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Full Paper

Moisture sorption of Thai red curry powder

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Abstract: Moisture sorption study was conducted on Thai red curry powder prepared by two different drying methods, viz. microwave and hot-air drying. Moisture sorption isotherms of the red curry powder at 30 °C and water activity in the range of 0.113-0.970 were determined by a static gravimetric method. The isotherms exhibited Type III behaviour. The moisture sorption data were fitted to several sorption models and a non-linear regression analysis method was used to evaluate the constants of the sorption equations. The fit was evaluated using the coefficient of determination (R^2), the reduced chi-square (χ^2) and the root mean square error (RMSE). The GAB model followed by the Lewiski-3 model gave the best fit to the experimental data. The monolayer moisture content, taken as the safe minimum moisture level in the red curry powder, was determined using the BET equation and was found to range between 0.080 - 0.085 gram water per gram dry matter.

Keywords: moisture sorption isotherm, monolayer moisture content, Thai red curry powder

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Introduction

Thai red curry paste is a well-known curry paste used to enhance several spicy Thai dishes. The paste is prepared from dried red chili, garlic, shallot, lemon grass, galangal, spices and additives such as salt and sugar, homogeneously blended to obtain an orange-red paste. It provides the colourful, spicy and authentic fragrance of certain dishes. Moreover, it has been reported that the major ingredients of this product such as chili [1-2], garlic [3], shallot [4], lemon grass and galangal root [5-6] are good sources of phenolic compounds. These compounds in herbs and spices have been found to be major contributors to human health with multiple positive biological effects such as antioxidant activity, antimutagenic and/or anticarcinogenic activity, and anti-inflammatory action [7-8]. In general, the red curry paste has a high moisture content and therefore is very perishable, having a limited shelf life. The growing popularity of Thai food around the world creates the need to preserve this product. Drying is one of the preservation methods that can extend the shelf life of the red curry paste. The dried paste is milled to a powder to be used mainly as a culinary supplement and has long storage life at room temperature.

During the processing and storage of agricultural products, physical, chemical and microbiological changes occur. The changes are influenced particularly by the moisture content and water activity of food material. Equilibrium moisture content of a food material is defined as its moisture content attained when the vapour pressure of water present in the food material has reached an equilibrium with its surroundings. It is a thermodynamic property and has practical significance in both drying and storage of foods. It is affected by the relative humidity and temperature. Water activity on the other hand is defined as the ratio of vapour pressure of water over the foodstuff to that of pure water at the same temperature. The relationship between moisture content and water activity in food at constant temperature and pressure is often expressed as a moisture sorption isotherm. It can give information on the sorption mechanism and the interaction of food with water. The typical shape of the sorption isotherm may change depending on the type of product and reflects the way in which water binds to the system [9]. The drying method can also significantly affect the sorption properties of some dry products such as model fruit powders (dried pectin-sugar gels) [10] and dried locust bean gum-pectin-starch composite gels [11].

Several equations have been used to describe the sorption isotherms of many food materials [12-16]. Some of these models are based on theories on the sorption mechanism; others are purely empirical or semi-empirical. However, none of these equations describes accurately the sorption isotherm over the whole range of water activity or for different types of food materials. According to Labuza, cited by Al-Muhtaseb et al. [12], no sorption isotherm model could fit data over the entire range of relative humidity because water is associated with the food matrix by different mechanisms in different water activity regions.

The information on the moisture sorption behaviour of food is essential for determining the interaction of water with food substances. It is also useful for food processing operations such as drying, mixing, packing and storage, since it can be used to calculate drying time and predict the behaviour of ingredients upon mixing. It can also help make packaging selection, model moisture changes that occur during storage, and estimate shelf life stability [16-17]. Furthermore, the monolayer moisture content or the minimum moisture level is of importance to the physical and chemical stability of dehydrated materials with regard to lipid oxidation, enzyme activity, non-enzymatic browning and structural characteristics [9].

The moisture sorption data for red curry powder are very rare in the literature. Therefore, in this paper, the investigation of the equilibrated moisture content of red curry powder at various relative humidity values and prepared by different drying methods is carried out. The suitability of various mathematical models for fitting the isotherm and the safe storage moisture content limits of red curry powder are also evaluated.

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Materials and Methods

Raw materials

Fresh Thai red curry paste was obtained from Namprick Maesri Partnership, Ltd. (245 Petkasem Road, Nakornpathom,Thailand) and stored at -60 ºC until use. The ingredients of this product consisted of dried red chili (35%), garlic (23%), shallot (20%), salt (7%), lemon grass (6%), spices (5%), sugar (3%) and galangal (1%). The moisture, crude fibre, ash, crude fat and protein (N x 6.25) of the product were determined by the methods of AOAC [18] and it was found to contain 70 % water, 9 % fibre, 8 % ash, 4 % fat and 3 % protein.

Sample preparation

The red curry paste samples were taken out of storage and thawed at room temperature to 20^{o}C. Fitty-five (±1) grams of the paste material were uniformly spread on a 180x180 mm translucent polyethylene sheet of 1-mm thickness and dried in a microwave oven (Hitachi, MR-30A, Thailand) or a hot-air oven (Path OV663, Thailand) to a final moisture content of approximately 8% by the following conditions:

Microwave drying: The samples were dried at three different levels of microwave output power (180, 360 and 540 W) with drying time of 23, 12 and 8 min respectively.

Hot-air drying: The samples were dried at three different drying temperatures (60, 70 and 80^o C) with constant air velocity of 9.02 m/s and drying time of 240, 180 and 130 min respectively.

Dried products were broken into small pieces, milled with an analytical mill (Retsch, ZM1000, Germany) and passed through a 0.25-mm sieve. The resulting powders were then sealed in aluminum foil bags to prevent moisture absorption and stored at -4 ºC for further studies.

Moisture sorption isotherms

Sorption isotherms were determined by a static-gravimetric method using air-tight glass jars, each containing a saturated salt solution. The salts used were $LiCl_2$, CH_3COOK, $MgCl_2$, K_2CO_3, KI, NaCl, KCl and K_2SO_4, which gave the water activity (a_w) values at 30°C of 0.113, 0.216, 0.324, 0.432, 0.679, 0.751, 0.836 and 0.970 respectively [9]. To determine the sorption, about 0.5 (± 0.001) gram of a sample of red curry powder was accurately weighed into a previously weighed aluminum pan. The pan was then placed on a plastic receptacle inside the jar over a saturated salt solution. The jar was then tightly closed and placed in an electric oven at 30°C. At high water activity ($a_w \geq 0.751$) a small quantity of toluene was placed in a capillary tube fixed in the jar to prevent microbial spoilage of the sample [19]. All samples were weighed every week until a difference of less than 0.001 gram in two consecutive weighings was achieved, when the moisture in the sample was assumed to be at equilibrium. After the equilibrium was reached, the moisture content was determined using the oven method by heating at 105ºC to constant weight [18]. All determinations were performed in triplicate.

The experimental data of all samples were fitted to ten sorption equations (seven two-parameter models, two three-parameter models and one four-parameter model) shown in Table 1. The parameters of the sorption models were estimated from experimental results using a non-linear regression analysis (Statistica for Windows 5.0 software, StatSoft, Inc. 1984-1995).

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Table 1. Sorption models used for fitting experimental data [9, 12-16]

Model name	Model equation
(Two parameters)	
Oswin	$W_e = A(a_w/1-a_w)^B$
Caurie	$W_e = \exp(A + Ka_w)$
Smith	$W_e = A + (B\ln(1-a_w))$
Lewicki-2	$W_e = A((1/a_w)-1)^{B-1}$
BET*	$W_e = X_m C a_w / [(1-a_w)(1-a_w+Ca_w)]$
Haslay	$a_w = \exp(-A/W_e^B)$
Henderson	$(1-a_w) = \exp(-AW_e^B)$
(Three parameters)	
GAB	$W_e = X_m CK a_w / [(1-Ka_w)(1- Ka_w + CKa_w)]$
Lewicki-3	$W_e = A[(1/(1-a_w)^B)-(1/(1+a_w^C))]$
(Four parameters)	
Peleg	$W_e = A(a_w)^C + B(a_w)^D$

Notes: a_w = water activity; W_e = moisture content at equilibrium (grams water per gram dry matter); X_m = monolayer moisture content (grams water per gram dry matter); *A*, *B*, *C*, *D* and *K* = moisture sorption constants

*Sorption data fitted for water activity ≤ 0.432

Statistical analysis

The goodness of fit of tested mathematical models to the experimental data was evaluated with the coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE) [14-15]. The higher the R^2 value and the lower the χ^2 and RMSE values, the better is the fit. The χ^2 and RMSE can be calculated as follows:

$$\chi^2 = \frac{\sum_{i=1}^{N} (W_{e,\exp,i} - W_{e,pre,i})^2}{N - z}$$

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N} (W_{e,\exp,i} - W_{e,pre,i})^2}$$

where $W_{e,exp,i}$ is the ith experimental moisture content at equilibrium, $W_{e,pre,i}$ is the ith predicted moisture content at equilibrium, N is the number of observations and z is the number of constants in the sorption model.

Results and Discussion

Sorption isotherms

The initial moisture content of microwave-dried and hot-air-dried red curry powders were found in the range of 0.082-0.086 gram water per gram dry matter. Moisture sorption isotherms of these samples are shown in Figure 1. As the initial moisture content of the red curry powder was

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low, adsorption was dominant. The equilibrated moisture content (W_e) of the red curry powder increased with water activity (a_w). This might be due to the fact that the vapour pressure of water present in samples increased with that of the surroundings. The moisture content increased very slowly with increase in water activity up to 0.432. From this point on there was a gradual increase in moisture content with increase in water activity up to 0.851, beyond which there was a steep rise in moisture in all samples.

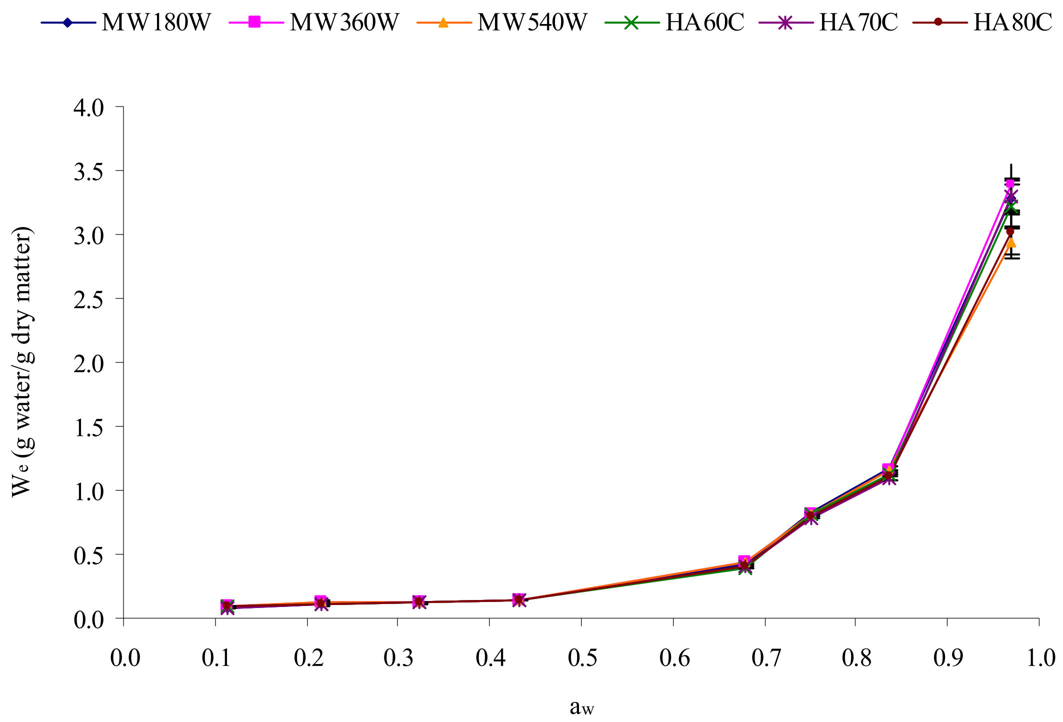

Figure1. Moisture sorption isotherms of Thai red curry powders prepared by microwave drying (MW) and hot-air drying (HA)

According to the classification of Brunauer et al. [12], all sorption isotherms obtained exhibited Type III behaviour, in which a small amount of water is adsorbed at low water activity and a larger amount is adsorbed at higher water activity, and once the bulk moisture point has been reached, the powder rapidly adsorbs large amounts of water vapour, causing it to deliquesce and leading to a steep rise in the third part of the curve, corresponding to the formation of hydrate [11]. The linear shape at the first part of the isotherms is caused by water adsorption on to the biopolymers and the sharp increase in water content at high water activity is due to the gradual dissolution of solutes such as salts and sugars [10]. These results suggest that the red curry powder is characterised by high hygroscopicity as a result of high solute content (salt and sugar) mostly in the amorphous state, which promotes undesirable effects (e.g. caking).

Al-Muhtaseb et al. [12] reported that foods rich in soluble components show isotherms with Type III behaviour owing to the solubility of the components in water. Similar isotherm behaviour has been found in crushed chilies [14], pistachio nut paste [19], model fruit powder [10,20],

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pineapple pulp powder [21], fruits rich in sugar such as grape, apricot and apple [22] and salted alligator meat [23].

It is known that the shape and position of an isotherm for food is influenced by sample composition, physical structure (crystalline or amorphous), pretreatment and method of processing [21]. According to Figure 1, however, the effect of drying method on the shape and position of the red curry powder isotherm is not evident. This means that the states of adsorbed water of the red curry powder during sorption process were not much affected by the method of drying. Moreover, all red curry powder samples had slight difference in the amount of equilibrated moisture content over the entire water activity levels, which indicated that the drying methods did not significantly affect the adsorption capacity of the samples either. Similar results were obtained by Debnath et al. [17] on freeze-dried, vacuum-shelf-dried and through-flow-dried onions. In contrast, Tsami et al. [10] found that freeze-dried pectin-sugar gels had a higher adsorption capacity than microwave-dried, vacuum-dried and convective air-dried samples in that order. Lee and Lee [24] and Giri and Prasad [25] also found that freeze-dried mushrooms had a higher adsorption capacity than microwave-dried and air-died ones in that order. Sundaram and Durance [11] found that the convective air-dried locust bean gum-pectin-starch composite gels had a higher adsorption capacity than freeze-dried and microwave vacuum-dried samples in that order up to 0.8 a_w level. These researchers suggested that moisture sorption capacity of the dry products was in accordance with structural properties such as shrinkage and porosity (total pore area and pore size distribution), which mainly depend on the drying method. Moreover, the effect of drying method on the sorption capacity of different materials may not be the same.

Fitting of sorption models to equilibrium moisture data

The experimental equilibrated moisture content data at any water activity of red curry powder from microwave and hot-air drying methods were fitted against the water activity on ten different sorption models listed in Table 1. The statistical test methods, the coefficient of determination (R^2), the reduced chi-square (χ^2) and the root mean square error (RMSE) were used to select the best fitting equation. The estimated parameters and statistical analysis of the ten models are presented in Table 2. The results show that the highest probability of fitting the experimental data with the highest values for R^2 and lowest values for χ^2 and RMSE are obtained with the GAB model for all the red curry powder samples. Mathematical comparison of the experimental and predicted results gives R^2 values ranging between 0.99639-0.99753 (average 0.99696), χ^2 values ranging between 0.00451-0.00580 (average 0.00504) and RMSE values ranging between 0.05308-0.06022 (average 0.05608). The fitted sorption isotherms for the model with the experimental data are illustrated in Figure 2.

Normally, parameters in the GAB equation have physical meaning: X_m is the monolayer content, C is the total heat of sorption of the first layer, and K is a factor correcting the properties of multilayer molecules with respect to the bulk liquid [19]. However, there are some other limit values for parameters C and K suggested by Lewicki [26] based on the mathematical analysis of the model. In order to guarantee a relatively good description of the isotherm and to fulfill the

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Table 2. Statistical results and estimated values of several model parameters for different drying conditions

Model	Parameter	Microwave drying			Hot-air drying		
		180 W	360 W	540 W	60 °C	70 °C	80 °C
Two parameters							
Oswin							
	A	0.33648	0.32630	0.34232	0.35039	0.34215	0.35615
	B	0.65178	0.66792	0.62815	0.64678	0.66175	0.61036
	R^2	0.98892	0.99200	0.98801	0.98878	0.99145	0.98526
	χ^2	0.01565	0.01184	0.01480	0.01662	0.01334	0.01746
	RMSE	0.10835	0.09425	0.10537	0.11164	0.10004	0.11443
Caurie							
	A	-5.58930	-5.82891	-5.32475	-5.48757	-5.70087	-5.06514
	B	6.95845	7.23285	6.61666	6.87698	7.12712	6.32436
	R^2	0.99335	0.99274	0.99290	0.99413	0.99344	0.99440
	χ^2	0.00939	0.01075	0.00877	0.00869	0.01025	0.00662
	RMSE	0.08392	0.08978	0.08108	0.08074	0.08766	0.07049
Smith							
	A	-0.30889	-0.32477	-0.26495	-0.31367	-0.33029	-0.24857
	B	-0.92524	-0.94499	-0.86580	-0.94819	-0.97144	-0.85031
	R^2	0.94904	0.94273	0.95534	0.95187	0.94578	0.96288
	$\chi 2$	0.06775	0.07996	0.05165	0.06701	0.07975	0.04109
	RMSE	0.22542	0.24488	0.19681	0.22418	0.24456	0.17555
Lewicki-2							
	A	0.33648	0.32630	0.34232	0.35039	0.34215	0.35615
	B	0.34822	0.33208	0.37185	0.35322	0.33825	0.38964
	R^2	0.98823	0.99152	0.98720	0.98806	0.99093	0.98422
	χ^2	0.01565	0.01184	0.01480	0.01662	0.01334	0.01746
	RMSE	0.10835	0.09425	0.10537	0.11164	0.10004	0.11443
BET							
	X_m	0.08017	0.08339	0.08464	0.08356	0.08321	0.08287
	C	429.62592	145.333057	1333229.36	107.06766	1326.3384	618734.8
	R^2	0.96880	0.91936	0.89922	0.95998	0.87758	0.84921
	χ^2	0.00002	0.00006	0.00006	0.00003	0.00009	0.00010
	RMSE	0.00328	0.00566	0.00570	0.00418	0.00666	0.00723
Haslay							
	A	0.17562	0.17495	0.17492	0.18406	0.18449	0.18302
	B	0.91551	0.92786	0.94602	0.90163	0.91205	0.91593
	R^2	0.96782	0.97037	0.96476	0.97085	0.96589	0.96384
	χ^2	2.12845	1.79900	1.86518	2.76614	2.43855	2.87668
	RMSE	1.26346	1.16157	1.18274	1.44035	1.35237	1.46885
Henderson							
	A	1.86038	1.89811	1.87708	1.80529	1.82196	1.82029

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Table 2. (Continued)

Model	Parameter	Microwave drying			Hot-air drying		
		180 W	360 W	540 W	60 °C	70 °C	80 °C
	B	0.78050	0.80097	0.81029	0.77582	0.79150	0.79160
	R^2	0.93792	0.94151	0.93691	0.94296	0.94013	0.94008
	χ^2	0.16648	0.23175	0.13049	0.15781	0.21300	0.08008
	RMSE	0.35335	0.41691	0.31283	0.34403	0.39968	0.24507
Three parameters							
GAB							
	X_m	0.51270	0.36958	0.45741	0.58185	0.42026	0.70660
	C	0.36373	0.55482	0.45222	0.32846	0.48915	0.28460
	K	0.91039	0.93380	0.90986	0.90335	0.92692	0.87733
	R^2	0.99658	0.99726	0.99639	0.99714	0.99753	0.99683
	χ^2	0.00580	0.00487	0.00535	0.00509	0.00463	0.00451
	RMSE	0.06022	0.05517	0.05781	0.05638	0.05379	0.05308
Lewicki-3							
	A	0.70377	0.62745	0.80473	0.75473	0.67691	0.96289
	B	0.46590	0.50227	0.41554	0.45390	0.48925	0.36552
	C	6.71382	6.71161	6.89649	6.75285	6.68133	7.03462
	R^2	0.99552	0.99672	0.99571	0.99595	0.99682	0.99576
	χ^2	0.00759	0.00582	0.00635	0.00720	0.00596	0.00603
	RMSE	0.06887	0.06033	0.06302	0.06706	0.06102	0.06140
Four parameters							
Peleg							
	A	1.91516	1.98273	1.77474	1.95455	2.02753	1.71775
	B	1.91516	1.98273	1.77474	1.95455	2.02753	1.71775
	C	6.06913	6.32743	5.76744	5.99412	6.22799	5.49316
	D	6.06913	6.32743	5.76744	5.99412	6.22799	5.49316
	R^2	0.98904	0.98822	0.98782	0.98978	0.98893	0.98933
	χ^2	0.02322	0.02617	0.02256	0.02269	0.02594	0.01896
	RMSE	0.10776	0.11440	0.10621	0.10651	0.11388	0.09737

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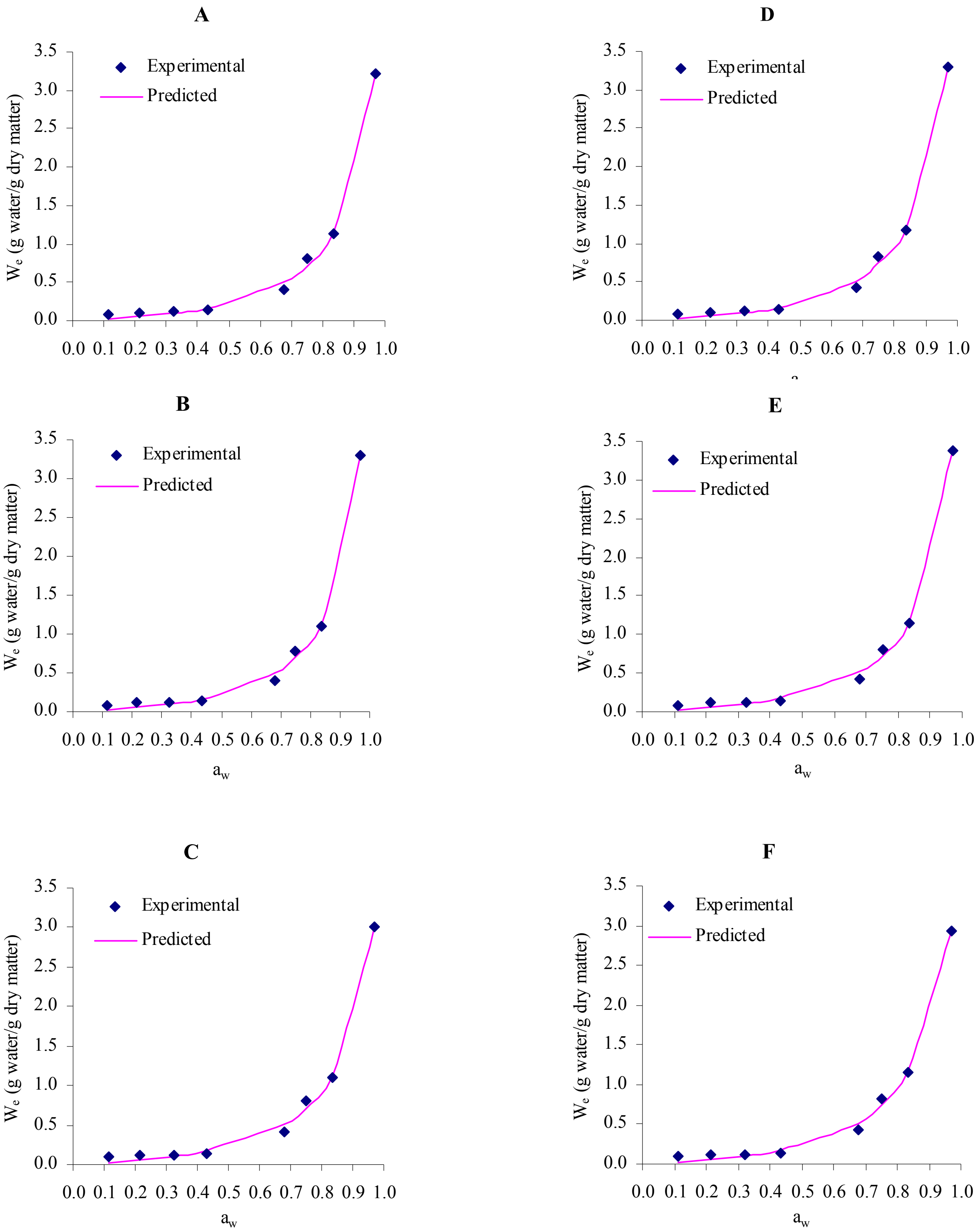

Figure 2. Comparison of experimental and predicted (GAB model) sorption isotherms of Thai red curry powder prepared by microwave drying at 180 W (**A**), 360 W (**B**), 540 W (**C**) and hot-air drying at 60 °C (**D**), 70 °C (**E**) and 80 °C (**F**)

requirements of the BET model as well as to assure that the estimated X_m values differ by not more than ± 15% from the true monolayer capacity, the above author stated that the parameters should assume values in the ranges $5.67 \leq C \leq \infty$ and $0.24 \leq K \leq 1$. In the present study, the estimated C results are not in accordance with the limit values and are therefore considered as not fulfilling the theoretical requirements. So the values of the GAB parameters obtained in this work lack any physical meaning. Similar results were found by Lewicki [26] for apple cellular fibre, carrot, coffee, mushroom, wheat bran flour and yeast isotherms. The physically impossible values of the GAB parameters have been reported by several researchers. The high value of X_m has been reported by Arslan and Toğrul [14] on the study of crushed chilies. Furthermore, the negative value of C and the value higher than unity of K have been found by Maskan and Göğus [19] on the study of pistachio nut paste.

The second best model that fits the experimental data of all the red curry powders is the Lewicki-3 model. Statistical data for the Lewicki-3 correlation are: R^2 ranging between 0.99552-0.99682 (average 0.99608), χ^2 ranging between 0.00582-0.00759 (average 0.00649) and RMSE ranging between 0.06033-0.06362 (average 0.06362). Lewicki [24] theorised that the Lewicki-3 model consists of two functions subtracted from each other assuming the two processes occur in parallel. The first process prevails at high water activity while the second plays a major role at low water activity. The model was found to give a higher probability of good fit for the experimental data compared to the GAB and Peleg equations. Nevertheless, no physical significance could be assigned to the parameters of the equation. On the other hand, the Henderson, Haslay and Smith equations provide the worst representations of the data.

Monolayer moisture content

The value of the monolayer moisture content (X_m) is of particular interest, since it indicates the amount of water that is strongly adsorbed to specific sites at the food surface. It is considered as the optimum value to assure food stability. For most dry foods, the rate of quality loss due to chemical reactions is negligible at the monolayer value. Therefore, this value is important for the storage of red curry powder, since at this moisture level water does not act as a solvent, being biologically inert.

The X_m value in this study was determined by using the BET equation and was found to range between 0.080-0.085 gram water per gram dry matter, the values at which the red curry powder keeps very well on storage for a long period of time. Tsami et al. [10] following adsorption at 25°C found for model fruit powder the X_m values between 0.060-0.097, which is the same in the order of magnitude as X_m estimated in the present work. The X_m values for lemon juice and pineapple powder, however, were between 0.146-0.166 gram water per gram dry matter following adsorption at 20-50°C [16,21]. Kaymak-Ertekin and Gedik [22] found for grapes, apricots and apples X_m values between 0.095-0.220 gram water per gram dry matter, and those for potato between 0.067-0.073 gram water per gram dry matter following adsorption and desorption at 30-60°C. The value of X_m for red curry powder thus seems to be lower than those for high-sugar fruits and fruit powder but higher than those for starchy foods.

Conclusions

This study presents data on moisture sorption of Thai red curry powder prepared by two different drying methods, i.e. microwave drying at 180, 360 and 540 W, and hot-air drying at 60, 70 and 80°C, over a range of water activity (0.113-0.970) at 30°C. It was found that the red curry powder exhibited Type III sorption isotherms which were not affected by the drying methods. The GAB model followed by the Lewicki-3 model was found to be most suitable for fitting the moisture sorption data. The monolayer moisture content derived from the BET model ranged between 0.080-0.085 gram water per gram dry matter. The moisture sorption data obtained could give useful information to guide the processing, packaging and storage of Thai red curry powder at ordinary temperature.

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