The Effect of Relative Humidity on Modified Atmosphere Packaging Gas Exchange

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Keywords: Postharvest, *Opuntia spp.*, permeability, respiration, diffusion, model

Abstract

A model to estimate gas profile of modified atmosphere packaged (MAP) prickly pear cactus stems was developed and calibrated. The model describes the transient gas exchange taking in consideration the effect of temperature (*T*) and relative humidity (*RH*) on film permeability ($^{F}P^{gas}$), respiration rate (R_x) and tissue permeance ($^{T}P^{gas}$). A diffusion cell was constructed to determine $^{F}P^{gas}$ to O_2 and CO_2 at the different conditions of T and RH. The integration of the T, RH and $^{T}P^{gas}$ to the model allowed a more precise description of the in-package gas concentration. The effect of T on $^{F}P^{gas}$, $^{T}P^{gas}$ and R_x is described by the Arrhenius equation. R_x and $^{T}P^{gas}$ decreased and $^{F}P^{gas}$ increased as RH increased. RH, in the range of 65 to 90%, has a marked effect on the rate of gas exchange, especially for CO_2, and consequently on the gas equilibrium inside MA packages.

INTRODUCTION

The application of modified atmosphere packaging (MAP) is expanding all over the world, as it provides an additional barrier to excessive loss of quality during storage and distribution. It has been studied and used for quite some time on a large number of different products with varying success. The effect of temperature and the levels of O_2 and CO_2 have been reported and modelled (Emond et al., 1991; Hertog et al., 1997; 1999; Lee et al., 1991; Peppelenbos et al., 1996). For all kinds of wrappings, products and conditions, the same basic relations can be used over and over again. However, the possible effect of relative humidity (RH) on the respiration and/or gas exchange in these packages remains to be investigated.

MATERIAL AND METHODS

Prickly pear cactus stems (*Opuntia spp.*) were stored at different T-RH combinations (5, 14, 20 and 25ºC, 65-90% at 5% intervals) in a closed system and the gas exchange was measured as a function of the O_2 and CO_2 levels. The permeance of cactus stem tissue was assessed in a small gas chamber firmly attached to the product tissue, placed inside a closed vessel system at different levels of RH. The film permeability at different RH levels was assessed according to standard ASTM methods.

RESULTS AND DISCUSSION

To account for the different effects of RH at different temperatures, all RH values were converted into vapour pressure deficit (VPD) using a standard equation. For the gas exchange induced by product respiration, the standard model of Lee et al. (1991); Peppelenbos et al. (1996), Hertog et al. (1997) was used. In an integral analysis comprising T, RH, O_2 and CO_2 levels simultaneously as explaining variables, the only parameter that was found to depend on RH was the maximal rate of gas exchange at reference T ($V_{m,ref}$). The relation with VPD is shown in eq. 1, indicating the “normal” dependence of V_m on temperature, with the additional dependence on VPD.

Proc. 3rd IS on Model IT
Eds.: M.L.A.T.M. Hertog and B.M. Nicolaï
Acta Hort. 674, ISHS 2005

$$V_m = V_{m,ref} \cdot VPD \cdot e^{\frac{Ea}{R'} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T} \right)} \quad \text{(eq. 1)}$$

The film permeability to O_2 and CO_2 could be described and analysed with eq. 2. Only for water vapour, an additional model was necessary to describe its behaviour (eq. 3) since the effect of RH on the permeance of water vapour was more of an exponential type.

$${}^F P^{gas} = {}^F P_0^{gas} + {}^F k^{gas} \cdot VPD \quad \text{(eq. 2)}$$

$${}^F P^{H_2O} = {}^F k_P^{H_2O} \cdot \left({}^F P_0^{H_2O} + {}^F k^{H_2O} \cdot exp^{\,{}^F k_{VPD}^{H_2O} \cdot VPD} \right) \quad \text{(eq. 3)}$$

The tissue permeance with respect to O_2, CO_2 and H_2O vapour could be described by the same eq. 2. Basically, the effect of VPD is linear over the complete range of RH and temperature applied in the experiments.

All analyses resulted in an explained part (R^2_{adj}) of around 90 %.

The results were further validated on data of actual MAP packed product at different T and RH storage conditions. The effect of low (65%) compared to high RH (90%) on film permeability is about a factor of 2. For water vapour it is even more. Tissue permeance also roughly doubled over that range of RH. As a consequence, finally, the gas exchange itself doubled over that range, especially the O_2 consumption.

Integrated MAP Model

Assuming that gas conditions in tissue and package are always faster at steady state than that over the package film, the integrated model can be conceived as a mass balance of diffusion over the film. The transport (flux) of gases (O_2, CO_2, H_2O vapor and N_2) through the film was modeled based on their diffusion (Fick's first law). Since the diffusion is in solid medium, the application of Henry's law may describe this process as a function of the permeability coefficient and the partial pressure of the gas (equation 4) (Hayakawa et al., 1975; Emond et al., 1991; Makino and Hirata, 1997; Zhu et al., 2002).

$$\frac{\partial [gas]_{pkg}}{\partial t} = \frac{P^{gas} \cdot A}{d \cdot V_{pkg}} \cdot \left([gas]_{atm} - [gas]_{pkg} \right) \quad \text{(eq. 4)}$$

During the diffusional transport through the film, the respiring product inside the package alters the gas composition, and adds to the overall change in gas composition inside the package. The respiration effect has therefore to be included in the integrated model. This leads to the general equation for any gas (eq. 5).

$$\frac{\partial [gas]_{pkg}}{\partial t} = \frac{P^{gas} \cdot A}{d \cdot V_{pkg}} \cdot \left([gas]_{atm} - [gas]_{pkg} \right) - \frac{\partial [gas]_{resp}}{\partial t} \cdot \frac{W}{V_{pkg}} \quad \text{(eq. 5)}$$

Validation of the Model

In a first set of experiments prickly pear cactus stems were packaged in Cryovac PD960 polyethylene films, with permeability of P_{O2} = 1.22-1.63 x 10^{-15} and P_{CO2} = 3.85-4.45 x 10^{-15} mol m m^{-2} s^{-1} Pa^{-1}, and gas changes were determined periodically at 5°C (Guevara et al., 2001). In a second set of experiments, prickly pear cactus stems were packaged in passive MAP (no addition of gases), and in semi-active MAP with CO_2 initial pressures of 20 kPa, 40 kPa or 80 kPa CO_2 using the Cryovac RS425 polyethylene film, with the same characteristics of permeability as that of the PD960 film. Similar conditions to first set of experiments (T, fruit weight and area, film area, thickness and free volume) were used (Guevara et al., 2003).

The combination 25ºC/65% RH presented the highest respiration rate, while the combination 5ºC/90% RH presented the lowest respiration rate (Fig. 1). No statistical differences were observed for R_{O2} as well as for R_{CO2} at 80, 85 and 90% RH at the different temperatures. However, the proposed function does not describe adequately R_{O2} and R_{CO2} at 5ºC (Fig. 1).

The parameters V_m, K_m and K_i for R_{O2} and R_{CO2} were estimated simultaneously as constants by a multi-response, multivariate non-linear regression analysis. With these parameters and applying the equation proposed by Lee et al. (1991), Hertog et al. (1999) and Peppelenbos et al. (1999), the maximum rate of O_2 consumption and CO_2 production can be predicted for any combination of O_2 and CO_2 concentrations at any T. With the current extension the RH outside the package is also included in the description and prediction.

V_m is the only parameter that depends on T. V_m increases with increasing T, with about the same energy of activation compared to the effects $^{T}P^{gas}$ and $^{F}P^{gas}$, and with increasing VPD (Table 1). Similar results were observed by Cisneros-Zeballos and Krochta (2002). Kang and Lee (1998) showed that higher respiration rates result in higher transpiration rates in apples, and R_{O2} and R_{CO2} were lower at elevated RH. This indicates that RH and respiration rate are closely related. In some products, the control of transpiration by maintaining high RH has a more profound effect compared to the reduction of O_2 levels (Cameron et al., 1995). A significant correlation was found between the data obtained experimentally and those generated by the function to describe the effect of T and RH on V_m (R^2_{adj} = 95.1%).

K_m and K_i values from R_{O2} and R_{CO2} did not display any trend as T and RH increased. Similar results in relation to T have been reported for broccoli (Jacxsens et al., 2000), blueberry (Beaudry et al., 1992), garlic (Lee et al., 2000) and apple, tomato and chicory (Hertog et al., 1999). Mahajan and Goswami (2001) reported an increase in K_m for R_{O2} as well as for R_{CO2}, and a decrease in K_i value for R_{O2} as well as for R_{CO2} in apples as T increased. Most probably this effect is caused by the classical stepwise and non-integrated analysis of the data used by these authors. The value of K_i was rather high, indicating only a very small effect of inhibition by CO_2 on the observed gas exchange.

The nature of the effect of RH and hence VPD on product respiration and gas exchange is not clear. Since the VPD inside product tissue is generally considered to be close to zero, most probably, the largest effect of VPD will be on the capacity of the tissue to transport all gases to and from the active reaction sites inside the tissue and cells. Following that reasoning it would be conceivable that RH affects the structure of the gas barriers by swelling of skin and tissue.

The results of the analysis of film permeability are shown in Table 2. The explained part (R^2_{adj}) is acceptably high, especially for H_2O permeability. All standard errors of estimates (s.e.) are acceptably low, below 10% of the estimated value.

The film permeability to O_2 ($^{F}P^{O2}$) and CO_2 ($^{F}P^{CO2}$) decreases linearly with increasing VPD (decreases with RH) at the different T (Fig. 2a, b). This is reflected in the negative values for $^{F}k_{VPD}^{gas}$ (Table 2). The permeability to water vapor ($^{F}P^{H2O}$, Fig. 2) decreases exponentially with increasing VPD (decreasing RH). In this case it is interesting to note that not only the slope of the curve depends on T, but also the asymptotic end value. This is reflected in the T dependence of $^{F}k_{VPD}^{H2O}$ (Ea_p). Since both the slope and the asymptotic end value depend on T with the same activation energy, the value $^{F}k_{VPD}^{H2O}$ at reference T had to be fixed to 1. These values are different for both aspects and are part of the estimated value for $^{F}P_{ref}^{H2O}$ and $^{F}k_{VPD}^{H2O}$. The values for the activation energy with respect to O_2 and CO_2 are both negative, indicating a decreased permeability with increasing T. For the water permeability the value of the activation energy is positive, indicating increasing permeability with increasing T.

The tissue permeance to O_2 ($^{T}P^{O2}$) did hardly change within the range of T and VPD applied, as can be taken from the very small range on the y-axis in Fig. 2. This is also reflected in the very small value estimated for $^{T}k_p^{gas}$. The small range of change probably also explains the low R^2_{adj} (55%) in the statistical analysis (Table 3).

The tissue permeance to CO_2 ($^{T}P^{CO2}$) exhibited a somewhat larger dependence on T and VPD (Fig. 2). An acceptable explained part of 88.1% was obtained (Table 3). Also, the permeance with respect to water vapor ($^{T}P^{H2O}$) did show a clear change with T and VPD, resulting in an explained part of 88.8%. All standard errors of estimates are relatively small (Table 3).

${}^{T}P^{O2}$, ${}^{T}P^{CO2}$ and ${}^{T}P^{H2O}$ increased with increasing VPD (decreasing RH) at the different temperatures (Fig. 2), which can be taken from the positive values of the ${}^{T}k_p^{gas}$ parameter. These results agree with the effects observed when using modified atmospheres: a high RH delays the respiration rate, thus decreases the metabolism of the tissue, and prolongs shelf life (Yahia, 1998).

The permeance decreases with increasing T, as can be taken from the negative Ea_p for all gasses studied. ${}^{T}P^{CO2}$ values were one order of magnitude higher than those for ${}^{T}P^{O2}$, which agree with the theory that the cuticle of fruits and vegetables has a differential permeability to the respiration gases (Lendzian and Kerstien, 1991). The proposed function (equations 1 to 3) properly describes the effect of T and RH on the V_m value, the permeability to O_2, CO_2 and H_2O vapor for the PD960 film and the tissue permeance to gases.

Validation of Integrated MAP Model

The application of the model was tested by comparing observed and predicted data (Table 4). Observed data (Guevara et al., 2001; 2003) were generated by packing prickly pear cactus stems in 2 Cryovac polyethylene films (PD960 and RS425) either passively (without the addition of gases) or semi-actively (with 20 kPa, 40 kPa or 80 kPa CO_2 in the package immediately after sealing). The O_2 concentration is overestimated and the CO_2 concentration is suitably described when the prickly pear cactus stems were packed in PD960 or RS425 films without adding gases (Fig. 3 and 4). Mean normalized bias values were 24.92% for O_2 and –10.45% for CO_2 in the PD960 film, and 30.84% for O_2 and –9.03% for CO_2 in the RS425 film (Table 4).

The applicability of the model was also tested on prickly pear cactus stems packaged in semi-active MAP with 20 kPa CO_2 immediately after sealing (Guevara et al., 2003). The O_2 concentrations are underestimated and the CO_2 concentrations are overestimated (Fig. 4), with normalized bias values of –12.89% and 11.38%, respectively (Table 4).

When applying the model to describe the gas profile of prickly pear cactus stems packaged in semi-active MAP with 40 kPa and 80 kPa CO_2, it was observed that it suitably describes the changes in O_2 (Fig. 5), with normalized bias values of -4.89% for 40 kPa CO_2 and -17.44% for 80 kPa CO_2 (Table 4). In the case of CO_2, the pressure is overestimated for 40 kPa, but is adequately estimated for 80 kPa (Fig. 5), with normalized bias values of 31.38% and –1.94%, respectively (Table 4).

CONCLUSIONS

The functions proposed describe the effect of T and RH (through VPD) on the permeability with respect to O_2, CO_2 and water vapor of the test film, the V_m value of the gas exchange, and the tissue permeance to the O_2, CO_2 and H_2O vapor. The integrated model suitably describes the changes in CO_2 concentration and overestimates the O_2 concentration in passive MAP of prickly pear cactus stems. However, when the pressure exceeds 20 kPa CO_2, the model adequately describes the changes in O_2 but overestimates the changes in CO_2 at 20 and 40 kPa. This might be due to high CO_2 pressure causing alterations in tissue metabolism. For 80 kPa CO_2 the model adequately describes the changes in O_2 and CO_2 changes. The temperature and RH integration and the small number of the parameters to be determined in the proposed model may help to apply the model for a great variety of situations involving different commodities. This approach should facilitate package designing for fresh produce, and therefore maximizing the benefits of MAP for horticultural products. RH around the MA package, e.g. in the display cabinet of retail stores, can have a major impact on the respiration and gas exchange of MAP packed products. This could well be the missing link in understanding the sometimes erroneous and incomprehensible results obtained with MA packages in practice.

Literature Cited

Emond, J.P., Castaigne, F., Toupin, C.J. and Desilets, D. 1991. Mathematical modelling of gas exchange in modified atmosphere packaging. Trans. ASAE, 34 (1), 239-245.

Hertog, M.L.A.T.M., Peppelenbos, H.W., Tijskens, L.M.M. and Evelo, R.G. (1997). A ready for use MAP-model dynamic in time and temperature with incorporated models for respiration and keeping quality. Proceedings of the CIPA International Congress for Plastics in Agriculture (pp. 521-528), 9-14 March, Tel Aviv, Israel.

Hertog, M.L.A.T.M., Peppelenbos, H.W., Evelo, R.G. and Tijskens, L.M.M. (1999). A dynamic and generic model of gas exchange of respiring produce: the effects of oxygen, carbon dioxide and temperature. Postharvest Biology and Technology, 14, 335-349.

Lee, D.S., Haggar, P.E., Lee, J. and Yam, K.L. (1991). Model for fresh products respiration in modified atmosphere based on principles of enzyme kinetics. Journal of Food Science, 56 (6), 1580-1585.

Peppelenbos, H.W., Tijskens, L.M.M., van 't Leven J. and Wilkinson, E.C. (1996). Modelling oxidative and fermentative carbon dioxide production of fruits and vegetables. Postharvest Biology and Technology, 9, 283-295.

Beaudry, R.M., Cameron, A.C., Shirazi, A. and Lange, D.L. (1992). Modified atmosphere packaging of blueberry fruit: Effect of temperature on package O_2 and CO_2. Journal of the American Society for Horticultural Sciences, 117, 436-441.

Cameron, A.C., Talasila P.C. and Joles, W. (1995). Predicting film permeability needs for modified atmosphere packaging of lightly processed fruits and vegetables. HortScience, 30, 25-34.

Cizneros-Zeballos, L. and Krochta, J.M. (2002). Internal modified atmosphere of coated fresh fruits and vegetables: Understanding relative humidity effects. Journal of Food Science, 67, 2792-2797.

Guevara, J.C., Yahia, E.M. and Brito de la Fuente, E. (2001). Modified atmosphere packaging of prickly pear cactus stems (Opuntia spp.). Lebensmittel-Wissenschaft und-Technologie, 34 (7), 445-451.

Guevara, J.C., Yahia, E.M., Brito, E. and Biserka, S. (2003). Effects of elevated concentrations of CO2 in modified atmosphere packaging on the quality of prickly pear cactus stems (Opuntia spp.). Postharvest Biology and Technology, 29 (2), 167-176.

Hayakawa, K., Hening, Y. and Gilber, S. (1975). Formula for predicting gas exchange of fresh produce in polymeric film package. Journal of Food Science, 40, 186-191.

Jacxsens, L., Devlieghere, F., De Rudder, T. and Debevere, J. (2000). Designing equilibrium modified atmosphere packages for fresh-cut vegetables subjected to changes in temperature. Journal of Food Science, 33, 178-187.

Kang, J.S. and Lee, D.S. (1998). A Kinetic model for transpiration of fresh produce in a controlled atmosphere. Journal of Food Engineering, 35, 65-73.

Lee, D.S., Kang, J.S., and Renault, P. (2000). Dynamics of internal atmosphere and humidity in perforated packages of peeled garlic cloves. International Journal of Food Science and Technology, 35, 455-464.

Lendzian, K.J. and Kerstiens, G. (1991). Sorption and transport of gases and vapors in plant cuticles. Rev. Environ. Contamination Toxicol, 121, 65-128.

Mahajan, P.V. and Goswami, T.K. (2001). Enzyme kinetics based modeling of respiration rate of apple. J. Agric. Eng. Res, 79 (4), 399-406.

Makino, Y. and Hirata, T. (1997). Modified atmosphere packaging of fresh produce with a biodegradable laminate of chitosan-cellulose and polycaprolactone. Postharvest Biology and Technology, 10, 247-254.

Yahia, E.M. (1998). Modified and controlled atmospheres for tropical fruits. Horticultural Reviews, 22, 123-183.

Zhu, M., Chu, M., Wang, S.L. and Lencky, R.W. (2002). Predicting oxygen and carbon dioxide partial pressures within modified atmosphere packages of cut rutabaga. Journal of Food Science, 67, 714-720.

Tables

Table 1. Results of statistical nonlinear regression analysis for gas exchange data, based on equations 2 and 4, for O_2 consumption y CO_2 production simultaneously.

	Estimate	s.e.
RQ	1.1423	0.0173
Vm_{ref}	18.375	0.454
K_m	3.248	0.371
Ea_m	83.34	1.76
K_i	31.12	4.11
R^2_{adj}	95.1	

s.e.= standard error of the estimates. N_{obs} 591;T_{ref} 20.

Table 2. Results of statistical nonlinear regression analysis for film permeability to O_2, CO_2 and H_2O vapour.

	O_2		CO_2			H_2O	
	Estimate	s.e.	Estimate	s.e.		Estimate	s.e.
${}^{F}P_0{}^{gas}$	9.975	0.2005	26.510	0.5371	${}^{F}P_{ref}{}^{H2O}$	35.433	4.766
${}^{F}k_{VPD}{}^{gas}$	-0.00518	0.00037	-0.0102	0.00099	${}^{F}k_{VPD}{}^{H20}$	1	fixed
Ea	-60.51	2.147	-76.00	3.1377	Ea_p	96.64	3.965
					α	-0.00675	0.000525
					${}^{F}P_0{}^{H2O}$	1.608	0.1160
R^2_{adj}	87.5		88.8		R^2_{adj}	95.1	
	Normalizing factor for all permeability value						
	·1E3		·1E3		·1E-14		

s.e.= standard error of the estimates. N_{obs} 48; T_{ref} 20°C.

Table 3. Results of statistical nonlinear regression analysis for tissue permeance to O_2, CO_2 and H_2O vapor.

	O_2		CO_2		H_2O	
	Estimate	s.e.	Estimate	s.e.	Estimate	s.e.
${}^{T}P_{ref}{}^{gas}$	5.038	0.0524	0.578	0.1266	1.187	0.0831
${}^{T}k_p{}^{gas}$	0.000483	0.000096	0.002646	0.000233	0.002804	0.000151
Ea_p	-68.14	6.194	-71.05	2.780	-27.85	2.259
R^2_{adj}	55.0		88.1		88.8	
	Normalizing factor for all permeance values					
	·1E-10		·1E-9		·1E-5	

s.e.= standard error of the estimates. N_{obs} 48; T_{ref} 20°C.

Table 4. Comparison of observed and predicted concentrations of O_2 and CO_2.

Film and modified atmosphere condition	Mean Normalized bias (%)		Mean normalized error (%)		Mean bias		Mean error	
	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2
PD960	24.92	-10.45	2.21	31.91	2.88	0.36	0.25	1.21
RS425	30.84	-9.03	30.86	33.99	3.26	0.02	3.26	1.01
RS425, 20 kPa CO_2	-12.89	11.38	14.1	11.65	-1.72	1.89	1.89	1.94
RS425, 40 kPa CO_2	-4.89	31.38	9.18	32.07	-0.56	6.92	1.07	7.2
RS425, 80 kPa CO_2	-17.44	-1.94	18.68	5.31	-1.38	-1.56	1.44	2.65

Figures

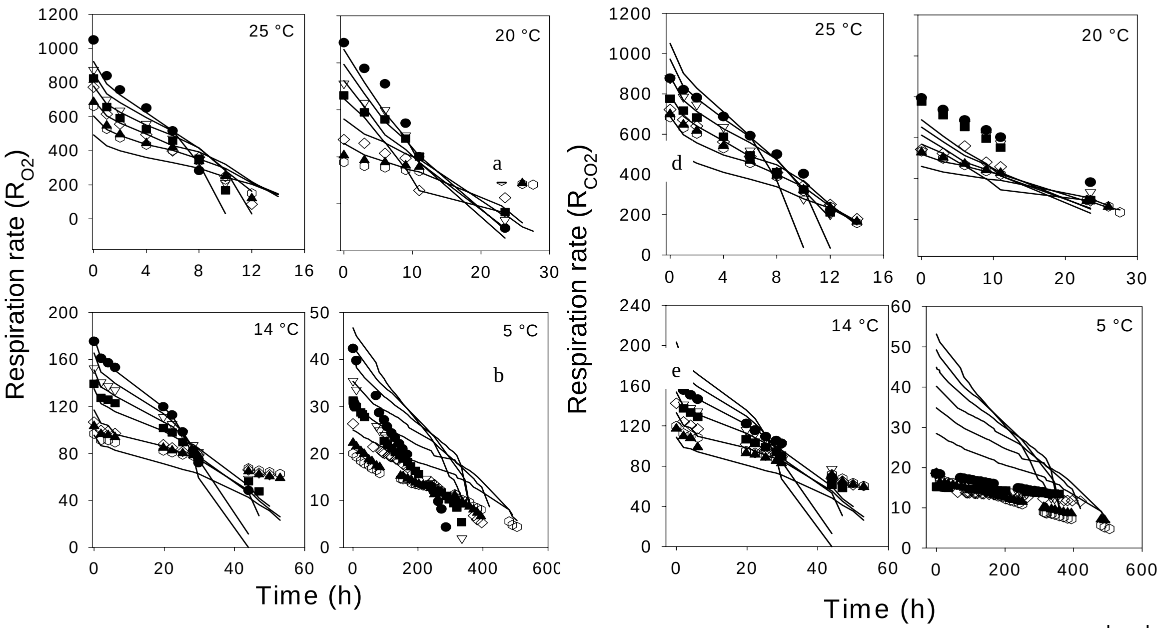

Fig. 1. Respiration rate (O_2 consumption, R_{O2} and CO_2 production, R_{CO2} in nmol kg^{-1} s^{-1}) at 5, 14, 20 and 25 °C and 65 to 90% RH. 65% RH (●),70% RH (▽), 75% RH (■), 80% RH (◇), 85% RH (▲) and 90% RH (⬡). Points are experimental data and lines are predicted results.

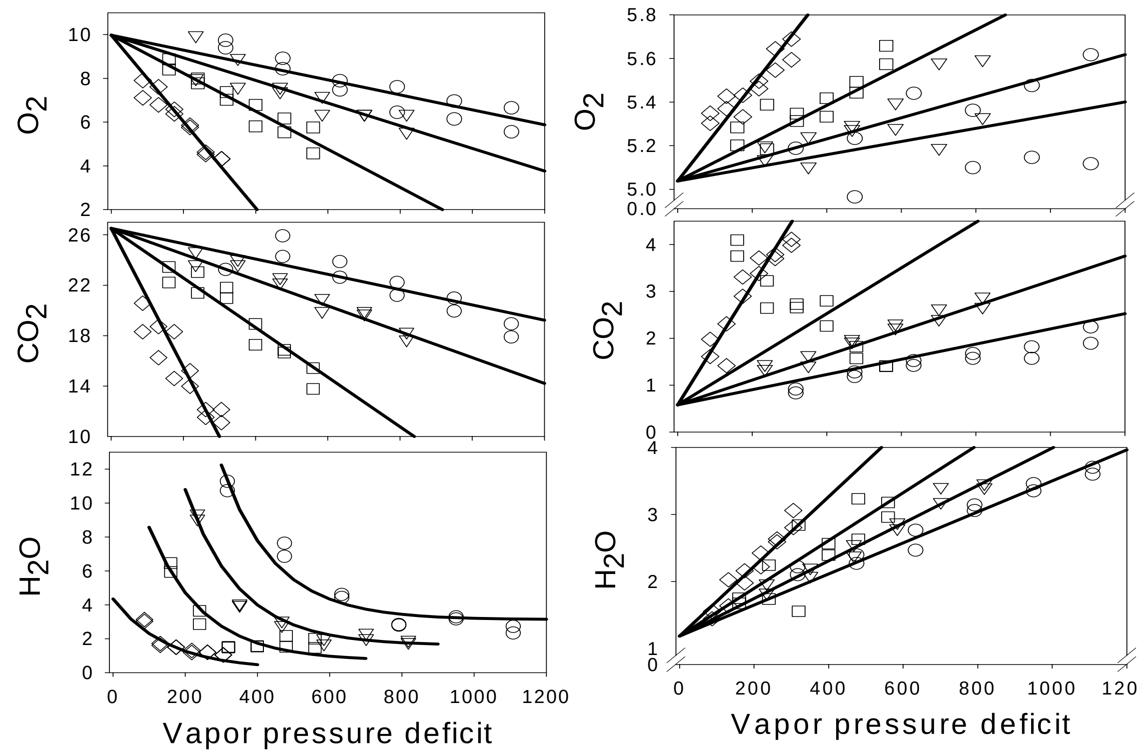

Fig. 2. Film permeability (mol m m^{-2} s^{-1} Pa^{-1}) to O_2 (a), CO_2 (b), H_2O vapor (c) and Tissue permeance (mol m^{-2} s^{-1} Pa^{-1}) to O_2 (d), CO_2 (e) and H_2O vapor (f). 25 °C (○), 20 °C (▽), 14 °C (□) and 5 °C (◇). Pints are experimental data and lines indicate the regression of the functions 5, 6 and 7 respectively.

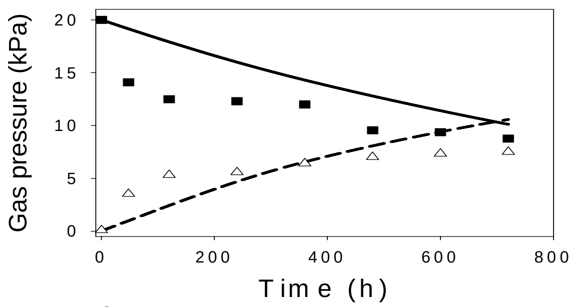

Fig. 3. Profile concentration for O_2 and CO_2 during packaging of prickly pear cactus stems in PD960 films. Symbols (O_2 ■, CO_2 △) indicate experimental data, while lines (O_2 ▬, and CO_2 .....) indicate predicted results (data from Guevara et al., 2001).

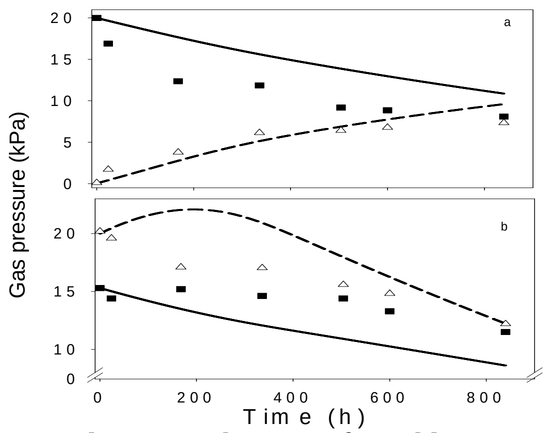

Fig. 4. O_2 and CO_2 changes during packaging of prickly pear cactus stems in RS425 films, a) passive MAP and b) semi-active MAP with 20 kPa CO_2 immediately after packing. Symbols (O_2 ■, CO_2 △) indicate experimental data, while lines (O_2 ▬, and CO_2 .....) indicate predicted results (data from Guevara et al., 2003).

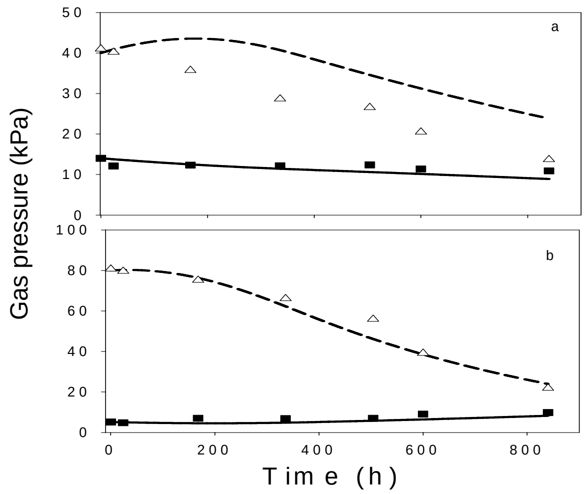

Fig. 5. Oxygen and CO_2 changes during packaging of prickly pear cactus stems in RS 425 films, a) semi-active MAP with 40 kPa CO_2 immediately after packaging, and b) semi-active MAP with 80 kPa CO_2 immediately after packaging. Symbols (O_2 ■, CO_2 △) indicate experimental data, while lines (O_2 ▬, and CO_2 .....) indicate predicted results (data from Guevara et al., 2003).