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Recovery of key components from real flavor concentrates by pervaporation

Manjuan She, Sun-Tak Hwang *

Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

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Abstract

Experimental study was conducted on pervaporation processes for recovering key flavor compounds from aqueous flavor systems for three real flavor systems (apple essence, orange aroma, and black tea distillate). Both continuous and batch operations were carried out. Key flavor compounds were identified and successfully recovered from the real flavor systems that were tested. Mass transfer equations for pervaporation were derived based on the nonequilibrium thermodynamics principles [L. Onsager, Reciprocal relations in irreversible process I, Phys. Rev. 37 (1931) 405; L. Onsager, Reciprocal relations in irreversible process II, Phys. Rev. 38 (1931) 2265]. Mathematical models for process simulation were developed. A material balance was applied to calculate recovery and loss percentages of flavor compounds. Flavor loss rate due to evaporation leakage was determined by fitting experimental data into a developed batch operation model. Separation performance for long-term operation was predicted based on the process simulation model. Significant flavor loss was observed in the pervaporation recovery process. Pervaporation design with better sealing and collection methods was highly recommended for process scale-up.

Keywords: Real flavor recovery; Pervaporation; Nonequilibrium thermodynamics; Process simulation

1. Introduction

In most developed countries there is a strong potential market for concentrated flavor products. Especially in the food and beverage industry, concentrated flavors are in demand because of prolonged shelf life, reduced packaging volume, and lower distribution and storage costs [3]. Food and beverage processing results in flavor change, so the addition of concentrated flavors is required to restore the original flavors to the final product [4]. Essential flavor ingredients are extracted from concentrated fruit and vegetable juices and can contribute from 35 to 70% of the flavor in different food products [5]. In addition, many natural flavor sources such as spices, herbs, fruits, and vegetables, have only one or several key compounds that significantly affect their perceived flavors. These compounds are called characteristic impart compounds (CICs), or simply key flavor compounds, and are main materials for the creation of new flavors. Flavor concentration is also an important method to recover CICs from natural resources [6].

Pervaporation for flavor concentration has been developed rapidly in the past 15 years. Researchers have successfully separated over 50 flavor compounds from model aqueous solutions in the laboratory and reported enrichment factors up to 100 [7]. At Lund University (Sweden), researchers from the food engineering department performed a series of studies in this area. In 1991, they began to concentrate apple juice aroma by pervaporation. They concentrated twelve selected flavor compounds and determined the enrichment factors. They found the alcohols had the lowest enrichment factors (2–22), the aldehydes had the medium values (16–67), and the esters had the highest enrichment factors, up to 100 [8]. They compared separation performances of six pervaporation membranes (PDMS-1060, PDMS-1070, PDMS-PT1100, POMS-PEI, POMS-PVDF and PEBA) and proved that the PDMS-PT1100, POMS-PEI, and POMS-PVDF membranes were the best ones for the pervaporation of a model apple juice aroma solution [9]. Benzaldehyde is an important flavor compound with the odor of bitter almond. Lamer et al. used pervaporation to concentrate benzaldehyde extracts and reported an enrichment factor up to 100 [10]. Baudot et al. [11] diluted two dairy flavor compounds (methylthiobutanoate and diacetyl) in aqueous solutions and concentrated them through a GFT silicalite-filled silicone composite membrane

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* Corresponding author. Tel.: +1 513 556 2791; fax: +1 513 556 1522.
E-mail address: shwang@alpha.che.uc.edu (S.-T. Hwang).

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and a GKSS PEBA homogeneous membrane. Rajagopalan and Cheryan [12] at the University of Illinois studied pervaporation of methyl anthranilate—a key flavor component of concord grapes—using three different membranes (PDMS-PC, PEBA, and PDMS-Zeolite membranes). They discovered that the fluxes and selectivities decreased linearly with an increase in downstream pressure, and increased with operating temperature. This relationship was not satisfied when the feed concentration was beyond 50 ppm where concentration polarization became serious [12]. The reason was that Rajagopalan and Cheryan did not consider the concentration polarization effect [12]. A research group in Germany concluded that pervaporation could be highly suitable for continuous recovery of very complex and delicate aromas during microbial fermentation [13].

Most of the above research work was done in the laboratory using model flavor solutions. Only few pervaporation reports of real flavors can be found in literature. There are two difficulties in the pervaporation concentration process to maintain the original flavor. One is how to keep all important flavor ingredients including some trace compounds. The other is how to retain the relative concentrations of different flavor compounds. In fact, none of the current concentration methods is able to exactly keep the original flavor after concentration; hence, flavor adjustment is necessary after concentration processes. The objective of real flavor pervaporation is to recover key flavor compounds as much as possible. In order to test and scale up the recovery process, both continuous and batch processes on real flavor pervaporation have to be carried out. In addition, process simulation is necessary for recovery performance prediction and future process scale-up. Material balance calculation is important for yield estimation and economic evaluations.

2. Theory

Based on the theory of nonequilibrium thermodynamics [1,2,14,15], the organic flux in a binary organic-water pervaporation system can be written as

$$N_i = L_1(P_i^{\mathrm{sat}}\gamma_i^{\infty}x_i - Py_i) + L_2(P_{\mathrm{w}}^{\mathrm{sat}} - Py_{\mathrm{w}}) + L_3[P_{\mathrm{u}} - (L_4P_i^{\mathrm{sat}} + P_{\mathrm{w}}^{\mathrm{sat}} - L_4P_{\mathrm{w}}^{\mathrm{sat}})] \quad (1)$$

where L_1, L_2, L_3 and L_4 are phenomenological coefficients. P_i^{sat} and $P_{\mathrm{w}}^{\mathrm{sat}}$ are the saturation vapor pressures of organic and water. P_{u} and P are the upstream and downstream pressures, respectively. γ_i^{∞} is the activity coefficient of a flavor organic at infinite dilution, x_i is the mole fraction of organic in the feed solution, and y_i and y_{w} are the mole fractions of organic and water in the permeate products.

The previous experimental results [16,17] indicated that the main driving force for the organic flux in pervaporation of dilute flavor organics was the organic fugacity difference. If the partial pressure of organics in downstream P_i can be neglected ($P_i \ll P_i^{\mathrm{sat}}\gamma_i^{\infty}x_i$) when operated at low downstream pressure, the organic flux Eq. (1) can be simplified:

$$N_i = \frac{Q_i}{l}P_i^{\mathrm{sat}}\gamma_i^{\infty}x_i \quad (2)$$

The above equation can be applied to multicomponent dilute flavor pervaporation if coupling effects are negligible [16]. The organic permeability Q_i is defined as

$$Q_i = L_1 l \quad (3)$$

where l is the thickness of the membrane.

Similar results can be obtained for the water flux. Enrichment factor for continuous steady-state pervaporation is expressed in the following equation:

$$\beta_i \equiv \frac{C_{i\mathrm{p}}}{C_{i\mathrm{b}}} \approx \frac{y_i}{x_i} \quad (4)$$

For the batch operations, a shell mass balance equation can be obtained as follows:

$$(VC_{\mathrm{tot}}x_i)|_{t=t_0} = N_iA_{\mathrm{p}}\Delta t + K_{\mathrm{L}i}x_i\Delta t + (VC_{\mathrm{tot}}x_i)|_{t=t_0+\mathrm{d}t} \quad (5)$$

where V is the volume of the feed solution, A_{p} is the membrane area, and C_{tot} is the total molar concentration of the feed solution (for dilute pervaporation C_{tot} becomes approximately the pure water molar density). $K_{\mathrm{L}i}$ is introduced as the flavor loss rate in the unit of mol/s, which represents how quickly the flavor organic compound is lost due to the system leakage, partial condensation, and incomplete collection in the pervaporation experiment. The following expression was derived from the combination of Eqs. (2) and (5). The total volume flux for dilute organic pervaporation hardly changes and it is practically the same as water flux. Therefore, the water concentration change in the downstream permeate product is negligible [16]:

$$-\left(\frac{K_{\mathrm{L}i}}{C_{\mathrm{tot}}} + a\right)x_i = V\frac{\mathrm{d}x_i}{\mathrm{d}t} \quad (6)$$

After integration, the above equation becomes

$$\ln\left(\frac{x_i}{x_{i0}}\right) = \left(\frac{a + (K_{\mathrm{L}i})/(C_{\mathrm{tot}})}{K_{\mathrm{V}}}\right)\ln\left(1 - \frac{K_{\mathrm{V}}}{V_0}t\right) \quad (7)$$

In Eqs. (5)–(7), x_i is the concentration of residue in feed tank, x_{i0} is the initial mole fraction of the flavor at the beginning of the batch operation, V_0 is the initial volume of the feed solution, and t is the operation time. The quantity a is a permeation rate constant that is defined by

$$a = \frac{Q_iP_i^{\mathrm{sat}}\gamma_i^{\infty}A_{\mathrm{p}}}{lC_{\mathrm{tot}}} - K_{\mathrm{V}} \quad (8)$$

where K_{V} is the total permeation volume flow rate ($\mathrm{d}V = -K_{\mathrm{V}}\mathrm{d}t$). For a short-term batch operation, the following equation results from the Taylor series expression of Eq. (7) after truncating the higher order terms [16]:

$$\ln\left(\frac{x_i}{x_{i0}}\right) \approx -\left(\frac{a + (K_{\mathrm{L}i})/(C_{\mathrm{tot}})}{V_0}\right)t \quad (9)$$

For predicting the recovery performance in a long-term operation, the residue percentage can be derived from Eq. (7) as follows: