

Moisture-sorption isotherms for paper-based components of transport packaging for fresh produce

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ABSTRACT: *This paper investigates the application of two common moisture-sorption isotherm models—both developed for food materials—to fiberboard components of transport packaging for fresh apples. Samples from several full-telescopic containers (outer corrugated sleeve, inner corrugated sleeve, molded pulp trays) were conditioned at temperatures between 1° C and 40° C and relative humidities between 43% and 95%. Moisture-sorption and -desorption isotherms were constructed from these data. One of the models provided an appropriate fit to the constructed isotherms. The isotherms developed during this study, and the fitted models, are relevant for studying the water-vapor interactions that occur among the transpiring fresh produce, the hygroscopic fiberboard packaging, and the high-humidity environments for storage of produce.*

KEYWORDS: *Fiber boards, isotherms, models, moisture, packaging, produce, water vapor.*

Corrugated fiberboard is used to fabricate packages for a wide range of products. Corrugated containers protect products from shock, vibration, and compressive forces during transportation and storage. In many cases, corrugated fiberboard boxes are designed solely for product containment, without any consideration given to the protec-

tive performance of the box under varying environmental conditions. It is well known that the crush and compressive strengths of corrugated fiberboard are seriously affected by moisture, and many researchers have derived factors and relationships to compare fiberboard boxes stored under different relative humidities.

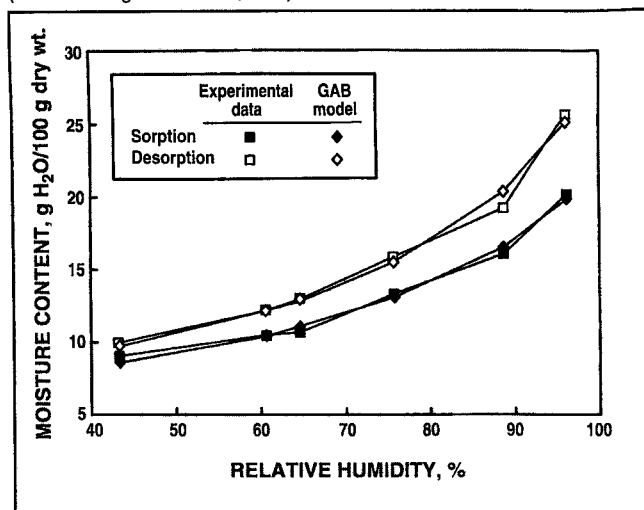
Packagers of fresh produce are among the most common users of corrugated fiberboard boxes, and horticultural products are among the most difficult to package effectively. Fresh horticultural products are extremely susceptible to mechanical damage and, unlike a number of other products, are stored and transported under conditions of high humidity and low temperature. Fresh produce constantly interacts with its surrounding environment through transpiration, and the transport packaging itself alters the product transpiration by either absorbing or liberating moisture into that environment.

Moisture-sorption isotherms relate the equilibrium moisture content of the fiberboard to the equilibrium relative humidity of the storage environment, thus providing a method of estimating the moisture content of the fiberboard given only the environment relative humidity and temperature. Knowledge of moisture-sorption and -desorption isotherms is important in the design of paper-based packaging for fresh produce for the following reasons:

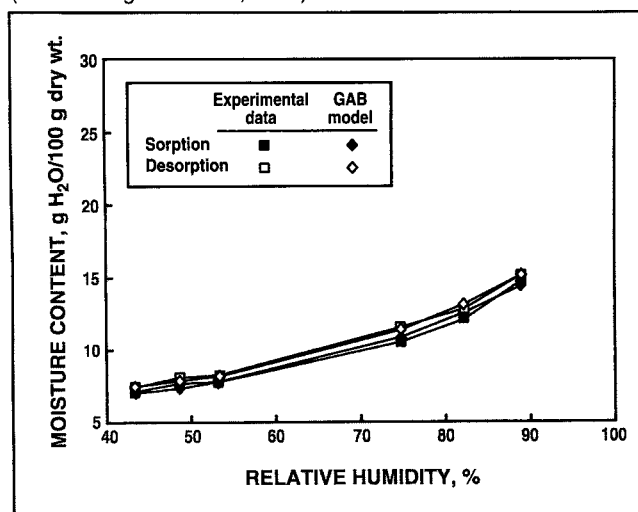
- Moisture is present in both the product and the distribution environment.
- The moisture content of the packaging can affect the degree of protection afforded to the product.

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1. Comparison of experimental data and GAB isotherm model (outer corrugated board, 1°C)



2. Comparison of experimental data and GAB isotherm model (outer corrugated board, 40°C)



- Moisture content is easier to measure than water activity and thus is routinely used in quality-control activities.

This paper investigates the application of two moisture-sorption isotherm models—both developed mainly for food materials—to fiberboard packaging for fresh produce. The models were applied to the three components (outer and inner corrugated sleeves and the molded pulp trays for setting layers of the produce) typically found in full-telescopic corrugated fiberboard boxes used for the packaging of fresh apples.

The specific objectives of this study were to

- Model the moisture-sorption and -desorption isotherms for the three components of typical full-telescopic containers for fresh apples.
- Determine the relationships among hysteresis, relative humidity, and temperature for these materials.

Background

Water activity and relative humidity

Water activity (a_w) is defined as the

I. Test temperatures, salt solutions, and corresponding relative humidities

Temp., °C	Relative humidity of saturated salt solutions, %					
	K_2CO_3	$Mg(NO_3)_2$	NaBr	NaCl	KCl	KNO_3
1	43.1	60.4	64.5	75.5	88.6	96.3
10	43.1	57.4	62.2	75.7	86.8	96.0
20	43.2	54.4	59.1	75.5	85.1	94.6
30	43.2	51.4	56.0	75.0	83.6	92.3
40	43.2	48.4	53.2	74.7	82.3	89.0

ratio of the water-vapor pressure of a material to the vapor pressure of pure water at the same temperature.

$$a_w = p/p_0 \quad (1)$$

where

p = vapor pressure of water exerted by the material at some temperature

p_0 = saturated vapor pressure of pure water at the same temperature.

This is related to equilibrium relative humidity (ERH) in that $ERH = a_w \times 100\%$. However, while water activity is an intrinsic property of the material, ERH is a property of the atmosphere in equilibrium with the material.

Because water-activity values are dependent on temperature, the temperature must be specified. The temperature dependence of water activity can be described by a modified

form of the Clausius–Clapeyron equation:

$$d\ln(a_w)/d(1/T) = -\Delta H/R \quad (2)$$

or

$$\ln(a_{w2}/a_{w1}) = (\Delta H/R)[(1/T_1) - (1/T_2)] \quad (3)$$

where

a_{wi} = water activity at temperature T_i

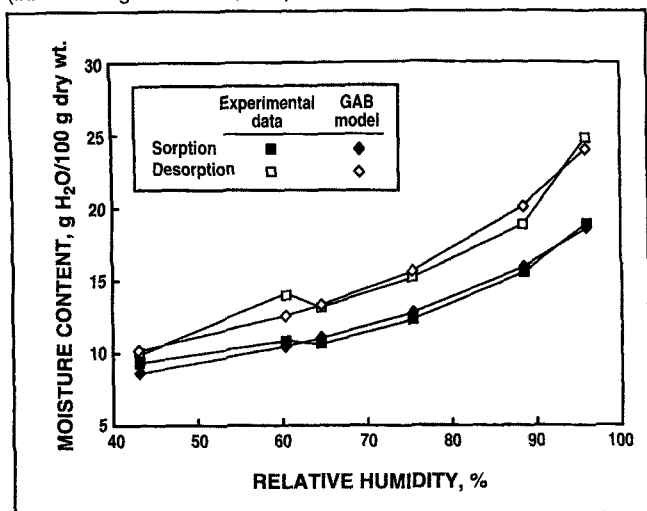
T = temperature, K

ΔH = isosteric net heat of sorption at the moisture content of the material, J/mol

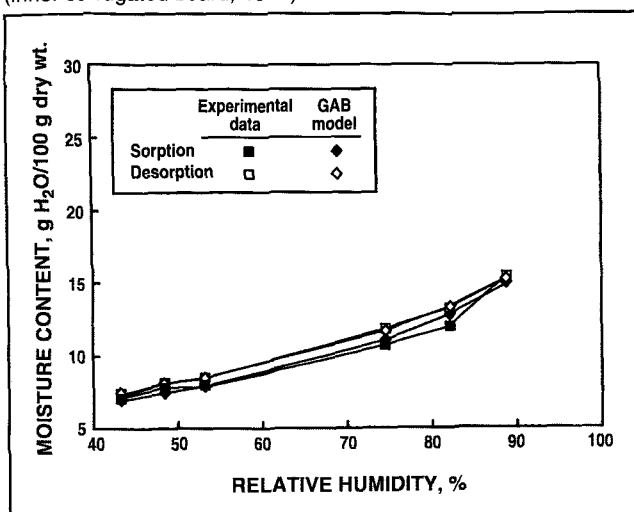
R = gas constant (8.314 J/mol·K).

From Eq. 2, a plot of $\ln(a_w)$ vs. $1/T$ at constant moisture content is linear. However such plots are experimentally not always found to be linear over wide temperature ranges (1).

3. Comparison of experimental data and GAB isotherm model (inner corrugated board, 1°C)



4. Comparison of experimental data and GAB isotherm model (inner corrugated board, 40°C)



Moisture content of corrugated fiberboard boxes

The effect of moisture content on the performance of corrugated fiberboard boxes has been extensively studied with respect to compression strength. Kellicutt and Landt (2) found that the box compression strength is linked to the moisture content of the corrugated fiberboard by Eq. 4.

$$\frac{P_2}{P_1} = \frac{10^{3.01 \cdot M_1}}{10^{3.01 \cdot M_2}} \quad (4)$$

where

P_i = ultimate compression strength of box at moisture content M_i .

Compressive strength reduction factors have also been derived for corrugated fiberboard boxes based on the relative humidity of the air in the storage environment (3). However, these approaches assume equilibrium between the box and the environment (4).

In the case of fresh produce, many packages are full-telescopic containers with two vertical layers of corrugated fiberboard. The outer layer is exposed to the storage environment, and the inner layer is exposed to the produce environment. If the inside and the outside of the box are not in equilibrium, then the inner and outer

boards are subjected to different relative humidities. It is also probable that the temperature at the inner and outer surfaces will be different, further contributing to a moisture-content differential.

Little work has been conducted on relating the moisture content of corrugated fiberboard to the equilibrium relative humidity in the storage environment, so that formulae such as Kellicutt and Landt's (Eq. 4) can be employed instead of other less quantitative methods. However, such techniques have been used in the area of food technology to relate the water activity and moisture content of foods for the purposes of, for example, product formulation and estimation of potential microbial growth.

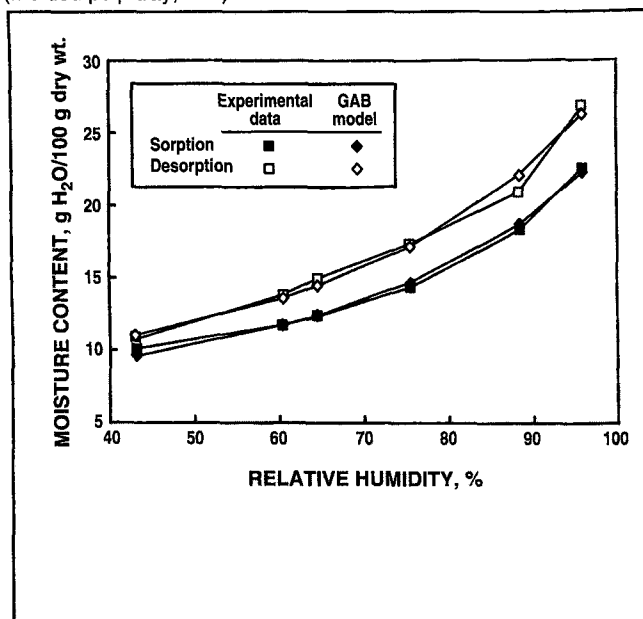
The moisture content of corrugated fiberboard has also been studied with respect to impact absorption. Marcondes (5) found that the moisture content significantly influences the cushioning characteristics of the material. However, these characteristics may or may not improve protection with increasing relative humidity, depending on the energy of the impact and the product/packaging contact area. These results are particularly important when packaging fresh horticultural produce, as the container must provide both compression resistance and shock-absorbing characteristics.

Moisture-sorption isotherms

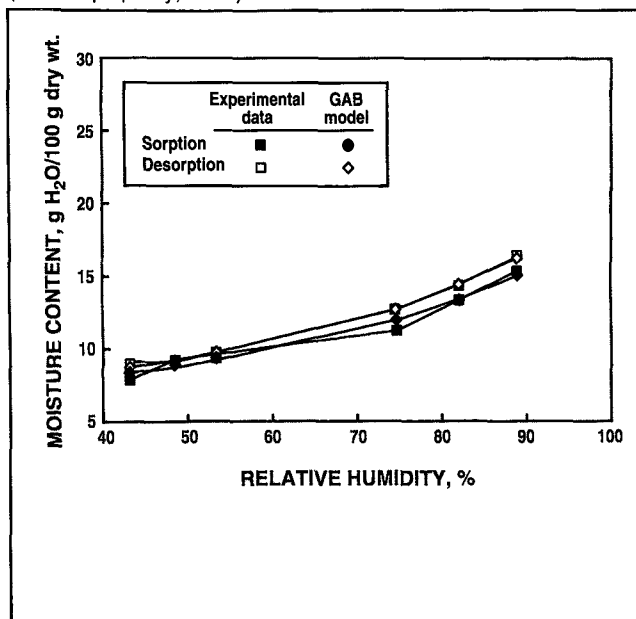
When a material is placed in an environment at a constant temperature and relative humidity, it will eventually come to equilibrium with that environment. The corresponding moisture content at steady state is called the equilibrium moisture content. A plot of this moisture content (expressed as mass of water per unit mass of dry material) vs. the corresponding water activity or equilibrium relative humidity at constant temperature results in a moisture-sorption isotherm.

A moisture-sorption isotherm prepared by the addition of water to a dry sample (adsorption) does not necessarily result in the same curve as an isotherm prepared by removal of water from a wet sample (desorption). This difference is referred to as hysteresis. Typically, at any given water activity, the moisture content of the material will be greater during desorption than during adsorption (1). This has important implications with respect to material stability, in that materials adjusted to the desired water activity or relative humidity by desorption rather than adsorption may deteriorate more rapidly because of their higher moisture content (6).

5. Comparison of experimental data and GAB isotherm model (molded pulp tray, 1°C)



6. Comparison of experimental data and GAB isotherm model (molded pulp tray, 40°C)



Since water activity is temperature dependent, it follows that moisture-sorption isotherms must also exhibit temperature dependence. Thus at any given moisture content, water activity increases with increasing temperature, in agreement with the Clausius-Clapeyron equation (Eqs. 2 and 3).

BET isotherm

Many relationships have been derived relating the water activity of a material to its moisture content. One of the most widely used relationships was the two-parameter BET (Brunauer-Emmett-Teller) isotherm.

$$m/m_0 = Ca_w / [(1-a_w)(1-a_w + Ca_w)] \quad (5)$$

where

m = equilibrium moisture content (dry-weight basis) at water activity, a_w

m_0 = moisture content of the monolayer (dry-weight basis)

C = a constant.

The BET equation has been used to estimate the monolayer value, which is equivalent to the number of primary sites for water sorption (7).

The term "monolayer" does not mean coverage of all dry matter with a closely packed single layer of water molecules. Rather, the term should be regarded as the maximum amount of water that can be strongly bound to the dry matter. Monolayer water constitutes a very small fraction of the total water in a high-moisture material (1).

GAB isotherm

Following an extensive review of sorption models, Van Den Berg and Bruin (8) recommended the use of the three-parameter GAB (Guggenheim-Anderson-de Boer) model, which fits data very well up to $a_w = 0.9$ in many cases (9). The GAB model is represented by Eq. 6.

$$m/m_0 = Cka_w / [(1-ka_w)(1-ka_w + Cka_w)] \quad (6)$$

where

m = equilibrium moisture content (dry-weight basis) at water activity a_w

m_0 = moisture content corresponding to saturation of all primary adsorption sites by one water molecule (equivalent to the BET monolayer)

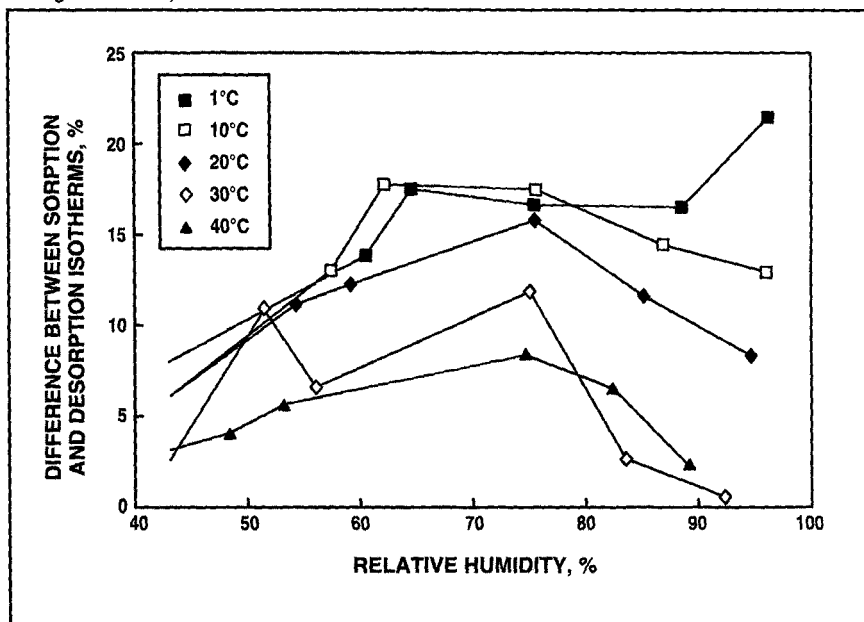
C = Guggenheim constant

k = factor correcting properties of the multilayer molecules with respect to the bulk liquid.

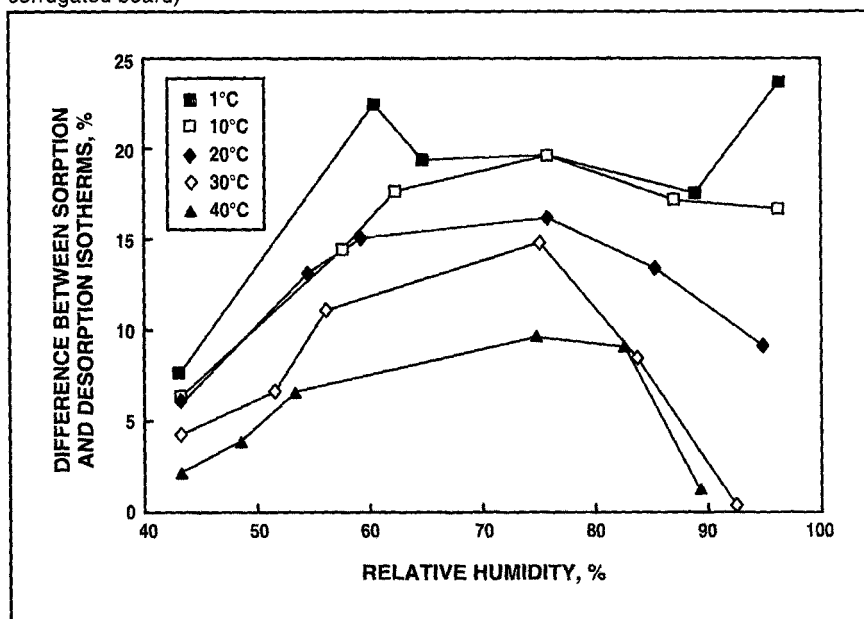
This model can be considered as an extension of the BET multimolecular model that takes into account the modified properties of the sorbed water in the multilayer region (6). It is reported to give a better evaluation for the amount of water tightly bound by the primary adsorption sites, m_0 (9).

In a comparison of the two models (10), the monolayer moisture content obtained by the BET (up to $a_w = 0.45$) and GAB (up to $a_w = 0.90$) models were not significantly different. The main advantage of the GAB model is that it offers an objective method for fitting sorption-isotherm data for many materials up to $a_w = 0.90$ and describes the temperature effect over a range of at least 40°C. These conditions are highly likely to occur during the transportation or storage of packaged produce. The final choice of model should be based on a compromise between the desired closeness of fit and the number of parameters involved.

7. Percentage difference between experimental sorption and desorption isotherms (outer corrugated board)



8. Percentage difference between experimental sorption and desorption isotherms (inner corrugated board)



Experiments

Tests were conducted on three outer corrugated boards, three inner corrugated boards, and four molded pulp trays used in full-telescopic boxes for the packaging of fresh apples. The boards were a single-wall construction consisting of kraft liners and 100% recycled media. The

outer boards were white coated and printed in two other colors, and the inner boards were not printed. Samples measuring 40 mm x 40 mm were taken from each board and tray type. These were placed in relative-humidity cells using the saturated salt solutions and temperatures shown in Table I (11). The test cells themselves consisted of sealed poly-

ethylene containers of 120-mL capacity. The samples were placed about 20 mm above the solution level.

Before testing, each sample was preconditioned for five days. The samples for the moisture-sorption isotherms were preconditioned using the K_2CO_3 (lowest humidity) solutions, and the samples for the moisture-desorption isotherms were preconditioned using the KNO_3 (highest humidity) solutions. Following preconditioning, the samples were exposed, at each testing temperature, to the relative humidities shown in Table I for 10 days.

The moisture-sorption and -desorption isotherms were constructed using the gravimetric method (continuous registration of weight changes). Each sample was replicated three times, and the mean values of the moisture contents were recorded.

The results were then entered into a spreadsheet software package, and the BET and GAB isotherm models were fitted to each sorption and desorption isotherm using the spreadsheet's built-in model-fitting tool. Model coefficients that would minimize the sum of the squares of the residuals (SSR) were obtained, where the residual is the difference between the observed moisture content and the model prediction. In each case, the initial guesses for m_0 , C , and k were taken as 1. Quadratic extrapolation to obtain initial estimates of the variables, central differencing to estimate partial derivatives, and a quasi-Newton gradient method of searching were used. All solved solutions were unconstrained.

Results and discussion

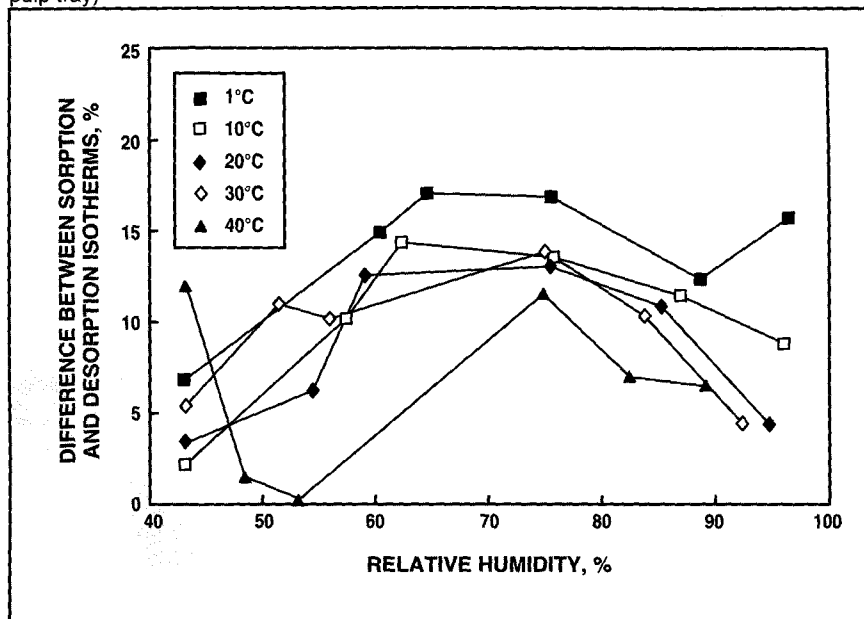
The BET isotherm model was found to be inadequate in describing the experimental data, as the individual residuals ranged from 1 g H_2O /100 g dry material up to 32 g H_2O /100 g dry material, an error in some cases of more than 100%. In contrast, the individual residuals for the GAB

model were found to be consistently less than 1 g H₂O/100 g dry material. The GAB model was therefore regarded as the more appropriate of the two in describing the experimental isotherm data. For this reason, the BET results are not presented here.

Figures 1 and 2 show the moisture-sorption and -desorption isotherms for the outer corrugated boards at 1°C and 40°C, respectively. Figures 3 and 4 show the isotherms for the inner corrugated boards at 1°C and 40°C, respectively, and Figs. 5 and 6 show the isotherms for the molded pulp trays at 1°C and 40°C, respectively. Comparison of the experimental data and the fitted GAB isotherm models shows that the GAB isotherm model appears to fit the experimental data very well. Observe that the isotherm ends do not meet, even though the sorption and desorption curves were constructed using data from the same materials. This occurs because the sorption curves were constructed from material that had been preconditioned at low humidity, while the desorption curves were obtained from material that had been preconditioned at high humidity.

Figures 7–9 show the percentage differences between the experimental sorption and desorption isotherms, i.e., hysteresis, at each temperature for the outer corrugated boards, inner corrugated boards, and molded pulp tray material, respectively. In all cases, the desorption moisture content is greater than the sorption moisture content, and the sorption moisture content is used as the basis for comparison. For all three materials, the percentage differences are generally least at the extreme relative humidities and greatest at intermediate relative humidities, as expected. In addition, the percentage differences are generally greater at low temperatures than at high temperatures, and generally greater for the corrugated boards than for the molded pulp. The large difference at high

9. Percentage difference between experimental sorption and desorption isotherms (molded pulp tray)



relative humidities and low temperatures indicates that samples exposed to high relative humidities gain more moisture than samples exposed to low relative humidities lose during the same period.

Table II shows the fitted GAB isotherm model coefficients for each package component at each temperature. From Table II, it can be seen that the values of m_0 tend to be lower for the sorption curves than for the desorption curves, and that m_0 also appears to decrease with temperature, as expected. However for C, the values for the sorption curves are higher than for the desorption curves. In addition, the values for the outer and inner corrugated boards are higher than for the molded pulp trays. There does appear to be some decrease in C with temperature, except in the case of the molded pulp desorption curve. There does not seem to be any variation in k with temperature, although it appears that the value of k for the sorption curves is greater than for the desorption curves. In contrast to these k coefficients, note that, from Eq. 5, the BET isotherm model assumes that k is equal to 1.

Table II also shows the SSRs and the mean of the individual residuals for each of the GAB sorption and desorption isotherms. Observe that both the SSRs and the mean of individual residuals are close to zero, which is expected of an adequate model. In contrast, the SSRs for the BET isotherm model were in the range 60–600 for the same data. It appears that the SSRs for the sorption isotherms are more closely constant across all temperatures than for the desorption isotherms, and although the SSRs for the desorption isotherms are lower (implying a more adequate model) above 10°C, they are higher at 1°C. Further study should be conducted to investigate the appropriateness of this model at subzero temperatures. Quantitative statistical analyses were not performed to test the adequacy of the fitted models, since each isotherm only comprised five temperatures.

II. GAB isotherm model equation coefficients, sum of squares of residuals, and mean residual for each isotherm

Temp., °C	Sorption					Desorption				
	Equation coefficients ^a			SSR ^b	Mean residual	Equation coefficients ^a			SSR ^b	Mean residual
	m ₀	C	k			m ₀	C	k		
Outer Corrugated Sleeve										
1	5.848	58,400	0.729	0.93	-0.02	6.476	15,300	0.768	1.82	-0.02
10	5.376	106,000	0.771	1.01	-0.03	6.312	15,900	0.767	0.13	0.00
20	5.262	106,000	0.773	0.71	-0.02	6.084	5,270	0.760	0.09	0.00
30	4.666	29,400	0.791	0.89	-0.03	5.334	7,310	0.750	0.53	0.00
40	4.698	35,200	0.758	0.51	-0.01	5.052	784	0.747	0.15	0.00
Inner Corrugated Sleeve										
1	6.022	80,000	0.700	1.31	-0.02	6.960	26,100	0.736	4.77	-0.02
10	5.336	103,000	0.768	1.34	-0.04	6.238	10,800	0.778	0.35	-0.01
20	5.260	212,000	0.774	0.96	-0.03	6.339	78.5	0.753	0.22	0.00
30	4.879	25,600	0.782	0.81	-0.02	7.161	9.22	0.676	0.05	0.00
40	4.668	22,400	0.770	1.41	-0.02	5.448	37.5	0.727	0.08	0.00
Molded Pulp Tray										
1	6.537	54,900	0.733	0.60	-0.02	7.554	640	0.739	1.67	-0.01
10	6.155	18,600	0.764	0.96	-0.03	7.304	36.9	0.747	0.04	0.00
20	6.016	22,600	0.769	1.36	-0.03	7.280	30.7	0.734	0.09	0.00
30	5.168	44,600	0.792	1.82	-0.04	7.443	13.7	0.676	0.04	0.00
40	5.849	2,690	0.686	1.40	-0.01	6.060	12,900	0.706	0.07	0.00

^aCoefficients for Eq. 6
^bSSR = sum of the squares of the residuals

Conclusions

The appropriateness of the GAB (Guggenheim-Anderson-de Boer) model to fit moisture-sorption isotherms for components of a transport package for fresh apples was investigated. Samples of outer and inner sleeves of a full-telescopic box and molded pulp trays were used to construct the isotherms.

The results show that, when compared with the BET (Brunauer-Emmett-Teller) isotherm model, the GAB isotherm model is more appropriate. In the range of temperatures and humidities studied, the great majority of the sums of the squares of the residuals between the experimental data and the fitted model were less than two, indicating a very good fit.

Further study should be conducted to (a) investigate the appropriateness of this model for temperature and humidity values that fall outside the ranges covered in this study and (b) assess the uncertainties in the fitted model estimates. ■

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