Moisture sorption and thermodynamic properties of *Camellia oleifera* seeds as influenced by oil content

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Abstract: Moisture sorption isotherms and thermodynamic properties of *Camellia oleifera* seeds as influenced by oil content were investigated. Moisture desorption and adsorption isotherms of *Camellia oleifera* seeds, kernels and shells from three varieties were determined using constant temperature and humidity chamber method at different temperatures (10°C, 25°C, and 40°C) with water activity ranging from 0.20 to 0.90. Six selected mathematic models were employed to fit the experimental data. The Peleg model gave the best results for both seeds and kernels and Langmuir model was the best for shells. The difference of equilibrium moisture contents at the same water activities during desorption and adsorption indicated the occurrence of hysteresis of adsorption processes and the equilibrium moisture contents tended to decrease with the increasing oil content and temperature. The binding energy and average capacity per unit mass decreased with increasing temperature and oil content. The relationships between water activity and the logarithm of sorption activity showed the capillary porous body characteristics of the seeds.

Keywords: *Camellia oleifera* seeds, moisture desorption and adsorption isotherms, equilibrium moisture content, oil content, thermodynamic property
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1 Introduction

Camellia oleifera Abel. which belongs to the genus *Camellia* of Theaceae, is commonly known as the oil-seed camellia or tea oil camellia. *Camellia oleifera* seed, together with oil palm, olive and coconut, is known as the most prominent woody edible oilseeds. The quality of *Camellia oleifer*a seeds during storage is greatly affected by storage conditions, including moisture content, environment temperature and relative humidity. In order to avoid the quality loss of stored *Camellia oleifera* seeds caused by insects, microbial and chemical spoilage, the control of moisture content and relative humidity during storage and processing is essential. The knowledge of the adsorption and desorption characteristics are beneficial for stability and acceptability of food products, prediction of shelf-life, drying process modeling, calculation of moisture changes that may occur during storage, and equipment design for drying, packaging and storage[1]. The moisture sorption isotherm is generated when the relationship between relative humidity (related to the water activity (a_w) of the material at the equilibrium state) of the environment and equilibrium moisture content (*EMC*) of the food is expressed in graphical format with fixed temperature[2]. For desorption processes, moisture inside materials evaporates to the atmosphere with low a_w and for adsorption processes, materials uptake moisture from the atmosphere with high a_w. These isotherms make it possible to predict the moisture content of food at a given a_w and temperature. Series of empirical and semi-empirical models have been applied to fit the sorption isotherm, such as Langmuir model[3], Chung-Pfost model[4], Brunauer-Emmett-Teller (BET) model[5], Guggenheim-Anderson-deBoer (GAB) model[6], Henderson model[7], Peleg model[8], Oswin model[9] and others.

Further analysis of sorption behavior by the application of thermodynamic principles can exhibit important information that provides an understanding of moisture properties and associated energy requirements of heat and mass transfer, food physicochemical and microbiological stability[10,11]. Thermodynamic parameters such as differential enthalpy and entropy, integral enthalpy and entropy, equilibrium spreading pressure, binding energy, sorption activity and average capacity per unit mass have been studied individually or jointly in previous reports of walnut[12], chestnut[13], peanut[14], *Zanthoxylum bungeanum* seeds[15] and wheat[16,17].

Sorption isotherms of *Camellia oleifera* seeds have been reported[18], however, only focused on adsorption isotherm and did not consider desorption characteristics. In addition, the effects of oil content which is significantly variant for different varieties on the sorption isotherms have not been reported, which might exert significant differences. Therefore, the objectives of this study were as to (1) obtain moisture desorption and adsorption isotherms of three varieties of *Camellia oleifera* seeds, as well as their kernels and shells and evaluate the best model to fit the experimental data;

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(2) explore the influence of oil content on sorption isotherms; (3) estimate the thermodynamic properties including binding energy, average capacity per unit mass, sorption activity.

2 Materials and methods

2.1 Materials and sample preparation

Samples of three varieties of *Camellia oleifera* seeds growing in the same area under the same conditions, namely *Old variety*, *Chanling* and *Ganzhouyou* denoted as Varieties 1-3, were obtained from Ganzhou, Jiangxi, China. Fresh seeds, with an average initial moisture content of 54.3%±2.1% (on wet basis) determined according to the decompression drying method[19], were used for desorption, while vacuum-dried seeds at 50°C for about 30 h with moisture content below 3% (on wet basis)[18] were used for adsorption. The oil content was 28.5%±0.4%, 31.3%±0.1% and 39.0%±1.2% for Variety 1, Variety 2 and Variety 3, and 49.7%±0.5%, 52.1%±0.2% and 54.2%±0.7% (on dry basis) for kernel of Varieties 1, 2 and 3, respectively, determined according to Soxhlet extraction method[20]. Both fresh and dried seeds were treated in three categories as seeds, kernels and shells. Both materials for desorption and adsorption were stored at 4°C until being used.

2.2 Moisture sorption determination

Sorption characteristics were determined using the constant temperature and humidity chamber method over the relative humidity range of 0.20 to 0.90[12]. In order to explore the sorption characteristics of *Camellia oleifera* seeds under different temperature conditions, the usual low, normal and upper limit storage temperature of 10°C, 25°C, and 40°C, respectively, were used according to the previous reports[18]. Triplicate samples of seeds, kernels and shells ((10±0.1) g, (10±0.1) g, (5±0.1) g, respectively) were weighed in an aluminum box and then placed into the constant temperature and humidity chamber (CTHI-150B, STIK (Shanghai) Co., Ltd., Shanghai, China) with specified a_w. In order to prevent fungal growth in the samples at high a_w, samples were dipped into a mercury chloride solution with a concentration of 0.1%, which does not affect the sorption characteristics.

2.2.1 Desorption procedure

A_w values used in this study were 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90. Aluminum boxes filled with seed, kernel and shell samples of weight as mentioned above were put into the constant temperature and humidity chamber with preset a_w at temperatures of 10°C, 25°C and 40°C, respectively. These samples were taken out of the chamber every 24 h to measure their weight using an analytical balance with a reading error of ±0.0001 g (FB224, Shanghai Sunny Hengping Scientific Instrument Co., Ltd., Shanghai, China) until the weight difference between two consecutive readings was no more than 0.01% of initial weight during approximately 5-20 d. The total time required for removing, weighing and replacing the samples in the chamber was approximately 15 s. After reaching equilibrium, the moisture content of each sample was determined by a vacuum oven at 65°C.

2.2.2 Adsorption procedure

The only difference between adsorption and desorption was that the samples (seeds, kernels and shells) were dried to lower moisture content.

2.2.3 Mathematical model

There are varieties of moisture sorption isotherm models for different food products. Six of them (Table 1), which are frequently used for oilseeds or nut[12], were employed to fit the desorption and adsorption experimental data of *Camellia oleifera* seeds.

Table 1 Mathematical models of desorption and adsorption models

Model	Mathematical equation	Reference
Chung-Pfost	$M_e = (n(b_0) - \ln(-\ln(a_w))) / b_2$	[4]
Oswin	$M_e = b_0[a_w / (1 - a_w)]^{b_1}$	[9]
GAB	$M_e = b_0 b_1 b_2 (a_w) / ((1 - b_1(a_w))(1 - b_1(a_w) + b_1 b_2 (a_w)))$	[6]
Henderson	$M_e = [-\ln(1 - (a_w)) / b_0]^{\frac{1}{b_1}}$	[7]
Peleg	$M_e = b_0(a_w)^{n_0} + b_1(a_w)^{n_1}$	[8]
Langmuir	$M_e = 1 / (1 / b_0 b_1 (a_w) + 1 / b_0)$	[3]

Note: b_0, b_1, b_2, n_0 and n_1 are parameters of these models; M_e is the equilibrium moisture content; a_w is the water activity

The goodness of the mathematical models was estimated by calculating statistical parameters including the residual sum of squares (*RSS*) and adjusted R-Square (Adj-R^2)[18]. The *RSS* value is very important in the non-linear regression process, with the fitting procedure being designed to achieve the minimum value. The maximum Adj-R^2 is considered to be a reasonable fit.

$$RSS = \sum_{i=1}^{N} (Y_i - \hat{Y}_l)^2 \tag{1}$$

$$\text{Adj} - R^2 = 1 - \frac{\sum_{i=1}^{N} (Y_i - \hat{Y}_l)^2 / (N-1)}{\sum_{i=1}^{N} (Y_i - \hat{Y}_l)^2 / (N-P)} \tag{2}$$

where, Y_i and $\hat{Y}_l$ are experimental and predicted values of desorption or adsorption equilibrium moisture content, respectively. *N* represents the number of experimental data and *P* is the number of coefficients in each model.

2.3 Influence of oil content on sorption isotherms

In order to explore the influence of oil content on the sorption behavior of *Camellia oleifera* seeds, the *EMC*s on oil-free dry basis (M_{of}) were calculated using Equation (3)[21]. Meanwhile, a comparative study of the *EMC*s of kernel slices (thickness less than 1 mm) and oil-free kernel slices (thickness less than 1 mm) was carried out using the same method as mentioned above. The oil-free kernel slices were obtained by Soxhlet extraction using petroleum ether as solvent at 45°C for 20 h after the dried seed kernels were cut into slices (thickness less than 1 mm)[20]. In addition, the Scanning Electron Microscopy (*SEM*) was employed for ultrastructure analysis of kernel and oil-free kernel slices. The process was as follows: The kernel or oil-free kernel slices were coated with a fine layer of gold using a Sputter gold coater (MSP-Mini, IXRF Systems, Inc., USA) for 45 s. The samples were observed using a *SEM* (SU3500, Hitachi, Japan) operated at an accelerated voltage of 15.0 kV.

$$M_{of} = \frac{M}{1 - O_c} \tag{3}$$

where, *M* is the moisture content, g/g (dry basis); O_c is the oil content, g/g (dry basis).

2.4 Thermodynamic properties

2.4.1 Binding energy

At constant temperature, when 1 mol water is removed from the material, the additional energy is called binding energy after removing latent heat of vaporization[22,23], which is evaluated by Equation (4):

$$L = -RTLn\varphi \tag{4}$$

where, *L* is the binding energy, J/mol; *R* is the universal gas constant (8.314 J/(mol·K)); *T* is the temperature, K; φ is relative humidity, %. The water activity of the material is equivalent to the relative humidity of the surrounding air when the material is in equilibrium.

2.4.2 Average capacity per unit mass

The average unit mass capacity refers to the change of moisture content of a material when the mass transfer potential of moisture changes a unit of measurement[23].

$$\bar{c}_m = \frac{\Delta M}{\Delta \theta_m} \tag{5}$$

where, $\bar{c}_m$ is the average unit mass capacity, mol/J; M is the moisture content on dry basis, g/g; θ_m is the joint mass transfer potential of moisture, J/mol. The joint mass transfer potential of moisture is expressed by the degree of mass exchange. With filter paper as standard material, the joint mass transfer potential of moisture at the maximum moisture content ($X_{\max}$) is defined as 100 mass transfer degrees (100°M). In filter paper with any moisture content (X), the joint mass transfer potential of moisture can be calculated using the following equation: $\theta_m = \frac{X}{X_{\max}} \times 100°\mathrm{M}$. The relationship between the joint mass transfer potential and relative humidity can be obtained from the adsorption isotherm of filter paper[23], and the moisture content of the material can be obtained from the corresponding sorption isotherm.

2.4.3 Sorption activity

Sorption activity refers to the increasing multiple of the distribution energy of 1 mol moisture when it is changed from the equilibrium vapor to the moisture in the sorption field. If moisture vapor is regarded as an ideal system, the adsorption activity is a measure of the deviation between the actual adsorption force field and the ideal system. The actual adsorption force field depends on the interaction among the adsorbed molecules and the interaction between these molecules and the adsorption surface. Therefore, the sorption activity can be regarded as the humid state characteristics of the capillary porous body[23].

$$a_s = \frac{1}{\ln\varphi}\ln\frac{M}{M_g} \tag{6}$$

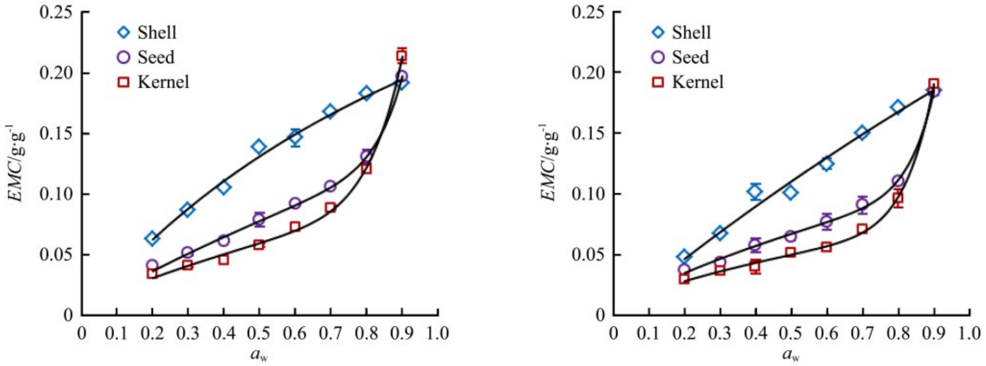
where, a_s is the sorption activity; M is the moisture content on dry basis, g/g; M_g is the gas saturated moisture content (on dry basis) of the material, g/g, which can be obtained from the corresponding sorption isotherm model.

3 Results and discussion

3.1 Desorption and adsorption isotherms

Figures 1-3 showed the experimental data and predicted data of *EMC* (dry basis) versus a_w range from 0.20-0.90 (desorption and adsorption) for the seeds, kernels or shells of Variety 3, respectively for example. The *EMC* at each a_w was the mean value of three replicates. Similar behaviors of desorption and adsorption isotherms were observed for all the 3 varieties at specific conditions, therefore the research results were selectively presented in this research.

In the initial segment (with low a_w) of the sorption isotherm curves, seeds and kernels absorb relatively lower amounts of moisture (Figure 1). Then, a sharp increase in the *EMC* could be seen at higher water activities (both of desorption and adsorption isotherms, a_w>0.70 at three temperatures). Similar behaviors have also been reported about other oilseeds and nuts, such as soybean[24], walnut[12], peanut[14], chestnut[13], macadamia nut[25], and so on. An approximate convex curve was observed in the isotherm of shells (Figure 1), which is similar to the results of Macadamia nut shell[26]. At a constant a_w, the shells had higher equilibrium moisture contents than that of the seeds and kernels, due to the difference in composition[27,28], specifically, the shells contained about 30% of Pentosan belonging to hydrotropic substance which helped the shells to absorb more moisture, while the kernels contained about 50% of oil belonging to hydrophobic substance in this study, which hindered the moisture absorption of the kernels.



a. Desorption isotherms b. Adsorption isotherms

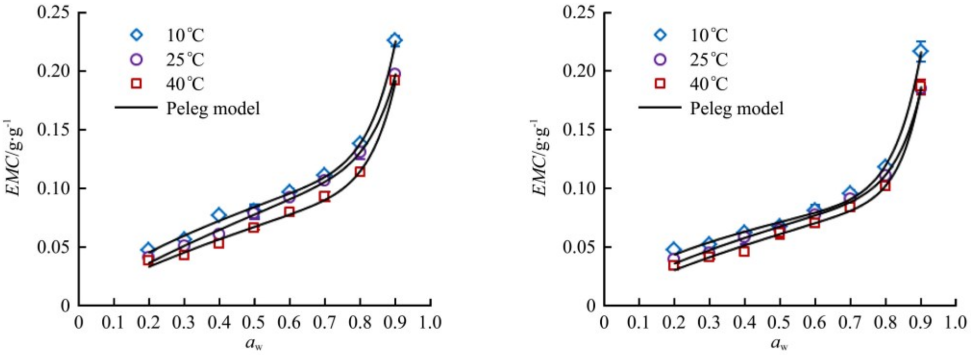
Note: Shell obeys Langmuir model, while the seed and kernel obey Peleg model.

Figure 1 Desorption and adsorption isotherms of Variety 3 at 25 °C

The sorption behavior of *Camellia oleifera* seeds and kernels could be described by sigmoid curve, belonging to Type II isotherm representing unrestricted monolayer-multilayer sorption, according to IUPAC classification[29]. However, the moisture sorption isotherm of the shell was Type I isotherm, similar to those of microporous solids with relatively small external surfaces[29], such as activated carbons, molecular sieve zeolites and certain porous oxides, the limiting uptake being governed by the accessible micro-pore volume rather than by the internal surface area.

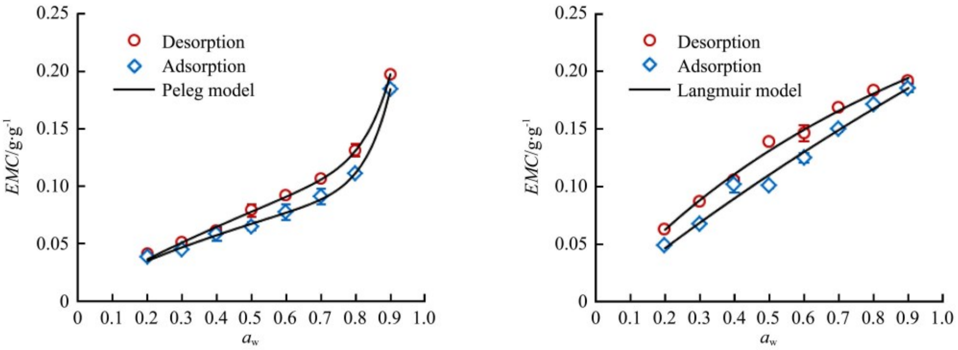
According to Figure 2, a_w (both desorption and adsorption) of the seeds increased with increasing temperature at constant *EMC*, for the moisture molecules become more active as the temperature increased[18]. Accordingly, for constant air relative humidity of the surrounding environment, the *EMC* of the *Camellia oleifera* seeds decreased with increasing temperature. However, the analysis of variance (ANOVA) showed that the effect of temperature on *EMC* was insignificant (p>0.05) in both desorption and adsorption processes, similar to the findings of Toğrul and Arslan[12].

Figure 3 shows that the adsorption progress exhibited obvious hysteresis over the entire range of a_w for the seeds (the kernels are similar to seeds) and shells of Variety 3 for example at 25°C. The hysteresis cycles for seeds could be classified as Type H3[29], where no limiting adsorption at high a_w and was often observed in aggregates of plate-like particles giving rise to slit-shaped pores. Capillary condensation theory might be introduced to present a better explanation for the hysteresis phenomena in foods although complex components affecting the moisture sorption capacity. Because of the delayed effect of capillary condensation, multilayer adsorption could be carried on the surface of particle until high a_w was reached. Once the condensation occurred, the state of the adsorbate was different and desorption curve followed a different path until the condensate became unstable at a critical value of a_w[16]. ANOVA showed a significant difference in desorption and adsorption data ($p<0.05$).



a. Desorption isotherms b. Adsorption isotherms

Figure 2 Desorption and adsorption isotherms of Variety 3 at three temperatures



a. Seeds b. Shells

Figure 3 Hysteresis effect of adsorption isotherms of the seeds and shells of Variety 3 at 25°C

3.2 Evaluation of fitting ability of sorption models

Six convention sorption models, including Chung-Pfost, Oswin, GAB, Henderson, Peleg and Langmuir model, were employed to fit the experimental data. The models were estimated based on the residual sum of squares (*RSS*) and adjusted R-Square (Adj-R^2). The lower calculated value of *RSS* indicated the higher agreement of the model to fit the experimental data. The fit accuracy was estimated by Adj-R^2, which lies in between 0 and 1 with the larger value corresponding to better goodness of the fit. The parameters of these models for Variety 3 were obtained and showed in Table 2.

According to the comparison in terms of the *RSS* and the Adj-R^2 of the fits, it could be concluded that all these models except for Langmuir were able to fit desorption and adsorption behaviors of the seeds and kernels. As shown in Table 2, Peleg model had the minimum *RSS* values and the maximum Adj-R^2 value when used to predict the moisture sorption isotherms of the seeds and kernels at 25°C, indicating that Peleg model was the most feasible to fit the sorption isotherms of the seeds and kernels over the a_w range from 0.20-0.90 at 25°C, similar behavior was observed on walnut kernels[12]. For shells, Langmuir model, suitable for Type I isotherm, was the most reasonable model to fit the experimental data, that is why Type I isotherms are also referred to as Langmuir isotherms, though this nomenclature is not recommended. The similar sorption behavior had been obtained for activated carbon exhibiting the typical Type I isotherm[29]. Figures 1 and 2 compared the experimental and predicted data employing Peleg model for the seeds and kernels, as well as Langmuir model for the shells. Though the sorption isotherms of different varieties of one species could not be represented with only one curve due to their different components, the sorption isotherms classification was the same and could be fitted by the same models.

3.3 Influence of oil content on sorption isotherms

As mentioned above, the oil content of three varieties of *Camellia oleifera* seeds (Varieties 1, 2 and 3), significantly different ($p<0.05$), was 28.5%±0.4%, 31.3%±0.1% and 39.0%± 1.2% (on dry basis), respectively. The *EMC* values of adsorption at the a_w range of 0.20 to 0.90 and temperature of 25°C were shown in Table 3 for example, which decreased with increasing oil content. Similarly, lower *EMC* was observed for walnut[12], sunflower[30] and soybean[24] samples with higher oil content.

While no significant difference was observed in the *EMC*s among the three varieties at certain conditions when the moisture content was expressed on an oil-free dry basis as in Table 3. This meant that when the oil was "removed", the sorption behavior of *Camellia oleifera* seeds were similar, possibly because that oil absorbs a negligible amount of moisture and does not hinder access of moisture molecule to some sorption sites[30].

Table 2 Parameters of models fitted to experimental sorption data of Variety 3 at 25°C

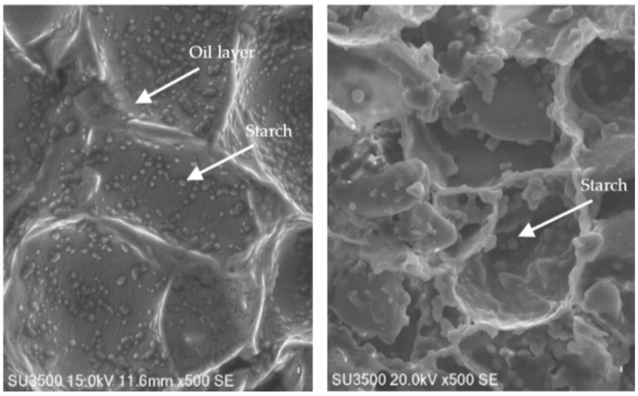
Model	Constants	Desorption			Adsorption		
		Seed	Kernel	Shell	Seed	Kernel	Shell
Chung-Pfost	b_0	2.8969	1.9751	8.5124	2.8969	1.9758	4.4371
	b_1	18.1371	15.5169	20.6565	18.1371	18.6555	18.3334
	RSS	0.0005	0.0020	0.0015	0.0005	0.0027	0.0013
	Adj-R^2	0.9667	0.9121	0.8840	0.9667	0.8361	0.9182
Oswin	b_0	0.0746	0.0590	0.1221	0.0664	0.0465	0.1015
	b_1	0.4366	0.5830	0.2496	0.4435	0.6228	0.3180
	RSS	0.0001	0.0002	0.0019	0.0004	0.0006	0.0021
	Adj-R^2	0.9953	0.9928	0.8506	0.9678	0.9661	0.8672
GAB	b_0	27.1876	0.0291	0.0792	0.0347	0.0231	0.0614
	b_1	0.2888	0.9591	0.6856	0.8964	0.9750	0.7697
	b_2	0.0140	242.5896	−3.92E20	6.89E15	9.62E15	−7.25E15
	RSS	0.0013	0.0001	0.0020	0.0002	0.0001	0.0025
	Adj-R^2	0.9013	0.9972	0.8110	0.9783	0.9894	0.8109
Henderson	b_0	21.8515	10.3585	96.4745	24.9914	10.7555	44.8003
	b_1	1.3389	0.9483	2.3690	1.3322	0.8848	1.8378
	RSS	0.0004	0.0008	0.0009	0.0012	0.0015	0.0010
	Adj-R^2	0.9714	0.9642	0.9305	0.9044	0.9089	0.9348
Peleg	b_0	0.2527	0.2799	−0.0402	0.2802	0.3964	−58.5557
	b_1	0.1345	0.0788	0.2353	0.0960	0.0772	0.2120
	n_0	11.7277	6.6108	4.8241	10.4513	11.4856	87.7314
	n_1	0.7877	0.5397	0.8255	0.5023	0.6212	0.9776
	RSS	0.0000	0.0000	0.0001	0.0001	0.0000	0.0004
	Adj-R^2	0.9966	0.9981	0.9891	0.9938	0.9977	0.9640
Langmuir	b_0	-	-	0.4882	-	-	2.2324
	b_1	-	-	0.7356	-	-	0.1019
	MSR	-	-	0.0001	-	-	0.0004
	Adj-R^2	-	-	0.9912	-	-	0.9757

Table 3 Equilibrium moisture content (*EMC*, adsorption) of kernel of *Camellia oleifera* seeds at 25°C

a_w	Kernel of different varieties			Kernel slices of Variety 3		
	Variety	*EMC* /g water·g dry solid^{-1}	Calculated *EMC* /g water·g oil-free dry solid^{-1}	*EMC* /g water·g dry solid^{-1}	Calculated *EMC* /g water·g oil-free dry solid^{-1}	*EMC* /g water·g oil-free dry solid^{-1}
0.90	1	0.2355 ± 0.0032^{a}	0.4680 ± 0.0064^{a}	0.1941 ± 0.0043^{b}	0.4234 ± 0.0093^{a}	0.3780 ± 0.0035^{a}
	2	0.2209 ± 0.0039^{b}	0.4616 ± 0.0081^{a}			
	3	0.1910 ± 0.0013^{c}	0.4169 ± 0.0029^{b}			
0.80	1	0.1201 ± 0.0067^{a}	0.2387 ± 0.0134^{a}	0.1167 ± 0.0021^{b}	0.2547 ± 0.0045^{a}	0.2390 ± 0.0027^{a}
	2	0.1160 ± 0.0055^{a}	0.2424 ± 0.0116^{a}			
	3	0.0968 ± 0.0076^{b}	0.2112 ± 0.0166^{a}			
0.70	1	0.0803 ± 0.0030^{a}	0.1596 ± 0.0060^{a}	0.0809 ± 0.0031^{b}	0.1766 ± 0067^{a}	0.1808 ± 0.00132^{a}
	2	0.0773 ± 0.0029^{ab}	0.1624 ± 0.0061^{a}			
	3	0.0709 ± 0.0030^{b}	0.1548 ± 0.0066^{a}			
0.60	1	0.0686 ± 0.00278^{a}	0.1363 ± 0.0055^{a}	0.0611 ± 0.0008^{b}	0.1333 ± 0.0017^{a}	0.1461 ± 0.0013^{a}
	2	0.0611 ± 0.0013^{ab}	0.1276 ± 0.0027^{a}			
	3	0.0559 ± 0.0025^{b}	0.1221 ± 0.0054^{a}			
0.50	1	0.0512 ± 0.0075^{a}	0.1018 ± 0.01149^{a}	0.0500 ± 0.0014^{b}	0.1091 ± 0.0030^{ab}	0.1223 ± 0.0188^{a}
	2	0.0522 ± 0.0100^{a}	0.1090 ± 0.0208^{a}			
	3	0.0519 ± 0.0035^{a}	0.1132 ± 0.0029^{a}			
0.40	1	0.0453 ± 0.0017^{a}	0.0900 ± 0.0033^{a}	0.0436 ± 0.0037^{b}	0.0952 ± 0.0081^{a}	0.1086 ± 0.0044^{a}
	2	0.0401 ± 0.0023^{b}	0.0838 ± 0.0048^{a}			
	3	0.0403 ± 0.0058^{b}	0.0880 ± 0.0127^{a}			
0.30	1	0.0387 ± 0.0069^{a}	0.0769 ± 0.0136^{a}	0.0380 ± 0.0012^{b}	0.0829 ± 0.0026^{a}	0.0948 ± 0.0021^{a}
	2	0.0367 ± 0.0003^{b}	0.0767 ± 0.0007^{a}			
	3	0.0367 ± 0.0001^{b}	0.0801 ± 0.0003^{a}			
0.20	1	0.0321 ± 0.0002^{a}	0.0637 ± 0.0004^{a}	0.0338 ± 0.0010^{b}	0.0738 ± 0.0022^{a}	0.0869 ± 0.0016^{a}
	2	0.0292 ± 0.0011^{a}	0.0610 ± 0.0024^{a}			
	3	0.0300 ± 0.0008^{a}	0.0655 ± 0.0019^{a}			

Note: $^{a\text{-}c}$: The same letter in the same column means no significant difference (p>0.05).

Further researches showed that the *EMC*s on oil-free dry basis of kernel slices calculated by using Equation (3) and *EMC*s of oil-free kernel slices were not different significantly, and were both higher than those of kernel slices of Variety 3 at 25°C. SEM observations indicated that the surface of the kernel cell was covered by oil (Figure 4). Meanwhile, the small starch granules were faintly visible below the oil layer. However, the starch granules of the oil-free kernel were exposed and formed large granules because of the oil extracting process. Though large starch granules were unfavorable for sorption behavior[31], the calculated *EMC*s on oil-free dry basis were lower than *EMC*s of oil-free kernel slices with the a_w less than 0.80. This is due to not only the hydrophobicity of oil but also the hindering for the entry of moisture molecules into seeds by steric hindrance effect in the presence of oil[21]. The behavior at high a_w became reversed as higher data were kept by calculated *EMC*s on oil-free dry basis at the same a_w, in agreement with the reported trends of pistachio kernel[32]. This is because that the decreased degree of crystallinity, resulted from the swelling of biopolymer caused by the plasticizing effect[33] of absorbed moisture that is enhanced by the presence of oil at high a_w, increasing availability of polar groups of the matrix to moisture molecules[34].



a. Kernel slice b. Oil-free kernel slice

Figure 4 Scanning Electron Microscopy images of kernel slice and oil-free kernel slice surface in magnification of 500×

3.4 Thermodynamic properties

3.4.1 Binding energy

The forms of bound water in materials are divided into three types: chemical bound water (binding energy is more than 5 kJ/mol), physical-chemical bound water (binding energy is about 3 kJ/mol) and physical-mechanical bound water (binding energy is with the energy level of 0.1 kJ/mol). According to the binding energy of water and material, different combinations of water and material can be distinguished[35].

According to Equation (4) and Peleg model, which fits best sorption isotherm of *Camellia oleifera* seeds, the binding energies of water in *Camellia oleifera* seeds at different moisture contents were calculated at certain temperatures (10°C, 25°C and 40°C) as shown in Table 4. All the binding energies of the three varieties of seeds (desorption and adsorption) were less than 5 kJ/mol at 10°C, 25°C and 40°C, over the *EMC* range from 0.04 g/g to 0.24 g/g, respectively, demonstrating that the chemical bound water is not the dominated form. When the equilibrium moisture content was higher than 0.12 g/g, the binding energy of water to matter, with the energy level of 0.1 kJ/mol, was relatively small and the water was taken as free water easy to be removed[36]. In addition, the binding energy of *Camellia oleifera* seeds decreased with the increasing temperature, which indicated that the seeds tend to lose water easily at high temperatures. At certain *EMC* and temperatures, the binding energy of the adsorption process was less than those of the desorption process due to the higher free moisture content of material after the adsorption process as compared to that of the desorption process, which might be an embodiment of the adsorption hysteresis.

For different varieties (the oil content from small to large in order as Variety 1, Variety 2, Variety 3, as shown in the above), at all the selected temperatures, the lowest binding energy of water was observed in the variety with the highest oil content during desorption and adsorption processes, which meant that the seeds with high oil content tend to lose water easily, explaining the phenomenon that *EMC* values decreased with increasing oil content from the thermodynamic point of view.

Table 4 Binding energy of water in *Camellia oleifera* seeds at different temperature (kJ/mol)

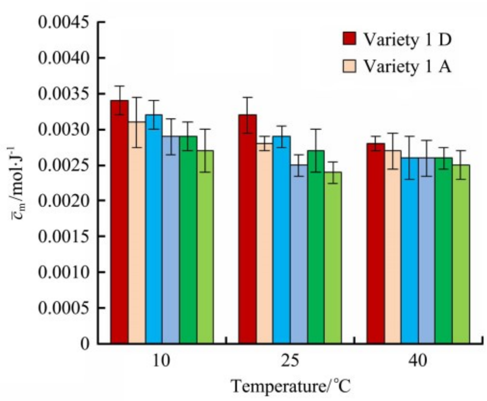
	Variety	T/°C	*EMC*/g water·g dry solid^{-1}										
			0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24
Desorption	1	10	5.0509	3.2550	2.0664	1.3873	1.0228	0.7986	0.6417	0.5230	0.4279	0.3490	0.2818
		25	4.5210	3.0582	2.0210	1.2543	0.8164	0.6099	0.4907	0.4099	0.3492	0.3009	0.2609
		40	4.3834	2.8018	1.7065	1.0493	0.7386	0.5670	0.4536	0.3698	0.3040	0.2498	0.2041
	2	10	4.8672	3.2224	2.0636	1.2678	0.8623	0.6551	0.5259	0.4341	0.3636	0.3066	0.2588
		25	4.2826	2.8136	1.7932	1.1418	0.8019	0.6099	0.4829	0.3901	0.3174	0.2581	0.2080
		40	4.2441	2.4263	1.3513	0.8954	0.6677	0.5230	0.4188	0.3379	0.2717	0.2160	0.1680
	3	10	4.2488	2.8257	1.8168	1.0761	0.6879	0.5159	0.4172	0.3493	0.2985	0.2577	0.2238
		25	3.7230	2.5024	1.6391	1.0139	0.6624	0.4871	0.3819	0.3093	0.2546	0.2105	0.1740
		40	3.6811	2.0382	1.0921	0.7313	0.5570	0.4462	0.3662	0.3037	0.2527	0.2097	0.1725
Adsorption	1	10	4.5491	2.7823	1.6018	1.0101	0.7425	0.5861	0.4787	0.3973	0.3322	0.2783	0.2319
		25	4.8367	2.8029	1.4218	0.8340	0.6175	0.4956	0.4125	0.3492	0.2986	0.2565	0.2205
		40	3.7904	2.1840	1.1264	0.7066	0.5400	0.4428	0.3752	0.3237	0.2821	0.2473	0.2174
	2	10	4.6709	2.7105	1.3780	0.8139	0.6080	0.4926	0.4135	0.3537	0.3058	0.2659	0.2316
		25	4.5959	2.6187	1.3456	0.8274	0.6061	0.4742	0.3814	0.3107	0.2532	0.2051	0.1639
		40	3.4585	2.0685	1.1421	0.7128	0.5300	0.4240	0.3509	0.2955	0.2510	0.2137	0.1820
	3	10	4.7298	2.3425	0.9725	0.6467	0.5098	0.4248	0.3633	0.3152	0.2759	0.2425	0.2138
		25	3.5866	2.1363	1.1453	0.6757	0.4934	0.3921	0.3231	0.2711	0.2300	0.1954	0.1661
		40	3.2372	1.8625	0.9570	0.6042	0.4657	0.3851	0.3290	0.2862	0.2516	0.2225	0.1976

3.4.2 Average capacity per unit mass and sorption activity

In order to calculate the average capacity per unit mass ($\bar{c}_m$) and sorption activity (a_s), the *EMC* and gas saturated moisture content (M_g) were obtained by the Peleg model for the three varieties over a_w range from 0.10 to 0.90 at 10°C, 25°C and 40°C, respectively. The mass transfer potential of water (θ_m) was 7.5 J/mol, 17.5 J/mol, 18.5 J/mol, 22.5 J/mol, 27.5 J/mol, 30.0 J/mol, 37.5 J/mol, 47.0 J/mol and 75.0 J/mol exceed a_w range from 0.1 to 0.90[15,23].

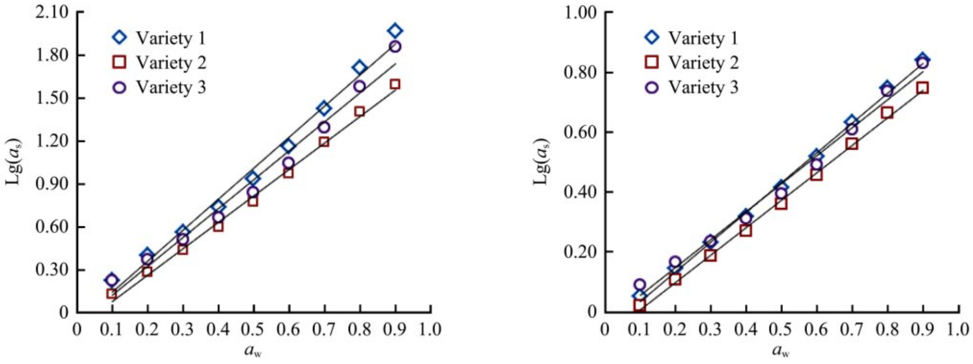
Figure 5 shows the calculated results of average capacity per unit mass ranging from 0.0024 mol/J to 0.0034 mol/J. The $\bar{c}_m$ decreased with the increasing temperature and oil content and was less in the adsorption process than that of the desorption process, which is corresponding to the binding energy. Reasonable pretreatment methods and drying methods can be selected based on the $\bar{c}_m$, which is important for the storage after drying of material[23].

According to Figure 6, a linear relationship was observed between a_w and Lg (a_s) of *Camellia oleifer*a seeds, demonstrating that *Camellia* seed was a typical capillary porous material, similar to cement sand, pulp and *Zanthoxylum bungeanum* Seeds[15]. Therefore, *Camellia* seeds showed capillary porous body characteristics, first of all, the effect of capillary pressure on fluid motion in media, which was important for the selection of drying model and calculation process[37].



Note: D and A represents desorption and adsorption, respectively.

Figure 5 Average capacity per unit mass for different varieties at 10°C, 25°C and 40°C



a. Desorption process

b. Adsorption process

Figure 6 Relationship between a_w and Lg (a_s) for different varieties at 25°C

4 Conclusions

Both of desorption and adsorption isotherms of *Camellia oleifera* seeds and kernels were in a sigmoid shape, belonging to Type II isotherm, while the shells showed Type I sorption isotherms. The equilibrium moisture content of the seeds, kernels and shells (desorption and adsorption) increased with the increasing water activity at constant temperature and decreased with increasing temperature at constant water activity. And the shells had higher equilibrium moisture contents than those of the seeds and kernels at the same condition. The adsorption process exhibited obvious hysteresis for the seeds, kernels and shells over the entire range of water activity. At 10°C, 25°C and 40°C, the Peleg model was found to be the most appropriate equation for fitting the sorption isotherms of the seeds and kernels over the water activity range of 0.20-0.90, while the Langmuir model was the best to describe sorption process of the shells.

The *EMC* values on dry basis decreased with increasing oil content at the whole water activity range. However, the differences in sorption behavior were not significant among the three varieties when the moisture content was expressed on an oil-free basis. Furthermore, the difference between calculated *EMC*s on oil-free dry basis and *EMC*s of oil-free kernel slices with water activity less than 0.80 which became reversed at higher water activity indicated that the steric effect related to the entry of water molecules and the degree of crystallinity related to the availability of polar groups of the matrix to water molecules in the presence of oil affects water adsorbed by the seeds.

The average capacity per unit mass and binding energy decreased with the increasing temperature. The binding energies of the three varieties of seeds (desorption and adsorption) which decreased with increasing moisture content were less than 5 kJ/mol at 10°C, 25°C and 40°C, over the *EMC* range from 0.04 g/g to 0.24 g/g indicating chemical bonds might not dominate. The linear relationships between water activity and logarithm of sorption activity demonstrated that *Camellia oleifer*a seeds belonged to the capillary porous body. Both average capacity per unit mass and binding energy decreased with the increasing temperature and oil content, indicating that the presence of oil decreased the amount of energy during moisture sorption processes in the seeds, and was less in adsorption process than that of desorption process indicating that the amount of energy involved in moisture desorption process was greater than that in adsorption process.

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