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The Performance of Pervaporative Aroma Recovery Units: Process Simulations

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ABSTRACT

Pervaporation is an emerging membrane-based separation technique which is very promising, for instance, for aroma recovery. Computer simulations of the behavior of large-scale pervaporation units for aroma recovery indicated that aroma concentrates can be produced by using this technique. For four of the five aroma compounds investigated, the degrees of recovery were high. The simulations showed that some process parameters, e.g., temperature, degree of aroma folding, and membrane material, strongly affect the performance of the process.

Key Words. Pervaporation; Aroma compounds; Simulations

INTRODUCTION

The use of hydrophobic membranes in pervaporation for the removal of organic compounds from aqueous solutions is of great interest in, for instance, the removal of organic contaminants from wastewaters. In the literature a large number of fundamental studies deal with this application, which has also been evaluated with respect to system performance, processing conditions, and costs (1–4). Pervaporation has, however, not been a success in this field although its performance is attractive. The reason for this is that several

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other techniques suitable for the task already exist, and pervaporation cannot compete with them in terms of economics (5).

The removal of alcohols, aldehydes, and esters by use of pervaporation has also received great interest for applications in food and biotech industry (6–8). One of the most promising applications for pervaporation in the food industry is aroma compound recovery or aroma compound concentration. This potential is also reflected in the large volume of fundamental research that has been carried out in this area (7–9). Not only can the quality of the beverage be improved by pervaporative aroma recovery, but there could also be economic benefits from producing a high-quality processed beverage. For instance, the retail price in Sweden of nonconcentrated juice is twice that of juices made from concentrates, which often have a poorer aroma. The production of a high-quality juice concentrate would therefore also be of economic interest. Aroma compounds are typically organic compounds, such as aldehydes, esters, and alcohols. Pervaporation for aroma recovery is thus very similar to removal of organic compounds from wastewaters using hydrophobic membranes. The objective of this study is to present estimates of the performance of a pervaporation plant for aroma recovery.

PROCESS DESCRIPTION

The situation considered is a process line for the production of concentrated apple juice. In this process, aroma compounds are recovered and put back into the final product in order to enhance its quality (10).

In order to simplify the discussion of the effects of different process parameters on process performance, a reference plant or reference situation was chosen. The aroma recovery unit considered is a pervaporation plant which produces a 100-fold aroma concentrate. The term "folding" is commonly used when discussing aroma recovery techniques as it gives an indication of the efficiency of the aroma recovery unit. If an aroma concentrate is 100-fold, it means that the volume of the aroma concentrate produced is 1% of the ingoing raw material stream. It does not, however, mean that the concentration of aroma compounds is 100 times higher in the concentrate compared with the ingoing raw material stream, i.e., it is not assumed that the recovery of aroma compounds is perfect (11).

In the calculations, the stream fed to the aroma recovery unit is considered to consist of water and five typical aroma compounds: isobutanol, isoamyl alcohol, *trans*-2-hexenal, ethyl acetate, and ethyl butyrate (12).

In a previous study (12), three commercially available membranes were found to be of interest for aroma recovery, i.e., POMS-PEI (GKSS, Geesthacht, Germany), PDMS-PT1100 (Hoechst Celanese Corp., Charlotte, NC, USA), and PDMS-1060 (Deutsche Carbone AG, Neunkirchen, Ger-

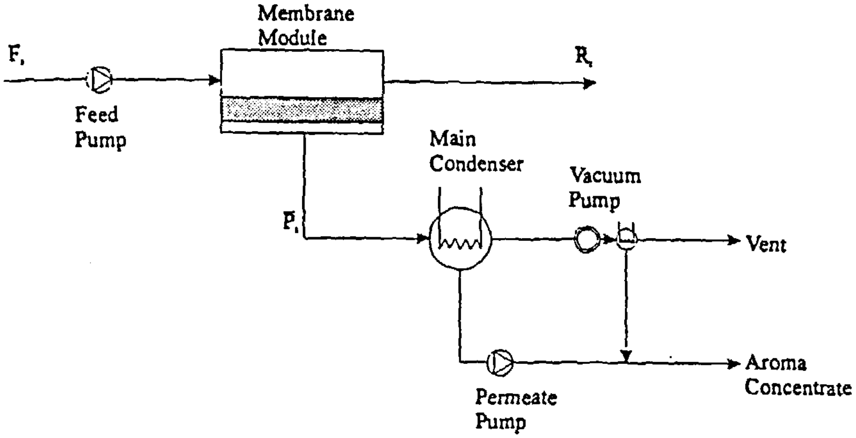

FIG. 1 Schematic drawing of pervaporative aroma recovery unit.

many). Of these, the POMS-PEI membrane has the highest selectivity for aroma compounds and was therefore chosen for evaluation in the reference plant. Simulations were also performed for the other membranes.

The pervaporative aroma recovery unit is outlined in Fig. 1. It consists mainly of feed pumps, membrane modules, a main condenser, a permeate pump, and a Roots vacuum pump. The feed pumps are assumed to be centrifugal pumps and the modules are assumed to be spiral ones. The main condenser is a spiral condenser. The permeate pump is necessary for the removal of the bulk of the permeate which is liquified in the main condenser. The Roots vacuum pump is a "dry" and oil-free diaphragm pump equipped with a secondary condenser on its vent side. The reason for this is that many aromas will not be liquified in the main condenser, which is operating at a low pressure, but will remain in a gaseous state and leave the condenser together with the vent gases. The aroma compounds will instead be transported through the vacuum pump, together with the vent gases, and condensed in the secondary condenser which operates at atmospheric pressure. The two condenser streams are assumed to be mixed together to form one aroma concentrate stream.

The flow rate in the reference situation is 46.26 mol/s, which corresponds to approximately 3000 kg/h. This is the capacity of many medium-sized aroma recovery plants in the beverage industry. The concentration of each aroma compound in the stream is 2 ppm (mole fraction) and the temperature of the stream is 40°C (313.15 K). The concentrations of the aroma compounds are not necessarily what would be found in most apple juices. On the contrary, apple juice contains a very large number of highly volatile compounds at normally very low concentrations, between 0.1 and 20 ppm, and the total concentration of aroma compounds is low, between 100 and 200 ppm. Furthermore, large variations in aroma compound composition and concentration occur due to variations in apple varieties, climate, soil, etc. (13). However, for pervaporation of dilute aqueous-organic feeds at a constant feed temperature, the cost in terms of membrane area is the same for any decimal reduction of the feed concentration of an aroma compound. In other words, the membrane area necessary for reducing the feed concentration of an aroma compound from 50 to 5 ppm is the same as when reducing it from 5 to 0.5 ppm. Furthermore, in the calculations presented, we do not discuss the efficiency of the pervaporation unit in terms of concentrations in the feed or in the concentrate, but rather in terms of aroma recovery. The term aroma recovery, AR_i, is defined as how much of the aroma compounds are transferred from the ingoing feed stream to the aroma concentrate, i.e., the permeate,

$$AR_i = \overline{P}_i/\overline{F}_i \tag{1}$$

The reference temperature is a very low temperature for aroma recovery plants, which are normally operated in a temperature range between 40 and 100°C (10). One of the advantages of pervaporation for aroma recovery is that it can offer mild process conditions, i.e., low temperatures, in order to avoid thermal damage to the aroma compounds. The reference situation temperature was therefore chosen to be at the lower end of the temperature range of commercially available aroma recovery plants.

The permeate pressure in the plant is 7 mbar. This pressure was chosen because of the main condenser. The main condenser determines the permeate pressure; the lower the condenser temperature, the lower the permeate pressure. A low permeate pressure is desirable as this increases the mass transfer rate across the membrane. However, as the aroma concentrate in the situation considered consists mainly of water, it will freeze if the temperature is too low. In order to avoid this, the condenser temperature should be above the freezing point. The equilibrium pressure of water at 0°C is 6.1 mbar, and the reference permeate pressure was consequently chosen to be 7 mbar.

The importance of concentration polarization in pervaporation is well known. In the reference plant it was chosen to work with a concentration polarization modulus (CPM_i, defined below) of 0.8.

THE SCALE-UP MODEL

The scale-up calculations were performed using heat- and mass-transfer models as well as heat and mass balances for the pervaporation process.

Local Mass Transfer

The flux of a component i, J_i^{M}, from the feed to the permeate can be described by the basic flux equation (14–19).

$$J_i^{\mathrm{M}} = k_{\mathrm{ov},i}^{\mathrm{M}}(P_{\mathrm{f},i}^{\mathrm{b}} - P_{\mathrm{p},i}^{\mathrm{b}}) \tag{2}$$

in which $k_{\mathrm{ov},i}^{\mathrm{M}}$ is an overall mass transfer coefficient and $P_{f,i}^{\mathrm{b}}$ and $P_{\mathrm{p},i}^{\mathrm{b}}$ are the partial pressures of component i in the feed and permeate, respectively.

Note especially that

$$P_{\mathrm{f},i}^{\mathrm{b}} = \gamma_{\mathrm{f},i} X_{\mathrm{f},i}^{\mathrm{b}} P_{0,i} \tag{3}$$

Except for *trans*-2-hexenal, the pure component equilibrium pressures, $P_{0,i}$, were obtained from Gmehling and Onken (20) in the form of the Antoine equation,

$$\log P_{0,i} = A + \frac{B}{t + C} \tag{4}$$

The pure component equilibrium pressure for *trans*-2-hexenal was estimated with a two-parameter, corresponding-states equation for vapor pressure, according to Reid et al. (21). This was done for a number of temperatures and fitted to an Antoine-type equation.

For a number of multicomponent aroma mixtures, Bruin (22) showed that the activity coefficient, $\gamma_{\mathrm{f},i}$, for a given aroma compound is not affected by the presence of the other aroma compounds in the mixture. This is due to the normally very low concentrations of aroma compounds in apple juice, and from a practical viewpoint, the aroma compounds often can be considered at infinite dilution (23). Originating from this, the activity coefficients were estimated using the UNIFAC method (21). The activity coefficients were thus estimated for binary mixtures of one aroma compound and water, i.e., it was assumed that the presence of other aroma compounds in the feed did not affect the activity coefficient of any given aroma compound. The activity coefficient of water was assumed to be equal to unity. In order to account for the temperature dependence of the activity coefficients, an exponential fit of the estimated values in the temperature range 5 to 50°C was employed according to

$$\gamma_{\mathrm{f},i} = \gamma_{0,i} \exp\left(\frac{E_{\mathrm{a},i}^{\gamma}}{T}\right) \tag{5}$$

The model described above should give acceptable values for the activity coefficients if the feed stream mainly consists of water and aroma compounds. Such feed streams could, for instance, be loss streams or aroma strip streams originating from the main process during apple juice processing. If the raw juice is considered as a feed stream, it should be remembered that it could also contain solutes such as carbohydrates, acids, and ethanol. Carelli et al. (23) compared the activity coefficients of some aroma compounds in model solutions containing such solutes with the ones of the binary mixture of the aroma compound and water. In general, the presence of these solutes results in increases of the activity coefficients of the aroma compounds. In the present study this would mean that the driving forces for mass transfer become larger, and that higher degrees of aroma recovery would be obtained.

The partial pressure of an aroma compound in the vapor permeate can be obtained from Dalton's equation

$$P^{\mathrm{b}}_{\mathrm{p},i} = Y^{\mathrm{b}}_{\mathrm{p},i} P_{\mathrm{p}} \tag{6}$$

As a molar frame of reference is used for the basic flux equation, the mole fraction $Y^{\mathrm{b}}_{\mathrm{p},i}$ is given by

$$Y^{\mathrm{b}}_{\mathrm{p},i} = J^{\mathrm{M}}_{i} / \sum_{j} J^{\mathrm{M}}_{j} \tag{7}$$

In the literature, the overall mass transfer coefficient, $k^{\mathrm{M}}_{\mathrm{ov},i}$, is normally considered to be composed of a mass transfer coefficient for the liquid feed boundary layer, $k^{\mathrm{M}}_{\mathrm{f},i}$, and a mass transfer coefficient for the membrane, $k^{\mathrm{M}}_{\mathrm{m},i}$, according to

$$\frac{1}{k^{\mathrm{M}}_{\mathrm{ov},i}} = \frac{1}{k^{\mathrm{M}}_{\mathrm{f},i}} + \frac{1}{k^{\mathrm{M}}_{\mathrm{m},i}} \tag{8}$$

The mass transfer coefficient of the membrane describes the mass transfer of a component from a position in the liquid feed infinitely close to the membrane to a position in the vapor permate infinitely close the the membrane. This coefficient thus contains information on the absorption of the component into the membrane, its diffusion through the membrane, and finally its desorption to the membrane. It has been observed in the literature that this mass transfer coefficient of the membrane can be considered to be independent of the feed composition and the feed temperature (19), and this view was adopted in this study. The mathematical description of the mass transfer in the liquid feed boundary layer can easily be described by Sherwood correlations (19, 24) for circular and rectangular channels. In the situation considered in this study, pervaporation using spiral-wound modules, the description of mass transfer in the liquid feed boundary layer is not straightforward. For such systems it can be shown to be highly dependent on a number of factors, such as crossflow velocity, geometry of the flow channel, feed spacers in the flow channel, spacer height or spacer morphology, the number of leafs, and leaf length and leaf width; the correlations observed cannot be considered as general (16, 25). It is, however, a fact that the overall mass transfer coefficient up to a certain flow rate can often be observed to be logarithmically dependent on the flow rate. As no general theory or description for the boundary layer mass transfer in spiral-wound modules exists, and in order not to complicate the evaluation by limiting the performance to a certain manufacturer's design but still not have an unrealistic number of parameters to investigate, a concentration polarization modulus, CPM_i, was defined according to

$$\mathrm{CPM}_i = k^{\mathrm{M}}_{\mathrm{ov},i}/k^{\mathrm{M}}_{\mathrm{m},i} \tag{9}$$

A value of the concentration polarization modulus of 0.80, which is used in the reference situation, consequently corresponds to a situation were concentration polarization reduces the overall mass transfer coefficient by 20% compared with its maximum value. During the calculations the concentration polarization modulus was assumed to be equal for all aroma compounds and also to be temperature independent. This is a simplification of any real situation, but we think that it is justified as its use gives an indication of the effects of concentration polarization in the considered situation. Concentration polarization was not considered for water.

Heat Consumption

As the permeate mainly consists of water and very small amounts of aroma compounds, the heat consumption in the pervaporation process was considered to be due only to the mass transfer of water. The heat consumed was assumed to be equal to the sum of the heat of vaporization and the heat of isothermal expansion of the permeate, as shown in a previous study (26), i.e.,

$$q_{\mathrm{proc}} = q_{\mathrm{vap}} + q_{\mathrm{exp}} \tag{10}$$

A linear fit of the heat of vaporization of water in the temperature range between 5 and 50°C was adopted from Schmidt and Grigull (27),

$$q_{\mathrm{vap}} = 56788.19 - 42.72T \quad (\mathrm{J/mol}) \tag{11}$$

The heat of expansion was assumed to be isothermal and was calculated according to

$$q = nRT\ln(P^{\mathrm{b}}_{\mathrm{f,aq}}/P^{\mathrm{b}}_{\mathrm{p,aq}}) \tag{12}$$

Global Mass and Heat Balances

A simulation program which calculates the global mass and heat balance for a pervaporation unit was written, and it is shown schematically in Fig. 2. The program requires the partial feed flows to the unit, the temperature of the feed, the permeate pressure, the concentration polarization modulus, and

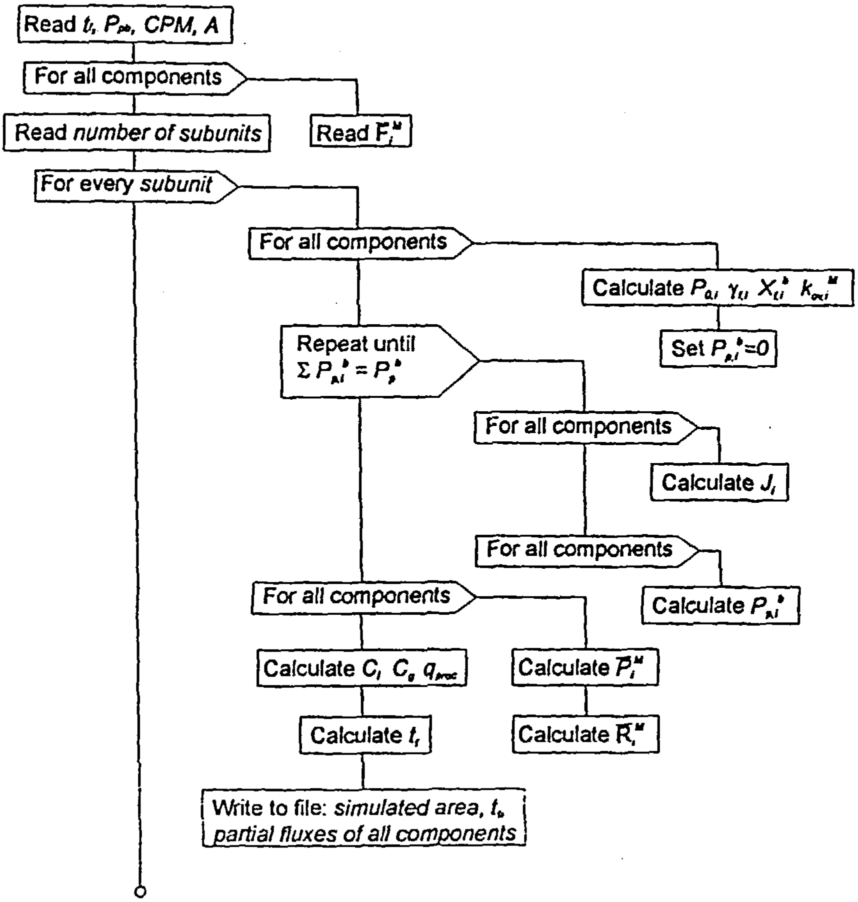

FIG. 2 Schematic presentation of the algorithm used in the simulation program. Details and programmer's tricks are not presented.

the requested membrane area in the unit. The unit is then split up into a number of subunits in which transport properties are considered to be constant. From the ingoing temperature and feed flows, equilibrium pressures, activity coefficients, feed concentrations, and mass transfer coefficients are calculated. These are used to iteratively calculate the partial fluxes of aroma compounds and water in such a way that the specified total permeate pressure is equal to the sum of partial pressures. A local mass balance is calculated for the subunit to determine the partial retentate streams from it:

$$\overline{F}_i^{\mathrm{M}} = \overline{R}_i^{\mathrm{M}} + \overline{P}_i^{\mathrm{M}} \tag{13}$$

where $\overline{F}^{\mathrm{M}}$, $\overline{R}^{\mathrm{M}}$, and $\overline{P}^{\mathrm{M}}$ are the feed, retentate, and permeate flows, respectively.

A heat balance is then calculated using the determined streams and the local heat consumption in the subunit:

$$\overline{F}^{\mathrm{M}}\mathbb{C}_l t_f = \overline{R}^{\mathrm{M}}\mathbb{C}_l t_r + \overline{P}^{\mathrm{M}}(\mathbb{C}_g t_f + q_{\mathrm{proc}}) \tag{14}$$

The heat balance gives the temperature of the retentate leaving the subunit, t_r. Effects due to temperature polarization and radial temperature gradients were not considered. Polynomial fits on literature data for the heat capacities (J/mol·°C) of liquid and vapor water in the temperature range 0 to 50°C were adopted from Schmidt and Grigull (27) according to

$$\mathbb{C}_l = 143.0423 - 0.4352T + (7.0348 \times 10^{-4}T^2) \quad (\mathrm{J/mol\cdot°C}) \tag{15}$$

$$\mathbb{C}_g = 32.8161 + (6.6438 \times 10^{-7}T) + (1.0698 \times 10^{-5}T^2) \quad (\mathrm{J/mol\cdot°C}) \tag{16}$$

Finally, the global mass and heat balances are corrected for the flows of mass and heat determined in the subunit, and the program moves on to the next subunit. In doing so, the partial retentate flows and retentate temperature from the preceding subunit are taken as feed characteristics. In order to speed up the simulations, calculations for a given aroma compound were stopped when 95% of it had been transferred to the permeate flow, i.e., the aroma concentrate, if this happened before the requested membrane area had been reached.

The input data for the simulations are mass transfer characteristics of three membranes for five aroma compounds and water as presented in an earlier study (12). These data are presented in Table 1, together with literature and estimated data for physical properties.

Finally, it should be mentioned that the permeate pressure $P_{\mathrm{p}}^{\mathrm{b}}$ was considered to be equal for all points on the permeate side of the membrane. For spiral-wound pervaporation modules it is known that a considerable increment in permeate pressure can be observed toward the leaf end if the design of the permeate chamber is non-optimal (15), a fact that might result in overestimation of the module performance. The situation is very much similar to the one earlier described for the mass transfer in the liquid feed boundary layer, i.e., it can be observed to be dependent upon the geometry of the permeate chamber, the spacers in the permate chamber, spacer height or spacer morphology, the number of leafs, leaf length, and leaf width. However, such effects can be minimized by careful design, especially for low flux applica-

TABLE 1
Properties of the Permeating Components

	$k^{M}_{m,i}$ (mol/m²·s·mbar) (12)			Antoine equation coefficients[a] (20)			Activity coefficient correlation (21)	
Compound	POMS-PEI	PDMS-PT1100	PDMS-1060	A	B	C	$\gamma_{0,i}$	E_i^γ (J/mol·K)
Isobutanol	5.7×10^{-5}	1.1×10^{-4}	8.9×10^{-5}	8.53516	1950.940	237.147	11.43	463.73
Isoamyl alcohol	2.4×10^{-4}	3.8×10^{-4}	2.9×10^{-4}	7.38170	1373.780	174.333	18.87	614.26
trans-2-Hexenal	2.9×10^{-4}	3.5×10^{-4}	2.9×10^{-4}	7.75757	2044.093	273.150	21.95	851.03
Ethyl acetate	2.3×10^{-5}	5.7×10^{-5}	2.1×10^{-5}	7.10179	1244.951	217.881	58.33	282.15
Ethyl butyrate	6.1×10^{-4}	6.9×10^{-4}	4.3×10^{-4}	7.24537	1470.930	215.719	58.99	640.61
Water	3.4×10^{-5}	1.2×10^{-4}	8.7×10^{-5}	8.07131	1730.630	233.426	—	—

[a] *The constants specified for the Antoine equation give the pressure in mmHg.*

tions such as those considered in this study. For this reason and in order to simplify the concentration polarization phenomenon, simplification on the permeate pressure was introduced.

SCALE-UP RESULTS AND EFFECT OF PROCESS PARAMETERS

Simulations were done to study the influence of such parameters as feed flow, temperature, permeate pressure, folding degree, and membrane material on the behavior of the reference plant/situation, the conditions of which are specified in Table 2. These factors were varied one by one in order to illustrate the behavior of a pervaporative aroma recovery unit. Simulations were carried out for each parameter in terms of the membrane area required to achieve the requested folding, and in terms of the recovery of the aroma compounds.

Reference Plant/Situation

The pervaporative recovery of aroma compounds as a function of membrane area is presented in Fig. 3. As can be seen from this figure, the aroma

TABLE 2
Reference Plant/Situation

F	Folding	T_f	P_p (mbar)	$X^b_{f,i}$	CPM_i	Membrane
46.26 mol/s (3000 kg/h)	100	40°C (313.15 K)	7	2×10^{-6}	0.8	POMS-PEI

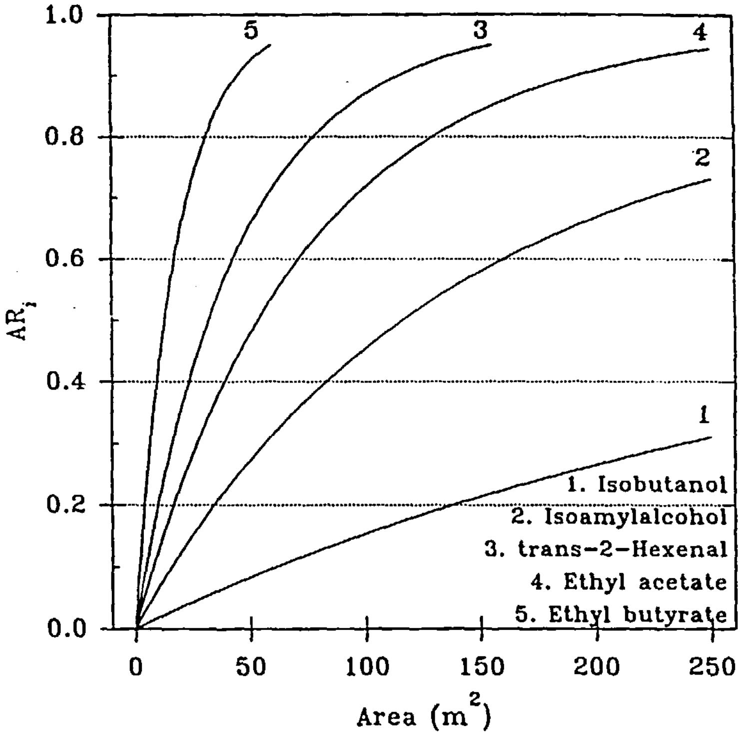

FIG. 3 Aroma recovery as a function of membrane area for the reference situation. A membrane area of 244 m^2 is required to produce a 100-fold aroma concentrate.

compounds which exhibited the highest enrichment in our previous study of different membrane materials (12), i.e., ethyl butyrate, ethyl acetate, and *trans*-2-hexenal, were quite easy to transfer to the permeate, even with small membrane areas. The aroma compounds which were not enriched to the same degree in the same study, i.e., isobutanol and isoamyl alcohol, were not transferred to the aroma concentrate to the same extent.

In order to produce an aroma concentrate which is 100-fold, i.e., a permeate flow of 0.46 mol/s (30 kg/h), a membrane area of 244 m^2 is required. Under this condition the recoveries of isobutanol, isoamyl alcohol, *trans*-2-hexenal, ethyl acetate, and ethyl butyrate were 0.31, 0.73, >0.95, 0.94, and >0.95, respectively. The temperature of the retentate stream was 33.7°C (306.85 K).

Effect of Concentration Polarization

As the aroma concentrate produced is mainly composed of water (over 99.9% in these simulations), the effect of concentration polarization on the area necessary to produce a 100-fold aroma concentrate will be negligible. In other words, as water is not affected by concentration polarization, the area necessary to produce a certain amount of permeate will not be affected by concentration polarization. Concentration polarization does, on the other hand, affect the mass transfer of the compounds preferentially permeated through the membrane, i.e., the aroma compounds, in an undesirable way. The effect of concentration polarization is presented in Fig. 4 for different values of the concentration polarization modulus, CPM_i. The effect is such that, for a folding of 100, concentration polarization is of greatest importance for the recovery of aroma compounds which are less enriched, relatively speaking. The reason for this is that even if concentration polarization reduces

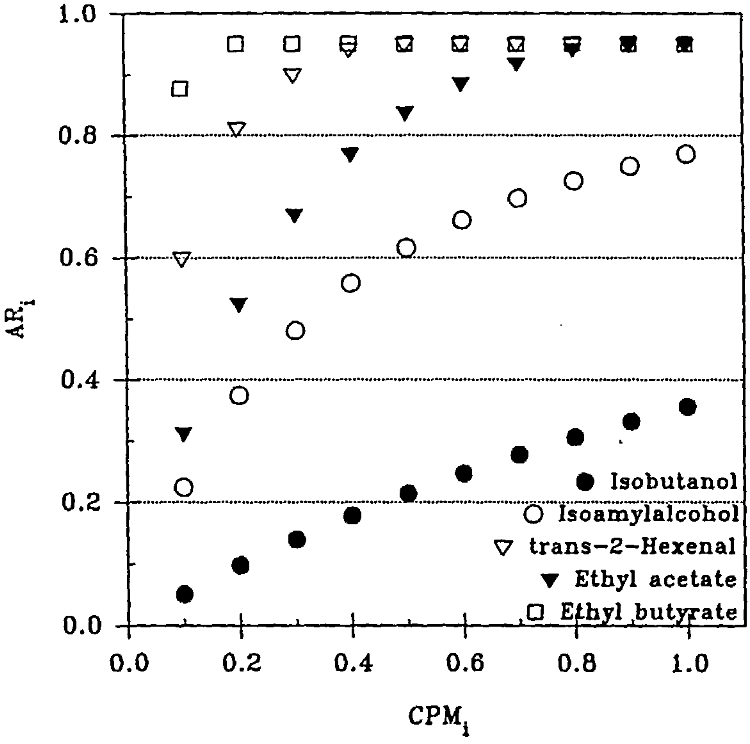

FIG. 4 Effect of concentration polarization modulus on aroma recovery.

the mass transfer of the highly permeating components, e.g., ethyl butyrate or ethyl acetate, by a certain factor, their overall mass transfer coefficients will still be so high that they are fully transferred to the aroma concentrate when it is 100-fold. For less highly permeating aroma compounds, e.g., isobutanol and isoamyl alcohol, which are not fully transferred to the aroma concentrate at optimal conditions, the recovery will be even less, the greater the concentration polarization.

Effect of Feed Flow

As the membrane itself determines the flux for both water and the aroma compounds, the area must be increased if the feed flow increases and it is desirable to maintain the folding degree. Due to linearities in the global mass and heat balances to the feed flow, the local mass transfer properties will also be affected linearly by the feed flow. As the feed flow increases from 15.42 to 154.2 mol/s, the required membrane area increases from 81 to 810 m^2. The aroma recoveries and retentate temperatures will consequently not be affected by the feed flow, under the assumption that all other process variables are unaffected. The result is that when producing a 100-fold aroma concentrate, the only parameter affected when manipulating the feed flow is the membrane area required.

Effect of Feed Temperature

In these simulations it was assumed that the molar-based mass transfer coefficient of the permeating components was not affected by temperature (19). Changes in fluxes are instead due to changes in the parameters responsible for the gradients in partial pressures across the membrane. As these properties, i.e., pure component equilibrium pressures and activity coefficients in the feed, have nonlinear effects on the local mass transfer, the performance of the pervaporation unit was considerably affected by changes in the feed temperature. The most drastic effect was observed for the membrane area required to produce a 100-fold aroma concentrate (Fig. 5). When simulating a feed inlet temperature of 20°C (293.15 K), the required area was 1121 m^2, which is considerably larger than that in the reference plant (40°C), which was 244 m^2. By increasing the feed inlet temperature to 60°C (333.15 K), the membrane area requested decreased to 80 m^2. This behavior can mainly be attributed to the strong increase in the driving force for the mass transfer of water across the membrane as the feed temperature is increased. When changing the feed temperature, the ability of the process to recover some of the aroma compounds is affected (Fig. 6). In the case of *trans*-2-hexenal and ethyl butyrate, the aroma recovery is still high and changes in the mass transfer properties due to temperature changes in the feed are not significant. The recovery of isobutanol remains low and almost constant with temperature.

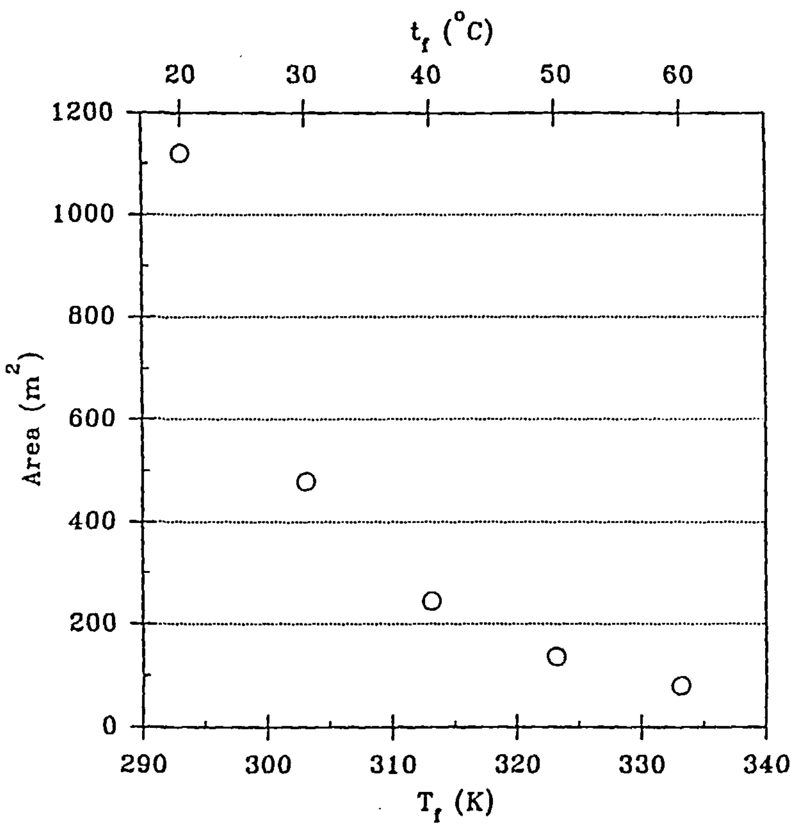

FIG. 5 Membrane area required for producing a 100-fold aroma concentrate as a function of inlet feed temperature.

The reason for this is that the mass transfer properties of isobutanol are changed in a similar way to the mass transfer properties of water. Interestingly, the recovery of isoamyl alcohol can be increased by increasing the feed temperature. This is, of course, due to the fact that the driving force of isoamyl alcohol increases faster with increasing temperature than that for water. Similarly, the recovery of ethyl acetate decreases with increasing feed temperature. However, this is only significant at temperatures above 40°C (313.15 K). The reason for this is the opposite of the reason described for isoamyl alcohol.

Effect of Permeate Pressure

The performance of a pervaporative aroma recovery unit was, to a large extent, dependent on the flow of water through the membrane. This was also found to be the case when investigating effects of permeate pressure. The equilibrium pressure of water at 40°C (313.15 K) is 74 mbar, which is relatively high in comparison with the permeate pressures investigated in these simulations. The reduction in driving force for the mass transfer of water across the membrane is consequently small when the total permeate pressure is increased to 10 mbar. Similarly, the driving force for mass transfer across the membrane is increased as the permeate pressure falls below 7 mbar, resulting in a decrease in the membrane area required. According to the simulation algorithm, the membrane area required to produce a 100-fold aroma concen-

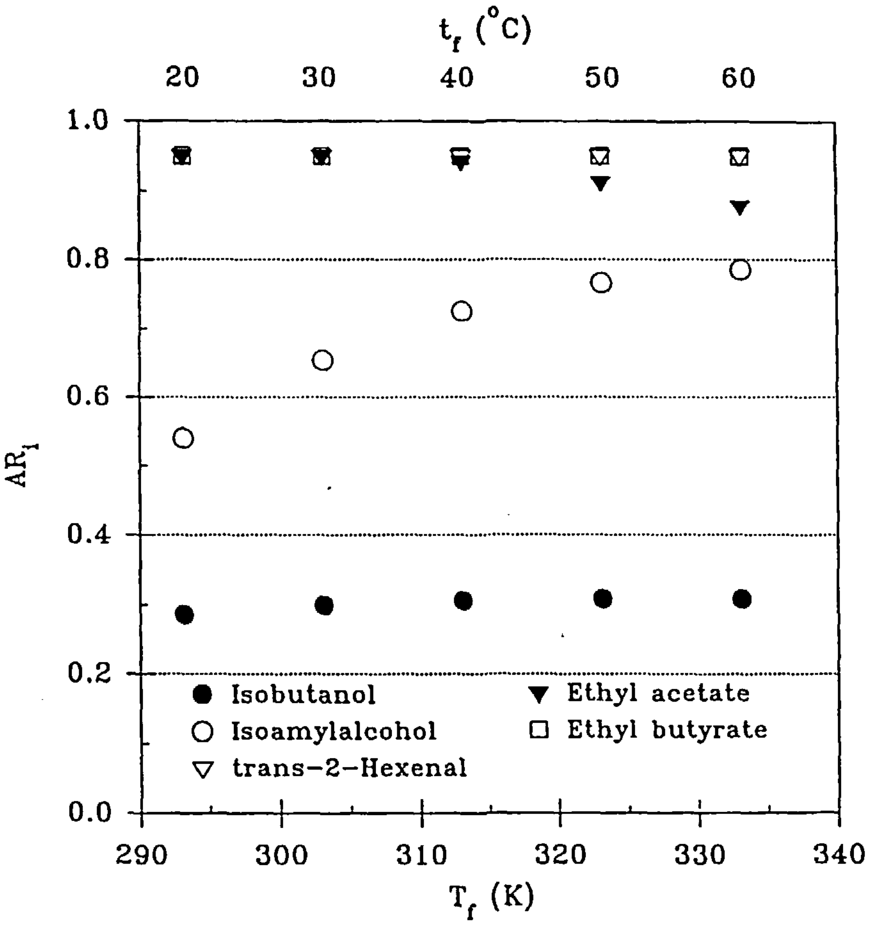

FIG. 6 Effect of feed temperature on aroma recovery.

trate increases from 232 to 257 m^2 if the permeate pressure is increased from 4 to 10 mbar. If permeate pressures in the lower range discussed above were to be established in the system described earlier, the permeate would freeze in the condenser due to condensation temperatures falling below 0°C. An alternative could be to use an interstage compressor between the pervaporation modules and the condenser, as suggested by Hickey and Gooding [4]. The recovery of the aroma compounds is only slightly affected by changes in the permeate pressure (Fig. 7). The reason for this is that the aroma concentrate is mainly made up of water and that the flow of water across the membrane, to some extent, determines the gradients in partial pressures of aroma com-

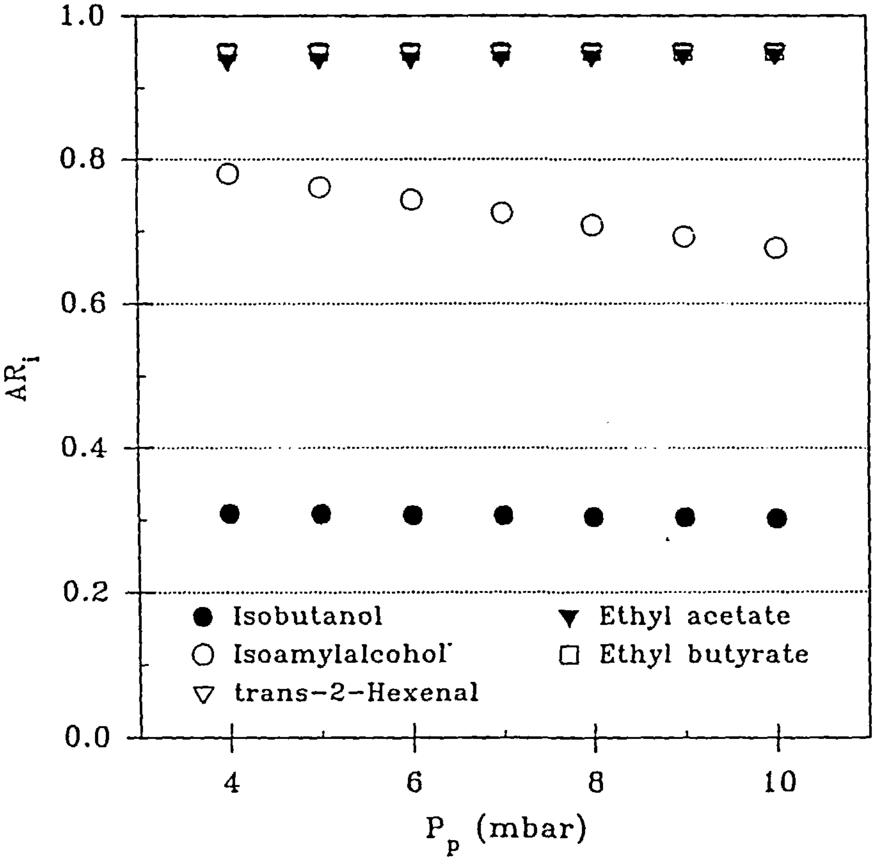

FIG. 7 Effect of permeate pressure on aroma recovery for 100-fold aroma concentrates.

pounds across the membrane. If the simulations presented here are investigated more thoroughly, it can be seen that the relations between the relative partial pressure gradients of aroma compounds and water across the membrane are fairly constant during the simulations although small differences occur, for instance for isoamyl alcohol. This is due to the fact that the mass transfer of aroma compounds across the membrane is determined by the feed and permeate partial pressures. The partial permeate pressures of the aroma compounds are, however, not directly determined by the total permeate pressure. They are instead determined by a balance between the mass transfer rates of aroma compounds and the mass transfer rate of water. The mass transfer rate of water across the membrane is determined mainly by the total permeate pressure; no significant effects of the presence of aroma compounds could be observed. This is due to their low concentrations in the feed and the permeate. The result is that the mass transfer rate and partial permeate pressure of an aroma compound is in equilibrium with, and not independent of, the other. The relative partial pressure gradient is thus largely determined by the mass transfer of the aroma compound itself, whereas the actual gradient in partial pressure, to a large extent, is caused by the mass transfer of water.

Effect of Folding Degree

As mentioned earlier, folding is a measure of how much of the aroma-containing feed is removed as an aroma concentrate. Folding degrees of 50, 100, and 200 correspond to permeate flows which are 2, 1, and 0.5% of the feed flow, respectively. A lower folding degree consequently corresponds to a larger mass of total permeate, which in turn corresponds to the requirement of a larger membrane area (Fig. 8). The membrane area required increases greatly when the degree of folding is lowered. It is, however, not inversely proportional to the folding degree, as could be expected if the heat balance of the system had been neglected. Heat consumption reduces the feed temperature, which in turn reduces the local flux; the larger the membrane area, the greater the reduction in local flux. The retentate temperature is given as a function of folding degree in Fig. 8. As the folding degree decreases, the removal of permeate increases, which results in increased recoveries of aroma compounds (Fig. 9). One way of reducing the effect of the temperature drop in the feed at low folding degrees is to heat the feed at intervals. This is a common way of maintaining a high flux when large permeate flows, in relation to the feed flow, are required.

Effect of Feed Concentration

As the aroma concentrate is mainly made up of water, the membrane area required to produce a 100-fold aroma concentrate is not significantly affected

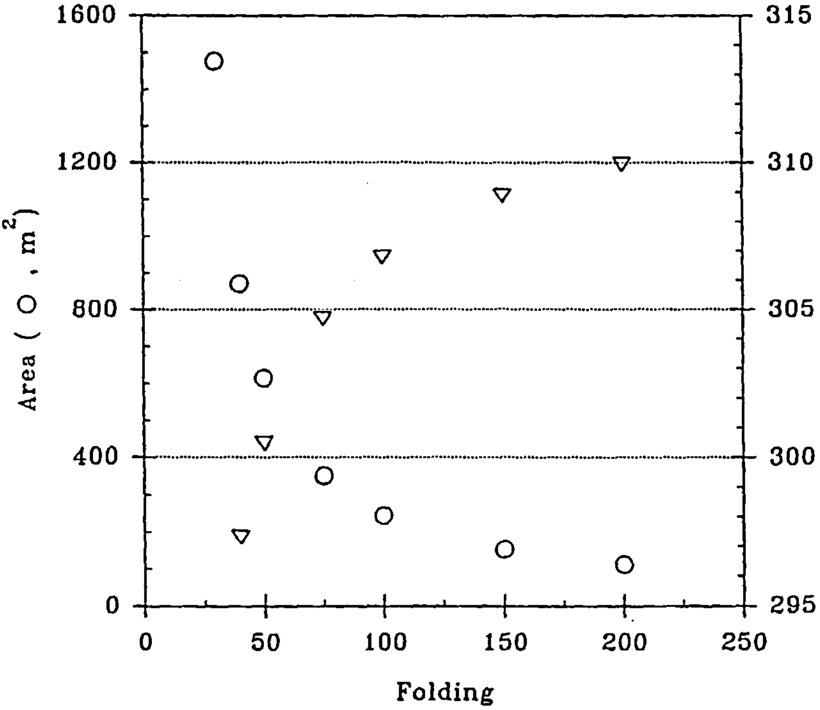

FIG. 8 Effect of folding degree on the membrane area required and on the retentate temperature.

by changes in the feed concentration of aroma compounds. This is also the case if the aroma recovery is evaluated as a function of feed concentration of aroma compounds.

Effect of Membrane Material

In the simulation results presented so far, the calculations were based on the mass transfer properties of the POMS-PEI membrane (GKSS, Geesthacht, Germany). This membrane was chosen as it had the highest selectivity for aroma compounds. However, two other membranes, PDMS-PT1100 (Hoechst Celanese Corp., Charlotte, NC, USA) and PDMS-1060 (Deutsche Carbone, Neunkirchen, Germany), also showed interesting properties regarding aroma recovery (12). The aroma compound selectivities of these membranes were poorer, but their mass transfer rates were higher than those for the POMS-PEI membrane. The difference in membrane mass transfer rates for the three membranes makes the use of the concentration polarization modulus, CPM_i, less useful because a certain value of CPM_i does not correspond to the same feed flow conditions for these three membranes. In the simulations presented below, it was instead assumed that concentration polarization did not affect the performance, i.e., $CPM_i = 1$. Comparison of the membrane materials is thus fairer because the performance of the process in these simulations is only determined by the membrane itself.

As already mentioned, the mass transfer rates, or more precisely the mass transfer coefficients, of the three membranes differ. This strongly affects the membrane area required to produce a 100-fold aroma concentrate. As shown above, the area of POMS-PEI membrane required is 244 m^2. For the PDMS-

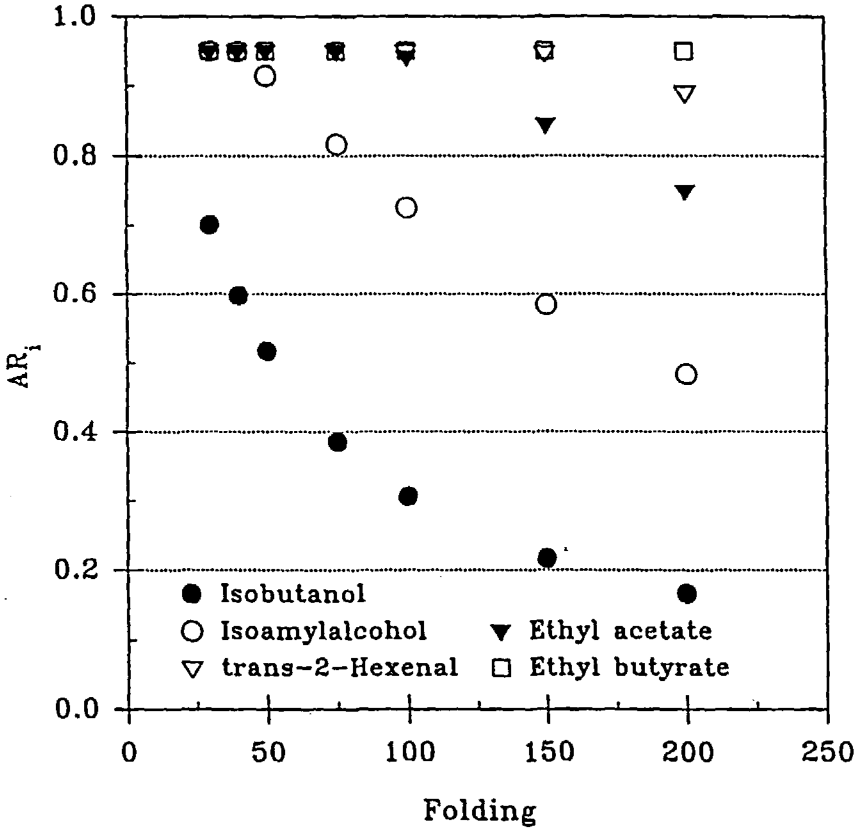

FIG. 9 Effect of folding degree on aroma recovery.

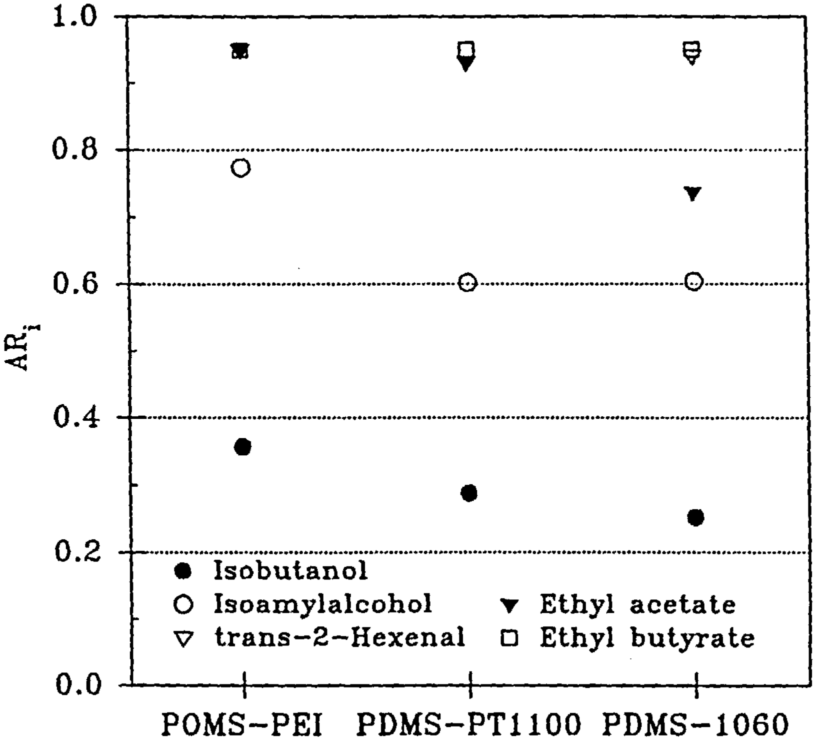

FIG. 10 Aroma recovery as a function of membrane material. $CPM_i = 1.0$.

1060 and the PDMS-PT1100 membranes, the corresponding areas are 97 and 74 m^2, respectively. The aroma compound selectivities of the two latter membranes were lower than those for the POMS-PEI membrane. This affects the aroma recovery for these membranes in a negative way compared with the POMS-PEI membrane (Fig. 10). Except for ethyl butyrate, all aroma recoveries were lower for the PDMS-1060 and the PDMS-PT1100 membranes. Especially noteworthy are the considerably lower recoveries of isoamyl alcohol for both the membranes and the lower recovery of ethyl acetate for the PDMS-1060 membrane. It should also be remembered when inspecting Fig. 10 that the data presented were obtained without concentration polarization. Including concentration polarization would lead to a reduction in the aroma recoveries.

Although the PDMS-1060 and the PDMS-PT1100 membranes do not give high aroma recoveries, their high mass transfer rates make them interesting.

This is mainly due to the fact that a much smaller membrane area is required, a fact which has great importance for the capital cost of a pervaporative aroma recovery unit. The selectivity of the membranes for aroma compounds is probably very closely linked to the material of which the membranes are manufactured. It is therefore unlikely that the selectivities of the PDMS-1060 and the PDMS-PT1100 membranes can be improved to give the same selectivity as the POMS-PEI membrane. It is probably easier to improve the mass transfer rate of the POMS-PEI membrane. The easiest way of doing this would be to reduce the thickness of the active layer, a modification which also could affect the selectivity of the membrane. An alternative to reducing the membrane thickness would be to operate the pervaporation unit at higher feed temperatures. This would, however, affect the aroma recovery, as discussed above.

CONCLUSIONS

Process simulations of large-scale plants for pervaporative aroma recovery indicated that it is possible to produce aroma concentrates with high degrees of aroma recovery. The simulations showed that some process parameters, e.g., process temperature, degree of aroma folding, and choice of membrane material, strongly affect the performance of the process.

SYMBOLS

k^{M}	mass transfer coefficient ($\mathrm{mol/m^2 \cdot s \cdot mbar}$)
n	number of moles or permeating components (mole)
q	specific heat (J/mol)
t	temperature (°C)
A	coefficient in the Antoine equation (—)
AR	aroma recovery (—)
B	coefficient in the Antoine equation $[(^{\circ}\mathrm{C})^{-1}]$
C	coefficient in the Antoine equation (°C)
$\mathbb{C}$	heat capacity (J/mol·°C)
CPM	concentration polarization modulus (—)
E_a	energy of activation (J/mol)
$\overline{F}^{M}$	feed flow (mol/s)
J^{M}	flux or permeate flow rate per unit membrane area ($\mathrm{mol/m^2 \cdot s}$)
P	pressure (mbar)
$\overline{P}^{M}$	permeate flow (mol/s)
R	gas constant (J/mol·K)
$\overline{R}^{M}$	retentate flow (mol/s)
T	temperature (K)

X	mole fraction/concentration in liquid state (—)
Y	mole fraction/concentration in vapor state (—)

Greek Letter

γ	activity coefficient (—)

Subscripts

aq	water
exp	expansion
f	feed or feed side
g	gas/vapor state
i	component
j	component
l	liquid state
m	membrane
ov	overall
p	permeate or permeate side
proc	process
r	retentate
vap	vaporization
0	standard state

Superscript

b	bulk

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