Acta Agrophysica, 2009, 14(2), 393-402

SORPTIVE PROPERTIES OF TYPE 2000 WHEAT AND RYE FLOURS

Aneta Ocieczek[1], *Robert Kostek*[2]

[1]Gdynia Maritime University, ul. Morska 83, 81-225 Gdynia
e-mail: daszenka@am.gdynia.pl
[2]University of Technology and Life Sciences in Bydgoszcz
Al. Prof. S. Kaliskiego 7, 85-796 Bydgoszcz

Abstract. This paper presents a comparative analysis of sorptive properties of type 2000 wheat and rye flours. The main aim of the study was to examine the influence of the raw material on the sorptive properties of the flours. Flours which were used as specimens were produced in a laboratory at identical milling conditions. The following parameters of sorption were identified: monolayer capacity with the corresponding water activity, energy constant, specific sorption surface, size and volume of capillaries. Certain differences of sorption parameters of the flours were found, however they can be neglected from a practical point of view.

Keywords: wheat flour, rye flour, sorptivity, GAB (Guggenheim, Anderson, De Boer) model

INTRODUCTION

Milled grain material usually consists of grain batches of various physical and chemical properties. Flour obtained from these mixtures, of various physical and chemical properties of the ingredients, usually has higher technological properties than flour received from separate components of the mixture. Preparing mixtures also gives the opportunity to produce product of uniform quality and properties. Therefore, assessment of flour as a commodity brings order to the flour market, ensuring the consistence of the trade object with its definition and its qualitative determinants.

The issue of flour quality is related with the role of packages, conditions of storage and distribution of flour and other materials used in bakery. Therefore it is important that all the elements of grain processing technological chain should be involved in solving the problem of flour quality. Effective actions must aim at achieving sufficient economic benefits.

OBJECTIVE

The main aim of the study was to find differences of sorptive properties of flours (type 2000) obtained from wheat and rye. According to the applied model in the experiment, flours obtained under the same milling conditions may have different sorptive properties, because it was assumed that grain type diversity significantly affects vapour sorption. A practical aspect of the problem was to present the differences in the way that various storage conditions affect the qualitative features of the material under study. Sorptive properties of flours affect their storage stability and keeping time.

MATERIAL

Wheat (MP) and rye flour (MZ) of type 2000, obtained by grinding whole grains, i.e. without removing the bran, were used as the study material.

Both of the flours were produced in a laboratory, with a MLU Bühler six-passage laboratory mill. The flours were obtained by mixing particular passage flours. Following the milling, the flours were stored for 5 days at 10°C and subsequently sorptivity analyses were conducted.

All the reagents used in preparing the saturated salt solutions were analytical grade.

METHODS

Sorption isotherms for the flours under study were determined with a static-desiccator method using saturated salt solutions (Labuza 1983). The preparations were stored at constant relative humidity ($0.07 \leq a_w \leq 0.98$) and constant temperature of 20 and 30°C (Świtka 1992, Tyszkiewicz 1987). Equilibrium state was established in the system after 30 days. Thymol was placed in hygrostats with water activity exceeding 0.7 to protect the samples from microflora growth (Ocieczek 2007, 2008).

The sorption process parameters, such as monomolecular layer capacity with the corresponding water activity and energy constant, were determined based on the GAB (Guggenheim, Anderson, De Boer) sorption model. The model is described by the following equation:

$$\frac{v}{v_m} = \frac{c_e k a_w}{(1 - k a_w)(1 - k a_w + c_e k a_w)} \qquad (1)$$

where:

v – equilibrium water content (g water (100 g d.m.)$^{-1}$),

v_m – monolayer capacity (g water (100 g d.m.)$^{-1}$),
c_e – energy constant,
k – constant,
a_w – water activity.

The parameters of the equation were identified from empirical data. Identification was performed with non-linear regression, using the Monte Carlo algorithm. Owing to such an approach it is possible to avoid the estimation process being stopped by a local minimum. Unlike in the classical method applied in food sciences, it is possible to match the GAB model in coordinates v - a_w. Minimisation of the sum of squares of remainders was adopted as the objective function. The criterion is most widely applied in statistical analysis (Ocieczek and Kostek 2009).

The specific surface of the adsorbent was calculated based on the volume of adsorbed water and so-called water settling surface, with the following equation:

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

where:
a_{sp} – sorption specific area ($m^2 \cdot g^{-1}$);
N – Avogadro's number ($6.023 \cdot 10^{23}$ molecules·mole^{-1});
M – water molecular weight (18 g·mol^{-1});
ω – water settling surface ($1.05 \cdot 10^{-19}$ m^2·molecule^{-1}).

Size and volume of capillaries of the material under test were determined from the isotherms in the capillary condensation area. Calculations were performed from the Kelvin equation:

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

where:
v – equilibrium water content (g water(100 g d.m.)$^{-1}$);
σ – liquid surface tension at temp. T (N·m^{-1});
r_k – capillary radius (m);
R – gas constant (8.314 J·(mol·K)$^{-1}$);
T – process temperature (K) (Ościk 1979, Świtka 1992).

RESULTS AND DISCUSSION

Flour is a hygroscopic material which may absorb or resorb water vapour, depending on water content and air saturation. Bran is even more hygroscopic.

Chemical composition of wheat and rye flour is different. 97% wheat flour contains more (9.8%) protein than 97% rye flour (7.3%), more fat (2.8% and 2.2%, respectively), less carbohydrates (70.3% and 73.2%, respectively), more digestible fibre (1.9% and 1.4%, respectively), and has a higher ash content (1.7% and 1.4%, respectively) (Gąsiorowski 1994, 2004).

Therefore, an assumption was made that different types of flour obtained in the same milling conditions may react differently to water vapour.

Comparison of the sorptive properties is based on the assessment of the following:

⇒ Position of adsorption isotherms against one another (Tab. 1, Fig. 1, 2, 3, 4),

⇒ Parameters of adsorption isotherms determined from the GAB model and the derivatives (Tab. 2),

⇒ Selected structural characteristics of the analysed flours (Tab. 2).

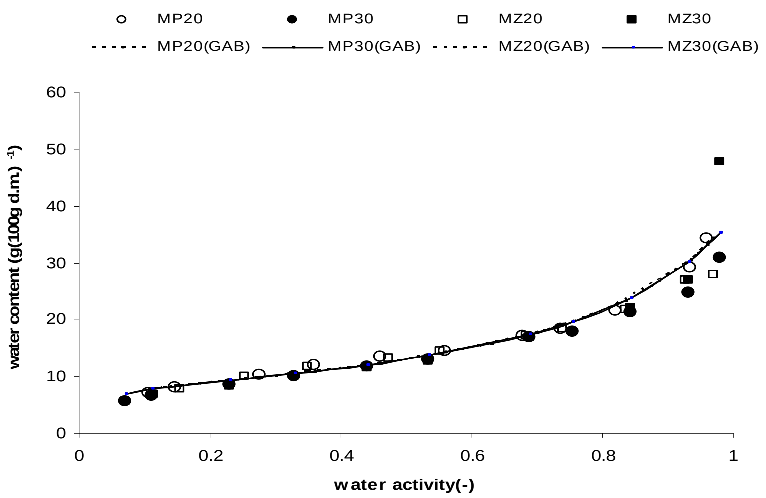

Fig. 1. Sorption isotherms of flours

MP20 – wheat flour in 20ºC (empiric data)
MP30 – wheat flour in 30ºC (empiric data)
MP20 GAB) – wheat flour in 20ºC (GAB model)
MP30(GAB) – wheat flour in 30ºC (GAB model)
MZ20 – rye flour in 20ºC (empiric data)
MZ30 – rye flour in 30ºC (empiric data)
MZ20(GAB) – rye flour in 20ºC (GAB model)
MZ30(GAB) – rye flour in 30ºC (GAB model)

The isotherms determined in the experiment revealed a sigmoid course of the process, typical of other products with a high starch content (Erbas *et al.* 2005, Ocieczek 2007, 2008).

The curves indicate low diversity of the sorptive properties of the analysed flours in both thermal conditions of the experiment (Fig. 1). Preliminary assessment of the results provided surprising results; the analysed flours were different in terms of their chemical composition.

The main component of flours which affects their hygroscopic properties is starch which may absorb up to 30% of water from high humidity air. The ability of starch to absorb water increases with the extent of damage to its granules. The content of reducing sugars in wheat flour is lower than in rye flour. Their presence affects the water-matrix interactions. The pentosane content in rye flour is higher than in wheat flour (8.5-10.2% and 4.9-7.5%, respectively). They are the main constituents of mucus, which can absorb high amounts of water. However, they reduce the ability of proteins and starch to swell. The average mucus content in rye flour is 2.8%, whereas in wheat flour it is much lower (ca. 0.5%) (Gąsiorowski 1994, 2004).

Therefore, the sorption curves were analysed in three areas: monomolecular and multilayer adsorption and capillary condensation (Fig. 2, 3, 4).

A certain effect of temperature on the sorptive properties of the analysed flour was observed in the monolayer adsorption region.

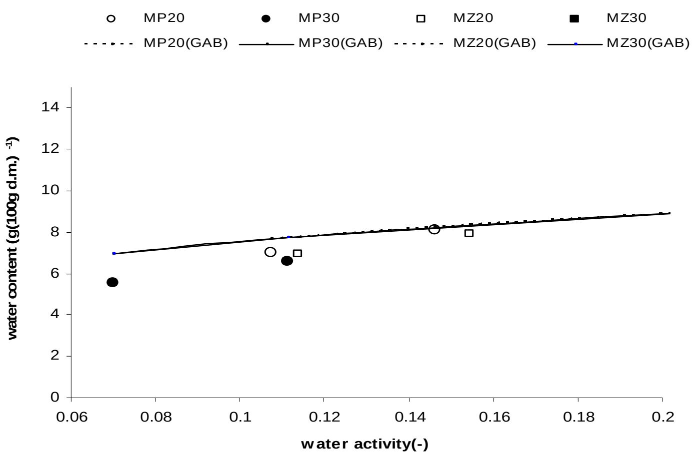

Fig. 2. Monolayer adsorption

When the temperature increased by 10°C, the sorptive properties of both the flours were found to decrease. However, no difference was found between the rye flour and wheat flour in this area. In order to verify those claims, the Student t-test was performed for the difference between the average values at equal variances ($p<0.05$) (Łomnicki 2006). No significant difference was found to exist between the mean water content in the analysed flours in all the analysed variants. The calculations showed that no statistically significant differences exist between the sorptive properties of rye flour and wheat flour, tested at temperatures of 20 and 30°C, in the region of monomolecular adsorption.

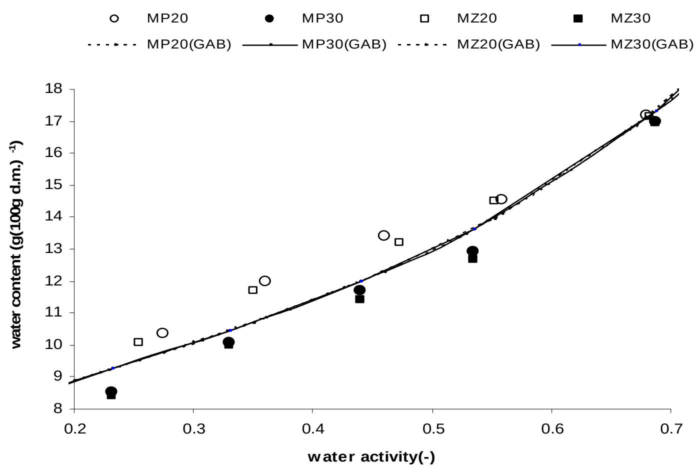

Fig. 3. Multilayer adsorption

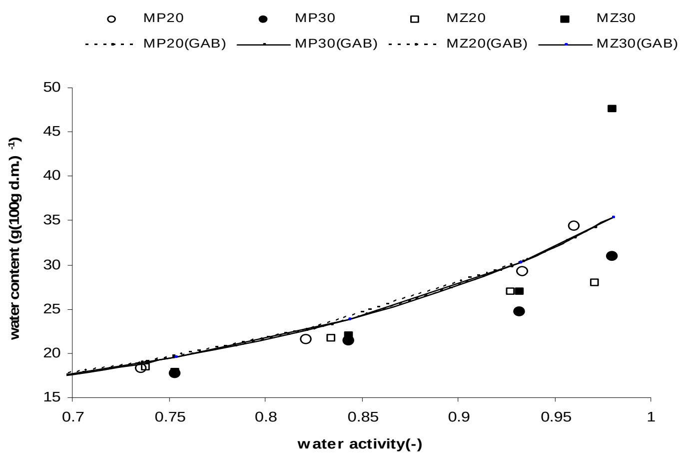

Fig. 4. Capillary condensation

A certain influence of temperature on the sorptive properties of the analysed flours was also observed in the multilayer adsorption area. However, no differences were found between the sorptive properties of rye flour and wheat flour. In order to verify those claims, a similar statistical procedure was applied. No significant difference was found to exist between mean water content in the flour in all the analysed variants. There were no statistically significant differences in the multilayer adsorption area between the sorptive properties of wheat flour and rye flour, analysed at temperatures of 20 and 30°C.

The statistical analysis of the results in the region of capillary condensation yielded the same picture as in the other regions.

Another element of the study was to estimate the parameters of adsorption isotherms, determined from the GAB model, and their derivatives. The GAB model takes into account the modified properties of the adsorbent in the multilayer adsorption area. It also properly reflects the shape of water sorption isotherms in food systems in the a_w range from 0 to 0.90. It can be used for determination of the monomolecular layer capacity and for determination of energy phenomena which accompany the sorption. Owing to this, it is possible to extrapolate results onto other temperatures. GAB transformation is applicable in a wider range (than for the BET model) at a specific satisfying degree of representation of empirical data. The applied GAB model transforms empirical data and makes it possible to perform calculations which help to determine the adsorbent structure and changes of the energetic state of the system (adsorbent-adsorbate) in the adsorption process.

Based on the sorption isotherms throughout the whole a_w range, the GAB equation was established and the degree of its matching was determined (mean square error, Pearson's linear correlation coefficient) with the empirical data and the GAB equation parameters (v_m, c_e, a_w, k) were calculated. The results are presented in Table 1.

The monolayer capacity (v_m) is determined not only by the amount of specific components with numerous polar sites, but also by their physical state and interactions between them. The monolayer capacity was greater for rye flour than for wheat flour. Mechanical damage of starch granules, protein content and the presence of mucus determine the availability of polar sites (Erbas *et al.*2005, Hebrard *et al.* 2003, Roman-Gutierrez *et al.* 2003). The monolayer capacity provides grounds for analysing various aspects of physical and chemical decaying of dry food products (Mathlouthi 2001).

Water activity which corresponded to a monolayer assumed higher values in rye flour than in wheat flour, which may indicate its lower storage stability.

The energy constant c_e reflects a physical character of the adsorption process when it assumes values close to 20 $kJ \cdot mole^{-1}$; it indicates a chemical character of the process when its values are close to 200 kJ·mole^{-1} (Atkins 2003, Ościk 1970, Paderewski 1999). The results achieved in this experiment provide grounds for the conclusion that in the analysed case, the process of physical adsorption takes place.

Table 1. Parameters of the GAB equation and structural characteristics of the studied flours

Parameter	MP20	MP30	MZ20	MZ30
c_e	65.0	34.5	25.1	32.7
k	0.785	0.746	0.688	0.757
v_m (g water (100 g d.m.)$^{-1}$)	8.15	8.11	9.62	8.06
a_w at v_m	0.140	0.195	0.242	0.197
RMS	7.98	4.47	1.63	0.793
R^2	0.99	0.98	0.99	0.99
Specific surface of sorption (m^2 g^{-1})	286	285	338	283
General capacity of capillaries (mm^3 (100 g d.m.)$^{-1}$)	85.0	76.9	76.6	96.6
Radius of capillaries about $a_w = 0.85$ (nm)	6.5	7.5	7.2	7.7

Source: Own research.

Based on the v_m, the specific surface of sorption was calculated. The results (Tab. 1) show that rye flour has a higher specific surface of sorption than wheat flour. Moreover, analysis of the results leads to the conclusion that mesocapillaries are the dominant form of capillaries in both cases.

Based on the Kelvin equation, the corresponding radiuses of capillaries and the characteristic parameters of the capillaries were calculated (Tab. 1). At 20°C, the total capillary capacity for wheat flour was higher than rye flour. The relationship was reversed at 30°C. The effect was probably caused by considerable changes in the structures of some components of the flours under test, caused by their interactions with water molecules. At $a_w = 0.82$-0.84, i.e. at the beginning of the capillary condensation process, capillaries with radiuses ranging from 6.5 nm to 7.5 nm were filled in the wheat flour, whereas the radiuses of capillaries filled in the rye flour ranged from 7.2 nm to 7.7 nm. No estimate was made of the most probable capillary radius, as the shape of the obtained structural curves prevented effective differentiation.

Apart from the amounts of particular components of the product, their state and interrelations are very important. It can be therefore assumed that the absence of any significant differences of the sorptive properties of the flours is a result of the domination of one component (starch) and the interrelations between the other components (protein, pentosanes) (Hebrard *et al.* 2003, Roman-Gutierrez *et al.* 2003).

CONCLUSIONS

1. The shape of the sorption isotherms for both the flours is sigmoid. The values of energy constant for the GAB equation indicated a physical (~25-65) nature of the process. The monomolecular layer capacity was higher for the rye flour, which is a result of a higher value of the sorption specific surface for the flour. Increasing the temperature resulted in a decrease of the monolayer capacity. Water activity, which corresponds to the monolayer, is higher for the rye flour, which in turn indicates its lower storage stability.
2. The capillary volume for the wheat flour is higher than that for the rye flour. Increasing the temperature reduced the capillary volume of the wheat flour and increased the capillary volume of the rye flour. The beginning of the capillary condensation of the wheat flour was accompanied by filling of capillaries with lower radiuses as compared to the rye flour.
3. In conclusion, it can be noted that the flours under test were different in terms of their sorptive properties; however, the differences were not statistically significant.

REFERENCES

Atkins P.W., 2003. Physical chemistry (in Polish). PWN, Warszawa.

Erbas M., Ertugay M.F., Certel M., 2005. Moisture adsorption behaviour of semolina and farina. Journal of Food Engineering, 69 191-198.

Gąsiorowski H., 1994. Rye. Chemistry and technology (in Polish). PWRiL, Poznań.

Gąsiorowski H., 2004. Wheat. Chemistry and technology (in Polish). PWRiL, Poznań.

Hebrard A., Oulahna D., Galet L., Cuq B., Abecassis J., Fages J., 2003. Hydration properties of durum wheat semolina: influence of particle size and temperature. Powder Technology, 130 211-218.

Labuza T., 1983. Standard procedure for isotherm determination. Food Research, 28(4), 258.

Łomnicki A., 2006. Introduction to statistics (in Polish), PWN, Warszawa.

Mathlouthi M., 2001. Water content, water activity, water structure and the stability of foodstuffs. Food Control, 12, 409-417.

Ocieczek A., 2007. Comparison of sorption properties of semolina and farina. Acta Agrophysica, 9(1), 135-145.

Ocieczek A., 2008. Evaluation of the usability of sorption isotherms for specification of weight growth in noodle products. Acta Agrophysica, 11 (1), 147-157.

Ocieczek A, Kostek R., 2009. The effect of micronization on sorptive properties wheat cellulose. Inżynieria i Aparatura Chemiczna, 48 (40), 108-109.

Ościk J., 1979. Adsorption (in Polish) PWN, Warszawa.

Paderewski M., 1999. Processes of adsorption in chemical engineering (in Polish). WNT, Warszawa.

Roman-Gutierrez A., Sabathier J., Gilbert S., Galet L., Cuq B., 2003. Characterization of the surface hydration properties of wheat flours and flour components by the measurement of contact angle. Powder Technology, 129 37-45.
Świtka J., 1992. Impact of selected technological factors on sorption properties of dried creamery products (in Polish). Scientific WSM work in Gdynia. Gdynia.
Tyszkiewicz S., 1987. Activity of water of foodstuffs. Definition. Method of the absolute measurement. Patterns (in Polish). Przemysł Spożywczy, 2, 51-53.

WŁAŚCIWOŚCI SORPCYJNE MĄKI PSZENNEJ I ŻYTNIEJ TYP 2000

Aneta Ocieczek[1], Robert Kostek[2]

[1]Katedra Organizacji Usług Turystyczno-Hotelarskich, Akademia Morska w Gdyni
ul. Morska 83, 81-225 Gdynia
e-mail: daszenka@am.gdynia.pl
[2]Katedra Maszyn Specjalnych i Ochrony Środowiska,
Uniwersytet Technologiczno Przyrodniczy w Bydgoszczy
Al. Prof. S. Kaliskiego 7, 85-796 Bydgoszcz

Streszczenie. W pracy przedstawiono porównawczą ocenę właściwości sorpcyjnych mąki pszennej i żytniej typ 2000. Celem pracy było zbadanie wpływu surowca na własności sorpcyjne mąki. Materiał badawczy stanowiły mąki wyprodukowane w warunkach laboratoryjnych przy zastosowaniu jednakowych warunków przemiału (młyn laboratoryjny MLU Bühler). Metody badań obejmowały wyznaczenie wybranych parametrów takich jak: pojemności monowarstwy wraz z odpowiadającą jej aktywnością wody, stałej energetycznej, powierzchni właściwej sorpcji, rozmiarów i objętości kapilar. Stwierdzono pewne różnice parametrów procesu adsorpcji dla obydwu mąk, które okazały się jednak mało istotne z praktycznego punktu widzenia.

Słowa kluczowe: mąka pszenna, mąka żytnia, sorpcyjność, model GAB (Guggenheim, Anderson, De Boer)