

EQUILIBRIUM MOISTURE CONTENTS OF PURELINE, HYBRID, AND PARBOILED RICE

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ABSTRACT. *Equilibrium moisture contents of long- and medium-grain rough rice of both pureline and hybrid cultivars, and a parboiled rough rice of unknown cultivar, were measured in a near-static air environment at five temperatures (10°C, 20°C, 30°C, 45°C, and 60°C) and relative humidities in the range of 10% to 70% using a gravimetric method. Results showed that there were no consistent significant differences between the equilibrium moisture contents of pureline and hybrid or medium- and long-grain rice cultivars. However, the equilibrium moisture content of parboiled rice was significantly less than that of non-parboiled rice for almost all air conditions. Nonlinear regression analysis was used to estimate empirical constants of five models used for describing grain sorption isotherms. The appropriateness of each model in describing the equilibrium data was evaluated using root mean square errors and residual patterns. The modified Chung-Pfost equation best described equilibrium data of non-parboiled samples, followed by the modified GAB, modified Oswin, modified Halsey, and modified Henderson equations. The modified Chung-Pfost and modified GAB equations were equally effective when describing equilibrium data of individual cultivars.*

Keywords. *Equilibrium moisture content, Isotherms, Parboiled, Sorption.*

In the mid-south U.S. rice-producing region, the moisture content (MC) of rough rice at harvest usually ranges between 15% and 24% (all moisture contents are expressed on a wet basis unless specified otherwise). To minimize respiration and growth of undesirable micro-organisms, the MC of harvested rice must be reduced to less than 13%. Drying is accomplished in either on-farm systems, where rough rice is aerated in bins for extended periods using ambient air, or in commercial drying systems, which utilize elevated temperatures (Inprasit and Noomhorm, 2001). For safe long-term storage, rough rice is stored in an environment where MC and temperature are controlled to prevent deterioration (Sun and Byrne, 1998). Rewetting can occur during storage, especially near the ventilation inlet, leading to growth of undesirable micro-organisms that cause reduction in quality, including yellowing and odor development (Labuza, 1975). The control of MC and temperature during storage of rough rice is, therefore, very important (Sun and Byrne, 1998).

Equilibrium moisture content (EMC), defined as the moisture content at which rice kernels are neither gaining nor losing moisture, depends on the temperature and relative humidity (RH) of the air surrounding the kernels. A thorough knowledge of the relationship between EMC and equilibrium

relative humidity (ERH) at a given temperature is required to facilitate proper modeling and optimization of rough rice drying and aeration processes (Sun and Woods, 1997a, 1997b).

Mathematical models are vital in describing EMC/ERH/temperature relationships for various agricultural products and are frequently used in drying and aeration applications (Iguaz and Versada, 2007; Aviara et al., 2004, 2006; Basunia and Abe, 2001; Sun and Byrne, 1998; Sun and Woods, 1994; Chen and Morey, 1989). Models are used to describe: (1) the thermodynamic properties of air, (2) heat and mass transfer between grain and air, and (3) the equilibrium state between grain and air. ASABE Standard D245.6 (*ASABE Standards*, 2007) lists the modified Chung-Pfost, modified Halsey, modified Henderson, and modified Oswin equations as models that can be used for describing grain sorption data (table 1). In addition, the modified GAB equation (Jayas and Mazza, 1993) has been successfully used to describe equilibrium data of agricultural materials (Aviara et al., 2004, 2006) and has also been recommended for modeling grain sorption data (Iguaz and Versada, 2007; Multon, 1998; Van der Berg, 1984; Weisner, 1985; Speiss and Wolf, 1987).

However, no single equation has been found that can satisfactorily describe EMC/ERH/temperature relationships for different grains over a wide range of temperatures and RHs (Sun and Woods, 1994). Significant variations in EMCs result from differences in cultivar, kernel dimensions, chemical composition, and pre-drying treatments. For example, the long-grain rice cultivar Lemont was found to have greater EMC compared to the long-grain cultivar Newbonnet for the same air conditions, while the medium-grain cultivar Bengal was found to have greater EMC compared to the long-grain cultivars Kaybonnet and Cypress at all experimental temperatures (Lu and Siebenmorgen, 1992). Parboiled rice was shown to have lesser EMC compared to non-parboiled rough rice (Reddy and Chakraverty, 2004). Differences in EMCs

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Table 1. Equilibrium models used for describing grain sorption data.

Name	Equation ^[a]
Modified Henderson ^[b]	$MC_{d.b.} = \left[\frac{\ln(1 - RH)}{(-A)(T + B)} \right]^{\frac{1}{C}}$
Modified Chung-Pfost ^[b]	$MC_{d.b.} = \frac{-1}{C} \ln \left[\frac{-(T + B) \ln RH}{A} \right]$
Modified Oswin ^[b]	$MC_{d.b.} = (A + B \cdot T) \left[\frac{1 - RH}{RH} \right]^{\frac{-1}{C}}$
Modified Halsey ^[b]	$MC_{d.b.} = \left[-\frac{\exp(A + B \cdot T)}{(\ln RH)} \right]^{\frac{1}{C}}$
Modified GAB ^[c]	$MC_{d.b.} = \frac{A \cdot B \cdot \left(\frac{C}{T} \right) \cdot RH}{(1 - B \cdot RH) \left[1 - B \cdot RH + \left(\frac{C}{T} \right) \cdot B \cdot RH \right]}$

^[a] $MC_{d.b.}$ is equilibrium moisture content expressed on a dry basis; RH is relative humidity expressed as a decimal; T is temperature ($^{\circ}C$); and A , B , and C are grain-specific empirical constants.

^[b] Listed ASABE Standard D245.6 (*ASABE Standards*, 2007).

^[c] Described by Jayas and Mazza (1993).

between cultivars were reportedly more prominent at RHs greater than 40% (Fan et al., 2000). At high RH, cultivars with high amylopectin/amylose ratios (waxy rice) have been reported to have greater EMCs than cultivars with high amylose/amylopectin (non-waxy rice) ratios (Juliano, 1964); amylopectin is more hygroscopic than amylose and thus retains more moisture (Wolff et al., 1951). In addition to chemical composition, variations in EMCs of rice samples from the same cultivar grown during different years have been attributed to physical properties of starch in the endosperm, which is reportedly influenced by ambient temperatures during the kernel filling stage (Halick, 1961; Suzuki et al., 1963).

To improve the robustness of models describing EMC, empirical constants need to be estimated from data collected over a wide range of temperatures and RHs and for different rice cultivars and conditioning treatments (Iguaz and Versada, 2007; Basunia and Abe, 2001; Sun and Byrne, 1998; Sun and Woods, 1994; Chen and Morey, 1989; Chirife and Iglesias, 1978). Therefore, the objectives of this study were to: (1) measure the EMC of long- and medium-grain rough rice of commonly-grown pureline and hybrid cultivars, and parboiled rice of unknown cultivar, at different air temperatures ($10^{\circ}C$, $20^{\circ}C$, $30^{\circ}C$, $45^{\circ}C$, and $60^{\circ}C$) and RHs in the range of 10% to 70%, (2) estimate the empirical constants of five isotherm models (table 1) from the experimental data using nonlinear regression analysis, and (3) evaluate the suitability of each model for describing EMC data of rough rice for the range of temperatures and RHs studied.

MATERIALS AND METHODS

SAMPLE COLLECTION AND PREPARATION

Long- and medium-grain pureline cultivars (Wells and Jupiter, respectively) and a hybrid long-grain cultivar (CLXL730) were harvested in Arkansas in the fall of 2007 at MCs ranging from 17% to 24%. In the spring of 2008, a long-

grain parboiled rough rice of unknown cultivar was obtained from Riceland Foods, Jonesboro, Arkansas, at 29% MC. All samples were cleaned (MC Kicker Grain Tester, Mid-Continent Industries, Inc., Newton, Kans.) and dried to MCs ranging from 11.6% to 12.8% on screens held in an environment where temperature and RH were maintained by an air control unit (model AA-558, Parameter Generation & Control, Inc., Black Mountain, N.C.) at $25^{\circ}C$ and 56%, respectively. The samples were stored in sealed plastic tubs ($0.22 m^3$) at $4^{\circ}C$ for four months. Before the EMC experiments, approximately 30 g of rough rice was obtained from each bulk sample and MC was determined by drying duplicate 15 g subsamples for 24 h in a convection oven (Shellblue, Sheldon Mfg., Inc., Cornelius, Ore.) held at $130^{\circ}C$ (Jindal and Siebenmorgen, 1987).

EQUILIBRIUM APPARATUS

A schematic of the system used to conduct the EMC experiments is shown in figure 1. The apparatus consisted of a 900 L oven (ESL 4CA Platinum Temperature and Humidity Chamber, Espec, Hudson, Mich.) capable of automatically maintaining temperature in the range of $-35^{\circ}C$ to $150^{\circ}C$ ($\pm 0.5^{\circ}C$) and RH in the range of 6% to 98% ($\pm 1\%$). The instrumentation that controls temperature and RH are built into the system; hence, desired conditions can be changed via the control panel. The air in the oven was circulated at $0.38 m^3 s^{-1}$, and conditions were monitored using a digital temperature and RH probe (Hygro-M2, General Eastern, Woburn, Mass.). The probe was calibrated using potassium sulfate, sodium chloride, and lithium chloride solutions (Merck, Darmstadt, Germany) prior to the start of the experiments.

A weighing and data collection system, separate from the automated temperature and RH oven, was constructed in-house and installed in the oven chamber. It consisted of 19 thin-beam, full-bridge load cells (LCL-227G, Omega Engineering, Inc., Stamford, Conn.), each with a capacity of 227 g, which were mounted 10 cm apart on aluminum bars attached to a 3.8 cm thick laminated plywood frame. Each load cell was connected to a data logger (CR3000 Micrologger, Campbell Scientific, Logan, Utah). The load cells were calibrated using standard masses (Fisher Scientific, Pittsburgh, Pa.) that ranged from 1 to 50 g. Rice samples spread in square baskets ($8.9 cm \times 8.9 cm \times 2.9 cm$ high) fabricated from 6.4 mm welded-wire mesh (4 mesh per 2.5 cm) were suspended on the load cells using 0.67 mm (gauge 23) wires. The baskets were lined with brass wire mesh (80 openings per 2.5 cm, 1.4 mm wire dia.). Loggernet software (version 3.3.1, Campbell Scientific, Logan, Utah) was used to record digital signals from the load cells and the temperature and RH probe at 5 min intervals.

At the start of each experiment, the baskets containing the rice samples were placed inside an open-top box ($54.6 cm \times 54.6 cm \times 25 cm$ high) made from 1.25 cm thick plywood. Once the samples were loaded into the baskets and suspended, a linear actuator (LACT12P, IEI, Taiwan), connected to the open-top box via a cable, was activated to raise the box. In the elevated position, the laminated plywood frame from which the load cells were suspended served as the top cover of the box, forming a tight seal, and thereby enclosing the baskets to prevent inadvertent loss of moisture during the oven stabilization period. When the desired temperature and RH were attained, the box was lowered to expose the samples contained in the baskets.

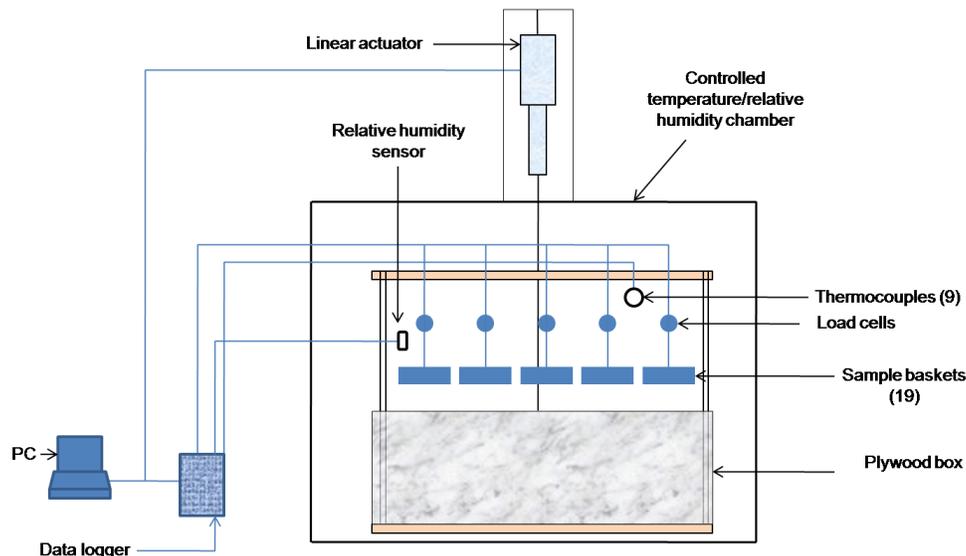


Figure 1. Schematic of the system used to conduct equilibrium moisture content experiments.

EQUILIBRIUM MOISTURE CONTENT DETERMINATION

Equilibrium moisture contents of all samples were determined at temperatures of 10°C, 20°C, 30°C, 45°C, and 60°C and 10% to 70% RH. Samples (15 g) from each rice lot were conditioned in each sample basket per run. The samples and baskets were weighed every 5 min until the change in mass was less than 0.01 g. The average duration required to reach equilibrium varied from 10 to 35 days, depending on the temperature and RH. The final MCs of the samples were determined using the oven method previously described (Jindal and Siebenmorgen, 1987) and were defined as the EMCs for a given temperature and RH. Each experiment was replicated.

STATISTICAL ANALYSIS

The experimental variables included rice cultivar (pureline and hybrid), cultivar type (medium-grain and long-grain), processing treatment (parboiled and non-parboiled), and air conditions (temperature and RH). The main effects of all variables on EMC were determined using ANOVA (JMP 8.0.1, SAS Institute, Inc., Cary, N.C.). Significance was established at $\alpha = 0.05$ unless otherwise specified. The empirical constants (A , B , and C in table 1) of the five EMC models evaluated were estimated from the experimental data using the nonlinear regression analysis platform in JMP (JMP 8.0.1, SAS Institute, Inc., Cary, N.C.).

RESULTS AND DISCUSSION

EQUILIBRIUM MOISTURE CONTENT

The EMC data are presented in table 2 as averages of four values, i.e., two replicated EMC measurements, with each measurement comprising two oven-MC duplicates. Greater EMCs were observed at greater RHs for the same temperature, and lesser EMCs were observed at greater temperatures for the same RH, as expected. Equilibrium isotherms are shown in figure 2, where effects of temperature and RH are indicated. The equilibrium data for non-parboiled rice samples (averaged across cultivars Jupiter, Wells, and CLXL730) from the present study were comparable to EMCs obtained

for the same air conditions in previous studies by Iguaz and Versada (2007) and Putranon et al. (1979) (fig. 3).

EFFECT OF CULTIVAR AND PROCESSING

Differences in EMCs for the medium-grain cultivar Jupiter compared to the long-grain cultivars Wells and CLXL730 were mostly non-significant ($p > 0.05$). There were no consistent significant differences ($p > 0.05$) between the EMCs of pureline (Wells) and hybrid (CLXL730) cultivars. However, the EMC of parboiled rice was significantly less ($p < 0.05$) than that of non-parboiled rice for almost all temperature and RH conditions (table 2). Similar results have been reported by Reddy and Chakraverty (2004) and Houston and Kester (1954). The lesser EMCs observed for the parboiled rice may be attributed to the presence of retrograded gelatinized starch that has less water-holding capacity compared to unaltered starch (Lamberts et al., 2006).

ESTIMATION OF EMPIRICAL CONSTANTS AND EVALUATION OF ISOTHERM MODELS

Empirical constants A , B , and C of the EMC equations listed in table 1 were estimated from the experimental data using nonlinear regression analysis. The suitability of the equations was evaluated using the root mean square error (RMSE). In addition, residual patterns were considered as qualitative criteria in evaluating the appropriateness of these models (Chia-Chung, 2001; Aviara et al., 2004).

Estimates of parameters A , B , and C of the EMC equations, and the indices used to evaluate these models, are shown in table 3. Based on minimizing RMSE, for temperatures ranging from 10°C to 60°C and RHs from 10% to 70%, the modified Chung-Pfost equation was the best model for describing equilibrium data of non-parboiled rice samples, followed by the modified GAB, modified Oswin, modified Halsey, and modified Henderson equations. However, the modified Chung-Pfost and modified GAB equations gave nearly identical RMSE values (< 0.80) that were superior to the other three EMC models when describing EMC data of individual cultivars, suggesting that both models were appropriate on an individual-cultivar basis. The residual plots

Table 2. Equilibrium moisture contents (EMCs) of pureline cultivars Jupiter and Wells, hybrid cultivar CLXL730, and parboiled rough rice of unknown cultivar exposed to temperatures from 10 °C to 60 °C and relative humidities from 9% to 72%. Each value is an average of four measurements, i.e., two EMC replications with each replicate moisture content being duplicated using an oven procedure. For each temperature and relative humidity combination, values across individual rows followed by the same lowercase letter are not significantly different.

Air Temperature (°C)	Relative Humidity (%)	Equilibrium Moisture Content (% wet basis) ^[a]			
		Parboiled (long grain) (MC _i = 12.8%)	Jupiter (medium grain) (MC _i = 12.1%)	Wells (long grain) (MC _i = 11.8%)	CLXL730 (long grain) (MC _i = 11.6%)
10.0	10.2	6.7 b	8.5 a	8.0 a	8.2 a
10.0	17.3	7.3 b	9.0 a	8.6 a	9.1 a
10.0	28.2	8.4 b	10.0 a	9.7 a	10.9 a
10.0	49.4	10.4 b	11.7 a	11.3 a	12.4 a
10.0	68.5	12.8 a	13.6 a ^[b]	13.0 a ^[b]	13.0 a ^[b]
20.3	9.7	6.6 b	7.2 b	7.4 b	7.3 b
20.1	18.3	7.0 b	7.2 b	8.0 a	8.1 a
20.1	28.5	8.4 b	8.8 b	9.3 a	9.6 a
20.7	49.8	11.3 b	11.8 a	12.3 a	12.4 a
19.8	69.8	12.4 b	13.8 a	13.6 a ^[b]	13.5 a ^[b]
30.0	10.1	4.6 b	5.5 a	5.3 a	4.8 a
30.2	19.2	6.7 b	7.6 a	7.8 a	7.6 a
30.0	28.9	6.9 b	8.2 a	8.1 a	8.3 a
30.0	50.3	9.7 b	10.2 a	10.3 a	10.4 a
29.9	69.1	12.3 a	12.9 a ^[b]	12.7 a ^[b]	12.9 a ^[b]
45.0	10.0	3.9 b	4.9 a	4.7 a	4.4 b
46.1	18.7	4.6 b	5.8 a	5.7 a	5.4 a
45.1	30.2	6.6 b	7.4 a	7.6 a	7.4 a
45.3	50.0	8.7 b	9.6 a	9.6 a	9.7 a
44.7	71.8	11.3 b	11.8 a	11.7 a	11.6 a
60.0	10.3	2.8 b	4.0 a	3.7 a	3.6 a
60.1	20.0	4.7 b	5.6 a	6.1 a	5.6 a
60.2	29.6	5.1 b	6.4 a	6.2 a	6.7 a
60.4	49.6	8.1 b	8.6 a	8.6 a	8.5 a
59.9	71.6	9.1 b	10.5 a	10.6 a	10.8 a

^[a] MC_i is the initial sample moisture content.

^[b] Adsorption equilibrium moisture content.

of the modified Chung-Pfost and modified GAB equations followed random patterns and were deemed acceptable from this criterion. Several studies have reported similar observations. Iguaz and Versada (2007) reported the modified GAB and modified Chung-Pfost equations to be most appropriate in describing EMC of rough rice at temperatures ranging from 40 °C to 80 °C. Basunia and Abe (2001) reported the modified Chung-Pfost equation as best in the range of 12 °C to 51 °C. Sun (1999) identified the modified Chung-Pfost as most appropriate for describing EMC/ERH sorption isotherms of wheat, shelled corn, rice, and rapeseed. Jayas and

Mazza (1993) reported the modified Chung-Pfost equation as the best for describing EMC data of oats at 10 °C to 55 °C.

Sorption isotherms of non-parboiled and parboiled rough rice, determined by the modified Chung-Pfost equation with statistically estimated *A*, *B*, and *C* values, are shown in figures 4a and 4b, respectively. The EMCs of parboiled rice samples were generally one percentage point less than those of non-parboiled rice samples for almost all experimental air conditions. For example, at 60 °C and 10% RH, the average EMC of non-parboiled rice samples was 3.8%, while that of parboiled samples was 2.8%.

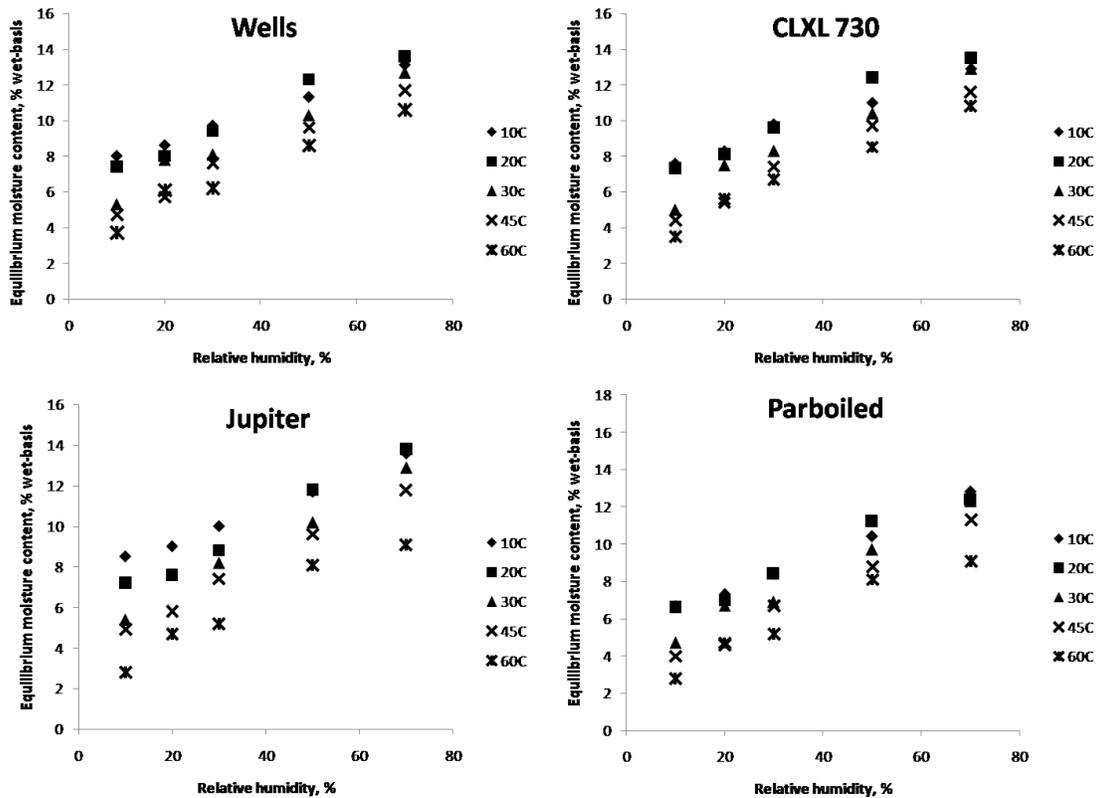


Figure 2. Equilibrium data of long-grains Wells (pureline) and CLXL730 (hybrid), medium-grain Jupiter (pureline), and parboiled rice of unknown cultivar exposed to temperatures ranging from 10°C to 60°C and relative humidities from 10% to 70%. Equilibrium data are expressed on a wet basis.

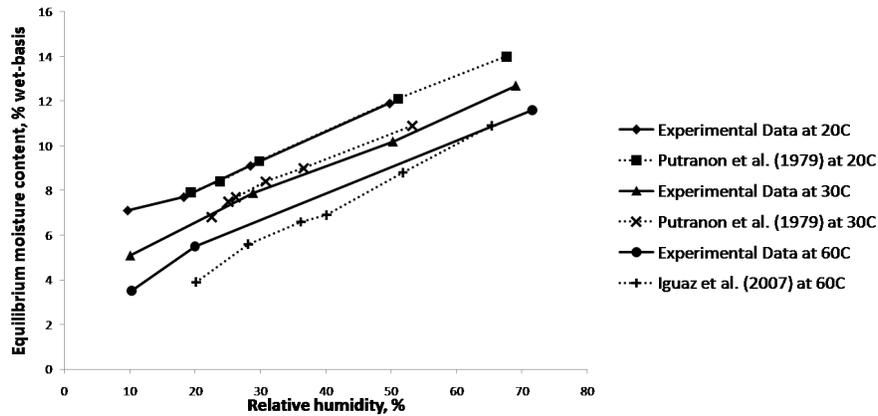


Figure 3. Equilibrium data for non-parboiled rice samples (averaged across cultivars Jupiter, Wells, and CLXL730) from the present study compared to data from Iguaz and Versada (2007) and Putranon et al. (1979) for temperatures ranging from 10°C to 60°C. Equilibrium data are expressed on a wet basis.

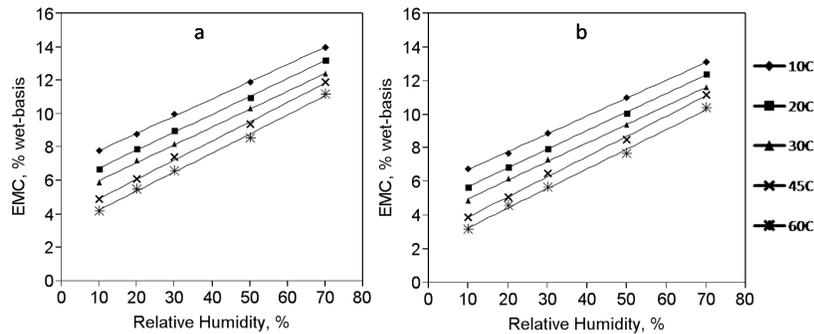


Figure 4. Equilibrium isotherms (expressed on a wet basis) predicted by the modified Chung-Pfost equation. The isotherm predictions are based on model constants *A*, *B*, and *C* listed in table 3 for (a) non-parboiled rough rice (pooled Jupiter, Wells, and CLXL730 cultivars) and (b) parboiled rough rice.

Table 3. Estimated coefficients of the modified Chung-Pfost (MCP), modified Henderson (MH), modified Oswin (MO), modified Guggenheim Anderson DeBoer (MGAB), and modified Halsey (MHa) equations, and the statistical parameters used to evaluate the models.

Rice Lot	Model	Estimated Model Constants ^[a]			Statistical Coefficients	
		A	B	C	RMSE	Residual Plot Pattern
Pureline (medium grain) Jupiter	MCP	475.1747	16.9175	0.2336	0.464	Random
	MH	1.1784×10^{-4}	12.4788	2.9563	0.772	Random
	MO	14.684	-0.0978	3.8320	0.657	Random
	MGAB	11.7793	0.3828	590.3383	0.704	Random
	MHa	6.3369	-0.0221	2.4937	0.702	Random
Hybrid (long grain) CLXL730	MCP	501.7992	23.6330	0.2279	0.736	Random
	MH	1.2454×10^{-4}	19.7259	2.8692	0.948	Random
	MO	14.2852	-0.0886	3.7527	0.862	Random
	MGAB	11.2528	0.4134	587.7960	0.724	Random
	MHa	6.1548	-0.0196	2.4594	0.995	Trend
Pureline (long grain) Wells	MCP	519.4373	20.6428	0.2355	0.655	Random
	MH	1.0296×10^{-4}	16.4011	2.9766	0.883	Random
	MO	14.3952	-0.0912	3.8826	0.772	Random
	MGAB	11.3953	0.3947	629.1636	0.726	Random
	MHa	6.3821	-0.0208	2.5348	0.877	Trend
Pureline and hybrid (long grains) CLXL730 and Wells	MCP	511.7649	22.1226	0.2316	0.942	Random
	MH	1.135×10^{-4}	18.0306	2.9219	0.889	Random
	MO	14.3406	-0.0899	3.8166	0.794	Trend
	MGAB	11.3237	0.4042	607.7889	0.703	Random
	MHa	6.2669	-0.0201	2.4966	0.909	Trend
Non-parboiled rice (all of the above lots pooled)	MCP	498.9584	20.3125	0.2322	0.611	Random
	MH	1.1518×10^{-4}	16.0667	2.9326	0.841	Random
	MO	14.455	-0.0925	3.8219	0.740	Random
	MGAB	11.4659	0.3975	601.7981	0.691	Random
	MHa	6.2906	-0.0208	2.4958	0.835	Random
Parboiled	MCP	406.902	23.6172	0.2303	0.684	Random
	MH	3.4322×10^{-4}	19.5649	2.5603	0.879	Random
	MO	13.2783	-0.0908	3.3586	0.735	Random
	MGAB	10.1469	0.4599	443.9290	0.811	Random
	MHa	5.3244	-0.0198	2.2059	0.849	Random

^[a] To estimate coefficients A, B, and C, the equilibrium data from this study were first converted from wet (w.b.) to dry basis (d.b.) using the following formula: $MC_{d.b.} = (100 \times MC_{w.b.}) / (100 - MC_{w.b.})$. As such, the coefficients in this table can be used in conjunction with the models in table 1 to yield EMCs expressed on a dry basis:

CONCLUSION

Measuring the rough rice EMCs of long- and medium-grain pureline cultivars Wells and Jupiter, respectively, hybrid long-grain cultivar CLXL730, and parboiled rice of an unknown cultivar revealed that the EMC of parboiled rough rice was generally one percentage point less than that of non-parboiled rough rice for all experimental air conditions. There were no consistent significant differences in EMCs of long- and medium-grain or pureline and hybrid cultivars at any given air condition. Of the five EMC models investigated, the modified Chung-Pfost equation best described the experimental EMC data, although the modified GAB equation was similar in accuracy to the modified Chung-Pfost when describing EMC data of individual cultivars.

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