

## ENRICHMENT OF PINEAPPLE AROMA COMPOUNDS FROM MODEL SOLUTIONS BY SWEEPING-GAS AND VACUUM- PERVAPORATION

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Our experiments were based on a model solution containing five of the main pineapple aroma components. Both sweeping-gas pervaporation and vacuum-pervaporation methods were carried out. Measurements were performed at different temperatures and feed flow rates. The purposes of this study were to examine applicability of the two pervaporation methods in reference to the pineapple aroma recovery, the effects of the operating parameters on the process, and modelling the pervaporation process by resistance-in-series model. Higher enrichment could be reached with vacuum-pervaporation than the sweeping-gas method. The separation process is determined by the diffusion of compounds in the membrane, thus the resistance in the boundary layer at liquid side is negligible. Based on performed experiments, the pervaporation process can be applied in beverage industry for aroma recovery.

**Keywords:** pervaporation, aroma recovery, enrichment, model solution, pineapple

Consumer expectations regarding both the nutritional and organoleptic properties are increasing constantly, but it is not always considered by the suppliers of food industry. The aroma is one of the most important features of fruit juices, and is directly connected to the quality of the product and the consumer's acceptance. Some fruits contain hundreds of volatile flavours, mostly in traces; however, these chemical compounds could determine their basic characteristics (AROUJALIAN & RAISI, 2007). Fruit juices have been traditionally concentrated by multi-stage vacuum evaporation up to a final concentration of about 60 °Brix. In this way not only the storage life of the product increases, but the transport and holding expenses decrease significantly (PEREIRA et al., 2006). Among the different types of evaporators, tube falling film evaporator is particularly suitable for the production of fruit juice concentrate. During juice concentration by evaporation process, losses of aroma compounds can occur due to the high temperature, thus deteriorating the quality of the concentrate (BÖRJESSON et al., 1996). In beverage industry rectification equipment and diffusion assisted aroma rectification equipment are usually used for aroma recovery, although these have very high energy and space consumption (RAISI et al., 2008).

Liquid mixtures can be separated by pervaporation, evaporating a part of the mixtures through a non-porous membrane (HUANG, 1991). During the method called "vacuum-pervaporation" low pressure is kept at permeate side with vacuum, and during the method called "sweeping-gas pervaporation" a carrier gas is circulated that delivers the permeate away. The liquid feed becomes vapour passing through the membrane. The permeate can be condensed by a cold surface, rendering the permeate into liquid phase. The possibility of

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using pervaporation for the recovery of natural aroma compounds in the food industry has been widely recognized. The using of hydrophobic membranes to recover aroma compounds from aqueous model solutions has been successfully demonstrated for alcohols, lactones, esters, aldehydes, ketons, sulphur compounds, and hydrocarbons (BAUDOT et al., 1999). The number of publications covering aroma recovery by hydrophobic pervaporation using the original natural source as feed is far more limited (LIPNIZKI et al., 2002). The research on pervaporation for aroma recovery has so far been mainly based on experimental studies with model solutions composed from the “key components” on the basis of the aroma profile of the natural juice, like strawberry (ISCI et al., 2005), pineapple (PEREIRA et al., 2005), and testing and selection of membranes (OVERINGTON et al., 2008; SATO et al., 2008). Using pervaporation it is not necessary to apply high temperature, so it can be used for heat-sensitive and volatile materials (BÉLAFI-BAKÓ et al., 2000, 2002). The pervaporation membranes are highly selective regarding the volatile aroma compounds, and their operation conditions are mild, which gives the benefit of less space and energy need (SHUJUAN et al., 2005; YANG et al., 2006). In the future this process could be an important element in beverage and other industries, too (DIBAN et al., 2008).

The aims of this research were to investigate the influence of the operational parameters (feed flow rate and feed temperature) on the pervaporation process, to compare the separation efficiencies (permeate flux, separation factor) of sweeping-gas and vacuum-pervaporation methods for pineapple aroma recovery, and modelling the separation process by resistance-in-series model.

## 1. Materials and methods

### 1.1. Measurement methods

The experiments were carried out with model aqueous solutions containing five of the main pineapple aroma compounds (HUI, 2010). Pineapple is one of the most popular subtropical fruits cultivated and consumed worldwide. The fruit is consumed fresh as well as in the food industry for the production of canned fruit, jam, and concentrated juice. Table 1 shows some of the properties of the chosen aroma compounds and their concentrations in the model solutions.

Table 1. Characteristics of the selected pineapple aroma compounds and their concentration in the model solutions

Pineapple aroma components	Ethanol	i-Amyl alcohol	Methyl 2- methyl butanoate	Methyl hexanoate	Ethyl acetate
Concentration (ppm)	10.0	2.0	14.0	8.0	2.0
Molecular formula	C <sub>2</sub> H <sub>6</sub> O	C <sub>5</sub> H <sub>12</sub> O	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>
Molar mass (g mol <sup>-1</sup> )	46.07	88.15	116.15	130.18	88.11
Density (g cm <sup>-3</sup> )	0.789	0.810	0.885	0.885	0.897
Boiling point (°C)	78.4	131.1	115.0	151.0	77.1

The separation of the aroma compounds was done by a laboratory pervaporation equipment (Fig. 1) using both sweeping-gas pervaporation and vacuum-pervaporation methods. The PDMS coated ceramic membrane tubes were obtained from Pervatech BV (Netherlands). The organophilic membrane having a length of 50 cm is placed in a tubular pervaporation module. The active area of the membrane is 110 cm<sup>2</sup>. Two pervaporation membranes were installed in parallel in order to separate the model solutions with greater efficiency.

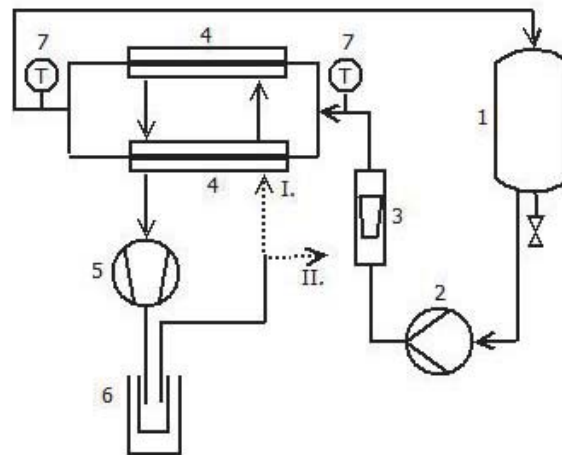


Fig. 1. Laboratory pervaporation equipment: (I.) Sweeping-gas pervaporation method, (II.) Vacuum-pervaporation method, (1) Feed tank, (2) Variable speed drive pump, (3) Flow-rate meter, (4) Pervaporation membranes, (5) Vacuum pump, (6) Cold trap, (7) Thermometers

The measurements were performed at five different temperatures (30, 40, 50, 60, and 70 °C) and three different feed flow rates (150, 300, and 600 l h<sup>-1</sup>). The concentrations of aroma compounds were constant during all pervaporation experiments. Each experiment was run for two hours, while permeate was condensed and collected in a cold trap by liquid nitrogen (-196 °C). The condensed frozen permeate was melted and weighed. The concentration of the permeate was determined by using a HP 5890 Series II. gas chromatograph equipment.

### 1.2. Separation efficiency

The characteristics of pervaporation can be described by factors like permeate flux and separation factor.

$$J_p = \frac{m_p}{A \times t}; \quad \alpha = \frac{C' \times (1 - C)}{C \times (1 - C')}$$

where  $J_p$  is the permeate flux (kg m<sup>-2</sup> h<sup>-1</sup>),  $m_p$  is the weight of permeate (kg),  $A$  is the membrane surface (m<sup>2</sup>), and  $t$  is the pervaporation time (h). The  $\alpha$  is the separation factor (-),  $C'$  and  $C$  are the concentrations of the aroma compound at the permeate and feed side, respectively (m/m, %).

### 1.3. Mathematical modelling

The resistance-in-series method is used to model the pervaporation process. To describe the mass transfer processes of a membrane, both the concentration and the partial vapour pressure are suitable. Pervaporation vapour pressure as a driving force is better to characterise the separation process of dilute solutions (WIJMANS et al., 1996).

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

where  $J_i$  is the permeate flux of component “i” through the membrane ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $Q_{OV,i}$  is the overall mass transfer coefficient of component “i” with driving force of partial vapour pressure ( $\text{mol m}^{-2} \text{Pa}^{-1} \text{s}^{-1}$ ),  $p_{L,i}$  and  $p_{G,i}$  are the partial vapour pressures of component “i” at feed and permeate side (Pa).

The total resistance is the sum of the boundary layer resistances and the membrane resistance. Resistance of the gaseous boundary layer can be neglected. The mass transfer through the membrane can be described by resistance-in-series model as follows (Ji et al., 1994):

$$\frac{1}{Q_{OV,i}} = \frac{1}{Q_{L,i}} + \frac{1}{Q_{Mem,i}}$$

where  $Q_{OV,i}$  is the overall mass transfer coefficient of component “i” with driving force of partial vapour pressure ( $\text{mol m}^{-2} \text{Pa}^{-1} \text{s}^{-1}$ ),  $Q_{L,i}$  is the mass transfer coefficient of component “i” with driving force of partial vapour pressure at liquid side ( $\text{mol m}^{-2} \text{Pa}^{-1} \text{s}^{-1}$ ),  $Q_{Mem,i}$  is the mass transfer coefficient of component “i” with driving force of partial vapour pressure in membrane ( $\text{mol m}^{-2} \text{Pa}^{-1} \text{s}^{-1}$ ).

The resistance of membrane with driving force of partial vapour pressure:

$$\frac{1}{Q_{Mem,i}} = \frac{1}{Q_{OV,i}} - \frac{1}{Q_{L,i}}$$

## 2. Results and discussion

The performance of the membrane is described by the flux of compounds through the membrane. In pervaporation, the most important parameter is the feed temperature. Figures 2 and 3 illustrate the effect of the operation temperature on the permeate fluxes of each aroma compound in case of sweeping-gas and vacuum-pervaporation. The higher permeate fluxes could be reached at  $600 \text{ l h}^{-1}$  with both separation methods. Increasing the temperature raises the mass of the membrane permeability. It can be seen that fluxes of all compounds increase as the feed temperature is enhanced. Comparing the separation methods it can be established that using vacuum-pervaporation shows higher separation efficiency than pervaporation with carrier gas.

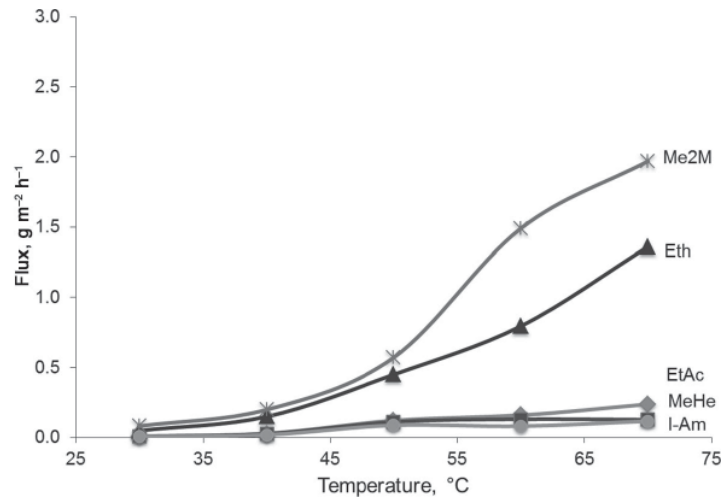


Fig. 2. Effect of feed temperature on permeate flux at 600 l h<sup>-1</sup> using sweeping-gas pervaporation. ▲(Eth): ethanol; ●(I-Am): i-amyl alcohol; \* (Me2M): methyl 2-methylbutanoate; ■(MeHe): methyl hexanoate; ◆(EtAc): ethyl acetate

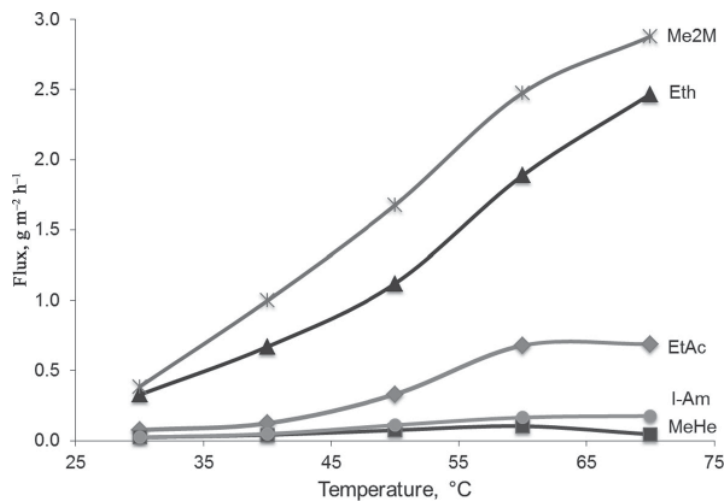


Fig. 3. Effect of feed temperature on permeate flux at 600 l h<sup>-1</sup> using vacuum-pervaporation. ▲(Eth): ethanol; ●(I-Am): i-amyl alcohol; \* (Me2M): methyl 2-methylbutanoate; ■(MeHe): methyl hexanoate; ◆(EtAc): ethyl acetate

The separation factors are compared for sweeping-gas pervaporation (Fig. 4) and vacuum-pervaporation (Fig. 5) at the feed flow rate of 600 l h<sup>-1</sup>, and the feed temperature of 50 °C. Examining the values of separation factor, selectivity increases with the feed flow rate. Ethyl acetate and methyl 2-methylbutanoate were separated with the highest efficiency. Most aroma components had higher separation factors with vacuum pervaporation method. Similar tendencies were determined for all operations.

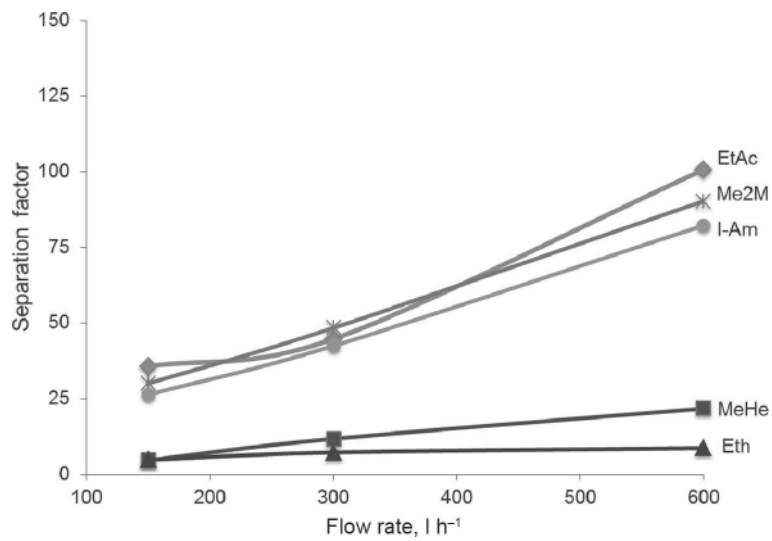


Fig. 4. Effect of feed temperature on separation factor of the investigated pineapple aroma compounds at 50 °C using sweeping-gas pervaporation. ▲(Eth): ethanol; ●(I-Am): i-amyl alcohol; ✱ (Me2M): methyl 2-methylbutanoate; ■(MeHe): methyl hexanoate; ◆(EtAc): ethyl acetate

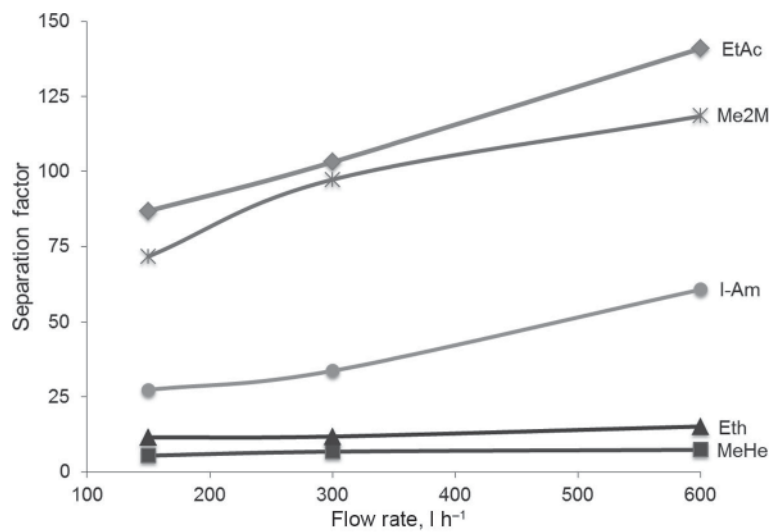


Fig. 5. Effect of feed temperature on separation factor of the investigated pineapple aroma compounds at 50 °C using vacuum-pervaporation. ▲(Eth): ethanol; ●(I-Am): i-amyl alcohol; ✱ (Me2M): methyl 2-methylbutanoate; ■ (MeHe): methyl hexanoate; ◆(EtAc): ethyl acetate

The calculated resistances for methyl 2-methylbutanoate are shown in Figs. 6 and 7. It can be noted that both overall and membrane resistances are much higher than resistances at the liquid side in case of sweeping-gas and vacuum-pervaporation, too. The pervaporative

resistance is affected by the resistance of the membrane, thus the resistance in the boundary layer at liquid side is negligible. Membrane resistance was lower using vacuum-pervaporation method. This can also be observed for the other aroma compounds.

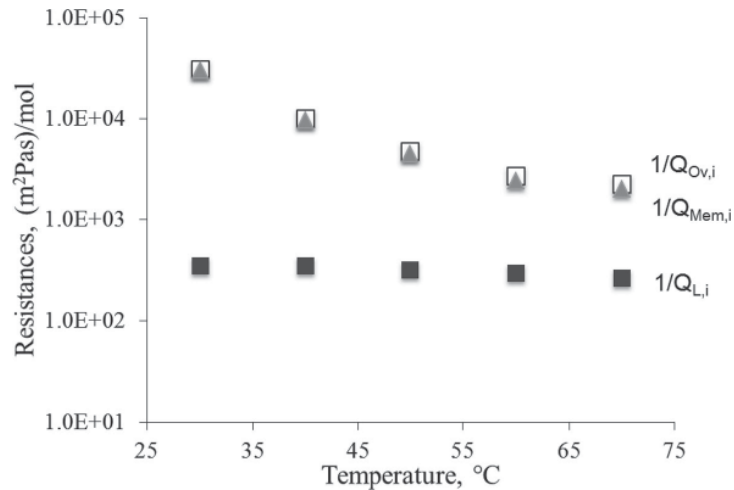


Fig. 6. Resistance as a function of temperature related to methyl 2-methylbutanoate using sweeping-gas pervaporation: ( $Q_{Ov,i}$ ): overall mass transfer coefficient of component „i” with driving force of partial vapour pressure; ( $Q_{Mem,i}$ ): mass transfer coefficient of component „i” with driving force of partial vapour pressure in membrane; ( $Q_{L,i}$ ): mass transfer coefficient of component „i” with driving force of partial vapour pressure at liquid side

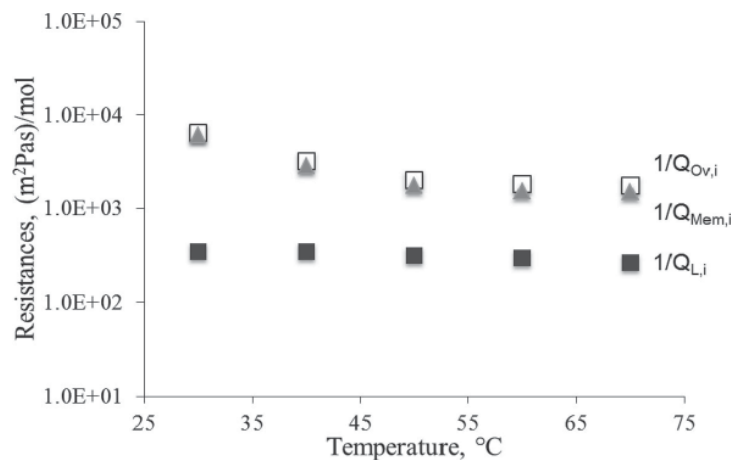


Fig. 7. Resistance as a function of temperature related to methyl 2-methylbutanoate using vacuum-pervaporation: ( $Q_{Ov,i}$ ): overall mass transfer coefficient of component „i” with driving force of partial vapour pressure; ( $Q_{Mem,i}$ ): mass transfer coefficient of component „i” with driving force of partial vapour pressure in membrane; ( $Q_{L,i}$ ): mass transfer coefficient of component „i” with driving force of partial vapour pressure at liquid side

### 3. Conclusions

It can be concluded from the experimental data that both pervaporation methods are applicable for the enrichment of the selected compounds from model solutions. Increasing temperature

has favourable effect on the permeate flux and selectivity. Higher enrichment could be reached with vacuum-pervaporation than with the sweeping-gas method. It can be established that the mass transfer is determined by the membrane, so the pervaporative resistance is influenced by the behaviour of the membrane only. Investigation of aroma compounds recovery from real fruit juices, deeper mathematical modelling, examination of other membranes, and economic analysis are necessary for industrial scale up.

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