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# COMPARISON OF SORPTION PROPERTIES OF SEMOLINA AND FARINA

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Abstract. The examined flours were characterized by variable chemical composition resulting from the genetic variety. The semolina (hard wheat flour) and farina (soft wheat flour) sorption isotherms were determined with the use of the static-dessicatory method at 20°C. The equilibrium water content significantly depended on the product type and water activity. A distinct increase of the water content was found in both examined types of flours at $a_w$ about 0.75. Probably above the level of $a_w$ = 0.75 there appeared the phenomenon of capillary condensation. On the basis of the BET equation there was determined the capacity of a monolayer (semolina – 5.53 and farina – 5.88 g·(100 g.s.s)$^{-1}$) and on its basis the specific surface of sorption (semolina – 194.2 and farina – 206.6 m$^2$ g$^{-1}$). There was also determined the general capacity of capillaries in the area of capillary condensation, recording higher values of this parameter for farina. On the basis of Kelvin equation the structure of examined flours was identified, defining the most probable radius of capillaries and indicating the radius of capillaries which are filled in the initial phase of condensation.

Keywords: semolina, farina, isotherms of sorption, monolayer capacity, specific surface of sorption, water activity, the energy constant, BET

## INTORDUCTION

The interest in the differences between the sorption properties of semolina and farina results from increased demand for pasta which makes an important element of everyday diet.

The culinary quality of pasta products is primarily determined by their colour, smell and taste, depending on the consumer's private habits. Nevertheless, the consumers are likely to observe the product's right texture once it has been cooked which will be demonstrated by lack of sticky or overcooked (soft) forms.

The post-cooking pasta quality depends definitely on the parameters of the technological process but also on the properties of the respective flour (Troccoli *et al.* 2000).

Up to the late 1980s, the Polish market was dominated by pasta products based on flour obtained from domestic wheat (farina). Market changes enabled the import of western products which displayed new, more sought qualities. In such circumstances, the domestic food industry specialising in pasta was forced to improve the quality of their products. Those measures resulted first of all in using the semolina in the production process. However, the use of high quality raw materials, among others semolina, involved a rise in the prices of final products. Thus, the producers have been continually looking for new opportunities of using domestic flours for the production of pasta.

The sorption property of flour is a particularly important parameter conditioning the rheological properties of pasta products, because this parameter is a resultant of the structure, composition and biophysical properties of proteins and their interaction with other elements of flour, i.e. with starch, lipids and non-starch polysaccharides (Troccoli *et al.* 2000).

## OBJECTIVE

The objective of the research reported herein was the determination of differences in sorption properties of semolina and farina on the basis of the isotherms of sorption and other parameters determined on their basis.

## RESEARCH MATERIAL

The research material were two kinds of flour obtained from *Triticum vulgare* ordinary wheat and *Triticum durum Desf* hard wheat. Both wheat types were the 2005 crops. Both flour types were used for industrial production of pasta by one of the leading Polish producers.

Taking into regard the influence of granulometric composition of flours on the course of isotherms of sorption (Hebrard *et al.* 2003), there was determined the share of individual factions of molecules in the mixture (Tab. 1).

**Table 1.** Granulometric distribution of semolina and farina – f (mm)

| Kind of flour | 0.6>f>0.43 | 0.43>f>0.2 | f<0.2 |
|---|---|---|---|
| Semolina | 1.113% | 83.897% | 14.990% |
| Farina | 1.562% | 78.604% | 19.834% |

Source: Own juxtaposition on the basis of the sift analysis.

All reagents used for the analyses and the preparations for the saturated salt solutions were pure reagents for analyses.

## RESEARCH METHODS

The contents of water, protein, reducing sugar, fat, starch and ash were determined according to AACC (Krełowska-Kułas 1993).

The run of the sorption isotherms of tested flours was outlined by means of static dessicator method using saturated salt solutions. The scope of research embraced the activity of water in the range of 0.07 to 0.98. The temperature of tests was 20°C. The duration of establishing the balance of the arrangement was 30 days. The obtained results were processed using the STATISTICA program (Świtka 1992, Tyszkiewicz 1987).

The BET equation parameters were determined, on the basis of empirical data, with the use of the minimum chi-square method. Fitting the empirical data to the BET equation was characterized on the basis of the average error of estimation (Se), coefficient of determination ($R^2$) and the index of correlation (R) (Makać *et al.* 2000).

In order to determine the parameters of the process of sorption, such as the capacity of monomolecular layer including the corresponding activity of water and the energy constant, the BET equation was used:

$$a = \frac{\nu_m c \frac{p}{p_s}}{(1 - \frac{p}{p_s})[1 + (c-1)\frac{p}{p_s}]} \tag{1}$$

where:
$a$ – adsorption (kg $kg^{-1}$),
$\nu_m$ – maximum adsorption magnitude corresponding to the complete surface coverage in monolayer of adsorbate (kg $kg^{-1}$),
$c$ – constant, related exponentially to the difference between the heat of adsorption the first and following layers, accepted to be constant and equal to the heat of condensation,
$p$ – vapour pressure of the adsorbed chemical compound in its gas phase (Pa),
$p_s$ – the adsorbed chemical compound vapour pressure over the liquid in balance with the adsorption temperature (Pa) (Ościk 1979, Paderewski 1999).

Knowing the volume of water vapour adsorbed at a temperature lower than the boiling temperature and the so-called surface of water sitting, the specific surface of the adsorbent was calculated on the basis of the following equation:

$$a_{sp} = \omega \frac{v_m}{M} N \tag{2}$$

where:
$a_{sp}$ – specific surface sorption ($m^2$ $g^{-1}$),
$N$ – Avogadro number ($6.023 \cdot 10^{23}$ molecules·$mol^{-1}$),
$M$ – water molecular mass (18 g $mol^{-1}$),
$\omega$ – surface of water sitting ($1.05 \cdot 10^{-19}$ $m^2$ $molecule^{-1}$) (Paderewski 1999, Tyszkiewicz 1987).

The size and capacity of capillaries of teste
d material were determined on the basis of the run of isotherms of adsorption in the area of capillary condensation. Calculations were made on the basis of the Kelvin equation:

$$\ln \frac{p}{p_s} = \frac{2\sigma v}{r_k RT} \tag{3}$$

where:
$v$ – molar volume of adsorbed water (kg $kg^{-1}$),
$\sigma$ – surface tension of liquid at temperature T (N $m^{-1}$),
$r_k$ – adius of the capillary (m)
$R$ – gas constant (8.314 J $(mol\ K)^{-1}$),
$T$ – temperature of the process (K) (Paderewski 1999).

The graphic interpretation of the obtained number pairs (*V-r*), called the structural curve, made the basis for the determination of capillary radius (*dV/dr-r*) with the use of the graphic differentiation of the distribution curves method. The maximum values for the distribution curves corresponded to the most frequently occurring pore radii (Świtka 1992).

## DISCUSSION OF RESULTS

The comparison of the sorption properties was based on the assessment of:

- chemical composition of examined products (Tab. 2)
- mutual positions of the adsorption isotherms determined at 20°C (Tab. 3, Fig. 1),
- parameters of adsorption isotherms determined following the BET model (Tab. 4),
- structural characteristics of tested products determined with the use of Kelvin equation (Tab. 5).

Considering the genetic non-homogeneous composite nature of examined flours there was determined the content of their basic elements. Chemical composition of tested products is presented in Table 2.

**Table 2.** Results of the Student t differences test between the mean contents of chemical component of the studied flours (g $(100g)^{-1}$)

| Feature | Semolina | | | Farina | | | $t_c$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $x_{mean}$ | SD | V (%) | $x_{mean}$ | SD | V (%) | $t_{0,05}$ | $t_{0,02}$ | $t_{0,01}$ | $t_{0,001}$ | $t_e$ |
| Water | 13.03 | 0.241 | 1.85 | 10.84 | 0.32 | 2.98 | 2.10 | 2.55 | 2.88 | 3.92 | 16.54 |
| Protein | 9.62 | 1.228 | 12.76 | 7.16 | 0.45 | 6.22 | 2.31 | 2.90 | 3.36 | 5.04 | 5.77 |
| Fat | 1.54 | 0.130 | 8.43 | 1.32 | 0.13 | 10.16 | 2.31 | 2.90 | 3.36 | 5.04 | 2.37 |
| Carbohydrates | 2.87 | 0.289 | 10.09 | 3.74 | 0.26 | 7.01 | 2.31 | 2.90 | 3.36 | 5.04 | 4.48 |
| Starch | 72.31 | 3.607 | 4.99 | 76.44 | 2.88 | 3.77 | 2.31 | 2.90 | 3.36 | 5.04 | 1.79 |
| Ash | 0.62 | 0.065 | 10.40 | 0.50 | 0.05 | 9.32 | 2.31 | 2.90 | 3.36 | 5.04 | 3.12 |

Source: Own juxtaposition on the basis of the chemical analyses.
$x_{mean}$ – mean value,
SD – standard deviation,
V(%) – coefficient of variation.

The tested flours form a highly significantly ($p<0.001$) diversified material with regard to the content of water and protein, significantly diversified with regard to the content of fat ($0.02<p<0.05$), reducing sugar ($0.001<p<0.01$) and ash ($0.01<p<0.02$), and not differentiated ($p>0.05$) with regard to the content of starch. Genetic diversity of semolina and farina is reflected in the chemical composition of tested flours. The lack of significant diversity with regard to the dominating element, i.e. starch (Tab. 2), was an important feature of tested flours. Therefore, it was assumed that the differences in the run of the sorption isotherms were determined by the differences in the amount of the remaining elements.

Analysis of the significance of differences ($p<0.05$) in the run of the sorption isotherms was the basis for rejecting the zero hypothesis about the lack of differences between average content of water in tested products at determined levels of $a_w$ (Tab. 3). Thus it was assumed that the differences in sorption properties of tested flours resulted from differences in the content of protein, fat, reducing sugars and ash.

The resultant of sorption properties of individual chemical elements of flours was the isotherm of sorption describing the mechanism of water bonding while it is being absorbed by flour (Erbas *et al.* 2005). Outlined isotherms (Fig. 1) reflected the process of physical adsorption which takes place on porous solid (Erbas *et al.* 2005, Paderewski 1999). The shape of curves characteristic for the 2nd type of isotherms was the effect of this process. Sigmoidal curves of sorption indicate the phenomenon of formation of multinuclear layers of water on the surface of both tested flours. Other authors also received the same results (Erbas *et al.* 2005, Hebrard *et al.* 2003).

**Table 3.** Results of the Student t differences test between the mean water contents at specific $a_w$ levels

| $a_w$ | Semolina | | | Farina | | | $t_e$ | $t_c$ |
|---|---|---|---|---|---|---|---|---|
| | $x_{mean}$ | SD | V | $x_{mean}$ | SD | V | | |
| 0.069 | 3.119 | 0.036 | 1.167 | 3.422 | 0.103 | 3.012 | 5.559 | 2.306 |
| 0.111 | 4.321 | 0.029 | 0.689 | 4.788 | 0.082 | 1.714 | 10.69 | 2.306 |
| 0.231 | 6.557 | 0.030 | 0.461 | 7.380 | 0.079 | 1.066 | 19.53 | 2.306 |
| 0.330 | 8.104 | 0.073 | 0.901 | 8.802 | 0.219 | 2.483 | 6.059 | 2.306 |
| 0.440 | 9.509 | 0.044 | 0.462 | 10.37 | 0.157 | 1.528 | 10.52 | 2.306 |
| 0.548 | 11.23 | 0.076 | 0.674 | 11.90 | 0.310 | 2.608 | 4.158 | 2.306 |
| 0.699 | 13.12 | 0.041 | 0.313 | 13.99 | 0.149 | 1.065 | 11.30 | 2.306 |
| 0.754 | 13.78 | 0.049 | 0.357 | 15.08 | 0.136 | 0.900 | 18.03 | 2.306 |
| 0.851 | 16.15 | 0.063 | 0.392 | 17.69 | 0.270 | 1.659 | 11.10 | 2.306 |
| 0.932 | 20.20 | 0.111 | 0.517 | 21.60 | 0.266 | 1.232 | 9.708 | 2.306 |
| 0.979 | 21.40 | 0.502 | 2.483 | 21.99 | 0.435 | 1.979 | 2.788 | 2.306 |

*Source: Own research*

The adsorption of moisture by both flours grew in line with increase of $a_w$. The phenomenon of absorption of moisture from the environment was conditioned by a considerable amount of protein and starch in the examined flours. These components, being macromolecules rich in polar places (groups -OH or -H), make it possible to adsorb moisture considerably.

However, semolina was characterized by a lower sorptive capacity than farina in the entire scope of $a_w$. According to Erbas et al (Erbas *et al.* 2005) it could be caused by higher content of protein in semolina related to its considerable hardness in comparison to farina. Probably it is the hardness of particles of semolina which obstructs the process of water diffusion, thus limiting the volume of sorption (Roman-Gutierrez *et al.* 2003).

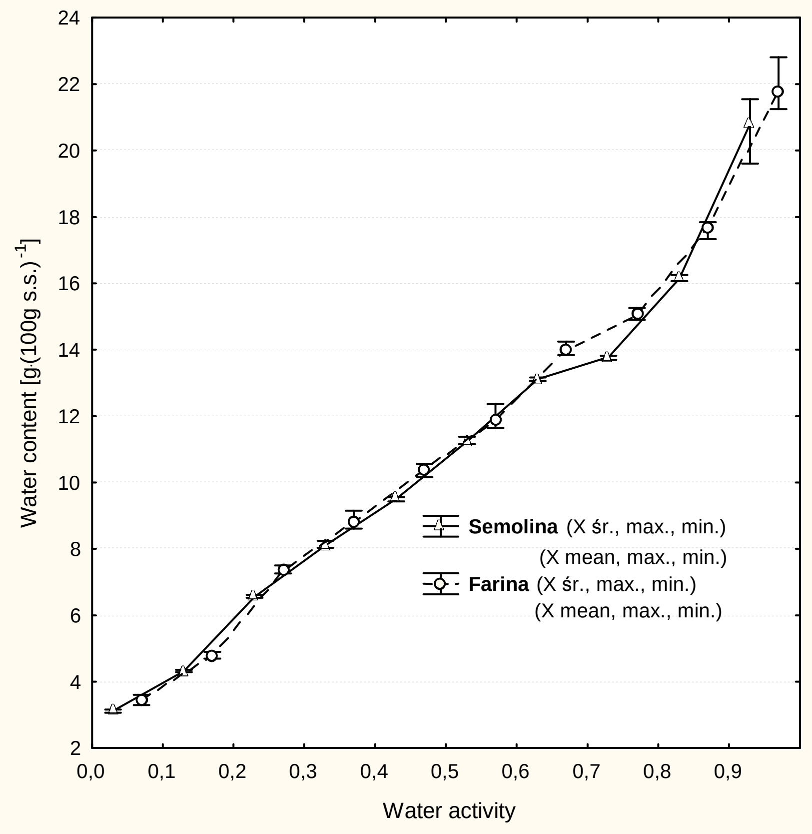

**Fig. 1.** Sorption isotherms of semolina and farina

Above the level of 0.75 $a_w$ the effect of sorption became particularly distinct. One may suppose that above 0.75 $a_w$ in both flours there occurred the phenomenon of capillary condensation.

On the basis of the run of the sorption isotherms in the range of 0.07-0.54 $a_w$ the BET equation was determined, defining the degree of its appropriateness ($R^2$, R, just) to empirical data and the parameters ($V_m$, $c$, $a_w$) of the BET equation were calculated. The results are presented in Table 4.

The value of the coefficient of determination ($R^2$) demonstrated that about 98% of the changeability of water in both tested samples was determined by the activity of water. Very high values of the index of correlation (R~99%) proved that the correlation between tested variables was very strong. The value of the average error estimation (Se) informed that empirically determined contents of water differed from those determined by means of BET function by an average of about 0.33 (semolina) and 0.48 (farina) g (100 g s.s.)$^{-1}$.

**Table 4.** Parameters of the BET equation of the studied flours

| Kind of flour | $R^2$ | R | Se | $V_m$ | c | $a_w$ |
|---|---|---|---|---|---|---|
| Semolina | 0.99 | 0.99 | 0.333 | 5.53 | 20.79 | 0.207 |
| Farina | 0.98 | 0.99 | 0.479 | 5.88 | 25.66 | 0.193 |

*Source: Own results*

The monolayer capacity ($V_m$), which can be determined on the basis of the BET equation, concerns the sorption capacity of the adsorbents and makes an indication as to the availability of polar spots by the water vapour. Being familiar with the notion of the monolayer, one will be able to analyse other aspects of the physical and chemical decay processes of various food products (Mathlouthi 2001).

In the analysed variant of the experiment the capacity of the monolayer of semolina was smaller than that of farina, in spite of the significantly higher content of protein in semolina. Erbas et al (Erbas *et al.* 2005) received similar results. In the temperature of 35°C and 60°C the capacity $V_m$ of semolina was smaller than that of farina. However, the investigation by Hebrard et al (Hebrard *et al.* 2003) indicate that proteins of wheat flour are characterized by about five times bigger hydration capacity than the starch of wheat flour. It can be surmised that not only the amount of particular elements rich in polar spaces influenced the capacity $V_m$ but also their physical state. So mechanical damage, to which the grains of wheat are exposed during grinding, could contribute to the change of the physical state of individual elements of flour. As a result, the capacity of the monomolecular layer became the resultant of the amount of individual elements and their physical state conditioning the availability of polar places.

In semolina the activity of water corresponding to monolayer had higher values than in farina. This fact can indicate lower storage permanence of semolina (Mathlouthi 2001).

The energy constant (c) reflects the difference between enthalpy of desorption from the monolayer and enthalpy of vaporization of liquid adsorbent. The value of enthalpy of the process of physical adsorption is about 20 kJ mole$^{-1}$. Generally such a small change of enthalpy does not influence the identity of physically adsorbed molecules. However ,one should consider that the presence of surfaces may trigger their deformations.

In the process of chemical adsorption molecules make chemical bonds with the surface. The enthalpy of chemisorption is much higher than that of physicsorption. Typical value is about 200 kJ mole$^{-1}$ (Atkins 2003).

The obtained results let us suppose that in the studied case there was only a process of physical adsorption. However, in order to be certain of the character of the occurring phenomena, spectroscopic examinations should be carried out.

On the basis of $V_m$ there was calculated the specific surface of sorption. The obtained results (Tab. 5) demonstrated that farina was characterized by a bigger specific surface. At the same time the development of specific surface of sorption of tested flours let us suppose that in both cases the dominating form of capillaries are mesocapillaries (Paderewski 1999).

On the basis of the Kelvin equation there were determined the characteristic parameters of capillaries from the isotherm of adsorption describing the area of the capillary condensation (Tab. 5), because this equation enables to recalculate the equivalent weight of relative pressures to the radii of corresponding capillaries (Paderewski 1999).

**Table 5.** Structural characteristics of the studied flours

| Kind of flour | Specific surface of sorption ($m^2$ $g^{-1}$) | General capacity of capillaries ($mm^3$ (100 g s.s.)$^{-1}$) | Radius of capillaries at around $a_w$ = 0.75 (nm) | Most probable radius of capillaries (nm) |
|---|---|---|---|---|
| Semolina | 194.2 | 71.53 | 2.911 | 2.121 |
| Ffarina | 206.6 | 74.96 | 3.186 | 2.353 |

Source: Own results.

Farina was characterized by a bigger general capacity of capillaries compared with semolina. At $a_w$ = 0.75, when presumably there started the process of capillary condensation, in semolina capillaries with the radius of ca. 2.90 nm filled up, whereas in farina – those with the radius of ca. 3.19 nm. Moreover, the most probable radius of capillaries in semolina was ca. 2.12 nm, whereas in farina – 2.35 nm. It can be assumed that the differences in chemical composition of flours are conditioned by the genetic diversity of cereals, influencing also the structure of obtained flours.

## CONCLUSIONS

1. The isotherms of sorption of semolina and farina had sigmoidal shape, characteristic for high-starch products. The shape of the curves of sorption indicates the course of the multi-layered adsorption and the porous structure of examined products.

2. The adsorption of moisture by both flours grew together with increase of $a_w$. However, semolina was characterized by lower equivalent weight value of moisture than farina in the entire scope of $a_w$.
3. The capacity of monomolecular layer calculated on the basis of BET equation was higher in the case of farina. As a consequence, the value of the specific surface area of sorption of farina was also higher.
4. The activity of water corresponding to the capacity of monomolecular layer of tested flours may suggest that farina has higher storage permanence.
5. The value of the energy constant of BET equation indicated a typically physical character (~21-25.5) of the investigated process.
6. Farina was characterized by a greater capacity of capillaries than semolina. At the beginning of the process of capillary condensation in farina there were filled up capillaries of bigger radius than in semolina. Moreover, in farina there dominated capillaries with bigger radius than in semolina.
7. Summing up, it should be stated that tested flours, being genetically composite, differed in their sorption properties.

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# PORÓWNANIE WŁAŚCIWOŚCI SORPCYJNYCH SEMOLINY I FARINY

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Streszczenie. Badane mąki charakteryzowały się zróżnicowanym składem chemicznym będącym skutkiem różnorodności genetycznej. Izotermy sorpcji semoliny (mąka z pszenicy twardej) i fariny (mąka z pszenicy miękkiej) zostały wyznaczone metodą statyczno-eksykatorową w temperaturze 20°C. Równowagowa zawartość wody była istotnie zależna od typu produktu oraz aktywności wody. Wyraźny wzrost zawartości wody stwierdzono w obu badanych mąkach przy $a_w$ około 0.75. Prawdopodobnie powyżej $a_w = 0,75$ następowało zjawisko kondensacji kapilarnej. W oparciu o równanie BET wyznaczono pojemność monowarstwy (semolina – 5,53 i farina – 5,88 $g \cdot (100\ g\ s.s.)^{-1}$) i na jej podstawie powierzchnię właściwą sorpcji (semolina – 194,2 i farina – 206,6 $m^2 \cdot g^{-1}$). Określono również ogólną objętość kapilar w obszarze kondensacji kapilarnej stwierdzając wyższe wartości tego parametru dla fariny. W oparciu o równanie Kelvina wyznaczono strukturę badanych mąk określając najbardziej prawdopodobny promień kapilar oraz wskazując promień kapilar ulegających wypełnieniu w początkowej fazie zjawiska kondensacji.

Słowa kluczowe: semolina, farina, izotermy sorpcji, pojemność monowarstwy, powierzchnia właściwa sorpcji, aktywność wody, stała energetyczna, BET