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Research Article

Moisture sorption characteristics and storage study of grape seeds flakes

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Abstract

The current scientific research is focused on the sorption isotherms, monolayer moisture content and storage study of full-fatted grape seeds flakes (FGSF) of different grape variety locally grow in Bulgaria (Mavrud, Cabernet Sauvignon, Syrah, Merlot, Dimyat and Sauvignon Blanc). To determine the sorption characteristics of FGSF, we are used a static gravimetric method of saturated salt solution and relative humidity from 0.11 to 0.90 at three different temperatures – 10, 25 and 40°C. In the condition of constant water activity and increasing temperatures, the sorption capacity of the product decrease. We are recommend the modified Henderson model for description of sorption isotherms of FGSF. The monolayer moisture content (MMC) values are obtained by linearization of Braunauer-Emmett-Teller (BET), in the range of $MMC_{ads} = 2.32 \div 3.41$, $MMC_{des} = 2.59 \div 3.68$.

The three months storage study of samples was monitored at moisture value reduced to a value corresponded to the calculated monolayer moisture content. FGSF was packed in a co-extruded barrier film with copolymer covering for heat sealing, in the conditions for storage - temperature 18 ÷ 25°C and relative humidity 45 ÷ 55%. No living cells of pathogenic organisms (*Escherichia coli*, *Staphylococcus aureus* and *Salmonella* spp.) or apparent molding were detected. The flour particle size has not changed either.

Keywords: grape, grape seeds, grape seeds flakes, sorption isotherms, bioactive compounds, enological by-product

Abbreviations:

FGSF - full-fatted grape seeds flakes

MMC - monolayer moisture content

BET - Braunauer-Emmett-Teller

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Introduction

The bioactive compounds have a beneficial effect on the human immune system used as a preventative measure against certain illness states (cancer, cardiovascular disease, diabetes, etc.) (Sousa et al. 2014; Zheng and Li 2015). A typical example for a product (part of a healthy diet) is the flakes. They are part of daily consumption in adolescents and adults in some countries such as the United States, Germany and France. Flakes are intended for direct using and they do not require supplemental heat treatment (Fast 1990). Nowadays, the businesses are focusing increasingly on recycling biodegradable waste products from different spheres of food productions. Moreover, the grape by-product, it seems to be an excellent source of bioactive compounds. The winemaking is a widespread industry in all countries of the world, including Bulgaria. Approximately 20% of the grapes are an unnecessary and pollution waste (Teixeira et al. 2014; Tournour et al. 2015). In the past years, the winemaking sub-product, has been used for fat extraction, while the defatted residue has been used for livestock breeding (source of dietary fiber) (Song et al. 2017; Wang et al. 2017). Grape seeds, retrieved after fermentation of wine, provides a new ways of applications for search and development in food industries, namely as food additives with anticancerogenic properties, exhibiting antioxidant activity, antibacterial activity and aromatic properties (Cádiz-Gurrea et al. 2017; Ricci et al. 2017). Due to influence of the respective climatic and soil characteristics, terroir, technological operation, (i.e. natural and human factors) gives the uniqueness of each lot of harvested grape seeds. Physical, chemical and microbiological stability of the flour structure depends on the amount of water and the mode of interaction with the product (Silva et al. 2014). The relation between moisture content of the product and the main parameters of the air, are considered when the product is in a state of equilibrium with ambient air and its humidity is relative (static sorption process). According to literature review, the equilibrium humidity decreases when a temperature increasing, in conditions of constant water activity. Research on the speed chemical reactions in food products show that for a large number of product exist a low value of relative humidity. Therefore, the quality of the product has not changed either. This value of the moisture corresponded to monolayer moisture content (MMC). This is an important sorption characteristic which influence directly on the stability of the product. Meanwhile, the oxidation of lipids is significantly decrease with a moisture below or corresponding at MMC (Decagon 2011; Labuza 2012). Data analysis on sorption characteristics and in the particularity MMC of food products, provide information about predicting, establishing and selecting storage regimes to ensure the stability and preservation of their nutritional values (Sharma et al. 2018). After reference research we didn`t find information on sorption characteristics, monolayer moisture content, storage study of FGSF of Bulgarian grape varieties. Thus, the aim of the present study was to determine sorption characteristics, monolayer moisture content, storage study (traceability of changes in microbial load, granulometric composition, moisture content) on FGSF of Bulgarian grape varieties.

Materials and Methods

Materials. Grape seeds flakes (of different grape varieties of Bulgarian origin, namely Mavrud, Cabernet Sauvignon, Syrah, Merlot, Dimyat, Sauvignon Blanc) were delivered by experimental institute located in Parvenets, Bulgaria. Grape seeds were extracted after alcoholic fermentation of wine as an oenological by-product. They was dried under atmospheric conditions and pressed with a reconstructed mill roll [using 2 smooth shafts with a differential difference of 0.05/each roller rotates at different speeds, the difference between them for 1 rpm (rotation per minute) is 1.5 mm to 5 mm]. The applied pressure was between 200 and 280 tons. Grape seeds flakes were full fat (19.33%) and their high fat content was confirmed by Soxhlet extractor at the Department of Technology of Grain, Fodder, Bread and Confectionery Products at the University of Food Technologies, Plovdiv, Bulgaria. The product was packaged in a co-extruded barrier film with copolymer covering for heat sealing designed for food industry, produced by Itaplast "ET - Ilko Tyanevita Plast", Assenovgrad, Bulgaria.

Procedure. The equilibrium moisture content (EMC) of the FGSF was determined at 10, 25 and 40ºC and a_w= 0.11 ÷ 0.90. The static gravimetric method was applied (Wolf 1985). For the adsorption process, the FGSF was dehydrated in a desiccator with P_2O_5 at a room temperature for 20 days prior to the beginning of the experiment. The desorption isotherms were determined on samples hydrated in a glass jar over distilled water at a room temperature. Samples of 1 ÷ 0.02 g were weighed in weighing bottles. The weighing bottles were then put in hygrostats with eight saturated salt solutions (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $MgNO_3$, NaBr, NaCl, KCl) used to obtain constant water activity environments (Bell and Labuza 2000). All of the used salts were of reagent grade. At high water activities (a_w > 0.70) crystalline thymol was placed in the hygrostats to prevent microbial spoilage of the FGSF. The hygrostats were kept in thermostats at 10, 25 and 40÷0.2ºC. Samples were weighed (balance sensitivity ÷ 0.0001 g) every three days. Equilibrium was ascertained when three consecutive weight measurements showed a difference less than 0.001 g. The moisture content (%) was determined according to AOAC 960.39 (AOAC 1990).

Analysis of data. The following models were used to verify 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:

M is the average moisture content, % d.b.;

a_w is the water activity, decimal;

A, B and C are coefficients;

t is the temperature, ºC.

A nonlinear, least squares regression program was used to fit the FGSF models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the average relative error P (%); the standard error of moisture (SEM) and the randomness of residuals (Chen and Morey 1989):

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

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

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

where:
Mi and $\hat{M}_i$ are experimentally observed and predicted by the model value of the EMC;
N is the number of data points;
A, B and C are coefficients.
df is the number of degree of freedom (number of data points minus number of constants in the model).

The monolayer moisture content (MMC) for each temperature is calculated by using the Brunauer-Emmett-Teller (BET) equation and the experimental data for water activities up to 0.45 (Bell and Labuza 2000; Brunauer et al. 1938):

$$M = \frac{M_e C a_w}{(1-a_w)(1-a_w+Ca_w)} \quad (8)$$

where:
M is the MMC, % d.b.;
a_w is the water activity, decimal;
C is the coefficient.

The microbial load. The microbial load of the product was determined during the three-month storage via:

Mesophilic aerobic and facultative anaerobic bacteria, according to Bulgarian State Standard (BSS) EN ISO 4833-2:2014;
Yeasts and fungi, according to (BSS) EN ISO 21527-2:2011;
Escherichia coli, according to (BSS) EN ISO 16649-2:2014;
Salmonella spp., according to (BSS) EN ISO 6579:2003;
Coagulase-positive *staphylococci*, according to (BSS) EN ISO 6888-1:2005.

Flour particle size. Flour particle size was determined with „ProMel LP – 200" sieve analysis equipment. Based on preliminary analysis, the set of sieves was determined as well as their size. The sieving of the sample in the apparatus continues for ten minutes if it amounts to 100 g. All tests were run in triplicate.

Results and Discussion

Moisture sorption analysis of FGSF. The obtained mean values of EMC (equilibrium moisture content), based on triplicate measurements for the respective water activity and temperature, are presented in Figure 1 for adsorption and in Figure 2 for desorption.

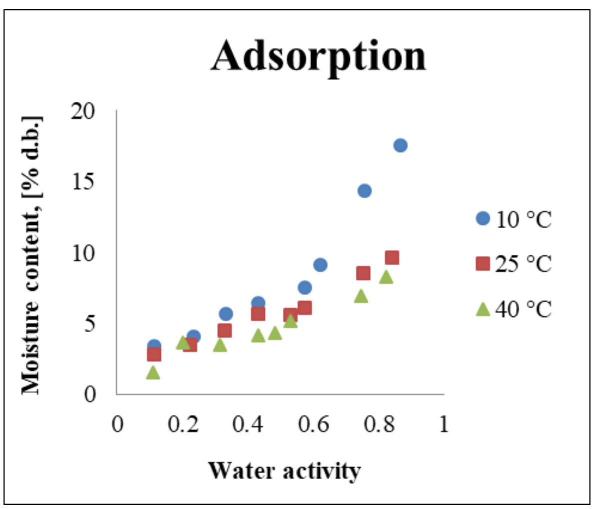

Figure 1. Sorption isotherms at 10, 25 and 40°C for Adsorption

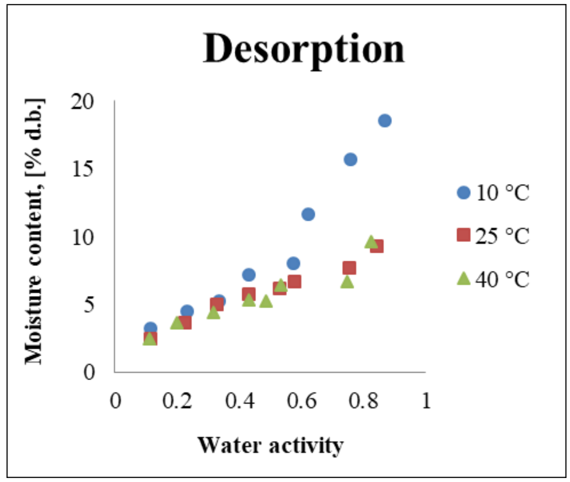

Figure 2. Sorption isotherms at 10, 25 and 40°C for Desorption

The EMC values increase with an increase in the temperature at constant aw. Similar trends for many foods have reported in the literature (Al-Muhtaseb et al. 2002; Durakova and Menkov 2005). The coefficients for the three-parameter modified models, P and SEM values are presented in Table 1 for adsorption and Table 2 for desorption. The results show that the lowest P and SEM values were obtained with the Henderson model. The graphical analysis of the residues demonstrates that the distribution is random for the model, which means that this modified model is suitable for the description of FGSF sorption isotherms (Fig. 3 and 4). We recommend the Henderson model, because of its lower values of the coefficients.

To calculate the BET monolayer moisture content (MMC), the model (8) is linearly transformed:

$$\frac{a_w}{(1-a_w)M} = P + Qa_w \qquad (9)$$

Based on the coefficients of the linear equation, the MMC for the respective temperature is calculated and the results are presented in Table 3.

As a result of the linearization of the BET model and the calculated monolayer humidity of the FGSF, the shelf life was increased and proven to dry out the test product to a maximum humidity close to the MMC.

Table 1. Model coefficients (*A*, *B*, *C*), average relative error (P, %), standard error of moisture (SEM) and Correlation coefficient (R) for adsorption

Model	*A*	*B*	*C*	P	SEM	R
Oswin	8.709116	-0.112632	0.417988	11.29	0.97	0.972
Halsey	3.273199	-0.022710	1.769954	12.29	1.12	0.975
Henderson	**0.000830**	**14.97965**	**1.725401**	**10.09**	**1.16**	**0.974**
Chung-Pfost	205.5701	0.316150	21.57597	11.69	1.74	0.964

Table 2. Model coefficients (*A*, *B*, *C*), average relative error (P, %), standard error of moisture (SEM) and Correlation coefficient (R) for desorption

Model	*A*	*B*	*C*	P	SEM	R
Oswin	9.412511	-0.118359	0.397866	17.88	1.55	0.942
Halsey	3.108822	-0.016192	1.687673	16.58	1.92	0.958
Henderson	**0.000672**	**17.99822**	**1.712982**	**10.05**	**1.14**	**0.964**
Chung-Pfost	271.3555	0.293390	35.50427	15.82	2.21	0.937

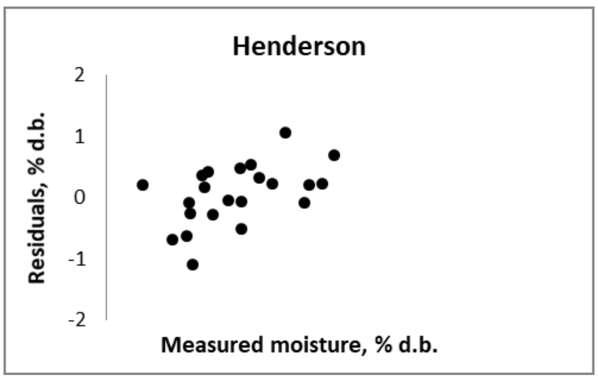

Figure 3. Plot of residuals fit of modified Henderson model to adsorption data.

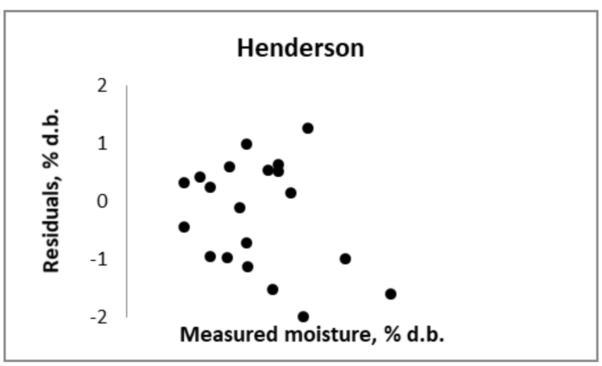

Figure 4. Plot of residuals fit of modified Henderson model to adsorption data.

Table 3. BET monolayer moisture content MMC (% d.b.) of FGSF at several temperatures

t **(°C)**	**Adsorption**	**Desorption**
10	3.41	3.68
25	2.32	2.59
40	2.43	2.96

For the aims of the present study, initial humidity was reduced from 8.36% to 3.53% - corresponding to already calculate MMC. We were monitored the parameters a storage for 3 months. The FGSF were subjected to selected microbial, fungal testes and changes in flour particle size distribution, as well.

The microbial load. In the Table 4, it was presented the results of the microbiological analyzes for a three-month period of storage of FGSF at a humidity of 3.53% at a temperature of 18÷25°C and relative humidity of 45÷55%. The product under investigation is packaged in plastic bags.

A microbiological analysis was performed for samples stored in the selected conditions – temperature = 18÷25°C and relative humidity of 45÷55% for 3 months. During a certain period of storage, microbiological parameters such as "Total numbers of mesophilic aerobic and facultative anaerobic bacteria", "*Escherichia coli*",

Table 4. Microbiological parameters of FGSF for three-month storage at 18÷25°C and relative humidity 45÷55 %

Sample/ Day	Total numbers of mesophilic aerobic and facultative anaerobic bacteria, CFU/g	*Escherichia coli*, CFU/g	*Staphylococcus aureus*, CFU/g	*Salmonella sp.* / 25 g	Yeasts, CFU/g	Fungi, CFU/g
Day 1	8.0×10^4	<10	<100	Not detected	<10	8.0×10^3
Month 1	3.0×10^5	<10	<100	Not detected	<10	5.0×10^3
Month 2	3.5×10^5	<10	<100	Not detected	<10	4.0×10^3
Month 3	9.3×10^4	<10	<100	Not detected	<10	6.0×10^3

"*Staphylococcus aureus*", "*Salmonella*", "Fungi and yeasts" are determinated. The results of the storage was monitored on the 1st day, 1st month, 2nd and 3th months of the storage of FGSF, showed wat *Salmonella* sp. is not detected and the presence of *Escherichia coli* and coagulase-positive staphylococci is below the allowable rate on the first day of storage and on the 3th month.

The results of the microbiological analyzes show that FGSF natural waste product after alcoholic fermentation in wine elaboration may be stored under the conditions presented in the present experiment for a three-month period without disturbing their microbiological safety.

Flour particle size. In Table 5 are presented the results of percentage distribution of the quantity of break stock of FGSF. During the storage, there is also increased in the amount of largest-size fractions over 355 μm. We defined that the product is suitable for incorporation as a functional ingredient to base flour whose size is over 180 μm.

During the storage period, we find a change in moisture content results. In the first 30 days, the humidity of the sample gradually increase from 3.53 % to 5.87%. After one-month, the results are in the range from 5.87 % to 6.24 %, which we believe is due to the packaging. In the present study, the maximum values of the moisture content for three-month storage is 6.24 %.

Table 5. Granulometric composition and moisture content FGSF during three-month storage

№	*Particales size, μm*	*Quantity of break stock, %*		
		1 Day	**1 Month**	**3 Months**
1	***1000***	0.94	1.05	0.78
2	***800***	6.30	5.70	5.56
3	**670**	12.03	11.41	5.46
4	**560**	12.59	12.74	15.30
5	**450**	17.86	18.54	25.15
6	**355**	48.08	47.81	46.88
7	**280**	0.00	0.57	0.58
8	**200**	1.47	1.24	0.29
9	**180**	0.58	0.38	−
10	less than **150**	0.13	0.57	−
	Moisture content, %	3.53	5.87	6.24

Conclusions

The sorption capacity of FGSF decrease with an increase in temperature at constant water activity.

The modified Henderson model is suitable for describing the relationships between the EMC, the water activity and the temperature of the FGSF.

According to sorption isotherms obtained for 10, 25 and 40°C, MMC is calculated with BET equation.

During the three-month storage of the FGSF in plastic bags (at temperature 18÷25°C and relative humidity 45÷55%), we were not detected living cells of pathogenic organisms or apparent molding. The percentage distribution of flour was not change considerably.

According to reported results, this flour is available for consummation after 3 months storage period for the conditions of the present experiment.

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