

Concentration of Flavor Compounds by Pervaporation

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Concentrated flavor distillates and extracts are important products for simulating natural flavors in the flavor industry. Usually, these flavor distillates and extracts originate as dilute solutions with the concentration of flavor compounds less than 300 ppm. The concentration method of conventional evaporation has the shortcomings of heat deterioration for heat-sensitive flavor compounds and flavor loss due to solvent evaporation. Pervaporation, which is a novel membrane separation method, has been successfully applied to extract dilute organics from wastewater. When the same process is applied to flavor concentration, it has the potential of effectively resolving the previously mentioned problems. Compared with other concentration processes, such as adsorption, evaporation, steam distillation, vacuum distillation, solvent extraction, and air stripping, pervaporation has the advantage of low energy consumption due to small amounts of evaporating materials. Also no additional separation treatment is required for the recovery of solvents or adsorbents [1]. Over 50 flavor compounds have been successfully separated from aqueous solutions in laboratory settings [2]. In order to scale up the experimental results obtained in the laboratory for industrial applications, operating conditions such as downstream permeate pressure, feed flow rate, feed concentration, and operating temperature need to be optimized. Reliable simulation models are necessary to predict the influence of these operating conditions on the outcome of pervaporation [3]. In addition, concentration polarization and possible coupling phenomena should also be included in a comprehensive study of pervaporation of dilute flavor organics [4].

In our investigation, dilute aqueous solutions of single and multiple flavor compounds are concentrated by pervaporation. Tested flavor compounds include ethyl-butyrate, trans-2-hexenal, benzaldehyde, cis-3-hexenol, phenethyl alcohol, and methyl anthranilate, which represent three major categories of flavor compounds (esters, aldehydes, and alcohols). Only the first four compounds, which have relatively high Henry's law constants, can be effectively concentrated by pervaporation at an ambient temperature of 20–23°C. Pervaporation did not work for the last two less volatile compounds. Due to the different thermodynamic properties (saturated vapor pressure and activity coefficient) of these flavor compounds, the effects of operating conditions on the organic flux and the enrichment factor varied significantly. Four polydimethyl siloxane (PDMS) membranes and one polyoctylmethyl siloxane (POMS) membrane were tested and their separation performances compared. Pervaporation flux was measured for these flat sheet membranes with different support layers and thicknesses, using a stainless steel permeation cell. The cell was suitably designed for membrane characterization using a cross-flow mode and had an effective area of 50 cm². Testing results illustrate that the membrane performance depended not only on the functional layer but also on the support layer. In the performance comparison among five different membranes, for dilute ethyl butyrate pervaporation, PDMS (functional layer 4μm)-PVDF-PP (support layer) membrane

produced the highest total flux while POMS (functional layer 10 μ m)-PVDF-PP (support layer) membrane showed the highest enrichment factor. Flavor loss rate due to evaporation was determined from a batch operation experiment. Calculation results indicate that considerable flavor organic loss was present in the current batch operation; thus a better design is required to reduce the flavor loss.

The effects of operating conditions on the dilute flavor pervaporation process were investigated and relevant mathematical models were developed. The effects of downstream permeate pressure on the separation performance were correlated with simple mass transfer equations based on the non-equilibrium thermodynamic formalisms [5]. In the model, a relative permeability was defined as the ratio of flavor permeability over water permeability. Depending on whether it is larger or smaller than unity, the increase of permeate pressure has a positive or negative effect on the enrichment factor. Most experimental results indicated a general trend of decreasing organic flux with the increase of permeate pressure. However, for flavor compounds with high Henry's law constants, the effects of permeate pressure on organic flux were negligible. Therefore relatively high permeate pressure is preferable in order to decrease energy consumption.

The effects of feed concentration were also investigated. Generally speaking, the degree of concentration that is defined as enrichment factor decreases when feed concentration increases. However, this effect was too small to be observed because of the very dilute nature of feed concentration, which resulted in very little change of organic concentration and negligible volume fraction of organics. Therefore, in our case, the mass transfer driving force (fugacity difference) increased linearly with the increase of feed concentration. Since both the boundary layer resistance and the membrane resistance remained unchanged, the organic fluxes increased linearly with the feed concentration, but the enrichment factors remained constant. As for the operating temperature optimization, increasing temperature significantly increased permeate fluxes of both water and organics. Temperature effects on the organic fluxes were successfully correlated with the operating temperature by utilizing a modified Arrhenius equation. The POMS membrane exhibited stable overall membrane permeances under the operating temperature of 22~50 $^{\circ}$ C, while in the same temperature range the permeances of PDMS membranes continuously decreased as temperature increased. POMS membrane achieved more stable separation results on enrichment factors and proved to be a better choice for high temperature pervaporation compared to PDMS membranes.

The organic and water fluxes at different feed flow rates were measured to investigate the effects of hydrodynamic conditions and concentration polarization phenomena. The feed flow rate had a negligible effect on the water flux due to the dilute solute concentration in the feed solution. However, the significant effect of the feed flow rate on organic flux proved the existence of a mass transfer boundary layer on the feed side of the membrane. A modified concentration polarization model derived from a steady state flux equation was applied to calculate the liquid boundary layer thickness on the feed side and the organic mass transfer coefficient in the membrane. The resistance in-series model was used to separate the mass transfer resistance of liquid boundary layer from the mass transfer resistance of the membrane. Modeling results showed that the boundary layer resistance was in the same order of magnitude as the membrane resistance and could not

be neglected. It was also evident from the modeling work that the mass transfer resistance of the boundary layer is controlled by hydrodynamic conditions and that the boundary layer thickness decreases as the feed flow rate increases. At the same time, calculated intrinsic membrane permeability is a characteristic property of membrane materials. Based on the modified concentration polarization model, the effects of membrane properties and other operating conditions were analyzed. It was concluded that the boundary layer thickness was affected not only by the bulk flow parallel to the membrane surface, but also by the permeation flux perpendicular to the membrane surface. The mass transfer boundary layer thickness decreased with the increase of intrinsic membrane permeance. The mass transfer coefficient in the boundary layer increased when more permeable membranes were used. When the experimental study was extended from single component to multicomponent mixtures that resembled real flavor systems, no obvious coupling effects were detected for the pervaporation of dilute multiple flavor organics. The water flux and organic fluxes behaved independently and did not affect each other when separation performances of multicomponent systems were compared to those obtained from single component systems. Thus, coupling terms do not need to be included in the mass transfer equations for dilute flavor pervaporation, which means the same flux equations and concentration polarization models can be applied to both single- and multicomponent pervaporation systems.

In conclusion, this work clearly shows that the performance of a flavor pervaporation process depends on the thermodynamic properties of flavor organics, the operating conditions (such as downstream permeate pressure, feed flow rate, feed concentration, and operating temperature), and the membrane permeation properties such as the intrinsic membrane permeance for organics and the membrane permeance for water. The experimental data were successfully correlated and modeled through the non-equilibrium thermodynamic formalisms, the resistance in-series model, and the concentration polarization model.

References

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