https://doi.org/10.17221/170/2023-CJFS

Modelling of desorption isotherms for dried meat: New approach and newly applied model

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Citation: Richtr P., Bauer J., Henke S., Ševčík R. (2024): Modelling of desorption isotherms for dried meat: New approach and newly applied model. Czech J. Food Sci., 42: 55–63.

Abstract: In this paper, desorption isotherms of two jerky products were studied (whole-muscle jerky – sample 1 and minced jerky – sample 2). The work focused on the comparison of the Dynamic Dewpoint Isotherm (DDI) method and the Saturated Salt Slurry (SSS) method and testing the newly applied model for modelling desorption isotherms for dried meat. Data were statistically processed using 8 models [Guggenheim-Anderson-de Boer (GAB), Double Log Polynomial (DLP), Henderson, Chin, Smith, Oswin, Hasley, and newly applied model] and statistically evaluated using coefficient of determination (R^2), root mean squared error (RMSE) and mean relative percentage deviation (P-value). The DLP model (25 °C) reached $R^2 \geq 0.999$, P-value ≤ 1.84 for DDI, and $R^2 \geq 0.998$, P-value ≤ 4.37 for SSS method. The GAB model reached $R^2 \geq 0.997$, P-value ≤ 2.58 for DDI, and for SSS method the GAB model reached $R^2 \geq 0.998$, P-value ≤ 5.47. The new model reached P-value ≤ 5.73 for DDI and P-value ≤ 3.48 for SSS method. All models reached the P-value < 10% except for Smith and Chin models. The DDI method and newly applied model prove to be a suitable and precise approach to the evaluation of isotherms of dried meat products.

Keywords: jerky; DDI method; SSS method; sorption models

The production and popularity of dried meat are widespread throughout the world. Traditionally, dried meat was produced by drying in the sun, mainly in conditions where it was not possible to store the meat at lower temperatures (Heinz and Hautzinger 2007). One of the most famous products is beef jerky, which originates in North America. Nowadays, jerky is produced using different types of raw materials (beef, pork, poultry, game, etc.) together with different types of spices and marinades with the addition of functional additives such as antioxidants and stabilisers (Hui et al. 2012). Other examples of dried meat include African biltong, charque from Latin America, bresaola from Italy, pastirma from Turkey, and many others (Roberts and Dainty 1996; Aksu et al. 2020).

It is advisable to use lean muscle to produce jerky. All fat and connective tissue should be removed. To facilitate slicing, the meat can be partially frozen. Slices of sliced meat, or minced meat, are then marinated (a mixture of salt and various spices – pepper, soy

Supported by the grant of Specific university research (Grant Nos: A2_FPBT_2023_041 and A1_FPBT_2023_004).

https://doi.org/10.17221/170/2023-CJFS

sauce, garlic, chili, sugar, and other seasoning ingredients) ideally for 12 h at refrigerated temperatures (Lim et al. 2014). Flavoured meat is then dried. The United States Department of Agriculture (USDA) recommends drying the meat at 70 °C for an hour at least to minimise the risk of alimentary disease caused by pathogenic microorganisms. In industrial production, jerky is dried with hot flowing air on perforated metal trays in drying chambers for approximately 6–8 h (Hui et al. 2012). From the microbial aspect of dried meat, the most important factor is the correct reduction in water activity (a_w) and, therefore, the knowledge of sorption isotherms both in the technological production process and in dried meat, as well as for the proper packaging and subsequent adsorption of water. The USDA recommends a water activity of less than 0.7, which results in the inhibition of fungal growth (Nummer et al. 2004). The jerky should be stored in a hermetically sealed container with reduced oxygen content and no moisture access. The packaging should include an oxygen absorber (Hui et al. 2012).

Water activity of dried meat products is lower than in fresh meat and knowledge of this parameter is a very important factor guaranteeing the practical sterility against microbial deterioration of the product and ensuring the safety of the product during the expected shelf life of the product (Schmidt and Lee 2012; Berk 2018). Therefore, knowledge of sorption isotherms and their measurement are required to model the drying processes (Reid 2020). The sorption isotherm defines the relationship between water activity and water content at a given temperature. This relationship is unique and complex for each product due to different interactions between water and solids at different water content (Al-Muhtaseb et al. 2002; Kaymak-Ertekin and Gedik 2004). Gravimetry is the most common technique used for this purpose (Fontana and Carter 2020).

The Saturated Salt Slurry (SSS) method is a static method for measuring sorption isotherms. The principle is to achieve the equilibrium between environment and material. In a desiccator, known relative humidity is created by using different saturated solutions of salts. Reaching equilibrium is determined gravimetrically (Lewicki and Pomaranska-Lazuka 2003; Schmidt and Lee 2012; Bauer et al. 2022).

The Dynamic Dewpoint Isotherm (DDI) method is based on measuring sorption isotherms using gravimetric analysis and measuring water activity with a chilled mirror hygrometer. The principle of the method is to moisten the sample (absorption) in advance with saturated air and to dry the sample (desorption) with air passing through a moisture absorber. A small change in water activity is recorded in each step (change to a_w = 0.002) (Carter and Fontana 2008; Romani et al. 2016; Bauer et al. 2022).

MATERIAL AND METHODS

Dried meat production. Two samples of jerky were produced – whole-muscle jerky (sample 1) and jerky made of minced meat (sample 2). Sample production was carried out twice at the Department of Food Preservation, University of Chemistry and Technology (UCT) Prague. The beef round (H1) was used to produce sample 1. The meat was sliced 0.5 cm thick; the slices were mixed with marinade and placed in the tumbler for 10 min. The marinade recipe was as follows: 9 kg of water was added to 100 kg of meat (local purveyor), 1 kg of apple vinegar, 0.6 kg of curing salt (TRUMF International, Czech Republic), 2 kg of spice mixture I (yeast extract, sugar, pepper, garlic dextrose, smoky aroma, hardened palm fat) (Raps, Germany), 0.2 kg of spice mixture II (dextrose, edible salt, chives, onion, leek) (Hubka-Petrášek a vnuci, Czech Republic).

The beef neck was used to produce sample 2 and the meat was minced on a cutting machine (HL-G 12 SS; Maso-Profit, Czech Republic) with a diameter of cutting plate holes 3 mm. The minced meat was mixed with a marinade identical to sample 1 and then evacuated (vacuum-sealed bag Vacstar S-210; Herold, Czech Republic) and marinated for 16 h at 6 °C. Subsequently, slices (15 × 3.2 cm) were prepared from the minced meat using a jerky maker (Excalibur, USA). Both samples were placed on drying grids in dehydrator (EXC10 EL; Excalibur, USA) and dehydrated at 68 °C for 5 h to the relative humidity of 80%.

Physicochemical analyses. Moisture, water activity, pH, and weight loss were analysed in both samples. Raw products were analysed every hour of drying (n = 6). The pH value was determined using the pH meter (KNICK Portavo 904; Knick Elektronische Messgeräte, Germany) with the needle probe (SE 104 N; Knick Elektronische Messgeräte, Germany) while the temperature was measured using a temperature sensor (Pt 1000 ZU 0156; Ellab, Denmark). The water activity was measured with the a_w meter (Aqualab 4 TEV; Aqualab, USA) at 25 °C. Drying process was at 105 °C in the dryer (HS 32 A; AST CZECH, Czech Republic) until a constant weight loss. The weight loss was recorded gravimetrically.

The colour measurement of the dried meat was carried out using the reflectance spectrophotometer

https://doi.org/10.17221/170/2023-CJFS

Table 1. Selected sorption models

Author	Equation	Author	Equation
Halsey	$M = -\left(\frac{A}{\ln a_w}\right)^{\frac{1}{B}}$	Chin	$M = \frac{A}{\ln a_w} + B$
Henderson	$M = \left[\frac{\ln\left(1 - a_w\right)}{-A}\right]^{\frac{1}{B}}$	Oswin	$M = A\left(\frac{a_w}{1 - a_w}\right)^B$
Smith	$M = A - B\ln\left(1 - a_w\right)$	GAB	$\frac{M}{M_m} = \frac{ABa_w}{\left(1 - Ba_w\right)\left(1 - Ba_w + ABa_w\right)}$
DLP	$M = A + B\times x + C\times x^2 + D\times x^3$	Henke	$\varphi = A\tanh\left(\frac{w}{B} + Cw^2\right)$

DLP – Double Log Polynomial; GAB – Guggenheim-Anderson-de Boer; M – equilibrium moisture content (g H_2O per 100 g dry basis); a_w – water activity; M_m – monolayer moisture content (g H_2O per 100 g dry basis); A, B, C, D – constants; $x = \ln[-\ln(a_w)]$; ϕ – relative humidity of air, $\phi = a_w \times 100$; w – moisture content in the material, $w = (M/100)/[1+(M/100)]$
Source: Sopade 2001; Al-Muhtaseb et al. 2002; Nurtama and Lin 2010

(CM-5; Konica Minolta, Japan) in the visible spectrum range (360–740 nm). Each sample was measured ten times (at different sample locations) in the CIE colour system $L^*a^*b^*$ in SCI mode. The values of the parameters lightness (L^*), red/green value (a^*), and blue/yellow value (b^*) were recorded, by means of which the colour deviation (ΔE) was calculated.

Desorption isotherms. Two methods were selected to measure desorption isotherms: DDI and SSS methods. Samples 1 and 2 were measured by the DDI method on the AquaLab Vapour Sorption Analyzer (Decagon Devices, USA) at 25 °C and a_w range of 0.97 to 0.5 with a resolution of 0.005. For the SSS method samples 1 and 2 were measured at 25 °C in desiccators with different water activity. Saturated salt solutions were prepared: magnesium chloride (a_w = 0.342), potassium carbonate (a_w = 0.451), sodium nitrite (a_w = 0.601), sodium chloride (a_w = 0.762), potassium chloride (a_w = 0.859), potassium nitrate (a_w = 0.944). The samples were placed in the desiccators to settle to a given relative humidity. Toluene prevents the spoilage of the samples in desiccators. Three pieces of each sample were measured at the same time and the mass change was observed gravimetrically.

Models of desorption isotherms. The experimental data were applied to the following 8 models: Double Log Polynomial (DLP), Halsey, Henderson, Guggenheim-Anderson-de Boer (GAB), Chin, Smith, Oswin, and the newly applied model inspired by its use for the description of the sugar moisture isotherm (Henke et al. 2018), whose equations are shown in Table 1. The experimental data were first evaluated using the Moisture Analysis Toolkit (Aqualab, USA) and then transferred to the MATLAB software (version 2019b), where linearised forms of equations were used to calculate the constants.

Statistical analysis. MATLAB software was used for data processing and to obtain a statistical parameter. The statistical parameters were the following coefficient of determination (R^2), root mean squared error (RMSE), and mean relative percentage deviation (P-value). P-values less than 10% indicate acceptable models (Delgado and Sun 2002, Jena and Das 2012).

$$R^2 = 1 - \frac{\Sigma\left(\hat{M}_i - \bar{M}\right)^2}{\Sigma\left(M_i - \bar{M}\right)^2} \quad (1)$$

$$\text{RMSE} = \sqrt{\frac{\Sigma\left(\hat{M}_i - \bar{M}\right)^2}{n}} \quad (2)$$

$$P = \frac{100}{n}\sum_{i=1}^{n}\frac{\left|M_i - \hat{M}_i\right|}{M_i} \quad (3)$$

where: M_i – experimental moisture content; $\hat{M}_i$ – predicted moisture content; n – number of observations; $\bar{M}$ – mean value of experimental moisture content.

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RESULTS AND DISCUSSION

Dried meat production. The main difference was the production cost of each product. The production cost of sample 1 is 1.4 times higher compared to sample 2. From a technological point of view, the advantage of sample 2 is an easier technological production thanks to the grinding of the raw material and preparation of its slices. The texture was another difference between the finished minced product and the whole muscle product. The whole muscle products were stiff and harder to chew. The minced products were fragile, and their consumption was more pleasant. Minced product fragility is clearly visible at the top of Figure 1. We can see that both whole muscle and minced products shrink during the drying process. However, minced products are more fragile and therefore probability product integrity dame is higher.

Physicochemical analyses. The water content of raw sample 1 was 74.6 ± 0.1 g per 100 g total and for sample 2 it was 74.8 ± 0.1 g per 100 g total. The final moisture content of sample 1 was 27.8 ± 0.1 g per 100 g total and 29.7 ± 0.1 g per 100 g total for sample 2. A similar trend was reported in the study (Ščetar et al. 2013). The average water activity of the raw material for both samples was 0.993 ± 0.002. The water activity of final sample 1 was 0.856 ± 0.002 and for sample 2 it was 0.811 ± 0.002. This indicates a faster drying time for the minced sample. The water activity is considered suitable according to Decree No. 69/2016 Coll., Czech Republic. The pH value for the second batches for sample 1 was 5.57 ± 0.02 and 5.58 ± 0.03 for sample 2. The final pH values for sample 1 were 6.26 ± 0.02 and 5.99 ± 0.01 for sample 2. The ΔE of the final minced product (sample 1) is 10.70 and for the whole muscle product (sample 2) it is 12.58.

Desorption isotherms. The DDI method measured sample 1 and 2 at 25 °C in the water activity range of 0.95–0.5 with a resolution of 0.005 and recorded 100 values for both samples. The experimental data was

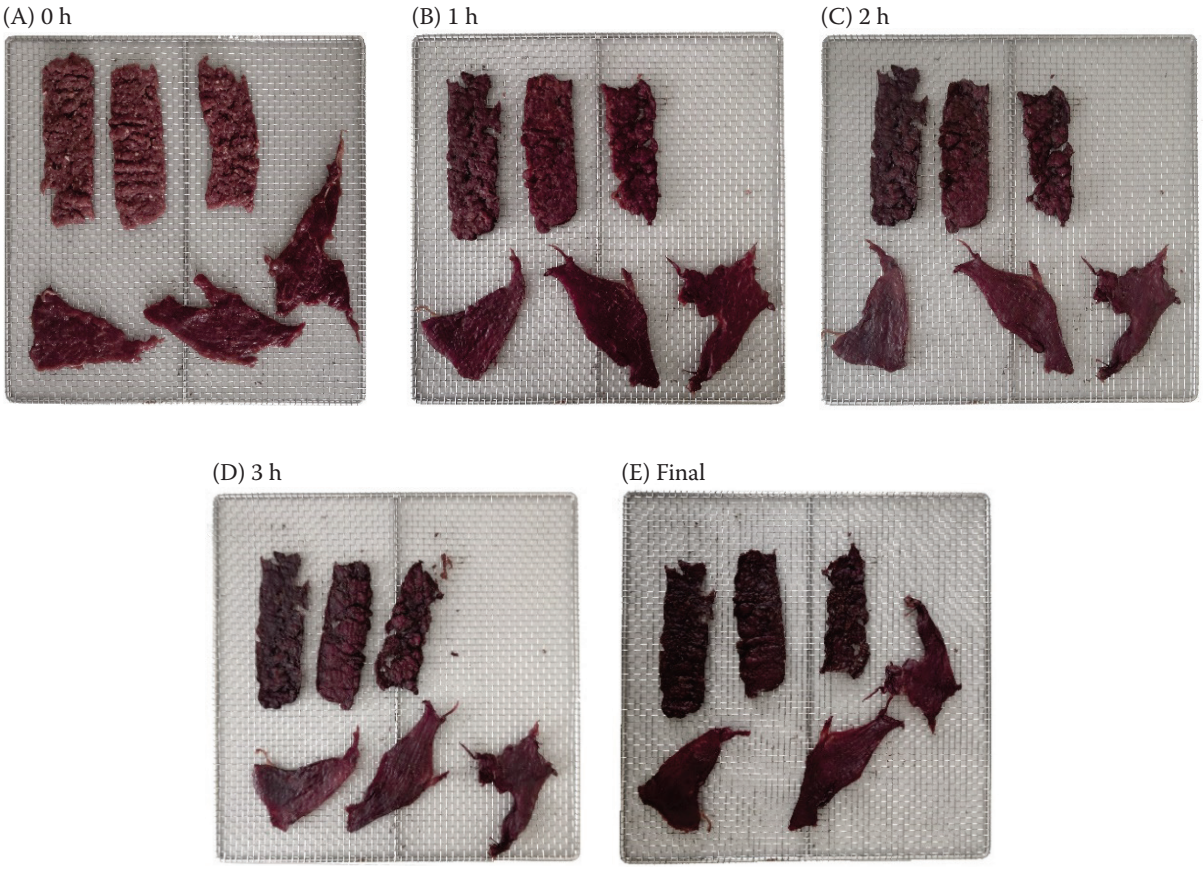

Figure 1. Evolution of jerky sample appearance during the drying process – After (A) 0 h, (B) 1 h, (C) 2 h, (D) 3 h, and (E) final sample

Whole-muscle jerky (sample 2) is placed at the bottom of each photography; jerky from minced meat (sample 1) is placed at the top of each photography

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fitted to the MATLAB software for 7 different sorption models (GAB, DLP, Henderson, Chin, Smith, Oswin, Halsey) and one new model (Henke et al. 2018), first applied in the case of dried meat sorption. The constants of the sorption models together with the statistical parameters are shown in Table 2. The standard method was used for both samples at 25 °C. The SSS data were evaluated in the same way as the DDI method. Figures 2A and 2B compare the measured data by the DDI and SSS methods and their interpenetration by the DLP and GAP models, respectively, for each sample. The DLP and GAB models appear to be the most accurate for the measured desorption isotherms. The SSS method shows a higher moisture content for

Table 2. Model constants and statistical parameters of desorption isotherms of sample 1 and sample 2 measured by Dynamic Dewpoint Isotherm (DDI) and the Saturated Salt Slurry (SSS) methods at 25 °C

Sample	Method	Model	Constants					Statistical parameters		
			A	*B*	*C*	*D*	M_m	R^2	*P*-value	RMSE
1	DDI	GAB	0.072	0.875	–	–	52.334	0.999	2.58	0.3580
		DLP	2.939	–1.175	9.504	0.201	–	0.999	1.84	0.3652
		Henke	85.828	0.077	–17.847	–	–	0.872	5.73	4.5295
		Hender	0.318	0.503	–	–	–	0.999	1.78	0.4189
		Halsey	1.229	1.276	–	–	–	0.931	0.93	0.1211
		Smith	–2.023	30.666	–	–	–	0.974	18.35	2.6862
		Chin	–5.466	–1.394	–	–	–	0.984	11.99	2.1174
		Oswin	5.249	1.076	–	–	–	0.986	0.69	0.0913
	SSS	GAB	4.163	0.930	–	–	9.730	0.999	5.47	0.6355
		DLP	9.882	–10.806	3.517	–0.302	–	0.999	0.88	0.8809
		Henke	94.735	0.243	3.040	–	–	0.994	3.31	2.0612
		Hender	0.084	0.819	–	–	–	0.994	15.07	1.8449
		Halsey	0.830	2.020	–	–	–	0.950	2.50	0.2160
		Smith	–3.667	25.051	–	–	–	0.983	22.28	3.2791
		Chin	–4.131	8.970	–	–	–	0.945	46.09	5.5480
		Oswin	13.623	0.649	–	–	–	0.988	1.09	0.1046
2	DDI	GAB	0.047	0.870	–	–	80.000	0.997	0.91	0.8689
		DLP	1.536	–9.428	0.977	–2.202	–	0.999	0.64	0.3542
		Henke	87.177	0.087	–15.060	–	–	0.914	4.44	3.6682
		Hender	0.317	0.500	–	–	–	0.998	4.12	0.6933
		Halsey	1.172	1.401	–	–	–	0.985	0.60	0.0857
		Smith	–20.298	30.610	–	–	–	0.961	18.36	3.2182
		Chin	–5.709	–1.552	–	–	–	0.994	6.56	1.2131
		Oswin	5.903	1.022	–	–	–	0.993	0.42	0.0600
	SSS	GAB	1.827	0.924	–	–	9.792	0.998	4.90	1.1267
		DLP	6.937	–9.925	4.335	–0.018	–	0.998	4.37	0.9877
		Henke	101.126	0.167	–5.462	–	–	0.995	3.48	2.0179
		Hender	0.118	0.751	–	–	–	0.997	11.99	1.2215
		Halsey	0.959	1.846	–	–	–	0.950	3.67	0.2499
		Smith	–5.163	25.018	–	–	–	0.983	35.26	2.9959
		Chin	–3.969	6.387	–	–	–	0.945	62.46	5.3058
		Oswin	10.189	0.751	–	–	–	0.989	1.34	0.1823

M_m – monolayer moisture content; R^2 – coefficient of determination; RMSE – root mean squared error; GAB – Guggenheim-Anderson-de Boer; DLP – Double Log Polynomial

https://doi.org/10.17221/170/2023-CJFS

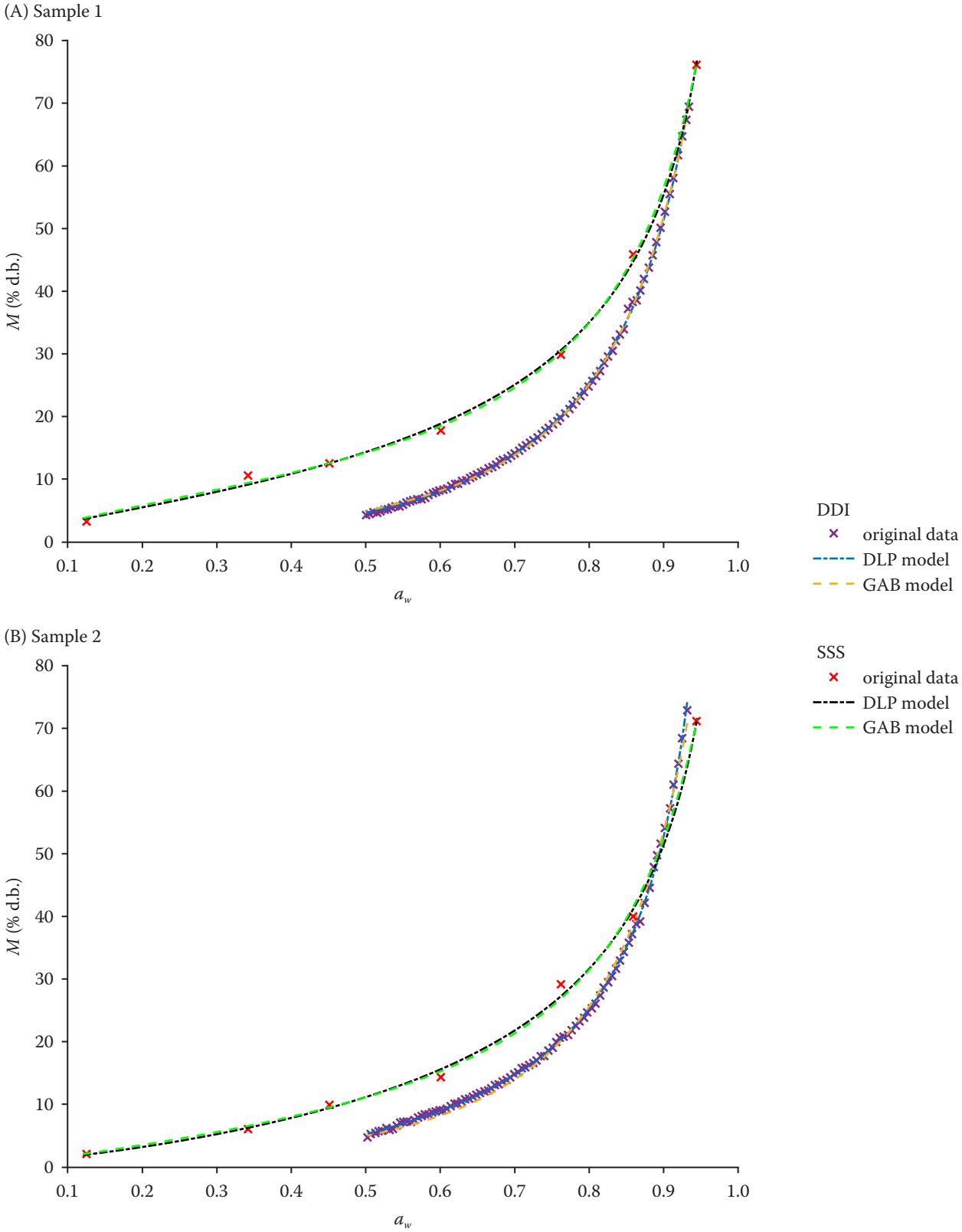

Figure 2. Desorption isotherms predicted by Guggenheim-Anderson-de Boer (GAB) and Double Log Polynomial (DLP) models and comparison with experimental data measured by Dynamic Dewpoint Isotherm (DDI) and the Saturated Salt Slurry (SSS) methods at 25 °C for (A) sample 1 and (B) sample 2

M – equilibrium moisture content; d.b. – dry basis; a_w – water activity

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water activity below 0.85, which could be caused by the longer period that was needed for the samples to settle, also the room humidity can differ in that long period of time, or the water can be in the moist; this circumstance shows the benefits of DDI measuring method. Figure 3 shows the original data (SSS method) and the fit of the newly tested model.

Scarce publications exist that accurately measure sorption isotherms (Aykın-Dinçer and Erbaş 2018). In practice, the standard static method is the usual approach for creating sorption isotherms of meat products. However, this method only records a limited number of isothermal points (Ahmat et al. 2014; Musavu Ndob and Lebert 2018). Furthermore, there is a lack of data regarding sorption isotherms obtained by the DDI method for dried meat products or with a high resolution of 0.005 for water activity (Aykın-Dinçer and Erbaş 2018; Bauer et al. 2022). Presently, DDI-generated sorption isotherms are available only for certain products such as starch (Cristina Duarte Marques et al. 2020).

If the *P*-value is less than 10%, the model is generally accepted (Jena and Das 2012). In addition to the Smith and Chin models, the DLP, GAB, Halsey, and Oswin models have a *P*-value less than 10% for both DDI and SSS methods. The Henderson model seems to be a suitable model for the DDI but not for the SSS method. The Smith and Chin models appear not to be useful for modelling the desorption of dried meat. The most suitable model for jerky products is the DLP model, where the R^2 value was ≥ 0.999, RMSE reached ≤ 0.3652 and the *P*-value ≤ 1.84 for DDI method and R^2 was ≥ 0.998, RMSE was ≤ 0.9877 and the *P*-value ≤ 4.37 for SSS method. Statistical parameter values of the GAB model reached R^2 ≥ 0.997, RMSE ≤ 0.8689, and *P*-value ≤ 2.58 for DDI method and for SSS method the values reached R^2 ≥ 0.998, RMSE ≤ 1.1267, and *P*-value ≤ 5.47.

Using the newly applied model (Henke), R^2 value was ≥ 0.872 and *P*-value ≤ 5.73 for DDI method while R^2 was ≥ 0.994 and *P*-value ≤ 3.48 for SSS method. The Henke model appears to be suitable for the SSS method, where the water activity (in the model ϕ – relative humidity of air) is in a wide range (0.1–0.9), but not for the DDI method (water activity range of 0.5–0.9). The Henke model is applicable, but it is not so suitable as DLP, GAB, Oswin, and Henderson models. Compared to literature (Kabil et al. 2012; Ahmat et al. 2014) where desorption isotherms were measured for similar

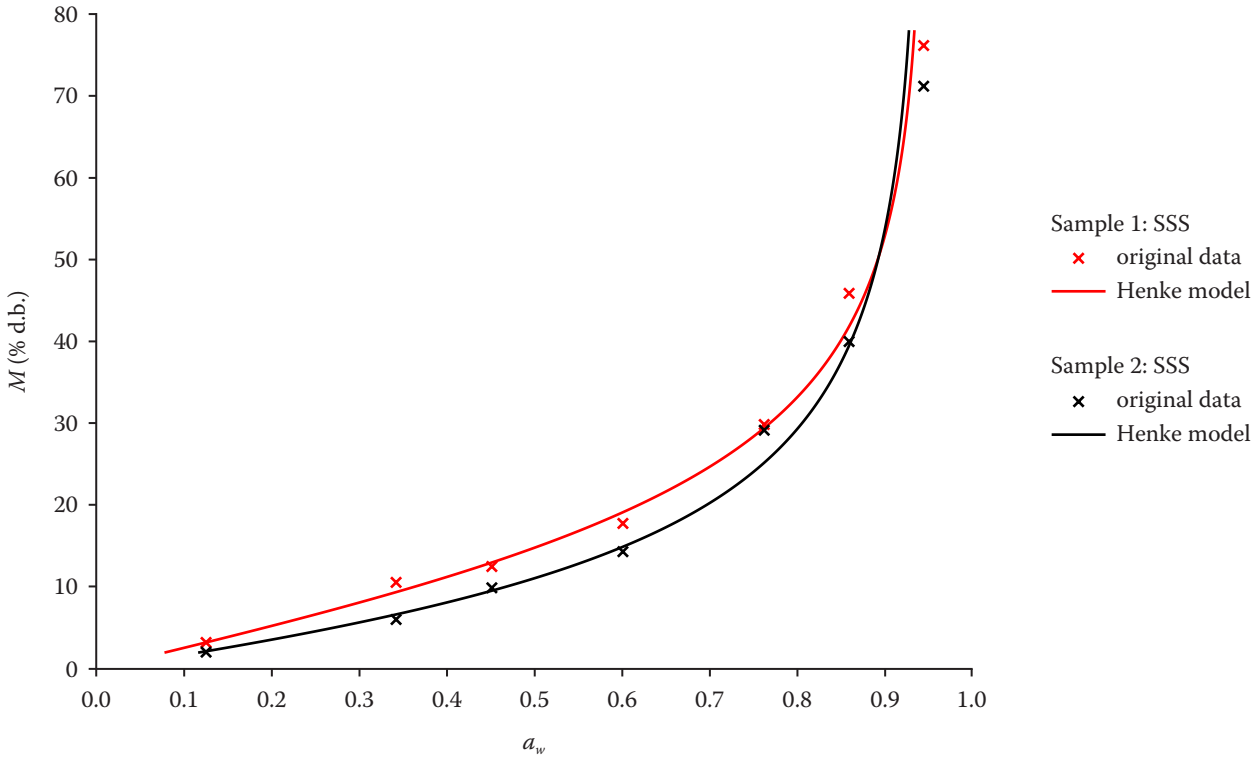

Figure 3. Comparison of the experimental desorption isotherms of sample 1 and sample 2 and the desorption isotherms predicted by the Henke model at 25 °C

M – equilibrium moisture content; d.b. – dry basis; a_w – water activity; SSS – Saturated Salt Slurry

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matrices. The DDI method was used for similar meat products, however in this study the products have lower *P*-values (*P* parameter is lower, which means our models fit the data more accurately) (Kabil et al. 2012).

The DLP and GAB models were chosen for the graphs because they demonstrated the highest accuracy and the best fit with the measured data. Figures 2A and 2B show the experimental data with prediction (model DLP and GAB) of the desorption isotherms for samples 1 and 2 using the DDI and SSS method. The difference between data points measured by DDI and SSS methods is not negligible for either sample. In the region of high water activity (0.85–0.95) the differences are small, however with decreasing water activity the difference becomes more significant. This is caused by different nature of the used methods, where DDI is a dynamic method and SSS is a static method. The static method needs a long period of time (several days) to reach the equilibrium within the sample, on the other hand, the dynamic method is very fast. Thus, the behaviour of the samples may vary with different exposure times to high or low humidity. The desorption isotherm can also be affected by some other processes such as dissolution or crystallisation, but these can be observed only by the SSS method. The DDI method does not necessarily achieve the equilibrium, for example in case of slow vapour diffusion from the sample. However, the nature of the method is closer to the real conditions, where the conditions change dynamically (Carter and Fontana 2008). A possible explanation for the difference may be the salt crystallisation during desorption observed by SSS method, but not by DDI method. Either a mathematical model of drying or further experiments are needed to determine the origin of the difference. Figure 3 shows the original data (SSS method) and the fitting to the newly applied model.

The most suitable models for the modelling of desorption isotherms for dried meat are the DLP and GAB models. Specifically, the DLP model proves to be highly precise in predicting desorption isotherms for dried meat products. Similar outcomes were observed in a study conducted by (Aykın-Dinçer and Erbaş 2018). The newly used model is based on the than function, therefore it is applicable only to the samples where some experimental data points are in the region of water activity under 0.5. The statistical parameters for the SSS method are in the accepted region, and the model can be considered a suitable model for the desorption of water from meat products with low water activity of the samples. Although sample 1 and sample 2 differ in the processing technology, the desorption isotherms (measured by the DDI method) do not show any significant differences. The DDI method offers several key advantages, primarily its efficiency as each sample can be measured within 12 h. In contrast, the SSS method requires a much longer time, specifically 40 days. Another benefit is the quick and straightforward sample preparation process, along with the faster measurement speed compared to the gravimetric approach used in the SSS method. Although it has only seven measured points, in contrast to 100 values used in the DDI desorption method, statistical data reveal that the SSS method remains highly accurate for certain types of models. Both methods were compared, and model parameters were presented that can be used based on the needs of the application.

CONCLUSION

In this paper, two different Jerky-type dried meat products were studied, which differed in the production process. Desorption isotherms were measured in the final samples by the DDI and SSS methods, followed by modelling (DLP, GAB, Halsey, Henderson, Oswin, Smith, Chin) and testing the newly applied model (Henke et al. 2018). The most suitable models for these types of dried meat products are the DLP and GAB models, where the DLP model (25 °C) reached $R^2 \geq 0.999$, *P*-value ≤ 1.84 for DDI method and $R^2 \geq 0.998$, *P*-value ≤ 4.37 for SSS method. The GAB model reached $R^2 \geq 0.997$, *P*-value ≤ 2.58 for DDI method, and for SSS method the GAB model reached $R^2 \geq 0.998$, *P*-value ≤ 5.47. Other suitable models for both methods are the Henderson, Halsey, and Oswin models. The newly proposed model reached *P*-value ≤ 5.73 for DDI and *P*-value ≤ 3.48 for SSS and it can be used to model the sorption isotherms for dried meat products. The DDI method is a much faster measuring method for sorption isotherms, which is beneficial when used in practice. Another advantage of the DDI method is the ease of sample preparation. The experimental data and predicted model parameters from this study should help meat producers to improve the technological process, analytical determination and to optimise the conditions of storage.

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Received: October 13, 2023
Accepted: February 14, 2024
Published online: February 27, 2024