

## **A CAPE tool to simulate the pervaporation process for recovering an aroma contributor of orange juice**

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### **Abstract**

Flavor and odor components of foods are often lost during processing, which leads to a final product with poorer quality when compared to fresh made ingredients. It is not a different scenario in orange juice and other beverage industries. Heating processes cause severe physical and chemical losses of the natural characteristic flavour of orange juice. Methods, that use lower heat, present thermal damage reduction and must be investigated to establish parameters to the future commercial processes. Membrane separation processes can be considered a promising alternative for this challenge in orange juice manufacturing and aroma processing. Comparative study of quantitative data of volatiles to odor threshold data suggested Ethyl Butyrate (EB) is one of the key contributors to fresh orange aroma. The recovery of the key contributors as EB before evaporation or pasteurization steps creates quality improvement opportunities. The freshness of juice can be improved with enriched aroma fraction add back or even commercialized this folded fraction. Pervaporation is an attractive technology for thermal sensitive products. This process is based on a selective transport through a membrane associated with permeate evaporation on the downstream side of the membrane. The liquid feed mixture is maintained in contact with one side of a membrane and the permeate is continuously and selectively removed from the other side in vapor phase by a vacuum pump. Pervaporation process using a poly (dimethylsiloxane) membrane was simulated for understanding separation and recovery of EB from a binary mixture (EB-water). It was applied a Fortran simulator named PERVAP. The software allowed the calculation of selectivity and permeate flux. PERVAP assumes that the permeation flow is a function of the diffusion coefficient of penetrant components in the membrane. The diffusion coefficient was predicted considering the free-volume theory and assumed constant in the membrane. Equations proposed were validated against literature experimental data for EB-water mixture.

Keywords: pervaporation, juice, aroma, membrane, simulator

## 1. Introduction

The fresh flavor of orange juice is sensitive to heat treatment used during processing. The juice undergoes compositional changes that invariably cause a negative quality impact in the original flavor and aroma of the fresh juice. Of the volatile components important to flavor, esters and aldehydes are the primary contributors to fresh orange juice, although other components could also be important (Nisperos-Carriedo and Shaw 1990, Shaw et al. 1993). Multivariate relationships between chemical composition and sensory characteristics were investigated and conclusions were elaborated on basis of measurements on orange juice. Acetaldehyde, ethyl-3-OH-hexanoate, valencene, ethyl butyrate (EB), and ethyl caproate were pointed as the largest sensory impact compounds. If one had to choose, the most important would be ethyl butyrate based on its level relative to its sensory threshold (Burgard 1995).

Pervaporation has been considered an interesting alternative process for the current industrial options for aroma recovery, distillation, partial condensation, solvent extraction, adsorption, or a combination thereof. It is a separation process based on a selective transport through a dense membrane associated with a recovery of the permeate from the vapour phase. A feed liquid mixture contacts one side of a membrane; the permeate is removed as a vapor from the other side. Transport through the membrane is induced by the vapor pressure difference between the feed solution and the permeate vapor. This vapor pressure difference can be maintained in several ways. In the laboratory, a vacuum pump is usually used to draw a vacuum on the permeate side of the system. Industrially, the permeate vacuum is most economically generated by cooling the permeate vapor, causing it to condense; condensation spontaneously creates a partial vacuum. The most accepted mechanism transport model is the solution-diffusion model which can be divided into three steps, (a) sorption into the membrane at the upstream side, (b) diffusion through the membrane, and (c) desorption into a vapour phase at the downstream side. Thus, selectivity and permeation rate are governed by solubility and diffusivity of each component of the feed mixture to be separated. Solubility is a thermodynamic property and diffusivity is a kinetic property. More recently, pervaporation has been used to the extraction of aroma compounds biotechnologically produced or recovered from perfumery wastes and PDMS (polydimethylsiloxane) was reported as the most used material in the available literature studies on aroma recovery (Baudot and Marin 1997, Baker 2004, Huang 1991, Pereira et al. 2006). The aim of this work was to simulate organophilic pervaporation process to recover ethyl butyrate from a diluted aqueous binary mixture. A FORTRAN software named PERVAP based on a predictive pervaporation modelling was applied (Alvarez 2005; Alvarez et al. 2003, 2006). PERVAP was, originally, developed and validated for non-diluted mixtures. Therefore, this is the first process study using the software in diluted conditions.

## 2. Materials and Methods

### *PERVAP software*

The software was developed using Fortran (Compaq Visual Fortran Professional Edition 6.6.a) in Separation Process Development Laboratory (LDPS) at State

University of Campinas (Alvarez, 2005). The mathematical model is based on solution-diffusion mechanism. Predictions were applied for the following parameters: (a) the diffusion coefficient in the membrane is predicted by free-volume theory; (b) binary interaction parameters between the components and polymer by group contribution method, value used for predicting membrane diffusion coefficient; (c) the activity coefficients in feed (upstream) obtained by UNIFAC group contribution method. d) EB free-volume parameters were estimated using pure component viscosity and temperature data available in literature (Djojoputro 2005).

#### *Inputs used for simulating the process*

The PDMS membrane (GKSS Research Centre, Germany) and process parameters were investigated using experimental data as comparative standard (Sampranpiboon et al. 2000). The operational conditions for simulation were: operating temperature: 303.15 K; downstream pressure (permeate): 0.3997 kPa and membrane thickness: 10  $\mu\text{m}$ .

#### *Diffusion coefficient prediction in the membrane*

The diffusion coefficient of component  $i$  (EB) in the membrane,  $D_i^m$ , is predicted by the free-volume theory described by the equation (1) (Vrentas and Duda, 1977 and 1979):

$$D_i^m = D_0(1-\phi)^2(1-2\chi\phi)\exp\left(\frac{-E}{RT}\right)\exp\left(-\frac{\omega_1\hat{V}_1^* + \xi\omega_2\hat{V}_2^*}{\frac{K_{11}}{\gamma}\omega_1(K_{21}-T_{g1}+T) + \frac{K_{12}}{\gamma}\omega_2(K_{22}-T_{g2}+T)}\right) \quad (1)$$

#### *Estimation of free-volume parameters for solvent and PDMS*

The six free-volume parameters (three for each solvent and three for polymer) were calculated applying the following theories: (a) PDMS:  $(K_{22} - T_{g2})$  and  $K_{22}/\gamma$  were calculated by Hong (1995) using viscosity and temperature data of pure polymer, this approach is expressed in terms of the Williams-Landel-Ferry (Williams et al., 1955) equation. The free-volume parameters for polymers are simply related to the WLF constants as proposed by Duda et al. (1982). (b) EB and Water:  $(K_{21} - T_{g1})$  and  $K_{21}/\gamma$  were calculated for each component. These parameters were obtained using viscosity and temperature data of pure component. Doolittle (1951) postulated that viscosity should be related to the amount of free volume in a system and derived the Vogel (1921) equation from free volume concepts. Hong (1995) presented an equation adopting Doolittle's expression and using nomenclature of Vrentas and Duda (1977, 1979) leads to equation (2) for the solvent viscosity. (c)  $V_1^*$  and  $\hat{V}_2^*$ : The two critical volumes were estimated as the specific volumes of the solvent and polymer at 0K

using group contribution methods (Haward, 1970 and Hong, 1995).  $\xi$  and  $\phi_l$  were calculated applying concepts presented by Vrentas and Duda (1977, 1979).

$$\ln \eta_1 = \ln A_1 + \frac{(\gamma \hat{V}_1^* / K_{11})}{(K_{21} - T_{g1}) + T} \quad (2)$$

### *Prediction of binary interaction parameter ( $\chi$ ) for EB-PDMS and water-PDMS*

The prediction of binary interaction parameter for EB/polymer was accomplished using group contribution equation of state. In this approach is assumed that the molecular binary interaction parameter ( $\chi_{12}$ ) is constant and independent of temperature and concentration. The  $\chi_{12}$  is calculated with binary group parameters  $m$  and  $n$ , and group binary interaction parameters  $\alpha_{mn}$ , expressed in equation (3) and (4) (High and Danner 1989):

$$\chi_{12} = \sum_m \sum_n \Theta_m^{(M)} \Theta_n^{(M)} \alpha_{mn} \quad (3)$$

$$\Theta_m^{(M)} = \frac{\sum_i n_m^{(i)} Q_m}{\sum_k \sum_i n_k^{(i)} Q_k} \quad (4)$$

where  $\Theta_m^{(M)}$  is the superficial group fraction area of  $m$  in the mixture,  $n_m^{(i)}$  is the number of groups ( $m$ ) of component  $i$  and  $Q_m$  is the superficial area parameter of group  $m$ . The group surface parameter UNIFAC,  $Q_k$ , were calculated as presented in Reid. et al. (1987).

### *Overview of fundamental process modeling equations*

In PERVAP software the mass transport in boundary layer is neglected. Thus, the following equations (5 and 6) are assumed to calculate permeate fluxes for component  $i$  (EB) and  $j$  (water):

$$J_i = \frac{D_i^m}{\ell \bar{\gamma}_i^m} \left( x_{i,F} \gamma_{i,F} - \frac{x_{i,F} \alpha p}{1 + (\alpha - 1)x_{i,F}} \right) \quad (5)$$

$$J_j = \frac{D_j^m}{\ell \bar{\gamma}_j^m} \left( x_{j,F} \gamma_{j,F} - \frac{(1 - x_{i,F}) p P_i^{sat}}{P_j^{sat} [1 + (\alpha - 1)x_{i,F}]} \right) \quad (6)$$

The selectivity was calculated on basis of flux equations of components  $i$  and  $j$  using equation (7):

$$\alpha_{i,j} = \frac{D_i^m \bar{\gamma}_j^m \left( \gamma_{i,F} x_{i,F} + \frac{x_{i,F} \alpha p}{1 + (\alpha - 1)x_{i,F}} \right) (1 - x_{i,F})}{D_j^m \bar{\gamma}_i^m \left( \gamma_{j,F} x_{j,F} - \frac{(1 - x_{i,F}) p P_i^{sat}}{P_j^{sat} [1 + (\alpha - 1)x_{i,F}]} \right) x_{i,F}} \quad (7)$$

### 3. Results and Discussion

The predicted and estimated free-volume parameters data applied to run the simulations are presented in Table 1. The parameters presented in extended abstract before this version were here corrected. Ethyl butyrate permeate fluxes presented a satisfactory adjustment compared to experimental data. Permeate flux profile is illustrated in Figure 1. Water permeate fluxes are presented in Figure 2. For water the simulated fluxes remained practically constant and did not presented a “good” adjustment compared to experimental data. It does not mean that the model is not capable to simulate process with reliability enough to provide preview directions for pilot or even industrial trials.

Components	$\hat{V}_1^*$	$K_{11}/\gamma$	$K_{21} - Tg_1$	$Do$	$\chi$	$\xi$	$E$
EB	0.919	$1.090 \times 10^{-3}$	-35.00	$0.50 \times 10^{-4}$	0.038	2.096	0
water	1.071	$2.180 \times 10^{-3}$	-152.29	$8.55 \times 10^{-4}$	0.003	0.236	0

Table 1- Free-volume parameters estimated and predicted applied for predicting the diffusion coefficient.

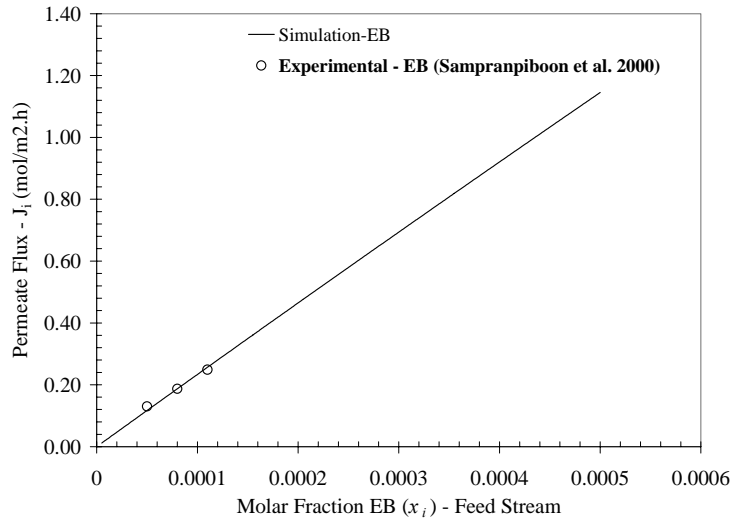


Figure 1 – Permeate fluxes of ethyl butyrate at different feed concentration.

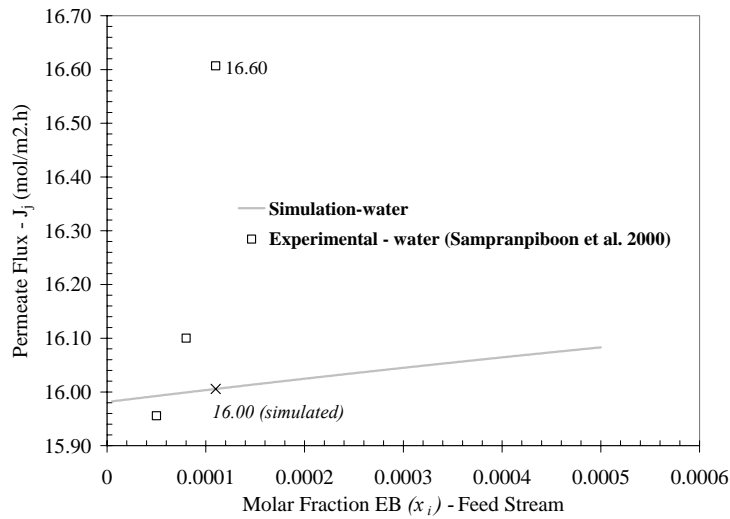


Figure 2 – Permeate flux of water at different ethyl butyrate feed concentration.

Several studies have reported that the water flux remains constant, i.e., it is independent of the concentration of organic components for the case of dilute solutions (Pereira et al. 2006). The simulated selectivity results did not fit precisely in experimental results because the permeate water flux deviation. Selectivity results are plotted in Figure 3. Membrane presented a preferential selectivity for EB and relatively low fluxes if compared to water fluxes. On the other hand, the separation is better as lower as the concentration EB, consequently, higher selectivity values are expected.

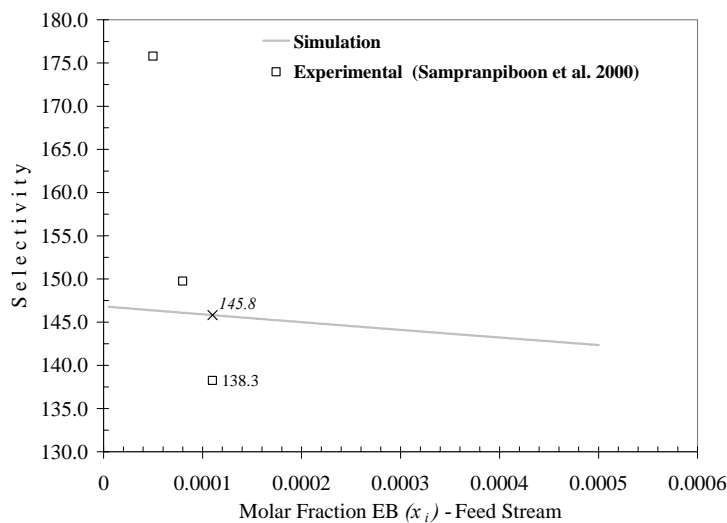


Figure 3 – Pervaporation process – Selectivity (Separation Factor)

#### **4. Conclusion**

Pervaporation technique is a promising technique for concentrating aroma fraction or even to recovery key compounds directly from diluted food industry streams (e.g., fruit juices). Environmental application for separating organic compounds can also be considered (e.g., phenol removal from wastewater). The PDMS membrane presented a satisfactory result in experimental and simulated study. The program outputs encourage future investigations to evaluate process performance for different binary systems. The software can be a valuable tool to understand variables behavior at many process scenarios. Future PERVAP improvement actions must consider the boundary layer modeling possibility since the version applied in this work neglected this diffusion phenomenon. The capability to simulate multi-component mixtures will be an important research issue.

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#### **Nomenclature**

$D_i^m$  = diffusion coefficient of component  $i$  in membrane ( $\text{cm}^2/\text{s}$ )

$D_j^m$  = diffusion coefficient of component  $j$  in membrane ( $\text{cm}^2/\text{s}$ )

$D_0$  = preexponential factor ( $\text{cm}^2/\text{s}$ )

$E$  = energy required to overcome attractive forces from neighboring molecules ( $\text{cal/mol}$ )

$J$  = permeate flux ( $\text{mol}/\text{m}^2 \text{ h}$ )

$K_{11}$  = solvent free-volume parameter ( $\text{cm}^3/\text{g K}$ )

$K_{21}$  = solvent free-volume parameter (K)

$K_{22}$  = polymer free-volume parameter (K)

$K_{12}$  = polymer free-volume parameter ( $\text{cm}^3/\text{g K}$ )

$\ell$  = membrane thickness (m)

$p$  = permeate relative pressure

$P^{sat}$  = vapor pressure (kPa)

$Q_m$  = surface area parameter of group  $m$

$Q_k$  = group surface parameter UNIFAC

$T$  = temperature (K)

$T_{g1}$  = solvent glass transition temperature (K)

$T_{g2}$  = polymer glass transition temperature (K)

$x_{i,F}, x_{j,F}$  = mole fraction of component  $i$  and  $j$  in the feed stream

$\hat{V}_1^*$  = specific critical hole free-volume of solvent required for jump ( $\text{cm}^3/\text{g}$ )

$\hat{V}_2^*$  = specific critical hole free-volume of polymer required for jump ( $\text{cm}^3/\text{g}$ )

#### *Greek Letters*

$\gamma$  = overlap factor for free-volume

$\gamma_{i,F}$   $\gamma_{j,F}$  = activity coefficient of components  $i$  and  $j$  (calculated by UNIFAC)

$\bar{\gamma}_i^m$  = activity coefficient in membrane for component  $i$  (m<sup>3</sup>/mol)

$\bar{\gamma}_j^m$  = activity coefficient in membrane for component  $j$  (m<sup>3</sup>/mol)

$\omega$  = mass fraction

$\xi$  = ratio of critical molar volume of solvent jumping unit to that of polymer jumping unit

$\phi$  = volume fraction

$\chi$  = interaction parameter of Flory-Huggins

$\Theta_m^{(M)}$  = surface area fraction of group  $m$  in mixture

$\Theta_n^{(M)}$  = surface area fraction of group  $m$  in mixture

$\alpha$  = selectivity

$\alpha_{mn}$  = group binary interaction parameters

### Subscripts

$i$  = ethyl butyrate

$j$  = water

$l$  = solvent

$2$  = polymer

## 5. References

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