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Dynamic vapor sorption isotherms of medium grain rice varieties

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ABSTRACT

It is known that the two popular medium rice varieties, namely M202 and M206, in California have different fissuring resistances. Therefore, the main goal of this study was to investigate the sorption behavior of these two varieties by a new approach using dynamic vapor sorption (DVS) method for elucidating the differences in fissuring resistance. The moisture sorption isotherms of rough, brown and white rice and husk were determined at 25 °C over a water activity range of 0–0.98. Although it was found that the sorption isotherms of different forms of M202 and M206 were similar, M202 absorbed and desorbed moisture faster than M206 which might make it more susceptible to fissuring. All obtained moisture sorption isotherms exhibited the sigmoid (Type II) shape and hysteresis was observed for all forms of rice. Absorption curves obtained using DVS method were compared with the traditional saturated salt solution (SSS) method. For all forms of rice, the maximum difference for equilibrium moisture content value between two methods was observed at 0 and 98% relative humidities, which was approximately 8–11% and 7–9%. Although at a single relative humidity point equilibrium with DVS was attained much faster than SSS method, obtaining a full isotherm with more than 10 data points might make SSS method more feasible for low diffusion materials. Among the select equations to describe sorption behavior of different forms of rice, Peleg equation gave the best fit for all forms of rice.

1. Introduction

California is the second largest rice producing state in USA and the rice industry annually contributes more than $1.8 billion to the economy with yearly production averaging more than 2.0 million metric tons and more than 90% of the rice grown in California is medium grain variety (Anon, 2011). The economic value and milling quality of rice are directly assessed by the head rice yield which is affected with fissures developed in the field or during post-harvest operations. It is believed that fissure development is closely related to the moisture absorption and desorption which happen when the rice is exposed to different relative humidity (*RH*) conditions (Kunze & Calderwood, 1985). In order to aid in mitigation of the fissure formation and also for design, modeling and optimization of rice processing it is important to know the relationship between equilibrium moisture content (*EMC*) of rice and equilibrium relative humidity (*ERH*) of the surrounding air at a certain temperature, described with sorption isotherms (Furmaniak, Terzyk, Golembiewski, Gauden, & Czepirski, 2009; Iguaz, Rodriguez, & Virseda, 2006; Kunze & Wratten, 1985; Sun, 1999).

There are several different methods to determine the sorption isotherms of food materials (Rahman & Sablani, 2009). Many authors (Aguerre, Suarez, & Viollaz, 1983; Bianco, Pollio, Resnik, Boente, & Larumbe, 1997; Engels, Hendrickx, & Tobback, 1987; Gencturk, Bakshi, Hong, & Labuza, 1986; Iguaz & Virseda, 2007; Reddy & Chakraverty, 2004) preferred gravimetric static methods using saturated salt solution (SSS) wherein a sample of known mass is stored in an enclosure, such as a desiccator, and is allowed to reach equilibrium with the surrounding atmosphere of known *RH* maintained by the solutions. The sample is weighed at regular intervals until a constant weight is reached, which is assumed to be the equilibrium point. The main drawbacks of this kind of system are slowness of the equilibrium process, the possibility of mold or bacterial growth on samples at high *RH* and difficulty in measuring the absorption and desorption isotherms for the same sample (Rahman & Sablani, 2009). In order to accelerate equilibrium time of food material, Haque, Sudeepa, Shimizu, and Kimura (2006) placed a fan within the chamber and reduced the equilibration time by 40–60%. Furthermore, mold or bacterial growth could be

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avoided by placing a UV lamp inside the chamber (Togrul & Arslan, 2006) or by spraying or mixing sodium azide onto food material or into solutions.

Lewicki and Pomaranska-Lazuka (2003) showed that although opening and closing a desiccator and weighing a sample took approximately 2 min, this action caused exchange of air contained in the desiccator with the surrounding ambient air. Therefore, when multiple samples were stored in the desiccator, compared to the first sample the next samples' water content can be over- or under-estimated up to 15%. In order to minimize disturbances and to accelerate the equilibrium process within the chamber, Togrul and Arslan (2006) used a radial fan to circulate the fog (atomized water and air mixture) inside chamber. The disturbance caused by opening and closing the desiccator can also be avoided by weighing the sample in situ via a scale attached to the sample holder (Rahman & Sablani, 2009).

It was shown by Prakash, Bingol, and Pan (2011) that at different *RH* the moisture diffusivity values of medium grain rice ranged from 10^{-11} to 10^{-12} m^2/s. Moreover, Arlabosse, Rodier, Ferrasse, Chavez, and Lecomte (2003) stated that when the apparent diffusion coefficient of a material is less than 10^{-9} m^2/s, a difficulty occurs to reach the thermodynamic equilibrium with the SSS method. Dynamic vapor sorption (DVS) method could overcome the disadvantages encountered with the SSS method. DVS system has been used in the pharmaceutical industry since 1994. The DVS system does not require the use of saturated salt solutions in order to provide the desired *RH*, but instead, a mixture of dry nitrogen and saturated water vapor, whose proportions are precisely controlled by mass flow controllers, is used. Due to small chamber and sample size and continuous flow of dry nitrogen and saturated water vapor mixture over the sample, the equilibration is more rapid, which avoids the risk of molding at high *RH*, and therefore enables the measurement of the same sample for absorption and desorption isotherms. Many authors used DVS method for different materials: wheat flour and wheat components by Roman-Gutierrez, Mabille, Guilbert, & Cuq (2003); food grade crystalline sucrose by Yu, Kappes, Bello-Perez, and Schmidt (2008); the native dent starch and corn gluten meal by Teoh, Schmidt, Day, and Faller (2001); sponge cakes by Guillard, Broyart, Bonazzi, Guilbert, and Gontard (2003). However, to the best of our knowledge, up to this date DVS method has not been used for evaluating sorption behavior of rice kernels. Therefore, considering the above-mentioned advantages of DVS method over the SSS method and the lack of a study in literature were the driving motives to investigate DVS method's feasibility for obtaining isotherms for different forms of rice.

There are many theoretical, semi-empirical and fully empirical mathematical equations developed to model the relationship between water activity (a_w) and *EMC*. Each model has success in predicting the *EMC* data for a particular foodstuff at a given range of *ERH* and temperatures. Among these models, the theoretical Guggenheim–Anderson–de Boer equation (Anderson, 1946; De Boer, 1953, pp. 61–81; Guggenheim, 1966, pp. 186–206), namely the GAB model, has shown a good fit to the isotherms in a broad range of a_w and was used by several researchers to model sorption isotherm of rice (Gencturk et al., 1986; Iguaz & Virseda, 2007; Reddy & Chakraverty, 2004). Besides GAB equation, other equations, such as Henderson, Caurie, Oswin and Peleg equations, were also found suitable to model sorption isotherms of rice (Aguerre et al., 1983; Engels et al., 1987; Togrul & Arslan, 2006).

Although both M202 and M206 are early maturing Calrose type medium grain varieties, it is known that M206 is more fissure resistant than M202 (Greer, 2010; Mutters, Thompson, & Plant, 2006). A better understanding of these two varieties' sorption behavior at different *RH* environments could help to the development of new processing methods or storage conditions that could increase the head rice yield. Thus the objectives of this study were to i) investigate the fissuring resistance differences of different forms of M202 and M206 by comparing absorption and desorption isotherms using the DVS method, ii) compare the DVS method with the traditional SSS method and iii) test the ability of different moisture sorption isotherm equations for predicting *EMC* of different forms of M202 and M206 and moreover select the model that best fits to the experimental data.

2. Materials and methods

2.1. Rice samples

Two medium varieties, namely Californian M202 and M206 were chosen as the raw material for the current study. Rough rice (RR) was obtained directly from California Rice Experiment Station (Biggs, California) with a moisture content ranging between 13.6 and 16.3 (g/100 g dry matter). Brown rice (BR) and white rice (WR) were prepared by dehusking with a husker (Yamamoto, Japan) and then milling with a rice mill (Yamamoto, Japan), respectively. The RR, BR and WR were kept in plastic bags and stored at 4 °C until used. During storage the moisture content of the rice decreased to between 11.5 and 14.0 (g/100 g dry matter). The husk was obtained by manually dehusking the RR before each experiment.

2.2. Dynamic vapor sorption method

A Dynamic Vapor Sorption equipment (DVS Advantage-1, Surface Measurement Systems, PA, USA) was used to obtain *EMC* of rough, brown and white rice and the husk. The weights of RR, BR and WR used for experiments, for M202 were 30.06 ± 0.80, 24.57 ± 0.71 and 20.97 ± 0.47 mg, respectively, and for M206 were 31.14 ± 0.50, 25.02 ± 0.72 and 22.30 ± 0.57 mg, respectively. For each experiment, three rice kernels or husk from at least three different rice grains were placed into the pan of the equipment. The relative humidity was changed from 0 to 98% and, then to 0% at a 20% *RH* step and the temperature was kept constant at 25 °C which is in line with the conditions selected by different authors (Arlabosse et al., 2003; Roman-Gutierrez, Guilbert, & Cuq, 2002). It was assumed that the equilibrium was reached when the change in sample mass as a function of time was lower than 0.002%/min. It was observed that except 0% *RH* for rough rice of both M202 and M206 and 98% for rough and brown rice for M206, where the equilibrium was considered to be achieved at 0.005%/min, the above-mentioned criteria was met for all of the experiments. The time necessary to reach aforementioned equilibration conditions ranged approximately from 400 to 1500 min (Fig. 1). All of the experiments were done at least in triplicate.

2.3. Saturated salt solution method

In order to validate our experimental findings with the DVS method, we have carried out the traditional saturated salt solution method to obtain absorption isotherm of M206 variety. To achieve 7 different relative humidity environments, desiccant (anhydrous calcium sulfate), aqueous solutions of KOH, $MgCl_2$, $Mg(NO_3)_2 \cdot 6H_2O$, NaCl and KCl and pure water were used to have *RH* of 0, 11, 33, 61, 76, 85 and 100%, respectively. In order to prevent fungal growth at relative humidities over 54%, sodium azide was mixed into solutions. Rough, brown and white rice of M206 variety, which were pre-equilibrated at 0% *RH*, were put into glass dishes which were placed above the solutions in closed containers at 24.0 ± 0.3 °C. The samples were stored in the containers for 3 weeks. The experiments were duplicated.

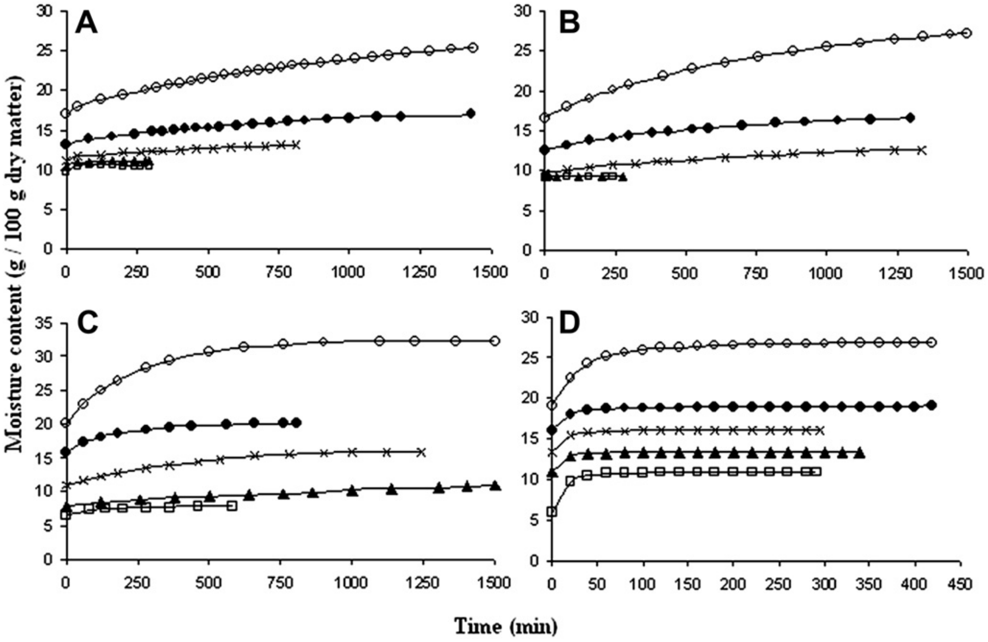

Fig. 1. Absorption rates of different forms of M206 variety at different relative humidities A) Rough rice, B) Brown rice, C) White rice, D) Husk (□: 20%; ▲: 40%; x: 60%; ●: 80%; ○: 98% relative humidity).

2.4. Mathematical models

In this study we evaluated the suitability of two-parameter Caurie, Halsey and Oswin equations; three-parameter GAB (Guggenheim, Anderson, de Boer) equation and four-parameter Peleg equation to describe moisture sorption isotherms of different forms of M202 and M206 varieties (Table 1). The fitting of the selected equations to the experimental data was done by using the *nls* built-in function of R software (R Development Core Team, R Foundation for Statistical Computing, Vienna, Austria).

2.5. Statistical analysis

The quality of fitting of experimental data to the selected mathematical models was tested with 3 different criteria, namely, coefficient of determination (R^2), the mean relative percent error (P_e) and root mean square error (*RMSE*). *RMSE* and P_e were calculated as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(M_e^i - M_p^i\right)^2}{N}} \tag{1}$$

Table 1
Selected mathematical models to describe sorption isotherms of different forms of rice.

Model	Reference
$\ln\left(\frac{1}{M}\right) = -\ln(a \cdot M_0) + \frac{2a}{M_0}\ln\left(\frac{1-a_w}{a_w}\right)$	Caurie (1981)
$a_w = \exp\left(\frac{-b}{M^a}\right)$	Halsey (1948)
$M = a \cdot \left(\frac{a_w}{1-a_w}\right)^b$	Oswin (1946)
$M = \frac{M_0 C K a_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$	GAB (Anderson, 1946; De Boer, 1953, pp. 61–81; Guggenheim, 1966, pp. 186–206)
$M = a \cdot a_w^b + c \cdot a_w^d$	Peleg (1993)

M: Moisture content (g/100 g dry matter). M_0: Monolayer moisture content (g/100 g dry matter). a_w: Water activity. *a*, *b*, *c*, *d*: Constants. *K*: Constant in GAB equation.

$$P_e = \frac{100}{N}\sum_{i=1}^{N}\frac{\left(M_e^i - M_p^i\right)}{M_e^i} \tag{2}$$

where M_e is the experimental *EMC*, M_p is the predicted *EMC*, and *N* is the number of experimental data points.

3. Results and discussion

3.1. Sorption isotherms

The sorption isotherms of different forms of M202 and M206, obtained by DVS method, are shown in Fig. 2. According to the classification of Brunauer, Deming, Deming, and Troller (1940) moisture sorption isotherms of different forms of M202 and M206 exhibited the sigmoid (Type II) shape. Furthermore, analyzing the isotherms on the basis of $a_w/M - a_w$ plots showed Type II-b shape according to Blahovec and Yanniotis (2009) classification.

For all forms of M202 and M206, desorption curves were above the absorption curves, thereby formed the hysteresis loop, which has been observed by several authors for different foodstuffs (Kachru & Matthes, 1976; Siripatrawan & Jantawat, 2006; Togrul & Arslan, 2006). The hysteresis loop extended over the entire water activity range; however it was the most prominent in the 0.20–0.80 a_w region, which is in line with the findings of Togrul and Arslan (2006). The average magnitudes of hysteresis of M202 and M206, which were found by computing the hysteresis loop area in the 0–0.98 region by using the trapezoidal integration method, were 2.03, 1.37, 1.85 and 1.21 hysteresis units for RR, BR, WR and husk, respectively. The magnitude of hysteresis is related to the nature and state of the components in foodstuffs (Al-Muhtaseb, McMinn, & Magee, 2002). It was further found that, there was no significant difference between the magnitudes of hysteresis for different forms of M202 and M206 that could be due to similar chemical compositions in terms of protein, fat, carbohydrate and ash content where the total protein, fat, carbohydrate and ash contents of M202 and M206 were 5.75, 2.86, 85.49, 5.90 (g/100 g

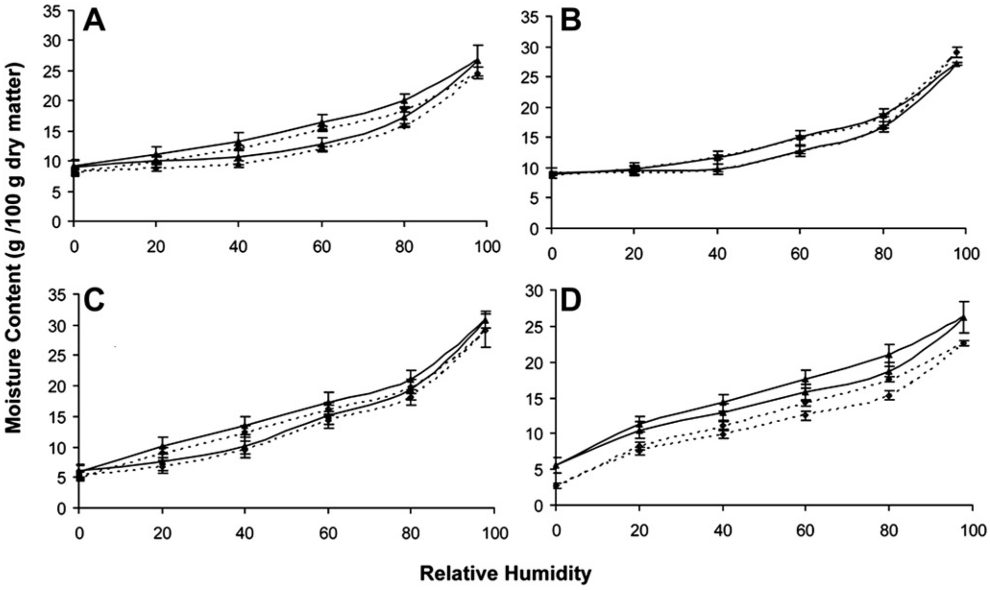

Fig. 2. Sorption isotherms of different forms of M202 and M206 varieties, A) Rough rice, B) Brown rice, C) White rice and D) Husk (--◇--: M202; ▲: M206).

dry matter) and 5.79, 2.87, 85.50, 5.83 (g/100 g dry matter), respectively. It is thus far seen that the chemical composition and sorption behavior of M202 and M206 are very similar.

The rice grain is hygroscopic in nature, it physically responds to moisture changes by expanding or shrinking. It has been shown that even a 1% moisture content change can produce stresses in the grain (Kunze & Calderwood, 1985). Kunze and Calderwood (1985) further reasoned that rapid changes in moisture content, such as rapid drying, can aggravate fissuring. During the harvest season, the relative humidity in Californian valleys could change from 90% in the early morning to 10% in the afternoon. Therefore, the rice kernels absorb moisture when the relative humidity is high and then desorb it when the relative humidity decreases. It is clearly seen from Fig. 3 that M202 variety absorbs and desorbs moisture faster than M206 which might make it more susceptible to fissuring.

Dong, Lu, Liu, Koide, and Cao (2010) showed that the shape and the amylose content of a rice variety play major role in forming fissure resistance. The longer the length and the higher the amylose content of the grain, make it more resistant to fissuring. It has been reported by California Rice Research Board (CRRB, 2010) that the apparent mean amylose content of M206 (17.70 ± 0.60, g/100 g dry matter) is higher than M202 (16.50 ± 1.00, g/100 g dry matter). CRRB (2010) further reported that on the average for rough, brown and white rice M206 (8.56 ± 0.17, 6.22 ± 0.06, 5.84 ± 0.00 mm) is longer than M202 (8.33 ± 0.20, 6.09 ± 0.13, 5.70 ± 0.12 mm), which, along with its higher amylose content, could also make it more fissure resistant.

Fig. 2 shows that as the a_w increased the *EMC* also increased at an increasing rate, with the exception of absorption at 20% *RH* for M202 BR. Kunze and Hall (1965) showed that BR could be moved through a 10% increment to different *RH* environments in 24 h periods without producing fissures; however, the authors concluded that if the increments in *RH* were greater than 10%, fissuring of grains was observed. Therefore it can be hypothesized that sudden increases in ambient relative humidity, especially over 40% ambient *RH*, will cause significant moisture gradients that could cause fissuring for all forms of rice. However, changes in ambient conditions below 40% for RR and BR and similarly below 20% for WR, might not cause fissuring since grains neither absorb

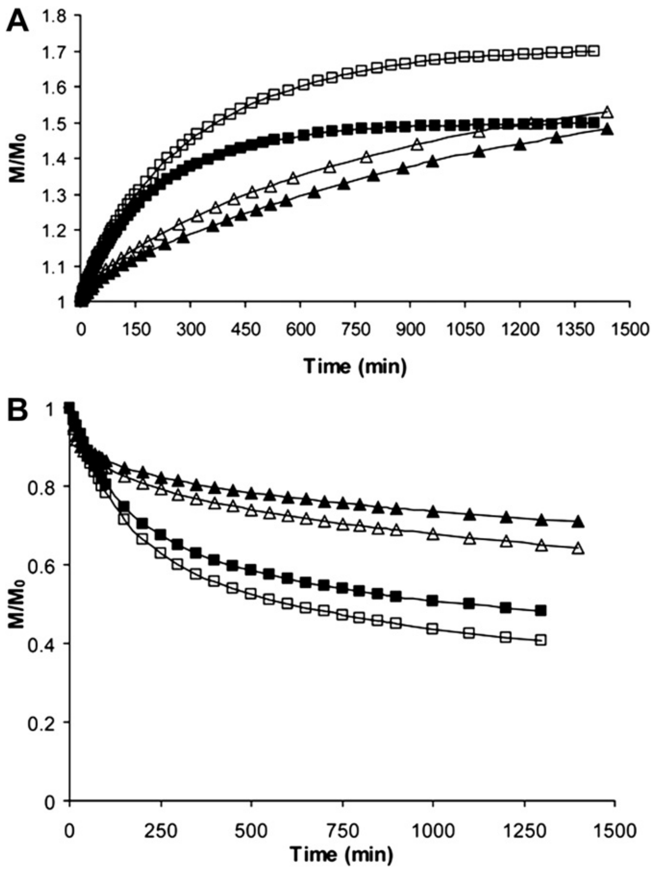

Fig. 3. Comparison of A) absorption (at 98% relative humidity) and B) desorption (at 0% relative humidity) rates of M202 and M206 rough and white rice (Δ: M202 rough rice; ▲: M206 rough rice; □: M202 white rice; ■: M206 white rice) (*M*: moisture content at time *t* (g/100 g dry matter; M_0: initial moisture content at respective relative humidity (g/100 g dry matter)). For the desorption curve initial moisture contents for M202 rough and white rice were 11.6 and 11.8 (g/100 g dry matter), respectively, and for M206 rough and white rice were 14.1 and 14.0 (g/100 d dry matter). For the adsorption curve initial moisture content can be read from Fig. 2 as equilibrium moisture content at 80% relative humidity.

nor desorb significant amount of moisture, therefore the moisture gradients could be assumed to be too low to cause fissuring. Therefore, in different *RH* environments, such as combine hopper, field cart, transport truck or holding bin the ambient *RH* should be carefully controlled in order to avoid fissuring which could lower the market value of the rice.

3.2. Comparison of DVS and saturated solution methods

Equilibration times for different forms of M206 variety using DVS ranged from 400 to approximately 1500 min (Fig. 1). Compared to weeks of equilibration time reported in the literature for rice (Gencturk et al., 1986; Iguaz & Virseda, 2007), DVS has the apparent advantage of more rapidly reaching the equilibrium conditions at different *RH* levels due to continuous flow of nitrogen and water vapor mixture over the product. However, it should be noted that, although at a certain *RH* level equilibration time for DVS was faster than SSS method, the time to obtain a full isotherm depends on the number of *RH* steps, during which the product needs to reach the moisture equilibrium. In our experiments we had a total of 11 *RH* levels and therefore obtaining a full isotherm for different forms of rice took approximately 6–10 days.

It has been reported that when the apparent diffusion coefficient of the material is less than 10^{-9} m^2/s, internal diffusion becomes a limiting factor which thereby could result in a difference between the SSS and DVS methods (Arlabosse et al., 2003). Keeping in mind that since diffusion coefficients of different forms of rice were smaller than 10^{-9} m^2/s (Prakash et al., 2011), a difference between SSS and DVS methods could already be anticipated. We have observed that at 0 and 98% *RH*s for all forms of rice there were approximately 8–11% and 7–9% differences, respectively, between DVS and SSS methods (Fig. 4). For RR and BR the differences between SSS and DVS were higher at a water activity range of 0.40–0.80 than the lower or higher water activities. Although Prakash et al. (2011) reported the highest diffusion coefficient of WR at a water activity range of 0–0.20, it was interesting to note that for WR as the *RH* increased, the difference between DVS and SSS methods decreased.

Although for most of the DVS experiments the change in sample mass as a function of time was lower than 0.002%/min, a criteria recommended by the manufacturer, it is seen from Fig. 1A and B that, unlike Fig. 1C and D, at the end of each *RH* level the curves are not completely parallel to *x*-axis implying that the perfect equilibrium conditions were not reached. It could, therefore, be that during absorption SSS method's curves were above the DVS method's curves, implying that the grains absorbed more moisture (Fig. 4). However, if the duration of the equilibration during DVS method was extended to obtain a better equilibration curve, which would significantly increase the experiment time, the *EMC*s for RR and BR would be slightly different than those obtained during this study. For example we have observed that extending the equilibration time for RR from 1490 (0.005%/min) to 4375 min (0.0033%/min) at 0% *RH* reduced the *EMC* from 9.22 to only 8.56 (g/100 g dry matter).

These results show that DVS method is suitable for WR and husk since at all *RH* levels perfect equilibration was reached. On the other hand, for RR and BR at 0 and 98% *RH* levels perfect equilibrium conditions were not reached even though the *RH* step time was extended to 4375 min. Therefore, for materials with very low diffusion coefficients, smaller than 10^{-9} m^2/s, we recommend the use of DVS method for experiments with only few number of *RH* data points. On the other hand, for full isotherms of low diffusion materials, i.e. experiments with more than 10 *RH* data points, use of SSS is recommended.

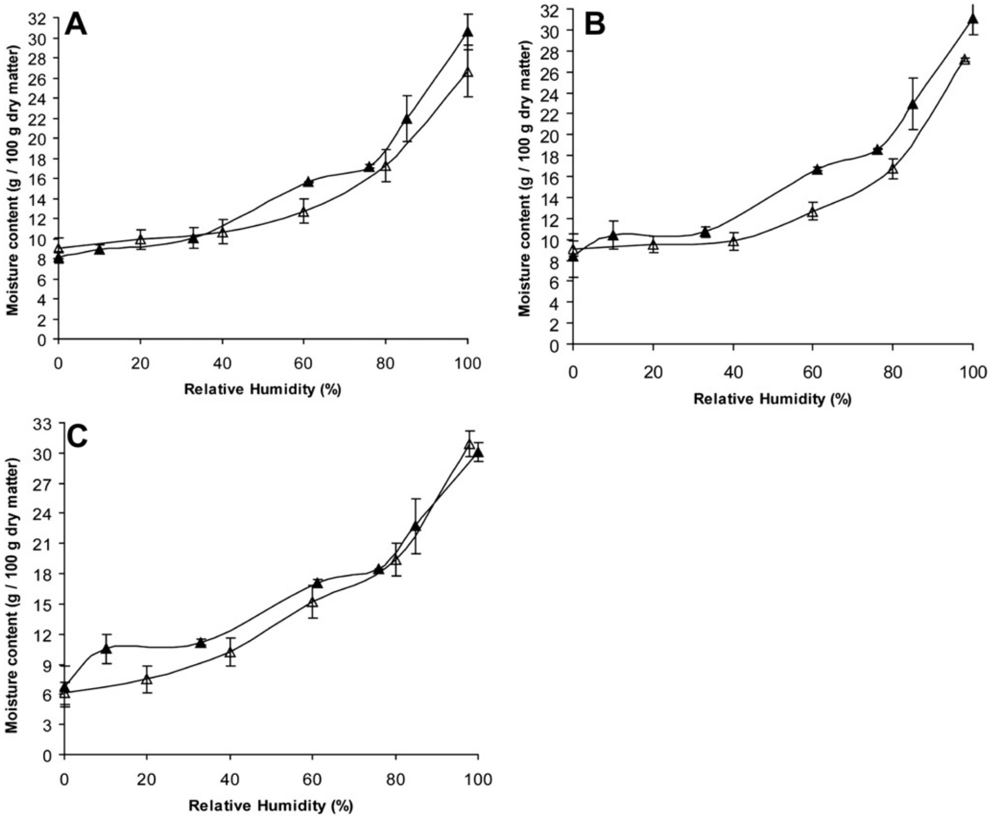

Fig. 4. Comparison of DVS and SSS methods for different forms of M206 variety: A) Rough rice, B) Brown rice and C) White rice (Δ: DVS method; ▲: SSS method).

Table 2
Coefficients and statistics of mathematical models for sorption isotherms of M202.

Model	a_w range	Parameters	RR-A	RR-D	BR-A	BR-D	WR-A	WR-D	Husk-A	Husk-D
Caurie	0.20–0.98	a	1.078	1.077	1.230	1.308	1.443	1.361	1.083	1.182
		M_0	10.394	12.523	9.903	11.321	8.938	11.193	10.162	11.296
		R^2	0.982	0.962	0.978	0.992	0.956	0.962	0.976	0.926
		P_e	5.354	4.651	6.651	10.676	18.117	12.331	4.151	11.279
		RMSE	1.828	1.635	1.735	10.626	53.221	20.956	0.563	13.185
Halsey	0.20–0.98	a	3.988	4.621	3.504	3.974	2.841	3.654	3.881	4.014
		b	9396	99,820	3292	18,439	551	8285	6085	12,663
		R^2	0.976	0.920	0.983	0.973	0.910	0.916	0.937	0.868
		P_e	4.353	6.652	5.424	4.959	11.445	9.155	7.214	10.810
		RMSE	1.433	3.466	2.422	1.738	9.029	5.781	2.128	7.245
Oswin	0.20–0.98	a	11.214	13.499	11.607	13.393	11.087	13.607	10.760	12.047
		b	0.208	0.172	0.237	0.209	0.278	0.217	0.208	0.189
		R^2	0.982	0.962	0.978	0.992	0.956	0.962	0.976	0.926
		P_e	4.462	3.876	11.607	13.393	6.570	4.621	3.727	5.862
		RMSE	1.670	1.493	0.237	0.209	3.233	2.126	0.838	2.781
GAB	0.20–0.98	K	0.720	0.695	0.785	0.730	0.793	0.755	0.778	0.735
		C	16,739	16,739	31,877	24,578	32,431	23,272	27,824	22,704
		M_0	7.350	8.250	6.950	8.306	6.730	7.950	5.710	6.750
		R^2	0.995	0.998	0.986	0.994	0.967	0.989	0.993	0.990
		P_e	7.448	5.069	10.088	4.306	9.017	11.914	24.215	29.801
		RMSE	2.168	1.342	4.768	1.373	2.055	4.239	5.841	9.480
Peleg	0.20–0.98	a	15.140	16.150	11.626	16.631	19.682	10.284	8.768	6.182
		b	4.510	0.300	0.165	0.331	0.706	8.985	8.113	4.751
		c	10.853	9.295	19.680	14.432	11.871	20.854	15.406	17.204
		d	0.136	4.056	5.552	6.456	9.368	0.527	0.457	0.462
		R^2	0.998	0.997	0.996	0.997	0.997	0.999	0.999	0.999
		P_e	1.912	1.406	3.024	2.213	3.372	1.538	1.320	0.958
		RMSE	0.306	0.194	0.768	0.543	0.791	0.373	0.203	0.086

A: Absorption, D: Desorption.

3.3. *Mathematical modeling*

Five sorption isotherm models were used for the analysis of the *EMC–ERH* relationship for rough, brown and white rice and husk of M202 and M206. The coefficients and statistics of the equations for these two varieties are given in Tables 2 and 3, respectively. If the value of P_e is less than 5, Lomauro, Bakshi, and Labuza (1985) and Ayranci and Duman (2005) considered the model to be a good/excellent fit to the experimental data. Furthermore, Siripatrawan and Jantawat (2006) assumed a model to be suitable if P_e value is less than 10. It is seen from Fig. 5 that for RR and BR, regardless of the number of parameters, all of the selected models gave suitable

Table 3
Coefficients and statistics of mathematical models for sorption isotherms of M206.

Model	a_w range	Parameters	RR-A	RR-D	BR-A	BR-D	WR-A	WR-D	Husk-A	Husk-D
Caurie	0.20–0.98	a	1.112	1.112	1.192	1.309	1.500	1.373	0.962	1.046
		M_0	11.095	13.210	10.510	11.557	9.414	11.923	12.716	13.926
		R^2	0.979	0.972	0.974	0.983	0.960	0.971	0.984	0.938
		P_e	5.092	3.352	5.449	12.494	19.968	10.977	14.982	8.380
		RMSE	2.568	1.401	1.894	22.445	69.254	17.015	24.046	7.671
Halsey	0.20–0.98	a	4.130	4.790	3.839	4.130	2.936	3.867	4.713	4.862
		b	19,686	233,685	8129	26,154	874	19,996	154,303	343,591
		R^2	0.980	0.935	0.977	0.954	0.918	0.930	0.950	0.884
		P_e	4.213	5.659	5.296	5.449	10.601	7.676	5.056	8.192
		RMSE	1.738	2.929	1.884	2.306	8.642	4.625	1.812	6.054
Oswin	0.20–0.98	a	12.342	14.686	11.869	13.239	11.980	14.772	14.022	15.361
		b	0.201	0.168	0.215	0.198	0.270	0.208	0.173	0.158
		R^2	0.979	0.972	0.974	0.983	0.960	0.971	0.984	0.938
		P_e	5.092	3.352	5.479	3.461	6.381	3.950	2.784	4.457
		RMSE	2.344	1.279	2.748	1.176	3.365	1.785	0.758	2.470
GAB	0.20–0.98	K	0.731	0.650	0.752	0.710	0.792	0.780	0.650	0.690
		C	26,836	18,742	20,000	23,589	20,000	21,417	2500	16,739
		M_0	7.565	9.954	7.100	8.430	7.435	7.650	9.403	9.350
		R^2	0.988	0.999	0.986	0.997	0.977	0.991	0.994	0.996
		P_e	7.606	1.761	8.328	2.928	9.056	12.107	3.597	14.497
		RMSE	2.657	0.312	3.131	0.649	2.591	7.573	0.806	7.553
Peleg	0.20–0.98	a	11.358	10.214	17.751	16.158	20.072	21.631	18.433	20.076
		b	0.086	4.429	4.680	0.321	0.650	0.478	0.356	0.361
		c	16.826	17.427	11.043	12.380	13.145	11.386	9.382	6.948
		d	4.477	0.283	0.103	5.282	8.070	8.686	7.737	4.508
		R^2	1.000	0.999	0.997	0.998	0.996	0.999	0.999	0.999
		P_e	0.953	1.231	2.588	1.880	3.756	1.542	1.225	0.871
		RMSE	0.223	0.190	0.552	0.356	1.010	0.429	0.235	0.105

A: Absorption, D: Desorption.

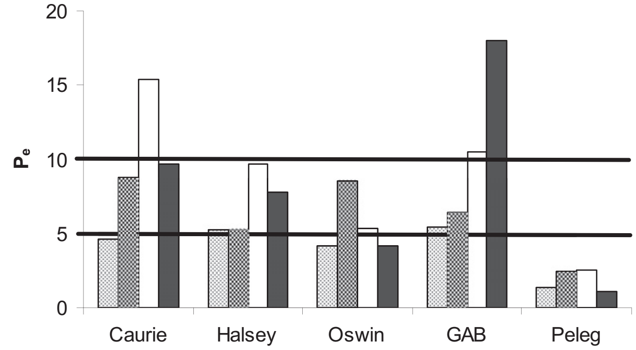

Fig. 5. Suitability comparison of two-, three- and four-parameter equations for fitting to rice isotherms (▨: rough rice; ▩: brown rice; □: white rice; ■: husk).

fits. Except Caurie and GAB equations, sorption isotherms of WR can be adequately described by Halsey, Oswin and Peleg equations. All of the two-parameter equations were suitable for rice husk, whereas the four-parameter equation, namely the Peleg equation, gave good/excellent fit. Among the selected equations, Peleg equation gave the best fit for all forms of rice. Fig. 6 shows the experimental and Peleg-equation-predicted absorption isotherms for RR and WR for M206 variety. It is seen that the prediction and experimental curves almost overlapped implying a perfect prediction. Similar patterns were also observed for experimental and prediction curves for both BR and Husk of both M202 and M206 varieties.

The GAB equation is an extension of the two-parameter (M_0, C) BET model, taking into account the modified properties of the sorbate in the multilayer region through the introduction of a third parameter, namely K. Most of the K values in the literature fall into the narrow range of 0.56–1.00 depending on water activity range and temperature (Chirife, Timmermann, Iglesias, & Boquet, 1992). Furthermore, the values of K for the various starchy materials, such as rice, fall into a narrower range of 0.65–0.75 (Chirife et al., 1992; Gencturk et al., 1986; Timmermann, Chirife, & Iglesias, 2001). In this study, the K values of different forms of M202 and M206 fell into the range of 0.650–0.793 (Tables 2 and 3). The monolayer moisture content (M_0) is a vital data for storage with minimum quality loss for a maximum period of time. On the average M_0 calculated by Caurie equation were 30% higher than did by GAB equation for all forms of both varieties. GAB and Caurie M_0 of different forms of M206 was higher than M202, except during the desorption of white rice computed with GAB. Cogburn (1985) and Genkawa, Uchino, Inoue, Tanaka, and Hamanaka (2008) stated that to be able to store rice over 3 months, rough and brown rice should be dried to moisture contents lower than 12 and 11 (g/100 g dry matter), respectively, which are slightly over the M_0 values found by GAB and Caurie equations (Tables 2 and 3). Therefore it can be expected that different forms of M202 and M206 could have a long shelf-life without compromising the quality if they are dried to a moisture content, computed from the average GAB and Caurie M_0 values.

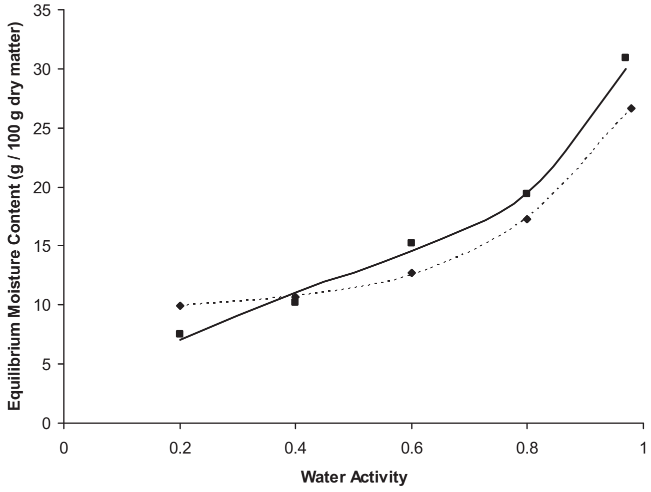

Fig. 6. Experimental and predicted (Peleg equation) absorption isotherms of M206 variety (◆: RR experimental data; dashed line: model prediction for RR; ■: WR experimental data; solid line: model prediction for WR).

4. Conclusions

Different forms of M202 and M206 exhibited Type II isotherms. Hysteresis was observed for all forms of rice. At 25 °C the equilibrium moisture content increased with an increase in water activity. For all forms of M202 and M206, the four-parameter Peleg model gave the best fit to the experimental sorption data at a water activity range of 0.20–0.98. All of the studied models gave suitable fits for rough and brown rice. The equilibrium moisture contents found with DVS method well agreed with the traditional SSS method except in water activity range of 0.40–0.80 for rough and brown rice whereas for white rice as the water activity increased the agreement of two methods increased. The knowledge of the equilibrium moisture contents of different forms of M202 and M206 could allow rice processors to determine the optimum processing, storage and transportation conditions.

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