ZESZYTY PROBLEMOWE POSTĘPÓW NAUK ROLNICZYCH 1995 z. 427, 137-143

WATER SORPTION ABILITY OF SEEDS, FLAKES AND PRESS-CAKES OF RAPESEED*

J. Sadowska, A. Ostaszyk, J. Fornal

Institute of Animal Reproduction and Food Research, Polish Academy of Sciences, Tuwima 10, 10-718 Olsztyn, Poland

Abstract. The water sorption isotherms of seeds, flakes and press-cakes of rapeseed from small farm oil plant were studied. The sorption isotherms of all press-cakes examined could have been identified as the III type curves in BET classification. Empirical Smith's equation was found to describe best the moisture sorption behaviour of rapeseed press-cake. Small differences were observed between the moisture adsorption isotherms of whole and ground (raw flakes) seeds. A distinct decrease of roasted flakes and an increase of adsorbed moisture in press-cakes was found. The moisture adsorption of press-cakes from unhulled seeds is higher than on oil-cakes obtained from hulled seeds, in which higher mechanical cell destruction and oil leakage were observed. An addition of bran to press-cakes caused an increase of moisture adsorption.

Keywords: rapeseed, rapeseed flakes, oil cake, moisture sorption isotherms

LIST OF SYMBOLS

A, B	- constants in empirical equations
a_w	- water activity
C	- Guggenheim constant in BET equation
EMC	- equilibrium content of water (g/100 g dry matter)
ERH	- equilibrium relative moisture (-)
H_1	- condensation heat of pure water vapour (kJ/kg)
H_q	- total heat of sorption of the multilayer water molecules (kJ/kg)
H_m	- total heat of sorption of water molecules in the first layer (kJ/kg)
k	- factor correcting including multilayer adsorption of water molecules
W	- water content (g/100 g dry matter)
W_m	- water content corresponding to saturation of all primary adsorption sites by one water molecule (g/100 g dry matter).

INTRODUCTION

Recently small oil production plants, which process either own material (e.g., rapeseed) or produce untypical oils, have been set working. Press-cake - a waste product - is usually a valuable addition to fodder. The variability of physical properties is important in both scientific knowledge of plant material physics and practical applications, particularly in estimation of storage conditions and improving of material processing and equipment.

The moisture adsorption of raw materials and food plays a major role in storage (determination of the appropriate values a_w prevents the development of microorganisms and unfavourable chemical and enzymatic processes) and processing. Knowledge of moisture adsorption and desorption isotherms is used in food engineering for drying optimization. Application

---

*This work was supported by the State Committee for Scientific Research, Poland, under grant No. 5 S307 058 04

of Brunauer-Emmett-Teller's (BET) and Guggenheim-Anderson-de Boer's (GAB), equations which have been derived from principles in adsorption theory, is limited in practise because of material and ambient moisture. Especially at high relative air humudity the experimentally estimated equilibrium moisture content (EMC) of the material varies considerably from the values calculated with these equations. Thus, the prediction of empirical and semi-empirical equations or constants of the existing equations is a widely used solution to this problem. The aim of this study was therefore to evaluate the moisture adsorption isotherms for products obtained during rapeseed pressing.

MATERIAL AND METHODS

Three series of samples collected during the processing of commercial rapeseed harvested in 1994 made the research material (Table 1). Two series included rapeseeds, raw and roasted flakes and an oil-cake, obtained during two production batches at a farm oil plant in Szestno. The line equipment and machines had been produced and installed by Krupp GmbH. The third series, press-cakes obtained from hulled seeds with the addition of bran, was produced on a semi-industrial scale in our laboratory. The basic equipment and press had been designed and manufactured for small farm oil plants by BISPOMASZ, Bydgoszcz, Poland.

Table 1. Characteristics of samples

Sample number	Samples	Fat content (%)	Protein content (%)
1	Seeds I	44.6	
2	Raw flakes I	46.6	
3	Roasted flakes I	47.9	
4	Press-cake I	10.1	30.3
5	Seeds II	45.6	
6	Raw flakes II	47.4	
7	Roasted flakes II	46.7	
8	Press-cake II	9.9	28.5
9	Press-cake from whole seeds - W_1	9.8	36.7
10	Press-cake from hulled seeds - W_2	18.0	25.2
11	W_2 + 5 % bran	16.5	35.6
12	W_2 + 10 % bran	12.6	41.1

The moisture sorption data were produced at 20 ±0.5 °C using a series of the following saturated salt solutions: LiCl, $CaCl_2$, $MgCl_2 \cdot 6H_2O$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl, K_2CrO_4, K_2SO_4, which provided the relative humidities of 0.11, 0.29, 0.43, 0.53, 0.65, 0.75, 0.86, and 0.97, respectively. A sample of approximately 1.0 g was put onto a small hard filter paper disc and suspended over the salt solution in a tightly closed desiccator. The weight changes in the sample were recorded until equilibrium was assumed, i.e., the difference between two consecutive sample weights was less than 1 mg/g dry matter in triplicate. The sample dry matter content was determined by the drying method [8]. All determinations were made in triplicate. Statistical calculations were performed using SPSS for Windows, ver. 5.0.1 program, using the analysis of nonlinear regression.

RESULTS

According to many authors the BET equation is of limited application for describing the moisture adsorption isotherms of food products as its accurracy above a_w= 0.5 is low [4,9]. Lewicki presents good adsorption isotherms for rice, oat, barley, and dry malt analysed by the BET method and classifies the curves as the IIIrd type in BET classification. Applying this method to determine the sorption isotherms for some dried food appeared unsuccessful. The negative values of constant *C*, which are excluded in physical interpretation were calculated [5]. The equation GAB has been preferred lately, as it comprises a wider range of water activity (for a_w<0.9). It should be noted that it is often limited for food products [3,4,9]. However, Jayas *et al.* [3] using this equation to describe the adsorption isotherms for flax seed, emphasised that above a_w = 0.8 only the GAB equation has appeared best fitted for the experimental data.

All moisture adsorption isotherms of the examined seeds, flakes and oil-cakes had a similar shape with the slightly marked inflexion point. Thus, Brunauer-Emmett-Teller's (BET) and Guggenheim-Anderson-de Boers's (GAB) equations were used for mathematically describing isotherm:

$$\frac{W}{W_m} = \frac{Ca_w}{(1-a_w)\,(1-a_w+Ca_w)} \qquad (1)$$

$$\frac{W}{W_m} = \frac{k\,Ca_w}{(1-k\,a_w)\,(1-k\,a_w+k\,Ca_w)}\,. \qquad (2)$$

The physical interpretation of constants C and k in Eq. (2) is :

$$C = c'\,\exp\,[(H_1 - H_m)/RT] \qquad (3)$$

$$k = k'\,\exp\,[(H_1 - H_q)/RT]\,. \qquad (4)$$

According to the initial calculations, it has been reported that these equations fit the experimental data (determinantion coefficients always exceeded 0.9) but all calculated values of the C constant in both equations were negative. These results do not comply with the results of the authors mentioned above, but similar results were obtained in previous research concerning the water sorption ability of high-fat oil cakes [10]. Differences might result from the wide range of water activities set up $0.11<a_w<0.97$ or the method of isotherm prediction (static method). Selection of the appropriate equation depends on many factors, i.e., a determination method applied, the range of equilibrium relative humidity set up for the experiment or the appropriate classification of curve types, etc. Lewicki *et al.* [6] noticed that the inflexion point in sorption curves for dry apples, carrot, potatoes and milk disappear very quickly and the IV type isotherms of these products became the II type curves during 12-week storage. Lagaudaki and Demetzis [4] also present, in pictures of sorption izotherms obtained by the static method and CIGC (Computerised Inverse Gas Chromatography), a slightly different shape of the curves done according to the data obtained by these methods.

The appropriate empiric equation was applied to describe the course of moisture sorption isotherms. Yang and Cenkowski [11] prefer the Halsey's equation to present their results concerning the successive adsorption and drying cycles of rapeseeds. Thus, the calculations were performed using the Helsey's equation in the form of:

$$EMC = \{A\,\ln\,[\ln(a_w\,100)]\}^{B}\,. \qquad (5)$$

Additionally, the Chung-Pfost's and Smith's equations were proposed as they are useful in a wide range of water activity:

$$a_w = \exp\,[-A\,\exp(-B\,EMC/100)]$$

$$0.20<a_w<0.75 \qquad (6)$$

$$EMC = A - B\,\ln(1-a_w)$$

$$0.30<a_w<0.75\,. \qquad (7)$$

The constants of the equations for the samples examined were calculated using non-linear regression analysis. The values with standard error and determination coefficients we presented in the Tables 2-5. All determination coefficients are high but the standard errors of constants only in Smith's equation are low. According to the calculations, the Smith's equation describes, with the highest accurracy, the course of adsorption moisture in the whole range of a_w (physical sense is not attributed to the equation constants).

It was established that the differences in sorption moisture isotherms for whole and ground (raw flakes) are unimportant. They are smaller than the differences in sorption isotherms for seeds of different origin (Fig. 1a, Table 4). A similar phenomenon is presented by Apostolopoulos and Gilbert [1] who found that the size of particles did not affect the moisture sorption ability of dry, ground coffee. Thus, it may be assumed that for raw plant materials, both the adsorption isotherms and the final quantity of adsorbed moisture depend on cell and tissue structure. Increasing the active surface through grinding, without damaging the structure of most cells, can have a stronger effect on the adsorption

Table 2. The constants of the Chung-Pfost's equation for seeds, flakes and press-cakes

Sample	Equation constants				Determination coefficient
	A		B		
	value	std. error	value	std. error	R^2
Seeds I	0.205	0.0522	-4.214	0.3748	0.9620
Raw flakes I	0.221	0.0759	-4.436	0.5442	0.9300
Roasted flakes I	0.285	0.0767	-4.202	0.4395	0.9481
Press-cake I	0.222	0.0519	-6.252	0.5227	0.9662
Seeds II	0.184	0.0247	-3.915	0.1778	0.9898
Raw flakes II	0.144	0.0486	-3.547	0.3776	0.9464
Roasted flakes II	0.194	0.0466	-3.4893	0.2878	0.9672
Press-cake II	0.210	0.0522	-6.010	0.5256	0.9632

Table 3. The constants of the Chung-Pfost's equation for modified press-cakes

Press-cake	Equation constants				Determination coefficient
	A		B		
	value	std. error	value	std. error	R^2
W_1 - from whole seeds	0.133	0.0270	-4.885	0.3055	0.9808
W_2 - from hulled seeds	0.123	0.0295	-4.3950	0.3167	0.9639
W_2 + 5 % bran	0.131	0.0410	-4.489	0.4293	0.9563
W_2 + 10 % bran	0.122	0.0295	-4.6137	0.3359	0.9742

Table 4. The constants of the Smith's equation for seeds, flakes and press-cakes

Sample	Equation constants				Determination coefficient
	A		B		
	value	std. error	value	std. error	R^2
Seeds I	3.98	0.463	5.24	0.276	0.9863
Raw flakes I	3.78	0.691	5.57	0.413	0.9733
Roasted flakes I	2.57	0.427	5.35	0.255	0.9888
Press-cake I	5.06	0.814	8.23	0.504	0.9617
Seeds II	4.18	0.309	4.82	0.184	0.9927
Raw flakes II	4.62	0.584	4.41	0.349	0.9696
Roasted flakes II	3.52	0.474	4.31	0.283	0.9789
Press-cake II	5.45	0.848	7.73	0.514	0.9788

rate than the quantity of the adsorbed moisture. Distinct differences occurred in the case of roasted flakes and press-cakes, although the character of the changes was different (Fig. 1b, Table 4). A clear decrease was found for the roasted flakes, whereas a distinct increase of the adsorbed moisture was observed for the oil-cakes. Fornal *et al.* [2] describe the differences of structure and mechanical properties of roasted flakes, that are the result of simultaneous mechanical and heat activity. Protein denaturation and higher cell destruction was observed in material subjected to hydrothermal processes. Both mentioned phenomena may limit the ability of moisture sorption of roasted flakes. Particle fragility

Table 5. The constants of the Smith's equation for modified press-cakes

Press-cake	Equation constants				Determination coefficient
	A		B		
	value	std. error	value	std. error	R^2
W_1 - from whole seeds	6.77	0.288	6.05	0.172	0.9960
W_2 - from hulled seeds	6.40	0.306	5.45	0.182	0.9944
W_2 + 5 % bran	6.38	0.310	5.73	0.185	0.9948
W_2 + 10 % bran	6.79	0.374	5.72	0.223	0.9924

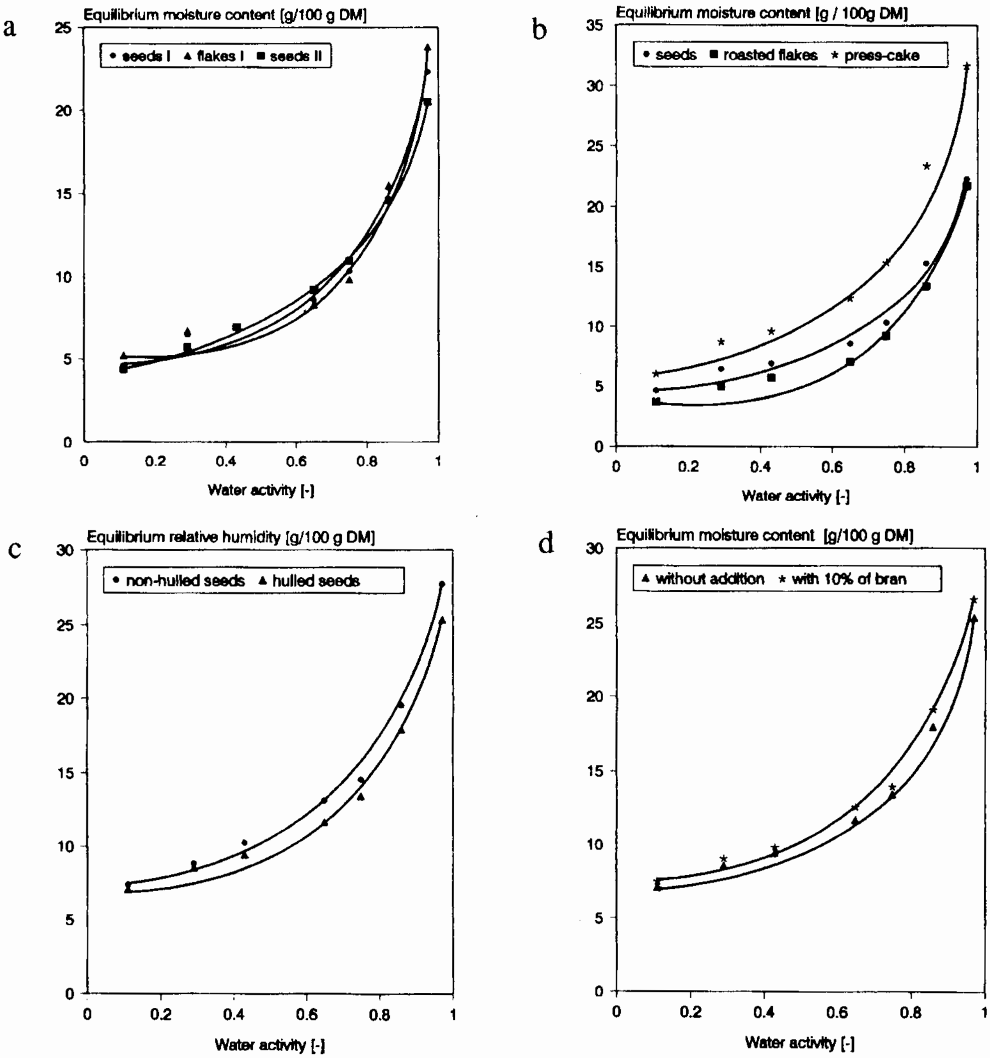

Fig. 1. Water sorption isotherms for: whole and grinded rapeseeds (a), rapeseed seeds, roasted flakes and press-cake (b), non-hulled and hulled rapeseeds (c), rapeseed press-cakes without addition and with 10 % of bran (d).

and fat leakage, causing particle agglomeration and oil spot enlargement, were probably reasons for the active sorption surface diminishing. Additionally, partial denaturation might diminish hydrophilic protein activity. The moisture sorption ability of rapeseed press-cake was higher than other products examined and depended on both a high degree of fineness and low fat content in press-cake.

It was confirmed that the moisture adsorption on oil-cakes from unhulled seeds is higher than on oil-cakes obtained from hulled seeds (Fig. 1c, Table 5). Press-cake from hulled seeds was characterised by a higher agglomeration ability resulting from higher cell destruction and oil leakage. Particle agglomeration caused both the diminishing of the active surface and the mechanical coating of hydrophylic protein by oil. The addition of bran to press-cakes from the hulled seeds caused an increase of moisture adsorption (Fig. 1d, Table 5). A bran with a porous structure, low fat and high cellulose content might limit this unfavourable effect. It seems that a higher content of protein, being the main hydrophilic compound of the materials examined had a similar result.

CONCLUSIONS

The moisture adsorption isotherms for seeds, flakes and press-cakes in the examined range of water activity a_w were the most accurately described by the empirical Smith's equation.

Small differences were observed between the moisture adsorption isotherms for the whole and ground (raw flakes) seeds. The differences between roasted flakes and press-cakes were clear. A distinct decrease of absorbed moisture for the roasted flakes and increase for press-cakes was found.

It was shown that the moisture adsorption on press-cakes from unhulled seeds is higher than oil-cakes obtained from hulled seeds, where higher mechanical cell destruction and oil leakage were observed. The addition of bran to press-cakes caused an increase of moisture adsorption. The porous structure, low fat content and high cellulose content in bran might limit unfavourable effects.

REFERENCES

1. **Apostopulos D., Gilbert S.G.**: Frontal Inverse Chromatography as used in studying water sorption of coffee solubles. J. Food Sci., 53, 882-884, 1988.
2. **Fornal J., Sadowska J., Jaroch R., Kaczyńska B., Winnicki T.**: Effect of rapeseed drying on their mechanical properties and technological usability. Int. Agrophysics, 8(2), 215-224, 1994.
3. **Jayas D.S., Mazza D., White, N.D.G.**: Equilibrium moisture content-equilibrium relative humidity relationship of flax seed. ASAE Papers, 89-6603, 1989.
4. **Lagaudaki M., Demertzis P.G.**: Equilibrium moisture characteristics of dehydrated food constituents as studied by a modified inverse gas chromatographic method. J. Sci. Food Agric., 65, 101-109, 1994.
5. **Lewicki P.**: A method for calculate constans in the BET equation applicable to the type III isotherms of the BET classification. Acta Alimentaria Polonica, 3(27), 67-77, 1977.
6. **Lewicki P.P., Lenart A., Mroczek T.**: Badanie wpływu czasu i wilgotności powietrza w metodzie statyczno-eksykatorowej na kształt izoterm sorpcji wody wybranych produktów spożywczych. Przemysl Spożywczy, 34, 22-25, 1980.
7. **Mazza G., Jayas D.S., Oomah B.D., Mills J.T.**: Comparison of five three-parameter equations for the description of moisture sorption data of mustard seeds. Int. J. Food Sci. Technol., 29, 71-81, 1994.
8. Official Methods of Analysis of the AOAC (Ed.: K. Helrich). 2, 777, 1990.
9. **Riganakos K.A., Kontominas M.G.**: GC study of the effect of specific heat treatment on water sorption by wheat and soya flour. Z. Lebensmittel-Untersuchung und-Forschung, 198, 47-51, 1994.
10. **Sadowska J., Ostaszyk A., Fornal J.**: Moisture sorption isotherms of rapeseed high-fat press-cake. In: Proc. Semin. 'Properties of Water in Foods', Warsaw, Poland, 1995
11. **Yang W.H., Cenkowski S.**: Effect of successive adsorption cycles and drying temperature on hygroscopic equilibrium of canola. Canad. Agric. Eng., 35(2), 119-126, 1993.

ZDOLNOŚĆ ADSORBOWANIA WILGOCI PRZEZ NASIONA, PŁATKI I WYTŁOKI RZEPAKOWE

Badano przebieg izoterm adsorpcji wilgoci dla półproduktów i produktów finalnych otrzymanych podczas wytłaczania nasion rzepaku w małych olejarniach farmerskich.

Materiał do badań stanowiły przemysłowe nasiona rzepaku ze zbiorów 1994 r. oraz produkty ich przerobu w olejarniach farmerskich tj. płatki, wytłoki i wytłoki z dodatkiem otrąb.

Ustalono, że przebieg izoterm absorpcji wilgoci w całym zakresie równowagowej wilgotności względnej najwiemiej opisuje empiryczne równanie Smitha (którego stałym nie przypisuje się sensu fizycznego) i zaliczono je, wg klasyfikacji BET, do krzywych III typu. Różnice przebiegu izoterm adsorpcji wilgoci dla nasion całych i płatków surowych są niewielkie, mniejsze niż różnice przebiegu izoterm adsorpcji wilgoci dla różnych nasion. Zanotowano natomiast znaczący spadek zdolności absorbowania wilgoci dla płatków parowanych, którego przyczyną mogła być ich kruchość wynikająca z jednoczesnego oddziaływania czynników mechanicznych i termicznych. Stwierdzono, że adsorpcja wilgoci na wytłokach z nasion obłuszczonych jest niższa niż na wytłokach z nasion niełuszczonych. Cząstki wytłoku z nasion obłuszczonych mają skłonność do aglomeracji spowodowaną silniejszą destrukcją komórek i wydzieleniem się większej ilości wolnego oleju, co powoduje zarówno zmniejszenie powierzchni aktywnej, jak i mechaniczne oblepienie cząstek hydrofilnego białka. Dodatek otrąb do wytłoków z nasion obłuszczonych spowodował zwiększenie adsorpcji wilgoci. Prawdopodobnie ten niskotłuszczowy, wysokobłonnikowy, o bardziej porowatej strukturze dodatek częściowo zniwelował wymienione wyżej niekorzystne oddziaływania.

Słowa kluczowe: nasiona rzepaku, płatki rzepakowe, wytłok rzepakowy, izotermy sorpcji wilgoci.