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ORIGINAL ARTICLE

Development and validation of a comprehensive model for map of fruits based on enzyme kinetics theory and arrhenius relation

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Abstract MAP is a dynamic system where respiration of the packaged product and gas permeation through the packaging film takes place simultaneously. The desired level of O_2 and CO_2 in a package is achieved by matching film permeation rates for O_2 and CO_2 with respiration rate of the packaged product. A mathematical model for MAP of fresh fruits applying enzyme kinetics based respiration equation coupled with the Arrhenious type model was developed. The model was solved numerically using MATLAB programme. The model was used to determine the time to reach to the equilibrium concentration inside the MA package and the level of O_2 and CO_2 concentration at equilibrium state. The developed model for prediction of equilibrium O_2 and CO_2 concentration was validated using experimental data for MA packaging of apple, guava and litchi.

Keywords MAP · Fruit respiration · Film permeability · Modelling · Shelf life

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Notations

A_p	Surface area of the packaging film, m^2
E	Mean relative deviation modulus, %
E_a	Activation energy, kJ g^{-1} mol^{-1}
E_{ap}	Activation energy of gas transmission rates for O_2 and CO_2 (kJ/kg-mole)
GTR	Gas transmissions rates of films (cm^3/m^2 h ΔC) at temperature T_{abs}
GTR_p	Gas transmission rates pre-exponential factor for O_2 and CO_2 (cm^3/m^2 h ΔC)
$K_{m(O2)}$	Michaelis-Menten constant for O_2 consumption, % O_2
$K_{m(CO2)}$	Michaelis-Menten constant for CO_2 evolution, % O_2
$K_{i\ (O2)}$	Inhibition constants for O_2 consumption, % CO_2
$K_{i\ (CO2)}$	Inhibition constants for CO_2 evolution, % CO_2
R_{O2}	Respiration rate, ml [O_2] kg^{-1} h^{-1}
R_{CO2}	Respiration rate, ml [CO_2] kg^{-1} h^{-1}
Y_{O2}	O_2 concentration inside the package (cm^3 per cm^3 of air)
Z_{CO2}	CO_2 concentration inside the package (cm^3 per cm^3 of air)
T	Storage time in h
Δt	Time difference between two gas measurements
V_f	Free volume of the respiration chamber in ml
W	Weight of the fruit in kg
R	Universal gas constant, 8.314 kJ kg^{-1} mol^{-1} K^{-1}
R_{CO2}	Respiration rate, ml [CO_2] kg^{-1} h^{-1}
R_{exp}	Experimental respiration rate, ml kg^{-1} h^{-1}
R_m	Model parameter of enzyme kinetic

R_{pre}	Predicted respiration rate, ml kg^{-1} h^{-1}
R_{O2}	Respiration rate, ml $[O_2]$ kg^{-1} h^{-1}
R_p	Respiration pre-exponential factor
T	Storage temperature, °C
T_{abs}	Storage temperature, K
t	Storage time, h
Δt	Time difference between two gas measurements
V_f	Free volume of the respiration chamber, ml
$V_{m\ (CO2)}$	Maximum respiration rate for CO_2 evolution, ml/kg-h
$V_{m\ (O2)}$	Maximum respiration rate for O_2 consumption, ml/kg-h
$Y_{O2}{}^{a}$	O_2 concentration in the atmospheric air (cm^3 per cm^3 of air)
$Z_{CO2}{}^{a}$	CO_2 concentration in the atmospheric air (cm^3 per cm^3 of air)
$Y_{O2}{}^{eq}$	Equilibrium/optimum O_2 concentration attained in the package
$Z_{CO2}{}^{eq}$	Equilibrium/optimum CO_2 concentration attained in the package
W_p	Weight of the fruits in MA package, kg
V_{fp}	Free volume in the package, cm^3
X	Thickness of the film, cm
OTR	Oxygen transmission rates
CTR	Carbon dioxide transmission rates
P_{O2}	O_2 permeability of packaging material (cm^3. m^{-2} . h^{-1}. [Conc. diff. of O_2 in volume fraction]$^{-1}$)
P_{CO2}	CO_2 permeability of packaging material (cm^3. m^{-2}. h^{-1}. [Conc. diff. of O_2 in volume fraction]$^{-1}$)
dY_{O2}/dt	Rate of change of O_2 concentration 'Y_{O2}' within the package at time 't' of storage (cm^3 per cm^3 of air. h^{-1})
dZ_{CO2}/dt	Rate of change of CO_2 concentration 'Z_{CO2}' within the package at time 't' of storage (cm^3 per cm^3 of air. h^{-1}) respectively
N	Number of respiration data points

Introduction

Modified-atmosphere packaging (MAP) of fresh commodity refers to the technique of sealing actively respiring produce in polymeric film packages to modify the O_2 and CO_2 levels within the package atmosphere. It is often desirable to generate an atmosphere low in O_2 and/or high in CO_2 to influence the metabolism of the product being packaged, or the activity of decay-causing organisms to increase storability and/or shelf life (Kader et al. 1989; Mangaraj et al. 2009). In addition to atmosphere modification, MAP vastly improves moisture retention, which can have a greater influence on preserving quality than O_2 and CO_2 levels (Mangaraj and Tripathi 2013). Furthermore, packaging isolates the product from the external environment and helps to ensure conditions that, if not sterile, at least reduce exposure to pathogens and contaminants (Mahajan et al. 2007).

MAP is a dynamic system during which respiration and permeation occur simultaneously. In a properly designed MAP, after a period of transient state an equilibrium state is established. At equilibrium, the amount of O_2 entering into the package and that of CO_2 permeating out of the package become equal to the amount of O_2 consumed and that of CO_2 evolved by the packaged fruit, respectively (Yam and Lee 1995; Del Nobile et al. 2007). Respiration rate of the commodity, permeability of packaging film, mass of the produce packed inside the package, area of the packaging film, surrounding gas composition, optimum level of O_2 and CO_2 concentration, storage temperature etc. affect the equilibrium gas concentration (Yam and Lee 1995; Jacxsens et al. 2000; Mangaraj et al. 2013a) and they are taken as input parameters for developing mathematical model.

Different mathematical models were developed to describe the mass balance of O_2 and CO_2 concentration inside the package during storage. These model parameters were considered for theoretical design of MAP of commodity. Cameron et al. (1989) employed O_2 depletion method for determining O_2 consumption in a closed system for tomatoes and optimized the package parameters based on the gas exchange model. Christie et al. (1995) proposed a material balance equation that relates the package film permeability and produce metabolism to the in-package gas concentrations. Song et al. (2002) developed a MAP model based on mass balances and the transport phenomenon across the package and solved it numerically using Adams-Moulton's numerical technique. The reasons for choosing the Adams-Moulton's numerically technique in this MAP model is due to the fact that it is useful for the solution of the differential equation to calculate and predict the variation of oxygen and carbon dioxide concentration with time. This method is very accurate for solving the higher order differential equation that form in MAP modeling process.

Rocculi et al. (2006) developed the models applying Michaelis-Menten's equation and Arrehnius's type expression to describe the mass balance of O_2 and CO_2 concentration inside the MA package for minimally processed apple packed in multilayer pouches. Torrieri et al. (2007) studied the effect of temperature, oxygen, red coloration process and post-harvest storage time on the respiration rate of fresh-cut Annurca apples for developing suitable MAP. Mahajan et al. (2007) developed software for MAP design of fresh and fresh-cut produce for selecting suitable packaging materials. Techavises and Hikida (2008) developed a mathematical

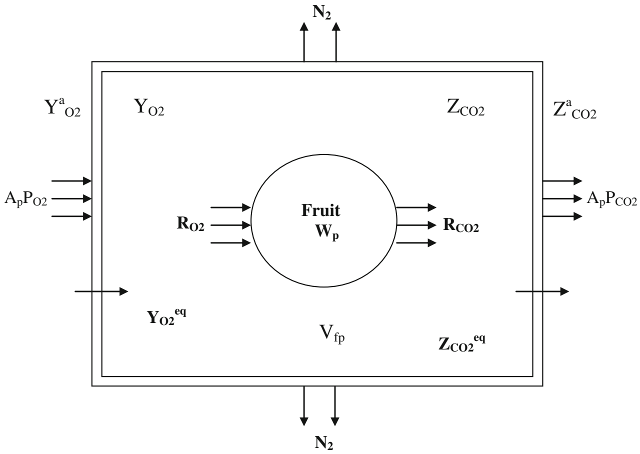

Fig. 1 Diagrammatic representation of gaseous exchange in MAP system

model based on Fick's law for predicting O_2, CO_2, N_2, and water vapor exchange in film packaging with macroscopic perforations.

A systematic theoretical design and modeling is needed to establish conditions for the success and benefit of MAP for a particular produce (Exama et al. 1993; Mahajan et al. 2007). Such a design and analysis could provide closely the characteristic of the commodity, film properties and optimized packaging parameters. Simulation of a MAP system is the most appropriate method to allow a correct MAP design and consequently obtain a successful commercial product (Cameron et al. 1989; Makino and Iwasaki 1997; Del Nobile et al. 2007).

Considering these approaches in mind a global model for MA packaging of fruits was proposed. The proposed model coupled to the principle of enzyme kinetics equation that describes the dependence of respiration rate on gas composition, temperature (and eventually time) and models that describes the dependence of packaging material on temperature; with the mass balance equations that describes the gaseous exchange in MAP. Using this model the variation of O_2 and CO_2 inside the MA package and the time to reach equilibrium level could be predicted accurately at any storage temperature.

Materials and methods

Respiration rate model

The Michaelis-Menten type equation based on principle of enzyme kinetics with uncompetitive type of inhibition, wherein CO_2 does not bind with the enzyme but reacts with enzyme substrate complex (Lee and Wicker 1991), was the model fitted to the experimental respiration data (Peppelenbos and Leven 1996; Mangaraj and Goswami 2011a, b). The relevant enzyme kinetics models are shown Eqs. (1) and (2).

$$R_{O2} = \frac{V_{m(O2)} \times Y_{O2}}{k_{m(O2)} + \{1 + ([Z_{CO2}])/k_{i(O2)}\}Y_{O2}} \tag{1}$$

$$R_{CO2} = \frac{V_{m(CO2)} \times Y_{O2}}{k_{m(CO2)} + \{1 + ([Z_{CO2}]/k_{i(CO2)})\}Y_{O2}} \tag{2}$$

The temperature dependence of the model parameters of the above Michaelis-Menten equations was quantified using an Arhhenius model (Mangaraj and Goswami 2008).

$$R_m = R_p \exp\left[\frac{E_a}{R \times T_{abs}}\right] \tag{3}$$

Model for gas transmission rates

The gas transmission rates (OTR/CTR) of polymeric film are temperature dependent and hence Arrhenius-equations of the following type were fitted to the experimental data to depict the relationship of GTR with temperature (Exama et al. 1993).

$$GTR = GTR_p \exp\left[\frac{-E_{aGTR}}{RT_{abs}}\right] \tag{4}$$

Table 1 Activation energy and pre-exponential factor of Arrhenius-type equation for different model parameters of uncompetitive inhibition

Arrhenius parameter	$v_{m (O2)}$	$v_{m (CO2)}$	$k_{m (O2)}$	$k_{m (CO2)}$	$k_{i (O2)}$	$k_{i (CO2)}$
Apple						
E_a (kJ/g-mole)	30.06	25.10	20.45	11.88	−20.23	−16.84
R_p (ml [O_2] kg^{-1} h^{-1})	5.2×10^6	9.1×10^5	3.8×10^4	1.7×10^3	1.7×10^{-3}	9.2×10^{-3}
Guava						
E_a (kJ/g-mole)	27.89	26.69	14.58	18.02	−17.54	−16.40
R_p (ml [O_2] kg^{-1} h^{-1})	3.7×10^6	1.9×10^6	4.5×10^3	1.4×10^4	5.0×10^{-3}	7.0×10^{-3}
Litchi						
E_a (kJ/g-mole)	42.24	39.45	17.76	16.36	−18.17	−10.44
R_p (ml [O_2] kg^{-1} h^{-1})	2.59×10^9	6.17×10^8	2.33×10^4	9.19×10^3	2.9×10^{-3}	1.1×10^{-1}

Design variables in MAP

The variables involved in the MA package design are: the surrounding gases composition ($Y_{O2}{}^{a}$ and $Z_{CO2}{}^{a}$), temperature (T), O_2 consumption rate and CO_2 production rate (R_{O2} and R_{CO2}), the optimum gas composition to be attained in the package ($Y_{O2}{}^{eq}$ and $Z_{CO2}{}^{eq}$), weight of the fruits in package (W_p), surface area of the packaging film (A_p), free volume of the package (V_{fp}), thickness of the film (x), gas transmission rates of film to O_2 and CO_2 (OTR and CTR). The ultimate aim of this design was to select suitable films for a 1±0.1 kg fill weight so that the equilibrium concentrations of O_2 and CO_2 are reached within shortest possible time and these concentrations lie within the range required for maximum shelf life of stored fruits (Das 2005; Mangaraj et al. 2009; Mangaraj et al. 2011). The package size of 1±0.1 kg was considered based on survey conducted at the local market.

Target level of MA package air composition for fruits

The recommended level of gas concentration in CA/MA storage of apple, guava and litchi for maintaining quality and extending shelf-life are 1–3 and 3–5 %; 2–5 and 2–5 %; 3–5 and 3–5 % O_2 and CO_2, respectively (Mangaraj and Goswami 2009a, b; Singh and Pal 2008; Shivakumar et al. 2007) with N_2. On the basis of preliminary investigations and the sub-optimal package air composition it was found appropriate for designing the optimal MA packages for apple, guava and litchi with target air composition of 3 %O_2 and 3 % CO_2; 5 %O_2 and 4 % CO_2; 5 %O_2 and 5 % CO_2 in N_2, respectively.

Development of MAP model for fruits

Respiration of the fruits and the gas permeation through the packaging film takes place simultaneously during MA packaging. In general, the relative humidity in the internal package atmosphere is higher than the external atmosphere. Hence some amount of water vapor may permeate out of the package, depending upon the WVTR of the polymeric film. The mathematical modeling of gaseous exchange for respiratory gases (O_2 and CO_2) has been attempted here. The diagrammatic representation of the gaseous exchange in MAP is shown in Fig. 1.

The concept is that once the fruit is sealed inside the package the O_2 and CO_2 concentration gradients develop due to the fruit respiration and the polymeric film serves as the regulator of O_2 flow into the package and the flow of CO_2 out of the package. At a given temperature and for a considerably small length of transient period, the rates of O_2 consumption (R_{O2}) and the rate of CO_2 evolution (R_{CO2}) of the packaged fruits depend greatly on O_2 concentration (Y_{O2}) and CO_2 concentration (Z_{CO2}). Considering that there is no gas stratification inside the packages and that the total

Table 2 Activation energy and pre-exponential factor of Arrhenius-type equation for selected polymeric films

Parameters for Arrhenious equations	Polymeric films with their thickness															
	BOPP-30 μ		BOPP-45 μ		PVC-25 μ		PVC-35 μ		PVC-50 μ		LDPE-40 μ		LDPE-60 μ		PVDC-40 μ	
	OTR	CTR	OTR	CTR	OTR	CTR	OTR	CTR	OTR	CTR	OTR	CTR	OTR	CTR	OTR	CTR
E_a (kJ/g-mole)	50.09	53.36	52.96	66.84	49.65	51.40	51.89	53.84	51.65	53.99	51.61	54.01	51.40	54.38	46.84	50.82
GTR_p (cm^3/m^2 h ΔC)	7.58×10^{10}	1.34×10^{12}	1.55×10^{11}	2.06×10^{14}	9.52×10^{11}	1.22×10^{13}	1.57×10^{12}	2.18×10^{13}	9.90×10^{11}	1.58×10^{13}	5.52×10^{11}	8.51×10^{12}	3.34×10^{11}	6.38×10^{12}	1.54×10^{8}	2.94×10^{9}

pressure is constant (Mahajan et al. 2007; Mangaraj et al. 2011), the differential mass balance equations that describe the O_2 concentration changes in a package containing respiring product are:

Rate of O_2 entry into package space—Rate of O_2 consumed by product
= Rate of O_2 accumulation inside package space

That is,
$$A_p P_{O2}\left(Y^a_{O2}-Y_{O2}\right)-W_p R_{O2} = V_{fp}\left(\frac{dY_{O2}}{dt}\right) \quad (5)$$

$$\text{Or}\left(\frac{dY_{O2}}{dt}\right) = -\left(\frac{W_p}{V_{fp}}\right)R_{O2} + \left(\frac{A_p P_{O2}}{V_{fp}}\right)\left(Y^a_{O2}-Y_{O2}\right) \quad (6)$$

Similarly, the CO_2 concentration changes in a package can be written as,

Rate of CO_2 generated by the fruits—Rate of CO_2 leaving out of the package space
= Rate of accumulation CO_2 inside package space
That is,

$$W_p R_{CO2}-A_p P_{Co2}\left(Z_{CO2}-Z^a_{CO2}\right) = V_{fp}\left(\frac{dZ_{CO2}}{dt}\right) \quad (7)$$

$$\text{Or}\left(\frac{dZ_{CO2}}{dt}\right) = \left(\frac{W_p}{V_{fp}}\right)R_{CO2}-\left(\frac{A_p P_{CO2}}{V_{fp}}\right)\left(Z_{CO2}-Z^a_{CO2}\right) \quad (8)$$

The Eqs. 6 and 8 were coupled to the enzyme kinetics models that describes the dependence of respiration rate on gas composition, temperature (and eventually time) i.e. Eqs. 1, 2 and 3 and models that describes the dependence of packaging film on temperature, i.e. Eq. 4 constitute the basic of development MAP models. Now substituting the Eqs. 1, 2, 3 and 4 appropriately in Eqs. 6 and 8 we have:

$$\left(\frac{dY_{O2}}{dt}\right) = -\left(\frac{W_p}{V_{fp}}\right)\times\left\langle\frac{\left(R_{pvmO2}\times\exp\left[\frac{-E_{avmO2}}{R\times T_{abs}}\right]\right)\times Y_{O2}}{\left(R_{pvmO2}\times\exp\left[\frac{-E_{akmO2}}{R\times T_{abs}}\right]\right)+\left\{1+\left[[Z_{CO2}]\ \left(R_{pkiO2}\times\exp\left[\frac{-E_{akiO2}}{R\times T_{abs}}\right]\right)\right]\right\}\times Y_{O2}}\right\rangle + \left(\frac{A_p\times\left(OTR_p\times\exp\left[\frac{E_{aOTR}}{RT_{abs}}\right]\right)}{V_{fp}}\right)\times\left(Y^a_{O2}-Y_{O2}\right) \quad (9)$$

Table 3 Equilibrium concentration of O_2 and CO_2 predicted by the model and experimental observations for apple (PCG-LFR-1), guava (PCG-LFR-3) and litchi (PCG-LFR-5) packages

MA package fill weight of 1.00 kg						
Temperature (°C)	$Y_{O2}^{eq\text{-}pre}$ (%)	$Y_{O2}^{eq\text{-}exp}$ (%)	$Z_{CO2}^{eq\text{-}pre}$ (%)	$Z_{CO2}^{eq\text{-}exp}$ (%)	$t^{eq\text{-}pre}$ (h)	$t^{eq\text{-}exp}$ (h)
Apple						
10	3.11	3.17	3.53	3.74	60.00	66.00
15	3.14	3.22	3.51	3.68	54.00	58.00
20	3.31	3.24	3.59	3.74	46.00	50.00
25	3.30	3.17	3.90	4.17	40.00	42.00
Guava						
10	4.97	5.20	2.91	3.34	24.00	26.00
15	4.86	5.13	2.97	3.45	22.00	24.00
20	4.82	5.00	2.93	3.39	18.00	20.00
25	5.11	5.27	2.86	3.27	16.00	16.00
Litchi						
10	4.93	5.16	3.32	3.96	44.00	48.00
15	5.01	5.24	3.20	3.75	40.00	42.00
20	4.90	5.19	3.14	3.63	30.00	28.00

$$\left(\frac{dZ_{CO2}}{dt}\right)=\left(\frac{W_p}{V_{fp}}\right)\times\left\langle\frac{\left(R_{pvmCO2}\times\exp\left[\frac{-E_{avmCO2}}{R\times T_{abs}}\right]\right)\times Y_{O2}}{\left(R_{pkmCO2}\times\exp\left[\frac{-E_{akmCO2}}{R\times T_{abs}}\right]\right)+\left\{1+\left[Z_{CO2}\right]\left(R_{pkiCO2}\times\exp\left[\frac{-E_{akiCO2}}{R\times T_{abs}}\right]\right)\right\}\times Y_{O2}}\right\rangle-\left(\frac{A_p\times\left(CTR_P\times\left[\frac{E_{aCTR}}{RT_{abs}}\right]\right)}{V_{fp}}\right)\times\left(Z_{CO2}-Z^{a}_{CO2}\right) \tag{10}$$

Numerical analysis

Simultaneous solution of above differential equations would give variation of O_2 concentration, Y_{O2} (volume fraction), CO_2 concentration, Z_{CO2} (volume fraction) as a function of time, t (h). The typical functional relationship for R_{O2} and R_{CO2} as a function of Y_{O2} and Z_{CO2} is carried out numerically, using Adams numerical method, which is based on Taylor's formula (Piskunov 1981).

The estimated values of respiration model parameters R_p and E_a for O_2 consumption and CO_2 evolution, along with the weight of fruits (W_p) constitute the product parameters. The GTR_p, E_{aOTR} and E_{aCTR} of selected films were used as film parameters. Total surface area of film package (A_p) and the package head space (V_{fp}) served as input for package parameters, whereas, initial in-pack O_2 and CO_2 concentration (Y_{O2}, Z_{CO2}) and outside atmosphere (${Y_{O2}}^a$ and ${Z_{CO2}}^a$) served as environment parameters. As the MA package initially contained air, initial O_2 and CO_2 (Y_{O2} and Z_{CO2}) concentration were taken as 21 % (0.21 cm^3/cm^3 of air) and 0.03 % (0.0003 cm^3/cm^3 of air) respectively.

MA Packaging of selected fruits

Apple, guava and litchi of medium size harvested at commercial maturity were collected from the orchard and number-labeled for MA packaging (Mangaraj and Goswami 2009c). Five types of packages (PKG-LFR1, PKG-LFR2, PKG-LFR3, PKG-LFR4 and PKG-LFR5) of required size i.e. 24×19 cm for apple; 19×19 cm for guava and 28×22 cm for litchi for 1±0.1 kg fill weight were developed. Fruits were packaged and heat sealed. Impulse time was adjusted for different films for obtaining a clean seal. Silicon rubber septums were glued to the packages to facilitate gas sampling. The MA packages were labeled marked and kept in the incubator for subsequent storage study at 10, 15, 20 and 25ºC (Mangaraj et al. 2005; Mangaraj et al. 2012a, b; Mangaraj et al. 2013b).

The samples of package air were analyzed on Gas Chromatograph (Mangaraj and Goswami 2009a, b) for determining the variation of O_2 and CO_2 concentration in the package with time. The equilibrium concentration of O_2 (${Y_{O2}}^{eq}$) and CO_2 (${Z_{CO2}}^{eq}$) were subsequently determined. From the mathematical model of gaseous exchange in MAP, the values of Y_{O2}, Z_{CO2}, ${Y_{O2}}^{eq}$, ${Z_{CO2}}^{eq}$ and t_{eq} were predicted by employing MATLAB Programme. The predicted and the experimental values of Y_{O2}, Z_{CO2}, ${Y_{O2}}^{eq}$, ${Z_{CO2}}^{eq}$ and t_{eq} were compared for validation of the developed model.

Results and discussions

MAP modelling and analysis

With the objective of meeting MAP requirements of fruit the polymeric high, medium and low barrier hydrophilic films namely, low density polyethylene (LDPE), biaxially oriented polypropylene (BOPP), polyvinyl chloride (PVC), polyvinyledene chloride (PVDC) were procured from Reliance Food Industry, Kolkata considering various film characteristics (Exama et al. 1993; Mangaraj et al. 2009; Costa et al. 2011). Two different films were combined through the tailoring of film laminates to bring the gas transmission requirement of the laminates close to the required values (Mangaraj et al. 2012a, b; Mangaraj and Tripathi 2013, a, ba,b). Three types of film packages i.e. PCG-LFR-1 (BOPP-30 μ+PVC−50 μ) for apple; PCG-LFR-3 (BOPP-45 μ+PVC−25 μ) for guava; and PCG-LFR-5 (BOPP-30 μ+PVC−25 μ) for litchi of package size 24 cm×19 cm; 19 cm×19 cm and 28 cm 22 cm, respectively were chosen for experimental validation of proposed MAP model (Mangaraj et al. 2012a, b; Mangaraj and Tripathi 2013, a, b). The activation energy and pre-exponential factor of Arrhenius-type equation for different model parameters of enzyme kinetics of uncompetitive inhibition is presented in Table 1; moreover the activation energy and pre-exponential factor of Arrhenius-type equation for selected polymeric films is given in Table 2. These values were used for validating the developed global MAP model (Mangaraj and Goswami 2008, 2011a, b).

In this study a generalized global model was developed and verified against the MAP storage study data for apple, guava and litchi for 1±0.1 kg fill weight. The output obtained from this model was compared with the experimental data and used for predicting the equilibrium level of O_2 and CO_2 in MA packaging of different commodity carried out by some researchers.

Equilibrium concentrations of O_2 and CO_2 in MA packages

The predicted as well as experimental values of Y_{O2}^{eq}, Z_{CO2}^{eq} and t_{eq} for various MA packages for 1±0.1 kg fill weight at different storage temperatures have been presented in Table 3. The profile of package air composition with time predicted by the modelling of gaseous exchange in MAP for the packages PCG-LFR-1, PCG-LFR-3 and PCG-LFR-5 for apple, guava and litchi, respectively at 15ºC has been depicted in Fig. 2. Most of the packages have established equilibrium at such levels of O_2 and CO_2, which were fairly close to the target levels. The predicted and experimental values of Y_{O2}^{eq}, Z_{CO2}^{eq} were found to be higher than the target levels for all the MA packages. There was good agreement between predicted as well as experimental values of Y_{O2}^{eq} and Z_{CO2}^{eq}. The experimental values of Y_{O2}^{eq} varied between 3.10–3.31 % (0.031–0.033 cm^3 per cm^3 of air); 5.00–5.37 % (0.05–0.054 cm^3 per cm^3 of air); 4.95–5.28 % (0.049–0.053 cm^3 per cm^3 of air) whereas those of Z_{CO2}^{eq} varied between 3.34–4.17 % (0.0334–0.0417 cm^3 per cm^3 of air); 3.14–3.72 % (0.0314–0.0372 cm^3 per cm^3 of air); 3.56–4.20 % (0.0356–0.0420 cm^3 per cm^3 of air) for all types of MA packages for apple, guava and litchi, respectively at all the reference temperature levels. The equilibrium O_2 and CO_2 concentration obtained from the model was verified against the experimental data for MA packages of fruits. The mean relative deviation moduli between the equilibrium concentration of O_2 and CO_2 as predicted by the developed model and that obtained through experiments were found to be in the range of 5.92–8.6 % and 7.14–9.35 %, respectively. This indicated that, the developed model is in good agreement with the experimental data. The experimental as well as predicted variation of O_2 and CO_2 levels in MA packages PCG-LFR-3 at 15ºC storage temperatures has been shown in Fig. 3. During steady state period, the experimental values of O_2 and CO_2 were found to be nearly constant for an extended period of storage. By and large all types of MA packages have established dynamic equilibrium state without causing any unfavorable deviation from the target levels of O_2 and CO_2 at all the reference storage temperatures.

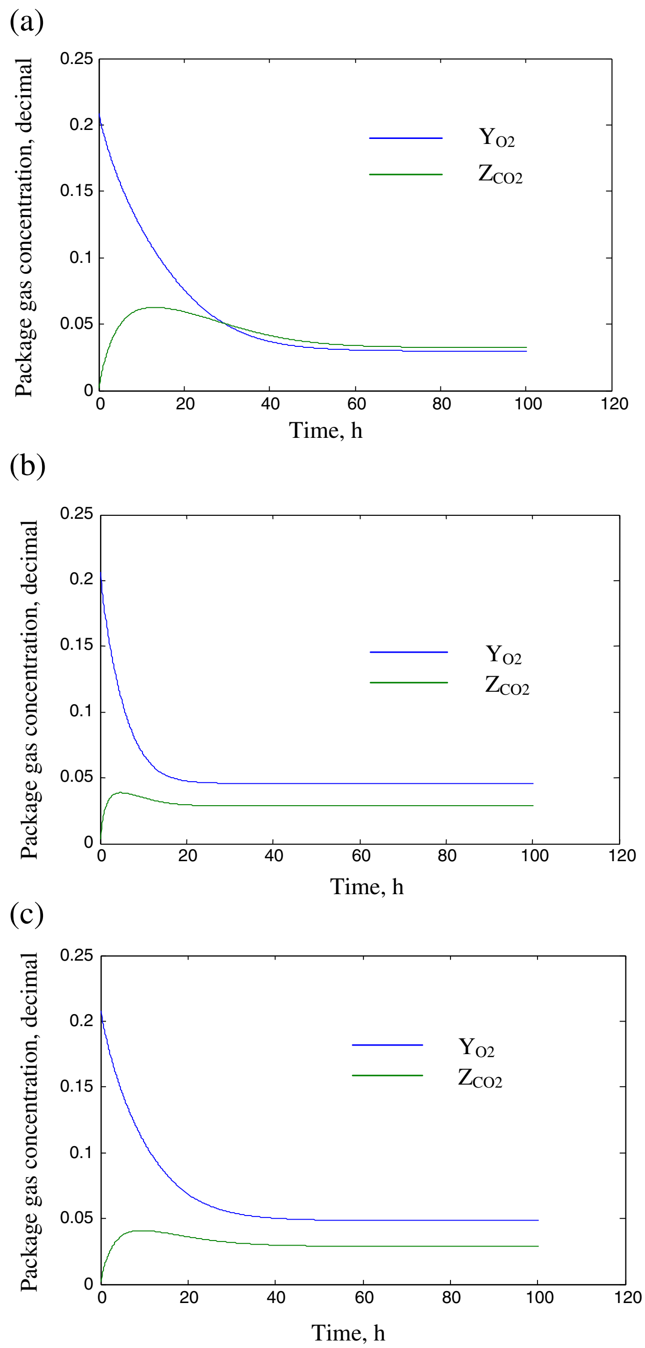

Fig. 2 (**a**, **b**, **c**): Predicted variation of O_2 and CO_2 with time by the model in MA packed apple, guava and litchi at 15ºC

Equilibrium time

The length of time taken by the MA package to establish dynamic equilibrium from the time of packaging is considered as equilibrium time. For various packages, the predicted values of equilibrium time were found to have varied between 36–72 h; 12–30 h; and 26–50 h, whereas those of experimental values varied between 34–80 h; 10–34 h and 24–56 for all types of MA packages for apple, guava and litchi, respectively at all the reference storage temperatures as given in Table 3. The mean relative deviation moduli for the equilibrium time as predicted by the developed model and that obtained through experiments were found to be 7.77, 7.17 and 2.47 % for apple, guava and litchi, respectively. This indicated that, the developed model is in good

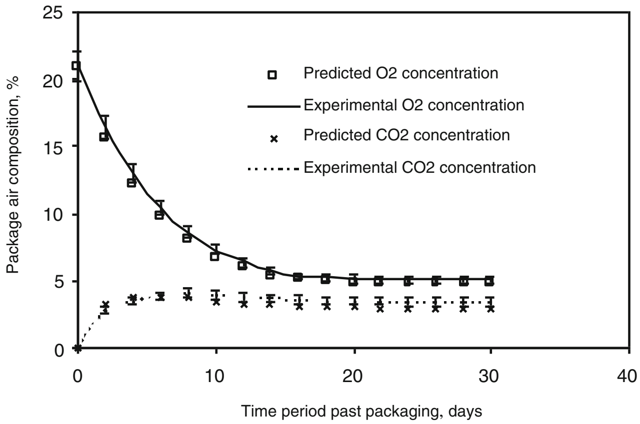

Fig. 3 Experimental and predicted variation in package air composition with time for guava (PCG-LFR-3) at 15ºC storage temperatures

agreement with the experimental data. There was some deviation of experimental values from the predicted ones. The development of quasi-equilibrium conditions and the variations in the free volume in the package (V_{fp}), because of the varying fill weight, were probably the cause of such deviations in equilibrium time (t_{eq}) values. In fact, small variations in V_{fp} are always possible in a flexible package. Hence, it is unrealistic to expect a constant value of V_{fp} in the flexible packages. It has been seen that the variation in O_2 affects both R_{O2} and R_{CO2} significantly. With the variation in R_{O2} and R_{CO2}, the O_2 consumption as well as the CO_2 evolution of the package varies which in turn affects O_2 and CO_2 level in the internal atmosphere of the package. Thus, as O_2 decreases, R_{CO2} reduces which in turn reduces CO_2 in the internal atmosphere of the package.

Reduction in CO_2 level tends to retrieve R_{CO2} slightly. However, the amount of reduction in CO_2 due to decrease in O_2 is greater than the amount of retrieved. As such, with the decrease in O_2 level CO_2 level also decreases, though by small amounts. Thus, though the equilibrium condition for CO_2 level appears to be approaching earlier than that of O_2 level but in true sense, CO_2 level becomes stable only when O_2 level attains equilibrium (Fig. 2 and 3). It implies that the equilibrium for both, O_2 and CO_2 is attained simultaneously in MA packaging. Also, in view of the fact that O_2 level has more pronounced effect on respiration rates than CO_2 level, the equilibrium time (t_{eq}) for O_2 level assume greater importance. The single equilibrium time (t_{eq}) approach advocated in this study is in agreeance with the study of (Rocculi et al. 2006; Torrieri et al. 2007; Gonzalez-Buesa et al. 2009; Tariq et al. 2009; Mangaraj et al. 2011).

Validation of model with other's work

Mahajan and Goswami (2001) has developed enzyme kinetics respiration model for red delicious apple. Using the values of model parameters the activation energy and respiration pre-exponential factor for O_2 consumption and CO_2 evolution was obtained. Substituting these values in Eqs. 9 and 10, with area of packaging film (A_p) as 0.11 m^2, mass of apple (W_p) of 1.00 kg, void volume of the package (V_{fp}) of 1,000 cm^3 the variation

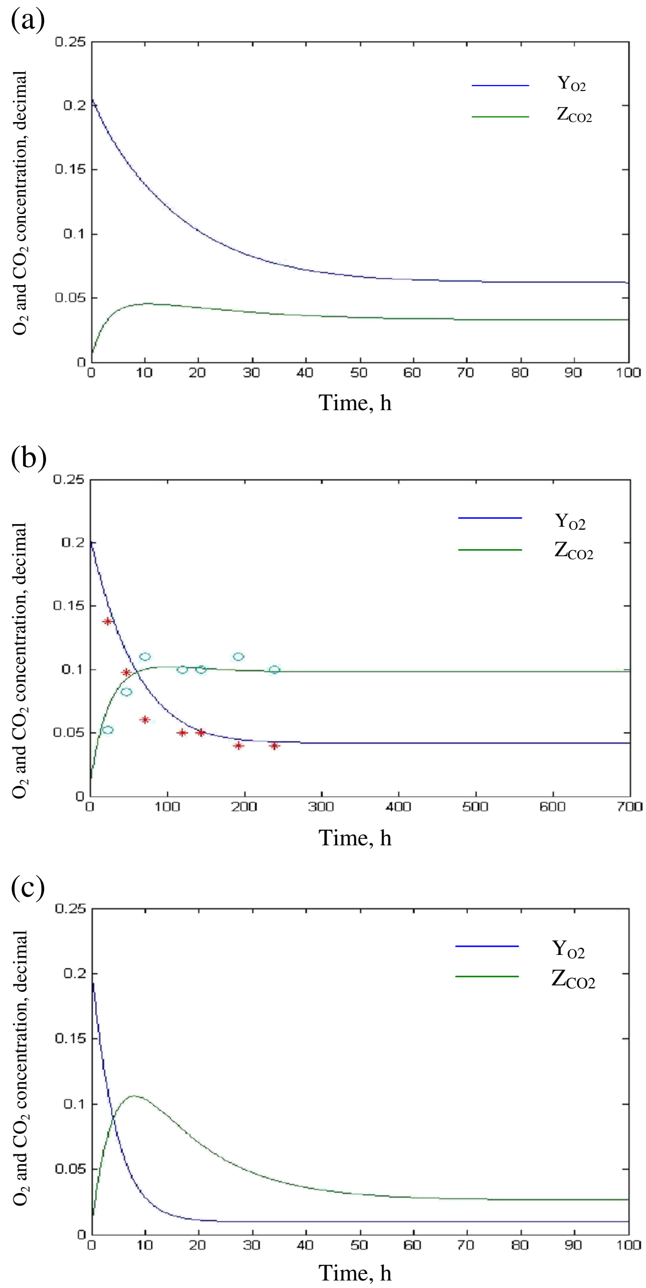

Fig 4 **a** Plot between O_2 and CO_2 with time for red delicious apple **b** Plot between O_2 and CO_2 with time for tomato **c** Plot between O_2 and CO_2 with time for button mushroom

of O_2 and CO_2 with time plot was obtained (Fig. 4a). It shows that (Fig. 4a) the model has achieved an equilibrium concentration of 6 % O_2 (0.06 cm^3 per cm^3 of air) and 4 % CO_2 (cm^3 per cm^3 of air) at 40 h and remains in equilibrium for 100 h. Geeson et al. (1985) conducted MA packaging study with tomato of weighing 390 g using 15 μ polyvinylchloride film having void volume of 550 cm^3 at a temperature of 10 °C. The equilibrium concentration of O_2 (4 %) and CO_2 (10 %) achieved inside the film package in 200 h using the developed model (Fig. 4b). Similarly, Rai and Paul (2007) worked on design and modelling of gaseous exchange in MAP for button mushrooms. They stored mushrooms of weight 500 g inside a 57 μLDPE film having a void volume of 545 cm^3 and area of packaging film of 0.11 m^2 at a temperature of 15 °C. They recorded the variation of O_2 concentration and CO_2 concentration with time inside the MA package. They found that O_2 concentration decreased and CO_2 concentration increased inside the package as the storage period progressed (Fig. 4c). The model suggested, that the dynamic equilibrium attained at 2 % oxygen and 4 % carbon dioxide level (Fig. 4c) and it maintained till 96 h of packaging. The mean relative deviation modulus for equilibrium gas concentration and time as predicted by the developed model and experimental values varied in the range of 4.7–8.5 % and 3.9–6.4 %, respectively indicating the good predictability of the developed MAP model.

Conclusions

A mathematical model for MA packaging of apple, guava and litchi applying enzyme kinetics based respiration equation coupled with the Arrhenious model was developed. The model was used to determine the time to reach to the equilibrium concentration inside the MA package and the level of O_2 and CO_2 concentration at equilibrium state. The equilibrium O_2 and CO_2 concentration obtained from the model was verified against the experimental data for MA packages of fruits. The mean relative deviation moduli between the equilibrium concentration of O_2 and CO_2 as predicted by the developed model and that obtained through experiments were found to be in the range of 5.92–8.60 % and 7.14–9.35 %, respectively for apple, guava and litchi fruits. This indicated that, the developed model is in good agreement with the experimental data. There were some deviations of equilibrium time between the predicted and experimental values may be attributed to the development of quasi-equilibrium conditions and the variations in the free volume in the package due to the varying fill weight. In fact, small variations in free volume are always possible in a flexible package. It has been seen that the equilibrium time for both, O_2 and CO_2 attained simultaneously in MA packaging. The model has been used for predicting the equilibrium level of O_2 and CO_2 in MA packaging of different commodity carried out by some researchers. These results further strengthen the model for its validation and wide application for fresh fruits and vegetables.

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