



HAL
open science

Hydration properties of wheat durum semolina : influence of granulometry and temperature

Anne Hebrard, Driss Oulahna, Laurence Galet, B. Cuq, Joel Abecassis,
Jacques Fages

► To cite this version:

Anne Hebrard, Driss Oulahna, Laurence Galet, B. Cuq, Joel Abecassis, et al.. Hydration properties of wheat durum semolina : influence of granulometry and temperature. 7th International symposium on agglomeration, May 2001, Albi, France. p.853-864. hal-01809101

HAL Id: hal-01809101

<https://hal.science/hal-01809101>

Submitted on 27 Sep 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hydration properties of wheat durum semolina : influence of granulometry and temperature

**HEBRARD¹ A., OULAHNA¹ D., GALET¹ L., CUQ B.,
ABECASSIS² J., FAGES¹ J.**

¹ Ecole des Mines d'Albi Carmaux - Centre Poudres et Procédés - Albi - France

² ENSAM - INRA - Unité Technologique des Céréales & Agropolymères - Montpellier - France

ABSTRACT

The processing of couscous is composed of various stage namely agglomeration, cooking and drying. During agglomeration process, particles of semolina are hydrated, mixed and rolled. Hydration contributes to the formation of interactions between particles that lead to agglomeration. Even so hydration properties of several food products have been studied, these of wheat semolina have never been investigated.

Hydration properties of semolina have been studied by water sorption isotherms which were coupled with others characterisations for a better understanding of the hydration mechanisms. Sorption properties, mass and time variation in relation with relative humidity have been measured by a dynamic vapour system.

Semolina presents type II isotherms as numerous food products [1]. This type of isotherms characterises the formation of additional layers adsorbed molecules. For a best understand of hydration mechanisms, the liquid / solid interactions can be modelled by G.A.B. equation.

The size of semolina particles influences mainly the kinetics of sorption: the finer the particles, the faster their kinetics of sorption. These variations are linked to physical properties. Increasing temperature in the range 25 – 45°C accelerates the kinetics of sorption. Furthermore, no irreversible transformation of semolina components occurred due to hydration. So, kinetics of sorption seems to be influenced by physical mechanisms, while the biochemical composition determines the amount of water sorbed.

RESUME

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 [1]. 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 G.A.B..

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 et 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, sorption, isotherm, kinetics, temperature, heat of sorption, internal transformation.

1. INTRODUCTION

Couscous is a traditional alimentary product developed in North Africa [2], that is prepared by mixing wheat durum semolina and water in a dish and subsequent rolling by hand until agglomeration of granules. The well-shaped and uniformly sized couscous granules are then steamed and sun dried. The industrial processing (*i.e.* hydration, mixing-agglomeration, sifting, steam cooking, drying, cooling and then packaging) has been designed to reproduce these traditional methods [3]. During the processing, hydration of semolina particles is an essential step as it contributes to the formation of interactions that conduct to the agglomeration of semolina in couscous. The knowledge and the control of interactions between water and durum wheat semolina are considered as key factors in managing this process.

A large number of published papers described the hydration properties of wheat flours [4, 5, 6] while no significant data are available for durum wheat semolina. Hydration properties of flours have been studied by using different techniques: by adding liquid water and centrifuging (*i.e.* water retention capacity), by adding liquid water and mixing (*i.e.* Farinograph absorption), or by equilibrium under different water vapour pressures (*i.e.* sorption isotherms). Water vapour sorption isotherms of wheat flours present a typical sigmoid shape that could be described by using classical models, such as the GAB models [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 few published papers described the kinetic aspects of wheat flour hydration. Kinetics data greatly depends on the experimental methods applied, and more particularly on type of water uptake: liquid water (*i.e.* Baumann method, soaking and centrifugation) or equilibrium in atmospheres at controlled RH [5, 8, 9, 10]. The initial rate of hydration has been estimated at 7 mg water/g (dm) /h, for wheat flour particles at 100% RH [10]. When the flour particles are directly in contact with liquid water at 25°C, hydration is much more faster, with an initial rate of 325 g water/g (dm) / h [10]. The hydration kinetics of flour particles have been considered to be controlled by water diffusion phenomenon [4]. Apparent diffusion coefficients ($4 \cdot 10^{-8} \text{ cm}^2 / \text{sec}$) have been calculated from the initial slopes of the water content against hydration time plots [5].

This value is in the same range of order as those found for hydrophilic materials. These apparent diffusion coefficients did not take into consideration the effects of sorption heat, distribution of particle size, shape irregularity, swelling and non-ideal behaviours [5].

Description of hydration properties for durum wheat semolina could be useful to control and to study the physico-chemical changes involved during the agglomeration process, and more particularly during the hydration stage. While hydration properties for wheat flour are partly described in published papers, no significant data are available for durum wheat semolina. Same behaviour between durum wheat semolina and wheat flour is not assured because the differences in particle size distribution and in content of damaged starch could affect the hydration properties. The objective of the current study was to investigate the water sorption properties of durum wheat semolina. Equilibrium sorption isotherms and dynamic hydration properties of durum wheat semolina (and of their size sub-fractions) were determined at different temperatures.

PRINCIPLE of sorption isotherms

Sorption isotherms of semolina were analysed by a gravimetric method, the automated dynamic vapour sorption system, DVS. The variation of mass and time at various relative humidity were measured.

For a given constant temperature, interchange of water occurs when the solid and air are not in equilibrium. It implies mass variation and time consumption, and proceeds until an equilibrium moisture content (EMC - equation 1) of the solid and equilibrium relative humidity (ERH) of the air are achieved.

$$EMC = (m-dm) / dm \text{ (equation 1)}$$

Where m is the moisture mass (g) of the solid and d.m. is the dry mass of the solid (g).

The relationship between EMC and ERH is described by sorption isotherm curves. In relation with the gas / solid system a wide variety of sorption isotherms forms can be obtained. Nevertheless, the majority of these isotherms, which results from physical sorption, may be grouped into six classes in the IUPAC classification [1]. So, a visual inspection of the isotherms informs about the nature of the solid system, the pore structure and the mechanisms of physio-sorption.

The moisture content of the sample placed in a given relative humidity is described, and particularly its maximal capacity of sorption. However, a variation of biochemical and/or physico-chemical difference between two particles could influence its properties of sorption. For example, if two particles have a different content in component with high capacity of water uptake, table I, they will have different capacity of sorption even if the same mechanisms of sorption are involved.

The time required to reach the mass equilibrium for a given relative humidity could be interpreted by the kinetics of sorption.

At 25°C	Components			
	Native starch	Damaged starch	proteins	pentosans
Capacity of water uptake (g H ₂ O / 100g dm)	44	200	215	1500

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

Temperature can influence sorption isotherms. Typically, the quantity of water sorbed at a given water vapour pressure increases when temperature decreases. So, these 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]. From two sorption isotherms at different temperatures, the heat of sorption can be calculated according to the Clausius Clapeyron equation. The heat of sorption give information about the amount of heat released or required to have a given moisture content. Furthermore, the "heat curve" gives information about the homogeneity of the surface.

In a specific case, the biochemical and structural transformations due to hydration can be identified by making successive cycle of adsorption - desorption and evaluate the water retained by the material at ERH=0%.

We investigate semolina sorption isotherms. These experiments coupled with results already obtained [12] permits a best understanding of the hydration mechanisms for semolina.

2. MATERIALS AND METHODS

2-1 Raw material

	Semolina and sub fractions (A1 - A3)			
	Semolina A	A1	A2	A3
Average diameter d50 (μm)	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	
Intra granular porosity		Non detectable		
Density (kg/l)		1.45		

Table II: Physico-chemical characteristics of semolina and its sub - fractions

Composition (% m.s.)	Semolina and sub fractions (A1 - 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	n.d.	0.13	0.12
Free lipids	1.4	2.4	1.5	1.1
Carbohydrate reducted	0.7	1.5	0.7	0.5
Ash	1.2	1.7	1.3	0.6

Tableau III: Biochemical composition of semolina and its sub - fractions

We experimented superior quality industrial semolina, A, as a whole and sub-divided in three fractions A1 (< 200 μm), A2 (200-400 μm) and A3 (> 400 μm). The physico-chemical, biochemical and structural properties of semolina and its sub-fractions A1, A2 and A3 have already been described [11]. The physico-chemical properties and biochemical composition of semolina are reported in tables I and II respectively.

The surface of semolina has been observed by environmental scanning electron microscopy [11]. The surface composition is heterogeneous. Mainly, two populations of granules starch, different in size, linked by a gluten matrix, have been identified. Small spherical granules of a size < 10 μm are distinct from large and oval granules of size between 20 and 40 μm . Occasionally, aleurons cells, which present an alveolus

structure, about 40 μm in size, have been observed. The surface ratio of this component is weak, about 2% of surface area.

2-2 Dynamic Vapour Sorption system

Adsorption data were measured gravimetrically using an automated Dynamic Vapour Sorption (DVS); (Surface Measurement Systems®) equipped with a video microscope system. This system permit to vary the relative humidity from 0 to 95% by mixing dry and saturated vapour gas flows. The mass variation of the sample and the time are recorded.

2-3. Water vapor sorption procedure

ERH varied between 0 and 95% in 11 stages at a nitrogen flow of 375 sccm (standard cubic centimeter). The progression to the next stage occurred for a change of mass lower than 0.002% in ERH, with a time minimum of 10 minutes and maximum of 360 minutes. At the end of each stage of equilibrium, images are taken. The mass of the sample and its initial moisture content are summarised in table IV.

	Semolina and sub fractions (A1 - 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

Table IV: Characteristics of semolina and its sub – fractions before DVS analysis

3. TYPE OF SORPTION ISOTHERMS

3.1. Semolina and its sub-fractions

3.1.1. General description

Adsorption – desorption isotherms at 25°C can be presented by plotting EMC versus ERH or A_w or ϕ_{water} versus ERH or A_w . EMC versus ERH and respectively ϕ_{water} versus A_w , for semolina A, are presented in figure 1 and 2 respectively. The isotherms of semolina sub-fractions present the same trend.

Water activity, A_w , is defined as:

$$A_w = ERH(\%) / 100 \text{ (equation 2)}$$

The volumic fraction of the solvent (water) in the solid, ϕ_{water} , is defined as:

$$\phi_{\text{water}} = 1 / [1 + (1/EMC) \cdot (\rho_{\text{water}} / \rho_{\text{solid}})] \text{ (equation 3)}$$

According the IUPAC classification [1], this system exhibits type II sorption isotherm. This type of isotherms characterises the formation of multiple layers of adsorbed molecules on a non-porous solid. More generally, the sigmoid shape of the isotherms and the hysteresis seems to be characteristic of wheat derivative, flour, starch, gluten and of natural high polymers such as proteins, starch and cellulose [4]. According to the specificity of the solid, regions describing the interactions of liquid / solid in a specific range of ERH, could be defined.

The initial convex region, region I, is the monolayer region, in which the water is bound by hydrophilic bonds on the polar sites of the components. In this phase, the water is the most strongly adsorbed and is immobile. Region II corresponds to the linear portion of the isotherm. Water added forms several additional layers. It represents water held by

the components. In the last concave region, region III, condensed water is trapped. Water is least strongly bound, the most mobile and is designed as bulk phase water.

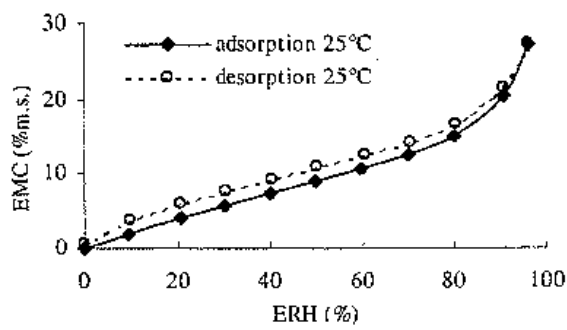


Figure 1: EMC = f(ERH)

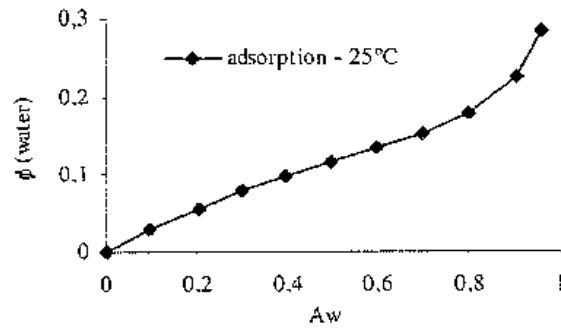


Figure 2: ϕ (water) = f(A_w)

Sorption isotherms for semolina A at 25°C

For this type of isotherms, a better precision of the monolayer value, can be determined by applying the G.A.B. equation [13].

Others equations can be applied such as the ENSIC model which describes the interactions between the liquid and the sorbent.

3.1.2. G.A.B. equation parameters

G.A.B. equation, with 3 parameters, is an extension of B.E.T. equation, which has been developed to fit sorption isotherms for A_w from 0 to 0.9.

The equation is:

$$X = (C.K.Mm.A_w) / [(1-K.A_w)(1-K.A_w + C.K.A_w)] \text{ (equation 4)}$$

With:

C : GAB constant linked to monolayer properties

K: GAB constant linked to multilayers properties,

Mm: water content of the monolayer (kg water/ kg dm)

Tableau V : G.A.B. equation parameters for semolina A at 25°C for the cycle of adsorption

Granulometry	Mm (kg water/kg dm)	K	C	R ²
0-200 μ m	0,0556	0,839	12,3	0,996
200-400 μ m	0,0540	0,829	9,2	0,996
400-630 μ m	0,0583	0,812	5,9	0,994
0-630 μ m	0,0589	0,828	9,5	0,993

$K < 1$ and $R^2 > 0.99$: the G.A.B. equation is a good fitting for sorption isotherms for A_w from 0 to 0.9.

The water content to saturate the monolayer, Mm, is independent of particle size. While K and C decrease when the size particle increases.

These values can be compared with the work on food powders [14]. They found that K varied between 0,98 for sodium carboxyméthyl cellulose and 0,56 for benzoyltetraglycin.

Compared with durum wheat semolina, flour and wheat present values of Mm and C stronger while the value of K are weaker.

Tableau VI : G.A.B. equation parameters for flour and wheat

Adsorption	T (°C)	Range of Aw	Mm(kg water/kg dm)	K	C
Flour	27	0,09-0,84	0,08	0,711	32,49
Wheat	25	0,33-0,94	0,07	0,821	37,39

4. KINETICS OF SORPTION

The kinetic of sorption is defined as the ratio of the mass variation by the time necessary to reach the equilibrium for a given relative humidity. Kinetics of water sorption of semolina A at 25°C are presented on figure 3.

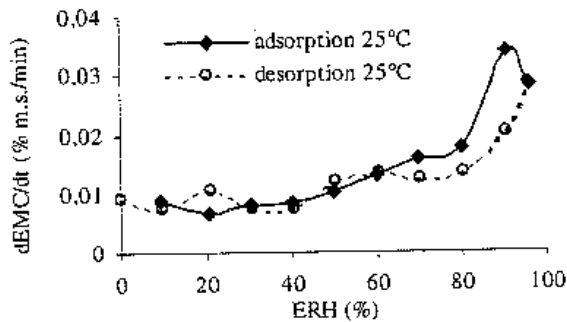


Figure 3: kinetics of sorption at 25°C for semolina A.

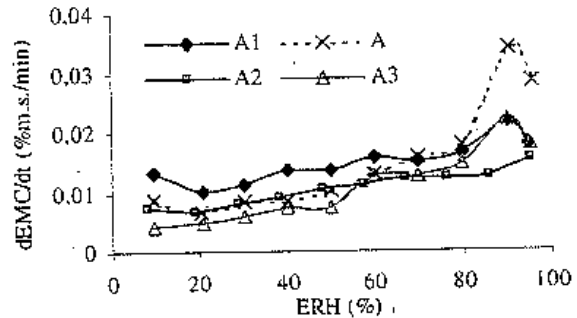


Figure 4: kinetics of adsorption at 25°C for sub-fractions of semolina A.

The kinetic of adsorption is slightly faster than that of desorption for ERH > 60%. However, they present the same trends.

The curves can be divided into three main parts. For ERH < 20 - 40% approximately, the kinetic is the longest, for ERH between 20 - 40% and 80% approximately, the kinetic increases and for ERH > 80%, the kinetic is the faster.

Kinetics can be explained by the main phenomena of water uptake described previously (3.1.1). The time to hydrate or dry the monolayer region, for ERH < 20% and the subsequent layer for ERH between 20 and 40% is longer than the time to hydrate additional layers, for ERH > 40%. So, once the first layers are formed, the formation of multilayers takes place quickly. For ERH > 80%, water is mobile, so hydration is the fastest.

The kinetics varies in relation with the size of the particles of semolina, figure 4. As defined previously, we distinct the three main phases. Fine particles present a small increase of kinetics between 20 and 80%, but it is the faster. The bigger the particles, the weaker the kinetics, for ERH < 20%, and the greater the increase between 20 and 80%. However, at 80%, fine and big particles present nearly the same kinetics of adsorption.

This notion of adsorption kinetics may be linked with the physical properties of the solid. On one hand, fine particles developed a larger surface area than big ones. So the spreading of water on the surface is quick. On the other hand, the diameter of small particles is lower than big ones. So, the diffusion of water into the particles is fast. These physical differences between small and big particles may be responsible for the adsorption kinetics.

These differences of sorption kinetics observed for the different size of semolina particles could be an important parameter for wetting in granulation process. The residence time of semolina in a wetting granulator could be limited by the kinetic of

water uptake by big particles. However, the effect of particle size can be reduced by scale transposition, from microscopic to macroscopic scale, and by the shirring of the granulator blades.

5. INFLUENCE OF TEMPERATURE

5.1. Sorption isotherms

Sorption isotherms for semolina were determined at three temperatures, 25, 35 and 45°C.

Independently of temperature, semolina presents type II isotherms with reversible hysteresis. Temperature seems to have no effect on the water content of semolina at a constant ERH. The content of water to saturate the monolayer is independent of temperature as well as K while C increases with the temperature, table VII.

Tableau VII : G.A.B. equation parameters for semolina at various temperature

Granulometry	T (°C)	Mm(kg water/kg dm)	K	C	R ²
0-630 µm	25°C	0,0589	0,828	9,5	0,993
0-630 µm	35°C	0,0622	0,789	6,9	0,999
0-630 µm	45°C	0,0569	0,850	10,5	0,998

5.2. Kinetics of sorption

Kinetics of sorption are influenced by temperature over the entire range of ERH, figure 5. The sorption kinetics at 35°C is located between those at 45°C and 25°C. On the whole, at 45°C, sorption kinetics are faster than that at 25°C. If we considered the three phases, we observed that for ERH < 20%, the temperature has no influence on the kinetics. For ERH > 20 %, the increase of temperature leads to faster sorption kinetics.

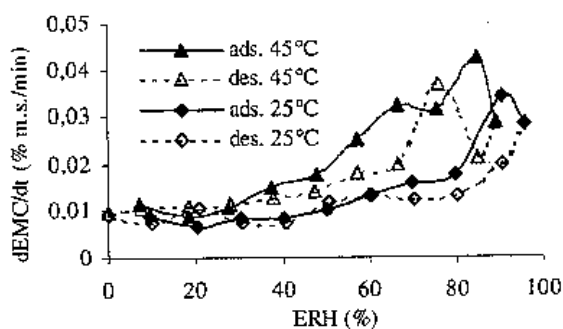


Figure 5: kinetic of sorption at 25, 45°C for semolina

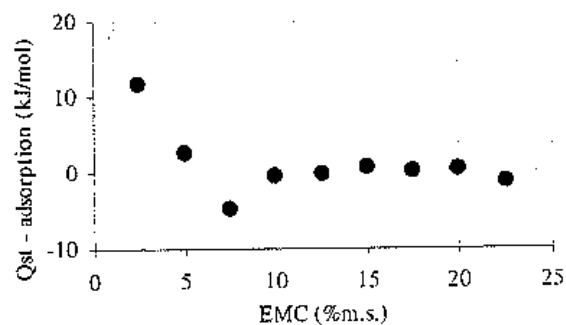


Figure 6: adsorption heat curve of semolina A

5.3. Conclusion

Temperature facilitates water exchange between the atmosphere and semolina but has no influence on the amount of water uptake. On the other hand, temperature in the range 25-45°C do not alter hydrophobicity, biochemical or structural properties of the components. The effect of temperature on kinetics can be explained by the increase of diffusion, mobility of water on the surface and into the particle due to temperature.

6. HEAT OF SORPTION

The isosteric heat of sorption is directly related to the energy of interactions between sorbant molecules and sorption sites. In turn, the energy of interaction can be suggestive of the mechanisms involved. The isosteric heat of sorption is calculated from two sorption isotherms at different temperature by means of the Clausius Clapeyron equation. (Equation 5)

$$Q_{st} = R \left[\delta(\ln P) / \delta(1/T) \right] \text{ (Equation 5)}$$

To apply this equation two assumptions must be made. The heat of sorption does not change with temperature and this equation is applied only when the moisture content of the system remains constant [11]. A semi-logarithmic plot of equilibrium pressure versus reciprocal absolute temperature at constant water uptake should give a straight line with a slope of Q_s/R .

When water is adsorbed, a quantity of heat, the heat of adsorption is released. While, when adsorbed water vapour is desorbed, a quantity of heat is taken up, the heat of desorption and is a measure of the heat or energy that must be added to adsorbed gas to break the intermolecular force.

Figure 6 presents the isosteric heat of adsorption as a function of the amount of water vapour adsorbed, it referred to as 'heat curves'. From this plot, we can determine the thermodynamics properties of the system and the nature of the adsorbent surface [13].

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 usually occurs. An energetically non-uniform surface possesses sites with different adsorption potentials that lead to a variation of the isosteric heat of adsorption at different loading, even in the monolayer region. Adsorption initially occurs on the most active sites, giving rise to the greatest interaction energy. As these sites are filled, adsorption proceeds on the less active site, giving off a smaller amount of heat. This hypothesis is analogous to that based on the Bruner, Emmett, Teller (B.E.T.) theory which assumes that the heat of adsorption for the first layer is greater than heats for subsequent layers.

The plot of isosteric heat of adsorption at different loading, figure 6, exhibits a steep initial drop 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 environmental microscopic observations [12]. We noted that to initialise water uptake an energetic level should be get over, a minimum quantity of heat is required.

Another hypothesis explains the decrease in heat of adsorption by the swelling of the adsorbent. The swelling process is highly endothermic and may use a quantity of the heat produced by the adsorption process.

7. COMPARAISON OF ENERGY: Heat of sorption and mixing energy

The total heat of sorption is the addition of the relative value of heat of sorption at each relative humidity. $Q(\text{total}) = \sum Q(\text{ERH})$ for ERH variant between 0 et 100%. The total heat of sorption evaluated by the isotherms of sorption about 8.81 kJ/mol H_2O or 158,5 J/g semolina. This value can be compared with the energy of mixing determined by calorimetry, which is about 5.12 J/g of semolina [18].

To calculate the heat of sorption in J/g of semolina, we use the following equations :

$$Q(\text{total}) \text{ (kJ/g } H_2O) = Q(\text{total}) \text{ (kJ/mole } H_2O) / \text{molecular mass of water}$$

At 25°C, we show that the capacity of water sorption by semolina at ERH = 90.5% and 96% is respectively 20.3% and 27.3%. By extrapolation, we can estimate the maximum capacity of water sorption by semolina at ERH = 100%, is about 32.4%. So 1 g of water is sorbed by 100/32.4 g of semolina.

$$Q(\text{total}) \text{ (kJ/g semolina)} = Q(\text{total}) \text{ (kJ/g H}_2\text{O)} / (100/32.4)$$

The energy of mixing determined by calorimetry is much lower than the heat of sorption evaluates by the isotherms of sorption. This strong difference is due to the way of hydration. By calorimetry method the product is directly immersed in excess water and blades facilitate the mixing and hydration of the particles. While in sorption method, particles adsorb water vapour from the atmosphere. No external forces facilitate the penetration of water into the particles. So, this process of hydration includes two steps which are energy consuming. First water vapour should condense on the surface of the particle then hydrate it.

8. STRUCTURAL AND BIOCHEMICAL ALTERATION

Hydration and temperature could alter the structural and biochemical properties of the solid. This modification should be linked with sorption properties of the solid and particularly with the quantity of water desorbed after adsorption. The water involved in the structural and biochemical change is retained by the material and could not be desorbed. So, to evaluate the structural and biochemical modification due to hydration two methods can be used. The first one consists of initially stored the sample in a given relative humidity to hydrate it at a specific moisture content. The second consists of making successive cycles of sorption. We have chosen the second method.

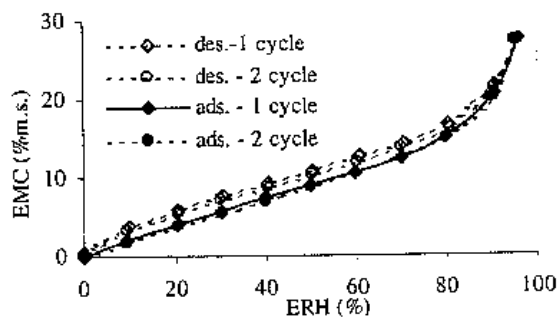


Figure 7: At 25°C

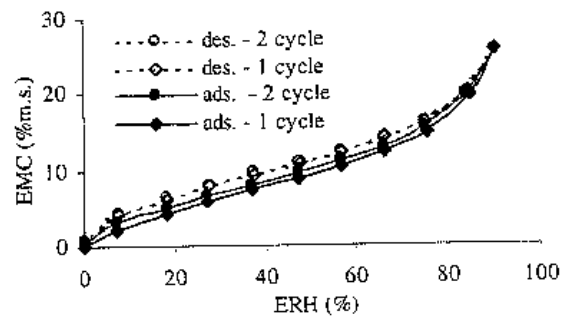


Figure 8: At 45°C

two successive cycle of adsorption – desorption for semolina A.

Tableau VIII : G.A.B. equation parameters for semolina A for two successive cycles of sorption

Granulometry	Adsorption cycle	T (°C)	Mm(kg water/kg dm)	K	C	R ²
0-630 μm	1 cycle	25°C	0,0589	0,828	9,5	0,993
0-630 μm	2 cycle	25°C	0,0516	0,843	9,4	0,991
0-630 μm	1 cycle	45°C	0,0569	0,850	10,5	0,998
0-630 μm	2 cycle	45°C	0,0602	0,845	16,3	0,997

Two cycles of adsorption – desorption have been made at 25 and 45°C. At 25°C as at 45°C, the two successive adsorption or desorption isotherms present no differences. After adsorption and desorption for the first and the second cycle, at ERH=0%, the product is completely dried, figure 7 and 8.

The value of M_m and C are independent of the number of cycle at 25 as at 45°C.

So, at 25 and 45 °C, the same phenomena of hydration are involved in the first and second cycles of sorption and no water is retained by the components of semolina. To conclude, no irreversible structural or biochemical change due to hydration, which could alter the capacity of sorption, could be observed at 25 or 45°C.

CONCLUSION

The purpose of this work was to determine the mechanisms of semolina hydration to have a better control of water uptake and drying of semolina.

Independently of the particles size, semolina presents type II sorption isotherms with a reversible hysteresis as numerous wheat derivative, flour, starch, gluten and natural high polymers such as proteins, starch and cellulose [6].

Components of semolina in relation with water swell, but not react in an irreversible way. For this reason, semolina can be considered as a chemically inert solid for water, during sorption, as numerous food products, in a range of temperature between 25 and 45°C.

So, the phenomenon of hydration is essentially physical. Since semolina has no intragranular porosity, two conclusions can be made. First, no water can accumulate into pores. Thus, the capacity of sorption is only determined by the biochemical composition. Secondly, after spreading, the distribution of water into the particle is a diffusional mechanism. Hence, the physical properties of the solid influence only the kinetics of sorption.

The mechanism of sorption can be divided into three main parts. For $ERH < 6\%$, water linked with the most hydrophilic components form a monolayer with the slowest kinetics of sorption. Subsequently, multilayers overlay the first one faster. Finally, for $ERH > 80\%$, water in the particle is mobile. In this part, the kinetics of sorption are the fast.

The particles size influences the kinetics this can be explained by physical consideration: the smaller the particles, the faster sorption kinetics. The temperature accelerates the kinetics of sorption. We can assume that increasing temperature facilitates diffusion and may increase the reactivity of semolina components.

This knowledge on the hydration capacity and kinetics and on the interactions solid / liquid will be used in granulation process in terms of amount of water added, mixing conditions and time required to have an homogeneous system.

Furthermore, the physico-chemical transformations during couscous manufacturing process should also modify the hydration properties. So, an evaluation of such transformation could be made by the sorption properties of couscous.

NOMENCLATURE

B.E.T : Bruner, Emmett, Teller

C : B.E.T. constant

EMC : equilibrium moisture content of grain

ERH : equilibrium relative humidity of the air

G.A.B. : Guggenheim – Anderson – de Boer

IUPAC :International Union of Pure and Applied Chemistry

m_{H_2O} : molecular weight of water (18 g / mol)

d.m. : dried mass (g)

$(P_w^v)_{sy}$: 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

REFERENCES

- [1] F. Rouquerol, J. Rouquerol, and K. Sing, Adsorption by powders and porous solids, principles methodology and applications, Academic press, 1999
- [2] Kaups S.M. and Walker C.E., Couscous in North Africa. *Cereal Foods World*, 31: 179, 1986..
- [3] Guezlane L., Selselet-Attou G., and Senator A., Etude comparée du couscous de fabrication industrielle et artisanale. *Ind. Cereales*, 43: 25, 1986.
- [4] Bushuk W. and Wikler C.A., Sorption of water vapor on wheat flour, starch, and gluten. *Cereal Chem.*, 34: 73-86, 1957.
- [5] Lomauro C.J., Bakshi A.S., and Labuza T.P., Moisture transfer properties of dry and semimoist foods. *J. Food Sci.*, 50: 397-400, 1985.
- [6] Riganakos K.A. and Kontominas M.G., Study of water sorption of flours (wheat and soy) using a hygrometric method: effect of relative humidity during heat treatment. *Z. Lebensm. Unters. Forsch.*, 204: 369-373, 1997.
- [7] Riganakos K.A., Demertzis P.G., and Kontominas M.G., Gas chromatographic study of water sorption by wheat flour. *J. Cereal Sci.*, 9: 261-271, 1989.
- [8] Pilosof A.M.R., Boquet R., and Bartholomai G.B., Kinetics of water uptake by food powders. *J. Food Sci.*, 50: 278-279, 282, 1985.
- [9] Bhattacharya S., Kinetics of hydration of raw and roasted corns semolina. *J. Food Eng.*, 25: 21-30, 1995.
- [10] Elizalde B.E., Pilosof A.M.R., and Bartholomai G.B., Empirical model for water uptake and hydration rate of food powders by sorption and Baumann methods. *J. Food Sci.*, 61: 407-409, 1996.
- [11] T.P. Labuza, A. Kaanane and J.Y. Chen, Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods, *Journal of food science*, 50, 385- 391, 1985
- [12] A. Hébrard, D. Oulahna et al., Etude morpho-granulométrique et structurale des semoules de blé dur- Propriétés d'hydratation et d'agglomération, en cours de publication.
- [13] N.H. Dural and A. L. Hines, Adsorption of water on cereal bread type dietary fibers, *Journal of food engineering*, Vol. 20,17-43, 1993
- [14] D.S. Chung and H.B.Pfost, Adsorption and desorption of water vapour by cereal grains and their products - part I : heat and free energy changes of adsorption and desorption, *Transactions of the Asae*, 549-551, 1967
- [15] D.W. Sun and J.L. Woods, The moisture content / relative humidity equilibrium relationship of wheat - a review, *Drying technology*, 11(7), 1523-1551, 1993
- [16] A. Roman-Gutierrez, J. Abecassis, B.Cuq, Facteurs physico-chimiques des propriétés d'hydratation des farines, *Industries des céréales*, 114, 11-13, 1999
- [17] J.C. Benezet, D. Oulahna, A. Hébrard, Etude par analyse thermique et microcalorimétrique de l'hydratation des semoules, en cours de publication.