Sorption characteristics of flour mixtures enriched with grape seeds flour of Bulgarian and French raw materials

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Определянето на равновесното влагосъдържание при три различни температури 10 °C, 25 °C и 40 °C чрез стандартен статичен гравиметричен метод и водна активност в диапазона от 0,1 до 0,9. Получените изотерми имат S-образен характер, т.е. те са от II тип, типичен за повечето хранителни продукти. Резултатите потвърждават закономерността, че сорбционият капацитет намалява с повишаването на температурата в условията на постоянна влажност. Мономолекулната влажност на брашнена смес се изчислява чрез линеаризиране на уравнението на Брунаер-Емет-Телер.
INTRODUCTION

Customers’ and producers’ interest has been recently growing in the ready-made mixtures (composed entirely of homogenized powder components). Their use does not require further mixing or specific storage conditions. The ready-made mixtures are preferred by both artisan and home bakeries facilitating the preparation of bread, bakery and confectionery products. The mixtures usually consist of basic flour (like whole grain flour) blended with functional ingredient powder. Modern consumers purchase the flour mixtures (from home and foreign producers) from hypermarkets and supermarkets, small neighborhood stores as well as specialized BIO shops. On the Bulgarian market there can be found mixtures for white bread, ciabatta, rye bread, spelt bread, country bread, gluten-free white bread, ready-made cakes etc. (Dimov, 2014).

According to recent scientific research the extract and the flour of the grape seeds are suitable for their incorporation in food products as a food ingredient (Aghamirzaei et al., 2015). Being rich in catechins and proanthocyanidins they enhance the potential health effects on the human body as well as extend the shelf life of the product (Ghouila et al., 2017; Wang et al., 2017). The grape seeds flour contains bioactive compounds favoring the human and animal physiological processes (Jayaprakasha et al., 2003). The oenological biodegradable waste product is gluten-free and suitable to be included in the diet of people suffering from celiac disease.

Numerous studies show that moisture affects texture, taste, flavor, quality and length of the shelf life (Labuza, 1980; Kurt, 2016). Water excess or shortage can lead to premature food spoilage (Hammerer et al., 2018). Furthermore, that primary indicator is monitored at different stages and at different frequencies (Li et al., 2018). Water activity plays an important role in the growth and development of the microorganisms as well as in the technological and thermo-physical properties of the products (Muangrat and Nuankham, 2018).

Flour is a hygroscopic material and constantly interacts with moisture in the environment during the process of production, transportation and storage. Eglezos, (2010) investigated the conditions affecting the microbiological safety during the production of wheat flour. The research reported the fact that the growth of microorganisms was significantly reduced when the product moisture content was below 12%. The influence of environmental parameters (temperature and relative air humidity) on the moisture content of the product is taken into account in order to select the best and adequate storage regime. These factors are the basis of the sorption characteristics studies that provide the necessary information on the conditions for processing, storing, packaging and transporting of different food products (Guo et al., 2010).

The main sorption characteristic is the equilibrium moisture content (Dupas-Langlet et al., 2016). The relation between the equilibrium moisture content (EMC) and the water activity \( \alpha_w \) is represented by an experimentally constructed sorption isotherm for a specified temperature \( t \) - EMC = \( f (\alpha_w, t) \). Large number of research articles prove that reducing the moisture content of the product to its corresponding monolayer moisture content maintains its best quality parameters (Decagon, 2011). Iglesias and Chirife, (1976) investigated the MMC on over 50 foods. Moreover, today such analyses exceed thousands (Bennamoun et al., 2018; Monte et al., 2018; Muangrat and Nuankham, 2018; Muzaffar and Kumar, 2016).

MATERIALS AND METHODS

Raw materials

Two flour mixtures of Bulgarian and French origin are made on the basis of whole grain flour with addition of 2.0% grape seeds flour. The Bulgarian whole grain flour is delivered by “The GoodMills Bulgaria” Ltd and the French whole grain flour “Farine de blé Complète type 150” is bought from the French market. Bulgarian defatted grape seeds flour (a mix of different grape varieties of Bulgarian origin, namely Mavrud, Cabernet Sauvignon, Syrah, Merlot, Dimyat, Sauvignon Blanc, derived after alcoholic fermentation) is delivered by an experimental institute located in Parvenets, Bulgaria. The grape seeds flour for
the French mixture is bought from the French market and packed by «Ecoidées Sarl». The present study is carried out at the University of Food Technologies – Plovdiv, Bulgaria and at the University of Burgundy, Dijon, France.

Due to the different specific parameters for the Bulgarian and the French raw materials - climatic, soil, grape and grain varieties characteristics suggest different composition of the components in the two flour mixtures. Therefore, this study examined the specific sorption characteristics of two new flour mixtures and was not a comparative study.

**Method and preparation of the samples**

The adsorption and the desorption isotherms are studied at 10 °C, 25 °C and 40 °C using a gravimetric - static method recommended by Project COST 90 (Wolf et al., 1985) and upgraded by Bell and Labuza, (2000). According to the standard method the equilibrium moisture content in food products, soil and building materials can be determined (Feng et al., 2013). One part of the samples is dehydrated in a vacuum desiccator over P₂O₅ at a room temperature before beginning the adsorption analysis. Simultaneously, the other part of the samples is hydrated in a desiccator over distilled water under the same conditions for the desorption analysis. Eight saturated salt solutions (LiCl, CH₃COOK, MgCl₂, K₂CO₃, MgNO₃, NaBr, NaCl, KCl), providing constant water environment activities within the range from 0.1 to 0.9, are prepared in a glass jar for each temperature and for each process used (Durakova, 2004). After partial drying and humidification process approximately 1.0000 g ± 0.0050 g of the mixtures are measured in aluminum weighing dishes. Each glass jar contained three samples together with one aluminum dish with thymol to prevent microbial spoilage. The glass jars are stored in a thermostat for one month until equilibrium is reached (Durakova and Gogova, 2012). The experimental layout for determination of the sorption characteristics is presented in Figure 1. According to AOAC 960.39 the moisture content was determined at 105 °C for 24h, expressed in % dry weight (AOAC, 1990).

**Mathematical modelling of the data**

According to a literature review four different modified models were selected for fitting of the sorption isotherms data, namely modified Chung-Pfost, modified Halsey, modified Oswin, modified Henderson, recommended by American Society of Agricultural Engineers (ASAE) (Igathinathane et al., 2005)

Modified Chung-Pfost

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

Modified Halsey

$$a_w = \exp \left[ -\exp \left( A + B \right) \right]$$

Modified Oswin

$$M = (A + B) \left( \frac{a_{w0}}{1 - a_w} \right)^c$$

Modified Henderson

$$1 - a_w = \exp \left[ -A \left( t + B \right) M^c \right]$$

where:

- $M$ is the average moisture content, %;
- $a_w$ is the water activity, decimal;
- $A$, $B$ and $C$ are coefficients;
- $t$ is the temperature, °C.

The different modified models were fitted through a non-linear least-squares regression program “Statistica” (Delchev et al., 2013). According to Lomauro et al. (1985) one of the basic criteria for determination of the models' equations is the average relative error ($P$, %). If the value $P$ is ≤ 10% the model is considered fit.
Moreover, Chen and Morey’s research included two more criteria to compare the suitability of the models, namely the standard error of moisture (SEM) and the randomness of residuals (Chen and Morey, 1989). Nowadays, the P (%), SEM and the randomness of residuals are taken into consideration in order to determine the suitability of the models (Durakova et al., 2013; Said et al., 2015):

\[
P = \frac{100}{N} \sum \left| \frac{M_i - \hat{M}_i}{M_i} \right| \tag{5}
\]

\[
SEM = \sqrt{\frac{\sum (M_i - \hat{M}_i)^2}{df}} \tag{6}
\]

\[
e_i = M_i - \hat{M}_i \tag{7}
\]

where:
- \(M_i\) and \(\hat{M}_i\) are experimentally observed and predicted by the model value of the equilibrium moisture content;
- \(N\) is the number of data points;
- \(df\) is the number of degree of freedom (number of data points minus number of parameters in the model).

According to a literature review the monolayer moisture content (MMC) is calculated through the linearization of Brunauer-Emmett-Teller (BET) equation (Eq. 8) including water activities over 0.45 (Eq. 9) for the three selected temperatures at 10°C, 25°C and 40°C (Brunauer et al., 1938; Peleg, 2020; Timmermann et al., 2001):

\[
M = \frac{M_e C a_w}{(1 - a_w)(1 - a_w + C a_w)} \tag{8}
\]

where:
- \(M\) is the equilibrium moisture content, %;
- \(M_e\) is the MMC, %;
- \(a_w\) is the water activity, decimal;
- \(C\) is the coefficient.

\[
\frac{a_w}{(1 - a_w)M} = P + Qa_w \tag{9}
\]

where:
- the coefficient \(P = \frac{1}{MC}\) \tag{10}
- the coefficient \(Q = \frac{C - 1}{MC}\) \tag{11}

The coefficients \(P\) and \(Q\) from equation 9 are processed constructing a least-squares graph through the program "Excel".

However, this scientific research did not find any information on the determination of the sorption isotherms of the flour mixtures enriched with enological waste product – grape seeds flour.

The aims of the current scientific research is to determine the sorption characteristics of new flour mixtures enriched with oenological waste product (grape seeds flour).

**RESULTS AND DISCUSSION**

The initial moisture content of the sample before starting the adsorption process is 4.04%, for the desorption process it is 16.49%, respectively. The results obtained from the Bulgarian flour mixture for both processes are presented in Table 1 and Table 2.

The equilibrium moisture content (EMC) of Bulgarian mixture is studied at different water activities from 0.1 to 0.9 and three most commonly used temperatures 10°C, 25°C and 40°C.

As it can be seen in Table 1 and Table 2 the EMC values decrease with increasing of the temperature values in the presence of constant water activity. Therefore, when the water activity values augment at constant-temperature condition, the EMC also increase.

The calculated coefficients \(A, B, C\) and the corresponding \(P\) and \(SEM\) values are presented in Tables 3 and Table 4 for each sorption process.

The lowest values of the both criteria \(P\) (≤10%) and \(SEM\) for adsorption process is at the modified Chung-Pfost, Oswin and Halsey models (Table 3).

The lowest values of \(P\) and \(SEM\) for desorption process are shown for the modified Chung-Pfost model (Table 4). Having assessed the models we can recommend the modified Chung-Pfost model as a suitable description of the sorption isotherms of the enriched Bulgarian mixture.
Table 1. Equilibrium moisture content EMC (%) of the Bulgarian flour mixture for adsorption at different water activities (a_w) and at different temperatures t (°C)

<table>
<thead>
<tr>
<th>Sel</th>
<th>10 °C</th>
<th>25 °C</th>
<th>40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a_w</td>
<td>EMC¹</td>
<td>SD²</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.113</td>
<td>4.41</td>
<td>0.07</td>
</tr>
<tr>
<td>CH₃COOK</td>
<td>0.234</td>
<td>5.10</td>
<td>0.14</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.335</td>
<td>6.16</td>
<td>0.13</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>0.431</td>
<td>6.65</td>
<td>0.07</td>
</tr>
<tr>
<td>MgNO₃</td>
<td>0.574</td>
<td>8.15</td>
<td>0.09</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.622</td>
<td>8.76</td>
<td>0.19</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.757</td>
<td>0.00</td>
<td>0.28</td>
</tr>
<tr>
<td>KCl</td>
<td>0.868</td>
<td>14.25</td>
<td>1.86</td>
</tr>
</tbody>
</table>

¹ Mean values based on three replications
² Average standard deviation values based on three replications

Table 2. Equilibrium moisture content EMC (%) of the Bulgarian flour mixture for desorption at different water activities (a_w) and at different temperatures t (°C)

<table>
<thead>
<tr>
<th>Sel</th>
<th>10 °C</th>
<th>25 °C</th>
<th>40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a_w</td>
<td>EMC¹</td>
<td>SD²</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.113</td>
<td>5.36</td>
<td>0.08</td>
</tr>
<tr>
<td>CH₃COOK</td>
<td>0.234</td>
<td>5.88</td>
<td>0.14</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.335</td>
<td>6.89</td>
<td>0.21</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>0.431</td>
<td>7.74</td>
<td>0.16</td>
</tr>
<tr>
<td>MgNO₃</td>
<td>0.574</td>
<td>9.54</td>
<td>0.22</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.622</td>
<td>9.93</td>
<td>0.13</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.757</td>
<td>10.67</td>
<td>0.16</td>
</tr>
<tr>
<td>KCl</td>
<td>0.868</td>
<td>13.20</td>
<td>0.49</td>
</tr>
</tbody>
</table>

¹ Mean values based on three replications
² Average standard deviation values based on three replications

Table 3. Bulgarian flour mixture: model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for adsorption process

<table>
<thead>
<tr>
<th>Modified three - parameter models</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>P</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oswin</td>
<td>7.74764</td>
<td>-0.04499</td>
<td>0.33714</td>
<td>8.18</td>
<td>0.55</td>
</tr>
<tr>
<td>Halsey</td>
<td>4.166290</td>
<td>-0.017423</td>
<td>2.192536</td>
<td>9.08</td>
<td>0.67</td>
</tr>
<tr>
<td>Henderson</td>
<td>0.000169</td>
<td>4.073694</td>
<td>2.652603</td>
<td>12.35</td>
<td>1.21</td>
</tr>
<tr>
<td>Chung-Pfost</td>
<td>375.3736</td>
<td>0.323554</td>
<td>37.69751</td>
<td>6.60</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Table 4. Bulgarian flour mixture: model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for desorption process

<table>
<thead>
<tr>
<th>Modified three-parameter models</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>P</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oswin</td>
<td>8.67764</td>
<td>-0.06242</td>
<td>0.28835</td>
<td>10.68</td>
<td>0.68</td>
</tr>
<tr>
<td>Halsey</td>
<td>4.45541</td>
<td>-0.02673</td>
<td>2.157853</td>
<td>10.92</td>
<td>1.23</td>
</tr>
<tr>
<td>Henderson</td>
<td>0.000182</td>
<td>1.873426</td>
<td>2.581853</td>
<td>10.72</td>
<td>1.04</td>
</tr>
<tr>
<td>Chung-Pfost</td>
<td>278.4272</td>
<td>0.321975</td>
<td>16.52974</td>
<td>4.77</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The linearization of the BET equation is presented in Figure 2 and Figure 3 for adsorption and desorption.

French flour mixture

The initial moisture content of the French mixture is reached – at dehydration over P₂O₅ it is 4.24% and at hydration over distilled H₂O is 14.49%, respectively. The EMC for both processes are shown in Figure 4 and in Figure 5.

The monolayer moisture content (MMC) are calculated on the basis of the coefficients of the linear equations (Brunauer et al., 1938; Bennamoun et al., 2018; Monte et al., 2018). Therefore, the values for the adsorption process are 3.79%, 2.54% and 3.16% and for the desorption process are 4.29%, 2.69% and 3.46% for the selected temperatures 10 °C, 25 °C, 40 °C, respectively.

Figure 2. Bulgarian mixture: linearization of BET equation for adsorption process

Figure 3. Bulgarian mixture: linearization of BET equation for desorption process

Figure 4. French flour mixture: Adsorption isotherms at three different temperatures

Figure 5. French flour mixture: Desorption isotherms at three different temperatures
Analyzing the Figures 4 and 5 data it could be seen that the temperature influenced the moisture content values. However, this fact (temperature) leads to decreasing the values of EMC within the range from 1% to 3%. Therefore, higher percentages again are observed at \( a_w > 0.7 \). According to Brunauer’s classification our adsorption and desorption curves possess an S-shape profile typical of the II\(^{\text{nd}}\) class (Brunauer et al., 1940).

The coefficients of the modified three-parameter models as well as the values of the average relative error and the standard error of the French mixture for the adsorption and for the desorption processes are presented in Table 5 and Table 6.

As shown in the Tables 5 and 6 and according to the suitability criteria of the models we can recommend the modified Oswin model for the adsorption process and for the desorption process – the modified Chung-Pfost model, respectively. According to the model suitability criteria these two models may be recommended for describing the sorption isotherms of the French flour mixture. The models presented are a confirmation of Chen and Morey’s statement (1985) that there is no universal model to be recommended for describing the sorption isotherms of all foods (Chen and Morey, 1989; Durakova et al., 2013; Said et al., 2015). The linearization of the known Brunauer-Emmett-Teller model based on the polymolecular theory for adsorption and desorption is presented in Figure 6 and Figure 7.

The calculated values of MMC are shown in Table 7.

<table>
<thead>
<tr>
<th>Table 5. French flour mixture: model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for adsorption process</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Oswin</td>
</tr>
<tr>
<td>Halsey</td>
</tr>
<tr>
<td>Henderson</td>
</tr>
<tr>
<td>Chung-Pfost</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6. French flour mixture: model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for desorption process</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Oswin</td>
</tr>
<tr>
<td>Halsey</td>
</tr>
<tr>
<td>Henderson</td>
</tr>
<tr>
<td>Chung-Pfost</td>
</tr>
</tbody>
</table>
as most food powders (Brunauer et al., 1940; Muangrat and Nuankham, 2018; Muzaffar and Kumar, 2016). Both mixtures have similar isotherms in the presence of water activity from 0.1 to 0.9.

The isotherms of all samples have an S – shaped profile, i.e. they are of the the II\textsuperscript{nd} class according to Brunauer’s classification.

The temperature affects the sorption capacity of the Bulgarian flour mixture and the French flour mixture. The equilibrium moisture content decreases with the increase of temperature in the presence of water activity.

The modified Chung-Pfost model is better for fitting sorption isotherms data for Bulgarian mixture. For French mixture – we can recommend the modified Oswin model for the adsorption process and the modified Chung-Pfost model for the desorption process.

The calculated monolayer moisture content (MMC) for the Bulgarian mixture is within the range from 2.54\% to 4.29\% and for the French mixture – from 2.67\% to 4.13\%.

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