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WATER ACTIVITY CHANGES OF MULTICOMPONENT FOOD MIXTURE DURING PROCESSING

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Abstract

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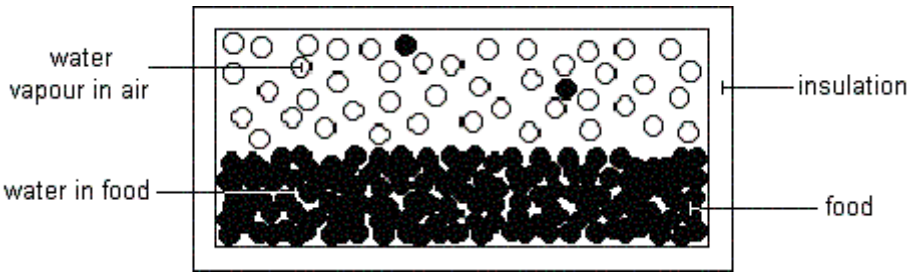
Water activity of multicomponent food mixture was analysed and measured. Samples of dry fermented sausages with two different starter cultures (*Pediococcus pentosaceus* + *Staphylococcus carnosus and Staphylococcus carnosus* + *Staphylococcus xylosus* + *Lactobacillus farciminis*) were tested during ripening (21 days) and storing (91 days). The basic raw materials were the same for all samples: lean beef meat, lean pork and pork fat in equal parts, nitrite salt mixture (2.5 %), and sugars (1.0 %). The method used for water activity tests was indirect manometric in a static environment. Moisture content of samples was measured using halogen dryer. The course of water activity and moisture content of sausages was variable during ripening and steady during storage. Diagrams showed gradual decrease of both parameters. Mathematical models of water activity and moisture content for storage of dry fermented sausages were developed and statistically verified. The influence of starter cultures was not significant.

modeling, moisture content, ripening, sausage, storage, temperature

Water activity is a valuable tool for food scientists and technologists because it can be used to predict potential changes in food stability; it can be used for storing method determination, packaging selection and also ingredient selection. Foods are both homogeneous and heterogeneous materials. For example sausage is a typical multicomponent food. There are frequently questions: What is the water activity of such heterogeneous mixtures, where each wet component has different thermal and water sorption properties? To explain simply the role of activity in food-water-vapour interaction considers the general setup simulating a food system shown in Fig. 1.



1: *Schematic representation of a closed food-water-vapour system at a constant temperature*

The solvent in the system is water, and food constituents such as salts, sugars, meats, proteins, carbohydrates, and others are the solutes. At a constant temperature, all components and water in the food have the same thermodynamic state as defined by chemical potential. In describing the state of any system, an important factor besides temperature, volume, concentration etc., is the free energy or Gibbs free energy, G = total energy (enthalpy factor) – unavailable energy (entropy factor) of the system (Hall, 1979; Štencl, 2000)

$$G = H - TS \quad (1).$$

In differential form, the expressions becomes

$$dG = dH - T\,dS - SdT \quad (2).$$

Enthalpy is equal

$$H = E + PV \quad (3)$$

or in differential form

$$dH = dE + PdV + VdP \quad (4).$$

When one recalls (3) and (4) and substitutes for dH, the expression for the differential dG becomes

$$dG = dE + PdV + VdP - TdS - SdT \quad (5).$$

For reversible change, where only pressure-volume work occurs, the first and second laws of thermodynamics give

$$dE = TdS - PdV \quad (6).$$

Substituting the value of dE into equation (5) and cancelling like terms gives as the final equation for differential change in Gibbs free energy of homogeneous system

$$dG = VdP - SdT \quad (7).$$

The Gibbs free energy of a multicomponent system undergoing any change will depend not only on temperature and pressure as defined by equation (7) but also on the amount of each component present in the system, e.g. number of moles n_i (Rao and Rizvi, 1995):

$$G = G(P, T, n_i) \quad (8).$$

A complete differential for the above equation would then be

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} dn_i \quad (9).$$

The partial molar Gibbs free energy $\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}}$ is called chemical potential of component i, μ_i, and represents the change in the total free energy per mole of component i added, when the temperature, total pressure, and numbers of moles of all components other than i are held constant:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} \quad (10).$$

Gibbs showed that for a simple system of one component and one phase or for a complex system of more than one component and existing in more than one phase, the necessary and sufficient condition for equilibrium is

$$\mu^{I}_{i} = \mu^{II}_{i} = \mu^{III}_{i} = \ldots \quad (11).$$

More correctly, the water in the system has the same thermodynamic state as defined by chemical potential. On a molar basis it is defined as (Čermák, 1979; Labuza, 1984)

$$\mu = \mu_0 + RT \ln a \quad (12),$$

where μ_0 is the chemical potential at some standard state, R is the gas constant, T is temperature and a is the thermodynamic activity of the particular substance.

Consequentially, at a constant temperature, all components and water in the food (Fig. 1) are in the thermodynamic equilibrium with each other in both the adsorbed and vapour phases. Considering only the water component in the two phases, their chemical potentials is equated, given by equation (13):

$$\mu_w(\text{vapour}) = \mu_w(\text{food})^{I}_{i} = \mu_w(\text{food})^{II}_{i} = \mu_w(\text{food})^{III}_{i} = \ldots \quad (13).$$

Since temperature was held constant, T is constant. In addition, μ_0 and R are constants; thus, the activity of water a_w in particular substances is also constant. Looking again at equation (12) with respect to state, it is possible to establish that the activity of the water in the headspace is also the same as it is in each particular substance:

$$a_w(\text{food})^{I}_{i} = a_w(\text{food})^{II}_{i} = a_w(\text{food})^{III}_{i} = \ldots = a_w(\text{air in headspace}) \quad (14).$$

Equation (14) represents the substance of common practical measurements of water activity (a_w) of foods

and biological materials in general (Kaminski and Strumillo, 1994; Wolf *et al*., 1990; Labuza, 1984). At equilibrium, the a_w (Iglesias and Chirife, 1982; Labuza, 1984) is related to the relative humidity of the surroundings atmosphere by

$$a_w = \frac{p}{p_0} = \frac{relative.humidity.(\%)}{100}\ [-] \qquad (15),$$

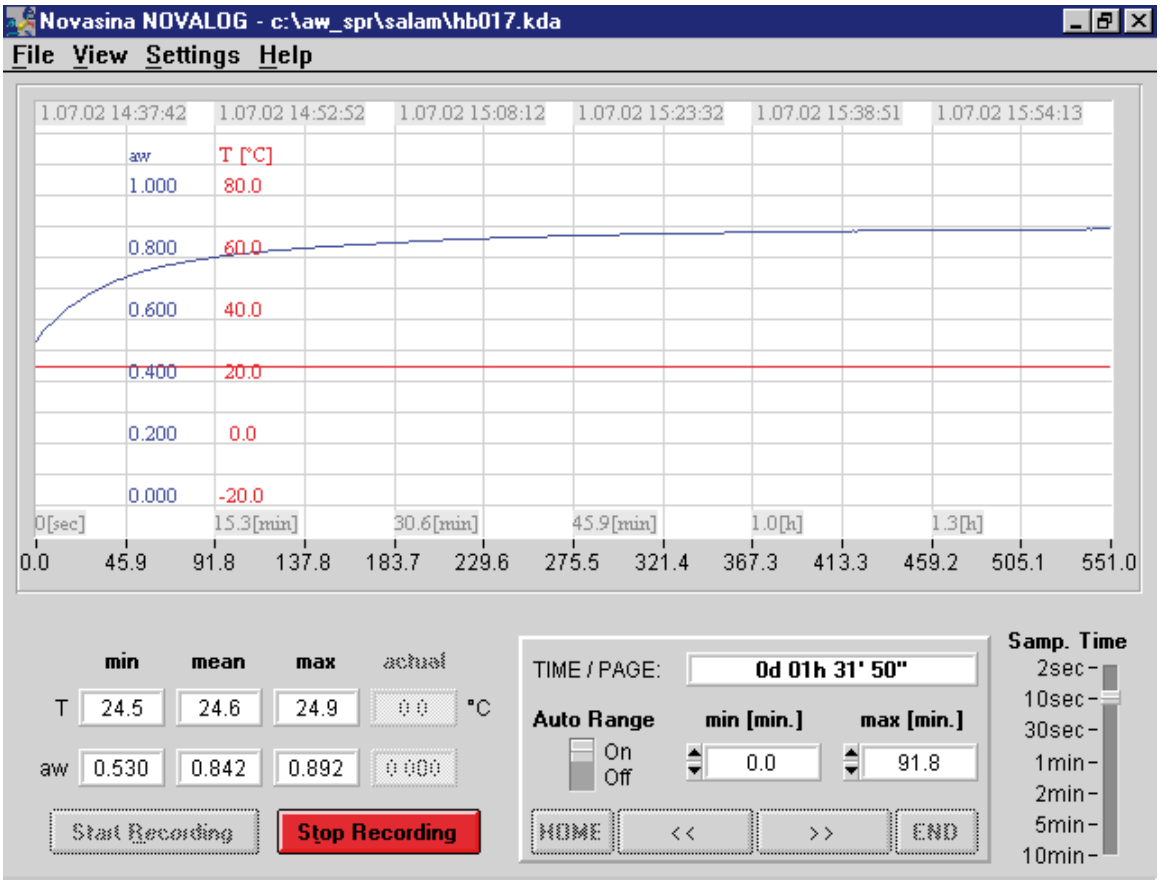
where p is the water vapour pressure exerted by the food material, p_0 the vapour pressure of pure water at temperature t_0, which is the equilibrium temperature of the system.

The objective of this study is to determine water activity changes of typical multicomponent food, dry fermented sausage, during ripening and storage, to measure simultaneously the moisture content of the samples tested, and further analyse and statistically evaluate recorded values.

MATERIAL AND METHODS

Two batches of dry fermented sausage "Herkules" were produced within a full-scale commercial production (Komprda *et al.*, 2004). The basic raw materials were the same for each batch: lean beef meat, lean pork and pork fat used in equal parts, nitrite salt mixture (2.5 %), and sugars (1.0 %). A special spicing mixture was applied according to the producer instructions. One of the two microbial starter cultures, *Pediococcus pentosaceus* + *Staphylococcus carnosus* (designated as HB) and *Staphylococcus carnosus* + *Staphylococcus xylosus* + *Lactobacillus farciminis* (HF), respectively, were admixed to the batch. Chopped and blended ingredients were stuffed into the cutisine casing. The diameter typical for the usual "Herkules" sausage production was kept 80 mm. All products ripened in the same temperature/humidity conditions (including smoking by the cold smoke): 27 °C/92 % 1st day, 20 °C/85 % 2nd to 12th day, and 12 °C /70 % until the 21st day (end of the ripening). Two pieces of each sausage were analysed zero, 7th, 14th and 21st day of ripening. The a_w-value and moisture content (MC) of samples were analysed immediately after refrigerated transportation from the producer to the laboratory. The rest of the sausages were stored at the room conditions for three months after the ripening. The samples were taken for further analysis in fortnight intervals. Each type of test was carried out in two repetitions in each of the two sausages.

Fully computerized laboratory device with a control software was used for the purpose of a_w tests, see Fig. 2.



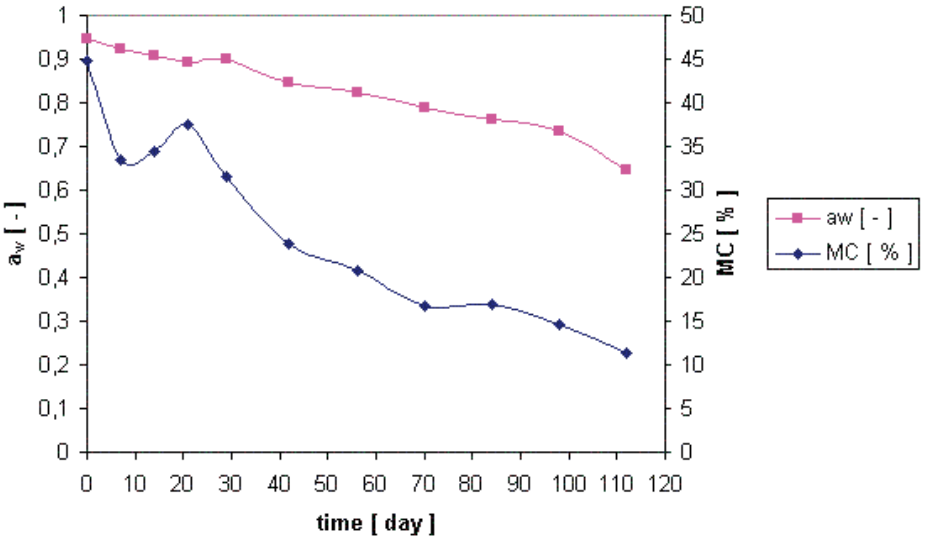
2: *Course of the a_w test*

The method used was indirect manometric in a static environment. The mass of samples was 3.0 ± 0.5 g and the temperature of testing 24.5 ± 0.1 °C. The MC (wet basis) was determined using a halogen dryer.

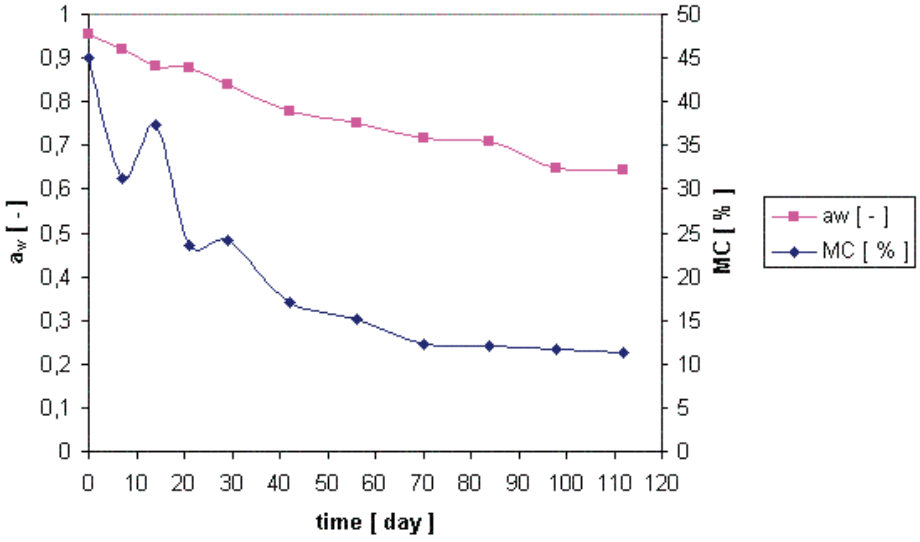
The linear regression for analysis of values measured was used.

RESULTS AND DISCUSSION

The experimental values of a_w and MC for sausages "Herkules" HB and HF are presented in Figs. 3 and 4, respectively.



3: *Course of a_w and MC tests of sausages HB during ripening and storage*



4: *Course of a_w and MC tests of sausages HF during ripening and storage*

Both diagrams show variable course of MC and a_w as well during ripening. It is in consequence of running chemical and biological processes, and varying near ambient air conditions. There was the temperature range from 27 to 12 °C and relative air humidity from 92 to 70 %. Temperature has significant influence on a_w in general, e.g. Štencl *et al.*, 1999; Iglesias and Chirife, 1976. A decrease of temperature causes a decrease of a_w for the same MC and vice versa. All components of mixture have the same value of a_w in the state of equilibrium between the material and environment, see Eqns. (13) and (14). MC of mixtures depends on water sorption properties of each component under specific near ambient air conditions. This is the main reason of high variability of this parameter during ripening process. Following storing conditions (temperature and relative air humidity) were stable already. Diagrams show gradual decrease of both parameters measured during this period. Decrease of MC and a_w of dry fermented sausage HB and HF describe Eqns. (16), (17) and (18), (19), respectively.

$$MC = 34.33-0.2132 * \tau \quad [\%] \tag{16},$$

$$a_w = 0.97-0.0027 * \tau \quad [-] \tag{17},$$

$$MC = 24.29-0.1348 * \tau \quad [\%] \tag{18},$$

$$a_w = 0.887-0.0023 * \tau \quad [-] \tag{19}.$$

Results of linear regression are presented in Tab. I and II.

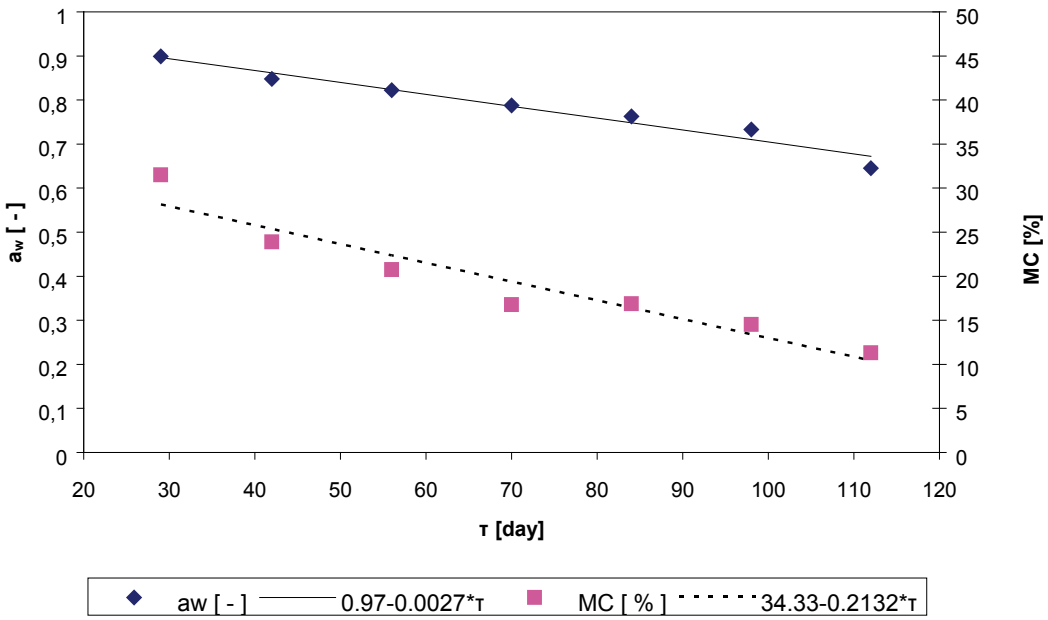
I: *Regression statistic of dry fermented sausage HB*

	MC [%]	a_w [-]
Correlation coefficient	0.952273	0.979255
Coefficient of determination	0.906823	0.950728
Standard error	1.247336	0.018378

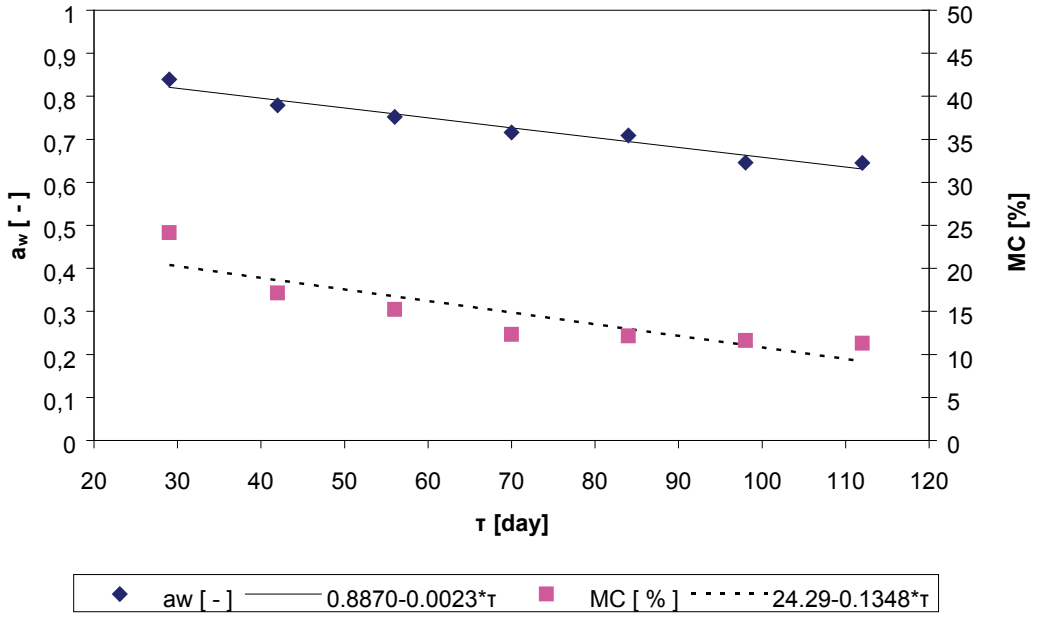
II: *Regression statistic of dry fermented sausage HF*

	MC [%]	a_w [-]
Correlation coefficient	0.873221	0.977289
Coefficient of determination	0.862515	0.955094
Standard error	1.473089	0.016305

Graphical models of MC and a_w for storing process are shown in Figs. 5 and 6.



5: *Course of a_w and MC of sausages HB, models for storage*



6: *Course of a_w and MC of sausages HF, models for storage*

LIST OF ABBREVIATIONS

a	Thermodynamic activity	R	Gas constant
a_w	Water activity	S	Entropy
E	Internal energy	T	Temperature
G	Gibbs free energy	V	Volume
H	Enthalpy	μ	Chemical potential
P	Pressure		

SOUHRN

Změny vodní aktivity vícesložkové potravinové směsi v průběhu zpracovávání

Vodní aktivita je významný parametr pro stanovování a predikci potenciálních změn mikrobiální stability potravin. Může být využita pro určování podmínek skladování, balení a také pro výběr ingrediencí. Při jejím určování se vychází vždy z rovnovážného stavu testovaného vzorku a prostředí, což platí obecně, tedy i u vícesložkových směsí. Změny vodní aktivity a souvisejícího obsahu vlhkosti byly analyzovány u vzorků trvanlivého fermentovaného salámu „Herkules“ vyrobeného se dvěma startovacími kulturami (*Pediococcus pentosaceus* + *Staphylococcus carnosus a Staphylococcus carnosus* + *Staphylococcus xylosus* + *Lactobacillus farciminis*) během zrání (21 dní) a skladování (91 dní). Základními surovinami pro jeho přípravu byly stejné díly hovězího a vepřového masa a vepřového tuku s přídavkem směsi solí (2,5 %) a cukrů (1 %). Vodní aktivita byla měřena nepřímou manometrickou metodou ve statickém prostředí. Obsah vlhkosti byl stanovován v halogenové sušárně. Zrání probíhalo při specifických podmínkách výrobce a skladování ve standardním neupravovaném prostředí. Průběh obou sledovaných veličin byl v době zrání kolísavý a při skladování stabilní. Pro skladování byly vytvořeny rovnice popisující změny vodní aktivity a vlhkosti v závislosti na čase. Matematické modely byly statisticky vyhodnoceny lineární regresní analýzou. Význam odlišných startovacích kultur neměl zásadní vliv na vodní aktivitu ani na vlhkost.

modelování, obsah vlhkosti, salám, skladování, teplota, zrání

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