Recovery of dairy flavor compounds by pervaporation using poly(ether block amide)

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During dairy products processing, many flavor compounds are lost due to their high volatility. Even a small amount of loss of flavor compounds may significantly affect products’ sensory quality. Since artificial flavors cannot satisfy consumers’ interest anymore, it is necessary to recover these flavor compounds before commercial processing from raw dairy recourses and then add them back to the final products.

Traditional flavor fractionation processes are based on extraction, distillation, partial condensation, and gas stripping [1,2]. Pervaporation, as a novel separation technique, was introduced as an alternative to the current separation technologies. Its major advantages include: the moderate operating temperature used in pervaporation can reduce the energy consumption; the mild temperature can also protect product integrity from thermal degradation, especially for heat sensitive compounds. In a pervaporation process, a feed liquid mixture contacts one side of a dense membrane, while the preferential permeate diffuses through the membrane and evaporates on the other side by using a vacuum pump. The non-permeated components in the retentate are usually recycled into the feed stream for further recovery.

Polyether block amide (PEBA) 2533 is a copolymer comprising 80 wt.% poly(tetramethylene oxide) and 20 wt.% nylon 12. Its general formula is shown in Figure 1 [3], where PA and PE represent polyamide and polyether segments, respectively. PEBA 2533 has a good selectivity of flavor compounds due to the strong affinity between the polyether segments and the flavor compounds.

Figure 1 Structure of PEBA

The objective of this study is to investigate the pervaporation performance of PEBA 2533 membrane on separating flavor compounds from dairy model solutions. The effects of independent variables like feed concentration and operating temperature, on organic flux and enrichment factor were studied. The coupling effect was also investigated by comparing the pervaporation results obtained in binary and multicomponent systems.

1 Experimental

Eight flavor compounds, which represent six categories of dairy flavor compounds (esters, ketones, aldehydes, acids, sulfur compounds and aromatic compounds), were recovered by pervaporation. The flavor compounds included ethyl hexanoate (EH), ethyl butanoate (EB), 2-heptanone (2-Hep), diacetyl, methyl sulfone (MS), indole, nonanal and hexanoic acid (HA). For single flavor compound
pervaporation, each flavor compound was diluted by deionized water to make a dilute flavor–water binary feed solution. For multicomponent pervaporation, the feed solution was prepared by mixing the eight organics with deionized water.

Pervaporation experiments with binary and multicomponent feed solutions were carried out at various flavor concentrations and temperatures. Figure 2 shows the schematic diagram of the experimental set-up for pervaporation separation. The PEBA membrane was mounted into the permeation cell. The feed solution was continuously circulated through the membrane cell and back into the 1000 mL feed tank. Vacuum was applied on the permeate side to generate pressure difference, which providing the driving force. The permeate sample was condensed in a cold trap immersed in liquid nitrogen (-196 °C), and analyzed by gas chromatography.

Figure 2 Schematic diagram of the pervaporation setup

2 Results and discussion

2.1 Influence of feed concentration

Pervaporation separation of flavor compounds from binary feed solutions with PEBA 2533 membrane was investigated at various feed concentrations and temperatures. Figures 3 (a) and (b) show the effect of the feed flavor concentration on the flavor permeation flux and enrichment factor, respectively.

All of the flavor compounds flux increases as the feed concentrations increase. That is because with the feed flavor concentration increasing, the partial pressure difference of the flavor compound between the two sides of the membrane increase, which leads to a higher driving force of the pervaporation process. The enrichment factors change little with the feed concentration, especially beyond 1000 ppm.

Moreover, the flux of the two esters (ethyl hexanoate and ethyl butanoate), one of the ketones (2-heptanone) and the aldehyde (nonanal) increase more significantly than other compounds when feed concentration increase; their enrichment factors are higher as well.
2.2 Influence of operating temperature

Operating temperature has a significant influence on flavor compound flux. The flavor flux increases obviously as temperature increases. This is because an increase in temperature generally increases both the diffusivity of the permeant and the thermal motion of the membrane polymer chains, which facilitates the movement of permeant.

2.3 Pervaporation with multicomponent feed solutions

The multicomponent feed solutions were prepared by mixing eight flavors and water in different mass ratios. Figure 4 shows the comparison between the flavors

**Figure 3** Effect of feed flavor concentration on (a) the flavor flux and (b) enrichment factor for binary flavor-water solutions using PEBA 2533 membrane.
enrichment factors obtained from binary and multicomponent systems (the organics concentration: nonanal 15 ppm, indole 100 ppm, EH 100 ppm, other flavors 500 ppm; five operating temperatures were tested, the results shown are average value of the enrichment factors under the five temperatures). It clearly shows that the enrichment factors of most flavors are lower in multicomponent system than in binary system, which indicates coupling effects exist under such flavor concentrations. This happens probably due to the competition and interaction between the flavor compounds when they penetrating the membrane.

Figure 4. The flavors enrichment factors obtained from binary and multicomponent systems (the organics concentration: nonanal 15 ppm, indole 100 ppm, EH 100 ppm, other flavors 500 ppm; the results shown are average value of the enrichment factors under the five temperatures).

Reference
DAIRY FLAVOR RECOVERY BY PERVAPORATION USING POLY(ETHER BLOCK AMIDE) MEMBRANE

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BACKGROUND

Traditional methods for recovering:
Distillation, partial condensation & gas stripping

Problems: product contamination and degradation, high energy consumption

Flavor Loss or degradation

Flavor recovery

Flavor added back

Flavoring ingredients

Food, medical and cosmetic industry.

Why pervaporation?
High selectivity, low energy consumption, mild operating temperatures and no damage to heat-sensitive flavors

OBJECTIVE

To investigate pervaporation as a mean of recovering flavor compounds from dairy model solutions, using an organophilic membrane material: poly(ether block amide) (PEBA).

• To determine how the operating conditions affected the pervaporation of each flavor compound.
• To compare the pervaporation behavior of single flavor component and multiple flavor components, in order to determine whether there is any “coupling effect” between permeating species.

Evaluation of pervaporation performance

• Flux \( (J) \)
Permeate flow rate of component \(i\) per unit membrane area.

\[ J = \frac{N_i}{A} \]

• Enrichment factor \( (\beta) \)
Ratio of component \(i\)’s concentrations in permeate and in feed.

\[ \beta = \frac{C_{pi}}{C_{fi}} \]

Pervaporative enrichment process is effective only when \(\beta > 1\).
• When the concentration of water flux and flavor flux, g/(m².h) increases with increasing temperature, these compounds can be successfully concentrated by pervaporation with the PEBA membrane.

• Flavor compounds with higher hydrophobicities are enriched more significantly with the PEBA membrane.

With an enhancement of feed concentration, MS and indole fluxes almost maintain the same; the flux of the other six compounds increase.

• Feed concentration affect EH and nonanal’s enrichment factors more significantly.

• When the concentration of feed flavor is increasing, both \( E_H \) and \( E_{HA} \) increase as well, while the other flavors’ enrichment factors decrease.

Flavor and water fluxes increase with increasing temperature.

**Arrhenius-type equation:**

\[
J = J_0 \exp \left(- \frac{E_a}{RT} \right)
\]

Where \( E_a \) is the activation energy of permeation, \( J_0 \) is permeation flux, \( J_0 \) is the pre-exponential factor, \( R \) is gas constant, and \( T \) is the absolute temperature.
If the activation energy of one flavor is higher than water, the enrichment factor of the flavor will increase as temperature goes higher, vice versa.

**CONCLUSIONS**

- PEBA 2533 has good pervaporation performance on concentrating dairy flavors, especially hydrophobic ones.
- The increase in feed concentration has positive effects to the flavor fluxes; however, its impact on enrichment factor varies from compound to compound, depending on the nature of the flavor molecule.
- Temperature affects the enrichment of dairy flavors as well. The temperature dependence of flavor and water fluxes obeys Arrhenius-type relationship. Flavors and water’s activation energy determines the changing trend of enrichment factor.
- In multicomponent pervaporation, the “coupling effect” between permeating species decreases the flavors enrichment.

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