International Food Research Journal 20(3): 1223-1227 (2013)
Journal homepage: *http://www.ifrj.upm.edu.my*

Sorption characteristics and some physical properties of caraway (*Carum Carvi* L.) seeds

*Rajamanickam, R., Kumar, R., Johnsy, G. and Sabapathy, S.N.

Food Engineering and Packaging Division, Defence Food Research Laboratory, Mysore – 570 011, Karnataka, India

Article history

Received: 4 October 2012
Received in revised form: 27 November 2012
Accepted:2 December 2012

Keywords

Sorption isotherm
*caraway (*Carum Carvi *L.)*
monolayer moisture
isotherm models
equilibrium moisture content

Abstract

Equilibrium moisture contents were obtained for Caraway (*Carum Carvi* L.) at 25 and 40°C experimentally over a range of relative humidity values of 23 – 85 %. Seven models were tested to fit the experimental data of caraway. The Peleg model showed the best fit with higher R^2 value and lowest root mean square error. Monolayer moisture contents, obtained from BET equation, were found to be 0.0488 and 0.0274 g water/g dry matter and surface area of monolayer is 170.90 and 95.83 m^2/g at 25 and 40°C respectively. Physical properties such as mass, volume, true density, geometric mean diameter, degree of sphericity and surface area of Caraway were measured.

Introduction

Caraway (*Carum Carvi* Linn) seed is a mature, dried schizocarpic fruit of a biennial herb of the parsley family, native to Europe and West Asia. In India, it is cultivated in Himachal Pradesh, in the hills and plains of North India and also in the hills of South India for its aromatic seeds. The caraway seeds have a characteristic odor and have an aromatic, warm and sharp taste. The seeds of caraway have been extensively used in food and in traditional medicines. They are widely added as spice to a variety of foods such as bread, yogurt, pickles, sauces and salads for flavoring. Caraway has been used since ancient in the treatment of digestive disorders. It is known as antiulcerogenic, antibacterial (Khayyal *et al*., 2001; Singh *et al*., 2002). The seeds have been reported to contain essential oils, fixed oil, flavanoids, saponins, alkaloids and proteins (Zargari, 1990). *Carum carvi* L. fruit is traditionally used to treat diabetes, cardiovascular disease and hypertension (Eddouks *et al*., 2002; Lemhadri *et al*., 2002). Since the highest beneficial values of caraway seeds, it must be protected in terms of moisture, mold growth and spoilage during storage and transportation.

The relation between moisture content to the water activity or equilibrium relative humidity, also called sorption isotherm, gives valuable information (Iglesias and Chirife, 1976a). Water sorption isotherms are important while considering drying, packaging and storage of food products (Bruin and Luyben, 1980). Since the food products are complex in nature, reliable sorption data obtained from experimental measurements are necessary for predicting their quality during storage.

Caraway seeds were widely used as a spice, due to its pungent and anise-like flavor and aroma. Normally these seeds contain low water content, which can be affected by the humidity and temperature conditions where it is stored. Undesirable changes in the moisture content occurring due to change in relative humidity and temperature can adversely affect the shelf life of these seeds. Reports about the sorption studies of caraway seeds are very scarce and their sorption data at different relative humidity conditions are very important to determine their drying and storage conditions. Hence the present study was undertaken to measure the equilibrium moisture content at various relative humidities, to fit the experimental data to sorption models. Further, physical properties such as shape, size, volume, area etc. are needed to design equipment for the harvesting, handling, conveying, separation, drying, aeration, storing and processing.

Materials and Methods

Raw material

Caraway seeds were procured from a local market

*Corresponding author.
Email: *rajamanickamkmu@gmail.com*
Tel: +91 821 2473150; Fax: +91 821 2473468

in Mysore city of India. The seeds were cleaned manually to remove all foreign matters such as dust, dirt and stones, as well immature, broken seeds.

Determination of initial moisture content of caraway seeds

The initial moisture content of the caraway seeds was determined by solvent distillation method using toluene as a solvent (AOAC 1990).

Physical properties of caraway seeds

Dimension

The major diameter (length) was defined as the largest dimension of the seed while the medium diameter (thickness) was the longest dimension in an axis perpendicular to that of the major diameter. The minor diameter (width) was then taken to be the largest dimension along a third axis perpendicular to both the major and medium diameters. To determine the dimensions, a grain mass of 1 kg was divided into 10 approximately equal portions. Ten seeds were then randomly picked from each of the ten portions and a digital vernier caliper and a micrometer screw gauge (Mitutoya Corporation, Japan) measuring to an accuracy of 0.01 mm and 0.001 mm were used to measure the major and medium and minor diameters for each seed respectively. The mean values of the dimensions were then determined and geometric mean diameter (D_g), degree of sphericity (ϕ) and surface area (S) of the seeds were calculated using Equations 1, 2 and 3 (Mohsenin, 1986).

$$D_g = (LWT)^{1/3} \quad (1)$$
$$\phi = ((LWT)^{1/3} / L) \quad (2)$$
$$S = \pi Dg^2 \quad (3)$$

where L, W and T are length, width and thickness of the seed.

Mass, volume and true density

Thousand kernel weights were determined by means of an electronic balance reading to 0.0001 g. The volume was determined by filling an empty 100 mL measuring cylinder with one thousand caraway seeds and the volume occupied was then noted. The true density was determined using the helium displacement method by Ultrapycnometer (Quanta Chrome Instruments, USA). Hardness was found out using Universal Testing Machine (LRX Plus, Lloyd Instruments, England).

Determination of equilibrium moisture content of caraway

The equilibrium moisture content (EMC) of the caraway was determined by keeping the approximately 4 to 5 grams of samples as is basis in desiccators containing 23 to 85% relative humidity obtained with saturated salt solutions (Greenspan, 1977). The salts used were: potassium acetate, magnesium chloride, potassium carbonate, magnesium nitrate, sodium nitrite, sodium chloride and potassium chloride corresponding to relative humidities of 22.51 ± 0.32, 32.78 ± 0.16, 43.16 ± 0.39, 52.89 ± 0.22, 64.4 ± 0.22, 75.29 ± 0.12 and 84.3 ± 0.30 at 25°C respectively. Chemicals used were procured from S.D. Fine Chemicals, Mumbai, India. All seven desiccators were kept in an incubator thermostatically controlled at 25ºC ± 2ºC and at 40ºC ± 2ºC. Samples were weighed with an accuracy of 0.0001 g, with a frequency of two days. The attainment of EMC was ascertained when three consecutive weight measurements shown a difference of less than 0.001 g. All the experiments were conducted in duplicate and the average value of EMC has been reported. The time required for the samples to reach equilibrium varied between 14 – 20 days. A small amount of sodium azide was kept inside, along with about 5 g of sample to avoid microbial growth above 70% relative humidity.

The monolayer moisture content of a food material provides the maximum moisture content upto which the product is more stable. It is a crucial parameter in the determination of the surface potential of moisture sorbed in food. It was a satisfactory specification for the lower limit of moisture in food. The monolayer moisture values were obtained by fitting the BET equation (Table 1).

The water surface area, S_0 in m^2/g of solid, was determined using the following expression as described by Labuza (1968).

$$S_0 = X_m \,.\, N_0 \,.\, A_{water} \,.\, 1/M_{water} \quad (4)$$

Where, X_m = monolayer value in g adsorbed / g solid,
M_{water} = mol. Weight of water = 18 g/mole
N_0 = avagadro's no. = 6 x 10^{23} molecules / mole
A_{water} = area of water molecule = 10.6 x 10^{-20} m^2.

$$\text{Hence, } S_0 = X_m\ 3.5 \times 10^3\ m^2 / g \quad (5)$$

Analysis of sorption data

A large number of models have been proposed in the literature for the sorption isotherms. Seven models were selected to fit the experimental values viz., BET, GAB, Oswin, Iglesian-Chirife, Henderson, Peleg and smith. The sorption models are shown in Table 1. The fitting of the selected equations to the experimental data was performed using Microsoft Excel 2007 and nonlinear estimation by GraphPad Prism version 6.00 for Windows (GraphPad Software, La Jolla California USA, www.graphpad.com).

Table 1. Selected isotherm equations for experimental data fitting

Model Name	Equation	Reference
BET	$X = (X_m.A.a_w)/((1-a_w)(1+(A-1)a_w))$	Brunauer *et al.*, (1938)
GAB	$X = (X_m.K.C.a_w)/((1-K.a_w)(1-K.a_w+K.C.a_w))$	Van den Berg (1981)
Oswin	$X=A(a_w/(1-a_w))^B$	Oswin (1946)
Iglesias-Chirife	$X=A+B(a_w/(1-a_w))$	Chirife and Iglesias (1981)
Henderson	$X=(-Ln(1-a_w)/A)^{1/B}$	Henderson (1952)
Peleg	$X=Aa_w^B+Ca_w^D$	Peleg (1993)
Smith	$X=A-(B*Ln(1-a_w))$	Smith (1947)

*X = equilibrium moisture content, X_m= monolayer moisture content, a_w = water activity, A, B, C, D and K = model coefficients

Validation of sorption models

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

$$RMSE = ((\sum_{i=1}^{N} (X_e^i - X_p^i)^2)/N)^{½} \quad (6)$$

$$MRE = 100/N(\sum_{i=1}^{N} (X_e^i - X_p^i)/ X_e^i) \quad (7)$$

where X_e^i and X_p^i are the measured and predicted equilibrium moisture contents respectively and N is the number of points. The higher values of coefficient of determination, and smaller values of MRE and RMSE gives the best fit of the models.

Results and Discussion

Physical properties

The moisture content of caraway seed was found to be 7.9 ± 0.14% on wet basis. The physical properties measured were shown in Table 2. The seed mean length, width and thickness were found to be 4.6507 mm, 1.0693 mm and 1.1794 mm respectively. Sphericity is an expression of a shape of solid relative to that of a sphere of the same volume and it is found to be 0.3879. The mass of thousand grain, volume of thousand grain, true density, geometric mean diameter (D_g) and surface area were 2.816 gm, 5.5 ml, 4.7364 g/ml, 1.8008 mm and 10.2142 mm². The hardness as found by universal testing machine was 51.083 N.

Sorption isotherm

Sorption isotherms of caraway in the relative humidity range of 23 – 85% and at temperature levels of 25 and 40°C are shown in Figure 1. Isotherm curves were found to be of sigmoid in shape and follows BET type II isotherm characteristics and all curves followed similar patterns as most food materials do (Brunauer *et al.*, 1940). Figure 1 shows that EMC decreases with the increase in temperature at all levels of relative humidity. The reason may be that the kinetic energy associated with water molecules present in caraway seeds increased with increasing temperature, which in turn, resulted in decreasing attractive forces, and consequently, escape of water molecules. This led to a decrease in equilibrium moisture content values with increase in temperature at a given relative humidity. Similar trend was reported for various food materials (Rahman and Labuza, 1999; Hossain *et al.*, 2001, Janjai *et al.*, 2010). Moreover, the BET monolayer moisture content of caraway is 0.0488 and 0.0274 g water/g dry matter and surface area of monolayer is 170.90 and 95.83 m²/g at 25 and 40°C measured respectively.

Table 2. Physical characteristics of *Carum Carvi* L., (Caraway)

Physical Property	Results
Length (mm)	4.6507 ± 0.2136
Width (mm)	1.0693 ± 0.0797
Thickness (mm)	1.1794 ± 0.1093
Geometric Mean Diameter (D_g)	1.8008 ± 0.0870
Sphericity	0.3879 ± 0.0246
Surface Area (mm²)	10.2142 ± 0.9759
1000 grain weight (gm)	2.816 ± 0.1856
1000 grain mass (ml)	5.5 ± 0.1
True Density (ρ_k) (g/cc)	4.7364
Hardness (N)	51.083 ± 11.068

*Mean ± Std. Dev.

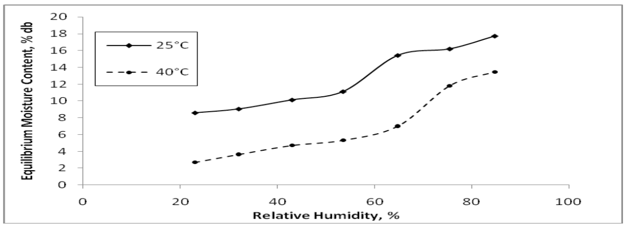


Figure 1. Experimental sorption isotherms for caraway at different temperatures

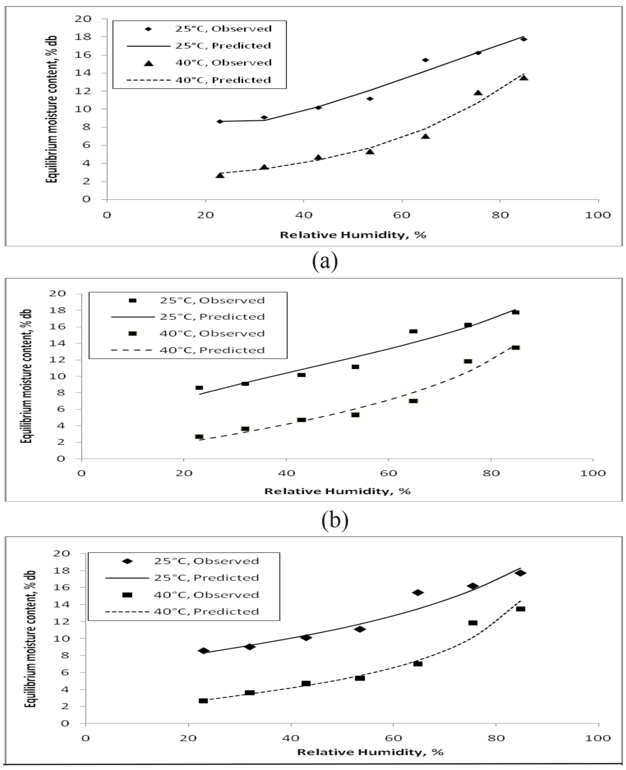
Fitting of sorption models

Statistically computed parameters for the seven isotherm models and their coefficient of determination (R^2), relative mean square error values are presented in Table 3. The parameters a, b, c and d are temperature dependent for all the models tested. In the case of Peleg model, the values of coefficient of determination are highest followed by Henderson and GAB model respectively. Further, minimum RMSE value was obtained for the Peleg model followed by Henderson and GAB model. Hence, Peleg model was found to be the best fit among the seven models tested. The Henderson model was the next to the Peleg model in terms of minimum RMSE and highest value of coefficient of determination. The agreement between the predicted and observed results is very good for the relative humidity range studied.

Table 3. The coefficients of the selected models, mean relative error (MRE), coefficient of determination (R^2) and root mean square error for caraway seeds

Models	Temperature (°C)	Parameters						
		A	B	C	D	MRE (%)	R^2	RMSE
BET	25	0.0488	-11.1048	-	-	3.4933	0.8702	0.3536
	40	0.0274	14.2247	-	-	5.3785	0.9498	0.2258
GAB	25	7.4983	67.955	0.7009	-	4.4794	0.9427	0.8309
	40	3.2639	7.4698	0.9221	-	6.3869	0.9601	0.7665
Oswin	25	11.58	0.2723			5.6777	0.9373	0.869
	40	5.436	0.5554			6.3365	0.9619	0.7496
Iglesias-Chirife	25	9.243	2.987			9.6113	0.8170	1.4840
	40	1.794	2.106			11.4189	0.9208	1.0801
Henderson	25	0.00204	2.359			5.825	0.9454	0.811
	40	0.1068	1.095			10.1689	0.9643	0.725
Peleg	25	0.1112	-2.32	20.85	0.9326	3.4131	0.9685	0.6162
	40	3.653	0.2026	17.36	3.126	7.6354	0.9750	0.6067
Smith	25	7.033	6.197			5.0077	0.9335	0.8948
	40	0.6641	6.976			8.2826	0.9668	0.6999

The predicted and observed equilibrium moisture contents are shown in figure 2a, 2b and 2c for the Peleg, Henderson and GAB models, respectively.



(a) (b) (c)

Figure 2. Predicted and measured sorption isotherms of caraway as per (a) Peleg, (b) Henderson and (c) GAB models at different temperatures

Conclusion

In conclusion, determined physical properties of caraway can be used to design of equipment for handling and processing. Different equations can be used to model the sorption data of caraway seeds. The Peleg, Henderson and GAB models described experimental isotherms of caraway seeds better for water activities 0.22 to 0.85 at 25 and 40°C. Temperature has a significant effect on the sorption isotherm of caraway seeds.

Acknowledgements

Authors are thankful to Director, DFRL for keen interest in the present study.

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