Moisture Isotherms and Heat of Desorption of Canola

Hamid Reza Gazor

Agricultural Engineering Research Institute. POB: 31585-845 Karaj, Iran
E- mail: hgazor@yahoo.com

ABSTRACT

Moisture desorption isotherms (EMC/ERH) of canola cultivar of 'Option 500' determined at 30, 40, 50 and 60 °C using the standard gravimetric static method over a range of relative humidity from 11% to 81%. The experimental desorption curves were fitted by four equations: modified Henderson, modified Chung–Pfost, modified Halsey and modified Oswin. The modified Oswin model was found as best model to describe desorption isotherms of canola. The net isosteric heat of desorption of canola was determined from the equilibrium data at different temperatures. It was observed to vary between 1.58 - 10.41 kJ/mol at moisture varying between 1.0 - 12.5 % d.b.

Keywords: Canola, desorption isotherms, isosteric heat

1. INTRODUCTION

Canola (*Brassica napus L.*) is an important oil crop grown in Canada, India, China, Europe and other regions of the world, and is ranked third in global production of oil crops (Kazan et al., 1999; Cardoza et al., 2003). In Iran, the area under cultivation of canola increases annually. For prevention of rancidity and to ensure good quality, canola must be harvested and dried in a short period in North of Iran. Drying has very important role in canola storage. In this step, moisture of kernels is reduced to about 7 % d.b., which would result in suitable condition for storage (Pagano et al., 1999; Ward et al., 1985).

The equilibrium moisture content (EMC) is useful to determine whether a product gains or loses moisture under a given set of temperature and relative humidity conditions. Therefore equilibrium moisture content is directly related to drying and storage. The equilibrium moisture content is dependent upon the temperature and related humidity of the environment as well as species, variety and maturity of the grain (Chakraverty, 1981; Iglesias and Chirife, 1982; Rahaman, 1995). Accurate information on equilibrium moisture content of different Iranian cultivars of canola at various relative humidity and drying temperatures are not available. There is a need for comprehensive study of the equilibrium moisture content of canola to understand its drying behaviour.

The net isosteric heat of sorption is also important information for drying, so it can be used to determine the energy requirements and provide information on the state of water within the dried product. The moisture content level of a product at which the net isosteric heat of sorption reaches the value of latent heat of sorption is often considered as the indication of the amount of bound water existing in the product (Wang and Brennan, 1991). The four empirically modified models that are used in literatures, are the most commonly used models (Sun and Byrne, 1998; Chen, 2000; Janjai et al., 2006; Ghodake et al., 2007).

Therefore, the present research was developed with the following objectives:
• Determine the effect of temperature on the moisture desorption isotherms of one Iranian canola seed cultivar 'Option 500' abbreviated as canola in this paper.
• Analyze the data with the help of four sorption isotherm equations available in the literature and find the most suitable model describing the isotherms of canola.
• Calculate the net isosteric heat of desorption of water from the experimental data.

2. MATERIALS AND METHODS

2.1 Experimental Procedure

The canola seeds used in the desorption experiments were collected randomly from a research farm in Gorgan province of Iran during the summer of 2008. The experiment was conducted by the Agricultural Engineering Research Institute (AERI), Karaj. The seed samples without any cracking, breaking and other physical damages were considered. They were carried out to laboratory in PE plastic bags. Canola 'Option 500' is an appropriate cultivar to be used in moderate climate especially in North of Iran. Naturally dried canola seeds were placed beside of distilled water in refrigerator at temperature 4 ºC for 15 days for primary conditioning. Toluene was used in sample preparation to avoid sample spoilage. The initial moisture content of the conditioned samples was determined about 25 % d.b. at the beginning of experiments using the standard method (AOAC, 1990). The selected sorption method was the static gravimetric technique, which was based on the use of saturated salt solutions to maintain a stable relative humidity after equilibrium was reached.

The water activity of the food is identical to the relative humidity of the atmosphere at equilibrium conditions and the mass transfer between the product and the ambient atmosphere is assured by natural diffusion of the water vapour. Seven saturated salt solutions (Table 1) were prepared corresponding to a wide range of water activities ranging from 0.11 to 0.83.

Table 1. Equilibrium relative humidity of saturated salt solutions *

	Temperature (ºC)			
Salt solutions	30	40	50	60
LiCl	0.1128	0.1121	0.1110	0.1095
CHC_3COOK	0.2161	0.2040	0.1920	0.1800
$MgCl_2.6H_2O$	0.3240	0.3160	0.3050	0.2930
K_2CO_3	0.4310	0.4330	0.4269	0.4212
$Mg(NO_3)_2$	0.5140	0.4842	0.4544	0.4730
NaCl	0.7510	0.7470	0.7434	0.7450
KaCl	0.8360	0.8230	0.8120	0.8025

* (Greenspan, 1977; Labuza et al., 1985)

Seven sealed glass bottles were used in this research. Each bottle was provided with a sample holder that was hanged up at the side of the bottle. Sample holder was kept above saturated salt solutions in order to avoid contact with salt solution. In all experiments, approximately 2.5 g of canola seeds was taken into the respective weighing cups. All these seven bottles were put in an oven supplied with circulation fan (Figure 1). The weight loss of all these samples in each bottle was monitored daily after ten days. The experiments were completed when less than 1 % weight change was found between two successive readings. This took about 15–30 days, depending on the nature of the samples and the temperature inside the oven. Three replications were kept for each sample and the average values of EMC have been reported. The EMC of each sample was determined with the help of an atmospheric drying oven using 130 °C for 3 h (Pagano et al., 1999). Experiments were conducted at temperatures of 30, 40, 50 and 60 °C.

Figure 1. Precision oven and sealed glass bottles used in the experiments

2.2 Analysis of Sorption Data

A large number of models have been proposed in the literature for the sorption isotherms (Iglesias and Chirife, 1982; Rahaman, 1995). In the present study, the description of the relationship between EMC, equilibrium relative humidity (ERH), and temperature for canola were verified according to the four models (Sun and Byrne, 1998; Sokhansanj et al., 1986; Chen, 2000; Ghodake et al.,2007; Basunia and Abe, 2001; Lahsasni et al., 2003) as shown in Table 2., where h_r is the relative humidity or decimal ERH, M_e is the equilibrium moisture content or EMC on dry basis, T is the temperature in ºC and C_1, C_2, C_3 are coefficients of models.

Table 2. Sorption isotherm models

Equations	Models
$h_r = \exp[-\exp(C_1 + C_2 T) M_e^{-C_3}]$	Modified Halsey
$1 - h_r = \exp[-C_1 (T + C_2) M_e^{C_3}]$	Modified Henderson
$h_r = \dfrac{1}{1 + [(C_1 + C_2 T)/M_e]^{C_3}}$	Modified Oswin
$h_r = \exp[-\dfrac{C_1}{T + C_2} \exp(-C_3 M_e)]$	Modified Chung–Pfost

2.3 Validation of EMC Model

The coefficients of the individual equations were determined by means of a standard regression technique. The various EMC models were evaluated for their suitability in predicting the EMC of the sample on the basis of the coefficient of determination (R^2), standard error of estimate (SEE) and mean relative of error (MRE). These statistical parameters were calculated employing the following equations (Chen, 2000; Ghodake et al., 2007; Basunia and Abe, 2001; Lahsasni et al., 2003; Sun and Byrne, 1998).

$$SEE = \sqrt{\frac{\sum_{i=1}^{N}(M_{i,\exp} - M_{i,pre})^2}{df}} \quad (1)$$

$$MRE = \frac{100}{n}\sum_{i=1}^{N}\left|\frac{M_{i,\exp} - M_{i,pre}}{M_{i,\exp}}\right| \quad (2)$$

Where, $M_{i,exp}$ is the ith experimental value of EMC; $M_{i,pre}$ is the ith value predicted by the model; N is the number of data points; n is the number of coefficients in each model; df is the degrees of freedom of regression model (N-n). It is generally considered that MRE values below 10 % indicate an adequate fit for practical purposes (Liu-Ping et al., 2005).

2.4 Determination of Net Isosteric Heat of Desorption

The net isosteric heat of desorption can be determined from moisture desorption data using the following equation, which was derived from the Clausius–Clapeyron equation (Adam et al., 2000; Janjai et al., 2006; Ghodake et al., 2007):

$$\frac{\partial \ln(h_r)}{\partial T} = \frac{Q_{st}}{RT^2} \quad (3)$$

Assuming that the net isosteric heat of desorption (Q_{st}) is temperature independent, integrating Eq. (3), gives the following equation:

$$\ln(h_r) = -(\frac{Q_{st}}{R})\frac{1}{T} + K \quad (4)$$

Using the computer softwares of Statistica 6.0 and Microsoft Excel 2003, the nonlinear optimization method was used to find out the best equation for the canola desorption isotherms and the net isosteric heat of desorption.

3. RESULTS AND DISCUSSION

3.1 Desorption Curves

The results of desorption experiments are presented in Figure 2. The equilibrium moisture content (EMC) increased with decreasing temperature at constant equilibrium relative humidity (ERH). Furthermore, at constant temperature, the EMC increased with increasing ERH. Similar results have been reported in the literature for the sorption curves of some crops (Basunia and Abe, 2001; Lahsasni et al., 2003; Ghodake et al., 2007).

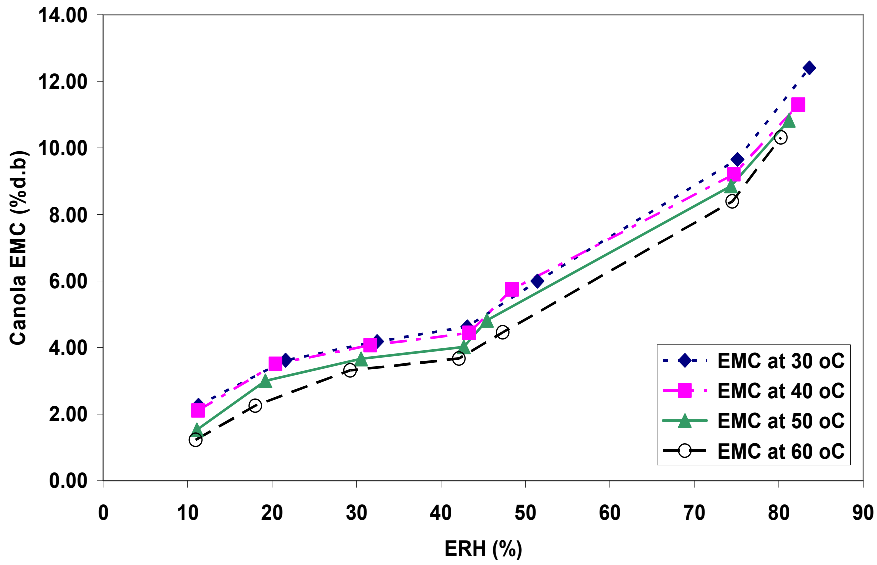

Figure 2. Influence of temperature on canola equilibrium moisture content (EMC)

3.2 Fitting of Sorption Models to Experimental Data

Desorption curves for canola were drawn as equilibrium moisture content against equilibrium relative humidity. These curves were used to estimate the coefficients of the different sorption models as shown in Table 2.

The coefficients of the modified Henderson, modified Chung–Pfost, modified Halsey and modified Oswin models, their mean relative error (MRE) and standard error of estimate (SEE) are presented in Table 3. It is clear from this table that the modified Oswin model gives better fit to the experimental data with highest R^2 and lowest values of MRE and SEE than other models.

Table 3. Coefficients and statistical evaluation of regression

Parameters	Modified Henderson	Modified Chung-Pfost	Modified Halsey	Modified Oswin
C_1	0.000526	502.1594	2.521234	6.954722
C_2	55.803240	105.6607	-0.009424	-0.032779
C_3	1.469770	0.27093	1.486269	2.126721
R^2	0.983	0.984	0.970	0.989
SEE	1.83	1.92	2.32	1.41
MRE (%)	8.12	7.57	11.66	7.42

Comparison between experimental values and predicted desorption isotherms by modified Oswin model for canola at 30, 40, 50 and 60 ºC is shown in Figure 3. Furthermore, modified Henderson and modified Chung–Pfost models obtained good fitting with experimental data. Similar results were reported for canola desorption isotherms by other researchers (Sun and Byrne, 1998; Sokhansanj et al., 1986).

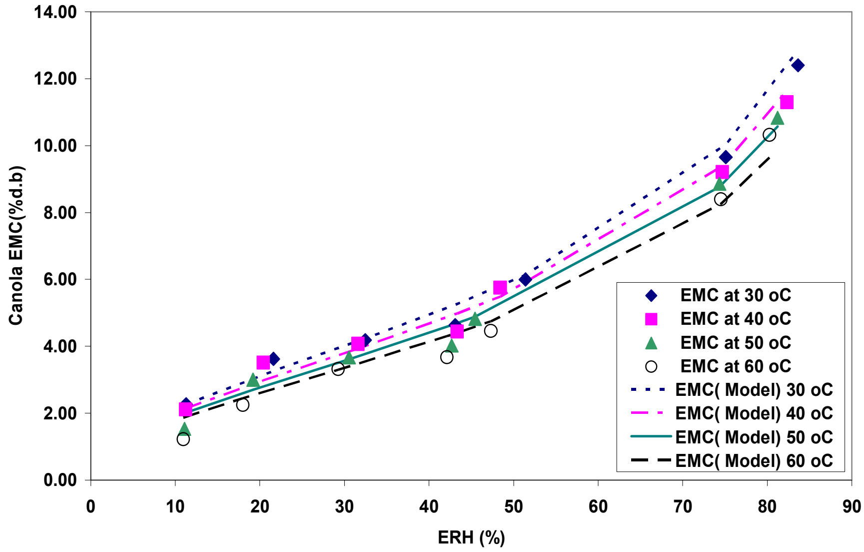

Figure 3. Experimental values and predicted desorption isotherms by modified Oswin model for canola at different temperatures

3.3 Heat of Desorption

The isosteric heat of desorption, Q_{st}, values were calculated from the slope of the plot between the values of ln(ERH) and 1/T at constant moisture content as shown in Figure 4 for canola. Data points correspond with desorption curves (fig.2).

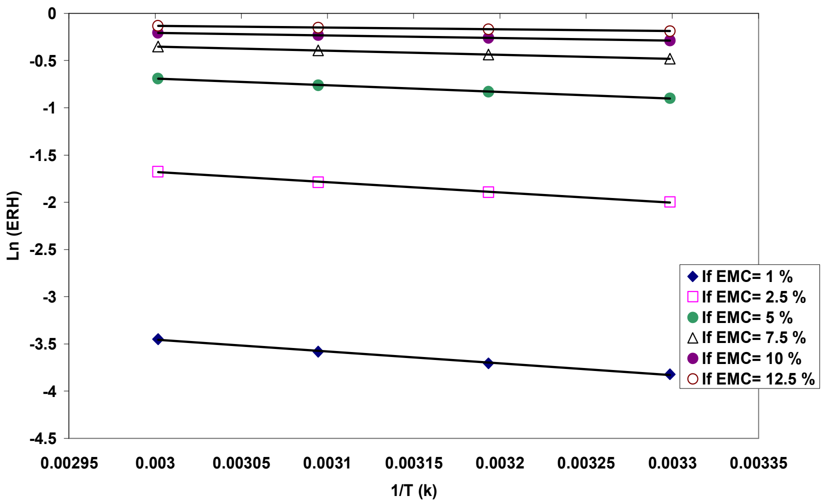

Figure 4. Ln(ERH) vs. 1/T graphs for calculating the heat of sorption of canola

ERH at different temperatures and moisture contents for canola are presented in Table 4.

Table 4. ERH at different temperature and moisture content for canola

Temperature (^oC)	Canola moisture content (%d.b) 1.0	2.5	5.0	7.5	10.0	12.5
30	2.20	13.60	40.68	61.91	75.00	82.79
40	2.51	15.00	43.59	64.70	77.10	84.42
50	2.82	16.69	46.73	67.51	79.33	86.00
60	3.20	18.73	50.09	70.38	81.40	87.61

The values of the net isosteric heat of desorption of canola for different moisture contents are presented in Table 5. Also, variations of the heat of desorption for canola with moisture content are shown in Figure 5.

Table 5. Variation of the net isosteric heat of desorption

Canola EMC (% d.b)	Q_{st} (kJ/mol)
1.0	10.41
2.5	8.98
5.0	5.85
7.5	3.62
10.0	2.30
12.5	1.58

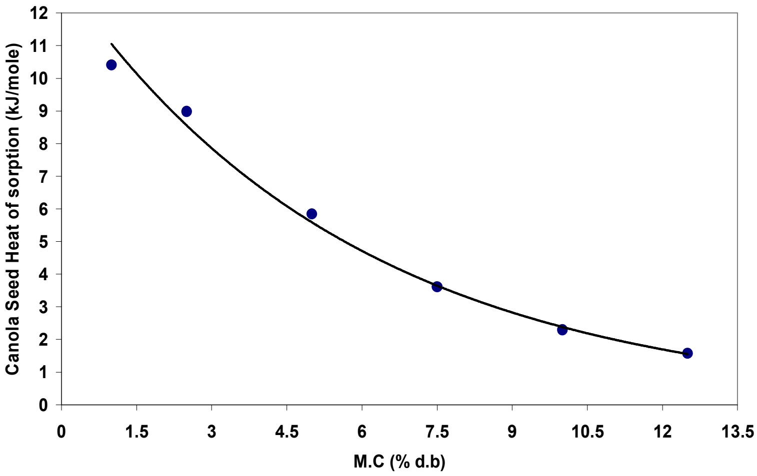

Figure 5. Net isosteric heat of desorption at different moisture content for canola

The isosteric heat of desorption of canola decreased with increase in material moisture content. The heat of desorption was higher at lower moisture contents. Similar results for many plants and food materials have been reported in the literature (Lahsasni et al., 2003; Ghodake et al., 2007; Janjai et al., 2006). The rapid increase in the heat of sorption at low moisture content was due to the existence of highly active polar sites on the surface of the food material, covered with water molecules forming a mono-molecular layer (Lahsasni et al., 2003). The net isosteric heat of desorption of water in canola seeds can be expressed mathematically as a function of moisture content (Ghodake et al., 2007; Janjai et al., 2006).

$$Q_{st} = 13.103\, e^{-0.1704\, M} \quad R^2 = 0.997 \tag{5}$$

This relation showed that the net isosteric heat of desorption of canola decreased exponentially with the increase of equilibrium moisture content.

4. CONCLUSIONS

The experimental results illustrated that the equilibrium moisture content (EMC) of canola seeds increased with decreasing temperature, at constant equilibrium relative humidity (ERH). Furthermore, at constant temperature, the EMC increased with increasing ERH.
Four isotherm models were fitted to experimental data. The modified Oswin model gave the best fit to the experimental data with highest R^2 (0.989) and lowest values of MRE and SEE compared to other models for sorption isotherms of canola for a wide range of water activity (0.11–0.81).
By applying the Clausius–Clapeyron concepts, the net isosteric heat of desorption was evaluated as an exponential function of moisture content. The net isosteric heat of desorption of canola varied between 1.58 – 10.41 kJ/mol at moisture varying between 1.0 – 12.5 % (d.b.).

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