Sorption isotherms of agricultural products

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Abstract

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The aim of the paper is to expand the theory of sorption and equilibrium moisture contents as well as to present the methodology of developing two types of sorption isotherms – I and II. The attention is also paid to the importance of the isotherms in the thermodynamics of drying and in the process of storage of agricultural products. Presented methodology of obtaining the isotherms is based on selected equations of the theory of adsorption and on the results of experimental measurements of equilibrium moisture content. Definition of the new isotherm II is introduced as dependence of equilibrium moisture content dry basis on time at constant temperature, constant relative moisture of the ambient air and stable biological properties (e.g. germination). The results show following graphic dependences: isothermal distort plane; sorption isotherm I of maize grains at various temperatures; moisture loss rate in dependence on time and sorption isotherm II. These theoretical dependences supported by experimental measurements broaden the scope of the theory of sorption and may be successfully applied in long-term storage of maize grains.

Keywords: equilibrium moisture; drying; thermodynamics; organic materials; drying curve

Agricultural products are characterised by high moisture content, which makes their long-term storage impossible. Therefore, post-harvest processing ends with a drying process with removal of free moisture and one part of bound moisture. Residual moisture content enables long-term storage without a decrease in quality. This value is of significant importance. Therefore, it is prescribed in technical standards that determine the max. volume and min. volume of moisture content. These values are in the range of equilibrium moisture content of a given material with the ambient atmosphere. Equilibrium moisture content is therefore an important parameter which is used in the thermodynamics of drying and also in the thermodynamics of storage.

For their research the authors studied excellent seminal works of drying theory, Czech from Valchař et al. (1967), Polish from Pabis (1982), Hungarian from Imre (1974) and German, in Slovak translation, from Maltry and Pötke (1966).

Remarkable publications about equilibrium moisture in agricultural products include those from Henderson (1952) and Štencl (2000a,b).

As a result, equilibrium moisture content was measured and relevant relationships were studied in the research. The paper presents complex theory of sorption isotherms with the intention to introduce this theoretical contribution to the experts in thermodynamics and to pass this knowledge to the workers in drying, especially to those who deal with long-term storage of agricultural products.

MATERIAL AND METHODS

Complex theory. In the theory of thermodynamics of organic materials, only the prescribed standard parameter for moisture content – moisture content dry basis with the relation, were used:

$$u = M_w/M_{db} \tag{1}$$

where:
u   – moisture content dry basis
M_w – moisture mass in the given material (kg)
M_{db} – mass of dry basis in the given material (kg)

The equilibrium moisture of the given material is moisture content dry basis relevant to the state of thermal equilibrium of the given material and ambient gas atmosphere.

Moisture in the material is free moisture on its surface and bound moisture inside this material, without moisture in chemical structures.

Adsorbed moisture is moisture on the surface of the material kept with molecular forces.

The curve of sorption isotherm is a graphic presentation of equilibrium moisture content in dependence on the relative moisture of ambient gas atmosphere φ at constant temperature *T*.

The equilibrium moisture of the given material is to be described with a universal relation (HAVELKA 1978):

$$u_e \cong F(T, \varphi, \tau, bio) \qquad (2)$$

where:
u_e – equilibrium moisture dry basis
F   – function
T   – temperature of the material and ambient atmosphere (K)
φ   – relative moisture of the ambient atmosphere
τ   – time from the end of drying process (days)
bio – parameter of biologic quality of this material

Post-harvest processing is performed in the way that this bio-parameter remains constant with the highest value in the whole process and also during storage.

The relation of *F*(*T*, φ, τ, *bio*) cannot be provided in an analytical form. In research works, sorption isotherm values are obtained from laboratory measurements of samples. The relation *F* gives a graphic description of an isothermal distort plane with *T* = const., *bio* = const. The scheme of this is shown in the coordinates *u*, φ, τ in Fig. 1.

Sorption isotherms. For the analysis of Eq. (2), a total differential of the following equation was used:

$$du_e = (\delta F/\delta T)dT + (\delta F/\delta\varphi)d\varphi + (\delta F/\delta\tau)d\tau + {} \\ + (\delta F/\delta bio)dbio \qquad (3)$$

In practice, only processes with *bio* = const are performed.

Two types of sorption isotherms were studied by the means of this relation of total differential and isothermal distort plane (Fig. 1).

Sorption isotherm I. This sorption isotherm is described with differential Eq. (4) and graphically presented as a section of isothermal distort plane with the level of given time τ scheme (Fig. 1).

The differential equation for this sorption isotherm is:

$$du_e = (\delta F/\delta\varphi)d\varphi; \; T = \text{const.}, \varphi = \text{const.}, bio = \text{const.} \quad (4)$$

The analytic relation is:

$$u_e = F_1(\varphi); \; T = \text{const.}, \varphi = \text{const.}, bio = \text{const.} \qquad (5)$$

This isotherm is used in the thermodynamics of drying. The course of this u_e (Eq. (5)) is to be stated only with laboratory measurements on a material sample.

The relation from HENDERSON (1952) was used:
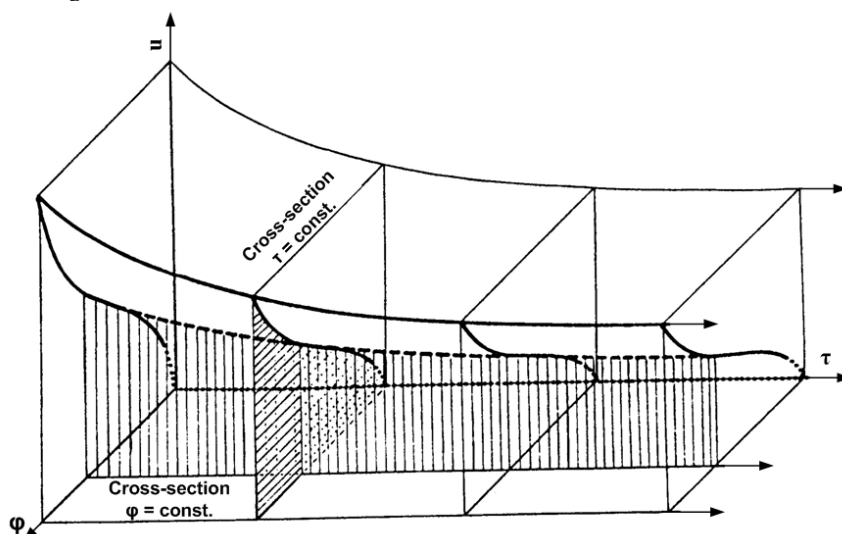
$$1 - \varphi = e^{-k \times T \times u^n} \qquad (6)$$

Fig. 1. Isothermal distort plane
τ – time; *T* – temperature; *u* – moisture content dry basis; φ – relative moisture of the ambient atmosphere

where:

e – base of natural logarithm

k, n – coefficients of the Henderson's relation

T – temperature of ambient air (K)

u – moisture content dry basis

For the derivation of sorption isotherm on another temperature, the following relation by means of the Henderson's equation was obtained:

$$u_e = u_{eI} \times (T_1/T)^{1/n} \tag{7}$$

Sorption isotherm II

Sorption isotherm II is a curve produced with the section of isothermal distort plane with the plane of φ = const. (scheme in Fig. 1).

The differential equation of this sorption isotherm is:

$$du_e = (\delta F/\delta\tau)d\tau; \; T = \text{const.}, \; \varphi = \text{const.}, \; bio = \text{const.} \tag{8}$$

The analytic relation of this is:

$$u_e = F_2(\tau); \; T = \text{const.}, \; \varphi = \text{const.}, \; bio = \text{const.} \tag{9}$$

The actual course from the laboratory measurement of samples of the given material was gained.

The analytic relation of u_e (Eq. (9)) as a curve of natural fall of moisture loss rate N^x was developed:

$$N^x = du_e/d\tau = -a \times (u_e - u_{e\infty}) \tag{10}$$

where:

N^x – moisture loss rate

du_e – differential of equilibrium moisture dry basis

$d\tau$ – differential of time

a – time constant of the given material

u_e – equilibrium moisture dry basis

$u_{e\infty}$ – equilibrium moisture dry basis at infinite time

With its integration, the relation for u_e was gained:

$$u_e = u_{e\infty} + (u_{e0} - u_{e\infty}) \times \exp(-a \times \tau) \tag{11}$$

Where:

u_e – equilibrium moisture dry basis

$u_{e\infty}$ – equilibrium moisture dry basis at infinite time

u_{e0} – equilibrium moisture dry basis at the beginning

a – time constant of the given material

τ – time

Isotherm II demonstrates the long-term course of equilibrium moisture at storage or at cooling. It

enables to calculate the mass of moisture produced in this process.

RESULTS AND DISCUSSION

Sorption isotherm I for maize

From laboratory measurements, the values of equilibrium moisture contents of maize grains at the temperature of 40°C were obtained. This isotherm is shown in Fig. 2. From these values, the values of constant k and n in the Henderson's equation with non-linear regression were calculated.

Henderson's equation:

$$\varphi = 1 - e^{-0.116393 \times T \times u^{2.092267}} \tag{12}$$

where:

φ – relative moisture of the ambient atmosphere

e – base of natural logarithm

T – temperature of ambient air

u – moisture content dry basis

With Eq. (7), the values for the temperatures of 10°C were calculated and presented in Fig. 2.

Sorption isotherm II for maize grains

The samples of maize from the previous section were used for the laboratory measurement of moisture losses in long-term storage. The value of u_e (equilibrium moisture dry basis) was obtained by exploratory calculations. From this the analytic relation for moisture loss rate was gained (Fig. 3):

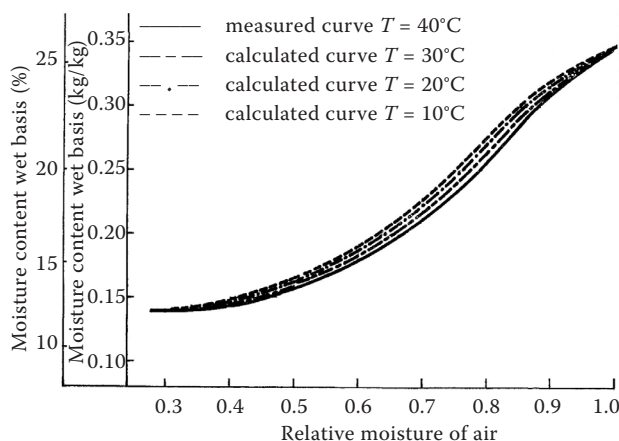$$N^x = -0.01546 \times e^{-(\tau/36.2)} \tag{13}$$

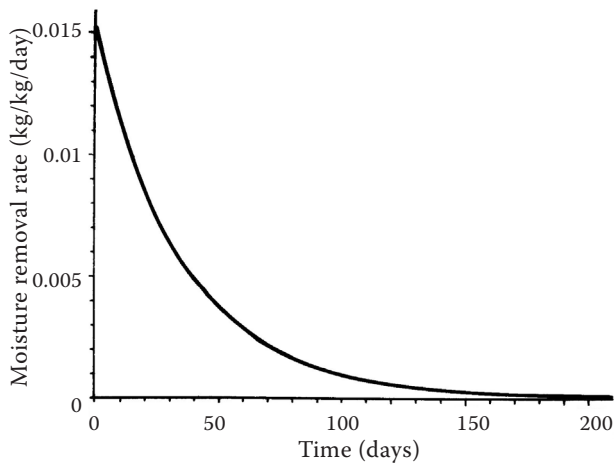Fig. 2. Sorption isotherms of maize grains

Fig. 3. Moisture loss rate of maize grains

where:

N^x – moisture loss rate

e – base of natural logarithm

τ – time

The analytic relation of equilibrium moisture content:

$$u_e = 0.1 + 0.56 \times e^{-(\tau/36.2)} \tag{14}$$

Graphic demonstration is presented in Fig. 4. The value of $u_{e\infty}$ is only an analytic calculating value.

In the course of long-term storage of agricultural products, one part of moisture content is released due to the biological activity of this material. This moisture must be removed to prevent deterioration of this material. This moisture is removed with cold airing. The flow of unsaturated air removes this moisture in continual or cyclic manner.

Similar situation is at cooling of agricultural products. With the knowledge of sorption iso-

therm I and sorption isotherm II, a considerably higher amount of moisture is to be removed than in the case of cold airing. The knowledge of these two sorption isotherms allows to calculate with the thermodynamics of wet air the course of this process and to propose an optimal technical solution of the storage equipment (Vitázek 2011).

The theory of sorption isotherm I is very objectively presented in the work of Nikitina (1963). Any similar method was not found in any relevant source. This method may be considered as an important improvement in the theory of sorption of humidity in the long-term processes in agriculture.

CONCLUSION

The drying of harvested grain and other agricultural products is carried out on the principle of drying curve and isotherm I. A long-term conservation of such materials is theoretically solved by means of isotherm II for the whole period of conservation.

Isotherm II enables to determine and analyse the conditions of the conservation process. Moreover, it deals with the disposal of spontaneous release of moisture by ambient air.

Process managers in dryers and storages of agricultural products use the knowledge of complex isothermal sorption in their practice. These basic principles considerably improve the process of drying and storage.

Conducted experiments and derived theory indicate a significant importance of further research into the thermodynamics of long-term conservation of all agricultural crops stored in great amounts.

References

Havelka J., 1978. Termodynamika dlhodobej konzervácie poľnohospodárskych produktov. [Thermodynamics of long-time conservation of agricultural products.] Acta Technologica Agriculturae: 189–197.

Henderson S.M., 1952. A Basic Concept of Equilibrium Moisture. In: Agricultural Engineering for January 1952: 29–32.

Imre I., 1974. Szárítási kézikönyv. [Manual of Drying.] Budapest, Müszaki Könyvkiado: 1122.

Maltry W., Pötke E., 1966. Technika poľnohospodárskeho sušiarenstva. [Technics of Drying in Agriculture.] Bratislava, SVPL: 490.

Nikitina L.M., 1963. Tablicy ravnovesnogo udelnogo vlagosoderžanija I energii svjazi vlagi s materialama. [Ta-
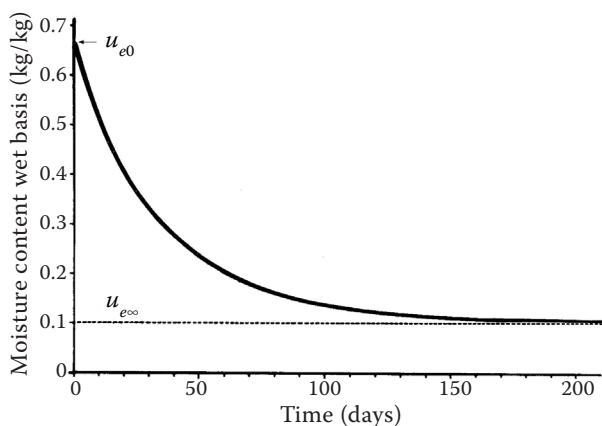
Fig. 4. Sorption isotherm II of maize grains

u_{e0} – equilibrium moisture dry basis at the beginning; $u_{e\infty}$ – equilibrium moisture dry basis at infinite time

bles of Equilibrium Moisture Contents and Binding Energy of Moisture with Material.] Moscow, Gosenergoizdat: 174.

Pabis S., 1982. Teoria kon wekcionogo suszenia produktov rolniczych. [Theory of Heat Conduction Drying of Agricultural Products.] Warszawa, PWRiL: 229.

Štencl J., 2000a. Equilibrium moisture content of *Festuca pratensis* in near ambient air drying conditions. Acta Technologica Agriculturae, *3*: 21–26.

Štencl J., 2000b. Equilibrium moisture content as a control parameter for a meadow grass drying process in a barn. Acta Technologica Agriculturae, *3*: 27–31.

Valchař J. et al., 1967. Základy sušení. [Basic Concepts of Drying.] Prague, ČVUT/SNTL: 396.

Vitázek I., 2011. Technika sušenia v teórii a v praxi – Obilniny. [Drying Technics in Theory and Practice – Cereals.] Nitra, SUA in Nitra: 102.

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