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# **Concentration of Dairy Flavours using Pervaporation**

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A thesis presented in partial fulfilment of the requirements for the degree of  
Doctor of Philosophy  
in  
Food Technology  
at Massey University, Auckland, New Zealand

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**2008**

## Abstract

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The food industry could potentially benefit from using pervaporation, a membrane process, to concentrate flavours. This research aimed to investigate its application for concentrating flavours in dairy process streams. Pervaporation experiments were carried out at a range of operating conditions, using hydrophobic membranes. The feed mixtures were either aqueous model solutions of dairy flavour compounds (acids, esters and ketones), complex model mixtures containing flavour compounds plus non-volatile dairy components, or real dairy products.

Flavour compound enrichment factors ranged from below one to above 30, with esters and ketones being concentrated more effectively than acids. Thus, the flavours could be partially fractionated based on their chemical structure. The permeation of acids was reduced by approximately 50% when the feed pH was increased to near their  $pK_a$  values.

For flavour compounds with lower molecular weights than approximately  $120 \text{ g mol}^{-1}$ , permeation was controlled mainly by sorption in the membrane; for larger compounds it was controlled mainly by diffusion through the membrane. The mass transfer of each flavour compound increased with temperature, following an Arrhenius-like relationship. The activation energy was a function of each compound's heat of sorption, its molecular weight, and the elastic modulus of the membrane. The activation energy was also related to the Arrhenius pre-exponential factor. Thus, fluxes could be estimated through empirical correlations.

The non-volatile feed composition was an important factor influencing the pervaporation performance. Milk protein isolate (4% w/v) or lactose (6% or 12% w/v) bound with the flavour compounds in the feed, thus lowering the enrichment of sorption-controlled compounds. Milk fat (up to 38% w/v, in the form of cream) reduced the enrichment of all the flavour compounds tested. Esters and ketones became unavailable for pervaporation as they partitioned into the fat phase; acids remained mainly in the aqueous phase, but their permeation was reduced because the added cream increased the feed pH.

Experiments with real dairy products showed that pervaporation could be used to concentrate diacetyl in starter distillate, and to selectively recover short-chain esters from ester cream. Of these two products, starter distillate is the more promising for use as a pervaporation feed stream.



# Acknowledgements

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I would like to thank my supervisor, Dr Marie Wong, and co-supervisors Dr John Harrison and Dr Lílian Ferreira, for all their help and encouragement during my PhD. Each of them provided valuable support, and helped me to become a better researcher. I would recommend any of them to future students as examples of excellent supervisors.

Thanks also to the other Fonterra staff who provided useful suggestions and discussion: Dr Vaughan Crow, Dr Ross Holland and Dr Paul Andrewes. I would also like to thank the laboratory staff at Massey and Fonterra, Helen Matthews and Andrew Broome, for helping my laboratory work to go smoothly.

Many long hours were spent in the chemistry laboratory at Massey University, and I thank the various staff, postgraduate students and fourth year students who provided company during that time. I am also grateful for the friendship of other PhD students who understood the ups and downs of the PhD process, particularly Christine Flynn, with whom I shared an office throughout most of my PhD.

Finally I must thank my parents for putting up with me living at home much longer than I should have.

This work was funded by Fonterra Co-operative Group Ltd and the Foundation for Research, Science and Technology (Technology Industry Fellowship programme; contract number FCGL0403). Pervaporation membranes were kindly supplied by GKSS-Forschungszentrum Geesthacht GmbH.

# List of publications and presentations

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## Peer-reviewed publications

Overington, A., Wong, M., Harrison, J., & Ferreira, L. (2008). Concentration of dairy flavour compounds using pervaporation. *International Dairy Journal*, 18(8), 835–848.

Overington, A.R., Wong, M., Harrison, J.A. & Ferreira, L.B. (2009). Estimation of mass transfer rates through hydrophobic pervaporation membranes. *Separation Science and Technology*, 44(4), 787–816.

## Conference presentations

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Concentration of dairy flavour compounds using pervaporation*. 5th NIZO Dairy Conference: Prospects for flavour formation and perception. Papendal, The Netherlands, 13–15 June 2007. (Poster and oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Modelling of pervaporation for concentration of flavour compounds*. IMSTEC 07: The 6th International Membrane Science and Technology Conference. Sydney, Australia, 5–9 November 2007. (Oral presentation).

Overington, A.. *Flavour concentration by pervaporation: Effect of feed solution characteristics*. Fonterra Science and Technology Seminar Series. Palmerston North, New Zealand, 12 June 2008. (Oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of feed solution characteristics on flavour concentration by pervaporation*. NZIFST Conference 2008: Food Sustainability. Rotorua, New Zealand, 24–26 June 2008. (Oral presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of dairy fat on pervaporative flavour compound concentration*. NZIFST Conference 2008: Food Sustainability. Rotorua, New Zealand, 24–26 June 2008. (Poster presentation).

Overington, A., Wong, M., Harrison, J. & Ferreira, L.. *Effect of feed solution characteristics on flavour concentration by pervaporation*. ICOM 2008: International Congress on Membranes and Membrane Processes. Honolulu, Hawaii, USA, 12–18 July 2008. (Oral presentation).

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# List of symbols and abbreviations

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$a$	Activity (dimensionless)
$a,b,c,d$	Empirical constants (Equations (2-22) and (B-10))
$A$	Membrane area ( $\text{m}^2$ )
$B$	Plasticising coefficient
$c$	Concentration ( $\text{mol m}^{-3}$ )
$C$	Flux correction factor (dimensionless)
$C_i$	Coupling factor (dimensionless)
$D$	Diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$df$	Driving force (dimensionless)
$d_h$	Hydraulic diameter (m)
$E_a$	Activation energy ( $\text{kJ mol}^{-1}$ )
$E_D$	Activation energy of diffusion ( $\text{kJ mol}^{-1}$ )
$f$	Frictional force (N)
$\Delta H$	Enthalpy change ( $\text{kJ mol}^{-1}$ )
$\Delta H_s$	Heat of sorption ( $\text{kJ mol}^{-1}$ )
$J$	Flux ( $\text{mg m}^{-2} \text{s}^{-1}$ or $\text{mol m}^{-2} \text{s}^{-1}$ )
$k$	Mass transfer coefficient ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$k'$	Mass transfer coefficient ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ )
$k_0$	Pre-exponential factor ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$k_D$	Darcy's law coefficient ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ )
$l$	Membrane thickness (m)
$L$	Phenomenological coefficient
$L_c$	Length of membrane cell (m)
$m$	Mass (kg)
$M$	Molecular weight ( $\text{g mol}^{-1}$ )
$M_0$	Elastic modulus extrapolated to a reference temperature (Pa)
$n$	Number of runs with one membrane piece
$N$	Number of carbon atoms
$p$	Partial pressure (Pa)
$P$	Permeability ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ )
$Pe$	Peclet number (dimensionless)
$PI$	Production index ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$PSI$	Pervaporation separation index ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$q$	Surface parameter (dimensionless)
$r$	Volume parameter (dimensionless)
$R$	Gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$Re$	Reynolds number (dimensionless)
$S$	Sorption coefficient (dimensionless)
$S_0$	Pre-exponential factor for sorption (dimensionless)
$\Delta S$	Entropy change ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ )
$Sc$	Schmidt number (dimensionless)
$Sh$	Sherwood number (dimensionless)
$Sl$	Slope of $J_i$ versus $n$ ( $\text{mg m}^{-2} \text{s}^{-1}$ )
$t$	Time (s)
$T$	Temperature (K)

$u$	Velocity ( $\text{m s}^{-1}$ )
$V$	Molar volume ( $\text{m}^3 \text{mol}^{-1}$ )
$w$	Mass fraction (dimensionless)
$x$	Mole fraction (dimensionless)
$y$	Number of molecules
$y_{\text{intercept}}$	y-Intercept of Figure 9-5
$z$	UNIQUAC coordination number (= 10)

### Greek letters

$\alpha$	Separation factor (dimensionless)
$\alpha_{\text{dist}}$	Relative volatility (dimensionless)
$\beta$	Enrichment factor (dimensionless)
$\gamma$	Activity coefficient (dimensionless)
$\delta$	Boundary layer thickness (m)
$\varepsilon$	Strain (dimensionless)
$\epsilon$	Empirical constant
$\eta$	Viscosity (Pa s)
$\theta$	Empirical constant
$\Theta$	Surface fraction (dimensionless)
$\lambda$	Empirical constant
$\mu$	Chemical potential ( $\text{J mol}^{-1}$ )
$\rho$	Density ( $\text{kg m}^{-3}$ )
$\sigma$	Shape factor
$\zeta$	Empirical constant
$\tau$ (with subscript)	Binary interaction parameter
$\tau$ (no subscript)	Defined by Equation (B-11) (dimensionless)
$\varphi$	Volume fraction of particles (dimensionless)
$\Phi$	Volume fraction of mixture component (dimensionless)
$\chi$	Flory-Huggins interaction parameter (dimensionless)
$\omega$	Empirical constant

### Superscripts

*	Modified (e.g. to account for hydrogen bonds)
/	In membrane
$\infty$	At infinite dilution
0	At reference conditions

### Subscripts

0	Initial or pre-exponential
<i>av</i>	Average for membrane pieces of the same type
<i>avail</i>	Available
<i>between</i>	Between separate membrane pieces of the same type

<i>bl</i>	In feed boundary layer
<i>c</i>	Critical
<i>f</i>	On feed side of membrane
<i>i</i>	Component <i>i</i> or membrane piece <i>i</i>
<i>int</i>	Intrinsic
<i>j</i>	Component <i>j</i>
<i>k</i>	Component <i>k</i>
<i>l</i>	Liquid phase
<i>m</i>	In membrane, or referring to membrane polymer
<i>max</i>	Maximum
<i>ov</i>	Overall
<i>p</i>	On permeate side of membrane
<i>s</i>	Solvent
<i>tot</i>	Total
<i>uncorrected</i>	Without applying flux correction factors
<i>v</i>	Vapour phase
<i>w</i>	Water
<i>within</i>	Within one membrane piece

### **Abbreviations**

EPDM	Ethylene-propylene-diene terpolymer
GC	Gas chromatography
GCMS	Gas chromatography-mass spectrometry
PAN	Polyacrylonitrile
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PEBA	Polyether-block-amide
POMS	Polyoctylmethylsiloxane
PTMSP	Poly(1-trimethylsilyl-1-propyne)
SPE	Solid phase extraction
SPME	Solid phase micro-extraction
UNIQUAC	Universal quasi-chemical