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Research Article

The Hygroscopic Properties and Sorption Isosteric Heat of Coix Seeds

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Abstract: Coix seeds are one of the most difficult-to-store cereal foods, and in order to maintain their quality during storage, the present study was conducted to determine the moisture adsorption and desorption isotherms of five varieties of coix seeds in the ranges of 10-35 °C and 11.3%-96.0% equilibrium relative humidity (ERH) using a static gravimetric method. The isotherms showed sigmoidal curves, and there was a hysteresis between adsorption and desorption isotherms. Six equilibrium moisture equations were used to fit the isotherms, and the Modified Chung-Pfost (MCPE), Modified Guggenheim-Anderson-deBoer (MGAB), Modified Henderson (MHE), Modified Oswin (MOE) and our developed modified Caurie (MCaurie) equations were suitable for fitting the data, among which MCPE was the best fitting equation. The monolayer water content decreased with increasing temperature, and the content of monolayer water, the density and layer number of adsorbed water, and the content of bound water for desorption were significantly higher than those of adsorption. The absolutely (ERH 65%) and relatively (ERH 70%) safe moisture contents (MC, wet basis, w.b.) of coix seeds were respectively 12.45%-12.82% and 13.15%-13.69% at 25 ℃. At equilibrium moisture content (EMC) less than 14.9% w.b., the desorption isosteric heats of coix seed were greater than the adsorption isosteric heats, and both decreased sharply in a hyperbolic form, approaching the latent heat of pure water at 14.9% w.b. The sorption isosteric heat of large-grain coix seed was slightly less than that of small-grain seed due to more cracks in the kernel back surface and more micropores in starch granular surface and resultantly more moisture sorption capacity. These results suggest that the desorptive and adsorptive behaviors of coix seeds should be differentiated for cooldown aeration, demoisturizing and remoisturizing operation, and the average isotherm can be used for common storage management.

***Keywords*:** coix seeds, hygroscopic properties, adsorption isotherm, sorbed water density, MCaurie equation

1. Introduction

Coix seed (*Coix lachrymajobi* L.), also known as adlay millet, bodhi beads, grass beads, and Job's tears, native to Southeast Asia, is widely planted in China, Japan, Korea and India [1]. It is a conventional crop and an annual gramineae plant that has been cultivated for over 6,000 years in China based on archaeological evidence [2]. Coix seed is an excellent medicinal and edible cash crop, known as the "King of the world's Gramineae Plant", with anti-oxidation, anti-tumor, hypoglycemic, analgesic and hemostatic effects [3-4]. It is not only rich in nutrients, but also

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contains esters, sterols, phenols, polysaccharides and other pharmacodynamic components, and confirmed by clinical pharmacological studies [1]. Coix seed is often used as a single agent because it has its specific constituents coixenolide and coixol [5]. It contains 17.8% protein, 52.16% starch, 7.76% fat and 2.62% ash, with 80.7% unsaturated fatty acids in total fatty acids content [1, 6-7]. China has 61,000-hectare of planting area for coix seed in recent years, and the annual production exceeds 0.5 million tons with an annual consumption is about 1 million tons [8]. The research on the storage conditions of coix seeds is being paid attention to due to the increasing their production. The quality of coix seed is easy to change in the storage process, such as easily broken, insect damage, and showing a rancidity taste, which have a serious impact on the storage quality and processing quality [9-10]. The main reason for this is the lack of research on coix seed's hygroscopic properties.

Equilibrium moisture isotherms are very important for designing drying operation models and equipment, predicting the shelf life of food and grains, selecting suitable storage conditions and packaging materials, and calculating thermodynamic parameters such as enthalpy and entropy [11-12]. The equilibrium moisture equations of staple cereals and oils have been evaluated in recent twenty years and are being gradually used for smart mechanical aeration design of different purposes like cooldowning, remoisturizing and demoisturizing aeration [13-14]. In this study, the adsorption and desorption equilibrium moisture isotherms of coix seed were determined to provide guidance for its reasonable drying, safe storage and packaging, and examine how changes in storage conditions influence quality parameters, and evaluate the importance of optimizing storage environments for preserving coix seed quality and extending shelf life.

2. Materials and methods

2.1 *Sample preparation and EMC determination*

Table 1. The samples in this study

No.	Species	Producing region	Initial MC (% w.b.)	
			Adsorption sample	Desorption sample
1	Xingren	Guizhou, China	6.06	20.46
2	Large-grain	Guizhou, China	3.63	16.81
3	Large-grain	Guizhou, China	7.17	21.27
4	Organic	Guizhou, China	3.53	16.16
5	Small-grain	Guizhou, China	6.65	20.20

The adsorption and desorption isotherms of coix seed were determined by static gravimetric method with saturated salt solutions for humidity control according to our previous study [15]. For adsorbed samples (Table 1), the initial samples were dehydrated to less 7.5% on wet basis (w.b.) moisture content (MC) with P_2O_5 solid at 35 °C. For the desorption samples, the initial samples were rehydrated to 16%-21% w.b. MC and stored at 4 °C for 2 weeks with mixing once a day. Nine saturated salt solutions were used to generate constant vapor pressures at five constant temperatures (10 °C, 20 °C, 25 °C, 30 °C and 35 °C). The equilibrium relative humidity of these nine saturated salts at different temperatures was shown in Table 2.

The obtained EMC/ERH data were used to make isotherm curves in Kaleidgraph for Windows version 4.54 software [16] with horizontal coordinates of equilibrium relative humidity and vertical coordinates of equilibrium water.

Table 2. The equilibrium relative humidity (%) produced by nine saturated salt solutions

Saturated soltion	10 ℃	20 ℃	25 ℃	30 ℃	35 ℃
Lithium choride	11.29	11.31	11.30	11.28	11.25
Potassium acetate	23.38	23.11	22.51	21.61	21.50
Magnesium chloride	33.47	33.07	32.78	32.44	32.05
Potassium carbonate	43.14	43.16	43.16	43.17	43.16
Magnesium nitrate	57.36	54.38	52.89	51.40	49.91
Cupric chloride	68.40	68.30	67.00	66.50	66.00
Sodium chloride	75.67	75.47	75.29	75.09	74.87
Potassium chloride	86.77	85.11	84.34	83.62	82.95
Potassium nitrate	95.96	94.62	93.58	92.31	90.79

Note: The data were cited from Li et al. [17]

2.2 *Determination of the optimal isotherm equations*

The best isotherm equation was determined by fitting the ads/desorption isotherms of coix seeds with the equations in Table 3, and the errors were calculated with the non-linear regression analysis of SPSS v17.0 software [18]. The fitting of the model was evaluated by determining coefficient (R^2), residual sum of squares (*RSS*), standard error (*SE*), mean relative percentage error (*MRE*), and residual distribution plot. R^2 is the basic criterion, *RSS* and *SE* determine the fit. The smaller the *MRE*, the better the model fits [19]. If the residual plot shows a random distribution, the model is better, otherwise, the model is bad when the residual plot has a patterned distribution [15]. The average statistical parameters were compared for the determination of the best sorption equation.

Table 3. The EMC equation used in this study

Model	Formula	Reference
MCPE	$EMC = (1/-C)\cdot\ln\left[\frac{(t+B)\cdot\ln\ (ERH)}{-A}\right]$	ASABE [20]
MGAB	$EMC = [A\cdot B\cdot(C/t)\cdot ERH]/[(1-B\cdot ERH)\cdot(1-B\cdot ERH+B\cdot(C/t)\cdot ERH)]$	Li [21]
MHAE	$EMC = [\exp\ (A+Bt)/-\ln\ (ERH)]^{1/C}$	ASABE [20]
MHE	$EMC = \left[\frac{\ln\ (1-ERH)}{-A\cdot(t+B)}\right]^{1/C}$	ASABE [20]
MOE	$EMC = (A+Bt)/\left(\frac{1}{ERH}-1\right)^{1/C}$	ASABE [20]
MCaurie	$EMC = \frac{(A+Bt)\cdot C_0}{\left(\frac{1}{ERH}-1\right)^{\left(\frac{2C_0}{A+Bt}\right)}}$	This study

Note: MCPE, Modified Chung-Pfost; MGAB, Modified Guggenheim-Anderson-deBoer; MHAE, Modified Halsey; MHE, Modified Henderson; MOE, Modified Oswin; Mcaurie, Modified Caurie; *EMC* is equilibrium moisture content (%d.b.); *ERH* is equilibrium relative humidity, decimal; *t* is temperature (°C). *A*, *B*, *C*, C_0 are equation parameters. MCaurie is our modified form from Caurie equation [22-23], $M_0 = A + Bt$, M_0 is monolayer moisture content (% w.b.), C_0 is adsorbed water density (g/cm^3); *N* is adsorbed water layers, $N = M_0/C_0$; $M_b = M_0 \cdot N$, M_b is the content of bound water or non-frozen water (%). ASABE, American Society of Agricultural and Biological Engineers

2.3 *Determination of monlayer moisture content, adsorbed water density and safe storage moisture content*

The original form of Caurie equation is,

$$EMC = \frac{M_0 \cdot C_0}{\left(\frac{1}{ERH} - 1\right)^{\left(\frac{2C_0}{M_0}\right)}} \tag{1}$$

where M_0 is monolayer moisture content (% w.b.), C_0 is adsorbed water density (g/cm^3). We made: $M_0 = A + Bt$, A and B are constants, t is temperature. The change in monolayer moisture content of coix seeds with temperature can be shown.

The five equations of MCPE, MHAE, MHE, MOE, and MGAB are three-parameter, temperature-dependent and reversible, the absolutely and relatively safe storage moisture content of coix seed were respectively analyzed in this study using MCPE, MGAB and MOE equations when 65% and 70% ERH at 25 °C were adopted.

2.4 *Determination of the isosteric heat of sorption*

MCPE and MOE equations can be used for calculating the isosteric heat of sorption due to easily seeking partial derivatives. The isosteric heat of sorption (h_s) for coix seed was analyzed according to previous reports [24] and calculated with the following equations,

$$\frac{h_s}{h_v} = 1 + \frac{p_s}{RH} \cdot \frac{dt}{dp_s} \cdot \left.\frac{\partial RH}{\partial t}\right|_M \tag{2}$$

$$h_v = 2501.33 - 2.363\ t \tag{3}$$

$$p_s = \frac{6 \times 10^{25}}{(273.15 + t)^5} \cdot \exp\left(-\frac{6800}{t + 273.15}\right) \tag{4}$$

$$\frac{dp_s}{dt} = \frac{p_s}{(t + 273.15)} \cdot \left(\frac{6800}{t + 273.15} - 5\right) \tag{5}$$

$$\left.\frac{\partial RH}{\partial t}\right|_M = \frac{A \cdot RH}{(t + B)^2} \cdot \exp\ (-\ C \cdot M) \tag{6}$$

$$\left.\frac{\partial RH}{\partial T}\right|_M = -\frac{1}{\left\{1 + \left(\frac{A + B \cdot T}{M}\right)^C\right\}^2} \cdot \left\{\frac{B \cdot C}{M}\left(\frac{A + B \cdot T}{M}\right)^{C-1}\right\} \tag{7}$$

where h_s is the isosteric heat of sorption (kJ/kg), h_v is the latent heat of free water vaporization (kJ/kg), p_s is the saturated vapor pressure (Pa), RH is relative humidity (decimal), t is temperature (°C). The h_v in equation (3) is dependent on temperature. A, B and C are the parameters of MCPE or MOE equation, and $\partial RH / \partial t\,|_M$ is related to the EMC equation, with this study adopting the modified Chung-Pfost equation (MCPE; Equation 6) and the modified Oswin equation (MOE; Equation 7).

2.5 *Scanning electron microscopy*

The individual coix seeds were cut and fixed on a sample table with conductive adhesive, and the sample surface was sprayed with gold particles using an ion sputtering (JEC-3,000 FC, Japanese Electronic LTD. Co., Japan). The surface morphology of the samples was observed by scanning electron microscopy (JSM-IT 700 HR, Japanese Electronic LTD. Co., Japan), and the accelerated voltage was 4.0 kV with the magnification of 500, 2,000 and 5,000 times.

2.6 *Statistical analysis*

The results were statistically analyzed using SPSS (version 17.0, [18]). One-way analysis of variance (ANOVA) and independent-sample *t*-tests were used to compare multiple and pairs of means, respectively.

3. Results

3.1 *Experimental moisture ads/desorption isotherms of coix seed*

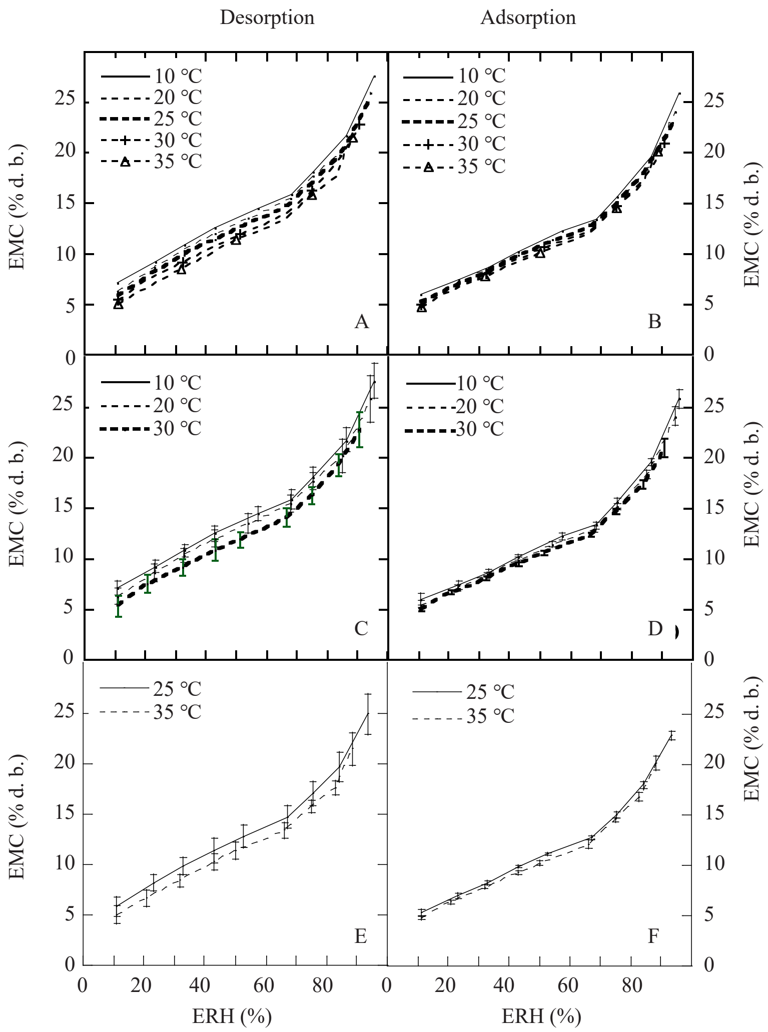
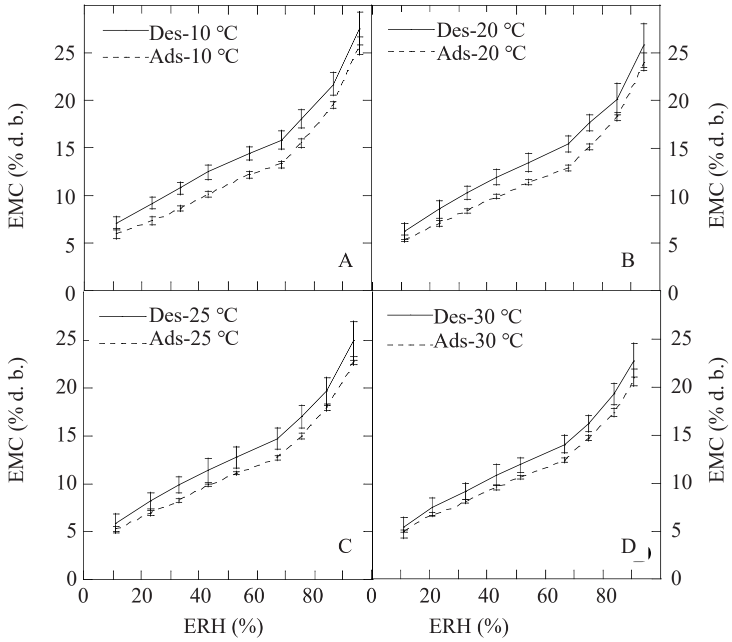


Figure 1. The measured average moisture desorption and adsorption isotherms of coix seeds

Figure 1 shows the average moisture adsorption and desorption isotherms of five coix seed samples at five temperatures. The measured EMC isotherms were influenced by the species and initial moisture content of the samples, and the experimental conditions of temperature and RH combination. The isotherms show a sigmoidal shaped curve with two inflection points respectively around 70% and 85% ERH (Figures 1A and 1B), indicating the glassy phase transition. When the temperature is constant, EMC increases with the increase of ERH, but when the ERH is constant, EMC decreases with the increase of temperature. The difference intervals between desorption isotherms for five temperatures were bigger than those of adsorption isotherms (Figures 1C to 1F). There was a significant hysteresis between the isotherms of adsorption and desorption (Figures 2A to 2D). These results suggest that the species of coix seeds have an insignificant effect on moisture sorption isotherms, but the significant difference between adsorption and desorption isotherms should be separately dealt with when they will be used to regulate the temperature and moisture content of bulk coix seeds during storage.



Note: Des, desorption; Ads, adsorption

Figure 2. The hysteresis between moisture desorption and adsorption isotherms of coix seeds

3.2 *Fitting of sorption equations to experimental sorption data*

The equations like MCPE, MHE, MGAB and MOE were suitable for fitting the moisture adsorption and desorption isotherms of coix seeds in that *MRE* was less than 10% with $R^2 > 0.967$ and random residual distributions (Tables 4-5). MHAE was suitable for adsorption isotherms of five samples due to *MRE* < 9.624%, $R^2 > 0.965$ and random residual distributions, but for the desorption isotherms of samples 2 and 4, *MRE* was greater than 10% and $R^2 < 0.940$, thus it is not suitable for these two samples. The MCaurie equations were suitable for both desorption and adsorption isotherm of coix seeds (Table 6), and the average water density (C_0, g/cm^3) of desorption was significantly higher than that of adsorption.

Table 4. The fitting results of desorption EMC data of coix seed with equations in the form of $M = f(rh, t)$

Equation	Samples	Equation parameters			Statistical parameters			*MRE*/%	Residual plot
		A	*B*	*C*	*RSS*	*SE*	R^2		
MCPE	1	374.162	32.816	0.173	18.7368	0.4461	0.9892	3.6941	*R*
	2	399.744	45.379	0.198	9.5007	0.2262	0.9927	3.5691	*R*
	3	1229.115	141.059	0.183	13.1806	0.3138	0.9912	2.7193	*R*
	4	466.371	44.282	0.197	12.2221	0.291	0.9908	3.3448	*R*
	5	524.455	50.628	0.188	9.1353	0.2175	0.9937	2.5381	*R*
MHAE	1	7.565	-1.28E-02	3.008	84.7296	2.0174	0.9513	9.7312	*R*
	2	6.626	-7.16E-03	2.915	93.7642	2.2325	0.9283	14.2406	*P*
	3	7.299	1.10E-03	3.046	16.3157	0.3885	0.9887	4.4715	*R*
	4	7.329	-1.01E-02	3.073	80.8022	1.9237	0.9393	10.7789	*R*
	5	7.451	-7.60E-03	3.075	75.1303	1.7888	0.9483	9.6066	*R*
MHE	1	4.086E-05	52.423	2.089	40.4134	0.9622	0.9768	6.1359	*R*
	2	5.825E-05	77.515	1.993	14.2435	0.3391	0.9891	4.6659	*R*
	3	1.206E-05	188.112	2.168	32.4627	0.7729	0.9784	5.2381	*R*
	4	4.124E-05	61.706	2.131	16.822	0.3853	0.9879	4.1599	*R*
	5	3.143E-05	71.912	2.144	19.0646	0.4539	0.9869	4.2305	*R*
MGAB	1	8.983	0.7153	448.424	45.6962	1.0881	0.9737	5.6703	*R*
	2	8.131	0.6907	278.341	12.0254	0.2863	0.9908	3.0959	*R*
	3	8.314	0.7288	928.473	17.3033	0.4119	0.9885	3.3468	*R*
	4	8.436	0.6909	399.192	21.3274	0.5078	0.9841	3.6834	*R*
	5	8.561	0.7056	498.692	18.8535	0.4489	0.9871	3.7681	*R*
MOE	1	14.571	-6.81E-02	3.632	38.3548	0.9132	0.9779	5.7908	*R*
	2	11.479	-3.50E-02	3.499	42.9562	1.0227	0.9671	9.2312	*R*
	3	12.979	-6.41E-03	3.711	21.4105	0.5098	0.9858	3.9918	*R*
	4	12.712	-4.66E-02	3.702	34.8744	0.8303	0.9738	6.4197	*R*
	5	13.252	-4.05E-02	3.712	30.2487	0.7202	0.9791	5.5825	*R*

Note: *A*, *B*, and *C* are the equation parameters; R^2, determining coefficient; *RSS*, residual sum of squares; *SE*, standard error; *MRE*, mean relative percentage error; *R*, random distribution; *P*, patterned distribution

Table 5. The fitting results of adsorption EMC data of coix seeds with equations in form of $M = f(rh, t)$

Eqns	Sample	Equation parameters			Statistical parameters				Residual plot
		A	*B*	*C*	*RSS*	*SE*	R^2	*MRE*/%	
MCPE	1	829.544	124.579	0.191	9.6488	0.2297	0.9931	3.0872	*R*
	2	1029.342	167.319	0.199	5.7457	0.1368	0.9954	2.5941	*R*
	3	1229.115	141.059	0.183	13.1806	0.3138	0.9912	3.5209	*R*
	4	1121.322	179.291	0.189	8.0914	0.1927	0.9942	2.6793	*R*
	5	1022.15	147.419	0.204	9.9839	0.2377	0.9918	3.0241	*R*
MHAE	1	6.075	6.96E-04	2.756	41.1087	0.9788	0.9701	8.05	*R*
	2	5.897	5.54E-04	2.741	44.2869	1.0545	0.9651	9.6231	*R*
	3	6.201	-1.20E-04	2.821	34.3514	0.8179	0.9724	6.8797	*R*
	4	6.045	1.43E-03	2.748	42.24	1.0057	0.9696	8.4421	*R*
	5	6.181	1.84E-03	2.845	49.0929	1.1689	0.9595	8.3737	*R*
MHE	1	3.836E-05	166.782	1.899	24.7178	0.5885	0.9821	5.9001	*R*
	2	4.398E-05	168.261	1.881	14.1634	0.3372	0.9889	4.3543	*R*
	3	3.673E-05	152.399	1.961	31.1797	0.7424	0.9749	6.2319	*R*
	4	3.535E-05	182.732	1.897	20.9822	0.4996	0.9849	5.3033	*R*
	5	2.950E-05	200.452	1.962	20.9756	0.4994	0.9827	5.3459	*R*
MGAB	1	6.634	0.7719	804.052	7.8469	0.1869	0.9943	2.7906	*R*
	2	6.449	0.7654	637.909	12.1142	0.2884	0.9905	3.7974	*R*
	3	6.486	0.7684	982.353	9.9653	0.2372	0.9919	3.4039	*R*
	4	6.696	0.7701	760.755	12.4196	0.2957	0.9911	3.9585	*R*
	5	6.594	0.7573	774.088	5.1737	0.1232	0.9957	2.3945	*R*
MOE	1	10.863	-7.71E-03	3.318	12.9932	0.3094	0.9905	3.7576	*R*
	2	10.313	-7.75E-03	3.295	12.2536	0.2918	0.9905	4.5867	*R*
	3	10.755	-9.97E-03	3.403	12.8863	0.3068	0.9896	3.5876	*R*
	4	10.829	-5.05E-03	3.309	11.0639	0.2634	0.9921	3.7767	*R*
	5	10.469	-2.87E-03	3.426	19.7954	0.4713	0.9837	4.3967	*R*

Note: *A*, *B*, and *C* are the equation parameters; R^2, determining coefficient; *RSS*, residual sum of squares; *SE*, standard error; *MRE*, mean relative percentage error; *R*, random distribution; *P*, patterned distribution

Table 6. Mcaurie parameters and statistical parameters

Mcaurie	Samples	Equation parameters			Statistical parameters		Residual plot
		A	*B*	C_0	R^2	*MRE*/%	
Desorption	1	11.692	-8.97E-02	1.349 ± 0.009[a]	0.9887	4.0788	*R*
	2	10.145	-6.74E-02	1.242 ± 0.011[ef]	0.9775	7.4207	*R*
	3	10.414	-2.80E-02	1.316 ± 0.009[b]	0.9882	3.2554	*R*
	4	10.703	-6.37E-02	1.261 ± 0.011[d]	0.9794	5.4128	*R*
	5	10.926	-6.12E-02	1.295 ± 0.009[c]	0.9859	4.4475	*R*
	Des-average	10.778	-6.19E-02	1.293 ± 0.008[c]	0.9891	4.3153	*R*
adsorption	1	9.095	-2.92E-02	1.271 ± 0.006[d]	0.9931	2.9889	*R*
	2	8.616	-1.94E-02	1.242 ± 0.007[ef]	0.9914	4.3825	*R*
	3	9.128	-2.89E-02	1.246 ± 0.006[ef]	0.9921	2.7931	*R*
	4	8.863	-1.91E-02	1.274 ± 0.006[d]	0.9931	3.4629	*R*
	5	9.044	-2.56E-02	1.233 ± 0.009[f]	0.9859	3.7549	*R*
	Ads-average	8.946	-2.44E-02	1.253 ± 0.006[e]	0.9932	3.1496	*R*
	Mean	9.879	-4.37E-02	1.274 ± 0.007[d]	0.9918	3.5955	*R*

Note: Des, desorption; Ads, adsorption. *A*, *B*, and C_0 are the equation parameters; R^2, determining coefficient; *MRE*, mean relative percentage error; *R*, random distribution. For desorption or adsorption samples, the values followed by different superscript letters are significantly different at $p < 0.05$, according to Duncan's multiple range test

3.3 *The best fitting equation for desorption and adsorption behavior of coix seeds*

Table 7. The orders of the adopted equations in form of $M = f(rh, t)$

Equation	Sorption	*RSS*	*SE*	R^2	*MRE*/%	Order
Mcaurie	Desorption	21.78617	0.51873	0.98480	4.82175	3
MCPE	Desorption	11.35598	0.27037	0.99232	2.98513	1
MHE	Desorption	24.60124	0.58268	0.98382	4.88606	4
MOE	Desorption	32.37420	0.77080	0.97758	6.08823	5
MHAE	Desorption	70.33457	1.67462	0.95247	9.77818	6
MGAB	Desorption	21.77850	0.51853	0.98560	3.80637	2
Mcaurie	Adsorption	10.97130	0.26125	0.99147	3.42198	3
MCPE	Adsorption	8.89372	0.21180	0.99342	2.91342	1
MHE	Adsorption	21.95527	0.52275	0.98305	5.40997	5
MOE	Adsorption	13.34958	0.31785	0.98963	3.96713	4
MHAE	Adsorption	41.76288	0.99437	0.96770	8.23542	6
MGAB	Adsorption	9.06127	0.21575	0.99303	3.18895	2

The average values of *RSS*, *SE*, R^2 and *MRE* for the five samples were compared in Table 7. The results show that the equations for desorption were ranked from highest to lowest: MCPE > MGAB > MCaurie > MHE > MOE > MHAE, and for adsorption MCPE > MGAB > MCaurie > MOE > MHE > MHAE. It is considered that MCPE is the best moisture sorption equation of coix seed and can be used to calculate sorption isosteric heat. Table 8 gives the coefficients of MCPE and MOE equations in different forms, the equations for the average of desorption and adsorption data can be used for common storage management.

Table 8. The parameters of better MCPE and MOE equations for coix seeds

Equation form	Types	MCPE parameter			MOE parameter		
		A	*B*	*C*	*A*	*B*	*C*
$M = f(rh, t)$	Desorption	505.437	51.179	0.187	12.998	-3.940E-02	3.652
$M = f(rh, t)$	Adsorption	947.698	142.765	0.197	10.643	-6.570E-03	3.348
$M = f(rh, t)$	Sorption	629.629	77.579	0.192	11.817	-2.276E-03	3.503
$rh = f(M, t)$	Desorption	466.159	44.803	0.188	14.025	-8.257E-02	3.275
$rh = f(M, t)$	Adsorption	989.367	133.7	0.208	11.181	-3.137E-02	3.127
$rh = f(M, t)$	Sorption	607.593	69.002	0.197	12.609	-5.726E-02	3.203
$rh = f(M, t)$	Large grain	932.069	99.363	0.203	12.595	-3.999E-02	3.403
$rh = f(M, t)$	Small grain	617.106	67.499	0.199	12.658	-5.784E-02	3.248

Note: *A*, *B*, and *C* are the equation parameters; Sorption is the average of adsorption and desorption

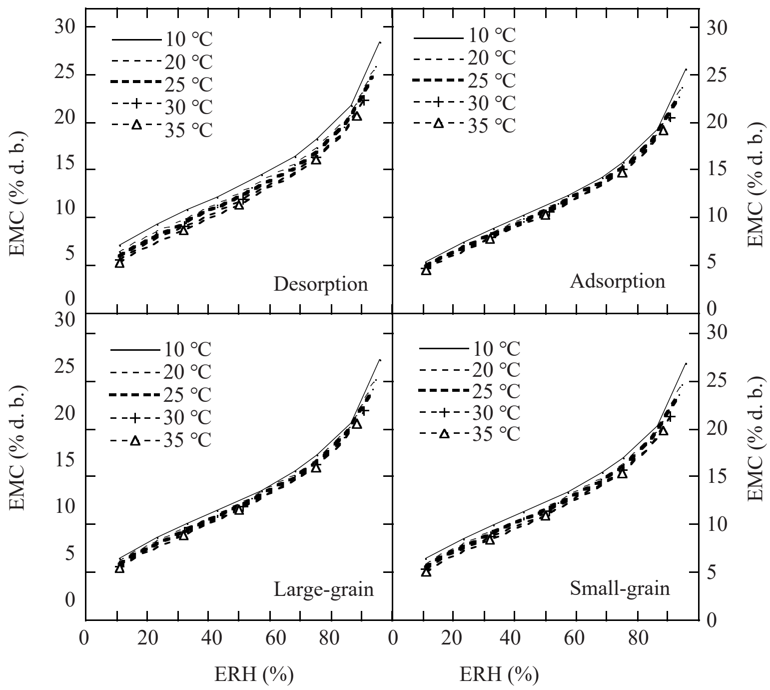


Figure 3. The MCPE-fitted moisture sorption isotherms of coix seeds

Figure 3 is the sorption isotherm of coix seed fitted by MCPE equation. The MCPE equation distinguished the effect of temperature on the sorption isotherms, and there was a significant lag between adsorption and desorption isotherms, but the difference between sorption isotherms of a small grain and large grain was small, hence the moisture adsorption and desorption MCPE equations for coix seed should be strictly distinguished in practice.

3.4 *The content of monolayer moisture sorption and safe storage moisture content for coix seeds*

Table 9. Monolayer water content, absorbed layers and bound water content in coix seeds

Type	Sample	Monolayer water content (% w.b.)							Absorbed layers (n)	Bound water (% w.b.)
		10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	Average		
Desorption	1	9.74	9.38	9.01	8.63	8.26	7.88	8.82 ± 0.70^{ab}	6.54	57.68
	2	8.65	8.37	8.09	7.80	7.51	7.22	7.94 ± 0.54^{bcde}	6.40	50.81
	3	9.20	9.09	8.97	8.85	8.74	8.62	8.91 ± 0.22^{a}	6.77	60.37
	4	9.15	8.88	8.62	8.35	8.08	7.81	8.48 ± 0.50^{abc}	6.73	57.07
	5	9.35	9.10	8.84	8.59	8.33	8.08	8.72 ± 0.48^{ab}	6.73	58.68
	Des-average	9.22	8.97	8.71	8.45	8.19	7.93	8.58 ± 0.48^{ab}	6.64	56.94
Adsorption	1	8.09	7.97	7.84	7.72	7.59	7.47	7.78 ± 0.23^{cde}	6.12	47.63
	2	7.77	7.68	7.60	7.52	7.44	7.35	7.56 ± 0.16^{e}	6.09	46.03
	3	8.12	8.00	7.88	7.75	7.63	7.51	7.82 ± 0.23^{cde}	6.27	49.02
	4	7.98	7.90	7.82	7.74	7.66	7.57	7.78 ± 0.15^{de}	6.10	47.48
	5	8.08	7.97	7.86	7.75	7.64	7.53	7.81 ± 0.21^{cde}	6.33	49.44
	Ads-average	8.01	7.90	7.80	7.70	7.59	7.49	7.75 ± 0.19^{d}	6.18	47.90
	Sorption-mean	8.63	8.45	8.26	8.08	7.89	7.71	8.17 ± 0.35^{bcd}	6.41	52.39

Note: Des, desorption; Ads, adsorption. For sorption samples, the values followed by different superscript letters are significantly different at $p < 0.05$, according to Duncan's multiple range test

Table 10. The relatively and absolutely safe storage moisture of coix seeds

Safe moisture (% w.b.)	Equation	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
Absolutely	MCPE	13.61 ± 0.87	13.29 ± 0.85	13.00 ± 0.84	12.73 ± 0.85	12.47 ± 0.87	12.23 ± 0.89
	MGAB	13.25 ± 0.63	13.11 ± 0.67	12.96 ± 0.71	12.82 ± 0.75	12.68 ± 0.78	12.55 ± 0.82
	MOE	12.99 ± 0.86	12.81 ± 0.86	12.63 ± 0.84	12.45 ± 0.84	12.27 ± 0.85	12.09 ± 0.87
Relatively	MCPE	14.36 ± 0.90	14.05 ± 0.87	13.76 ± 0.87	13.49 ± 0.87	13.24 ± 0.89	12.99 ± 0.91
	MGAB	14.09 ± 0.68	13.96 ± 0.72	13.82 ± 0.75	13.69 ± 0.79	13.56 ± 0.82	13.44 ± 0.86
	MOE	13.71 ± 0.92	13.52 ± 0.89	13.34 ± 0.87	13.15 ± 0.87	12.96 ± 0.88	12.77 ± 0.90

The moisture content of the monolayer, the number of adsorbed layers and the bound water content of coix seed were analyzed using our modified Caurie equation (Table 9). The moisture content of the monolayer sorption decreased with the increase of temperature, and the moisture content of the desorption monolayer was higher than that of the adsorption monolayer.The sorption layer number and bound-water content were 6.64 and 56.94% for desorption, 6.18 and 47.90% for adsorption, respectively.

MCPE, MGAB and MOE equations were used to analyze the safe stored moisture of five samples of coix seeds (Table 10). The absolutely and relatively safe moistures at 25 °C were 12.45%-12.82% w.b. and 13.15%-13.69% w.b. at 65% and 70% ERH, respectively.

3.5 *The changes in sorption isosteric heat of coix seeds with moisture content*

MCPE could clearly show the effect of temperature on the sorption isosteric heat curves of coix seeds. When the EMC was less than 17.5% d.b., the desorption isosteric heat of coix seed was greater than the adsorption isosteric heat (Figure 4A), and both of them decreased sharply in the hyperbolic form, approaching the latent heat of pure water at 17.5% d.b. (14.9% w.b.), the corresponding heat was about 2,500 kJ/kg, so the end point of drying coix seeds with high moisture content is 14.9% w.b. Compared with the significant difference of desorption and adsorption isotherms, the difference of moisture sorption isosteric heat curves between small grain and large grain were smaller (Figure 4B).

MOE could not show the effect of temperature on the sorption isosteric heat curves of coix seeds (Figures 4C and 4D). As with the MCPE, there was a big difference between the isosteric heat curves of moisture desorption and adsorption in coix seeds calculated with MOE model. In the range of 10% to 28% d.b. moisture content, the difference between the moisture sorption isosteric heat curves of large and small coix seeds became smaller.

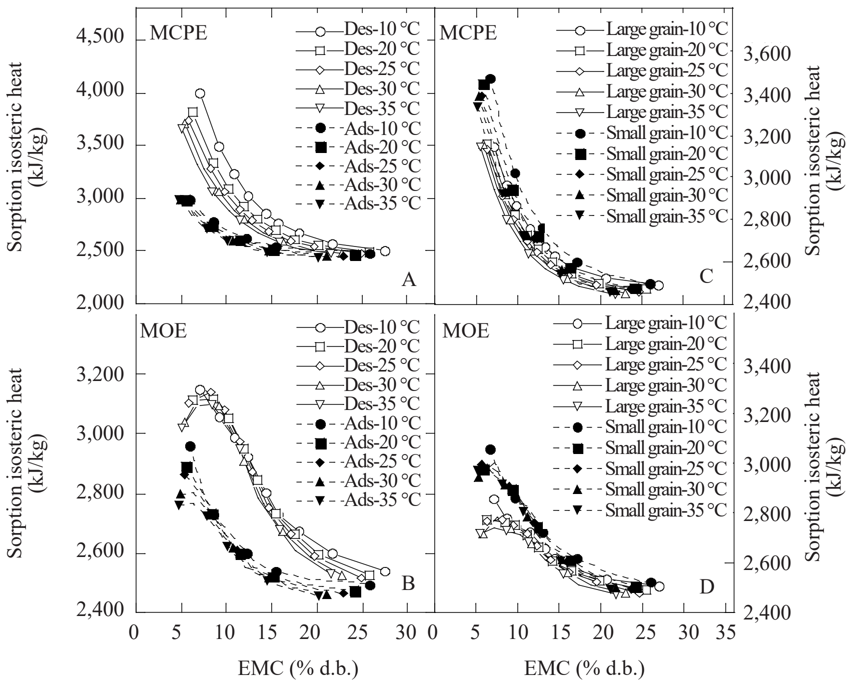
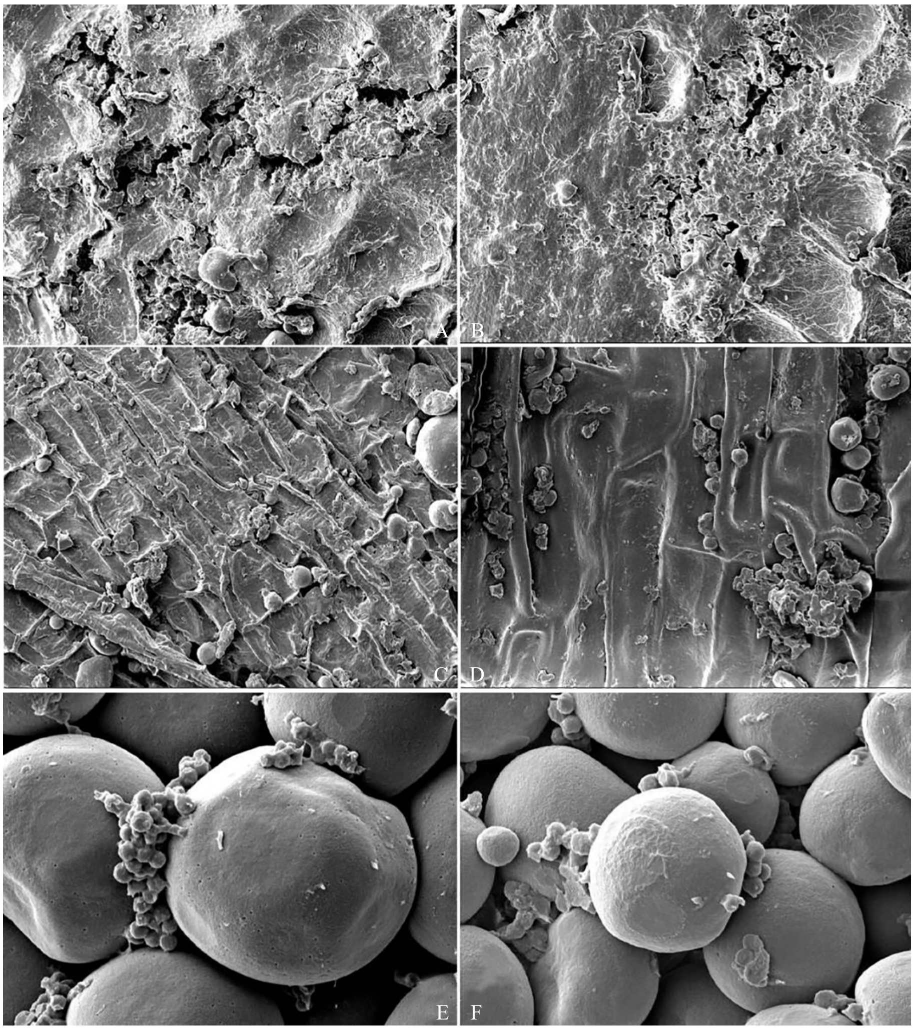


Figure 4. Moisture sorption isosteric heat curves of coix seeds

Compared with the small-grain coix seed, a large-grain coix seed had similar embryo surface, but had more cracks in back surface. To the cross section of a kernel, large-grain coix seed had larger starch granules and more micropores on the surface of starch granules. There structure characteristics might result in more water adsorption amount and less sorption isosteric heats in large-grain coix seeds when compared with a small-grain coix seeds (Figure 5).



Note: A. Back surface of large-grain (1,000 ×); B. Back surface of small-grain (1,000 ×); C. Embryo surface of large-grain (1,000 ×); D. Embryo surface of small-grain (1,000 ×); E. Starch granules of large-grain (5,000 ×); F. Starch granules of small-grain (5,000 ×)

Figure 5. Microscopic structure of coix seed

4. Discussion

Coix seed is one of the most difficult grains to store because it is prone to lipid peroxidation [3, 25]. Therefore, the storage conditions (temperature, light, moisture content, and package) and the changes in fatty acid composition of coix seed have been studied in China [8, 26-28]. In order to describe the process of drying, the effect on water activity, the ambient cooling of cereal grains like coix seeds, and to improve physical control in storage, a sound knowledge of the relationship between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) is essential. To our knowledge, we are the first study to determine the desorption and adsorption isotherms of Coix seed. Two inflection points around 70% and 85% ERH respectively occurred on the sigmoidal shaped isotherms indicate the transition from multilayer moisture sorption to solid solution sorption [29], which is useful to predict the quality and stability attributes of coix seeds. The linear region of the isotherms from 20% to 70% ERH can be used for developing an instrument for quick monitoring the moisture content of coix seeds [30].

The most useful way to define the EMC-ERH relationship is by fitting the data to a suitable equation [31]. American Society of Agricultural and Biological Engineers (ASABE) has recommended that five EMC equations like MCPE, MHAE, MHE, MGAB, and MOE can be used for fitting the moisture sorption isotherms of cereals [20]. In the present study, the equations like MCPE, MHE, MGAB and MOE were suitable for fitting the moisture adsorption and desorption isotherms of coix seeds in that *MRE* is less than 9.232% and $R^2 > 0.967$, with random residual distributions. MHAE was suitable for adsorption isotherms of five coix seed samples with $MRE < 9.624\%$ and $R^2 > 0.965$, but for the desorption isotherms of samples 2 and 4, *MRE* was greater than 10% and $R^2 < 0.940$, thus it is not suitable for these two coix seed samples, in spite that MHAE is commonly regarded to fit for the moisture sorption isotherms of oil seeds [12]. MCPE fit best to the desorption and adsorption isotherms of five varieties of coix seeds with average *MRE* of 2.9851% and 2.9134% and average R^2 of 0.9923 and 0.9934, respectively. MCPE is a three-parameter EMC equation and is used to calculate the sorption isosteric heats for showing the effect of temperature.

At 65% ERH and 25 °C, the absolutely safe moisture content (w.b.) of paddy, wheat, shelled corn and soybean was 13.11%, 12.75%, 12.67%, and 10.16%, respectively [12]. In the present study, the absolutely (65% ERH) and relatively (70% ERH) safe moisture content (w.b.) of coix seeds was analyzed as 12.45%-12.82% and 13.15%-13.69% at 25 °C, respectively, further demonstrating that coix seeds have the hygroscopic property of gramineae grain. To slow down the reaction of fat peroxidation, we suggest that coix seed can be stored at quasi-low temperatures (≤ 20 °C) and RH ≤ 65% whenever possible.

This study showed that the latent heat of coix seeds was similar to that of pure water at a moisture content (MC) of 14.9% w.b., which is drying endpoint and was significantly lower than the 17.5% w.b.MC of other cereal grains (wheat, rice, and corn) and soybeans, but higher than the 12.5% w.b. MC of peanut and rapeseed, and the 10% w.b. MC of sesame [12]. To reduce the unsaturated fat loss of coix seeds after harvest, the drying process should be carried out in two stages. The moisture content was reduced to 14.5% w.b. rapidly at first, and then 1.0%-1.5% moisture was lost through slow-speed process to achieve safe moisture content. The isotherms and equations of moisture adsorption and desorption of coix seeds can be also used in the design of bulk ventilation, mixing and packaging. The further study will explore the relationship between glass transition temperature of starch, fat, protein and cell wall polysaccharides of coix seeds during moisture sorption and their quality parameters.

5. Conclusion

This study provides a comprehensive analysis of the moisture adsorption and desorption isotherms of five varieties of Coix seeds, revealing sigmoidal curves with noticeable hysteresis between the processes. The Modified Chung-Pfost (MCPE) equation was the most accurate among the six equations evaluated for fitting the experimental data. The findings show that monolayer water content decreases with increasing temperature, with higher isosteric heats and moisture content for desorption than for adsorption. The study identified safe moisture contents for Coix seeds at 25 °C, essential for maintaining seed quality during storage. These insights are crucial for optimizing storage conditions, suggesting distinct consideration of desorptive and adsorptive behaviors and the use of average isotherms for effective storage management.

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Conflict of interest

Authors declare there is no conflict of interest at any point with reference to research findings.

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