

Behavior and Modelling of Humidity Isotherms of *Mangifera indica* L (Vimang®) Powder

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Abstract: The knowledge of the relationship between the equilibrium moisture content and the equilibrium relative humidity is very important in order to describe the drying process and the effect of water activity on safe storage. In this paper were obtained the moisture adsorption-desorption isotherms of Vimang® powder, using a standard dynamic method over a range of water activities from 0.54 to 0.83 at 25±0.1°C. Only were studied these values because are the range most frequently of relative humidity in Cuba. The sorption capacity of powder increased with the increase of water activity. The minimum water content obtained in the studied experimental conditions was 11.25 %. Taking into account that the maximum admissible value of the humidity content for the Vimang® raw material is 9 %, it is necessary to choose some adequate process drying parameters and to take special precautions during its storage and handling. The sorption isotherms for Vimang®, can be described by isotherms type II or III according to Brunauer's classification. Several sorption models were used to explain the sorption behavior involving water activity, moisture content and the temperature. The GAB model give best fit among all equations studied for the adsorption and desorption curves with a regression coefficient higher than 0.995.

Key words: Models • Moisture isotherms • Storage • Vimang®

INTRODUCTION

Equilibrium moisture content data is needed for the mathematical description of thin-layer drying and rewetting of natural products. Thin-layer drying and rewetting equations are used as part of partial differential equations for modeling deep bed drying. Hence a good knowledge of the relationship between the equilibrium moisture content (X_{eq}) and the equilibrium relative humidity (Y_r) of any natural product is of primary importance in order to describe the drying process and the effect of water activity on safe storage [1].

Moisture content at which vapor pressure of water present in the natural product, food, drug or other solid product is equal to that of the environment is called equilibrium moisture content [2]. The relationship between X_{eq} and the corresponding relative humidity at constant temperature yields the so-called moisture sorption isotherm. The sorption isotherm of most food and natural

product are nonlinear and, generally, sigmoidal. The phenomenon where the X_{eq} during both adsorption and desorption process is different is called hysteresis. The major factors affecting the shape of the isotherm are product composition, storage time and the number of successive adsorption and desorption cycles.

Water activity is commonly used to characterize the natural product quality and is defined as (equation 1):

$$a_w = \frac{P}{P_0} = \frac{Y_r}{100} \quad (1)$$

Where:

P is vapor pressure of water in the solid material at any given temperature, P_0 is the vapor pressure of pure water at that temperature, a_w is the water activity (dimensionless) and Y_r is the equilibrium relative humidity (%).

It is well known that, when a hygroscopic material is placed in air it gains or loose the moisture to the air until

it comes into moisture equilibrium with the surroundings. The movement of water vapor from a hygroscopic material to the surrounding air depends on the moisture content and composition of the material, as well as the temperature and humidity of the environment. Each material has a unique shape of sorption isotherms at different temperatures. The precise shape of sorption isotherm of a material is based on the physical structure and chemical composition of the material and also on extent of water binding within the material. Five types of isotherms were described by Brunauer *et al.* [3] but, the two isotherms most commonly found in natural products are types 2 and 4 [4].

The principal methods for obtaining water sorption isotherms for foods or natural product are gravimetric, manometric and hygrometric [5-6]. The traditional gravimetric method (static gravimetric method) consists of exposing the samples to atmospheres of saturated salt solutions or sulphuric acid solutions of known relative humidities [7]. This method is a lengthy and laborious process involving a series of repetitive weightings [2]. In the dynamic method the airflow around the samples makes the wetting and drying process faster and more controlled [8-9].

The sorption isotherms models are used to explain the adsorption behavior involving water activity, moisture content and also temperature [10-11]. It has been reported that more than 200 isotherm equations have been developed theoretically, semi-theoretically or empirically to model the relationship between X_{eq} or Y_r and temperature of different materials [12].

The sorption isotherm models may be classified according to the number of primary parameters that presents. Common forms of sorption isotherm models are the two, three and four-parameter models. The two and three parameter isotherm models were often earlier isotherm models modified to include the effect of temperature.

There has been increased interest in the research on natural products, including plant extracts, which might replace synthetic drug or be used as phytomedicine. *Mangifera indica* L (Anacardiaceae) grows in tropical and subtropical regions and its parts are commonly used in folk medicine for a wide variety of remedies. Vimang® is a commercial name of a powder obtained from the stem bark of selected varieties of *Mangifera indica* L. The antioxidant [13], analgesic [14], anti-inflammatory [15] and immunomodulatory [16] properties of Vimang® powder have been evaluated. Besides, it is used as nutritional supplement and phytomedicine.

The industrial extract is obtained by aqueous decoction and drying by spray dried [17]. Then, it is obtained a homogeneous brown powder which melts with decomposition from 215 to 218°C and has a particle size of 30-90 µm [17-18]. Vimang® powder has a defined composition polyphenols, terpenoids, steroids, fatty acids and microelements [18]. Inside the technology scheme obtained, to establish both drying and storage conditions are very important for guarantee an end product with a predefined quality specification. Carry on with engineering study there are necessary to know the behavior of this powder under values different of relative humidity.

The bibliographic analysis shows two reported relations with the sorption isotherms of the mango fruit. The first article presents a study about the determination of adsorption and desorption isotherms of three tropical fruits: banana, mango and pineapple for several values of relative humidity and four temperatures value [19]. The second paper details the sorption isotherms of Mango chips [20] obtained at 25 and 35°C temperatures and intervals humidity between 0.1-0.9%. Unfortunately, in the literature, there is no available information about sorption equilibrium moisture data for the powder obtained from the stem bark of *Mangifera indica*.

Therefore, our investigation was focused on the experimental determination of equilibrium moisture content of Vimang® powder at 25±0.1°C in the range of values of the environmental relative humidity from 54 to 83%, most common in Cuba. At least, different sorption isotherms models (Iglesias and Chirife, Oswin, Hasley, G.A.B., Langmuir, Henderson, BET, Kuhn and Smith) were used to describe the experimental adsorption-desorption equilibrium. The experimental equilibrium values obtained could be used in the establishment of operating conditions of spray drying process and the storage of the Vimang® with the objective to guarantee an end product with a predefined quality specification [17].

MATERIALS AND METHODS

Material: The stem bark of *Mangifera indica* L. was collected from plants grown in a fruit farm in Alquizar, Havana, Cuba. An extract of the stem bark is obtained by decoction using water as the solvent and drying by spray dried to obtain the Vimang® powder [17].

Moisture Sorption Isotherm: A dynamic method was used in the determination of the sorption isotherms as it provides the same (or better) results as the static method

in much shorter time [21]. The samples of natural product (2 g) were placed in capsules forming a thin layer evenly distributed with a thickness of less than 3 mm. The open capsules were introduced into the ovens and kept in darkness at constant temperature. Heraeus ovens with automatic control of temperature ($\pm 0.1^\circ\text{C}$) and relative humidity ($\pm 0.1\%$) were programmed to obtain values of relative humidities of 54, 60, 72 and 83% at $25 \pm 0.1^\circ\text{C}$ of temperature. Only were studied these values because are the range most frequently of relative humidity in Cuba. The initial moisture contents were 5 and 40% for the adsorption and desorption studies, respectively. The end of the adsorption (or desorption) process as assumed when the mass gain (or loss) of the weighted sample was less than $\pm 0.001\text{g}$ for two successive weighting [22]. Then, equilibrium moisture content was determined in a moisture determination balance with an infrared heater. Each experiment was replicated three times. The curves of the equilibrium humidity were obtained representing the corresponding equilibrium humidities vs. the tested relative humidities.

Isotherm Equation: The approaches proposed for mathematical description of sorption isotherms of several food and natural products are mainly based on theories of mechanism sorption, some of them being semi-empirical or empirical.

The following equations were chosen for the present study and are included in the ASAE Standard [23].

Lagmuir [24]

$$a_w \left(\frac{I}{X_{eq}} - A \right) = B \quad (2)$$

BET [25]

$$X_{eq} = \left(\frac{ABa_w}{(1-a_w)(1+(B-1)a_w)} \right) \quad (3)$$

G.A.B [26]

$$X_{eq} = \left(\frac{ABCa_w}{((1-B a_w)(1+(C-1)(B a_w)))} \right) \quad (4)$$

Halsey [27]

$$a_w = \exp \left(\frac{-A}{X_{eq}^B} \right) \quad (5)$$

Oswin [28]

$$X_{eq} = A \left(\frac{a_w}{(1-a_w)} \right)^B \quad (6)$$

Henderson [29]

$$1-a_w = \exp(-AX_{eq}^B) \quad (7)$$

Kuhn [22,30]

$$X_{eq} = \frac{A}{\text{Ln}a_w} + B \quad (8)$$

Smith [31]

$$X_{eq} = A-B.\text{Ln}(1-a_w) \quad (9)$$

Iglesias and Chrirife [32]

$$X_{eq} = A \left(\frac{a_w}{1-a_w} \right) + B \quad (10)$$

Minimum square method was used to estimate both the empirical constants value and confidence interval of all models discussed. The criterion used to evaluate the goodness of the fit was the regression coefficient.

RESULTS AND DISCUSSION

Sorption Isotherm: The equilibrium moisture contents (X_{eq}) of Vimang® powder at selected activity a_w (0.54-0.83) for temperature of 25°C are showed in Table 1. There was an increase in the equilibrium moisture content values with increase the activity of water. This behavior was observed for both adsorption and desorption curves. On the other hand, the equilibrium moisture content value for the adsorption process is lower than the desorption process at constant water activity values. This behavior was analogous to other pharmaceutical, food and vegetable products [8, 21].

Table 1: Equilibrium Moisture Isotherm Data of Vimang Powder Determined at 25°C

Curve	a_w	X_{eq} (%)	SD (%)
Adsorption	0.54	11.25	0.28
	0.60	13.68	0.03
	0.72	18.15	0.01
	0.83	24.87	0.33
Desorption	0.54	11.79	0.01
	0.60	13.76	0.23
	0.72	18.27	0.16
	0.83	28.19	0.99

SD: Standard deviation

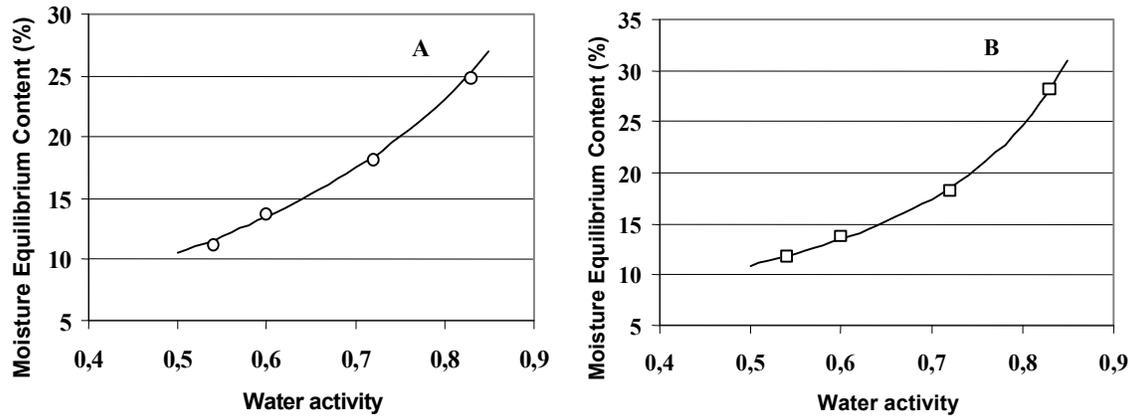


Fig. 1: Isotherms of humidities for the Vimang powder. Adsorption (○) and Desorption (□) moisture isotherms of VIMANG at 25°C. (—) predicted adsorption and desorption isotherms using GAB model

Table 2: Models and Parameters Values for all Studied Models

Models	Adsorption						Desorption							
	A	C.I.	B	C.I.	C	C.I.	R ²	A	C.I.	B	C.I.	C	C.I.	R ²
Lagmuir	-0.05	0.005	0.07	0.004			0.997	-0.06	0.01	0.08	0.01			0.982
BET	4.08	0.29	-3.1	1.2			0.959	4.62	0.16	-4.80	1.7			0.993
GAB	10.7	4.3	0.82	0.09	2.4	2.1	0.998	6.1	1.9	0.96	0.05	43.7	530	0.995
Halsey	-33.1	10.6	1.61	0.11			0.995	-18.5	4.2	1.38	0.07			0.995
Oswin	10.8	0.4	0.53	0.03			0.995	10.5	0.5	0.62	0.04			0.992
Henderson	0.06	0.006	1.07	0.04			0.998	0.08	0.02	0.92	0.08			0.985
Kuhn	-3.49	0.36	6.5	1.2			0.979	-4.32	0.22	5.05	0.74			0.995
Smith	1.08	0.58	13.4	0.5			0.998	-1.39	1.86	16.4	1.5			0.984
Iglesias and Chirife	3.52	0.37	8.1	1.1			0.979	4.36	0.23	7.0	0.7			0.995

The minimum water content obtained in the studied experimental conditions was 11.25%, which is in correspondence with an environmental humidity of 54%. Taking into account that the maximum admissible value of the humidity content for the Vimang® raw material is 9% [17], it is necessary to choose some adequate drying parameters and to take special precautions during its storage and handling.

Figure 1 shows the equilibrium isotherms at 25°C. As it can be seen from these curves, the Vimang® equilibrium moisture content does not differ whether the product is being wetted (adsorption) or dried (desorption) for values of water activity between 0.54-0.72. Therefore, the product not presents a hysteresis cycle of drying for these conditions. However, for environmental humidity values higher than 72% there not correspondence between both adsorption and desorption curves. A similar trend has been reported for various pharmaceutical products [33]. The isotherms of adsorption-desorption for Vimang® powder obtained in the range of relative humidity from 54 to 83% can be described by isotherms type II or III according to Brunauer's classification.

Moisture Sorption Models: The relationship between the equilibrium relative humidity and equilibrium moisture content at 25 °C was analyzed in terms of several mathematical models cited below for the moisture sorption isotherms (Table 2). The estimated parameters, the confidence interval (C.I) and the regression coefficient (R²) for the models are also shown. The GAB, Henderson and Smith models gave the best fit for the adsorption curve while that GAB, Halsey, Kuhn and Iglesias and Chirife models fit correctly the desorption equilibrium curve, among all studied models with regression coefficient value superior at 0.995 for both adsorption and desorption curve. Figures 1 present a comparison between the experimental and calculated values for the GAB models that correctly fit both desorption and adsorption curves. The agreement between the experimental and predicted results was excellent for the relative humidity range of 54-83% for both adsorption and desorption isotherms. All the models adequately explain the sorption behavior over the studied range of water activity.

CONCLUSION

The sorption isotherms of Vimang® powder have been experimentally obtained for first time. The equilibrium moisture content of this natural product was obtained using dynamic method over a range of water activities from 0.54 to 0.83 at $25 \pm 0.1^\circ\text{C}$. These data have been collected for a range of temperatures and relative humidity commonly used in the drying and storage of Vimang® powder in Cuba.

The moisture content increases when the water activity was increasing. The curves of sorption obtained can be described by isotherms type II or III according to Brunauer's classification. The best fit were obtained by the GAB, Henderson and Smith models for describing the adsorption curve while that GAB, Iglesias and Chirife, Halsey and Kuhn equations permitted describe correctly the desorption equilibrium curve.

Nomenclature:

a_w	water activity (dimensionless)
A, B, C	model parameters
P	vapor pressure of water in the food material at any given temperature (Pa)
P_0	vapor pressure of pure water at that temperature (Pa)
X_{eq}	equilibrium moisture content (%)
Y_r	equilibrium relative humidity (%)
C.I	confidence interval
R^2	regression coefficient

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