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Comparative analysis of sorption characteristics of Bulgarian grape seeds and flours and flakes produced by them

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Abstract. The present paper contains a comparative characteristics of results obtained from statics of the sorption characteristics of grape seeds and biologically active products obtained from them – full-fatted flour, defatted flour and full-fatted flakes. The statics of the sorption processes is conducted for three temperatures - 10°C, 25°C and 40°C and eight water activities in the range from 0.112 to 0.868. For all of the examined products the temperature rise leads to a decrease of their sorption capacity. For the description of the equilibrium curves of the examined products the three parametric modified models of Oswin, Halsey, Henderson, Chung-Pfost are used. By the method of the smallest squares, using a programme for nonlinear regression "*Statistica*", the coefficients of the used models are calculated, as on the basis of universally used criteria of suitability, a relevant model is recommended for each of the four Bulgarian products. The calculation of the values of the monolayer moisture content (MMC) in water activities below 0.5 is done through linearization of the Brunauer-Emmett-Teller (BET) model. The obtained results for MMC vary within the range from 2.34% to 4.96% dry substance (d.b.) for the processes of adsorption and desorption.

Keywords: sorption characteristics, functional flours, grape seeds.

1. Introduction

Recently more and more studies are focused on the prospecting of natural plant species with high content of nutrients, which to be treated and proposed as products of high quality, satisfying the body needs [1].

The sorption characteristics (equilibrium and monolayer moisture content) of the nutrients afford an opportunity for proper methods of their treatment and preservation to be optimized. The knowledge about the equilibrium moisture enables the proper deciphering of the regimes and methods for the product's treatment, preservation and packaging [2]. The dependence between the equilibrium moisture (M) and the water activity (a_w) is given from a skillfully built under definite temperatures sorption isotherm. The isotherms afford the examination of the character and the quantity of the different types connected water. For the first time the term "water activity - a_w" is suggested by Scott in 1952 and it is widely used in the monitoring of the Critical Control Points (CCP) in the Hazard Analysis and Critical Control Point (HACCP) [3]. The equilibrium moisture calculated in different conditions of the nutrients can be prognosticated through a mathematic model. The use of empirical models for specifically examined products restricts their applicability. This imposes the search of models, allowing the description of the sorption isotherms of a larger number of nutrients grouped under similar indices [4]. Scientific teams suggest over 200 empiric and theoretical models for description of the equilibrium isotherms [2; 5-7]. A large part of the publications are concentrated over the use of two parametric methods, which eliminate the influence of the temperature in their equations. However, the investigations prove that the temperature affects the equilibrium moisture, which imposes the two parametric methods to be modified into three parametric methods containing the temperature effect [8]. The sorption isotherms of different nutrients modeled by a great number of scientific teams, proves that there is no universal model, i.e. to describe the isotherms of different products or groups of products. The first to reach this conclusion in 1989 are Chen and Morey, which necessitates that in the processing of the results obtained from an experiment, there must be used several models and according to certain criteria: average relative error, standard error and residues distribution, the most fitted to be chosen [9]. These criteria are adopted till nowadays [10]. In Standard 245D of American Society of Agricultural Engineers (ASAE) for description of the equilibrium isotherms of products of plant origin, three parametric modified models of Oswin, Henderson, Halsey и Chung-Pfost are suggested [11-12].

The model of Brunauer-Emmett-Teller (BET), based on the theory for the poly molecular adsorption is also one of the widely used [6; 13]. It is proved that the BET model is generally used in the calculation of the monolayer moisture content (MMC) for a large number of products in water activity not higher than 0.5. The moisture value corresponding to the monolayer moisture content (MMC) is a sorption characteristics, which affects the product's stability [14-17]. In a large number of investigations it is proved that reducing the product to moisture corresponding to MMC in conditions for storage, preservation of its quality indices is achieved [18].

In the detailed literature survey there is not data base of a summarized comparison of the sorption characteristics of grape seeds of Bulgarian origin and flours and flakes produced by them in cultivation, which gave us a reason for the present elaboration.

2. Materials and methods

2.1. Materials

The targets of the present studies are grape seeds of Bulgarian origin extracted after alcohol fermentation of wine of the sorts Mavrud, Cabernet Sauvignon, Syrah, Merlot, Dimyat and Sauvignon Blanc, and the obtained products - full-fatted flakes, full-fatted flour and defatted flour. The analysed samples are provided from an experimental base – village of Parvenets, Municipality of Rodopi, Plovdiv. They are selected on the base of limited and/or lack of data after a detailed literature survey.

2.2. Methods

Nutrients' equilibrium isotherms indicate the dependence between the product equilibrium moisture and the water activity of the environment in determinate temperature.

A static gravimetric method, recommended by Project COST 90 [19] and up-dated by Bell & Labuza, (2000) [14] is used for the purpose of the present paper. The study provides information about the sorption characteristics – adsorption and desorption in temperatures of 10°C, 25°C и 40°C and

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eight different relative air moistures. The samples are preliminary dehydrated in desiccators over diphosphorus pentaoxide (P_2O_5) for 20 days with the purpose to investigate the process adsorption.

The samples are hydrated over distilled water (H_2O) for the same period – 20 days for the process of desorption. Aluminium weight containers, in which samples with a mass of 1±0.01g are measured, are used for the analysis. After that the containers are placed in hygrostats, in which relevant saturated solutions of salts are prepared in advance, upholding over their surface definite constant water activities (relative moistures of the environment) within the range from 0.112 to 0.868. In the hygrostats at a_w>0.6 thymol crystals are placed to prevent the product from microbiological damage for the whole period of the experiment.

2.2.1. Sorption isotherms modelling

The modified three parametric models of Oswin, Chung-Pfost, Halsey and Henderson are used for the description of the sorption isotherms.

Modified Chung-Pfost $$a_w = exp\left[\frac{-A}{t+B} exp(-CM)\right] \quad (1)$$

Modified Halsey $$a_w = exp\left[\frac{-exp(A+Bt)}{M^C}\right] \quad (2)$$

Modified Oswin $$M = (A + Bt)\left(\frac{a_w}{1-a_w}\right)^C \quad (3)$$

Modified Henderson $$1 - a_w = exp[-A(t + B)M^C] \quad (4)$$

where: *t* is temperature, °C; A, B and C - coefficients.

A programme for nonlinear regression by the method of the smallest squares "*Statistica*" (procedure "Nonlinear estimation") [20] is used to determine the coefficients of the models (A, B and C). Average relative error, standard error and residues distribution are the criteria applied for the estimation and comparison of the models:

Average relative error $$P = \frac{100}{N}\sum\left|\frac{M_i-\widehat{M}_i}{M_i}\right| \quad (5)$$

Standard error $$SEM = \sqrt{\frac{\sum(M_i-\widehat{M}_i)^2}{df}} \quad (6)$$

Residue $$e_i = M_i - \widehat{M}_i \quad (7)$$

where: M_iи $\widehat{M}_i$ are respectively the experimental and the predicted by the model equilibrium moisture; N – number of experiments; *df* – degrees of freedom (number of experiments minus number of coefficients).

The accidental and non-accidental distribution of residues is graphically represented. In model with the lowest values for P and SEM and accidental residues distribution, the relevant model can be recommended for description of the sorption isotherms of the examined product.

The model of Brunauer-Emmett-Teller (BET) (10) is transformed into linear type with the purpose of calculation of the monolayer moisture content values - MMC [21]:

Where: coefficients $$\frac{a_w}{(1-a_w)M} = P + Qa_w \quad (8)$$

$$P = \frac{1}{M_eC} \quad (9) \qquad \text{and} \qquad Q = \frac{C-1}{M_eC} \quad (10)$$

To receive the values of the coefficients P and Q of the linear equation, the experimental data at $a_w \leq 0.5$ and temperatures – 10°C, 25°C и 40°C are processed with the programme Excel by the method of the smallest squares. On the basis of the received results MMC of the examined products is calculated.

3. Results and discussion

The analysis of the sorption characteristics of the examined grape seeds and the biologically active components obtained from them indicates certain common objectives.

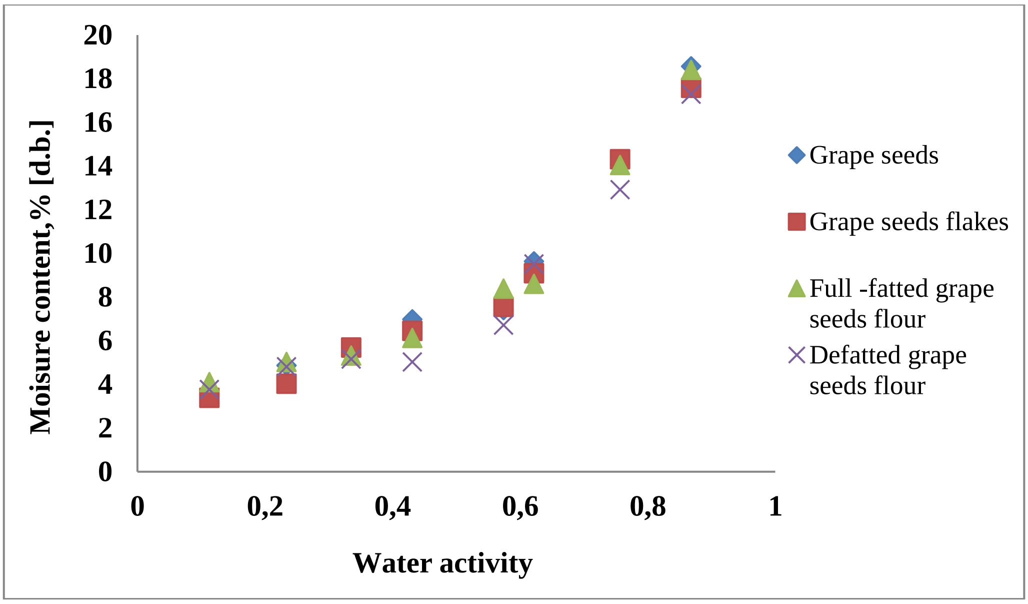


Figure 1. Adsorption isotherms of examined products at temperature of 10ºC

From the analysis of the received results for temperatures of 10°C, 25°C and 40°C and water activities within the range from 0.112 to 0.868, it can be indicated that the temperature rise for all examined products leads to the reduction of their sorption capacity. The explanation of this fact is probably the activation of the water molecules' mobility, which are respectively held with difficulty on the hard surface. All isotherms have clearly indicated S-figured character, i.e. they are from 2nd type according to the classification of Brunauer et al., (1940), like more of the nutrient powdered products [22]. The comparative graphic dependencies of the adsorption and desorption isotherms of all examined products received for 10°C are presented in Figure 1 and 2.

In analysis of the results it is reported that the examined grape seeds and the bioactive products obtained from them at a_w approximately 0.6 have almost equalized adsorption and desorption capacity. An interesting fact is that at $a_w > 0.8$ for the adsorption process the sorption capacity which is most strongly defined is measured for whole grape seeds, followed by full-fatted flour, full-fatted flakes and defatted grape seeds flour. For the desorption process we measured the most strongly defined sorption capacity for full-fatted grape seeds flakes, followed by defatted flour, full-fatted flour and the initial material – the whole grape seeds remain with the lowest capacity. For water activity $a_w = 0.6$ at fig. 2 the four examined products are with equal sorption capacity. In the comparison sorption isotherms for all examined products (grape seeds, full-fatted flakes, full-fatted flour and defatted flour) lower or more clearly expressed hysteresis is defined. As a summary of the different theories explaining the hysteresis effect, we came to the conclusion that it is a result from many factors interacting between each other. The received results for the other two temperatures – 25°C and 40°C for adsorption an desorption processes are similar too.

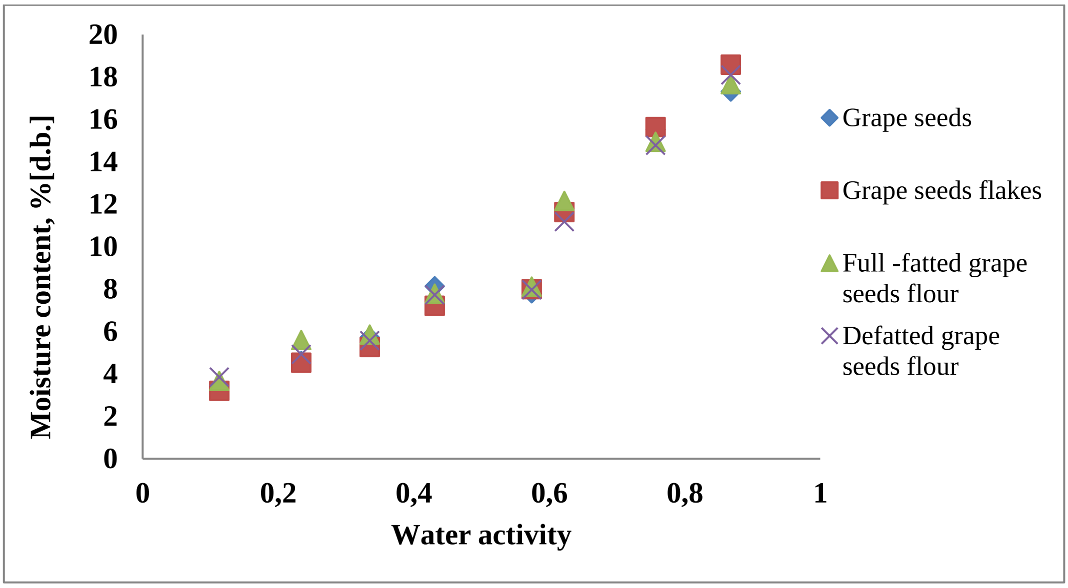
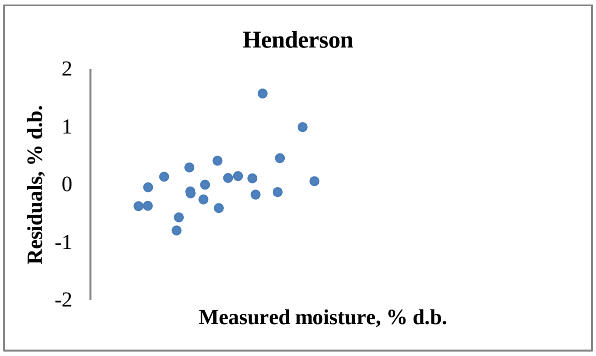
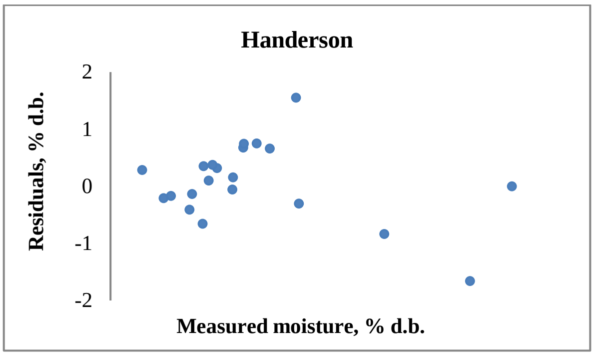


Figure 2. Desorption isotherms of examined products at 10°C

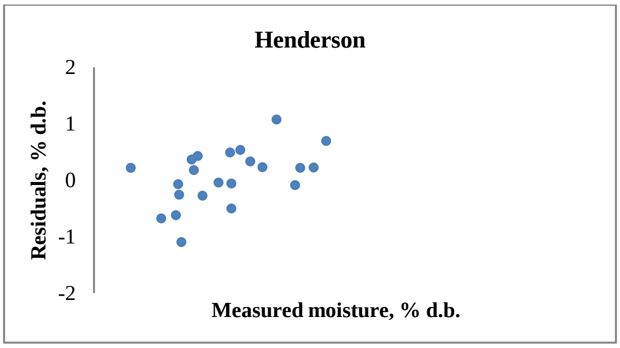


Adsorption



Desorption

Figure 3. Grape seeds: Residues distribution
* Residues larger than ± 2 are not presented



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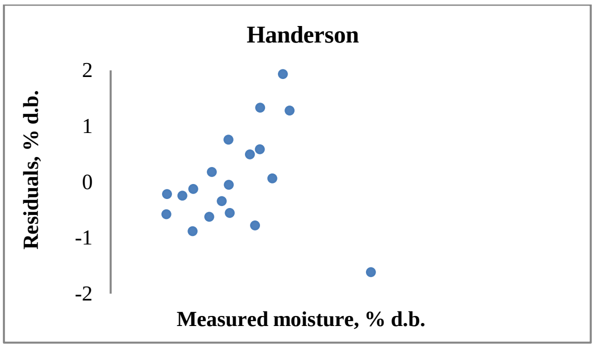
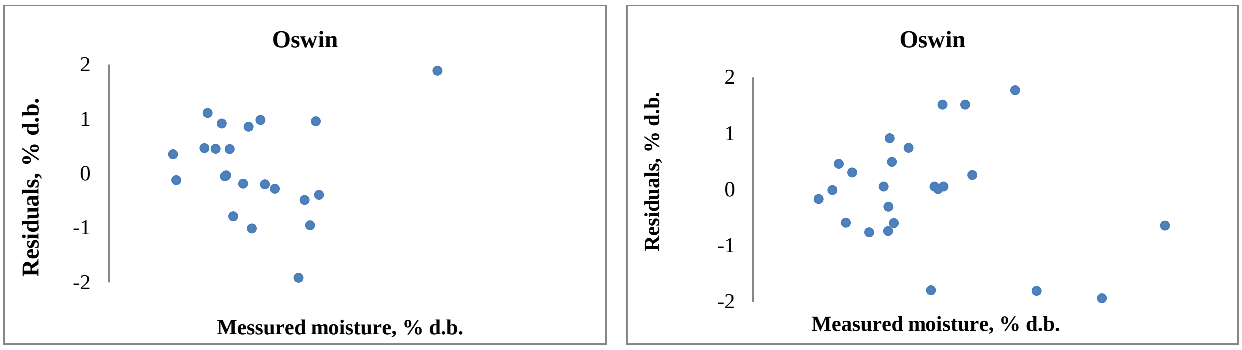


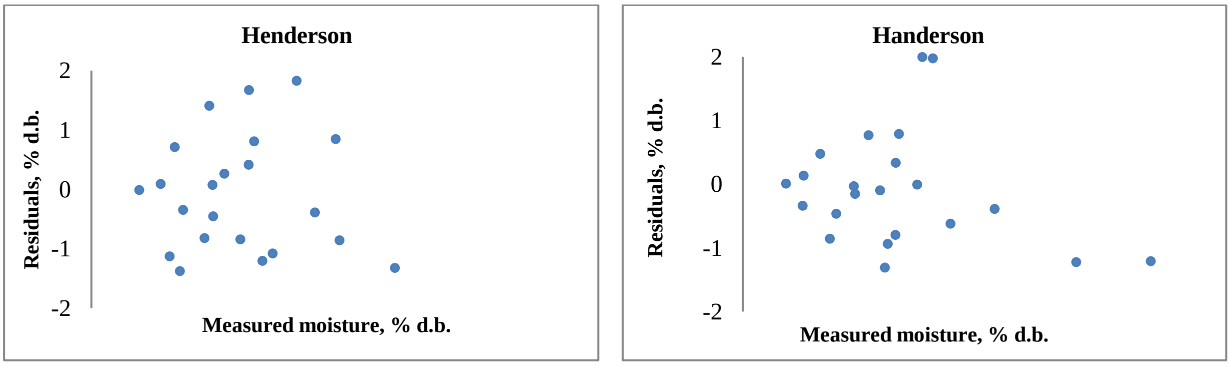
Desorption

Figure 4. Grape seeds flakes: Residues distribution
* Residues larger than ± 2 are not presented



Adsorption Desorption

Figure 5. Full-fatted grape seeds flour : Residues distribution
* Residues larger than ± 2 are not presented



Adsorption Desorption

Figure 6. Defatted grape seeds flour: Residues distribution
* Residues larger than ± 2 are not presented.

On the basis of statistic processing three parametric modified models for description of the four examined products sorption isotherms are recommended, namely: whole grape seeds, full-fatted grape seeds flour, full-fatted grape seeds flakes and defatted grape seeds flour.

Table 1. Coefficients (*A, B, C*) of recommended models for sorption isotherms description

Product	**Models**	**Process**	***A***	***B***	***C***
Grape seeds	Henderson	Adsorption	0.000959	9.608507	1.737924
		Desorption	0.001089	8.806570	1.610936
Grape seeds flakes	Henderson	Adsorption	0.000830	14.97965	1.725401
		Desorption	0.000672	17.99822	1.712982
Full-fatted grape seeds flour	Oswin	Adsorption	547.982	0.33870	61.6750
		Desorption	9.68658	-0.10298	0.35869
Defatted grape seeds flour	Henderson	Adsorption	0.000291	95.37602	1.564150
		Desorption	0.000696	18.61505	1.63518

The models are recommended on the basis of commonly accepted criteria for the lowest values for average relative error, standard error (table 1) and accidental residue distribution (figures 3,4,5 and 6).

The presented models confirm the Chen & Morey, (1989) statement that there is no universal model to be recommended for description of all nutrients sorption isotherms, including the obtained as derivatives of initial materials [5-6; 9].

The numerical values of the monolayer moisture content (MMC) presented in table 2 are calculated through linearization of the BET model and the received calculations. It is clear from the data in the table that the highest value of MMC is reported at temperature 10ºC, after which its values for temperatures 25ºC and 40ºC lower with approximately 1.3% for adsorption and approximately 1.5% for desorption process. The lowest values for the experiment's conditions are reported at temperature 25ºC. The full-fatted flakes from pressed grape seeds have the lowest values of MMC at temperature 25°C for the both processes. The highest values 4.33% d.b. is calculated for desorption process at 10°C for this analyzed product, too. For the three temperatures the values of MMC for desorption process are higher than its values for adsorption process. The reported data for grape seeds full-fatted flour show clearly defined hysteresis; for the three temperatures are higher for desorption than adsorption with from 0.2% d.b. до 1.2% d.b. We report the lowest values for adsorption and desorption at temperature of 25ºC for grape seeds Bulgarian full-fatted flour. Hysteresis is available for defatted flour but only for two temperatures – 10ºC and 25ºC. For temperature of 40ºC the received results are approximately equal and similar to value with the results for desorption for 10ºC.

Table 2. BET monolayer moisture content, % d.b. for adsorption and desorption processes of examined products for temperatures 10°C, 25°C and 40°C.

Product	**Process**	**10°C**	**25°C**	**40°C**
Grape seeds	Adsorption	4.03	2.46	2.59
	Desorption	4.96	2.34	3.03
Grape seeds flakes	Adsorption	3.95	2.62	2.67
	Desorption	4.33	2.78	3.23
Full-fatted grape seeds flour	Adsorption	3.34	2.48	3.11
	Desorption	4.59	2.70	3.55
Defatted grape seeds flour	Adsorption	3.41	2.54	4.53
	Desorption	4.58	2.75	4.25

As a result of the analysis we can summarize that the received results for all examined products indicate that the temperature does not affect the values of the monolayer moisture content. For all products an interesting fact is that the lowest values are calculated for temperature 25°C. The MMC values for examined whole grape seeds and powdered products obtained from them vary within the range from 2.34% d.b. to 4.96% d.b. for adsorption and desorption.

The sorption characteristics examination gives an important information for treatment, transportation and preservation which guarantees the nutrients' quality. The hygro-thermal equilibrium between relative air humidity and the examined products of Bulgarian origin – grape seeds, full-fatted grape seeds flakes, full-fatted flour and defatted flour for temperatures of 10ºC, 25ºC and 40ºC and aw = 0.10÷ 0.90, is studied for the first time.

The numerical values of the proposed models for description of the equilibrium isotherms of the examined products, make them usable for calculation of equilibrium moisture in the engineering practice.

The moisture value corresponding to the monolayer moisture content (MMC) is a sorption characteristic which influence positively the stability of the product [16-17]. The MMC calculated values are a good precondition for an extensive research about regimes and terms of preservation of the analyzed products.

4. Conclusions

Equilibrium isotherms are received for the processes adsorption and desorption for temperatures 10ºC, 25ºC and 40ºC and relative moistures within the range from 0.112 to 0.868 for grape seeds, full-fatted grape seeds flakes, full-fatted grape seeds flour and defatted grape seeds flour. It is established that the isotherms of all products are with *S*-graphic character, i.e., they are from 2nd type according to the classification of Brunauer et al., (1940). It is established that the temperature affects the sorption capacity of the grape seeds, full-fatted grape seeds flakes, full-fatted grape seeds flour and defatted grape seeds flour. With its increase at constant water activity the equilibrium moistures lower. On the basis of statistic processing and in accordance with the accepted criteria three parametric modified models for description of the four examined products sorption isotherms are recommended:

- For grape seeds, full-fatted grape seeds flakes and defatted grape seeds flour – modified model of Henderson;
- Full-fatted grape seeds flour – modified model of Oswin;

The values of MMC for the processes adsorption and desorption are calculated in the range within:

- Grape seeds: 2.34% ÷ 4.96%
- Full-fatted grape seeds flakes: 2.62% ÷ 4.33%
- Full-fatted grape seeds flour: 2.48% ÷ 4.59%
- Defatted grape seeds flour: 2.54% ÷ 4.58%

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