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MATHEMATICAL MODELLING OF MODIFIED ATMOSPHERE PACKAGING SYSTEMS FOR APPLES

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Process and Environmental Technology at Massey University.

> Ingeborg Merts B.Tech (Hons)

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ABSTRACT

ENZA New Zealand (International) is considering the use of modified atmosphere packaging (MAP) as an adjunct to cool storage for cartons of apples. The objectives of this study were to measure modified atmosphere development in apple cartons and to develop a mathematical model that could be used as a tool for package design and optimization.

Storage trials were carried out with film-lined cartons of 'Braeburn', 'Royal Gala', and 'Granny Smith' apples. Measured package O_2 and CO_2 concentrations showed excellent reproducibility for cartons with heat-sealed liners. Liners closed by folding produced less modified and less consistent package atmospheres, especially for thicker films (40 μ m versus 25 μ m). Macroscopic holes in the liners resulted in almost total loss of atmosphere modification, whereas microscopic holes resulted in smaller changes apparent for O_2 concentrations only. A high incidence of film damage could quickly erode any potential fruit quality benefits imparted by the liners.

Packing of warm rather than pre-cooled fruit resulted in much faster rates of atmosphere modification, without the development of unduly low O_2 or high CO_2 concentrations. The detrimental quality effects of slower cooling rates for film-lined cartons may outweigh any benefits of more rapid modified atmosphere development. Short-term exposures (less than 24 hours) to 20°C resulted in relatively short-lived and non-critical disturbances to package atmospheres. Periods of more than 3 days at 20°C led to a significant risk of anaerobic conditions or harmful CO_2 levels forming within the fruit, especially within the 40 μ m liners. Folding rather than heat-sealing of liners did not reduce this risk.

The MAP model simulated fruit respiration as a function of temperature and fruit O_2 and CO_2 concentrations; O_2 , CO_2 , N_2 , and water vapour exchange between the fruit, package, and external atmospheres; condensation of moisture within the package; and moisture sorption by paper-based packaging materials. Gas concentrations and temperature throughout (i) the fruit and (ii) the package atmosphere were each assumed to be uniform with position. The model can be applied to a wide range of packages under variable-temperature storage regimes. The model closely predicted observed trends in experimental data collected during the MA storage trials, but tended to under-predict CO_2 concentrations and performed less well under conditions of extremely modified atmospheres. Sensitivity analyses showed that this lack of fit was not greater than that which could be explained by uncertainties in respiration and permeability data. It is recommended that future work be aimed at resolving the worst of these uncertainties before a significant amount of effort is directed towards further model development.

The MAP model was considered sufficiently accurate for it to be usefully applied to the design and optimization of MAP systems.

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ERRATA

- p. x Sub-sections of section 8.2.1 should be numbered 8.2.1.1, 8.2.1.2, and 8.2.1.3.
- p. 13 Second-to-last line of second paragraph. 'Late harvested fruit were used in the trail...' should read 'Late harvested fruit were used in the trial...'.
- p. 33 Eq. 2.7. The symbol RQ_m should be RQ (as listed in the definition of symbols on p. 34).
- p. 37 Definition of symbols for Eq. 2.12. Units of $[i]_{ext}$ and $[i]_{int}$ should read $(m^3 \cdot m^{-3})$.
- p. 96 Eq. 6.14 should read

$$\frac{d(\epsilon V_n C_{O_2,f})}{dt} = k_{O_2} A_n (C_{O_2,p} - C_{O_2,f}) - \nu M_n$$

p. 114 Eq. 6.85 should read

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\alpha \left(\theta - \theta_e\right)$$

- p. 121 Throughout Chapter 7, the symbol ' ε ' represents the local error tolerance bound for the numerical solution method. Throughout the rest of the thesis ' ε ' represents the porosity of the fruit flesh (m³·m⁻³).
- p. 151 Section 8.2.2.1 should be numbered 8.2.1.1.
- p. 155 Section 8.2.2.2 should be numbered 8.2.1.2.
- p. 158 Section 8.2.2.3 should be numbered 8.2.1.3.

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NOMENCLATURE

This section lists the nomenclature used in the mathematical formulation of the MAP model (Chapter 6). Miscellaneous symbols used locally in Chapters 2, 4, 7, and 8 are defined in the text as necessary.

а	empirical parameter of the fruit surface area-volume correlation (Eq. 6.17)
A_{film}	total surface area for gas permeation through the packaging film (m ²)
Afruit	total fruit surface area (m ²)
Aholes	total area of holes in the packaging film (m^2)
A_n	individual fruit surface area (m ²)
Apack	average heat transfer area of the packaging materials (m ²)
Auray	effective tray surface area for moisture sorption (m ² ·tray ·1)
a_w	fruit water activity
aw, trav	tray water activity
b	empirical parameter of the fruit surface area-volume correlation (Eq. 6.17)
Bi	Biot number for heat transfer
Bi'	Biot number for mass transfer
C _{pa}	specific heat capacity of dry air (J·kg ⁻¹ ·K ⁻¹)
C _{pf}	specific heat capacity of the fruit flesh (J·kg ⁻¹ ·K ⁻¹)
C _{pt}	specific heat capacity of the dry trays $(J \cdot kg^{-1} \cdot K^{-1})$
C_{pv}	specific heat capacity of water vapour (J·kg ⁻¹ ·K ⁻¹)
C _{pw}	specific heat capacity of liquid water (J·kg ⁻¹ ·K ⁻¹)
Ċ	parameter of the GAB isotherm model (Eq. 2.22)
$C_{\text{CO2}, e}$	CO_2 concentration in the store atmosphere (kg $CO_2 \cdot m^{-3}$)
$C_{\text{CO2}, p}$	CO_2 concentration in the package atmosphere (kg $CO_2 \cdot m^{-3}$)
$C_{\text{CO}_{2,f}}$	CO_2 concentration in the fruit internal atmosphere (kg $CO_2 \text{ m}^{-3}$)
С _{Н:О. р}	concentration of water vapour in the package atmosphere (kg H_2Om^{-3})
С _{н:О, е}	concentration of water vapour in the store atmosphere (kg $H_2O m^{-3}$)
C_i	mass concentration of gas species i (kg·m ⁻³)
$C_{i.e}$	ambient concentration of gas species i (kg·m ⁻³)
$C_{i,p}^{0}$	initial package concentration of gas species $i (kg m^{-3})$
$C_{i,p}^{t}$	package concentration of gas species i at time t (kg·m ⁻³)
C _{N:, e}	N_2 concentration in the store atmosphere (kg N_2 m ⁻³)
$C_{N_2, p}$	N_2 concentration in the package atmosphere (kg N_2 m ⁻³)
$C_{0:,f}$	O_2 concentration in the fruit internal atmosphere (kg $O_2 \cdot m^3$)
$C_{02, e}$	O_2 concentration in the store atmosphere (kg O_2 m ⁻³)
$C_{O_{2}, p}$	O_2 concentration in the package atmosphere (kg $O_2 \cdot m^{-3}$)
D	mass diffusivity (m ² ·s ⁻¹)
D _{i, eff}	effective diffusivity of gas species <i>i</i> through holes in the packaging film $(m^2 \cdot s^{-1})$
D _{i, ref}	diffusivity of gas species <i>i</i> in air at temperature T_{ref} (m ² ·s ⁻¹)
D _{i. air}	diffusivity of gas species <i>i</i> in air $(m^2 \cdot s^{-1})$
D _{CO2} , eff	effective diffusivity of CO_2 through holes in the packaging film $(m^2 \cdot s^{-1})$
D _{H2O} , eff	effective diffusivity of water vapour through holes in the packaging film $(m^2 \cdot s^{-1})$

DN2 eff	effective diffusivity of N_2 through holes in the packaging film $(m^2 \cdot s^{-1})$
$D_{0, eff}$	effective diffusivity of O_2 through holes in the packaging film (m ² ·s ⁻¹)
E_{ai}	activation energy for permeation of gas species i (J-mol ⁻¹)
h	surface heat transfer coefficient (W·m ⁻² ·K ⁻¹)
h.	convective heat transfer coefficient at the external package surface $(W \cdot m^{-2} \cdot K^{-1})$
h	convective heat transfer coefficient at the fruit surface $(W \cdot m^{-2} \cdot K^{-1})$
h	latent heat of vaporization of water (J·kg ⁻¹)
h	convective heat transfer coefficient at the internal packaging-film surface
r*p	$(W \cdot m^{-2} \cdot K^{-1})$
Н	absolute humidity of the package atmosphere $(kg \cdot kg^{-1})$
k k	general rate constant (units variable)
k	fruit skin permeance to $CO_{\rm c}$ (m·s ⁻¹)
k	fruit skin permeance to O_2 (m·s ⁻¹)
k O2	fruit skin permeance to water vapour (sm^{-1})
ng, skin	mass transfer coefficient for moisture corntion at the tray surface (sm^{-1})
R _{g, tray}	mass transfer coefficient for moisture condensation at the fruit surface (sm^{-1})
Kg, fruit	mass transfer coefficient for moisture condensation at the inside surface of the
Kg, film	mass transfer coefficient for moisture condensation at the mistide surface of the
1-	packaging $\min(s \sin \beta)$
K _{ic}	competitive inhibition constant (kg CO_2 ·m ⁻³)
K_{iu}	half estimation constant (kg CO_2 m ⁻)
K _m	nair saturation constant (kg O_2 ·m ⁻)
K	parameter of the GAB isotherm model (Eq. 2.22)
	characteristic dimension (m)
m_i	net mass now of gas species i into the package by all mechanisms except bulk
55 (* 15)	flow (mol·s ⁻)
$m_{\rm CO_2}$	net mass flow of CO_2 into the package through fruit gas exchange, permeation,
	and diffusion (kg·s ⁻)
$m_{\rm H2O}$	net mass flow of H_2O into the package through truit moisture loss, permeation,
	diffusion, condensation/evaporation, and sorption/desorption (kg·s ⁻)
m_{N_2}	net mass flow of N_2 into the package through permeation and diffusion (kg s ⁻)
m_{O_2}	net mass flow of O_2 into the package through fruit gas exchange, permeation,
	and diffusion (kg·s·)
$M_{i, p}$	mass of gas species i in the package atmosphere (kg)
М _{со2, р}	mass of CO_2 in the package atmosphere (kg)
$M_{\text{H}_2\text{O}, p}$	mass of water vapour in the package atmosphere (kg)
M _{N3} p	mass of N_2 in package atmosphere (kg)
$M_{O_2, p}$	mass of O_2 in package atmosphere (kg)
M _{cond, f}	mass of condensate on the fruit surface (kg)
M _{cond. p}	mass of condensate on the inside packaging film surface (kg)
$M_{f. initial}$	initial total fruit mass (kg)
M_f	total fruit mass (kg)
M_n	individual fruit mass (kg)
M_p	mass of dry air in the package atmosphere (kg)
M_{tray}	tray dry mass (kg tray ')
M _{w. tray}	mass of water absorbed by the moulded-pulp trays (kg tray ⁻¹)
Mr_i	molecular mass of gas species $i (g \text{ mol}^{-1})$
Mr _c	molar mass of carbon (g·mol ⁻¹)

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Mr_{CO_2}	molar mass of CO_2 (g·mol ⁻¹)
Mr _{H-O}	molar mass of water (g·mol ⁻¹)
Mr_{N}	molar mass of N_2 (g·mol ⁻¹)
Mr _o	molar mass of O_2 (g·mol ⁻¹)
n_h	total molar flow into the package through holes in the packaging film $(mol \cdot s^{-1})$
'n.	net molar flow of gas species <i>i</i> into the package by all mechanisms except bulk
1	flow (mol·s ⁻¹)
nco	net molar flow of CO ₂ into the package through fruit gas exchange, permeation.
102	and diffusion (mol \cdot s ⁻¹)
n	net molar flow of H ₂ O into the package through fruit moisture loss, permeation.
TH:O	diffusion, condensation/evaporation, and sorption/desorption (mol·s ⁻¹)
n.	net molar flow of N_{2} into the package through permeation and diffusion
**N2	(mol·s ⁻¹)
n.	net molar flow of $\Omega_{\rm c}$ into the package through fruit gas exchange permeation
102	and diffusion (mols ⁻¹)
12	total number of moles of gas in the package atmosphere
N ioi	number of fruit in the package
N	number of moulded pulp trave per package
rv tray	saturated vapour pressure of water at the trav temperature (Pa)
P sat. tray	saturated vapour pressure of water at the packaging film temperature (Pa)
P sat. film	saturated vapour pressure of water at the fruit surface temperature (Pa)
Psat. f	saturated vapour pressure of water at the store air temperature (Pa)
Psat, e	saturated vapour pressure of water at the temperature (Fa)
Psat. p	saturated vapour pressure of water at the temperature of the package
n	annosphere (ra)
P _{w. tray}	partial pressure of water vapour hereath the fruit clin (De)
$P_{w,f}$	partial pressure of water vapour in the store etmosphere (Pa)
Pw.e	partial pressure of water vapour in the package atmosphere (Ia)
$P_{w, p}$	pressure (Pa)
P	pressure (1 a) pre-exponential factor for permeation of gas species $i (m^2 \cdot s^{-1})$
I 0, i P	atmospheric pressure (Pa)
atm D	nermeability of the packaging film to gas species $i(m^2 \cdot s^{-1})$
I i P	packaging film nermeability to $CO_{\rm c}$ (m ² ·s ⁻¹)
P	packaging film permeability to water vanour $(m^2 \cdot s^{-1})$
ин. Р	packaging film permeability to N. $(m^2 \cdot s^{-1})$
P N:	packaging film permeability to Ω_2 (m ² s ⁻¹)
P	package atmosphere pressure (Pa)
\hat{O}	cumulative Ω consumption (kg $\Omega \cdot kg^{-1}$)
0	temperature coefficient for respiration
\mathcal{E}_{10}	gas constant $(I \cdot mol^{-1} \cdot K^{-1})$
RH	relative humidity of the store air (%)
RH	relative humidity of the package atmosphere (%)
RO	mass-based respiratory quotient for aerobic respiration (kg·kg ⁻¹)
SA SA	empirical correction factor for evanoration of moisture from the fruit surface
t corr	time (s)
t	half cooling or warming time or half life (c)
*0.5 t	time at which holes in the packaging film are formed (s)
6.1	

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T	temperature (V)
I T	
I ref	reference temperature (K)
U_{pack}	overall heat transfer coefficient for the packaging materials (W m ·K ·)
ν	aerobic respiration rate (kg O_2 ·kg ⁻¹ ·s ⁻¹)
v_{max}	maximum aerobic respiration rate at the fruit temperature (kg $O_2 \cdot kg^{-1} \cdot s^{-1}$)
$V_{max,ref}$	maximum aerobic respiration rate at the reference temperature (kg $O_2 \cdot kg^{-1} \cdot s^{-1}$)
Vcarton	carton volume (m ³)
Vin	volume of gas species <i>i</i> in the package atmosphere (m^3)
Vcon	volume of CO ₂ in the package atmosphere (m^3)
Vulo	volume of water vapour in the package atmosphere (m ³)
V _N	volume of N_2 in the package atmosphere (m^3)
V _o	volume of O_2 in the package atmosphere (m ³)
$V_{02, p}$	individual fruit volume (m^3)
V n	minimum package atmosphere volume (m^3)
p, min	volume of the package atmosphere (m^3)
	volume of the package atmosphere (iii) maskage atmosphere volume at time $t_{\rm c}$ (m ³)
V p.h	package atmosphere volume at time t_h (iii)
W	respiratory near generation per unit mass of O_2 consumption (J·kg)
x	this have a fit have a
x_i	thickness of the <i>i</i> ^m layer of packaging material (m)
X_i	mole fraction of gas species i in the bulk flow through holes in the packaging
	film
$X_{\rm CO_2}$	mole fraction of CO_2 in the flow through holes in the packaging film
$X_{\rm H:O}$	mole fraction of water vapour in the flow through holes in the packaging film
X_{N_2}	mole fraction of N_2 in the flow through holes in the packaging film
X_{0}	mole fraction of O_2 in the flow through holes in the packaging film
XCO2, e	mole fraction of CO_2 in the store air (dry air basis)
XN2, e	mole fraction of N_2 in the store air (dry air basis)
Xoz e	mole fraction of O_2 in the store air (dry air basis)
X_m	parameter of the GAB isotherm model (Eq. 2.22)
Xtray	tray moisture content on a dry solids basis (kg·kg ⁻¹)
Y	fractional unaccomplished temperature change
Y'_i	fractional unaccomplished concentration change for gas species <i>i</i>
$\begin{bmatrix} i \end{bmatrix}$	volume concentration of gas species $i (m^3 \cdot m^{-3})$
[<i>i</i>].	volume concentration of gas species i in the store atmosphere $(m^3 \cdot m^{-3})$
$\begin{bmatrix} i \end{bmatrix}$	volume concentration of gas species <i>i</i> in the package atmosphere $(m^3 m^{-3})$
[CO']	volume concentration of CO ₂ in the store atmosphere $(m^3 \cdot m^{-3})$
$[U, U]_{e}$	volume concentration of water vanour in the store atmosphere $(m^3 \cdot m^{-3})$
$[H_2O]_e$	volume concentration of water vapour in the package atmosphere $(m^3 m^{-3})$
$[11_2 \bigcirc]_p$	volume concentration of N in the store atmosphere $(m^3 \cdot m^{-3})$
$\begin{bmatrix} 1 \\ 2 \end{bmatrix}_e$	volume concentration of Ω_2 in the store atmosphere (m ⁻³ m ⁻³)
$[O_2]_e$	volume concentration of O_2 in the store autosphere (in an)
C	constant in Eq. 6.82 (c ⁻¹)
u .	constant in Eq. 6.82
Y	Constant III Eq. 0.62
3	$\frac{1}{2} \frac{1}{2} \frac{1}$
η_f	iruit specific enthalpy (J·Kg ⁻)
n.	specific enthalpy of the package atmosphere (dry air basis) (J·kg ⁻¹)

 η_p specific enthalpy of the package atmosphere (dry air basis) (J·kg) η_{tray} specific enthalpy of the moulded-pulp fruit trays (dry mass basis) (J·kg⁻¹)

θ	store air temperature (°C)
θ_{f}	fruit temperature (°C)
θ_{film}	temperature of the packaging film (°C)
θ	initial temperature (°C)
θ_p	temperature of the package atmosphere (°C)
θ_{ref}	reference temperature (°C)
λ	thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$
λ	thermal conductivity of the i^{th} layer of packaging material (W·m ⁻¹ ·K ⁻¹)
ξ	empirical correction factor for gas diffusion through holes
0	initial fruit flesh density $(kg \cdot m^{-3})$

 $\begin{array}{ll} \rho_{f.\ initial} & \text{initial fruit flesh density } (\text{kg m}^{-3}) \\ \rho_{f} & \text{fruit flesh density } (\text{kg m}^{-3}) \end{array}$

 θ temperature (°C)