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Sorption Isotherm of Hybrid Seed Corn

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ABSTRACT

Isotherm data are used in solving heat and mass transfer problems that may be encountered during storage and drying processes as well as in dryer design. A study was performed on the basis of two factorial experiments for adsorption and desorption phenomena with three factors: hybrid (at 2 levels: three-way cross 647 and single cross 704), temperature (at 6 levels from 5 to 55°C) and relative humidity (RH) (at 5 levels from 10 to 90%). Glycerol solutions at different concentrations were used to maintain RH at the aforementioned ranges. Statistical analysis showed that temperature, RH and hybrid affected the equilibrium moisture content in both adsorption and desorption phenomena. Comparisons between means showed that hybrid 704 had higher EMC values than hybrid 647 at the same conditions. Fitting of non-linear models (Henderson, Chung-Pfost and Oswin) to the experimental data was conducted. The Oswin model was the best model for adsorption and desorption curves for hybrid 704 and the adsorption curve for hybrid 647. The best model for desorption curve for hybrid 647 was the Chung-Pfost model.

Keywords: Isotherm curves, adsorption, desorption, sorption models, equilibrium moisture content, temperature, relative humidity

INTRODUCTION

According to previous studies, controlling environmental conditions, especially temperature and relative humidity, is an important factor to control metabolic activity of seeds and also to inhibit microbial contamination during storage. Lack of control of storage environment results in respiration increase and vigour decrease, and under worse conditions leads to contamination and eventually deterioration of seed germ. Because of effectiveness of seed moisture content and RH on each other (in limited environments), and also because both of them are affected by temperature, access to isothermal models could be helpful to estimate moisture content of the crop promptly and consequently to have a successful and safe storage (Brooker et al. 1992 ; Copeland and McDonald 1995). In other words, Equilibrium moisture content (EMC) is a relevant physicochemical property that describes the moisture state of a hygroscopic material at equilibration on a moisture basis with its environment. EMC data have practical application, such as helping establish humidity bounds to inhibit microbial growth and mycotoxin production during storage (Boente et al. 1996).

The other important stage in postharvest technology of seed corn is drying in which parameters such as temperature, relative humidity of inlet air, final moisture content of seed, air velocity, etc. should be selected appropriately to have a cost competitive process and a dried product (seed) with minimum loss in vigour.

In a study by Thompson (1972), it was revealed that any increase in moisture content of seed corn and temperature reduces its storability, such that at 15.6°C, reduction of moisture from 28% to 15.5% improves its storability from 17 to 197 days. On the other hand, at moisture content of 15.5%, reduction of temperature from 23.9°C to 15.6° reduces storability from 81 to 197 days.

Molds are one of the most important categories of microorganisms that are responsible for seed contamination. According to studies, more than 100 genera of molds are responsible for cereal contamination during storage. Each genus needs a minimum and an optimum temperature and also an optimum RH for growth. The optimum temperature for most molds is in the range of 25 to 30°C. Some of these molds grow best at 37°C. The minimum temperature for growth and activity is not reported, but it is elucidated that some genera can grow at temperatures of about 0°C (Brooker et al. 1992).

Moisture isotherms describe the EMC as a function of the environment equilibrium conditions and are useful for biological systems (Bell and Labuza 2000; Lewis 1990). Chen and Morey (1989b) investigated isotherm curves for corn in the range of 5 to 45°C. The results indicated that the curves are different for different varieties. Also, factors of temperature and RH affected the curves. Hysteresis was observable from 10 to around 100% RH. The inconsistency and scattering of data obtained by Chen (2000) indicated the EMC / ERH properties of corn kernels and soybeans were affected by the variety, location, and other factors. In addition to the environmental conditions, grain components (minerals, lipids, starch and protein) and variety could be determinative factors for adsorption and desorption isotherms (Neubere, E.E. 1980). Evaluating goodness-of-fit of sorption models (Henderson, Chung-Pfost, Oswin and Kalsey models) on EMC/ERH data for cereals and oilseeds by Chen and Morey (1989a) resulted in that Halsey is the best model for crops rich-in protein and oil, and Oswin has the best precision for wheat and corn. However, Chung-Pfost and Henderson models were evaluated better models for crops rich in fiber and starch. In another research, seed corn isotherms were studied in the temperature range of 20 to 40°C and water activity (a_w) of 0.1 to 0.98. In this study, 6 models were evaluated for prediction of EMC of the samples and in the end, Hederson model was evaluated as the most precise model for this purpose. Also, it was reported that precision of each model could be different in adsorption and desorption phenomena (Sopade and Ajisegiri 1994).

Thus, because of the importance of isotherm curves in storage and drying of hybrid seed corn, this study was performed to: a) determine the effect of temperature, RH and variety on EMC of the crop, b) evaluate the fit of 3 models (Modified Henderson, Chung-Pfost and Modified Oswin equations) in estimating EMC for the adsorption and desorption phenomena.

MATERIALS AND METHODS

Two common varieties of seed corn in Khoozestan province in Iran namely: Single-cross 704 and Three-way-cross 647 were used in this study. Glycerol solutions were used to prepare controlled RH environment at a specified temperature. In order to determine ERH of a glycerol solution, an isolated container made of plexiglas was prepared. A 400 W electric heater was used to heat the internal environment of the container and the temperature was controlled by a Delta-Ohm thermostat (model: HD-4030, Italy) with a controlling capability of ±0.2°C in the range if -15 to 110°C. Also, a fan was used for better distribution of moisture and heat. After equilibration of glycerol solution with air in the container, its RH, dry bulb and wet bulb temperatures were measured using a hygrometer (Testo 405, Germany). Before doing measurements, the hygrometer was calibrated with standard solutions of sulphuric acid and glycerol solutions in the RH range of 10 to 90% and temperature range of 5 to 55°C (Lewis 1990; Perry and Green 1997). For more confidence, wet and dry bulb temperatures were also measured using wet and dry bulb thermometers, respectively and vapour pressure was calculated by the following equation:

$$P_w = P_{wb} - \frac{(P_B - P_{wb})(T_a - T_w)}{1555.56 - 0.722(T_w)} \qquad (1)$$

Where:

P_w = Partial pressure of water (kPa)
P_B = Barometric pressure (kPa)
P_{wb} = Saturated water vapour pressure at wet bulb temperature (kPa)
T_a = Dry bulb temperature (°C)
T_w = Wet bulb temperature (°C)

In order to measure P_B, a barometer (Lambrecht 604, Germany) with a precision of ±0.025 kPa was used. To determine P_{wb} the standard table of thermodynamic properties of saturated water was used (Perry and Green 1997). In performing experiments, solutions of glycerol with concentrations in the range of 24 to 98% (w/w) were prepared and consequently, their ERH and vapour pressure were determined at six levels of temperatures: 5, 15, 25, 35, 45, and 55°C. Then, some nonlinear univariate models, based on concentration of solutions, were obtained for relative humidity (RH) by fitting the observed data. In the end, needed concentrations of the solutions for providing five RH (10, 30, 50, 70 and 90%) levels at six temperature (5, 15, 25, 35, 45 and 55 °C) levels were determined using trial and error method. To inhibit contamination of dilute solutions by molds, two drops of saturated copper sulphate were used in each solution (Anonymous 1983).

In the second stage, the effect of environmental conditions on EMC of seed corn hybrids was studied on the basis of a factorial experiment including three factors: hybrids (647 and 704), temperature (at six levels from 5 to 55°C) and RH (at five mentioned levels from 10 to 90%); each treatment was performed in 3 replicates. EMC of the samples was investigated during adsorption and desorption, separately.

For each adsorption experiment, about 4 g dried sample and for each desorption experiment, about 5 g wet sample were accurately weighed. The sample was put on a perforated plate located in a glass jar containing glycerol solution (which provided the required RH and vapour pressure). The jars were put in a plexiglas container (equipped to a 800 W heater and temperature control system) at the adjusted temperature under static condition. After the samples reached stable condition (20 days), they were taken out of the jars and were weighed using a scale with a precision of ±0.001 g (Sartorius, Germany). To determine their moisture content, samples were dried in an oven (Memmert 600, Germany) at 103°C for 72 hours and moisture contents were reported on dry basis using the following equation (Chen and Morey 1989b):

$$M_d = \frac{W - W_d}{W_d} \times 100 \qquad (2)$$

W = total weight of sample (g)
W_d = weight of dry material (g)

The data obtained from observations, were analyzed on the basis of factorial (statistical) experiments for adsorption and desorption phenomena, separately. The means were compared using Duncan's multiple range test (P = 0.01).

Hysteresis phenomenon for each variety, as a quantitative property, was determined by the difference between adsorption and desorption moisture contents. At the final stage, a number of sorption models were fitted to the experimental EMC data to estimate EMC of seed corn hybrids using environmental conditions (temperature and RH). The models used are as follows:

a) Modified Henderson model:

$$RH=1- \exp(-A\times(T+C)\times M^{B}) \qquad (3)$$

b) Chung-Pfost model:

$$RH=\exp(-(A/(T+C)\times\exp(-B\times M)) \qquad (4)$$

c) Modified Oswin model:

$RH=1/[((A+B\times T)/M)^{C}+1]$ (5)

Where :

RH = Relative humidity
M = equilibrium moisture content
T = temperature (°C)
A, B, C = experimental constants

After fitting, the standard error of estimate (SEE) (equation 6) and mean relative deviation (MRD) (equation 7) were calculated.

$$SEE=\sqrt{\frac{SSE}{df}}=\sqrt{\frac{\sum_{i=1}^{n}(M_i-M_p)^2}{df}} \qquad (6)$$

$$MRD=\frac{1}{n}\times\frac{M_i-M_m}{M_i} \qquad (7)$$

Where M_i is the observed EMC, M_p is predicted EMC, df is degree of freedom and M_m is the mean of the observed data for EMC.

RESULTS AND DISCUSSION

Results indicated that glycerol can be used as a controlling agent for RH in the desired range. Subjection of the data for ERH regression provided by different concentrations (C = % w/w) of glycerol solutions at temperature range of 25°C and 45°C resulted in the following simple relationships:

T=25 °C : $RH=(102.11 - 1.02C)/(1 - 0.0075C)$, $R^2>0.99$ (8)

T=45 °C : $RH=(102.77 - 1.03C)/(1 - 0.0075C)$, $R^2>0.99$ (9)

The data indicated that the increase of glycerol concentration in the solution from 34.9%(w/w) to 97.6%(w/w) decreased RH and water vapour pressure from 90% to 10% and 21.38 to 2.38 mm Hg, respectively. However, performance of the solution in decreasing RH, is higher at high concentrations. For instance, at 25°C, concentration of the solution must be increased from 34.9% to 65.05% in order to decrease RH from 90% to 70%, However, to reduce RH from 30% to 10%, glycerol concentration must be changed from 90.6% to 97.6%(w/w).

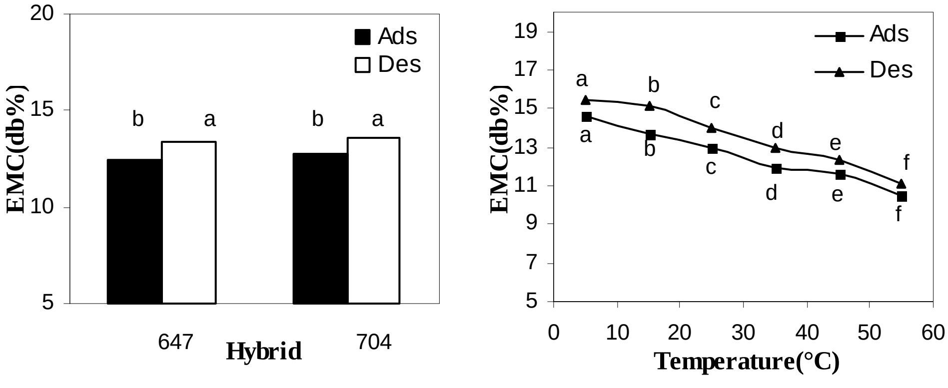
Adsorption

The results of analysis of variance for EMC are tabulated in Table 1. From Table 1 and Figure 1.a, hybrid corn significantly affected (P = 0.01) EMC, such that in adsorption stage, EMC of single-cross 704 and three-way cross 647 were 12.65% and 12.45%(db), respectively. The table also shows that the effects of temperature and RH on EMC of the hybrids are significant (P = 0.01). Increase of temperature from 5 to 55°C caused significant reduction in mean EMC values, such that it was reduced from 14.66%(db) at 5°C to 10.49%(db) at 55°C (Figure 1.b). Increased RH resulted in direct increase of EMC. However, due to higher slope of the EMC variation due to RH (dependent on water vapour pressure) compared to temperature, RH has greater impact on EMC values than temperature. The results agrees to the previous studies reported by Chen and Morey (1989a) and Sopade and Ajisegiri (1994).

Table 1. Analysis of variance for equilibrium moisture content during adsorption and desorption.

Source of Error	**DF**	**Mean square (Adsorption)**	**Mean square (Desorption)**
Hybrid	1	1.179**	1.054**
Temperature	5	42.065**	52.034**
RH	4	941.921**	923.159**
Hybrid*Temperature	5	0.031^{ns}	0.047^{ns}
Hybrid*RH	4	0.039^{ns}	0.009^{ns}
Temperature*RH	20	0.969**	1.065**
Hybrid*Temperature*RH	20	0.056^{ns}	0.025^{ns}
Error	120	0.063	0.055

**Significant at P = 0.01 ; ^{ns}Not significant at P = 0.01



(a) (b)

Figure 1.(a) Comparison of hybrids' mean equilibrium moisture content (wb%) during adsorption and desorption. (b) Comparison of mean equilibrium moisture content at different temperatures in adsorption and desorption.

The interaction of temperature and RH on EMC is significant (P = 0.01) (Table 1). Figure 3 indicates that at a fixed temperature, EMC increases due to the RH increase in a sigmoid trend and inversely, EMC increases when temperature declines at a fixed RH. Therefore, moisture content of the crop is controllable with controlling combination of the parameters (temperature and RH). Figure 3 also indicates that when temperature increases at a fixed EMC, ERH increases resulting from water activity increase in the seed which has a negative influence on its storability.

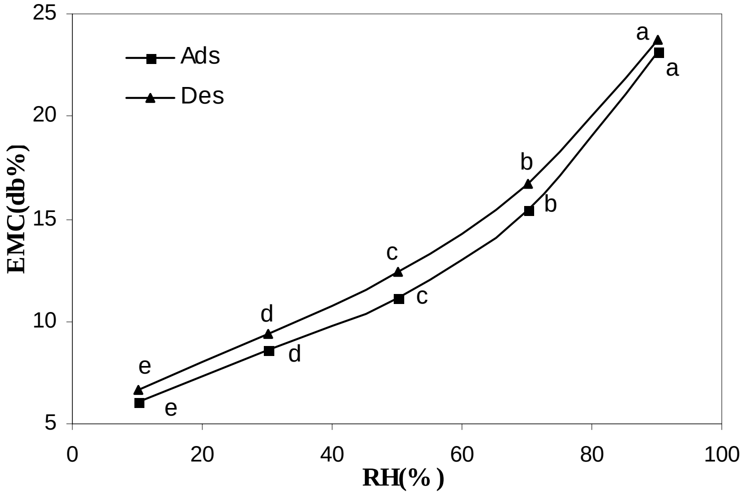


Figure 2. Relationship of mean equilibrium moisture content and relative humidity in adsorption and desorption.

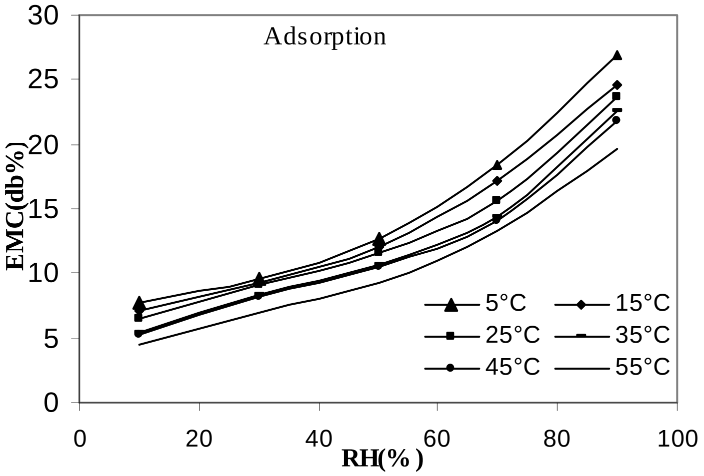


Figure 3. Relationship of mean equilibrium moisture content and relative humidity during adsorption.

Desorption

Desorption curves could be helpful in analyzing the drying process of the seed, as well as in dryer design and prediction of drying rate and time. Analysis of variance for desorption experiments are shown in Table 1. The results indicate that like adsorption, the effects of temperature, RH and hybrid on EMC are significant (P = 0.01). Also, RH had more impact on EMC values compared to temperature in the range investigated. The results are also shown in Figures 1, 2 and 4.

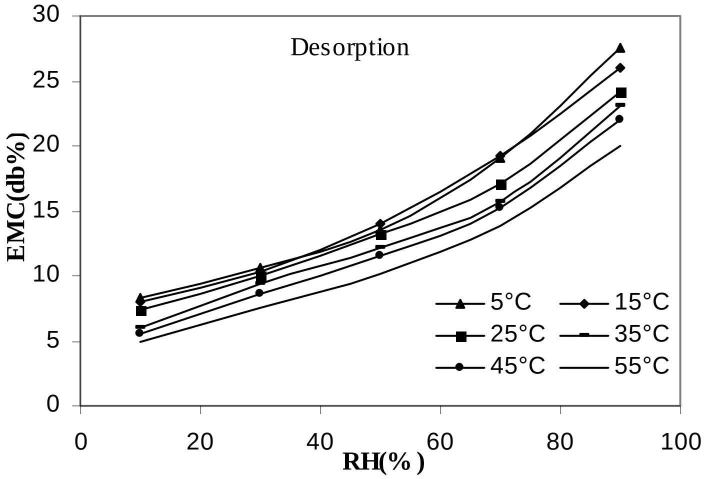


Figure 4. Relationship of mean equilibrium moisture content and relative humidity during desorption.

Hysteresis

Hysteresis changes due to ERH for both hybrids of 647 and 704 are shown in Figures 5 and 6. For both hybrids at a fixed temperature, ERH increase causes hysteresis to increase until about 70% ERH, and then hysteresis decreased at high ERH. The hysteresis at high temperature was not as high as those at low temperature.

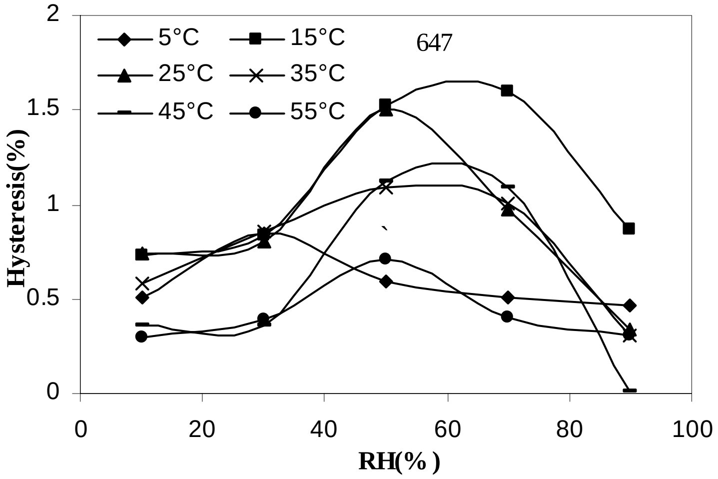


Figure 5. Hysteresis profiles with equilibrium relative humidity for hybrid 647.

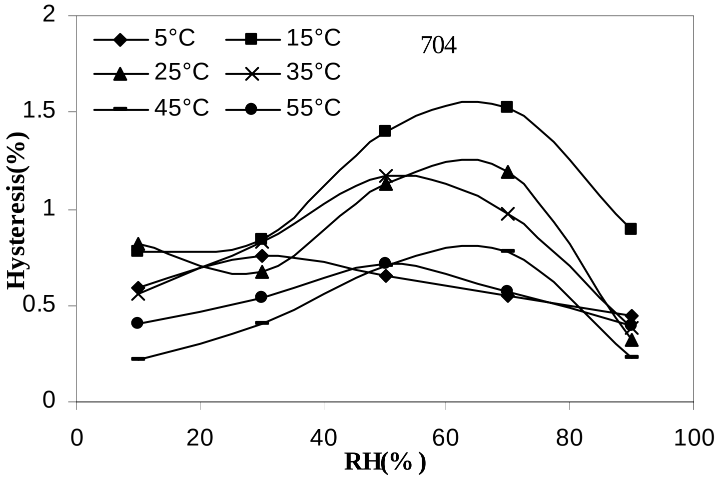


Figure 6. Hysteresis profiles with equilibrium relative humidity for hybrid 704.

Model Fitting

The results of fitting the three models of Henderson, Chung-Pfost and Oswin to the data obtained from experiments are shown in Table 2.

Table2. Estimated parameters for Henderson, Chung-Pfost and Oswin models.

Model	**Phenomenon**	**Hybrid**	**A**	**B**	**C**	**R^2**	**SEE**	**MRD**
Henderson	Adsorption	647	0.7974	2.060	44.649	0.994	1.224	0.083
		704	0.7173	2.075	51.412	0.995	1.156	0.052
	Desorption	647	0.8475	2.164	43.112	0.994	1.046	0.070
		704	0.7175	2.146	50.918	0.994	1.055	0.068
Chung-Pfost	Adsorption	647	493.18	19.056	51.269	0.996	1.112	0.069
		704	542.95	18.782	57.985	0.996	1.064	0.062
	Desorption	647	522.73	18.305	48.387	0.996	0.965	0.056
		704	560.73	18.011	54.991	0.996	0.982	0.056
Oswin	Adsorption	647	0.1357	-0.00075	3.067	0.998	0.531	0.039
		704	0.1367	-0.00071	3.079	0.998	0.533	0.038
	Desorption	647	0.1483	-0.00083	3.207	0.997	1.186	0.056
		704	0.1478	-0.00078	3.186	0.997	0.705	0.043

Based upon SEE and MRD, the Oswin model was the best model for adsorption and desorption curves for hybrid 704 and the adsorption curve for hybrid 647. However, the Chung-Pfost model was the best model for desorption curve of hybrid 647. Sopade and Ajisegiri (1994) studied the behaviour of different varieties of corn in water sorption process and reported that precision of each model could be different in adsorption and desorption phenomena. Sorption curves based on the predicted data using the best fitted models for both varieties are shown in Figures 7 to 10.

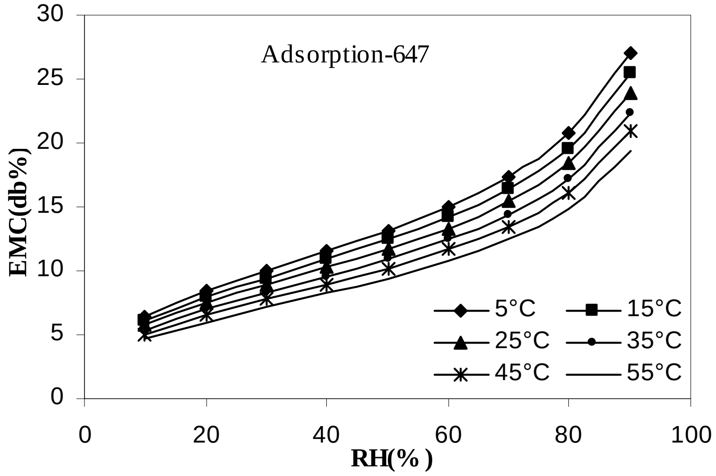


Figure 7. Predicted adsorption curves for hybrid 647 using Oswin model.

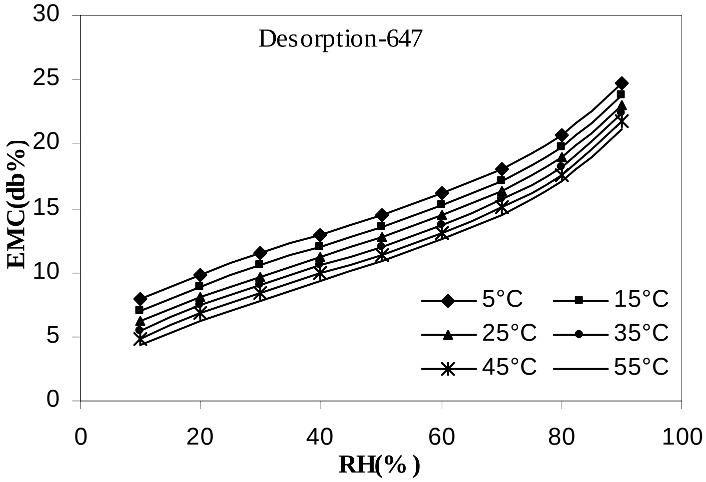


Figure 8. Predicted desorption curves for hybrid 647 using Chung-Pfost model.

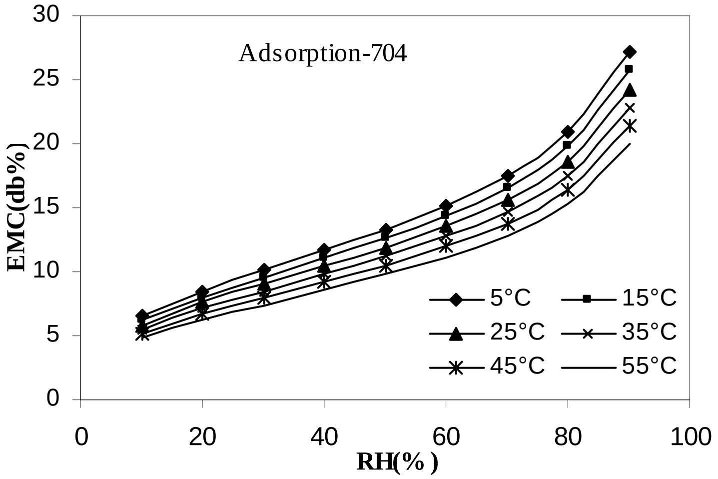


Figure 9. Predicted adsorption curves for hybrid 704 using Oswin model.

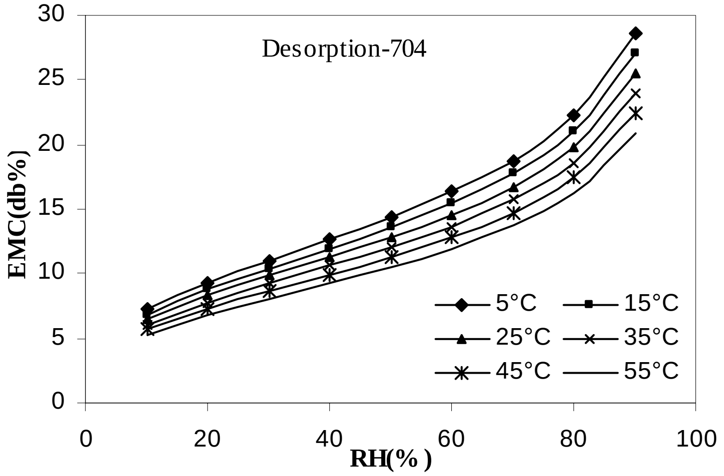


Figure 10. Predicted desorption curves for hybrid 704 using Oswin model.

Conclusion

Based upon the results of this study, hybrid, temperature and relative humidity are important factors affecting sorption isotherms of seed corn, and EMC of the crop is controllable by controlling combination of the parameters, especially temperature and RH. However, for each hybrid, relative humidity is the main environmental factor affecting the adsorption and desorption phenomena. Under the same environmental conditions, hybrid 704 provides lower ERH (resulting from lower a_w) compared to hybrid 647 and therefore, the former has better storability. The Oswin model is the best model for fitting to adsorption and desorption data for hybrid 704 and adsorption data for hybrid 647.,The Chung-Pfost model provided the best fit for desorption data for hybrid 647.

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