Moisture isotherms and heat of desorption of canola

Hamid Reza Gazor

(*Agricultural Engineering Research Institute. POB*: 31585-845 *Karaj- Iran*)

Abstract: Moisture desorption isotherms (EMC/ERH) of canola cultivar of option 500 determined at 30, 40, 50 and 60℃ 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 to be a better model to describe the desorption isotherms of canola. The net isosteric heats of desorption of canola were determined from the equilibrium data at different temperatures. 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.

Keywords: canola, desorption isotherms, isosteric heat of desorption

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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 and Stewart, 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 a very important role in canola storage. In this step, kernels moisture is reduced to about 7% d.b., which would be resulted in suitable condition for storage (Pagano，Rovhein and Crozza, 1999; Ward et al., 1985).

The equilibrium moisture content (EMC) is useful to determine whether a product gains or losses moisture under a given set of temperature and relative humidity conditions. Thus equilibrium moisture content is directly related to drying and storage. Different materials have different equilibrium moisture contents. 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 contents 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 contents of canola to understand its drying behaviour.

The net isosteric heat of sorption is also an 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 used in literatures, are the most commonly used models (Sun and Byrne, 1998; Chen, 2000; Janjai et al., 2006; Ghodake, Goswami and Chakraverty, 2007).

Therefore, the present research was developed with the following objectives:

• To determine the effect of temperature on the moisture desorption isotherms of one Iranian canola seed cultivar as option 500 that here in by abbreviated to canola in the paper.

• To 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.

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Corresponding author: Hamid Reza Gazor, Email: hgazor@yahoo.com

• To 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 isotherms experiments were collected randomly from a researching farm of Gorgan province of Iran in the summer of 2008. The experiment was conducted in Agricultural Engineering Research Institute (AERI) in Karaj. The seed samples considered without any cracking, breaking and other physical damages. They were carried out to a laboratory in PE plastic bags. Canola *Option 500* is an appropriate variety to use in moderate climate, especially in north of Iran. Naturally dried canolas were conditioned beside of distilled water in a refrigerator at a temperature of 4℃ for 15 days. 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 experiments start time by using the standard method (AOAC, 1990). The sorption method used the static gravimetric technique, which was based on the use of saturated salt solutions to maintain a fixed relative humidity when the equilibrium was reached.

The water activity of the food was identical to the relative humidity of the atmosphere at equilibrium conditions and the mass transfer between the product and the ambient atmosphere was 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 at 30, 40, 50 and 60℃ *

Salt solutions	Temperature/℃			
	30	40	50	60
LiCl	0.1128	0.1121	0.111	0.1095
CHC_3COOK	0.2161	0.204	0.192	0.180
$MgCl_2.6H_2O$	0.324	0.316	0.305	0.293
K_2CO_3	0.431	0.4330	0.4269	04212
$Mg(NO_3)_2$	0.514	0.4842	0.4544	0.473
NaCl	0.751	0.747	0.7434	0.745
KaCl	0.836	0.823	0.812	0.8025

Note: * Greenspan, 1977; Labuza et al., 1985.

Seven sealed glass bottles were used in this research. Each bottle was provided with a sample holder who was hanged up in the side of the bottle. Sample holder was kept above saturated salt solutions in order to avoid contact of the salt solution with it. For each of these experiments about 2.5 g of canola seeds was taken into the respective weighing cups. All these seven bottles were put in an Oven with precision 1℃ and circulation fan (Figure 1). The loss in weights 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 whose temperature was fixed at 130℃ and 3 h (Pagano, Rovhein and Crozza, 1999). Experiments were conducted at temperatures 30, 40, 50 and 60℃.

Figure 1 Precision oven and sealed glass bottles that 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; Sokhansanjet al., 1986; Chen, 2000; Ghodake, Goswami and Chakraverty, 2007; Basunia and Abe, 2001; Lahsasni et al., 2003) as shown in Table 2. In this table h_r is the relative humidity or ERH decimal, M_e is the equilibrium moisture content or EMC % d.b., T is the temperature ℃ and C_1, C_2, C_3 are coefficients of models.

Table 2 Sorption isotherm models

Equations	Models
$h_r=\exp[-\exp(C_1+C_2T)M_e^{-C_3}]$	Modified-Halsey
$1-h_r=\exp[-C_1(T+C_2)M_e^{C_3}]$	Modified Henderson
$h_r=\frac{1}{1+[(C_1+C_2T)/M_e]^{C_3}}$	Modified-Oswin
$h_r=\exp[-\frac{C_1}{T+C_2}\exp(-C_3M_e)]$	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 based on 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 Goswami and Chakraverty, 2007; Basunia and Abe, 2001; Lahsasni et al., 2003; Sun and Byrne, 1998):

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

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

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 a 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):

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

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

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

Computer software Statistica 6.0 and Microsoft Excel the nonlinear optimization method were 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 the desorption experiments are presented in Figure 2. The equilibrium moisture content (EMC) increases with decreasing temperature, at constant equilibrium relative humidity (ERH). Furthermore, at a constant temperature, the EMC increases with increasing ERH. Similar results were reported in the literature for the sorption curves of some crops (Basunia and Abe, 2001; Lahsasni et al., 2003; Ghodake Goswami and Chakraverty, 2007).

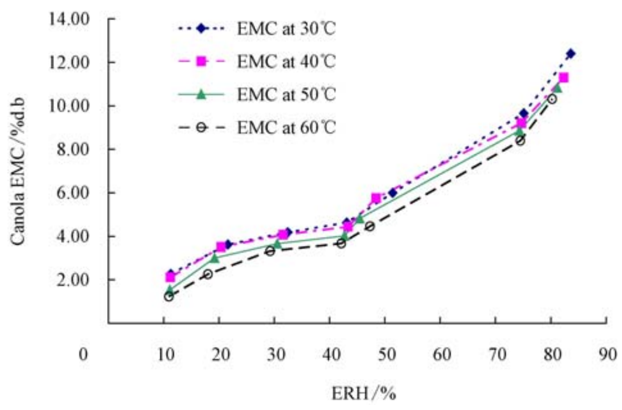

Figure 2 Influence of temperature on canola equilibrium moisture content (EMC)

3.2 Fitting of sorption models to experimental sorption data

The desorption curves for canola are drawn as equilibrium moisture content against the equilibrium relative humidity. These curves are 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 a better fit to the experimental data with highest R^2 and lowest values of MRE and SEE than other models for desorption isotherms of canola for a wide range of water activity.

Table 3 Model coefficients and Statistical results of equations fitted to the desorption isotherms of canola

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	0.97	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℃ were showed in Figure 3. Furthermore, modified Henderson and modified Chung–Pfost models have good fitting with experimental data. Similar results were reported for canola desoption isotherms by other researchers (Sun and Byrne, 1998; Sokhansanjet al., 1986).

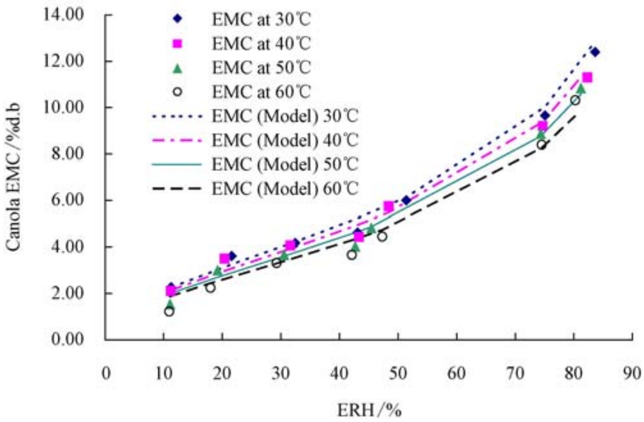

Figure 3 Experimental values and predicted desorption isotherms by modified Oswin model for canola at 30 , 40, 50 and 60℃

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(*RH*) and 1/*T* at constant moisture content as shown in Figure 4 for canola. The natural logarithms of ERH against reciprocal of absolute temperatures were determined from Figure 2 at various moisture contents.

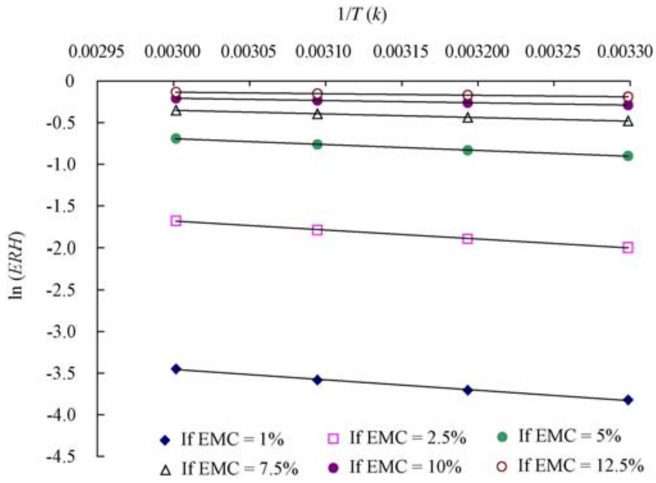

Figure 4 ln(*RH*) vs. 1/*T* graphs for calculating the heat of sorption of canola

ERH at different temperatures and moisture contents for canola are presented in Table 4. The values of the net isosteric heat of desorption of canola for different moisture contents are presented in Table 5. The variations of the heats of desorption for canola with moisture content are shown in Figure 5.

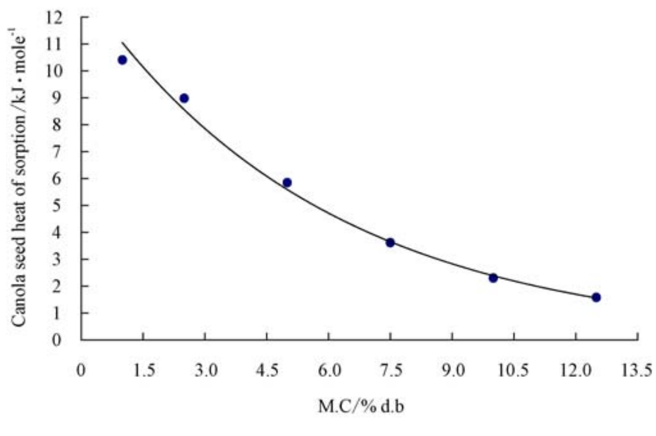

Figure5 Net isosteric heat of desorption at different moisture contents for canola

The isosteric heats of desorption of canola decrease with an increase in material moisture content. The heat of sorption is higher at lower moisture contents than at higher moisture contents. Similar results for many plants and food materials were reported in the literature (Lahsasni et al., 2003; Ghodake Goswami and Chakraverty, 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 surfaces of the food material, which were 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 Goswami and Chakraverty,2007; Janjai et al., 2006).

$$Q_{st} = 13.103e^{-0.1704M} \qquad (R^2 = 0.997)$$

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 a constant temperature, the EMC increased with increasing ERH.

The experimental data were fitted to four isotherm models. The modified Oswin model gave better fit to the experimental data with highest R^2 and lowest values of MRE and SEE than 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 heats of desorption were evaluated as a 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.).

Nomenclature

C_1, C_2, and C_3 model coefficients, dimentionless

d.b. dry basis

df degrees of freedom

EMC equilibrium moisture content, % d.b

ERH equilibrium relative humidity, % d.b

M moisture content, % d.b

$M_{i,\mathrm{exp}}$ ith experimental value of EMC

$M_{i,pre}$ ith value predicted by the model

MRE mean relative error

n number of coefficients in each model

Q_{st} net isosteric heat of desorption, kJ/mol

R universal gas constant, 8.314 J/(mol • K)

R^2 coefficient of determination

SEE standard error of estimate

t temperature, ℃

T absolute temperature, K

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