L is the thermal conductivity (W/m·K); λ_i is the thermal conductivity of the component i (W/m·K); λ_m is the thermal conductivity of the liquid mixture (W/m·K).

VISCOSITY

The viscosity of a pure liquid can be determined as a function of the temperature when there are two or more values of viscosity for determining the constants A and B . The Guzman-Andrade equation (14), presents maximum errors of 2%:

$$\eta = Ae^{B/T} \quad (19)$$

in which A is a characteristic constant of a substance, to be adjusted; B is a characteristic constant of a substance, to be adjusted; and T is the temperature (K).

The empirical equation of Kendall-Monroe is the best for calculating mixture viscosity (14):

$$\eta_m^{1/3} = \sum X_i \eta_i^{1/3} \quad (20)$$

in which X_i is the mass fraction of the component i ; η_i is the viscosity (cP); and η_m is the mixture viscosity (cP). This equation should not be used if $T_r > 0.75$.

Simulation Results of Falling Film Molecular Distillation Unit

Study of Tocopherols and Phytosterols from Crude DDSO

Figures 2 to 7 present simulation results of the quantity recovered of each component (except fatty acids) in the liquid and vapor phases in relation to its quantity in the feed stream (%) vs the operating temperature (°C) for feed flow rates ranging from 0.5 to 1.0 kg/h using the DISMOL simulator. Since fatty acids are the most volatile components and are recovered first at a lower temperature (approx 125°C), they were omitted in order to facilitate understanding the obtained results. By increasing the temperature, it is possible to recover tocopherols in the vapor phase with the diglyceride and the squalene. Phytosterols are recovered in the liquid phase, also called residue. Thermal decomposition was not calculated because, in these cases, it is very small.

It can be observed in Fig. 2 that for a feed flow rate of 0.5 kg/h and temperature of 170°C, the tocopherols were almost 100% recovered in the vapor phase (also called distillate). When the operating temperature was increased to 180°C (10°C above), part of the phytosterols began to be recovered in the vapor phase too; however, this is not of interest because at this temperature the phytosterols start to distillate and this reduces the purity of tocopherol. It was also observed that by increasing the feed flow rate from 0.5 to 1.0 Kg/h (100%) (Figs. 2–7), a lower quantity of phytosterols was recovered in the vapor phase at 180°C.

The main objective of our study was to recover tocopherols, but it is also possible to recover phytosterols, which are products with high added value, since they are used for the formulation of margarine and the syntheses of sexual hormones.

In addition, it was found that the higher the feed flow rate, the higher the required operating temperature to recover the same quantity of tocopherols (Figs. 2–7). Furthermore, for temperatures lower than 160°C, practically all phytoesterols remained in the liquid phase (residue stream). It is also verified that tocopherols and diglycerides have similar behaviors, which implies that in the final product this mixture is obtained. Regarding tocopherol recovery (in the vapor phase), the best operating temperature was near 170°C (feed flow rate = 0.6 kg/h); above this temperature, the problem of thermal decomposition can arise. Above a feed flow rate of 0.6 kg/h, the recovery decreases.

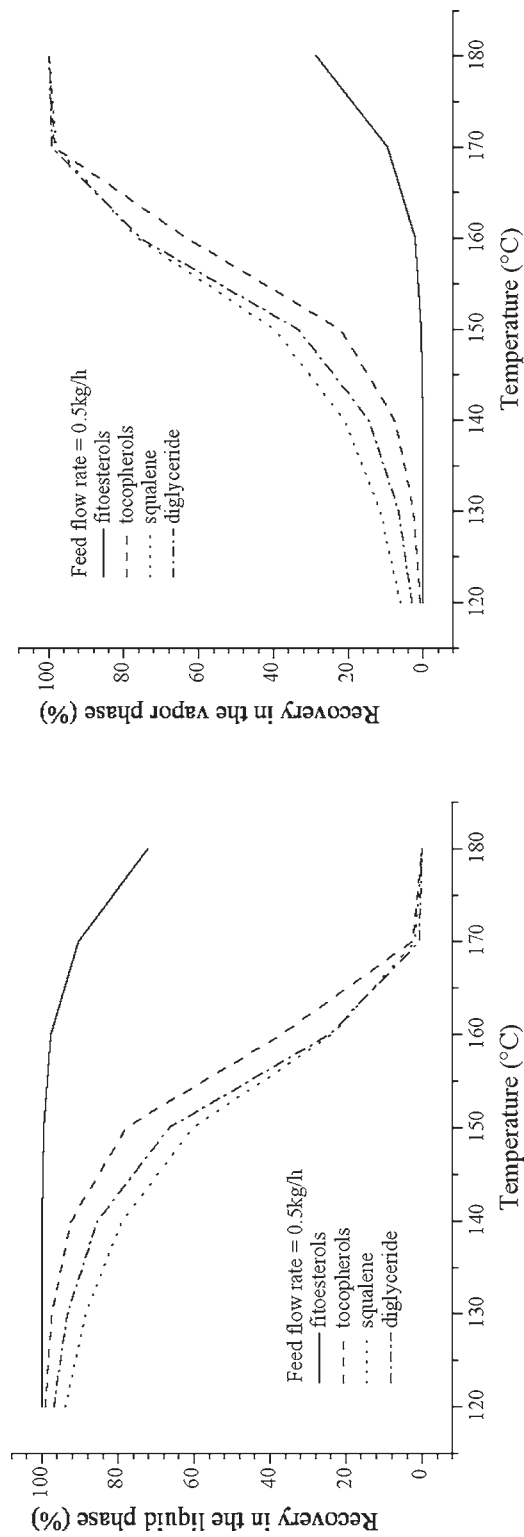


Fig. 2. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 0.5 kg/h.

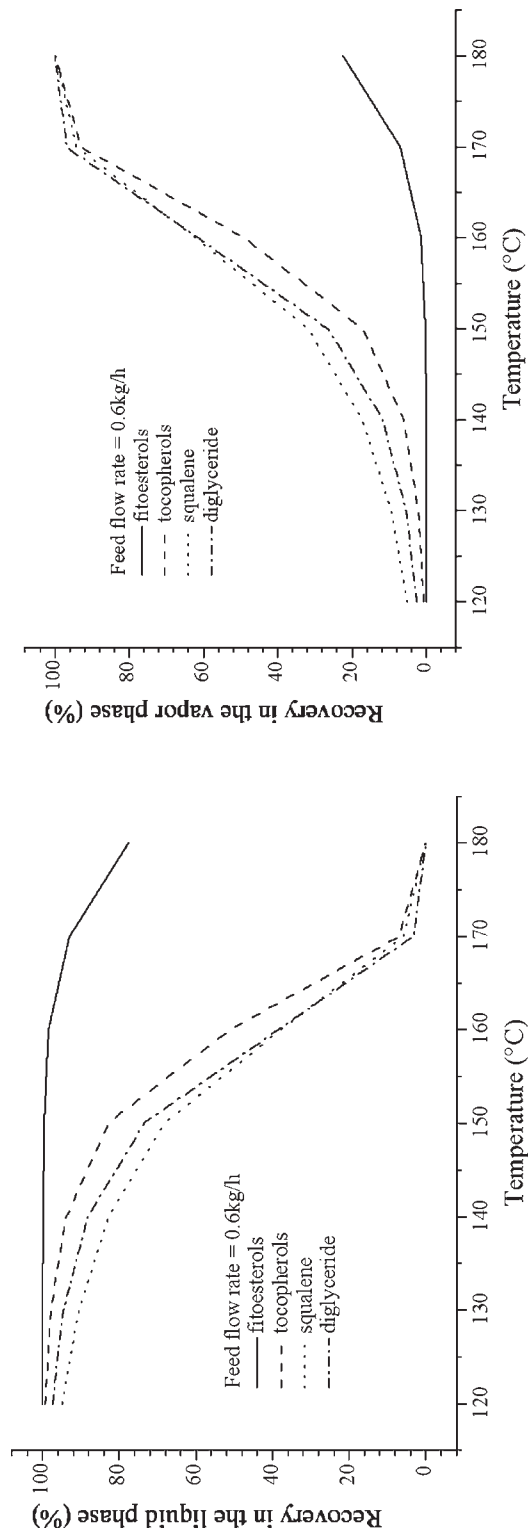


Fig. 3. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 0.6 kg/h.

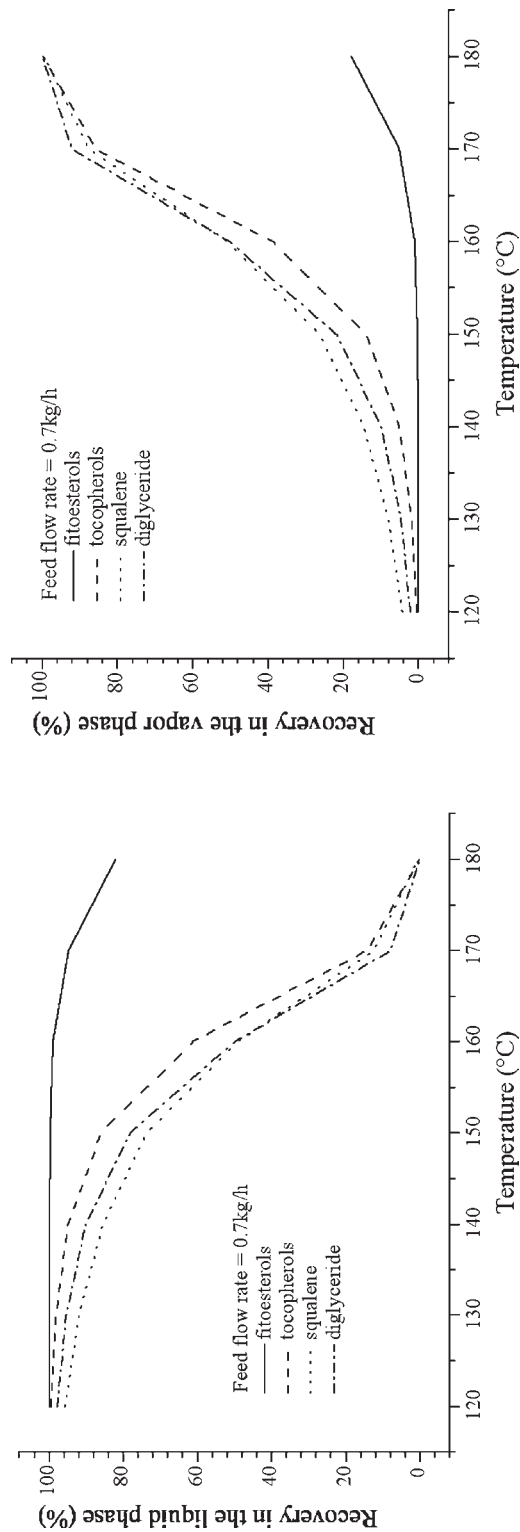


Fig. 4. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 0.7 kg/h.

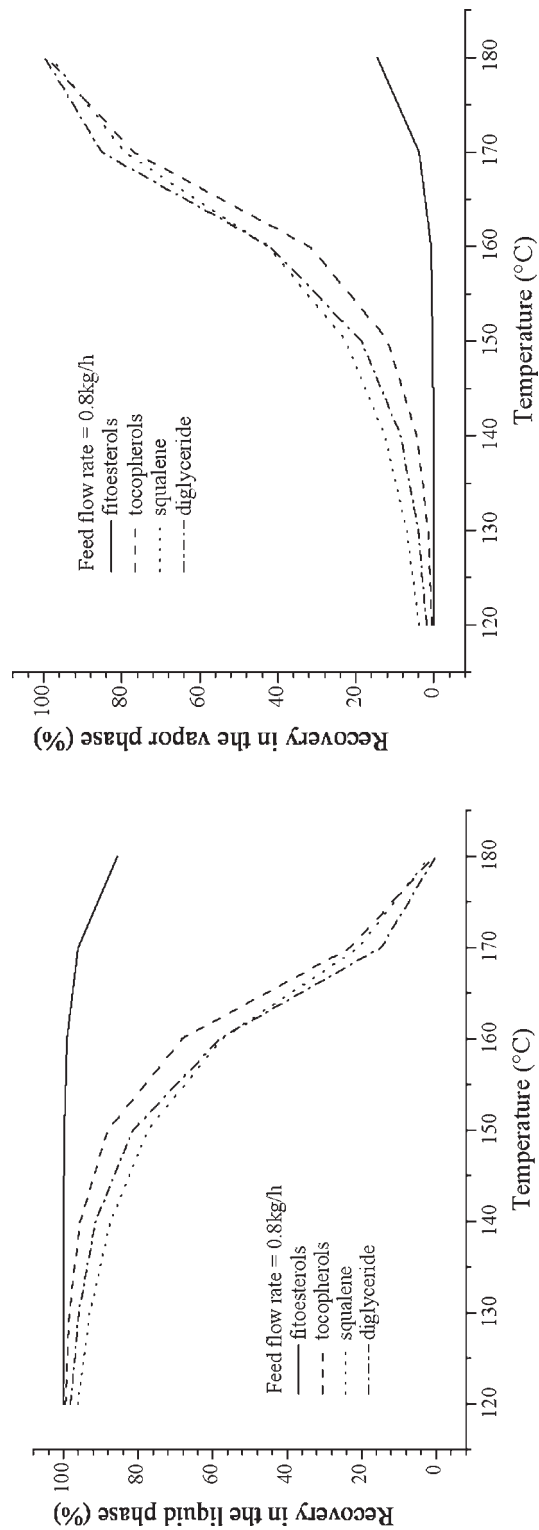


Fig. 5. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 0.8 kg/h.

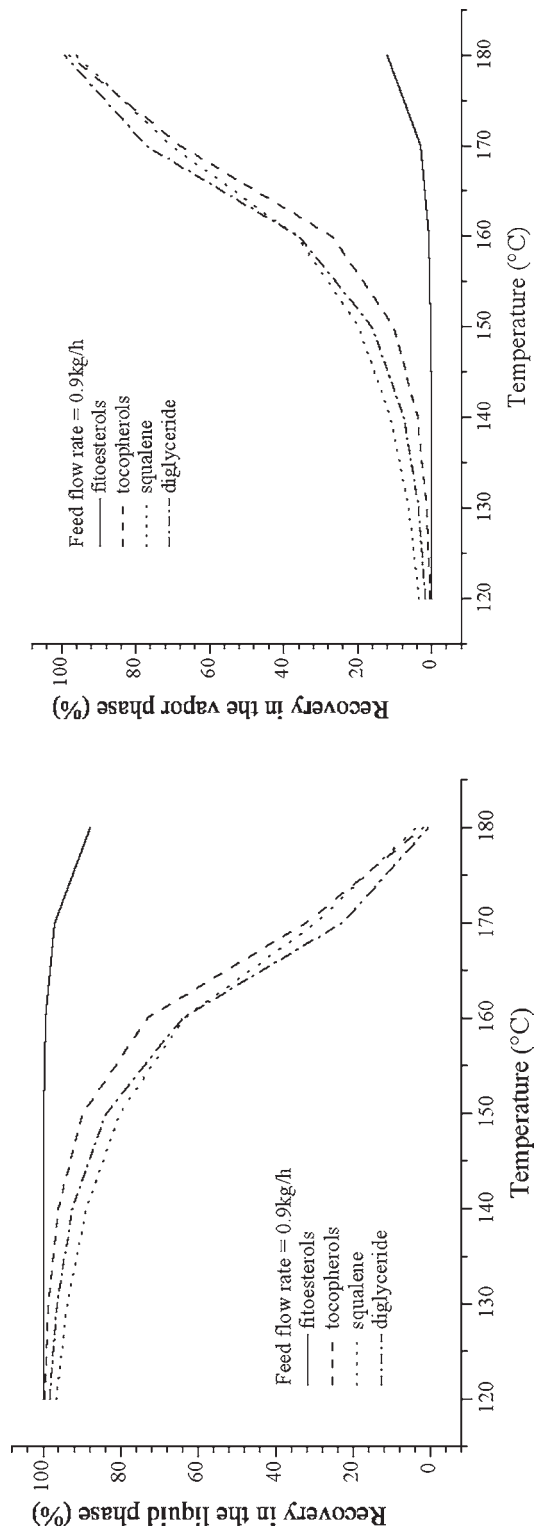


Fig. 6. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 0.9 kg/h.

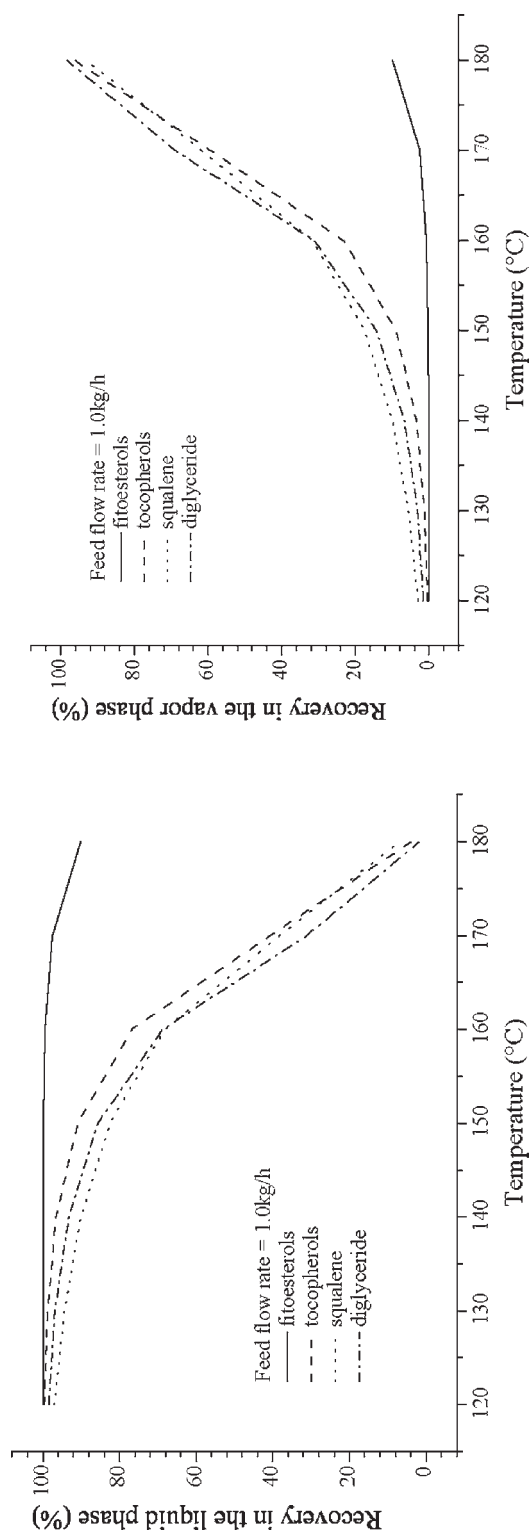


Fig. 7. Recovery of components in liquid and vapor phases in relation to quantity in feed vs temperature for feed flow rate of 1.0 kg/h.

Study of Tocopherol Concentration as Function of Distance Covered on Evaporator

Figures 8–10 show the curves of tocopherol concentration in the residue (% w/w) vs the percentage of the distance on the evaporator (from the feed point) for feed flow rate ranging from 0.5 to 1.0 kg/h for the falling film molecular distillation unit. The initial tocopherol concentration was 8.50% (w/w). For a feed flow rate of 0.5 kg/h (Fig. 8), it can be observed that at the end of the distillation, the tocopherol concentration in the residue will be higher, at 150°C (about 15% [w/w]). At 160°C, at 80% of the distillation, the tocopherol concentration reaches a maximum and then decreases, because the tocopherols are already recovered in the vapor phase. Figures 8–10 show that by increasing the feed flow rate at the same temperature (160°C), the tocopherol concentration can increase until it doubles the initial concentration (for a feed flow rate of 0.6 kg/h). From this point, it decreases, requiring an increase in the temperature to concentrate more (for a feed flow rate of 1.0 kg/h at 170°C). For all feed flow rates (Figs. 8–10), at 180°C, practically all the tocopherols are found in the vapor phase. With this study, it is possible to observe which temperature is the best in order to recover the fatty acids (first step = $\pm 125^{\circ}\text{C}$) and, then, recover the tocopherols in the vapor phase (distillate) and the phytosterols in the liquid phase (residue) (second step = $\pm 170^{\circ}\text{C}$). At the lowest temperature (120°C) the tocopherol recovery was minimum (about 5%). By increasing the feed flow rate from 0.5 to 1.0 kg/h (100%), the quantity of tocopherol in the residue at 170°C, e.g., increases, which means that the process performance has decreased.

Conclusion

The DISMOL simulator is a powerful tool for calculating the feasibility and performance of a process, as well as for identifying the best operating conditions to carry out the experiments. This means that it is possible to identify the operating conditions for recovering a large quantity of tocopherol. According to the results, a temperature of about 170°C and a feed flow rate of about 0.6 kg/h are the best operating conditions for the considered equipment. Simulation can result in a substantial reduction in the experimental time, process development, and optimization. The procedure for estimating the properties for complex systems is of crucial importance.

The results show that the feed flow rate and the temperature can be adequately chosen in order to obtain total tocopherol recovery. In addition, the behavior of the tocopherols on the evaporator as a function of the temperature and feed flow rate can be verified. In future works, the validation of the model and of the simulation will be demonstrated.

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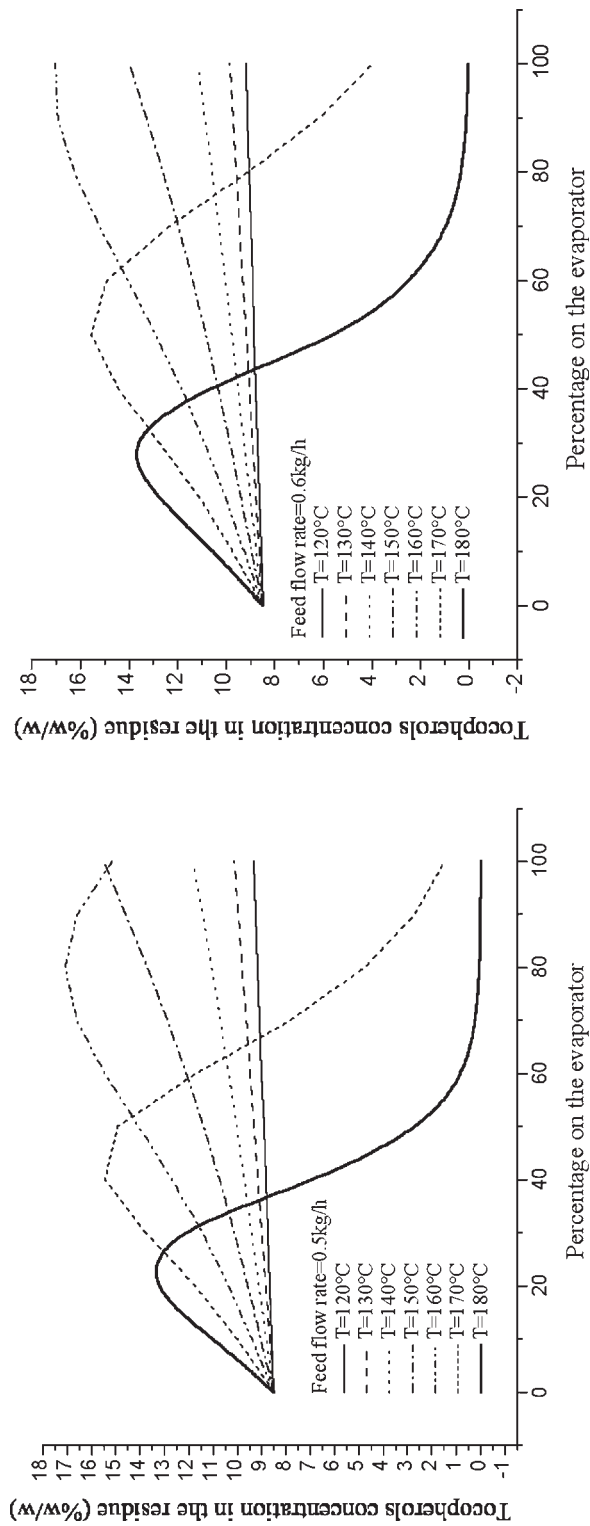


Fig. 8. Tocopherol concentration in residue vs distance covered on evaporator (%) for feed flow rate of (A) 0.5 and (B) 0.6 kg/h.

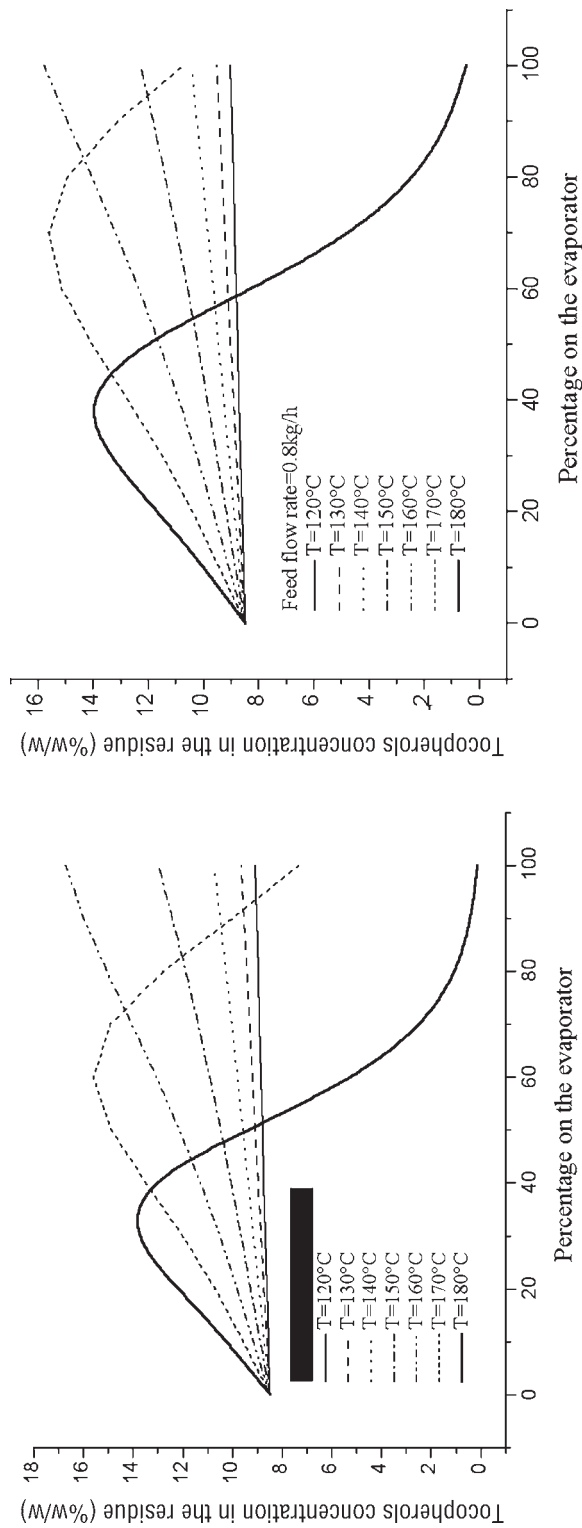


Fig. 9. Tocopherol concentration in residue vs distance covered on evaporator (%) for feed flow rate of (A) 0.7 and (B) 0.8 kg/h.

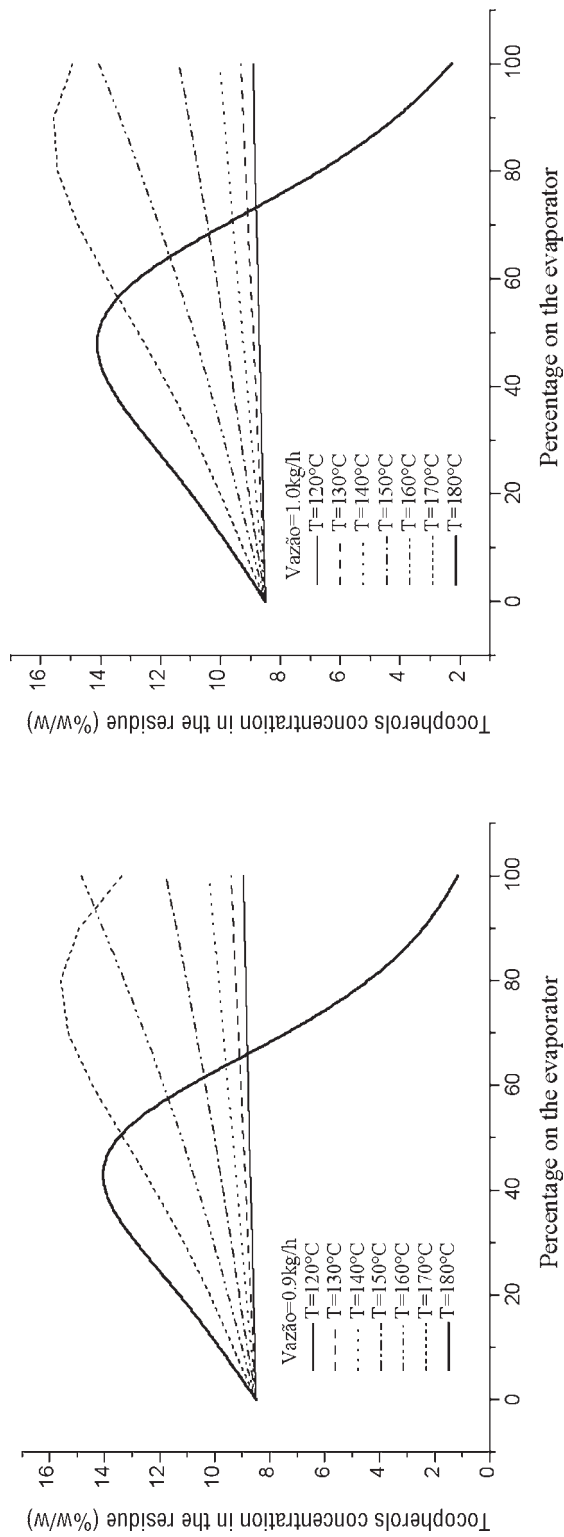


Fig. 10. Tocopherol concentration in residue vs distance covered on evaporator (%) for feed flow rate of (A) 0.9 and (B) 1.0 kg/h.

References

1. Cvengros J., Lutisan, J., and Micov, M. (2000), *Chem. Eng. J.* **78**, 61–67.
2. Batistella C. B. and Maciel, M.R.W. (1998), *Comput. Chem. Eng.* **22(Suppl.)**, S53–S60.
3. Batistella, C. B., Moraes, E. B., Maciel Filho, R., and Maciel, M. R. W. (2002), *Appl. Biochem. Biotechnol.* **98(1–3)**, 1187–1206.
4. Batistella, C. B., Moraes, E. B., Maciel Filho, R., and Maciel, M. R. W. (2002), *Appl. Biochem. Biotechnol.* **98(1–3)**, 1149–1159.
5. Batistella C. B. and Maciel, M. R. W. (1996), *Comput. Chem. Eng.* **20(Suppl.)**, S19–S24.
6. Batistella, C. B., Moraes, E. B., and Maciel, M. R. W. (1999), *Comput. Chem. Eng. (Suppl.)*, S767–S770.
7. Batistella, C. B., Maciel, M. R. W., and Maciel Filho, R. (2000), *Comput. Chem. Eng.* **24(2–7)**, 1309–1315.
8. Maciel Filho, R., Wolf-Maciel, M. R., and Batistella, C. B. (2001), FRAMOL Project, UNICAMP/CENPES/PETROBRAS/FINEP.
9. Winters, R. L. (1990), in *World Conference Proceedings, Edible Fats and Oils Processing, Basic Principles and Modern Practices*, David, R., ed., American Oil Chemists' Society, Champaign, IL, pp. 402–405.
10. Winters, R. L (1986), in *Proceedings of the World Conference on Emerging Technologies in the Fats and Oils Industry*, Baldwin, A. R., ed., American Oil Chemists' Society, Champaign, IL, pp. 184–188.
11. Ramamurthi S. and McCurdy, A. (1993), *JAOCs* **70(3)**, 287–295. 12. Batistella C. B. (1996), MS thesis, UNICAMP, Campinas, SP, Brazil.
13. Augusto, M. M. M. (1988), MS thesis, UNICAMP, Campinas, SP, Brazil.
14. Perry, R. H. and Chilton, C. H. (1980), *Manual de Engenharia Química*, Seção 13, Ed. Guanabara II, Rio de Janeiro, RJ, Brazil.
15. Reid, R. C., Prausnitz, J. M., and Poling, B. E. (1987), *The Properties of Gases and Liquids*, McGraw-Hill, New York, NY.
16. Erickson, D. R. (1995), in *Practical Handbook of Soybean Processing and Utilization*, AOCS Press, Champaign, IL, and United Soybean Board, St. Louis, MO, pp. 203–217, 307.
17. Perry, R. H. and Green, D. (1984), *Perry's Chemical Engineers' Handbook*, 6th Ed., McGraw-Hill, Malaysia.