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^{TM} 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^{TM} 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

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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.

Keywords: volatile compounds, pervaporation, salt effect, PDMS membrane

1. Introduction

Shellfish flavour is a high value food product. The liquid effluent of the seafood industry, produced during boiling process, contains important amounts of flavour 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 analysed 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 equation 1 [6]:

$$J_i = Q_{OV,i}\left(x_i \gamma_i p_i^s - y_i p_p\right) \tag{1}$$

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

$$\beta_i = w_{i,p} / w_{i,f} \tag{2}$$

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]:

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

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

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

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 i in the feed tank, $x_{i,o}$ is the initial mole fraction of component i 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:

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

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 equations (6) and (7) respectively:

$$\text{residue}\,(\%) = \left(1 - \frac{K_V}{V_O}t\right)^{1+\left(a+K_{L,i}/C_{tot}\right)/K_V} \cdot 100 \qquad (6)$$

$$\text{recovery}\,(\%) = \frac{1 + a/K_V}{1 + \left(a + K_{L,i}/C_{tot}\right)/K_V}\left[1 - \left(1 - \frac{K_V}{V_O}t\right)^{1+\left(a+K_{L,i}/C_{tot}\right)/K_V}\right]\cdot 100 \qquad (7)$$

3. Experimental section

3.1. Materials

An organophilic dense membrane was used in this study: PERVAP^{TM} 4060 (Sulzer Chemtech$^\circledR$, 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.

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^2 [9]. The temperature of the feed liquid mixture was kept constant ($\pm$ 0.5 ºC) 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^{-1}. 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/Vo) 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 ºC and 250ºC respectively. The oven was operated at programmed temperature, from 40ºC to 220ºC. 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^{TM} 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 analysed by varying the salt concentration in the feed. Finally some preliminary fractionation results by using two condensation steps are discussed.

4.1. Evaluation of PERVAP^{TM} 4060 membrane performance.

Effect of feed concentration

The effect of feed concentration was investigated in the range of 0.1 to 50 ppm at a fixed pervaporation temperature (26ºC) and permeate pressure (300 Pa). Since experiments were carried out at very dilute concentration, total permeation flux was close to water permeation flux and remained almost constant (0.0054 mol/m^{2}s) whatever the volatile compounds feed concentration.

Figure 1 shows the organic compounds permeation fluxes as a function of its feed concentration. It can be observed a linear relationship for all the compounds studied in this work (r^2 > 0.99 except for 2,3-pentanedione that shows a r^2 = 0.97). Since activity

coefficients at infinite dilution are constant, and the polymeric membrane swelling can be considered negligible, the pressure-normalized permeation flux (permeance) of the organic compounds and water, and consequently the separation factor, will remain constant.

Table 2 reports the enrichment factors and permeances obtained through the PDMS membrane. Benzaldehyde was found to have the highest enrichment factor and permeance. This way, Baudot and Marin [10] assessed that pervaporation membranes are very permselective for aldehydes containinig a benzene ring, which enhances their hydrophobicity and, consequently, their solubility in the pervaporation membrane. Ethyl acetate and 1-octen-3-ol also exhibit high separation factors. On the other hand, the selectivity for 2,3-pentanedione was found to be the lowest, with a separation factor value of 10.

Effect of pervaporation temperature

The operating temperature was varied in the range 26 °C to 40 °C. The experiments were carried out at three different feed concentrations (1, 5 and 10 ppm) and a fixed permeate pressure (300 Pa). Water permeation flux increased exponentially from 0.0054 mol/m^{2}s to 0.012 mol/m^{2}s in the temperature range studied in this work.

Figure 2 shows the effect of temperature on volatile compounds permeation flux at an organic feed concentration of 10 ppm. The effect of feed temperature can be described by an Arrhenius type equation:

$$J_i = J_{i,o} \cdot \exp\left(-\frac{E_{a,i}}{RT}\right) \qquad (8)$$

where $E_{a,i}$ is the apparent activation energy of permeation, $J_{i,o}$ the preexponential factor and T the absolute temperature. Table 3 reports the apparent activation energies for

permeation of aroma compounds and water for the PDMS membrane. This parameter characterizes the overall effect of temperature on the permeability and the driving force for permeation [11]. A higher value of the apparent activation energy indicates a more sensitive behaviour towards temperature changes. Table 3 shows that $E_{a,i}$ for most of the organic compounds is higher than that of water, except for benzaldehyde and ethyl acetate. However, these differences are not high. Therefore, it cannot be generalized for PDMS membrane that enrichment factors of volatile compounds increase with temperature, although for some of the volatile compounds, such as 1-octen-3ol, the increase of the enrichment factor with temperature is remarkable. This behaviour can be observed in Figure 3 that shows the enrichment factor at the four temperatures studied in this work at a fixed feed concentration of 10 ppm for all the volatile compounds. The effect of temperature on selectivity depends on changes of sorption of organic compounds on the membrane and its diffusion through the membrane. According to Feng and Huang [11] the activation energy of permeation, E_p, which characterizes the temperature dependence of the membrane, can be estimated by subtracting the heat of vaporization from the calculated apparent activation energy ($E_p = E_a - \Delta H_v$). The calculated activation energy follows the order: $E_{p,1\text{-penten-3-ol}}$ (-8.8 kJ/mol) < $E_{p,\text{ethylacetate}}$ (-8.6 kJ/mol) < $E_{p,\text{benzaldehyde}}$ (-5.3 kJ/mol) < $E_{p,\text{hexanal}}$ (-1.8 kJ/mol) < $E_{p,\text{ water}}$ (-0.5 kJ/mol) < $E_{p,1\text{-octen-3-ol}}$ (10.5 kJ/mol) < $E_{p,3\text{-methylbutanal}}$ (17.0 kJ/mol) < $E_{p,2,3\text{pentadione}}$ (28.1 kJ/mol). Negative values of E_p indicate that the membrane's permeability decreases with increasing temperature. E_p can be expressed as the activation energy of permeating compounds to diffuse through the membrane, E_D, plus the enthalpy of dissolution, ΔH_s ($E_p = E_D + \Delta H_s$) [11]. Enthalpy of dissolution is usually negative due to exothermic

sorption process; however the diffusion coefficient increases with increasing temperature. According to the level of contribution of both factors, E_p will be positive or negative [12]. Considering that for some of the volatile compounds the value of the activation energy of permeation is negative, it can be concluded that for PDMS membrane, temperature has greater effects on sorption than on diffusion. Similar results were obtained by She and Hwang [13] for PDMS membranes.

This fact can be also observed in Figure 4. This Figure shows the ratio of partial permeation fluxes obtained at 40 ºC and 26 ºC and also the contribution of the increasing driving force [14]. In general, the increase in partial permeation flux is mainly due to an increase in the driving force. For some of the volatile compounds a significant effect of temperature on sorption can be appreciated since the ratio of partial permeation fluxes is even lower than the corresponding increase in driving force. This result agrees with the observed trend of enrichment factors with temperature (Figure 3).

Effect of permeate pressure.

Permeate pressure was varied in the range of 300-1800 Pa at a fixed feed concentration (1ppm) and a fixed temperature (26ºC). Water permeation flux decreased from 0.0054 mol/m^{2}s to 0.0027 mol/m^{2}s. According to Eq. 1 increasing the permeate pressure will decrease the permeate flux. This fact can be observed in Figure 5 where organic permeation fluxes have been plotted as a function of permeate pressure. Figure 6 illustrates the effect of permeate pressure on separation factors for the volatile compounds. The effect of permeate pressure depends on the thermodynamic properties of the compounds. As a general trend, for organic compounds with low values of Henry's law constant (see Table 1) the pressure at the permeate side is not negligible regarding pressure at the feed side, and the driving force of the process decreases with

increasing permeate pressure. This behaviour can be observed for compounds such as 1-octen-3-ol, benzaldehyde and 1-penten-3ol, which have been found to be more sensitive to changes in permeate pressure. However, for other organic compounds, such as 3-methylbutanal, 2,3-pentanedione and ethyl acetate, enrichment factors have been found to remain more or less constant with permeate pressure. For these compounds, the driving force of the process remains almost constant in the pressure range studied in this work, due to the high values of the Henry's law constant (see Table 1). It must be pointed out that hexanal exhibits high values of the Henry's law constant, but enrichment factor tends to decrease with increasing permeate pressure.

4.2 Comparison of PERVAP^{TM} 4060 and POMS/PEI performance.

In this study, pervaporation has been performed through a PDMS membrane, while in a previous work, results were obtained by using a POMS membrane [4]. Table 2 compares the performance of PERVAP^{TM} 4060 and POMS/PEI membranes at a pervaporation temperature of 26ºC and a permeate pressure of 300 Pa. Volatile compounds from dilute aqueous solutions have been successfully concentrated by these two hydrophobic membranes. However, the POMS membrane produced lower total flux. According to She and Hwang [5] this can be due to the bulky octyl groups in the POMS polymer that could reject more water molecules from passing through the membrane.

As expected, membrane material has a great influence on the aroma profile of the permeate, as it can be seen from the different values of the enrichment factors for both polymers (Table 2). Table 2 presents the pervaporation separation index (Eq. 3) for the organic compounds obtained with the two different polymers. PERVAP^{TM} 4060 membrane exhibits higher pervaporation separation index than those corresponding to

POMS/PEI membrane due to the higher permeation flux through PERVAP^{TM} 4060. This Table also lists the pressure normalized flux, permeance, for both polymers. This parameter is recommended when comparing the separation performance of the membranes, since it allows distinguishing the effect of the nature of the membrane and the operating conditions. The permeances obtained in previous work with a POMS membrane [4] have been recalculated by using the new activitivy coefficients at infinite dilution recently published for the aroma compounds [7]. It can be observed from Table 2 that PERVAP^{TM} 4060 membrane presents higher permeances for all the aroma compounds than POMS membrane, concluding better performance for PERVAP^{TM} 4060.

Table 3 lists the apparent activation energies for both polymers. In general, E_a presents higher values for the POMS/PEI membrane showing that it is more sensitive towards changes in temperature. In fact diffusion contribution was found to be important in POMS membrane [4]. However, as it has been explained in section 4.1, for PDMS membrane, temperature has greater effects on sorption than on diffusion. Similar conclusions were raised by She and Hwang [13]. The effect of the permeate pressure on the process was found similar for both type of membranes.

The different permeate aroma profile obtained in the permeate for a 10 ppm feed concentration for all the aroma compounds at 26ºC and 300 Pa for both polymers, is compared in Figure 7. In this work, it was assumed that the contribution of all the organic compounds to the overall aroma is qualitatively the same, but in fact it would depend on their corresponding aroma threshold value. Therefore, the aroma profile of the feed solution consists in a regular heptagon whose distortion in the permeate

depends on the selectivity that the membrane shows for the different aroma compounds. From this Figure, it can be easily observed that the permeate aroma profile is more similar to the feed solution for PERVAP^{TM} 4060 than for POMS/PEI membrane.

4.3. Unsteady state batch pervaporation of dilute multicomponent solution.

Unsteady state pervaporation was carried out at a pervaporation temperature of 26ºC and a permeate pressure of 300 Pa. Aroma feed concentration was in the range 1 – 3 ppm for all the organic compounds and the membrane area to initial feed volume ratio was 0.23 cm^{-1}. Figure 8 shows how the residue concentration decreases as a function of time for batch operation. Experimental results were fitted to the model proposed by She and Hwang [5] (see section 2). Concentration polarization effect would probably takes place at the low concentration reached in the feed tank during the experiment. But in this work, enrichment factors were considered constant during the whole experiment.

According to She and Hwang [13], flavor loss rate, K_L, is evaluated considering the difference between ideal behavior, with no flavor loss ($K_L = 0$), and experimental data. From the difference in slopes of the straight lines ($\ln x_i/x_{i,o}$ vs t) between ideal and experimental data, organic compounds loss rate was determined. Permeation rate constant, a, was evaluated by equation 5 by using the permeability coefficients obtained in the previous steady state experiments (section 4.1). In Figure 8 solid lines represent the results obtained with Eq. 4.

Table 4 reports the values of the flavor permeation rate constant, a, flavor loss rate, K_L, and the residue (Eq. 6), recovery (Eq. 7) and loss percentage of the aroma compounds. The recovery percentage depends on flavor permeation rate and flavor loss rate [5]. Aroma compounds with high values of permeation rates (higher enrichment factors: 1-

octen-3-ol, benzaldehyde) present the highest recovery percentage after 11 h batch operation time. Ethyl acetate shows a high value of permeation rate constant; however its flavor loss rate is high which means lower recovery percentage than 1-octen-ol and benzaldehyde. 1-penten-3-ol presents high recovery yield due to its low flavor loss rate, similar to that of 1-octen-3-ol and benzaldehyde.

She and Hwang [5] reported loss percentage in the range of 4% to 54% for 2-methyl-1-butanol and ethyl acetate respectively by batch pervaporation through a POMS-PVDD-PP membrane after 10 h batch operation time. These authors consider that due to the volatile nature of these organic compounds, flavor loss is unavoidable. Therefore, it is expected that flavor loss is strongly dependent on the thermodynamic properties of aroma compounds. In this sense, aroma compounds with low Henry's constant values, 1-penten-3-ol, 1-octen-3-ol and benzaldehyde, show the lowest flavor loss rate. On the other hand, compounds with high Henry's constant values, presented high flavor losses, from 46 to 76%, depending on their permeation rate, since the higher the permeation rate, the lower the loss percentage.

In order to improve the low recovery yield that high volatile compounds present in this study, changes in the process design must be made. She and Hwang [5] proposed a better sealing, condensation and collection method in pervaporation process to reduce the flavor loss. Additionally, since production capacity of pervaporation processes depends on the residue mass, time and membrane area, higher membrane area would lead to higher flavor permeation rate, reducing the flavor loss percentage [15].

4.4. Effect of the salt content in the feed solution.

Brown crab boiling juice contains different nonvolatile components such as salts, e.g. sodium chloride (NaCl). The salt concentration in industrial brown crab boiling juice

was around 0.43 mol/kg. To study the effect of salt, pervaporation was carried out by varying the salt feed concentration in the range 0-0.85 mol/kg, at a fixed pervaporation temperature of 40ºC and a permeate pressure of 300 Pa.

There is a tradeoff in the salt feed concentration on the pervaporation performance. The positive effect of the presence of salts in the feed solution is related to the "salting out" effect. This effect is based on the reduction of the solubility of the organic compounds in aqueous solutions, increasing the activity coefficients of the organic compounds present in the feed solution. The negative effects are related to the increase in the density and viscosity of the feed solution and the fouling effect of the salts which could penetrate into the structure of the membrane. There are different studies in the literature considering the effect of salts on pervaporation performance. Most of the studies observed a positive effect on the membrane selectivity. However other studies reflected no changes or even fouling of the membrane [12, 16].

Water permeation flux remained more or less constant in the salt concentration range studied in this work. On the other hand, partial permeation fluxes of the organic compounds were found to slightly increase as the salt concentration in the feed increased. Based on this result, it can be concluded that the "salting out" effect could dominate over the retarding effect on mass transport in the salt concentration range studied in this work. In a previous work [7], it was found that activity coefficients at infinite dilution increase with NaCl concentration. This higher activity coefficient can generate higher driving force and higher permeation flux (Eq. 1). Based on these results, the enrichment factors of aroma compounds slightly increase within the salt concentration range considered in this work (Figure 9).

Kujawski and Krajewski [17] proposed the applicability of the empirical Setschenov equation:

$$\ln\left(\frac{\gamma_i^{\infty}}{\gamma_{i,o}^{\infty}}\right) = k_i c_s \qquad (9)$$

to describe the increase of organic permeation flux with salt concentration. In Eq. 9 γ_i^{∞} is the activity coefficient at infinite dilution in salty solutions, $\gamma_{i,o}^{\infty}$ the activity coefficient at infinite dilution in pure water, c_s the salt concentration and the proportionality factor, k_i, is the salting-out coefficient. This way the ln ($J_{i,\ salty\ solutions}$/$J_{i,non-saltysolution}$) can be plotted as a function of NaCl concentration and compared with data of the activity coefficients obtained in previous work [7]. Table 5 lists the slopes of these plots together with the values previously reported in the study of the activity coefficients at infinite dilution. It can be observed that the values of the slopes obtained for the ln ($J_{i,\ salty\ solutions}$/$J_{i,non-saltysolution}$) were lower than the values previously reported [7]. Therefore, blocking effect cannot be considered negligible. As an example Figure 10 represents the applicability of the Setschenov equation for ethyl acetate. In this Figure, the values of the activity coefficients at infinite dilution obtained in a previous work have been also plotted.

4.5. Multistage condensation of the aroma compounds.

In section 4.1 enrichment factors were reported in the range of 10 for 2,3-pentanedione to 39 for ethyl acetate. Marin et al. [18] proposed to modify the downstream section with a multi-stage condensation step to improve the pervaporation performance. In this work, some experiments have been performed by using two condensers placed in series. The components of the permeate vapour have different condensation potentials, thus

yielding an additional separation factor [19]. The distribution of water and organic compound in each condenser depends on the temperature of the first condenser, the volatility of the components, the flow of the condensable and inert gases in the permeate side and the stripping effect between condensers [20, 21].

Pervaporation experiments have been carried out at a fixed temperature of 26ºC and permeate pressure of 300 Pa. Feed concentration was about 1 ppm for all the organic compounds. Two different temperatures were tried in the first condenser -4 ºC and -10ºC.

Table 6 shows the permeation flux percentage collected in both condensers as a function of temperature in the first condenser. As it can be observed, the percentage collected in the first condenser increases as the condensation temperature in the first condenser decreases. Due to the efficiency in water removal in the first condenser, enrichment factors of the organic compounds collected in the second condenser improve considerably (Table 7) compared to one condenser. Table 7 also reports the separation factor that would be obtained on the basis of vapour-liquid equilibrium (VLE) at 40ºC. This relative volatility at infinite dilution, $\alpha_{i,w}^{\infty}$, is defined as:

$$\alpha_{i,w}^{\infty} = \frac{p_i^s}{p_w^s}\gamma_i^{\infty} \tag{10}$$

where p_i^s and p_i^w are the saturation vapour pressure of organic compounds and water respectively and γ_i^{∞} is the activity coefficient at infinite dilution. The separation factors obtained with one condenser were lower than the separation that would be achieved on the basis of VLE. However, with a two condensation step the new separation factors obtained are, for some of the compounds, even higher than the values of the relative volatility.

Concentration for the most volatile compounds in the permeate collected in the first condenser was very low. That indicates that most of the permeant molecules of these organic compounds were mainly collected in the second condenser probably due to a stripping effect. However, the concentration of the aromatic compounds in the second condenser is less than expected based on mass global balance with the results obtained with one condenser. This fact can be due to the very high loss rates found for these compounds in the studies performed in non-steady state (section 4.3). The non-steady state experiments revealed that the concentration of the high volatile compounds is largely conditioned by the time employed in each run due to the high value of the flavor loss rate. The operation time used in the fractionation experiments was longer than in the experiments carried out with one total condenser, due to the fact that insufficient quantities for the analysis were collected in the second condenser, especially in the experiments carried out at the lowest temperature in the first condenser.

5. Conclusion

PERVAP^{TM} 4060 membrane has been found to be effective to recover some key aroma compounds found in the brown crab boiling juice from a model dilute aqueous solution. The effect of feed concentration, pervaporation temperature and permeate pressure on pervaporation performance has been analyzed. An increase of the aroma feed concentration increases organic permeation flux due to an increase in the permeation driving force. Partial and total permeation flux increased with temperature and permeation flux decreased as permeate pressure increased.

The results obtained under steady state operation with PERVAP^{TM} 4060 were compared with those one obtained with a POMS/PEI membrane. Total permeation flux was higher

for PERVAP^{TM} 4060 membrane than for POMS/PEI. Based on the different effect of temperature for both types of membranes it was concluded that sorption contribution was more important for PERVAP^{TM} 4060 membrane than for POMS/PEI membrane.

From batch pervaporation experiments, it was found that the loss of volatile compounds increases with operation time. Loss percentage was high for volatile compounds with low permeation rate and high flavour loss rate. Higher membrane area would help to reduce the loss percentage.

The presence of NaCl slightly improved the efficiency of aroma recovery from dilute aqueous solutions. This fact can be attributed to the "salting out". However the increase in partial permeation flux is lower than the corresponding "salting out" effect concluding that blocking effect cannot be neglected.

Modifying the permeate circuit with a two condensation step can be an efficient way of improving the pervaporation performance, since it has been observed a considerable increase of the enrichment factors regarding one condensation step. However, the design must be optimized since important losses of some of the volatile compounds, especially the most volatiles, have been observed.

Further studies will be carried out with the industrial brown crab boiling juice to study the ability of pervaporation technique.

Nomenclature

a = permeation rate constant, $m^3 \cdot s^{-1}$ (Eq. 4)

A = membrane area, m^2

C_{tot} = total molar concentration in liquid phase, $mol \cdot m^{-3}$ (Eq. 4)

E_a = apparent activation energy of permeation, kJ·mol^{-1}

H = Henry's law constant, Pa

J = permeation flux, mol·s^{-1}·m^{-2}

k = salting out coefficient

K_L = flavor loss rate, mol·s^{-1} (Eq. 4)

K_V = total permeation volume flow rate, m^3·s^{-1} (Eq. 5)

Q_{OV} = pressure-normalized permeation flux, mol·s^{-1}·m^{-2}·Pa^{-1}

p = pressure, Pa

P.S.I. = pervaporation separation index

R = gas constant, kJ·mol^{-1}K^{-1}

T = absolute temperature, K

V = volume of feed solution, m^3

x, y = mol fraction

t = time, s

γ = activity coefficient

β = enrichment factor

subscripts

i = component

p = permeate

f = feed

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Table 1. Physicochemical properties of the volatile compounds. (MW = molecular weight, BP = boiling point, p^s = saturation pressure, γ^∞ = activity coefficient at infinite dilution, H = Henry's constant).

Compound	MW, g/mol	BP, ºC	$p^s_{26ºC}$, Pa	$\gamma^\infty_{26ºC}$	$H_{26ºC} \cdot 10^{-4}$, 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	13045	62	80.9

Table 2. Pervaporation parameters of PERVAP$^{\text{TM}}$ 4060. Comparison of PERVAP$^{\text{TM}}$ 4060 and POMS/PEI membranes (T_{PV} = 26ºC, p_p = 300 Pa).

Compound	PERVAP$^{\text{TM}}$ 4060			POMS/PEI		
	β	$Q_{OV,i} \cdot 10^7$ (mol/m^{2}sPa)	PSI (mol/m^{2}s)	β	$Q_{OV,i} \cdot 10^7$ (mol/m^{2}sPa)	PSI (mol/m^{2}s)
1-Octen-3-ol	36	18.5	$2.0 \cdot 10^{-1}$	120	8.6	$8.8 \cdot 10^{-2}$
1-Penten-3-ol	25	29.6	$1.4 \cdot 10^{-1}$	25	3.1	$1.9 \cdot 10^{-2}$
3-Methylbutanal	18	1.1	$1.0 \cdot 10^{-1}$	5	0.03	$3.9 \cdot 10^{-3}$
Benzaldehyde	51	35.8	$2.8 \cdot 10^{-1}$	93	7.5	$7.5 \cdot 10^{-2}$
2,3-Pentanedione	10	1.4	$6.8 \cdot 10^{-2}$	7	0.1	$5.2 \cdot 10^{-3}$
Hexanal	23	1.4	$1.3 \cdot 10^{-1}$	22	0.2	$1.7 \cdot 10^{-2}$
Ethyl Acetate	39	2.7	$2.2 \cdot 10^{-1}$	7	0.04	$5.6 \cdot 10^{-3}$
Water		17.5			2.0	

Table 3. Apparent activation energies of the volatile organic compounds for PERVAP^{TM} 4060 and POMS/PEI membranes.

Compound	E_a (kJ/mol)$_{PERVAP^{TM}\ 4060}$	E_a (kJ/mol)$_{POMS/PEI}$
1-Octen-3-ol	60.9	58.6
1-Penten-3-ol	48.2	84.8
3-Methylbutanal	54.4	87.7
Benzaldehyde	37.5	49.5
2,3-Pentanedione	66.3	155.0
Hexanal	47.9	79.6
Ethyl Acetate	26.7	86.8
Water	43.1	46.7

Table 4. Experimental results in batch pervaporation with PERVAP^{TM} 4060 (T_{PV} = 26ºC, p_p = 300 Pa, t = 11 h), a, K_L = parameters from Eq. 4

Compound	a (m^3/s)	K_L (mol/s)	Recovery (%)	Residue (%)	Loss (%)
1-Octen-3-ol	6.51·10^{-8}	3.83·10^{-4}	86	5	9
1-Penten-3-ol	4.50·10^{-8}	1.81·10^{-4}	81	13	6
3-Methylbutanal	2.83·10^{-8}	5.37·10^{-3}	24	1	76
Benzaldehyde	1.00·10^{-7}	3.02·10^{-4}	94	1	5
2,3-Pentanedione	1.24·10^{-8}	2.70·10^{-3}	21	8	72
Hexanal	3.76·10^{-8}	2.64·10^{-3}	44	3	53
Ethyl Acetate	7.19·10^{-8}	3.46·10^{-3}	54	0	46

Table 5. Salting out coefficients obtained from the curves that represent $\ln$ ($J_{i,\text{salty solutions}}$ /$J_{i,\text{non-salty solutions}}$) and $\ln$ ($\gamma_i^\infty / \gamma_{i,o}^\infty$) versus salt concentration in the feed solution.

Compound	k, ln ($J_i/J_{i,0}$)	k, ln ($\gamma_i^\infty / \gamma_{i,0}^\infty$)
1-Octen-3-ol	0.15	0.56
1-Penten-3-ol	0.26	0.37
3-Methylbutanal	0.31	0.39
Benzaldehyde	0.14	0.34
2,3-Pentanedione	0.40	0.43
Hexanal	0.19	0.62
Ethyl Acetate	0.25	0.58

Table 6. Percentage of permeate collected in both condensers at different temperatures in the first condenser.

T in the first condenser	% condenser one	% condenser two
$T_1 = -4\ ^{\circ}C$	79	21
$T_1 = -10\ ^{\circ}C$	90	10

Table 7. Comparison of enrichment factors obtained during the fractionation experiments in two condensers and one condenser ($T_{PV} = 26°C$, $p_p = 300$ Pa). Relative volatility at infinite dilution, $\alpha_{i,w}^{\infty}$, at 40°C

| Compound | $T_{1 =} -4°C$ | | $T_{1 =} -10°C$ | | $\beta_{one\ condenser}$ | $\alpha_{i,w}^{\infty}$ |
	β_1	β_2	β_1	β_2		
1-octen-3-ol	16	78	20	179	36	56
1-penten-3-ol	14	79	16	149	25	22
3-methylbutanal	<1	68	<1	139	18	293
benzaldehyde	18	132	17	347	51	33
2,3-pentanedione	<1	40	<1	54	10	147
hexanal	<1	97	<1	164	23	284
ethyl acetate	<1	145	<1	261	39	232

List of Figure captions:

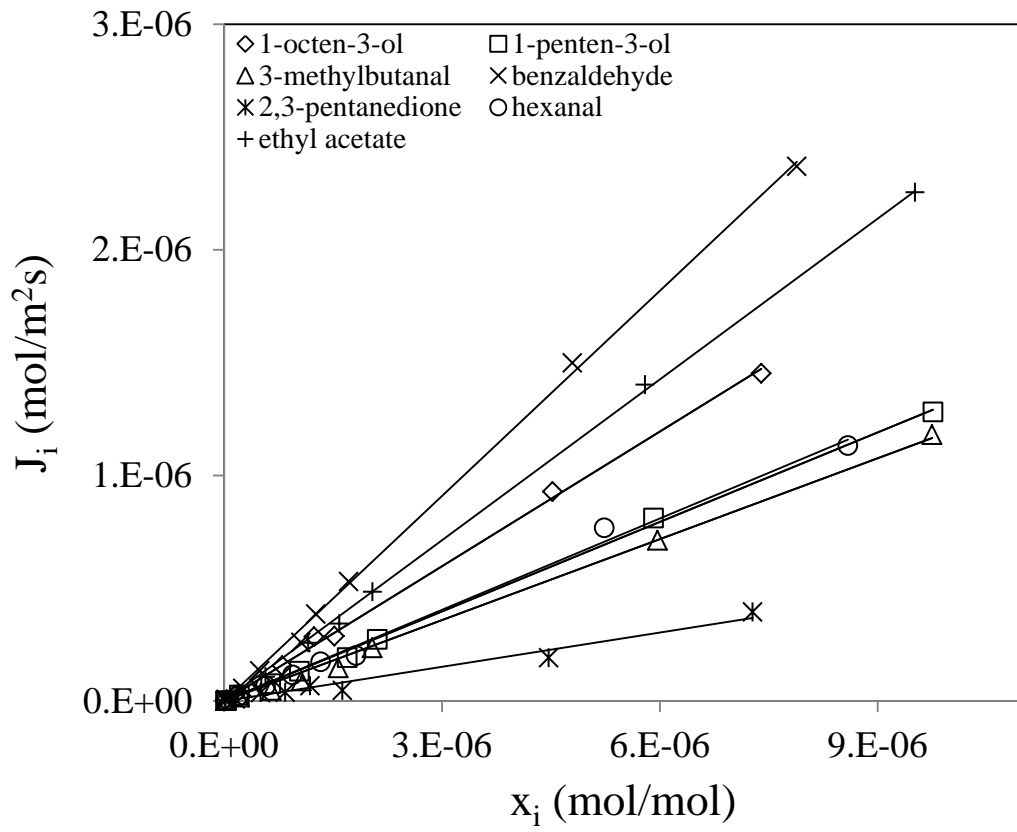**Figure 1.** Effect of volatile feed concentration on volatile compound permeation flux (T_{PV} = 26 ºC, p_p = 300 Pa) for PERVAP^{TM}4060.

Figure 2. Effect of pervaporation temperature on volatile compound permeation flux ($C_{i.\ feed}$ ≈ 10 ppm. p_p = 300 Pa) for PERVAP^{TM}4060.

Figure 3. Effect of pervaporation temperature on the separation factor of the volatile compounds ($C_{i.feed}$ ≈ 10 ppm, p_p = 300 Pa) for PERVAP^{TM}4060.

Figure 4. Effect of pervaporation temperature on the flux and driving force ratio for PERVAP^{TM}4060 (C_{feed} ≈ 10ppm, p_p = 300 Pa). DF =driving force of the process.

Figure 5. Effect of permeate pressure on partial permeation flux for PERVAP^{TM}4060 ($C_{i.\ feed}$ ≈ 1 ppm. T_{feed} = 26ºC). The continuous lines are to guide the eye.

Figure 6. Effect of permeate pressure on the enrichment factors of the volatile compounds for PERVAP^{TM}4060 ($C_{i.\ feed}$ ≈ 1 ppm. T=26°C).

Figure 7. Effect of membrane material on the permeate aroma profile (T = 26ºC, C_i = 10 ppm p_p = 300 Pa.

Figure 8. Evolution of feed concentration over time in the pervaporative recovery of aroma compounds (T_{PV} = 26ºC, p_p = 300 Pa, t = 11 h). The continuous lines represent the model proposed by She and Hwang [5].

Figure 9. Influence of salt concentration on the enrichment factor of the organic compounds for PERVAP^{TM}4060 (C_{feed} = 1ppm, T_{feed} = 40ºC. P_p = 300 Pa).

Figure 10. Comparison between the effect of salt concentration on ethyl acetate partial permeation flux (○) and activity coefficients at infinite dilution (▲).

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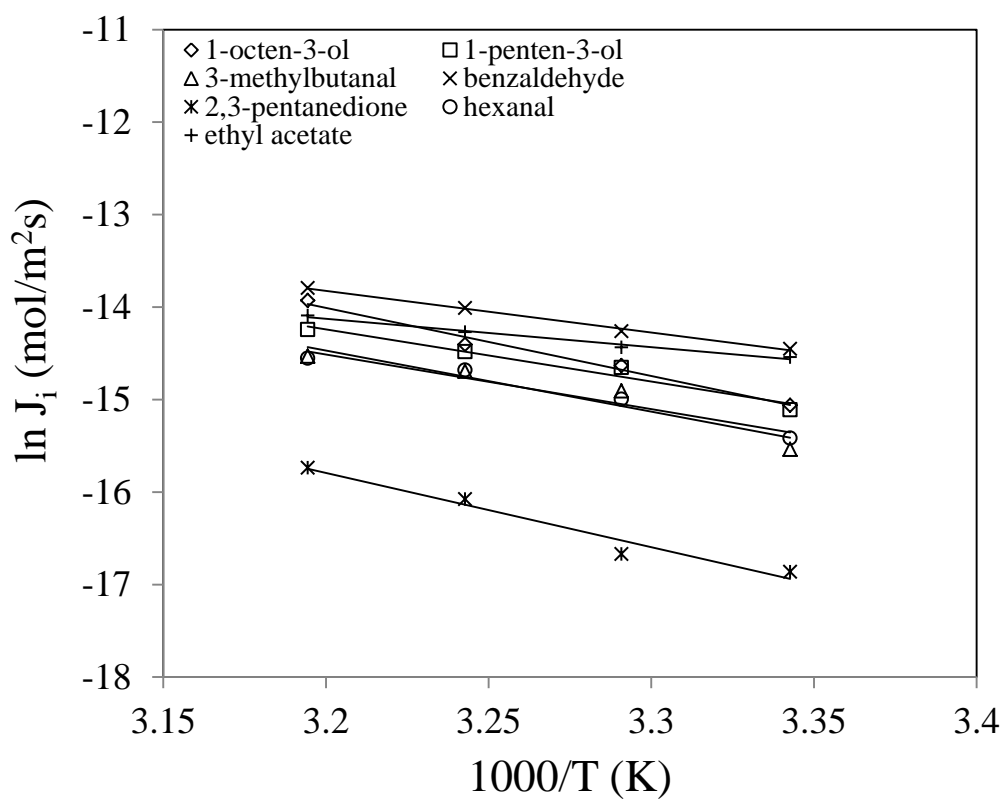
Figure 2. Effect of pervaporation temperature on volatile compound permeation flux ($C_{i.\ feed} \approx 10$ ppm, $p_p = 300$ Pa) for PERVAP[TM]4060.
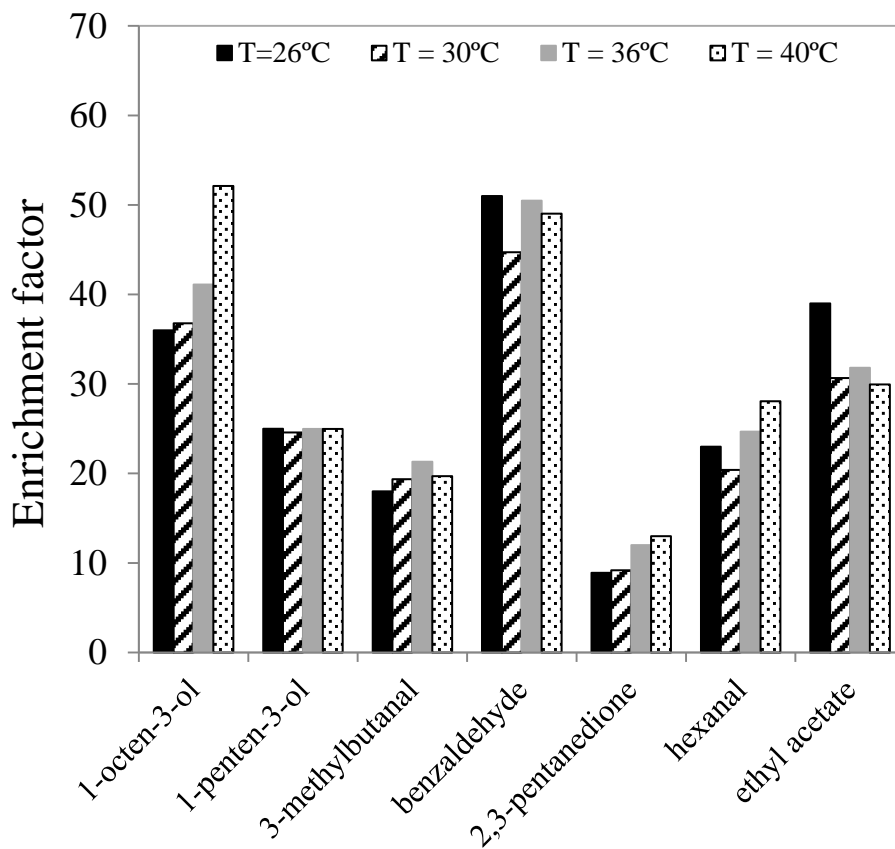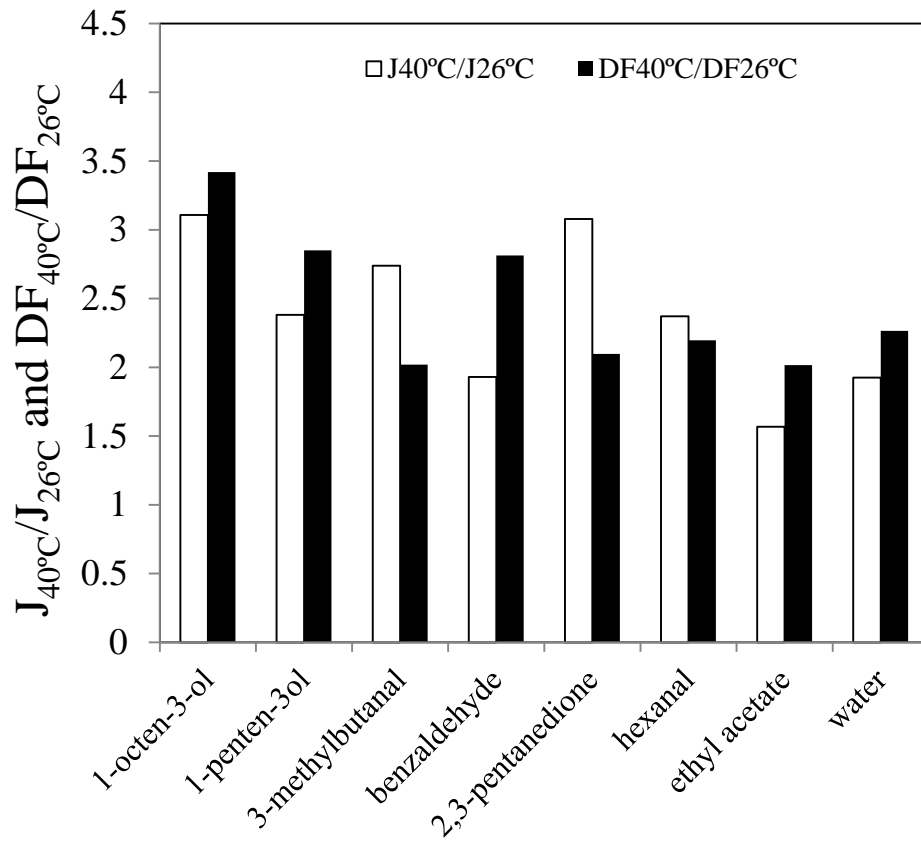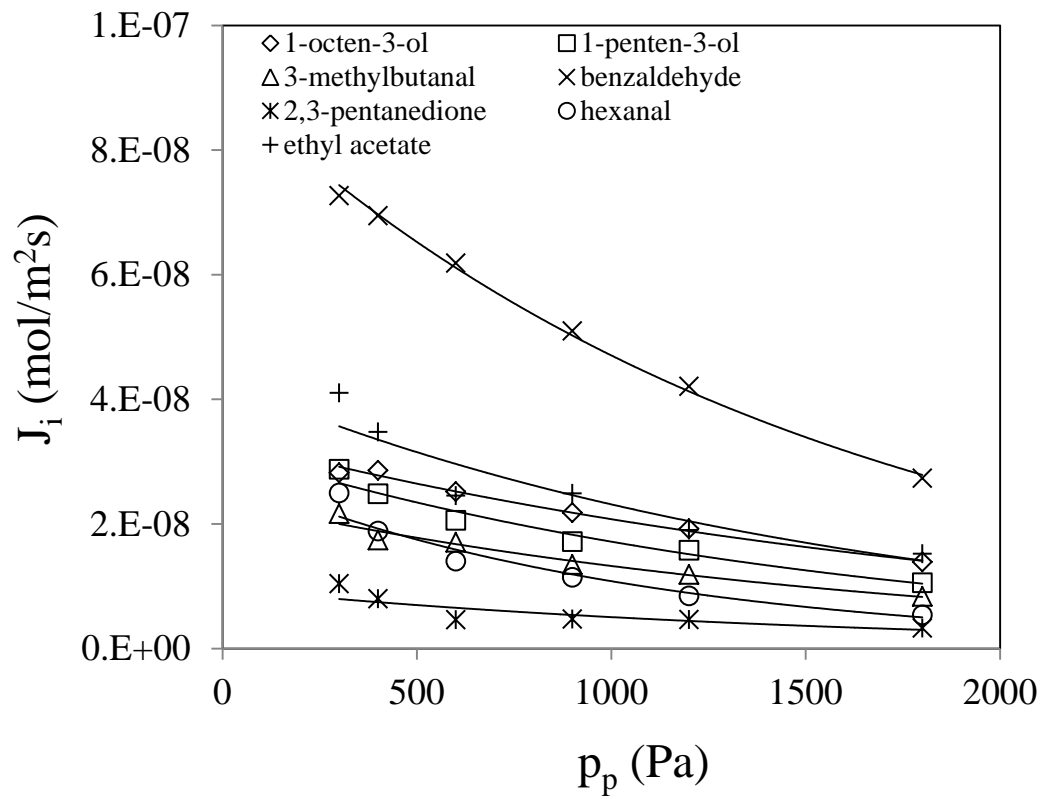
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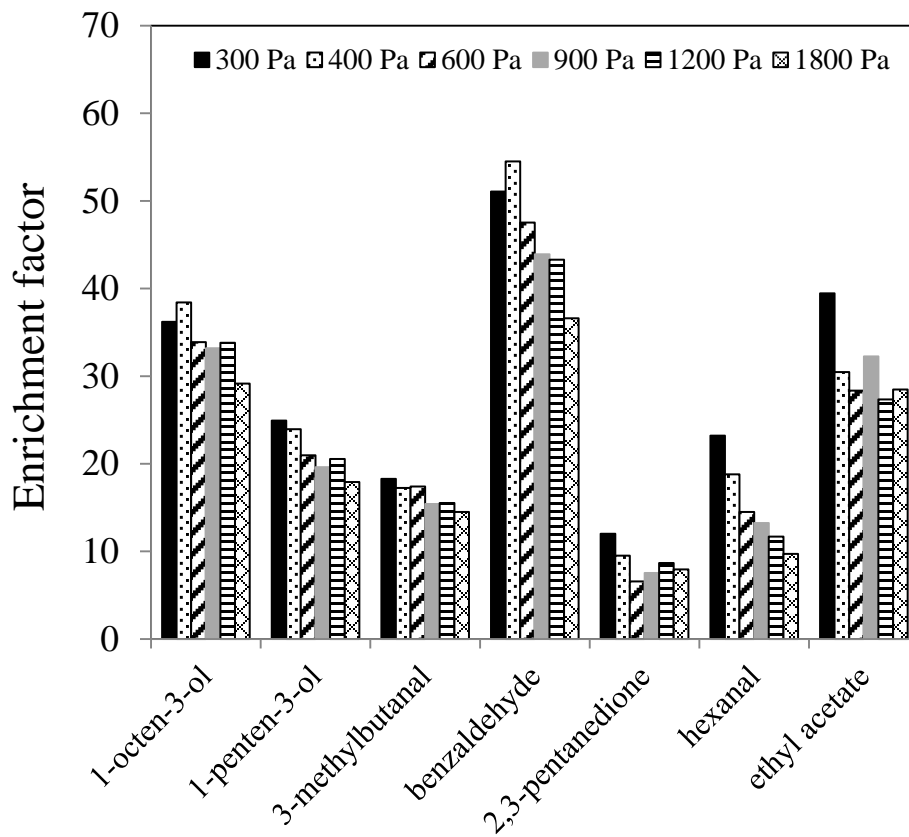
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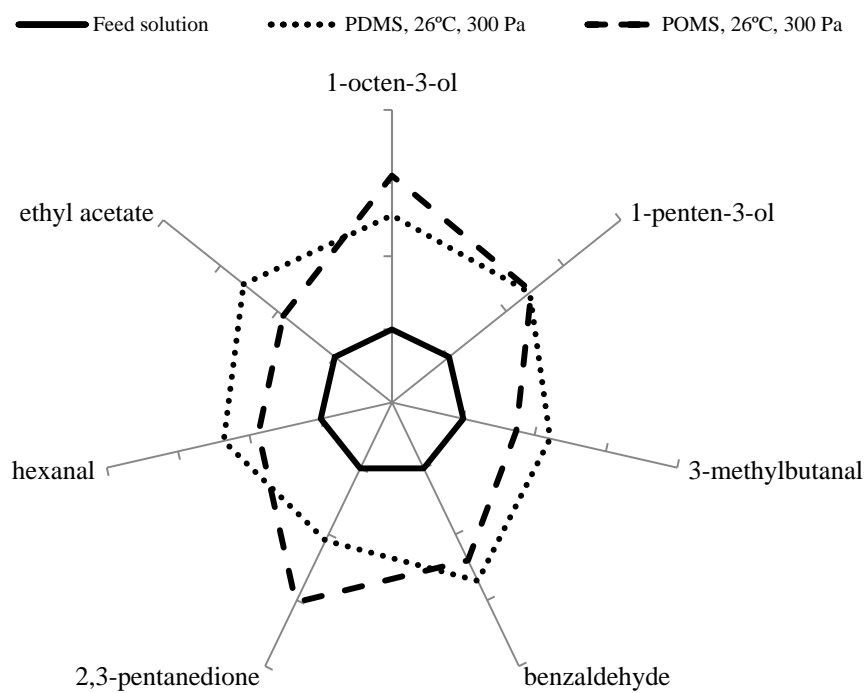
Figure 7. Effect of membrane material on the permeate aroma profile (T = 26ºC, C_i = 10 ppm p_p = 300 Pa.
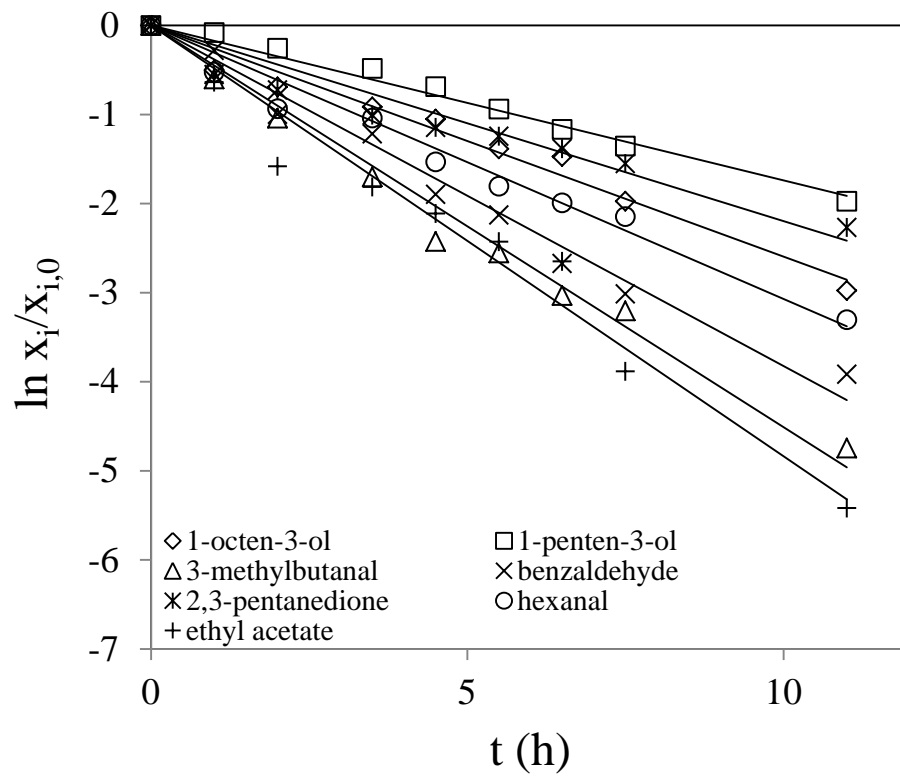
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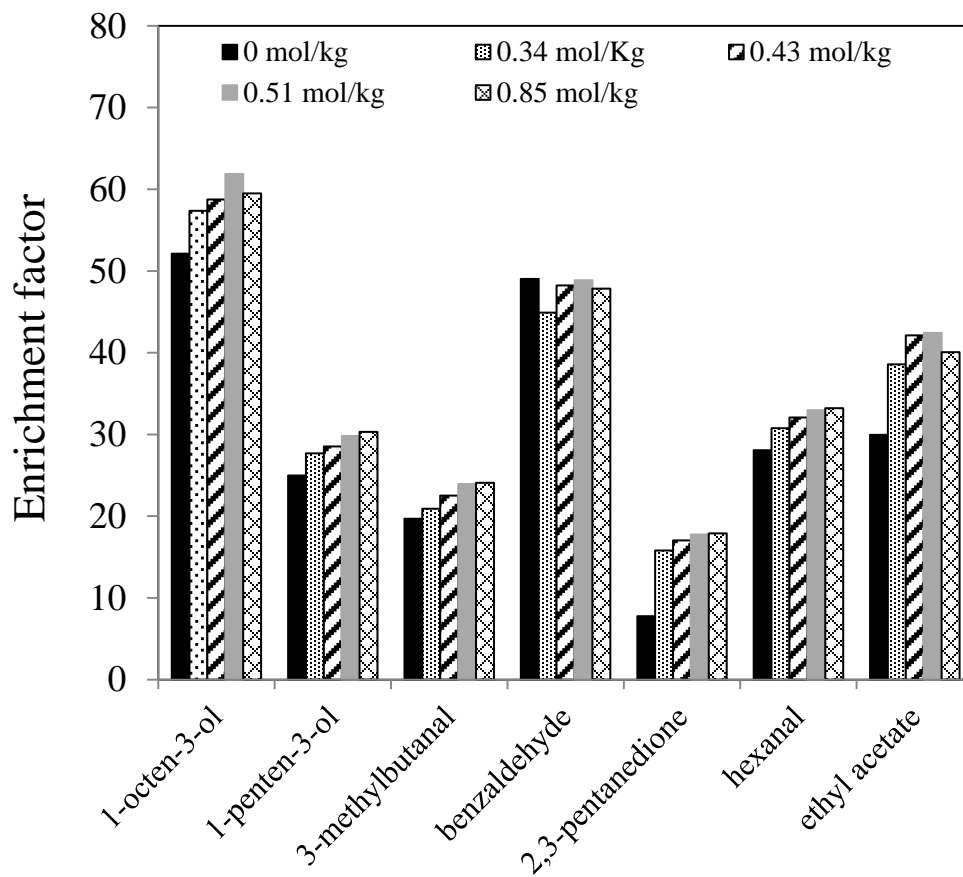
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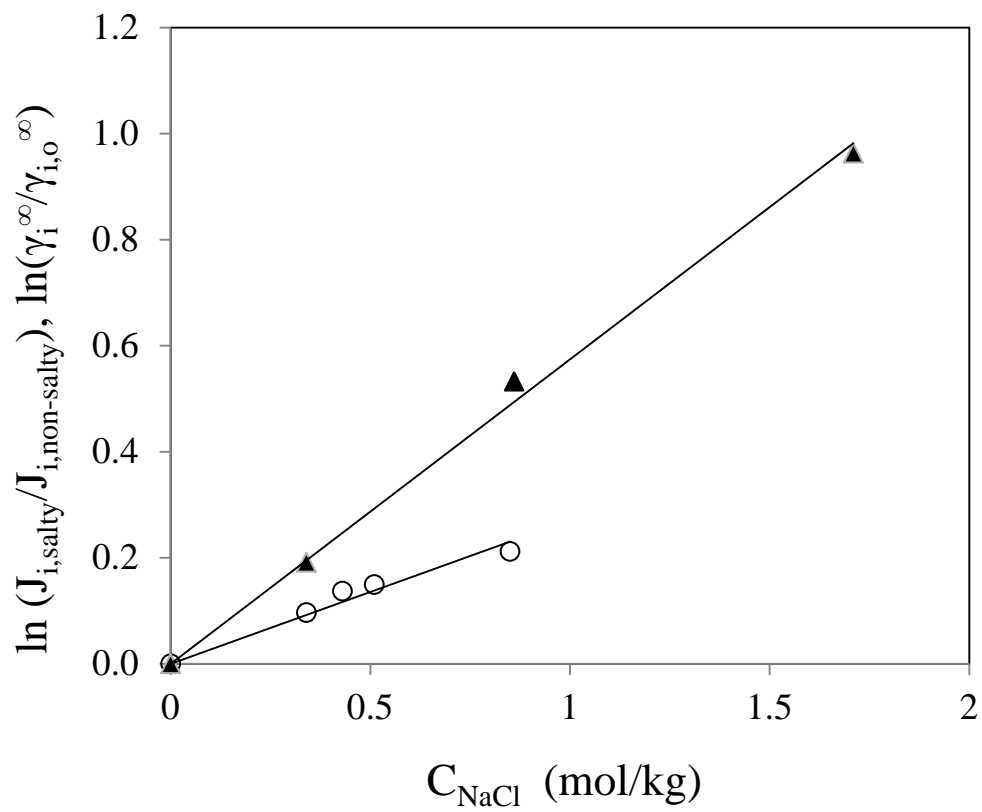
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