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Impacts of the size distributions and protein contents of the native wheat powders in their structuration behaviour by wet agglomeration

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Abstract – The control of the wet agglomeration processes of powders depends on the contribution of the characteristics of the native powders. The objective of this work is to specifically investigate the contribution of the size distribution ($d_{50}$ and span) and composition (the protein contents) of the native particles, on the dimensional and structural characteristics of the wet agglomerates. Different fractions of native semolina with contrasted size properties ($d_{50}$ and span) and protein content are used as raw materials. The wet granulation is conducted using a low shear granulator and liquid spraying condition at constant dimensionless spray flux. The structure properties are evaluated by the distribution of the measured values of the size, water content and compactness. We observed specific effects of the span and the median diameter of native powders on the size distributions of the wet agglomerates. Using small native particles ($d_{50} < 250 \mu m$) improves the homogeneity of the size distributions. Using slightly dispersed native particles (span < 1.0) leads to a better uniformity on the size distributions. Using semolina with high protein content could lead to a narrow size distribution by limiting the process of fragmentation and the formation of fragments in the bed. We showed that the mechanisms involved in the agglomeration process are similar whatever the size distribution and the protein content of the native powders.

Keywords – Wet agglomeration mechanisms; size distributions; protein contents; hydrotextural approach
1. Introduction

The wet agglomeration process is broadly used in a wide range of industrial applications (e.g. food processing, pharmaceutical industry, chemical and civil engineering, etc.). This process is used to increase the diameter of particles by adding a wetting liquid and mechanical energy to promote attractive interactions and mobility (Iveson et al., 2001). The wet agglomeration mechanisms present a multifactorial inference of many interacting variables, responsible of the process complexity (Benali et al., 2009; Palzer, 2011). The knowledge and the modelling of mechanisms involved in the agglomeration processes widely progressed since about twenty years (Sanders et al., 2009; Washino et al., 2013). The twin product/process approaches, developed within the framework of science and technology of powders, allow purposing dimensional and process control tools, which help to solve the industrial challenges (Hapgood et al., 2009; Mangwandi et al., 2012). These approaches improve very effectively empiricism even guided by the experimental designs.

The development of population balance approaches have allowed ensuring a complete prediction of the size distribution of the agglomerates (Gerstlauer et al., 2006; Tan et al., 2005). This approach remain based on a simplified phenomenology and very dependent on the capacity to estimate the values of the kernel coefficients (Braumann et al., 2010). The increase of the size is relatively well mastered at lab scale and it is possible to predict values such as the median diameter of the agglomerates.

The investigation of the agglomeration mechanisms also requires taking into consideration the changes in the morphology or the hydro-textural characteristics of the agglomerates, such as the compactness or the sphericity. Among the multiple phenomena occurring simultaneously during the wet agglomeration, how to identify a priori the limiting phenomenon or the preferential reactive mechanisms?

The wet agglomeration process requires the addition of water to generate capillary bridges, which promotes the cohesion between particles. Agglomeration mechanisms result from the spatial arrangement of the native particles with the binder components, promoting attractive interactions and links. The contribution of liquid bridges between native particles largely overtakes the physical forces and the van der Waals interactions (Hapgood et al., 2003). For food powders, besides the contribution of physical phenomena, the mechanisms also depend on the physicochemical reactivity of the molecules, which strengthens the adhesion forces between particles, by adding a significant contribution of the viscous forces (Cuq et al., 2013). When the food powders are hydrated, some of their molecules are able to undergo
irreversible physicochemical changes, such as solubilisation. The molecules have the capacity to establish with the surrounding molecules low energy interactions including hydrogen bonds, hydrophobic interactions, or ionic interactions. For examples, the wheat proteins can establish continuous macromolecular network when subjected to water addition and mixing, that contribute to irreversible mechanisms (Abecassis et al., 2012).

The couscous grains, a typical Mediterranean foodstuff, are produced by agglomeration process from durum wheat semolina. Recent works demonstrated different modes of agglomerate morphogenesis during the wet agglomeration of durum wheat semolina to produce couscous grains (Barkouti et al., 2014; Hafsa et al., 2015; Saad et al., 2011).

Agglomeration mechanisms developed during the wetting/mixing of durum wheat semolina generated differences in agglomerated structures. Their multiplicity leads to a very large polydispersity of the size of the wet agglomerates. This is at the origin of the very high ratio (up to 60%) of out of scope of wet agglomerates (too large or too small) that are observed during the industrial processing of the couscous grains. A narrow size distribution of the agglomerates is one of the main quality criteria for the elaboration. The quantification of the fluctuations in these parameters around their mean values stays a challenge.

Only few works deal to describe the influence of the characteristics (size distribution and protein content) of native semolina on the wet agglomeration process, in order to investigate the specific contributions of the physical and biochemical mechanisms. Lefkir et al. (2017) have compared the ability of three different durum wheat semolina of industrial quality to be agglomerated. The yield of the wet agglomeration was significantly affected by the characteristics of native semolina, although it was not possible to know if it was an effect of the protein content or of size distribution of the semolina.

The aim of this work is to describe the wet agglomeration mechanisms by analysing the experimental investigations, to understand how the initial characteristics (particle-size distribution and protein content) of the native durum wheat semolina impact the characteristics of the wet agglomerates. Experiments were conducted using different durum wheat semolina, with different size characteristics or protein contents. The wet agglomeration process was conducted by using a low shear mechanical mixer. Wet agglomerates are considered as multiphase media described as a solid granular matrix that could be saturated or unsaturated by two fluids: liquid and gaseous phases (Rondet, 2008; Ruiz et al., 2011). The hydro-textural states of the wet agglomerates are defined by the distribution of the values of water content (w), compactness (ϕ) and saturation degree (S).
2. Material and methods

2.1. Raw material

Durum wheat semolina of industrial quality (Panzani group, France) was used as "standard semolina". Four fractions of semolina with different particle size distributions were obtained by sieving the standard semolina over a column of 2 metallic sieves (0.315 and 0.25 mm). The fraction called "small semolina" was collected under the 0.25 mm sieve. The fraction called "low span semolina" was collected between the two sieves (0.25 and 0.315 mm). The fraction called "very coarse semolina" was collected over the 0.315 mm sieve. In addition, the fraction called "coarse semolina" was collected over the 0.25 mm sieve, after sieving the standard semolina over only one sieve at 0.25 mm. Three durum wheat semolina with different protein contents (called "very low protein semolina", "low protein semolina", and "high protein semolina") were also selected. These semolina were produced according to a standard milling process, using the durum mill pilot plant facility of the technological platform of the UMR IATE (Montpellier), from three different specific durum wheat grains (Miradoux, Daktar and Anvergur, respectively) produced in 2015 by the UMR AGIR (Toulouse) under the ANR Dur-Dur research project. All the semolina were stored in hermetic containers at 4°C until experiments.

The selected semolina were characterized using standardized methods (Table 1). The water content was determined according to the approved method 44-15A (AACC, 2000), by weighing after oven drying at 105°C for 24 h. The particle size distributions and their characteristics values ($d_{10}$, $d_{50}$ and $d_{90}$) were measured by a laser particle size analyser (Coulter TMLS 230, Malvern, England) at room temperature. The true density ($\rho_s$) was measured by using an nitrogen pycnometer. The total nitrogen content (TN) of semolina was determined by the Kjeldahl method, and the crude protein content was calculated according to TN x 5.7 based on the AFNOR method V 03-050 (AFNOR, 1970). All experimental measurements were carried out in triplicate.

The selected raw materials allow studying separately the effects of selected variables (median diameter, span, or protein content) to understand the effects of the physical and biochemical characteristics of the native particles on the wet agglomeration mechanisms.

2.2. Wet agglomeration process
The wet agglomeration of durum wheat semolina was carried out in a horizontal low shear mixer (Sercom, France) composed by a mixing a horizontal shaft axis positioned at 6.7 cm from the bottom of the tank (30 cm length, 11.5 cm width, 16.5 cm height), with 14 metal rotating paddle blades (4 cm length, 2 cm width, 7.5 cm gap between 2 blades) (Fig. 1). The direction of rotation of the shaft axis was inverted every 20 seconds to improve the effects of mixing and homogenization of the powder. The process can be qualified as low shear mixer because the mixing conditions do not lead to shear stresses as intense as those sitting within high shear mixers (Rondet et al., 2012).

A sample of 780 g of semolina was introduced in the mixing tank and first mixed for 2 min at constant mixer arm speed (100 rpm) to equilibrate the temperature at 20°C. The wet agglomeration was conducted at 100 rpm. Water was directly sprayed over the semolina under mixing, using a single-fluid atomizing system (Spraying Systems Co., France, ref. TPU 6501) to produce a flat spray of droplets. The flat spray nozzle was either connected to a regular water supply network with a stable pressure or to a peristaltic pump (520S/REM, Watson Marlow, France) in order to control the liquid flow rate. The water addition flow rate was 2.10^{-6} \text{m}^3\text{s}^{-1} and the diameter of droplets of water was estimated at 242 \mu m according to Mandato et al. (2012). The calculated d_{50\text{semolina}}/d_{50\text{droplet}} ratio was found to range between 0.5 when using the small semolina, and 1.6 when using the very coarse semolina. These process conditions induced a value of the dimensionless spray flux (\psi_a) close to 0.1 (Litster et al., 2001). Taking into consideration the characteristics of the liquid and the native powders, the ratio of drop penetration time to granular circulation time was estimated close to 0.01, whatever the semolina tested. When depicting these values on the nucleation regime map (Hapgood et al., 2003), the nucleation regime could be located just near the drop controlled zone.

The spraying time (about 2 min) was adjusted with respect to the targeted water content of the wet mass (0.45 g water/g dry matter). After the water addition step, a mixing stage at 100 rpm for 10 minutes was conducted to homogenize the entire wet mass. Samples of the wet agglomerates were collected immediately after the end of the mixing step.

### 2.3. Agglomerates characterization

**Size distribution** - Size distribution of the wet agglomerates was measured immediately after completing the wet agglomeration process. Samples of 250 g were collected and sieved over
a column of eleven metallic sieves of decreasing mesh $D_j \in (2, 1.25, 0.9, 0.8, 0.71, 0.63, 0.5, 0.4, 0.315, 0.25, \text{and} 0.160 \text{ mm})$ to separate the different structures. The subscript $j$ refers to the sieve number according to the mesh openings. The sieve column was manually shaken for 2 min. The size distribution was obtained by weighing the mass of the products collected on each sieve. The weight distribution according to size criteria was expressed as the percent of total weight. Measurements were conducted in triplicate. Immediately after sieving, products were sampled from the remaining on the sieves with 2, 1.25, 0.9, 0.8, 0.71 mm mesh openings, and are then characterized by their water content ($w_j$) and compactness ($\phi_j$).

**Water content** - The water content (g water / g dry matter) of wet agglomerates was determined on 3-5 g samples, by a drying method in an oven (RB 360, WC Heraeus GmbH, Hanau, Germany) at 105°C for 24 h (AACC Method 44-15A). Mean values were determined from triplicate.

**Compactness** - The compactness (i.e. the solid volume fraction: $\phi = \rho_s/\rho_s^*$) of wet agglomerates was determined on about 1 g samples, according to Rondet et al. (2009). The solid apparent density of the wet agglomerates ($\rho_s$) was measured by using a hydrostatic balance with paraffin oil, which ensures the wet agglomerates without penetrating them.

**Saturation degree** - The saturation degree is the ratio of the liquid volume to the pore volume of agglomerates: $S = V_w/(V - V_s)$, where $V_s$ and $V_w$ are respectively the volume of the solid phase and the volume of the liquid phase, in the apparent volume $V$ of the agglomerate.

### 2.4. Statistical analysis

The statistical significance of results was assessed using single factor analysis of variance (ANOVA). Multiple comparisons were performed by calculating the least significant difference using Microsoft Excel 2010, at a 5% significance level.
3. Results

3.1. Agglomeration of standard semolina

In the investigated experimental conditions (mean water content \( \bar{w} = 0.44 \)), the wet-agglomeration process of the standard semolina gives the size distribution of wet agglomerates depicted in Figure 2. The wet agglomerates are characterized by a large dispersion in size, from 200 to 2500 µm. The shape of the curve of the particle size distribution is clearly not unimodal, with the formation of different structures at characteristics diameters.

The water content and compactness of the wet structure (with diameter up to 710 µm) were measured for each class as a function to their diameter (Fig. 3). The water content of the wet structures was positively linearly correlated with their diameter (Fig. 3a). The compactness of the wet agglomerates was negatively linearly correlated with their diameter (Fig. 3b). Previous works have already demonstrated that in almost comparable process conditions, the agglomeration growth of semolina to produce couscous grains leads to increasing water content and decreasing compactness, according to an increase in the median diameters of the structures (Barkouti et al., 2014; Bellocq et al., 2017; Rondet et al., 2010; Saad et al., 2011).

In the present study at unique process water content, we observe that the structures obtained on the different sieves are characterized by the same trend.

Taking into consideration the specific shape of the particle distribution curve (Fig. 2) and the hydrotectural characteristics (Fig. 3) of the wet agglomerates of standard semolina, it makes possible to distinguish different types of structures according to their diameter (Benali et al., 2009; Iveson et al., 2001; Saad et al., 2011). The small structures (diameter < 0.5 mm) are the "native particles of semolina". Their water content is low and remains always smaller than the capillary condensation water content (0.21). The small structures can also contain slight amounts of fragments of the larger structures that could be generated by the mechanical erosion of larger structures due to the shear stresses during the wet-agglomeration. The structures called "fragments" (diameter close to 0.55 mm) are obtained by the breakage of the very large dough pieces due to the mechanical stress during process. The structures called "nuclei" (diameter between 0.63 and 0.9 mm) are structures obtained by primary association of the native semolina particles. The structures called "agglomerates" (diameter between 0.9 and 2 mm) are obtained by the association of fragments and/or nuclei. Their water contents are located between the values of capillary condensation (0.21) and the plastic limit \( w_p = 0.59 \) of durum wheat semolina. The very large structures (with diameter > 2.5 mm) are
called "the dough pieces". Their water content is higher than the plastic limit ($w_p$) of the semolina. The plastic limit is defined as the water content at which the sample maintains any applied deformation (Atterberg, 1911). The water content is then enough high to ensure their saturation (Rondet et al., 2013).

The weight proportion of these different fractions is presented in Table 2. The amount of the agglomerates is relatively low (only 27.2%). Similar low values are classically observed during the wet-agglomeration stage and are typical of the low process efficiency of the manufacture of the industrial couscous grains (Abecassis et al., 2012).

3.2. Influence of the diameter and the span of native particles

We investigated the impact of the size characteristics of the native particles, on the wet agglomeration mechanisms by testing the selected raw materials with different values of median diameter and/or span (Table 1). Experiments were conducted at similar mean water contents. These selected semolina were characterized by almost constant values of protein contents (between 12.3 and 13.0%). The wet-agglomeration process generates different curves of size distribution of the wet agglomerates as depicted in Figure 4. Whatever the characteristics of the raw materials, the wet structures are characterized by a large diversity in size and the curve of particle size distribution remain not unimodal.

The impacts of the median diameter or of the span on the weight fractions of the different structures (particles, fragments, nuclei, agglomerates, and dough pieces) are presented in Table 2. For each experiment, these different structures were also characterized by their water content and compactness as a function to their diameter (Fig. 5).

The impact of the span of the semolina (at similar median diameter) can be described by comparing the results obtained with the standard semolina and the low span semolina (Table 1). Using these two semolina with different span values (1.51 and 0.92) and almost similar median diameter (287 and 282 µm) generates similar wet agglomeration conditions according to the value of the diameter ratio ($d_{50\text{semolina}} / d_{50\text{droplet}} = 1.2$).

The present results demonstrated a significant effect of the span of the semolina on the weight fractions of the different structures (Table 2). The distributions of the hydrotextural properties (water content and compactness) as a function of the size are in the same range (Fig. 5). Besides, the homogenization of the population of native particles around the median diameter (i.e. lower span) seems to lead to a strong decrease of the population of the "small particles" and of the "fragments" for the benefit of "nuclei" (Table 2). This result suggests
that the process of nucleation/growth is favoured. The conditions in which it takes place still lead to the formation of "dough pieces" and to lower contents of "agglomerates".

The impact of the **median diameter** of the semolina (at almost similar span) can be investigated at low values of span or at high values of span. The comparison of the small semolina ($d_{50} = 129 \mu m$) and the standard semolina ($d_{50} = 287 \mu m$) is done at similar high values of span (1.58 and 1.51) (Fig. 4a). The comparison of the results obtained with the low span semolina ($d_{50} = 282 \mu m$), the coarse semolina ($d_{50} = 339 \mu m$), and the very coarse semolina ($d_{50} = 393 \mu m$) is done at similar low values of span (0.92, 1.02, and 0.77) (Fig. 4b).

Using these semolina generates very different wet agglomeration conditions, according to values of the diameter ratio ($d_{50\text{semolina}} / d_{50\text{droplet}}$) with values ranging from 0.5 to 1.6.

The decrease of the $d_{50}$ of the semolina leads to an increase of the population of "agglomerates" and to a decrease of the population of "dough pieces". Experiments carried out using the semolina with the smallest median diameter (small semolina) induced the disappearance of the population of "fragments" (Table 2). This result suggests that the process of nucleation/growth seems exclusive. Indeed, when drops of water are larger than the native particles (ratio $d_{50\text{semolina}} / d_{50\text{droplet}} = 0.5$), the nucleation is essentially controlled by the size of the drops, which aggregate the particles. The nuclei generated by this way join themselves and give more compact agglomerates (Fig. 5) with a better yield, as far as the production of dough pieces is strongly limited. These two different modifications of the semolina population follow preferentially the nucleation/growth mechanism in comparison to the mechanisms of dough formation/fragmentation. The ratio $d_{50\text{semolina}}/d_{50\text{droplet}}$ plays an important role in the nucleation regime which is here a “drop-controlled” and corresponds to a situation where the drop size controls preferentially the nucleation (Hapgood et al., 2003).

Experiments carried out using the semolina with the largest median diameter (low span semolina, coarse semolina, and very coarse semolina) were realized at high values of the ratio $d_{50\text{semolina}}/d_{50\text{droplet}}$ (up to 1). The increase of the diameter of semolina then generates a small increase in the weight fraction of the "dough pieces". The strongest trend comes from the increase of the weight fraction of the "fragment" in relation to the decrease of the weight fraction of the "nuclei". The increases of the weight fractions of "dough pieces" and "fragments", which have a pasty structure ("fragments" arising from the break of the "dough pieces"), induce lower compactness and higher water content than the other configurations (Fig. 5). These results indicate that the process leads to a higher heterogeneity in the agglomerated structures, due to the increase in the median diameters of the native particles.
3.3. Influence of the protein content of semolina

We investigated the impact of the protein content (between 7.7 and 13.8%) of the native semolina on the wet agglomeration mechanisms by comparing three raw materials (Table 1). The experiments were conducted at similar mean water content ($\bar{w} = 0.44$) and at almost similar values of median diameter (227 to 262 µm) and span (1.25 to 1.13) of semolina. The wet agglomeration process generates different curves of the size distribution of the wet agglomerates as depicted in Figure 6. Whatever the protein content, the wet agglomerates are characterized by a large diversity in size, and the curve of particle size distribution remain not unimodal.

The impacts of the protein content of the native semolina on the weight fractions of the different structures (small, fragments, nuclei, agglomerates, and dough pieces) are presented in Table 2. For each experiment, the different structures are also characterized by their water content and compactness as a function to their diameter (Fig. 7).

We observe a slight difference in the particle size distribution curve obtained with the three native semolina, which have different protein content (Fig. 6). The weight fractions of each wet structures remain very close to each other using the very low, low and high protein contents semolina. The hydrotextural characteristics of the wet structures (Fig. 7) are also similar as a function of the values of protein content of the native semolina. We can note that the high protein semolina slightly favours the population of "nuclei" and "agglomerates". "Fragments" are almost inexistenct and the amount of “dough pieces” is slightly lower by using the high protein semolina. This result suggests that the process of fragmentation is restricted. These effects could be explained by the fact that proteins would promote semolina particles stickiness and limit the process of fragmentation. Nevertheless, changes in the protein content of semolina do not appear to have a significant influence on wet agglomeration mechanisms and the contribution of biochemical mechanisms does not therefore appear to be dominant.
4. Discussion

4.1. Mechanisms of the wet-agglomeration of semolina

By reporting on a hydrotextural diagram all the experimental values of water content and compactness for the different structures produced by the wet-agglomeration process (Fig. 8), we observe that structures on each sieve follow the saturation curve (Ruiz et al., 2011). For each structure, the saturation degree is equal to 1.

Figure 9 depicts the hydrotextural diagram of the wet-agglomerates obtained for the experiments using the different semolina. Results show that the different collected structures also follow the saturation curve, which means that the saturation degree is equal to 1. Changing the size characteristics of semolina or the protein content of semolina does not change the position of the experimental data on the saturation curve.

The present work demonstrates that the mechanisms leading to these agglomerated structures are different from those found in previous studies. As described by Saad et al., (2011), an agglomeration mechanism of nucleation/growing takes place, but mechanisms of dough formation/fragmentation are also observed (Iveson et al., 2001).

Previous works in semolina agglomeration highlighted that the follow-up of both the textural and characteristic length (i.e. the diameter) of agglomerates allowed us identifying a fractal morphogenesis process (Barkouti et al., 2014; Rondet et al., 2010). The suggested model describing fractal growth of agglomerates can be written as: \( \phi = \phi_N \left( \frac{d_{50}}{d_{50N}} \right)^{Df-3} \), where \( Df \) was the fractal dimension of the generated agglomerates; \( d_{50} \) was the median diameter of the agglomerate population, \( \phi_N \) and \( d_{50N} \) were respectively the solid volume fraction and the median diameter of the nuclei (Rondet et al., 2010). Fractal structure of agglomerates elaborated by a wet agglomeration process had ever been highlighted (Pashminehazar et al., 2016; Turchiuli and Castillo-Castaneda, 2009). In the case of a fractal growth, this particular process involves nuclei association by homothetic scale up, where nuclei constitute the elementary structure of the generated agglomerates. Nuclei were identified after sieving and optical microscopy observations. Their median diameter and solid volume fraction were determined. This analyse is purposed to characterise the agglomerates.

Because small range of water contents has been explored, the present data are not completely related to growing mechanisms. The fractal dimension had been calculated: \( Df \sim 3 \). This value, which is an integer, is the fact of saturation. It indicates that agglomerate could be assimilated to geometrical structures in which nuclei do not play the role of a base unit.
The agglomeration mechanism of nucleation/growth, which takes place here, occurs in three major stages. (i) The nucleation stage is both depending on wetting/mixing parameters with physicochemical properties of fluid and surface particle (Ax et al., 2008; Chouk et al., 2009; Iveson et al., 2001). (ii) The growing stage could be described as the formation of large grains by the association of several nuclei following a fractal morphogenesis (Rondet et al., 2010; Saad et al., 2011). (iii) The “pasting” stage occurs by adding water and leads to the transformation of the agglomerates in dough pieces through percolation (Rondet et al., 2013; Ruiz et al., 2011). The transformation of agglomerates in dough structures results in a considerable increase in grain size and biochemical changes with the formation of partial dough structures involving the proteins inside the grains. The percolation mechanisms could be described as the formation of very large structures by hydration and adhesion. It can be associated with a mechanical deformation of large agglomerates to generate some dough pieces, when the water content is close to the plastic limit. The compactness of the dough pieces is smaller than that of agglomerates and nuclei (Fig. 8). These structures could exhibit stronger strain, and when they are maintained in condition of agitation within a bed of more compact particles, is going to favour their disintegration. This situation takes place generally in high shear mixer conditions, where the shear stress field does not allow the stability of dough (Iveson et al., 2001). The breakage mechanisms generate small-sized fragments, which are strengthened as observed on the size distribution curve (Fig. 2). Besides their slightly lower size, the difference with nuclei comes because having been very hydrated, they have a dough texture, whereas nuclei is made by associations of semolina particles. Fragments have lower water content and higher compactness than dough pieces, due to the strengthening of their structure during the mechanical agitation. As explained by Wade et al. (Wade et al., 2015) and Rondet et al. (Rondet et al., 2016), the breakage mechanism of dough pieces is able to generate granules with high intragranular compactness, due to the complete filling of intra-particle pores by the binder liquid, but the addition of further powders can reduce the liquid saturation of the granules. So generated, fragments can interact with nuclei and contribute to build agglomerates with the same growing mechanism as ever described. This paste/fragmentation mechanism could be compared to a nucleation by downsizing, by difference with the "classic" nucleation, which is a bottom-up mechanism (Iveson et al., 2001). We can notice that this phenomenon could be totally developed in low shear mixer to generate agglomerates (Rondet et al., 2016). In the case of this study, the spray process conditions associated to mixing process conditions generate a very significant population of
dough pieces (Fig. 2). It occurs here a concomitant paste/fragmentation mechanism, which
generates fragments, associated to nuclei in the growing process.

As mentioned in Barkouti et al. (2014), to identify the major mechanisms contributing to the
structure layout during the growing stage, it seems interesting to combine the fluctuations of
water content and compactness standard deviations. Figure 10 shows that for all the
structures considered fluctuations of compactness and water content are correlated, whatever
the semolina used as raw materials. Indeed, if the different types of structures (discriminated
by size, water content, and compactness) are interacting by binding, the fluctuations of
hydrotextural values would be independent. Nuclei and fragments contribute to the primary
step of growing. Then, the correlation results can be interpreted as the fact that the
agglomerates grow thanks to the association of structures that belong to the same category in
terms of hydro-textural characteristics. As hydrotextural properties are related to structural
size, the association law is based on an association by both size-class. However, as ever
mentioned, the structures are poorly fractal.

4.2. Specification of durum wheat semolina for wet agglomeration

The present results allow proposing some specifications for the durum semolina used for the
production of the couscous grains by the wet agglomeration process. The protein content
does not appear to be a significant factor impacting the wet agglomeration mechanisms. We
have only observed slight changes in the wet agglomeration process when using semolina
between 7.7% and 13.8% protein content. It was thus not possible to define a specification of
the protein content to control the wet agglomeration mechanisms. This work will have to be
completed by investigating the impact of the protein content of semolina on the final quality
of the couscous grains.

On the other hand, the size characteristics of the native semolina significantly affect the wet
agglomeration mechanisms. Changing the median diameter or the span of the native semolina
generates large impact of the agglomeration yields. The higher amount of the fraction of
agglomerates with diameter ranging between 1 and 2 mm was obtained when using semolina
with low median diameter and low span. Additional work will be conducted to evaluate the
impact on the final quality of the couscous grains.
5. Conclusion

This work deals with the study of the impact of particle-size distribution and protein content characteristics of semolina on the wet agglomeration process. The results demonstrate that the span and the median diameter of the native powder have a significant influence. As the median diameter increases, the ratio of the dough pieces and fragments in the bed increases and the ratio of nuclei and agglomerates decreases. The impact of the protein content is lower. The different structures generated by the agglomeration process result from two major modes of agglomeration: nucleation/growing and dough formation/fragmentation. We show that structures as nuclei or fragments could be individually identify because they differ essentially from their hydrotextural properties. An increase in the amount of dough pieces leads to an increase in the fragments and an increase of the polydispersity of the structures. The configuration leading to the higher amount of the agglomerates population corresponds to the low diameter semolina. The relative size of native particles is the major parameter to modulate the formation of the fragments. In the same way, semolina with higher protein content could strengthen the structure by favouring the stickiness between the semolina particles. The process of fragmentation is limited and the ratio of fragment in the bed decreases.

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Fig. 1. Sketch of the horizontal low shear mixer equipment.
Fig. 2. Distribution curve of the weight fractions as a function of the diameters of the wet agglomerates produced by the wet-agglomeration process of standard semolina.
Fig. 3. Distribution curves of the measured values of water content (a) and compactness (b), as a function of the diameter of the structures produced by the wet-agglomeration process of standard semolina.
Fig. 4. Impact of the (a) median diameter at constant span (small semolina) and the span at constant median diameter (low span semolina) and (b) of the median diameter (at constant span) of the native semolina, on the distribution curves of the weight fractions as a function of the diameters of the wet agglomerates produced by the wet-agglomeration process.
**Fig. 5.** Impact of the median diameter or diameter span of the native semolina on the distribution curves of the measured values of water content (a) and compactness (b), as a function of the diameter of the wet agglomerates produced by the wet-agglomeration process of different semolina. The dotted line is the value of the standard semolina.
Fig. 6. Impact of the protein content of the native semolina on the distribution curves of the weight fractions as a function of the diameters of the wet agglomerates produced by the wet-agglomeration process.
Fig. 7. Impact of the protein content of the native semolina on the distribution curves of the measured values of water content (a) and compactness (b), as a function of the diameter of the wet agglomerates produced by the wet-agglomeration process of different semolina. The dotted line is the value of the standard semolina.
Fig. 8. Hydrotextural diagram of the different structures collected on each sieve after the wet agglomeration of standard semolina.
Fig. 9. Hydrotextural diagram of the different structures collected on each sieve after the wet agglomeration of semolina with different size distributions (a) or with different protein contents (b).
Fig. 10. Variations of compactness standard deviation of agglomerates according to water content standard deviation for all trials.
Figure captions

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Fig. 6. Impact of the protein content of the native semolina on the distribution curves of the weight fractions as a function of the diameters of the wet agglomerates produced by the wet-agglomeration process.

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Fig. 8. Hydrotectural diagram of the different structures collected on each sieve after the wet agglomeration of standard semolina.

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Fig. 10. Variations of compactness standard deviation of agglomerates according to water content standard deviation for all trials.
Table 1

Physical and biochemical characteristics of the different selected durum wheat semolina.

|                    | $d_{50}$ (μm) | Span (λ) | True density ($\rho^*$) (g/cm$^3$) | Water content (g/g dry matter) | Proteins content (g/100 g dry matter) |
|--------------------|--------------|----------|-----------------------------------|-------------------------------|---------------------------------------|
| Standard semolina  | 287 (± 2)    | 1.51 (+/- 0.01) | 1.415 (± 0.003)                  | 0.173 (± 0.001)               | 12.4 (± 0.1)                           |
| Low span semolina  | 282 (± 2)    | 0.92 (+/- 0.04) | 1.447 (± 0.004)                  | 0.160 (± 0.004)               | 12.7 (± 0.1)                           |
| Small semolina     | 129 (± 1)    | 1.58 (+/- 0.02) | 1.461 (± 0.003)                  | 0.157 (± 0.001)               | 13.0 (± 0.1)                           |
| Coarse semolina    | 339 (± 2)    | 1.02 (+/- 0.01) | 1.451 (± 0.006)                  | 0.139 (± 0.001)               | 12.4 (± 0.2)                           |
| Very coarse semolina | 393 (± 1)  | 0.77 (+/- 0.00) | 1.453 (± 0.002)                  | 0.161 (± 0.001)               | 12.3 (± 0.1)                           |
| Very low protein semolina | 227 (± 3) | 1.13 (+/- 0.02) | 1.462 (± 0.003)                  | 0.178 (± 0.001)               | 7.7 (± 0.1)                            |
| Low protein semolina | 234 (± 3)  | 1.14 (+/- 0.02) | 1.448 (± 0.003)                  | 0.177 (± 0.001)               | 9.4 (± 0.1)                            |
| High protein semolina | 262 (± 3)  | 1.25 (+/- 0.02) | 1.458 (± 0.003)                  | 0.180 (± 0.001)               | 13.8 (± 0.1)                           |

Values are means (± standard deviation).

Values in column with the same letter were not significantly different (P<0.05).
Table 2

Impact of the characteristics of the native semolina on the weight fractions of the different structures produced during the wet agglomeration process.

| Weight fractions of the different structures after agglomeration | Small | Fragments | Nuclei | Agglomerates | Dough pieces |
|---------------------------------------------------------------|-------|-----------|--------|--------------|--------------|
| Standard semolina                                             | 22.7 (± 1.5) | 12.5 (± 2.0) | 10.9 (± 10.6) | 27.2 (± 0.3) | 19.3 (± 2.2) |
| Small semolina                                                | 0.3 (± 1.2) | 0.3 (± 2.6) | 36.5 (± 4.9) | 41.1 (± 3.6) | 7.6 (± 1.4) |
| Low span semolina                                             | 3.7 (± 1.0) | 1.7 (± 0.8) | 41.0 (± 26.0) | 27.6 (± 3.4) | 17.0 (± 1.7) |
| Coarse semolina                                               | 13.9 (± 0.5) | 12.6 (± 6.5) | 12.2 (± 1.0) | 27.9 (± 2.6) | 22.1 (± 2.0) |
| Very coarse semolina                                          | 28.0 (± 0.4) | 18.1 (± 0.0) | 7.4 (± 0.2) | 18.8 (± 0.3) | 20.6 (± 1.9) |
| Very low protein semolina                                     | 9.5 (± 0.1) | 7.3 (± 0.4) | 21.1 (± 1.1) | 34.8 (± 0.9) | 21.5 (± 1.1) |
| Low protein semolina                                           | 13.2 (± 0.2) | 5.6 (± 0.3) | 22.1 (± 1.1) | 31.3 (± 0.8) | 22.2 (± 1.1) |
| High protein semolina                                          | 1.3 (± 1.6) | 1.1 (± 0.1) | 26.8 (± 1.3) | 35.4 (± 0.9) | 16.6 (± 0.8) |

Values are means (± standard deviation).

Values in column with the same letter were not significantly different (P<0.05).