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# Hydration properties of durum wheat semolina: influence of particle size and temperature

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## Abstract

The hydration of semolina particles is an essential step in couscous processing which leads to binding between particles for the formation of agglomerates. Despite this importance, the hydration properties of such food products are rarely studied and in particular, durum wheat semolina has never been investigated.

Here we present a study of the hydration properties of durum wheat semolina by determination of water sorption isotherms, and other characterisation techniques to obtain a better understanding of hydration mechanisms. Equilibrium and dynamic sorption properties have been measured as a function of relative humidity by means of a controlled atmosphere microbalance. It is found that durum wheat semolina presents a type II isotherm [F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids Principles Methodology and Applications, Academic Press, 1999] indicative of multi layer adsorption. The Guggenheim Anderson de Boer (GAB) model is used to describe the isotherm and obtain a better understanding of hydration mechanisms and liquid/solid interactions.

The effects observed are related to physical properties of the semolina. In particular, the size of the semolina particles is found mainly to influence sorption kinetics: the finer the particles, the faster their sorption kinetics. Increasing temperature in the range 25–45 °C accelerates sorption kinetics. Furthermore, hydration causes no irreversible transformation of semolina components. Thus, absorption kinetics seem to be influenced by physical mechanisms, while the biochemical composition determines the amount of water sorbed.

## Résumé

Le procédé de fabrication du couscous se compose de plusieurs étapes: agglomération, cuisson, séchage. Au cours de l'agglomération, les particules de semoule sont hydratées, mélangées et roulées. Par hydratation, des liens se forment entre particules de semoule et permettent leur agglomération. Même si les propriétés d'hydratation de nombreux produits alimentaires sont connues, celles des semoules n'ont jamais été étudiées.

Les isothermes de sorption couplées à d'autres caractérisations permettent de comprendre les mécanismes d'interactions eau semoule. Les propriétés de sorption, variations de masse et de temps en fonction de l'humidité relative, ont été mesurées par une balance de sorption.

La semoule présente des isothermes de sorption de type II [F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids Principles Methodology and Applications, Academic Press, 1999]. La prise en eau s'effectue sous forme de plusieurs couches d'eau superposées. Pour une meilleure compréhension des mécanismes d'hydratation, les interactions liquide/solide peuvent être modélisées par l'équation de (GAB).

La taille des particules de semoule influence leur cinétique de sorption, plus les particules sont fines, plus leur cinétique de sorption est rapide. Ces différences sont liées aux facteurs physiques essentiellement. L'augmentation de la température accélère les cinétiques de sorption sans modifier la capacité de sorption. D'autre part, au cours de l'hydratation, pour une température comprise entre 25–45 °C, les composants de la semoule ne subissent pas de transformations internes irréversibles. La vitesse de prise en eau de la semoule est régie par des phénomènes physiques tandis que la composition biochimique influence la capacité de sorption.

*Keywords:* Semolina; Absorption; Isotherm; Kinetics; Temperature; Heat of absorption; Internal transformation

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## 1. Introduction

Couscous is a traditional food product from North Africa [2], which is prepared at home by mixing wheat durum semolina with water, followed by hand rolling to agglomerate and form granules. The well shaped and uniformly sized couscous granules are then steamed and sun dried. The industrial process for making couscous (i.e., mixing agglomeration, sifting, steam cooking, drying, cooling, and then packaging) has been designed to reproduce traditional methods [3]. The first part of the process, where the semolina particles are hydrated, is an essential step in bringing about interactions between particles leading to the agglomeration of semolina to form couscous granules. The knowledge and the control of interactions between water and durum wheat semolina can therefore be considered as a key factor in the overall process for making couscous.

A number of papers have been published on the equilibrium hydration properties of wheat flours [4, 6, 15], but no significant data is available for durum wheat semolina. Hydration properties of flours have been studied by different techniques: adding liquid water and centrifuging (i.e., water retention capacity), adding liquid water and mixing (i.e., farinograph absorption), following the equilibrium under different water vapour pressures (i.e., sorption isotherms). Water vapour sorption isotherms of wheat flours are found to present a typical “S” shape that corresponds to classical models such as the Guggenheim Anderson de Boer (GAB) model [6]. By using the GAB model, the monolayer water content of wheat flour was estimated at 7% (dm). An active site binding mechanism was favoured at low moisture contents, whereas water-water interactions were favoured at higher moisture content [7].

Only a few published papers have described the hydration kinetics of wheat flour. Kinetic data depends a great deal on the experimental method used, and more particularly on the type of water uptake: hydration by water addition (i.e., Baumann method, soaking and centrifugation), hydration by equilibration in controlled water vapour atmospheres [5, 8–10]. The initial rate of hydration for wheat flour particles, at 100% equilibrium relative humidity of the air (ERH), has been estimated at 7 mg (water) g<sup>-1</sup>(dm) h<sup>-1</sup> [10]. Hydration is faster when flour particles are brought directly in contact with liquid water, with an initial uptake rate of 325 g (water) g<sup>-1</sup>(dm) h<sup>-1</sup> at 25 °C [10]. The hydration kinetics of flour particles are considered to be controlled by water diffusion phenomena [4] and an apparent diffusion coefficient (4.10<sup>-8</sup> cm<sup>2</sup>/s) has been calculated from the initial slope of water content versus hydration time [5]. This value is of the same order of magnitude as those found for hydrophilic materials. However, this apparent diffusion coefficient does not take into consideration the effects of heat of absorption, distribution of particle size, shape irregularities, swelling, and non ideal behaviour [5].

Information on the hydration properties of durum wheat semolina would be useful for understanding the physico

chemical changes involved in the couscous agglomeration process and also be an aid to process control during the hydration stage. Contrary to wheat flour, no significant data is available for durum wheat semolina. In addition, it is not expected that durum wheat semolina will have the same behaviour as wheat flour because of the differences in particle size distribution and in the damaged starch content, which both have great influence on hydration properties. The objective of this paper is to investigate water sorption properties of durum wheat semolina for a better comprehension and control of semolina agglomeration processes. For this, equilibrium sorption isotherms and dynamic hydration properties of durum wheat semolina have been determined as a function of particles size and temperature of hydration.

## 2. Principle of sorption isotherms

When a solid is exposed to controlled conditions of relative humidity at given constant temperature, water exchanges occur between the solid and the atmosphere until equilibrium is reached. Under equilibrium conditions, the moisture content (EMC) of the solid is classically expressed by Eq. (1).

$$EMC = \frac{(M_{\text{solid}} - M_{\text{dry matter}})}{M_{\text{dry matter}}} \quad (1)$$

where EMC is the equilibrium moisture content (g water/g dry matter),  $M_{\text{solid}}$  is the mass of solid (g), and  $M_{\text{dry matter}}$  is the mass of dry matter (g). The relationship between EMC and ERH is classically described by sorption isotherms. For gas/solid systems, a wide variety of shapes of sorption isotherms can be obtained. Nevertheless, the majority of these isotherms, which result from physical sorption, may be grouped into six classes according to the IUPAC classification [1]. Thus, a visual inspection of the isotherm can give information about the nature of the solid, the pore structure, and the mechanisms of physiosorption. Sorption properties can be influenced by biochemical factors and/or physicochemical differences between two particles. For example, as shown in Table 1, if two particles have a different content in a component with high water sorption capacity, the particles could have different sorption capacities even if the same sorption mechanisms are involved.

Table 1  
Hydration capacity of the main components of wheat flour [16]

|                                                                 | Components of wheat flour |                |          |           |
|-----------------------------------------------------------------|---------------------------|----------------|----------|-----------|
|                                                                 | Native starch             | Damaged starch | Proteins | Pentosans |
| Capacity of water uptake at 25 °C (g H <sub>2</sub> O/100 g dm) | 44                        | 200            | 215      | 1500      |

The time required to reach equilibrium at a given relative humidity can be interpreted as the kinetics of sorption. Temperature is also known to influence sorption isotherms. Typically, the quantity of water absorbed at a given ERH increases when temperature decreases. Such products become less hygroscopic as temperature increases. An opposite trend is shown by some sugar containing foods, which become more hygroscopic at higher temperature because of the dissolution of sugars in water [11]. The heat of sorption can be calculated from sorption isotherms determined at different temperatures, according to the Clausius Clapeyron equation (Eq. (2)).

$$Q_s = R \left[ \frac{\delta(\ln P)}{\delta(1/T)} \right] \quad (2)$$

To apply this equation, two assumptions must be made. Firstly, the heat of sorption does not change with temperature, and secondly, the moisture content of the system remains constant [11]. A semi logarithmic plot of equilibrium pressure versus the reciprocal absolute temperature (at constant moisture content) should give a straight line with a slope of  $Q_s/R$ . The heat of sorption gives information on the amount of heat released or taken up to reach a given moisture content and about the homogeneity of the surface.

In some specific cases, the biochemical and structural transformations due to hydration can be identified by making successive cycles of adsorption desorption and evaluating the water retained by the material at 0% ERH. We have investigated semolina sorption isotherms. These experiments, coupled with previous results [12], give a better understanding of semolina hydration mechanisms.

### 3. Materials and methods

#### 3.1. Raw material

Superior quality industrial semolina A is used in the experiments both in its entirety and subdivided into three sieve fractions: A1 ([0 200]  $\mu\text{m}$ ), A2 ([200 400]  $\mu\text{m}$ ), and

Table 2  
Physicochemical characteristics of semolina A and its sub-fractions [12]

|                                              | Semolina A and sub-fractions (A1, A2, and A3) |     |     |     |
|----------------------------------------------|-----------------------------------------------|-----|-----|-----|
|                                              | Semolina A                                    | A1  | A2  | A3  |
| Average diameter d50 ( $\mu\text{m}$ )       | 300                                           | 157 | 325 | 470 |
| Scattering: (d90 d10)/d50                    | 0.9                                           | 1.2 | 0.7 | 1.3 |
| Specific area ( $\text{m}^2 \text{g}^{-1}$ ) | 0.05                                          |     |     |     |
| Intragranular porosity                       | non-detectable                                |     |     |     |
| Density ( $\text{kg/l}$ )                    | 1.45                                          |     |     |     |

Table 3  
Biochemical composition of semolina A and its sub-fractions [12]

| Composition (% m.s.)      | Semolina A and sub-fractions (A1, A2, and A3) |                |      |      |
|---------------------------|-----------------------------------------------|----------------|------|------|
|                           | Semolina A                                    | A1             | A2   | A3   |
| Starch                    | 86.1                                          | 83.3           | 85.6 | 86.9 |
| Damaged starch            | 5.9                                           | 9.3            | 5.0  | 4.6  |
| Proteins                  | 13.5                                          | 15.4           | 14.1 | 13.0 |
| Insoluble proteins in SDS | 6.7                                           | 5.9            | 7.8  | 6.9  |
| Total pentosans           | 1.7                                           | 1.9            | 1.6  | 1.3  |
| Solubles pentosans        | 0.12                                          | non-detectable | 0.13 | 0.12 |
| Free lipids               | 1.4                                           | 2.4            | 1.5  | 1.1  |
| Carbohydrate reduced      | 0.7                                           | 1.5            | 0.7  | 0.5  |
| Ash                       | 1.2                                           | 1.7            | 1.3  | 0.6  |

A3 ([400 ...]  $\mu\text{m}$ ). The physicochemical, biochemical, and structural properties of semolina and its sub fractions A1, A2, and A3 have been previously described [12]. The physicochemical properties and biochemical composition of semolina are reported in Tables 2 and 3, respectively. The semolina has also been examined by means of an environmental scanning electron microscope (ESEM) [12]. This shows that surface composition is heterogeneous and two populations of starch granules have been identified which differ in grain size and are bound by a gluten matrix. Small spherical granules, of < 10  $\mu\text{m}$  size, are distinct from large and oval granules, of size between 20 and 40  $\mu\text{m}$ . Occasionally, aleuron cells about 40  $\mu\text{m}$  in size which present an alveolar structure have been observed. The surface area ratio of this component is low, about 2% of surface area.

#### 3.2. Dynamic vapour sorption system

The sorption characteristics of semolina have been determined by a gravimetric method using a Surface Measurement Systems® automated Dynamic Vapour Sorption (DVS1000) which is a controlled atmosphere microbalance equipped with a video microscope system. In these experiments, the variation of mass of a sample of durum wheat semolina was measured as a function of time over a range of values of relative humidity by mixing dry and saturated vapour gas flows. The mass variation of the sample and the time are recorded.

#### 3.3. Water vapour sorption procedure

Water adsorption isotherms were determined at constant temperature (25, 35, or 45 °C) at a nitrogen flow of 375 standard  $\text{cm}^3$ . Samples (28–37 mg) were loaded and pre-equilibrated at 0% ERH by a continuous flow of dry air. Samples were then equilibrated at successive levels of relative humidity (from 10% to 95% in 11 steps). For each ERH level, the equilibrium conditions were defined when the change in sample mass as a function of time was lower than  $0.002\% \text{ min}^{-1}$  (with a 10 min minimum and 360 min

Table 4  
Characteristics of samples before DVS analysis

|                         | Semolina A and sub-fractions (A1, A2, and A3) |      |      |      |
|-------------------------|-----------------------------------------------|------|------|------|
|                         | Semolina A                                    | A1   | A2   | A3   |
| Initial moisture (% dm) | 2.9                                           | 1.7  | 0.4  | 0.2  |
| Mass of sample (mg)     | 29.9                                          | 29.8 | 28.6 | 36.9 |

maximum). The mass of the sample and its initial moisture content are summarised in Table 4.

## 4. Type of sorption isotherms

### 4.1. General description

Adsorption desorption isotherms can be presented by plotting the changes in moisture content versus ERH or by plotting the volume fraction of water ( $\phi_{\text{water}}$ ) versus water activity. For semolina A at 25 °C, moisture content versus ERH and  $\phi_{\text{water}}$  versus water activity are presented in Fig. 1a and b, respectively. Sorption isotherms of semolina sub fractions present similar trends.

Water activity,  $A_w$ , is defined as:

$$A_w = \text{ERH}(\%)/100 \quad (3)$$

The volume fraction of the solvent (water) in the solid,  $\phi_{\text{water}}$ , is defined as:

$$\phi_{\text{water}} = \frac{1}{[1 + (1/\text{EMC})]} \left( \frac{\rho_{\text{water}}}{\rho_{\text{solid}}} \right) \quad (4)$$

Based on the IUPAC classification [1], semolina presents type II sorption isotherms which are characteristic of the

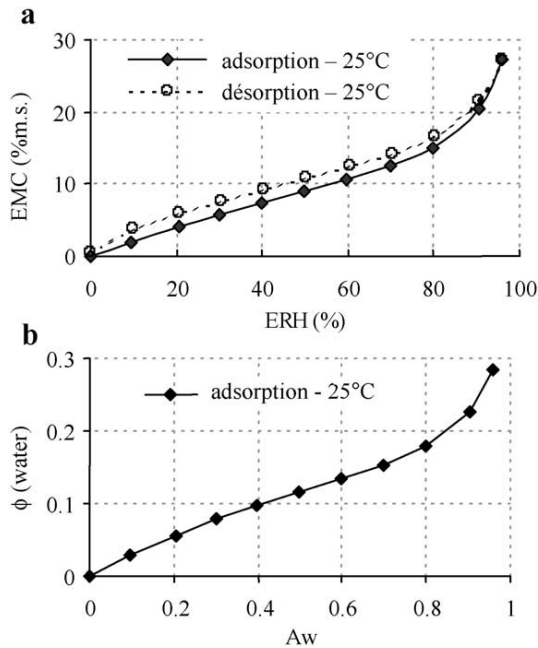


Fig. 1. Sorption isotherms for semolina A at 25 °C.

formation of multiple layers of adsorbed molecules on a non porous solid. More generally, wheat and products derived from wheat (flour, starch, gluten) have S shaped isotherms and show hysteresis. Natural high molecular weight polymers (such as proteins, starch, and cellulose) display the same behaviour [4].

According to the characteristics of the different components present in the solids, different regions can be identified depending on the expected liquid/solid interactions in a specific range of ERH. The initial convex region (region I) is the monolayer region in which the water is bound by hydrogen bonds on the polar sites of the solids. In this region, water is most strongly adsorbed and is immobile. Region II corresponds to the linear portion of the isotherm. Here the water forms several additional layers and corresponds to water held by the components. In the last concave region (region III), condensed water is held in weakly bound states, is mobile, and is classically designed as bulk phase water.

### 4.2. Parameters of the GAB equation

The relationships between water vapour adsorption capacities and equilibrium relative humidities were described by using the Guggenheim Anderson de Boer model (GAB) which has three parameters (Eq. (5)).

$$M = \frac{(M_0 C k a_w)}{(1 - k a_w)(1 - k a_w + C k a_w)} \quad (5)$$

$C$  is the Guggenheim constant,  $k$  is a constant correcting for the properties of the multilayer molecules with respect to the bulk liquid,  $M$  is the equilibrium water content (% dm), and  $M_0$  is the monolayer moisture content (% dm). The GAB equation was developed to fit sorption isotherms for  $a_w$  from 0 to 0.9. This equation can be used to calculate the values of the monolayer moisture content [13]. Other equations can be applied such as the ENSIC model which describes the interactions between the liquid and the sorbent.

The GAB equation was applied to sorption isotherms of semolina A and its sub fractions. The constants have been determined and are presented in Table 5. The value of  $k$  ( $< 1$ ) and the correlation coefficient ( $R^2 > 0.99$ ) show that the GAB equation gives a good fit to experimental semolina sorption isotherms (for  $0 < a_w < 0.9$ ). The water content to saturate the monolayer ( $M_0$ ) is independent of the particle size.  $k$  and  $C$  decrease when the particle size increases. These values can be compared with others reported for food powders [13]. Compared with flour and wheat, durum wheat

Table 5  
GAB equation parameters for semolina A at 25 °C-cycle of adsorption

| Particles size              | $M_0$ (kg water/kg dm) | $k$   | $C$  | $R^2$ |
|-----------------------------|------------------------|-------|------|-------|
| A1 (0 200 $\mu\text{m}$ )   | 0.0556                 | 0.839 | 12.3 | 0.996 |
| A2 (200 400 $\mu\text{m}$ ) | 0.0540                 | 0.829 | 9.2  | 0.996 |
| A3 (400 630 $\mu\text{m}$ ) | 0.0583                 | 0.812 | 5.9  | 0.994 |
| A (0 630 $\mu\text{m}$ )    | 0.0589                 | 0.828 | 9.5  | 0.993 |

Table 6  
GAB equation parameters for flour and wheat [13]

| Adsorption | $T$ ( $^{\circ}\text{C}$ ) | Range of $A_w$ | $M_0$<br>(kg water/kg dm) | $k$   | $C$  |
|------------|----------------------------|----------------|---------------------------|-------|------|
| Flour      | 27                         | 0.09 0.84      | 0.08                      | 0.711 | 32.5 |
| Wheat      | 25                         | 0.33 0.94      | 0.07                      | 0.821 | 37.4 |

semolina present the same values of  $M_0$  and  $C$ , while the values of  $k$  are similar, as shown in Table 6.

## 5. Sorption kinetics

The kinetics of water sorption (i.e., water vapour sorption rates) of semolina A and its sub fractions at 25  $^{\circ}\text{C}$  are presented on Fig. 2a and b, respectively.

Changes in water vapour sorption rates as a function of ERH during adsorption or desorption present similar trends. However from Fig. 2a, it can be seen that the rates of vapour adsorption are slightly higher than desorption rates when ERH >60% and more particularly when ERH >80%.

The curves can be divided into three main parts: the lowest values of sorption rates are observed for ERH <20%; sorption rates increase for ERH between 20% and 80%; the kinetics are the fastest for ERH >80%.

The trend of sorption kinetics versus ERH can be related to the main phenomena of water exchanges. The time to hydrate (or dry) the monolayer region, for ERH <20%, is longer than the time to hydrate additional layers, for ERH >20%. So once the first layer is formed, the formation of multilayers takes

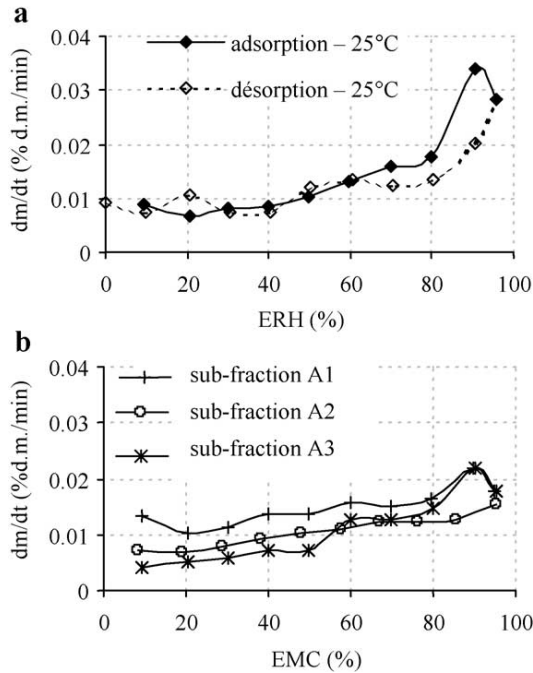


Fig. 2. Sorption kinetics at 25  $^{\circ}\text{C}$  for semolina A (a) and for sub-fractions of A (b).

place quickly. For ERH >80%, water is mobile, so hydration is the fastest. Changes in water vapour sorption rates as a function of ERH during adsorption or desorption for sub fractions of semolina A (Fig. 2b) present similar trends to those previously observed for semolina (Fig. 2a). Fig. 2b for sub fractions of semolina A also shows that the size of semolina particles influence sorption kinetics. Fine particles present a slight increase of kinetics between 20% and 80% ERH. These particles are characterised by the higher values of sorption rates. The bigger particles have lower values of sorption rates when ERH <20% and by the higher increase in rates when ERH increases from 20% to 80% ERH. However at 80% ERH, both the fine and coarse particles present nearly the same kinetics of adsorption.

Adsorption kinetics may be related to the physical properties of the solid. On one hand, fine particles have a larger surface area per unit volume (or mass) than coarse particles and consequently, have a greater surface area available to exchange water with the atmosphere. On the other hand, the time necessary for the water molecules to diffuse from the surface to the centre of particles is less for the smaller particles than for the larger particles. These physical differences between small and coarse particles may be responsible for the observed differences in adsorption kinetics. It may also be supposed that the values of water diffusion coefficient are affected by the particle size, but our results do not permit evaluation of the effect of particle size on diffusion coefficients.

These differences observed in sorption kinetics for semolina with different particle sizes could be an important parameter in the wetting stage in the granulation process. The residence time of semolina in a wetting granulator could be limited by the kinetics of water adsorption by big particles. However, this effect can be reduced by shearing due to the blades in the granulator.

## 6. Influence of temperature

### 6.1. Sorption isotherms

Sorption isotherms for semolina were determined at three temperatures: 25, 35, and 45  $^{\circ}\text{C}$ . Independently of temperature, semolina presents type II isotherms with hysteresis. Changes in temperature seem to have no effect on the water content of semolina at a constant ERH. The GAB equation was applied, and the value of the constants at 25 and 45  $^{\circ}\text{C}$  are presented in Table 7. As expected, the monolayer water

Table 7  
GAB equation parameters for semolina A at various temperatures of sorption

| $T$ ( $^{\circ}\text{C}$ ) | $M_0$ (kg water/kg dm) | $k$   | $C$  | $R^2$ |
|----------------------------|------------------------|-------|------|-------|
| 25                         | 0.0589                 | 0.828 | 9.5  | 0.993 |
| 35                         | 0.0622                 | 0.789 | 6.9  | 0.999 |
| 45                         | 0.0569                 | 0.850 | 10.5 | 0.998 |

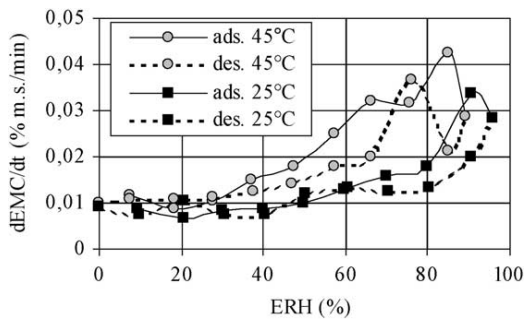


Fig. 3. Sorption kinetics at 25 and 45 °C for semolina A.

content is independent of temperature as well as  $k$ , while  $C$  increases with the temperature.

### 6.2. Kinetics of sorption

Kinetics of sorption are influenced by temperature over the entire range of ERH, as seen in Fig. 3. The sorption kinetics at 35 °C are intermediate between those at 45 and 25 °C. If we considered the three phases identified above, it can be seen that temperature has no influence on the kinetics for  $ERH < 20\%$ , while for  $ERH > 20\%$ , an increase in temperature leads to faster sorption kinetics.

### 6.3. Conclusion

Temperature seems to promote water exchange between the atmosphere and semolina but has no significant influence on the water sorption capacities. Changes in temperature in the range 25–45 °C do not alter the ability of semolina components to establish interactions with water. The effect of temperature on kinetics can be explained by the increase of diffusion and mobility of water in semolina particles.

## 7. Heat of sorption

Fig. 4 presents the isosteric heat of adsorption as a function of the amount of adsorbed water vapour. These plots are called “heat curves” from which we can determine

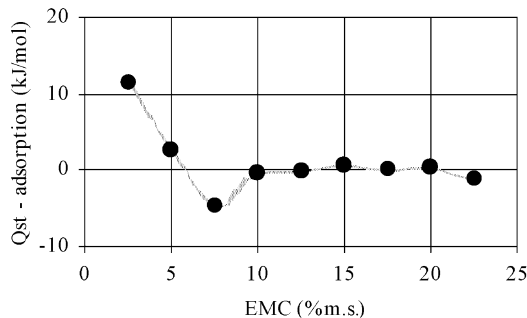


Fig. 4. Adsorption heat curve of semolina A.

the thermodynamic properties of the system and the nature of the adsorbent surface [14]. The isosteric heat of sorption is directly related to the energy of interactions between sorbent molecules and sorption sites. When water is adsorbed, a quantity of heat (the heat of adsorption) is released. And when adsorbed water is desorbed, a quantity of heat is taken up (the heat of desorption) which is a measure of the heat, or energy, that must be added to adsorbed gas to break the intermolecular force.

For an energetically uniform surface, heat curves are expected to yield a straight line, with zero slopes in the monolayer region, representing the heat of adsorption of the first layer. In the multilayer region, a decreasing curve is usually observed. An energetically non uniform surface possesses sites with different adsorption potentials that lead to a variation of the isosteric heat of adsorption at different loadings, even in the monolayer region. Adsorption initially occurs on the most active sites, giving rise to the greatest interaction energy. As these sites are progressively filled, adsorption proceeds on the less active site, giving off a smaller amount of heat. This hypothesis is in agreement with the Bruner Emmett Teller (BET) theory that assumes that the heat of adsorption for the first layer is greater than the heats of adsorption for subsequent layers.

Fig. 4 shows the isosteric heat of adsorption in the monolayer region, followed by a smooth decrease as the multilayers are formed and finally levels off. Such curves are the best indication of surface heterogeneity. This result is confirmed by ESEM observations [12]. It should be noted that a minimum quantity of heat is required to initialise water uptake. The decrease in heat of adsorption could be explained

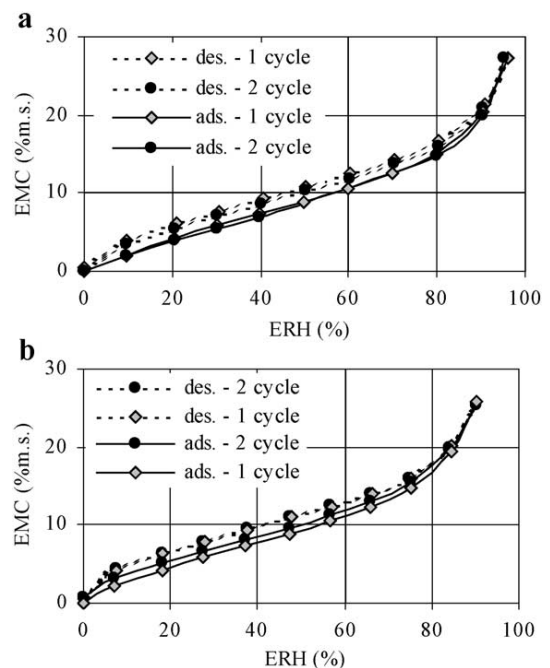


Fig. 5. Two cycles of sorption for semolina A at 25 °C (a) and 45 °C (b).

by the swelling of the adsorbent, as the swelling process is highly endothermic and may use heat produced by the adsorption process.

### 8. Heat of sorption versus energy of mixing

The total heat of sorption is the sum of the relative value of heat of sorption at each relative humidity:  $Q_{ST} = \sum Q_S(ERH)$ ; for ERH between 0% and 100%. The total heat of sorption evaluated by the isotherms of sorption is about 8.81 kJ/mol H<sub>2</sub>O or 158.5 J/g semolina (assuming that 100 g of semolina is able to adsorb 32.4 g of water at 100% ERH). This value can be compared with the energy of mixing determined by calorimetry, which is about 5.12 J/g of semolina [17].

The energy of mixing determined by calorimetry is much lower than the heat of sorption evaluated by the sorption isotherms. This large difference may be associated with the type of hydration in each case. In the calorimetry method, the product is directly immersed and hydrated in excess water. Furthermore, the stirrer blades facilitate mixing and hydration of particles. In the sorption method, particles adsorb water vapour from the atmosphere and there are no external mechanical forces that facilitate the penetration of water into particles. Thus, water vapour must first condense on the surface of the particle, then hydrate; these two steps are energy consuming.

### 9. Structural and biochemical alteration

Hydration and temperature may alter the structural and biochemical properties of the semolina. Such structural and biochemical changes will involve water retention and can be identified by comparing the quantity of water desorbed with respect to the quantity adsorbed. To examine these possibilities, samples have been exposed to successive cycles of adsorption-desorption.

Two cycles of adsorption-desorption have been made at 25 and 45 °C. At both temperatures, the two successive adsorption-desorption isotherms present no apparent differences, as indicated in Fig. 5. At ERH = 0%, after one or two adsorption and desorption cycles, the moisture content of product is the same (EMC = 0%) for the first and second cycle. As expected, the value of  $M_0$  and  $k$  are independent of the number of cycle at 25 or 45 °C, as shown in Table 8. Thus,

Table 8  
GAB equation parameters for semolina A for two successive cycles of adsorption at 25 and 45 °C

| Adsorption cycle | $T$ (°C) | $M_0$<br>(kg water/kg dm) | $k$   | $C$  | $R^2$ |
|------------------|----------|---------------------------|-------|------|-------|
| One cycle        | 25       | 0.0589                    | 0.828 | 9.5  | 0.993 |
| Two cycles       | 25       | 0.0516                    | 0.843 | 9.4  | 0.991 |
| One cycle        | 45       | 0.0569                    | 0.850 | 10.5 | 0.998 |
| Two cycles       | 45       | 0.0602                    | 0.845 | 16.3 | 0.997 |

no water is retained by semolina components and no irreversible structural or biochemical change occurs.

### 10. Conclusion

The aim of this paper is to determine the mechanisms involved in semolina hydration so as to obtain a better understanding and control of water uptake during the semolina agglomeration process. It is found that for all particle sizes tested, semolina presents type II sorption isotherms with hysteresis. As expected, the components of semolina swell in contact with water but hydration of semolina particles does not induce irreversible modifications. For this reason, as with numerous other food products, semolina can be considered to be a solid which is inert to water during sorption in a range of temperatures between 25 and 45 °C. The hydration of semolina particles is thus essentially a physical phenomenon, and since semolina shows no intragranular porosity [12]. First, water cannot penetrate into particles through pores and cannot accumulate in pores. Thus, the sorption capacity only depends on the water sorption capacity of the semolina components. Secondly, after adsorption of water on the surface of the semolina particles, water molecules penetrate inside the particle by diffusion.

The mechanism of sorption of water into dry semolina particles can be differentiated in three main domains of relative humidity. For a water content from 0% to 6% relative humidity, water molecules establish interaction with the most hydrophilic components and form a monolayer coverage with the slowest kinetics of sorption. Afterwards, multilayer absorption takes place and each layer rapidly covers the previous one. Finally, for ERH >80%, water is mobile in the semolina particles and the sorption kinetics are the fastest.

It is found that sorption kinetics depend on particle size. The increase in the rate of water uptake with smaller particles may be assumed to be due to the greater surface area per unit volume. Sorption kinetics are also influenced by temperature, and an increase in temperature accelerates sorption. It may be assumed that increasing the temperature facilitates diffusion of water molecules.

Knowledge of the hydration properties (capacity and kinetics) of wheat durum semolina and the solid/liquid interactions involved is useful for understanding the agglomeration process in terms of content of added water and time required to obtain an homogeneous system. Furthermore, it may be supposed that the significant physicochemical transformations induced by the industrial couscous processing should also modify the hydration properties. Evaluating these transformations can be made by the description of the water sorption properties of couscous.

#### Nomenclature

|     |                      |
|-----|----------------------|
| Aw  | water activity       |
| BET | Bruner Emmett Teller |
| C   | BET constant         |



|                         |                                                                            |
|-------------------------|----------------------------------------------------------------------------|
| EMC                     | equilibrium moisture content of grain                                      |
| ENSIC                   | Engaged Species Induced Clustering                                         |
| ERH                     | equilibrium relative humidity of the air                                   |
| ESEM                    | environmental scanning electron microscope                                 |
| GAB                     | Guggenheim Anderson de Boer                                                |
| IUPAC                   | International Union of Pure and Applied Chemistry                          |
| $M_{\text{solid}}$      | mass of solid (g)                                                          |
| $M_{\text{dry matter}}$ | mass of dry matter (g)                                                     |
| $(P_w^v)_{\text{sy}}$   | ratio of water vapour pressure in the system                               |
| $P_w^v$                 | vapour pressure of pure water                                              |
| $P$                     | pressure of the water vapour                                               |
| $P_0$                   | pressure of the water vapour in the atmosphere saturated with water vapour |

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### References

- [1] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids Principles Methodology and Applications, Academic Press, 1999.
- [2] S.M. Kaups, C.E. Walker, Cereal Foods World 31 (1986) 179.
- [3] L. Guezlane, G. Selselet-Attou, A. Senator, Ind. Cereales (1986) 25-43.
- [4] W. Bushuk, C.A. Wikler, Cereal Chem. 34 (1957) 73-86.
- [5] C.J. Lomauro, A.S. Bakshi, T.P. Labuza, J. Food Sci. 50 (1985) 397-400.
- [6] K.A. Riganakos, M.G. Kontominas, Z. Lebensm.-Unters. Forsch. 204 (1997) 369-373.
- [7] K.A. Riganakos, P.G. Demertzis, M.G. Kontominas, J. Cereal Sci. 9 (1989) 261-271.
- [8] A.M.R. Pilosof, R. Boquet, G.B. Bartholomai, J. Food Sci. 50 (1985) 278-282.
- [9] S. Bhattacharya, J. Food Eng. 25 (1995) 21-30.
- [10] B.E. Elizalde, A.M.R. Pilosof, G.B. Bartholomai, J. Food Sci. 61 (1996) 407-409.
- [11] T.P. Labuza, A. Kaanane, J.Y. Chen, J. Food Sci. 50 (1985) 385-391.
- [12] A. Hébrard, D. Oulahna, M.F. Samson, L. Galet, M.H. Morel, J. Abecassis, J. Fages, Recent. Prog. en Genie Procédés 15 (2001) 489-496.
- [13] N.H. Dural, A.L. Hines, J. Food Eng. 20 (1993) 17-43.
- [14] D.S. Chung, H.B. Pfost, Trans. ASAE, (1967) 549-551.
- [15] D.W. Sun, J.L. Woods, Dry. Technol. 11-7 (1993) 1523-1551.
- [16] A. Roman-Gutierrez, J. Abecassis, B. Cuq, Ind. Cereales 114 (1999) 11-13.
- [17] J.C. Benezet, D. Oulahna, A. Hébrard, Recent. Prog. en Genie Procédés 15 (2001) 323-330.