

SIMULATION OF DEACIDIFICATION PROCESS BY MOLECULAR DISTILLATION OF DEODORIZER DISTILLATE

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Abstract— A computer program has been developed to simulate the deacidification of sunflower deodorizer distillate. The developed mathematical model is based on momentum, mass and energy balances. The Langmuir-Knudsen constitutive equation was used in order to represent the kinetics of evaporation and condensation. Physical and transport properties have been evaluated using correlations, which are functions of temperature and composition. The obtained partial differential equation system was solved by means of the Crank-Nicholson technique, and the calculation programs employed were developed and debugged using Matlab 7.1.

The mathematical model was used to analyze the phenomena that take place during the molecular distillation process, and it also allowed studying the influence of operating variables on the performance of the process. In this investigation, we analyzed the influence of the operating temperature on purity and yield of the components. Trials at three evaporating temperatures (110 °C, 130 °C, and 140 °C) were carried out in a KDL4 (UIC) molecular distillation apparatus to verify the model.

Keywords — Molecular distillation, simulation, free fatty acids, tocopherols, sterols.

I. INTRODUCTION

Molecular distillation operation, which is also known as short-path distillation, is a useful separation technique in the purification of compounds which are thermally unstable and have low volatility. Molecular distillation is based on the evaporation of compounds in a mixture. These phenomena take place in two types of distillers: falling film or centrifugal. In the falling film method, one film is in contact with a heated surface and the other film is in contact with a cold surface. The cold surface is near the heated surface, at a distance shorter than the mean free path of the residue gas. The main operating characteristic is the working pressure, and it ranges from 10^{-2} to 10^{-4} KPa. Under these conditions, the volatility of the components increases and the operation temperature decreases, allowing the compounds to separate at lower temperatures. The molecules that leave the evaporation surface suffer virtually no collisions at lower operating pressures. As a result, the molecules take a short path before their condensation; that is, they arrive at the condenser surface in a brief period of time. It is for this reason that very high evaporation velocities are reached. Under these two conditions, short residence

time and low temperature, the thermal decomposition of the components is reduced and separation occurs at acceptable velocities (Weissberger, 1951; Perry *et al.*, 1984).

The separation level that is obtained in a molecular distillation process is not only a function of the volatility of the components, but it is also a function of the mass and heat transfers in the liquid phase and its molecular kinetics play an important role in the performance of the operation. When the liquid is evaporated, the vapor-liquid interface becomes cold and, in mixtures, it decreases the composition of the more volatiles components. This leads to the formation of driving forces for the diffusive transfer of mass and heat. All these resistances affect not only the evaporation velocity, but also the product purity (Bose and Palmer, 1984).

Advances in the theoretical modelling of this operation have been reported. Bose and Palmer (1984) showed that the existence of concentration and temperature gradients in the liquid phase decreases the separation efficiency. Bandarkar and Ferron (1991) worked in the mass and heating transference in a liquid film on a centrifugal still. Batistella and Maciel (1996) have shown results of efficiency and performance with two types of distillers. The pressure effect in the molecular distillation process has been analyzed by Cvengros and Lutisan (1995) using both Boltzmann proposals and the Maxwell distribution function for the molecular velocity in the vapor phase. Cvengros *et al.* (1997) used a model to theoretically analyze the operation of molecular distillation for binary mixtures.

Tocopherols and sterols are compounds with important economical value. They decompose at the high temperatures that are required in the conventional distillation operation (Yankah and Jones, 2001; Dunford, 2001). These compounds can be obtained from a by-product of the deodorization stage of the vegetable oil refining process: the 'deodorizer distillate'. Besides sterols and tocopherols, the distillate generally contains lighter compounds such as free fatty acids, and heavier components such as mono, di and triglycerides, and esters from sterols and pigments (Winters, 1994). This mixture must be treated with separation techniques in order to obtain the purified compounds. The separation of free fatty acids from the remaining components of the mixture is generally the first stage of distillation in the separation and purification process, because the fatty acids are more volatile than the rest of the components. However, the conventional distillation requires high

temperatures, which tocopherol decomposition. In this context, the molecular distillation method becomes a promising process.

Since these processes are carried out on multi-components mixtures, the application of mathematical models for the previous study of the operation is very complicated since it requires the use of many component properties. Consequently, the study of a simplification in the treatment is justified. The aim of this work is to analyze the deacidification process of sunflower deodorizer distillates through molecular distillation using a mathematical model and its respective experimental verification considering the multi-components mixture as a set of two identities.

II. METHODS

A. Mathematical Modelling

In Fig. 1 the performance of a falling film molecular distiller is shown in a schematic way. The transport equations, which describe the evaporation process in the film, are obtained using momentum, mass and energy balances.

To develop the mathematical model, the following assumptions have been made:

1. Condition of steady state throughout the process.
2. Temperature of condensation set low to avoid re-evaporation from the condensation surface.
3. A rectangular coordinates system to describe variables over the film, because thickness film is very small in comparison with the radius of the cylindrical evaporation surface.
4. Negligible collisions between molecules in the vapor phase.

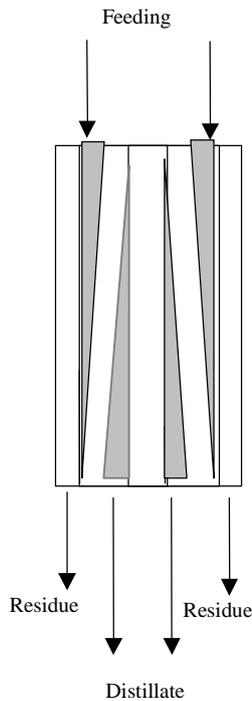


Figure 1: Molecular distillation equipment scheme.

A binary mixture (A+B) is considered. The main free fatty acids are considered as entity A (lighter compounds of the mixture), and the remaining less volatile components (the heavier ones) as the other entity (B). Their properties have been calculated considering the relative quantity of each component, in order to have averaged properties of each entity.

For movement description in the system considering laminar flow, the momentum balance is formulated as follows.

$$\mu \frac{\partial^2 v_y}{\partial z^2} + \rho \cdot g_y = 0 \quad (1)$$

with the following boundary conditions:

$$\begin{aligned} z = 0 \quad v_y|_{z=0} &= 0 \\ z = h \quad \frac{\partial v_y}{\partial z}|_{z=h} &= 0 \end{aligned} \quad (2)$$

From the continuity equation for component A of a binary mixture (A+B), the following is obtained:

$$v_y \frac{\partial x_A}{\partial y} = D_{AB} \frac{\partial^2 x_A}{\partial z^2}, \quad (3)$$

with the following conditions:

$$\begin{aligned} y = 0 \quad x_A|_{y=0} &= x_A^f \quad \forall z \\ z = 0 \quad \frac{\partial x_A}{\partial z}|_{z=0} &= 0 \quad \forall y \end{aligned} \quad (4)$$

where x_A^f is the molar fraction of A in the feed.

For boundary condition in $z=h$, Fick's first law for diffusion is used:

$$N_A|_{z=h} = x_A^s (N_A|_{z=h} + N_B|_{z=h}) - D_{AB} c \frac{\partial x_A}{\partial n}|_s, \quad (5)$$

where n represents normal direction to the evaporation surface and s represents the liquid surface.

The molar flow density for the components is expressed as a function of the evaporation rate:

$$\begin{aligned} N_A|_{z=h} &= x_A^s \cdot k_A \\ N_B|_{z=h} &= (1 - x_A^s) \cdot k_B \end{aligned}, \quad (6)$$

where x_A^s is the molar fraction of component A in the evaporation surface.

The evaporation rate of each component is evaluated by Langmuir, which is based on the kinetic gas theory:

$$\begin{aligned} k_A &= \frac{Pv_A(T^s)}{\sqrt{2\pi R M_A T^s}} \\ k_B &= \frac{Pv_B(T^s)}{\sqrt{2\pi R M_B T^s}} \end{aligned} \quad (7)$$

where T^s is the evaporation surface temperature.

As a result of formulating a global mass balance, a variation equation of molar total flow is obtained:

$$\frac{dI}{dy} = -2\pi R_l (x_A^s \cdot k_A + (1 - x_A^s) \cdot k_B) \quad (8)$$

where R_l is the average radius of the film. The boundary condition related to this equation is formulated as:

$$y=0 \quad I = I^f \quad (9)$$

where I^f is the feeding molar flow.

The energy balance equation for this system has the following form:

$$\rho c_v v_y \frac{\partial T}{\partial y} = k \frac{\partial^2 T}{\partial z^2} \quad (10)$$

The boundary conditions for this equation are:

$$\begin{aligned} y=0 \quad T &= T^f \quad \forall z \\ z=0 \quad T &= T^w \quad \forall y \end{aligned} \quad (11)$$

where T^f and T^w are feed and wall temperatures, respectively.

For boundary condition in $z=h$, the equation has the following shape:

$$\begin{aligned} z=h \quad \forall y \\ -k \frac{\partial T}{\partial n} \Big|_s = \Delta \hat{H}_{vA} x_A^s k_A + \Delta \hat{H}_{vB} (I - x_A^s) k_B \end{aligned} \quad (12)$$

The thickness value of the film, h , is related with molar flow I by means of:

$$I = \frac{2}{3} \pi \frac{\rho g R_l}{\nu} h^3 \quad (13)$$

In Fig. 2, the scheme of the net employed to solve the numerical method is shown. The partial differential equations were formulated in terms of the implicit finite difference method, considering the curved borders present in the falling films. The set of linear equations from finite difference scheme is solved by the Gauss-Seidel method.

The α value is determined by:

$$\alpha = h(j) - \Delta z \cdot n_z(j) \quad (14)$$

The equations used to formulate the condensation mathematical model are the conservation equations of mass, movement and energy already formulated for the evaporation film with the following changes:

1- The film initial velocity is zero.

$$y=0 \quad ; \quad z=0 \quad ; \quad v_y \Big|_{y=0} = 0 \quad (15)$$

2- The initial temperature is equal to the temperature of the cooling fluid:

$$y=0 \quad T = T_{con}^w \quad \forall z \quad (16)$$

3- Initial compositions of A and B can be determined from:

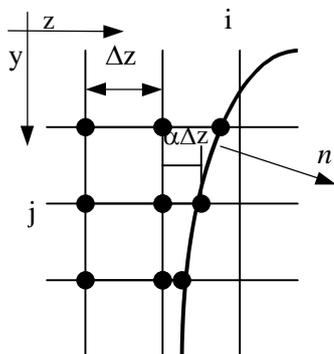


Figure 2: Scheme of the net employed to solve the numerical method.

$$y=0 \quad \frac{x_A}{x_B} \Big|_{y=0} = \frac{Pv_A(T_{con}^w) \sqrt{M_B}}{Pv_B(T_{con}^w) \sqrt{M_A}} \quad \forall z \quad (17)$$

The complete mathematical model has been numerically solved using MatLab 7.1. In order to determinate the physical properties, correlations available in bibliographical data were used. An average molecular weight was used taking into account the relative mass from the principal fatty acids in the deodorizer distillate (Madhavi *et al.*, 1996) and to represent the less volatile compounds, an average molecular weight was calculated taking into account the compositions of the more abundant ones (Lide, 1992). The average vapor pressure has been considered as a function of the temperature (Madhavi *et al.*, 1996). The compound's critical properties were calculated with Ambrose's proposal (functional group contribution) (Reid and Sherwood, 1968). The transport properties thermal conductivity, viscosity and diffusivity have been obtained by means of the Sheffy-Johnson, Thomas and Sitaraman-Ibrahim-Kuloor correlations, respectively (Reid *et al.*, 1987). Considering the thermodynamic properties, the heat capacity was obtained by means of the Chow-Bright correlation (Perry, 1984), the density by means of the Benson-Fishtine (Madhavi *et al.*, 1996) equation and the latent heat of evaporation by means of Vetere equation (Reid and Sherwood, 1968). All properties were averaged pondering with mass fractions. The unknown compounds were not considered for the determination of the properties average; instead, they were assigned the calculated average properties.

B. Experimentals

Analytical methods. With the aim of knowing the characteristics of raw material and the quality of the obtained product, the following analytical determinations were used, by means of AOCS methods: *Free fatty acids* (AOCS Cd 3d-63), *FFA composition* (AOCS Ce 1-62-gas chromatography method) and *Sterols, Tocopherols and Squalene* (AOCS Ce 7-87- gas chromatography method) (AOCS, 1994).

Raw material. A sample of deodorizer distillate was obtained from the sunflower oil refining process. The sample was liquid at ambient temperature and had a dark brown color, almost black. Table 1 shows the composition of the sample. Fatty acid distribution is shown in Table 2.

Molecular distillation. Molecular distillation was carried out in KDL4 (UIC) equipment (falling film, evaporation surface: 0.04 m², condensation surface: 0.02 m²). The distiller is equipped with wiper rollers of variable velocity. The vacuum system consists of a diffusion pump and a mechanical pump. These are capable of obtaining a maximum vacuum of 10⁻⁴ KPa, with a maximum feeding of 0.5 Kg/h. A scheme of this apparatus is shown in Fig. 3.

The experimental tests were planned in order to analyze the influence of the evaporator temperature. The feeding and condensation temperatures, the feeding

flow rate, the pressure and the velocity of wiper rollers were established according to those typically used in these kinds of applications. Operative conditions used in the trials are shown in Table 3.

Table 1. Composition of sunflower oil deodorizer distillate. (Deodorizer conditions: 3-4 torr, 240°C, 45 min)

| Component | Mass % |
|------------------------------|--------|
| α - Tocopherol | 3.87 |
| δ - Tocopherol | 1.17 |
| β, γ - Tocopherol | 2.72 |
| Total tocopherols | 7.76 |
| β - Sitosterol | 4.12 |
| Campesterol | 1.65 |
| Stigmasterol | 1.68 |
| Total sterols | 7.45 |
| Squalene | 2.65 |
| FFA (wt% acid oleic) | 35.08 |
| Others | 47.06 |

Table 2. Free fatty acid composition for sunflower oil deodorizer distillate.

| Fatty Acid (formula) | Mass(%) |
|----------------------|---------|
| Palmitic (16:0) | 11.31 |
| Stearic (18:0) | 6.02 |
| Oleic (18:1) | 21.61 |
| Linoleic (18:2) | 59.88 |
| Others | 1.18 |

C. Results and Discussion

Results of molecular distillation process at different evaporator temperatures from 100°C to 140°C are shown in Table 4. Mass balance and compositions of main components of these trials allow as comparing experimental results with theoretical results from the model developed. The physical parameters obtained in the application of the model for the sunflower deodorizer distillate used in the experimental trials at 120°C can be observed in Table 5. Vapor pressure variation with the temperature is reported in Table 6, which shows the value of vapor pressure for A and B at two operating temperature.

The change in the relative quantity of the heavier components in the residue at different non-dimensional vertical positions is shown in Fig. 4. This quantity shows the heavier remaining components in the residue at the vertical y-position. The results of three simula-

tions for three different evaporation temperatures are shown. At higher evaporation temperature, the evaporated quantity of all components was higher, so the amount of residue was lower.

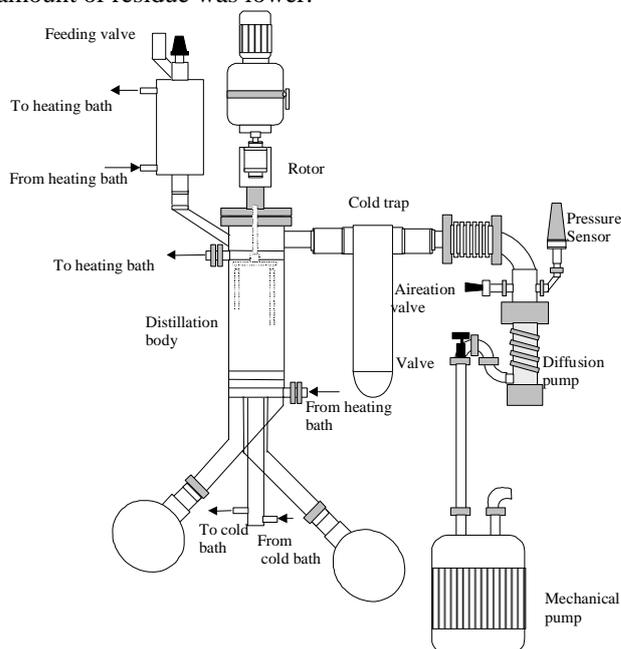


Figure 3: Scheme of molecular distiller

Table 3. Operating conditions for the process

| Parameter | Value |
|----------------------------|-----------|
| Feed flow rate [ml/min] | 1.9 |
| Feed Temperature [°C] | 45 |
| Condenser temperature [°C] | 25 |
| Pressure [mbar] | 10^{-2} |
| Rotor speed [rpm] | 130 |

Results of the corroboration of the model are shown in Fig. 5 through 8. Figure 5 shows the variation of the total evaporated quantity, which is relative to the feeding, with the evaporation temperature. Based on the simulation results, the total evaporated quantity is approximately 35 % at 107 °C. Trials at higher temperatures were later carried out in order to evaporate, at least, the desired quantity of distillate (similar to the quantity of the lighter compounds that was intended to separate in the distillate).

Table 4. Results of the molecular distillation process at different evaporator temperatures (from 100°C to 140°C). Mass balance and compositions.

| | 100°C | | 110°C | | 120°C | | 130°C | | 140°C | | |
|----------------------|-------|------|-------|-------|-------|------|-------|-------|-------|-------|-------|
| | F* | D | R | D | R | D | R | D | R | | |
| Mass (g) | 100 | 27.9 | 72.1 | 38.47 | 60.24 | 50.2 | 49.8 | 60 | 39.8 | 64.1 | 35.9 |
| Tocopherol % | 7.76 | 0 | 10.2 | 0 | 12.87 | 2.23 | 13.4 | 4.21 | 13.15 | 5.87 | 11.18 |
| Sterol % | 7.45 | 0 | 12.7 | 0 | 12.34 | 3.47 | 11.71 | 5.10 | 11.02 | 5.56 | 10.87 |
| Squalene % | 2.65 | 1.01 | 3.9 | 1.39 | 3.29 | 1.91 | 2.9 | 2.76 | 2.17 | 3.49 | 1.39 |
| FFA (wt% acid oleic) | 35.08 | 60.2 | 22.8 | 57.71 | 21.67 | 52.3 | 15.7 | 46.66 | 10.75 | 49.99 | 5.50 |

* F: Feed, D: distillate, R: residue.

Table 5. Set of physical, thermodynamic and transport parameters of A and B at 120°C.

| | M (gmol ⁻¹) | Pv (mbar) | ΔH_v (KJ/mol) | ρ (Kgm ⁻³) | μ (Pa.s) | k (W/m ² K) | D_{AB} (m ² /s) | Cp (KJ/Kg.°C) |
|---|-------------------------|----------------------|-----------------------|-----------------------------|-----------------------|------------------------|------------------------------|---------------|
| A | 278.4 | 0.043 | 101.6 | 829.7 | 0.003 | 0.146 | $2.45 \cdot 10^{-8}$ | 2.33 |
| B | 412.3 | $0.15 \cdot 10^{-3}$ | 54.4 | 1131.5 | $0.135 \cdot 10^{-3}$ | 0.068 | $1.75 \cdot 10^{-8}$ | 3.21 |

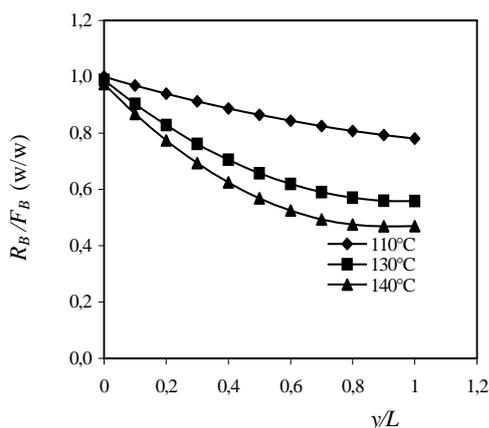


Figure 4: Variation of relative quantity of heavier compounds in the residue (R_B) with respect to the heavier compounds in the feeding (F_B) for three evaporating temperature.

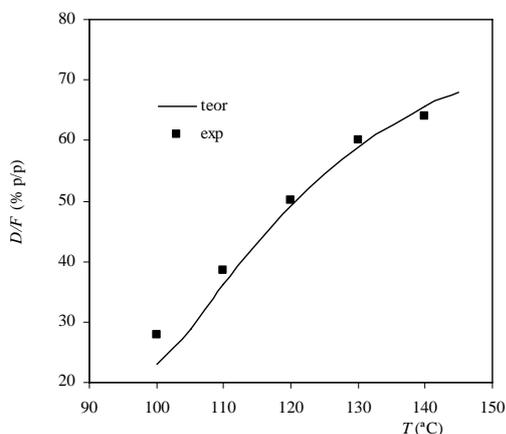


Figure 5: Variation of the total evaporated quantity with the evaporating temperature.

Table 6. Vapor pressure for A and B.

| | Pv (mbar) | |
|---|-----------|-------|
| | 120°C | 140°C |
| A | 0.043 | 0.185 |
| B | 0.010 | 0.042 |

The results of the final composition for residue and distillate at different temperatures are shown in Fig. 6. At higher temperatures, lighter compounds composition in the residue and in the distillate is lower. The more adequate temperature will depend on the particular objective of purification (to maximize the profitability of the process).

Figure 7 shows modeling and experimental results of mass flows of lighter compounds in the distillate and heavier compounds in the residue for different evaporation temperatures, relative to the respective feeding. Both flows should be as high as possible in order to get larger separation efficiency, but it does not occur simultaneously. There will be a technical trade-off solution.

The separation factor, F_s , is calculated as:

$$F_s = \frac{Y_A}{1 - Y_A} \frac{1 - X_{AF}}{X_{AF}} \quad (18)$$

F_s is shown in Fig. 8, in relation to the temperature. This factor suffers a larger decrease due to the resistance to the heat and mass transfer in the liquid. At higher temperatures, the factor decreases abruptly, so it is convenient to set this temperature in a value near to 110°C. This value allows for the evaporation of a distillate percentage to equal the percentage of the lighter compounds in feeding.

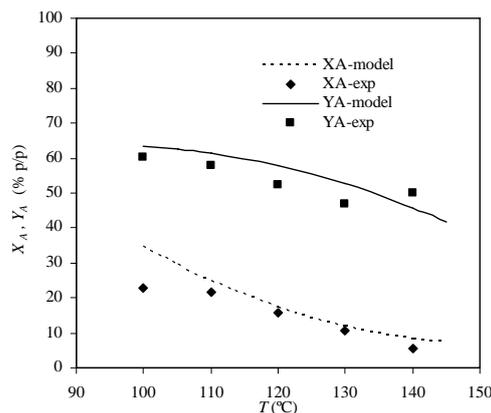


Figure 6: Final compositions in residue (X_A) and distillate (Y_A) at different evaporating temperatures.

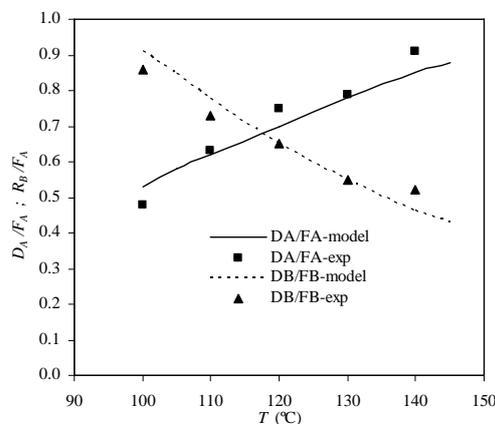


Figure 7: Mass flows of the lighter compounds (A) in the distillate and mass flows of heavier compounds (B) in the residue for different evaporating temperatures.

III. CONCLUSIONS

A computer mathematical modeling system to simulate the molecular distillation process was developed. It was used to study the deacidification operation of sunflower deodorizer distillate. The physical model allowed us to analyze the influence of evaporation surface temperature.

The model was experimentally verified, obtaining good accordance with the simulation model results and the data coming from the trials.

This methodology of analysis can be carried out to investigate improvements in the separation efficiency

with other influential parameters such as flow, condensation temperature and pressure.

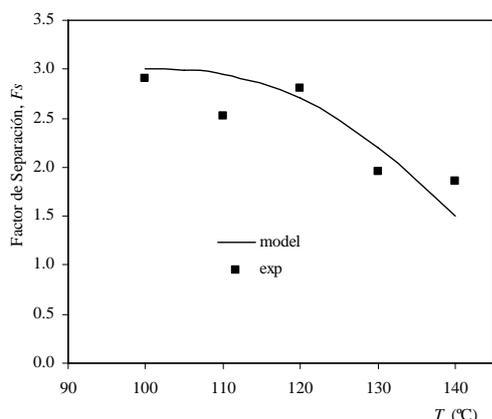


Figure 8: Separation factor as a function of the evaporation temperature.

NOMENCLATURE

- c = molar density, [mol/m³]
 h = film thickness, [m]
 k_i = rate of component evaporation, [mol/m²,s]
 k = thermal conductivity, [Joule/m,°C]
 L = evaporator high, [m]
 n_z = intervals on z direction
 v = velocity, [m/s]
 x_A = molar fraction of A component
 y = vertical coordinate, [m]
 z = horizontal coordinate, [m]
 c_v = heat capacity, [Joule/mol,°C]
 D_{AB} = diffusion coefficient, [m²/s]
 I = molar flow, [mol/s]
 M = molecular weight
 N = density of molar flow, [mol/m²,s]
 P_v = vapor pressure, [Pa]
 R = universal constant of gases
 T = temperature, [°C]
 ρ = density, [kg/m³]
 μ = viscosity, [kg/m,s]
 ν = cinematic viscosity, [m²/s]
 ΔH_v = latent heat of vaporization, [Joule/mol]
 Δz = horizontal increment, [m]

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