



# Concentration by pervaporation of brown crab volatile compounds from dilute model solutions: Evaluation of PDMS membrane

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## ABSTRACT

Pervaporation experiments with PERVAP™ 4060 membrane have been performed to study its ability to concentrate some aroma compounds identified in the brown crab boiling juice from a model dilute aqueous solution. The effect of feed concentration, pervaporation temperature and permeate pressure on the pervaporation performance of the membrane has been analyzed. The results obtained with PERVAP™ 4060 membrane were compared with experiments performed in a previous work with a POMS/PEI membrane. Membrane material seems to be a key factor in the permeate aroma profile. The presence of non-volatile compounds, such as sodium chloride, in brown crab boiling juice slightly improves pervaporation performance in the concentration range studied in this work. Batch pervaporation experiments prove that the flavor loss percentage during long operation time is high, especially for the most volatile compounds. Additionally, it has been shown that pervaporation can be significantly improved by modifying the permeant circuit by means of two stage condensation step.

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## 1. Introduction

Shellfish flavor is a high value food product. The liquid effluent of the seafood industry, produced during boiling process, contains important amounts of flavor components [1]. Brown crabs are found in the Eastern Atlantic and are heavily exploited commercially, being available throughout the year. This work is part of a wider study to consider the conversion of the brown crab effluent produced during boiling into a valuable volatile concentrate.

Membrane separation techniques represent a potential pathway for the production of a natural aroma concentrate and a disposable effluent [2,3]. In a previous study [4], organophilic pervaporation through a polyoctylmethylsiloxane membrane was shown to be able to concentrate some compounds of the brown crab boiling juice from a model dilute aqueous solution. In this work, pervaporation through a polydimethylsiloxane membrane has been performed to compare the ability of the two polymers, POMS and PDMS, to recover some aroma compounds found in the brown crab boiling juice from model dilute aqueous solutions.

The effect of some important variables that determine the final aroma profile, such as feed concentration, pervaporation temperature and permeate pressure has been studied. Brown crab boiling juice contains organic compounds and non-volatile compounds. The influence of the presence of non-volatile

components, such as salts (e.g.: sodium chloride) was also analyzed by varying the salt content in the feed solution.

For industrial applications, batch operation is preferred to a continuous operation if the aroma recovery is a short-term operation with relatively small amount of extracts [5]. In this work, batch process has been performed to recover aroma compounds from model solutions.

Finally, fractionation experiments have been also performed to improve the pervaporation performance by using a two condensation step at the permeate side.

## 2. Theory

Solution/diffusion model is used to describe the transport of permeating components through the membrane being proportional to the difference in partial vapor pressure at both sides of the membrane according to Eq. (1) [6]:

$$J_i = Q_{ov,i} (x_i \gamma_i p_i^s - y_i p_p) \quad (1)$$

where  $J_i$  is the partial permeation flux of component  $i$ ,  $Q_{ov,i}$  is its pressure-normalized permeation flux (permeance),  $x_i$  is its mole fraction in the feed,  $\gamma_i$  is its activity coefficient,  $p_i^s$  is its saturation vapor pressure at the feed temperature,  $y_i$  is its mole fraction in the permeate and  $p_p$  is the permeate pressure. In case of pervaporation of dilute aqueous solutions, activity coefficients at infinite dilution ( $\gamma_i^\infty$ ) are used as feed-side activity coefficients. In this work, the activity coefficients at infinite dilution in water

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were obtained from previous work in which activity coefficients at infinite dilution were obtained by using the headspace gas chromatography technique [7].

The separation performance of a pervaporation membrane, in case of dilute aqueous solutions, can be described in terms of the enrichment factor. The enrichment factor of a given component is the relationship between its concentration in permeate and the feed:

$$\beta_i = w_{i,p} / w_{i,f} \quad (2)$$

In dilute systems, as aroma recovery systems, the solvent enrichment factor is close to one; therefore aroma enrichment factors of organic compounds can be considered equal to the corresponding separation factors. There is usually an opposite trend between permeation flux and separation factor, i.e.: when one factor increases the other decreases. This way, a pervaporation separation index (P.S.I.) has been defined as a measure of the separation ability of a membrane [8]:

$$\text{P.S.I.} = J_{tot} \cdot \text{Separation factor} \quad (3)$$

To describe the batch operation systems, the following expression inferred by She and Hwang [5] was used:

$$\ln\left(\frac{x_i}{x_{i,o}}\right) = \left(-\frac{a + (K_L/C_{tot})}{V_o}\right)t \quad (4)$$

She and Hwang [5] introduced the term  $K_L$  to consider the flavor loss rate and represents how quickly the organic compound is lost due to several reasons such as system leakage, partial condensation or incomplete collection in the pervaporation system. In Eq. (4)  $x_i$  is the mole fraction of component in the feed tank,  $x_{i,o}$  is the initial mole fraction of component at the beginning of the process,  $V_o$  is the initial volume of the feed solution, and  $t$  is the operation time. The parameter  $a$  is defined as:

$$a = \frac{Q_{ov,i} p_i^s \gamma_i^\infty A}{C_{tot}} - K_V \quad (5)$$

where  $C_{tot}$  is the total mole concentration of the feed solution (for dilute systems  $C_{tot}$  becomes approximately the pure water molar density),  $A$  is the membrane area and  $K_V$  is the total permeation volume flow rate ( $dV = -K_V dt$ ). According to She and Hwang [5], the residue percentage and recovery percentage are calculated by Eqs. (6) and (7) respectively:

$$\text{residue (\%)} = \left(1 - \frac{K_V}{V_o} t\right)^{1 + (a + K_L/C_{tot})/K_V} 100 \quad (6)$$

$$\text{recovery (\%)} = \frac{1 + a/K_V}{1 + (a + K_L/C_{tot})/K_V} \left[1 - \left(1 - \frac{K_V}{V_o} t\right)^{1 + (a + K_L/C_{tot})/K_V}\right] 100 \quad (7)$$

### 3. Experimental section

#### 3.1. Materials

An organophilic dense membrane was used in this study: PERVAP™ 4060 (SulzerChemtech®, Switzerland), a membrane whose active layer is based on polydimethylsiloxane (PDMS).

A multicomponent dilute aqueous solution was prepared with seven selected volatile compounds [4] belonging to different chemical classes: 1-octen-3-ol (Sigma Aldrich, 98%), 1-penten-3-ol (Sigma Aldrich, 99%), 3-methylbutanal (Sigma Aldrich, 97%), hexanal (Sigma Aldrich, 98%), benzaldehyde (Sigma Aldrich, ≥ 99%), 2,3-pentadione (Sigma Aldrich, 98%) and ethyl acetate (Sigma Aldrich, HPLC grade). Some thermodynamic properties of the selected compounds are listed in Table 1.

**Table 1**

Physicochemical properties of the volatile compounds (MW=molecular weight, BP=boiling point,  $p^s$ =saturation pressure,  $\gamma^\infty$ =activity coefficient at infinite dilution,  $H$ =Henry's constant).

Compound	MW (g/mol)	BP (°C)	$p^s_{26\text{ °C}}$ (Pa)	$\gamma^\infty_{26\text{ °C}}$	$H_{26\text{ °C}} \times 10^{-4}$ (Pa)
1-Octen-3-ol	128.2	174–5	65	1779	11.6
1-Penten-3-ol	86.1	114.4	1348	38	5.1
3-Methylbutanal	86.1	92.5	7035	127	89.3
Benzaldehyde	106.1	178.8	181	504	9.1
2,3-Pentanedione	100.1	108	2918	133	38.8
Hexanal	100.2	128.3	1540	599	92.3
Ethyl acetate	88.1	77.1	13,045	62	80.9

#### 3.2. Pervaporation experiments

Pervaporation experiments were performed with a plate and frame laboratory stainless steel permeation cell (Sulzer Chemtech®) with an effective membrane area in contact with the feed mixture of 170 cm<sup>2</sup> [9]. The temperature of the feed liquid mixture was kept constant ( $\pm 0.5$  °C) by using a thermostat to heat the stirred tank feed reactor. The permeate was condensed on two parallel glass cold traps cooled by liquid nitrogen to ensure that permeate was fully collected. Permeate pressure was regulated with an air-inlet located between the condensers and the vacuum pump. For steady state operation the feed reactor has a 5 L capacity. This way, due to the small amount of permeate product, the concentration of the volatile compounds in the feed tank was kept approximately constant along operation. The feed flow rate was set to 70 kg h<sup>-1</sup>. This flow was enough to avoid concentration polarization in the concentration range studied in this work. For unsteady state operation the ratio membrane area to initial feed volume ( $A/V_o$ ) was higher than for steady state operation; thus feed concentration of volatile compounds continuously decreases as pervaporation takes place. In case of fractionation at the permeate side, two condensers were placed in series in one of the two parallel permeate circuits. The first condenser was cooled by a refrigerant bath using a Julabo FP50 cryostat. The second condenser was cooled with liquid nitrogen, acting as a total condenser. The chemical stability of the membrane was checked by measuring pure water flux at reference operating conditions.

#### 3.3. Sample analysis

Permeate and feed concentration was measured off-line using a Hewlett Packard (6890) gas chromatograph (GC) equipped with series connected thermal conductivity (TCD) and flame ionization (FID) detectors. Helium, 99.999% pure, was used as carrier gas. The GC column was a 007 FFAP 25 m × 0.25 mm bonded phase fused silica capillary column. The injector and detectors were kept at 200 °C and 250 °C respectively. The oven was operated at programmed temperature, from 40 °C to 220 °C. 1-hexanol was used as internal standard for analysis of the sample.

### 4. Results and discussion

First, the effect of different operating variables, such as feed concentration, pervaporation temperature and permeate pressure, on the pervaporation performance of PERVAP™ 4060 membrane is presented. Further, these results are compared with a previous work [4], where pervaporation was carried out with a POMS/PEI membrane. Afterwards, the results obtained in batch operation are presented. Then, the effect of sodium chloride is analyzed by varying the salt concentration in the feed.

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