Recovery of aroma compounds from model solution by pervaporation membrane

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Abstract

The aim of our study was to examine applicability of pervaporation in reference to the apple aroma recovery and the effects of the operating parameters on the process. Based on performed experiments the pervaporation, as membrane process, may be capable to reduce the loss of aroma compounds in the beverages production, due to its low operating temperature and high aroma recovery efficiency so organoleptic characteristics of the products would satisfy the growing consumer expectations as well. The studied main aroma compounds were i-amyl-alcohol, ethanol, butanol, i-butanol, ethyl-acetate, which could be separated with high selectivity. The values of activation energy of investigated compounds follow their order of polarity that requires further investigation. The data were analysed statistically, which showed negligible effects of flow-rate and initial concentration on the process.

Keywords

pervaporation · aroma · activation energy · recovery

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Introduction

The total soluble solid content of a fresh juice is usually about 11°Brix, therefore fruit juices have been traditionally concentrated by multi- stage vacuum evaporation up to a final concentration of about 60°Brix. The concentration step has to be introduced in the industrial processing so as to reduce storage, transportation, packaging costs and to prolong the shelf life of the fruit juices [13]. Disadvantages of this traditional method are loss of nutritional value, changing of colour and taste of fruit juices. The fruit aromas have important role and determine the organoleptic characteristics of beverages products. Nowadays rectification equipment is used for aroma recovery with good efficiency. However this process connected to multi-stage evaporation, needs very high energy and area. Therefore the pervaporation process may be able to substitute distillation method, because it meets the needs of lower energy consumption and high efficiency [5]. Liquid mixtures can be separated by pervaporation evaporating a part of the mixtures through a non-porous membrane [6,11]. This technique former known as mixture permeation is called today pervaporation emphasizing the fact that the permeate goes through a phase change.

By the processing of fruit juices physical and chemical losses of aroma compounds occur which results in an unwanted quality decrease of the final product. During heat treatment both the intensity and the character of aroma get deteriorated through the applied vacuum and high temperature [4,15].

Pervaporation is inherently available for separation of volatile organic compounds from even very dilute mixtures with high performance [2,16]. The pervaporative separation is highly selective towards aroma compounds and can operate under mild conditions [14,15,16]. Several studies investigated the aroma compounds recovery present in different fruit juices and reported high separation factors at low temperatures for multi-component mixtures by commercial pervaporation membrane [1,5,8,14]. Organophylic pervaporation is particularly suitable for the recovery of volatile compounds from their dilute solution [5,16].

The objective of this study is to investigate the effects of key parameters on the pervaporative recovery process of volatile

aroma such as feed temperature, permeate flow-rate and feed concentration of compounds from model solution using a commercial polydimethyl-siloxane (PDMS) membrane.

Experimental

The experiments were carried out with the aqueous solutions of selected aroma compunds with different concentration (Table 1) [4]. 3P experimental design was applied for expected non-linear relations between operational parameters as independent variables and key parameters below. The experiments were performed at 3 different temperatures: 20, 40, 60°C. The flow-rate of feed solution was set for 150, 200, 250 L/h. The applied laboratory scale pervaporation unit with flat-sheet membrane was operated by carrier gas method circulating air in closed circle at atmospheric pressure. The characteristics of selected membrane are shown in Table 2.

The carrier gas was circulated in the closed loop by a vacuum pump without lowering partial pressure at permeate side. Permeate in vapour phase was condensed in a cooler chilled by liquid nitrogen.

The characteristics of pervaporation can be described by factors like permeate flux (Eq. 1), separation factor (Eq. 2) and the temperature dependence of the process (Eq. 3, Arrhenius-equation) [1,10].

$$J_P = \frac{m_P}{F_m \cdot t} \quad (1) \qquad \alpha = \frac{c'(1-c)}{c(1-c')} \quad (2) \qquad J = J^* \cdot e^{-\frac{E_a}{R \cdot T}} \quad (3)$$

Where J_p is permeate flux [kg/(m²h)], m_p is the weight of permeate [kg], F_m is the membrane surface [m²] and t is the time of one experiment [h]. The α is the separation factor, c' is the concentration of permeate related to the compound passing faster through the membrane (organic compound), c is the concentration of feed related to the compound passing faster through the membrane. In the Arrhenius-equation J^* is the pre-exponential factor, E_a is the activation energy [kJ/mol], R is the universal gas constant [J/molK] and T is temperature in Kelvin degree.

Mathematical modelling

Our approach to simulate the mass transfer during pervaporational separation was the common and accepted resistance-in-series model (Fig. 2) [6,12]. This model is applicable with both membrane concentration and partial pressure to describe the mass transfer process. In case of pervaporation, partial pressure as a driving force characterises the process better which parameter was chosen for our simulation [9].

$$J_i = Q_{OV,i} \cdot A \cdot (p_{L,i} - p_{G,i}) \quad (4)$$

where J_i is the mol stream of (*i*) component through the membrane [mol/s], $Q_{OV,i}$ is the overall mass transfer coefficient of (*i*) component with driving force of partial vapour perssure [mol/(m²Pas)], A is the membrane surface (m²), $p_{L,i}$ is the partial

Tab. 1. Concentrations of applied aroma compunds in mixtures A,B and C

Apple aroma components	Mixture A ppm	Mixture B ppm	Mixture C ppm
Ethanol	30	40	50
Ethylacetate	35	45	50
n-Butanol	10	15	20
i-Butanol	15	20	25
i-Amyl alcohol	5	10	15

Tab. 2. Characteristics of examined membrane

Company	Type of membrane	Character	Active surface
Sulzer Chemtech	PERVAP-1060 sheet membrane	Organophilic	131 cm²

vapour pressure of (*i*) component at feed side (Pa), and $p_{G,i}$ is the partial vapour pressure of (*i*) component at permeate side (Pa).

Assuming that the resistance at permeate side is negligible [15,16], the mass transfer through the membrane can be desribed by linear resistance model as follows:

$$\frac{1}{Q_{OV,i}} = \frac{1}{Q_{M,i}} + \frac{1}{Q_{L,i}} \quad (5)$$

where $Q_{OV,i}$ is the overall mass transfer coefficient of (*i*) component with driving force of partial vapour pressure [mol/(m²Pas)], $Q_{L,i}$ is the mass transfer coefficient of (*i*) component with driving force of partial vapour perssure at liquid side [mol/(m²Pas)], and $Q_{M,i}$ is the mass transfer coefficient of (*i*) component with driving force of partial vapour perssure in membrane [mol/(m²Pas)].

The mass transfer coefficient of liquid side with the driving force of partial vapour pressure:

$$Q_{L,i} = \frac{\rho_{L,i}}{\gamma_i \cdot P_i^0} \cdot k_{L,i} \quad (6)$$

where $k_{L,i}$ is the mass transfer coefficient of (*i*) component with driving force of concentration-difference at liquid side (m/s), γ_i is the plasticization coefficient of (*i*) component at liquid side, P_i^o is the saturated vapour pressure of (*i*) component [19], $\rho_{L,i}$ is the molar density of the liquid.

$$k_{L,i} = \frac{Sh \cdot D_{i,j}}{d_e} \quad (7)$$

where Sh is the Sherwood-number, $D_{i,j}$ is the diffusivity of (*i*) component in (*j*) solvent by Wilke-Chang equation (m²/s) [18] d_e is the equivalent diameter of the membrane module at liquied side calculated by the geomethric relations of the membrane modul (m).

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Diffusivity can be calculated from the Wilke-Chang equation [20]:

$$D_{i,j} = \frac{(7,4 \cdot 10^{-12}) \cdot (\Phi_j \cdot M_j)^{0,5} \cdot T}{\eta_L \cdot V_L^{0,6}} \qquad (8)$$

where Φ_j is the association factor for solvent (water: $\Phi_j = 2,6$), M_j molar weight of solvent (kg/kmol), T is the temperature (K), η_L is viscosity of the mixture (Pa·s), and V_L is the molar volume of the mixture at normal boiling temperature (m³/kmol).

The Sherwood-number can be described by the equation from (7) in case of impermanent flow rate.

Results and discussion

Based on the resistance-in-series model detailed above the resistances of membrane, liquid side and the overall mass transfer process are the derivatives of mass transfer coefficients of the parts of the model.

Liquid side mass transfer coefficient was the highest with which its resistance was the lowest therefore the main determinative step of mass transfer process is the evaporation through the membrane. The separation factor which describes the efficiency of the process varied in different ranges for different compounds (Table 3) as ethanol had 3-10 times higher values than n-butanol. Usually ethanol separation factor is lower (10-20) in case of pervaporation [3]. The increased separation factor for ethanol can be explained by the presence of other compounds which as a coupling effect can modify the diffusivity as if they were alone [8]. All compounds were separated with an expected high efficiency which maximum was obtained at 60°C for all compounds. For this commercial organophylic membrane a particular water flux is characteristic which is a natural behaviour of the process since instead of the hydrophylic membranes the physical relationship of the water and membrane at the membrane surface allow water transport as well [17].

As it is illustrated by the surface respond of the experimental model (Figure 1) the separation efficiency is significantly ($p<0.05$) influenced by the operation temperature and insignificantly ($p<0.05$) depends on the other two operational conditions (feed concentration, feed flow-rate). The relationship between separation factor and the temperature can be described by an exponential function.

The capacity of the membrane is described by the flux of compounds through the membrane. From the compounds with different characteristic overall-, organic (for each compounds)-, and water flux can be calculated. Figure 2 illustrates the effect of operation conditions on the flux of ethyl-acetate.

The determinations of activation energies are from the logarithmic form of Arrhenius equation. The function derived from logarithmic form is linear from which slope is calculated the value of activation energy. For each compounds very similar

Tab. 3. Separation factor value ranges of compounds on different feed flow-rates and concentrations

Separation factor [-]	20°C	40°C	60°C
i-amyl-alcohol	0.9-5.6	5.4-10.5	8.9-24.1
ethyl-acetate	1.2-3.4	2.7-4.5	2.9-7.0
n-butanol	0.5-5.1	0.8-8.2	0.9-12.6
i-butanol	4.1-9.7	6.4-20.1	11.5-64.7
ethanol	15.9-61.6	28.8-76.8	33.4-96.1
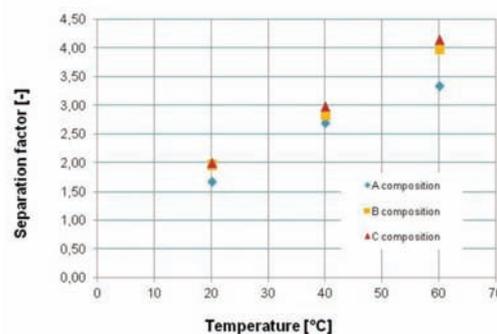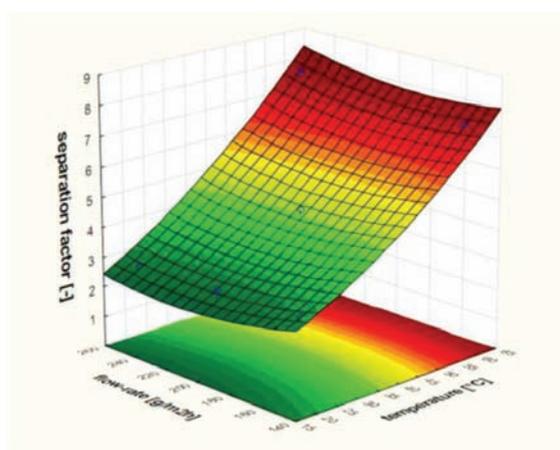
Fig. 1. Separation factor dependence of operational parameters regarding to n-butanol
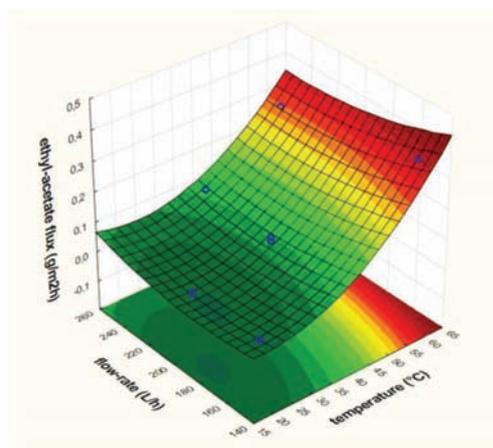
Fig. 2. Flux as a function of flow-rate, temperature in case of mixture A for ethyl-acetatel

slopes are calculated from almost parallel lines and the average of activation energies are summarized in Figure 3. The compounds are in order of increasing molecule polarity from bottom to top to illustrate the discovered relationship between the two parameters. This relation was also parallel by the increase of solubility in water for the compounds. As it was experienced from the results of mathematical modelling the mass transfer process is mainly influenced by the physico-chemical relationship of molecules in the solution with the membrane surface. The relationship between molecular polarity and activation energies needs further investigation to better understand the entire transport process.

Compound	Activation energy [kJ/mol]	Polarity order
water	48.3	
ethanol	51.2	
ethyl-acetate	62.0	
n-butanol	65.3	
i-butanol	69.0	
i-amyl-alchol	78.2	

Fig. 3. Activation energies of the compounds with molecule polarity increasing from bottom to top

Conclusions

It can be established by the experimental data that the examined membrane is applicable for separation the selected compounds from aqueous solution. The high enrichment rate let us say that this process can be applied in food-industry for aroma recovery. This study generated the need for further investigation of the mass transfer process and the optimisation of operational parameters. With the benefit of better understanding the process the economical aspects of the process is recommended to evaluate.

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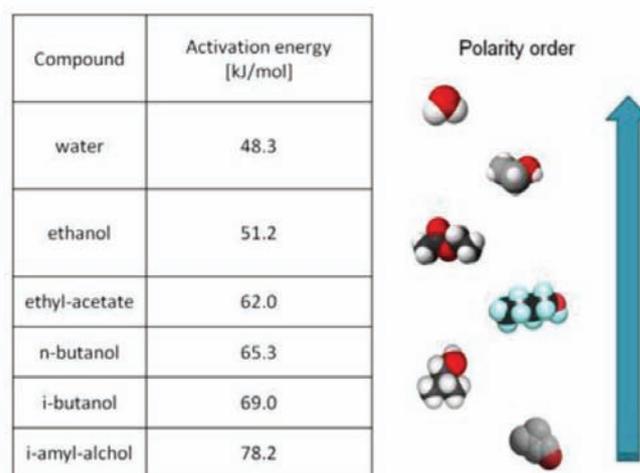
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