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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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## Highlights

Span and median diameter of the native powder have a significant influence on the size distributions of the wet agglomerates.

A high protein content of the native semolina could lead to a narrow size distribution of the wet agglomerates.

Hydrotextural diagram is used to demonstrate specific growth mechanisms.

The different structures generated by the agglomeration process result from two major modes of agglomeration: nucleation/growing and dough formation/fragmentation.

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

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7  
8       **Abstract** – The control of the wet agglomeration processes of powders depends on the  
9       contribution of the characteristics of the native powders. The objective of this work is to  
10       specifically investigate the contribution of the size distribution ( $d_{50}$  and span) and  
11       composition (the protein contents) of the native particles, on the dimensional and structural  
12       characteristics of the wet agglomerates. Different fractions of native semolina with contrasted  
13       size properties ( $d_{50}$  and span) and protein content are used as raw materials. The wet  
14       granulation is conducted using a low shear granulator and liquid spraying condition at  
15       constant dimensionless spray flux. The structure properties are evaluated by the distribution  
16       of the measured values of the size, water content and compactness. We observed specific  
17       effects of the span and the median diameter of native powders on the size distributions of the  
18       wet agglomerates. Using small native particles ( $d_{50} < 250 \mu\text{m}$ ) improves the homogeneity of  
19       the size distributions. Using slightly dispersed native particles (span  $< 1.0$ ) leads to a better  
20       uniformity on the size distributions. Using semolina with high protein content could lead to a  
21       narrow size distribution by limiting the process of fragmentation and the formation of  
22       fragments in the bed. We showed that the mechanisms involved in the agglomeration process  
23       are similar whatever the size distribution and the protein content of the native powders.

24  
25       **Keywords** – Wet agglomeration mechanisms; size distributions; protein contents;  
26       hydrotextural approach

27

## 28 1. Introduction

29

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

42 The development of population balance approaches have allowed ensuring a complete  
43 prediction of the size distribution of the agglomerates (Gerstlauer et al., 2006; Tan et al.,  
44 2005). This approach remain based on a simplified phenomenology and very dependent on  
45 the capacity to estimate the values of the kernel coefficients (Braumann et al., 2010). The  
46 increase of the size is relatively well mastered at lab scale and it is possible to predict values  
47 such as the median diameter of the agglomerates.

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

53 The wet agglomeration process requires the addition of water to generate capillary bridges,  
54 which promotes the cohesion between particles. Agglomeration mechanisms result from the  
55 spatial arrangement of the native particles with the binder components, promoting attractive  
56 interactions and links. The contribution of liquid bridges between native particles largely  
57 overtakes the physical forces and the van der Waals interactions (Hapgood et al., 2003). For  
58 food powders, besides the contribution of physical phenomena, the mechanisms also depend  
59 on the physicochemical reactivity of the molecules, which strengthens the adhesion forces  
60 between particles, by adding a significant contribution of the viscous forces (Cuq et al.,  
61 2013). When the food powders are hydrated, some of their molecules are able to undergo

62 irreversible physicochemical changes, such as solubilisation. The molecules have the  
63 capacity to establish with the surrounding molecules low energy interactions including  
64 hydrogen bonds, hydrophobic interactions, or ionic interactions. For examples, the wheat  
65 proteins can establish continuous macromolecular network when subjected to water addition  
66 and mixing, that contribute to irreversible mechanisms (Abecassis et al., 2012).

67 The couscous grains, a typical Mediterranean foodstuff, are produced by agglomeration  
68 process from durum wheat semolina. Recent works demonstrated different modes of  
69 agglomerate morphogenesis during the wet agglomeration of durum wheat semolina to  
70 produce couscous grains (Barkouti et al., 2014; Hafsa et al., 2015; Saad et al., 2011).  
71 Agglomeration mechanisms developed during the wetting/mixing of durum wheat semolina  
72 generated differences in agglomerated structures. Their multiplicity leads to a very large  
73 polydispersity of the size of the wet agglomerates. This is at the origin of the very high ratio  
74 (up to 60%) of out of scope of wet agglomerates (too large or too small) that are observed  
75 during the industrial processing of the couscous grains. A narrow size distribution of the  
76 agglomerates is one of the main quality criteria for the elaboration. The quantification of the  
77 fluctuations in these parameters around their mean values stays a challenge.

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

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

95

## 96 2. Material and methods

97

### 98 2.1. Raw material

99 Durum wheat semolina of industrial quality (Panzani group, France) was used as "standard  
100 semolina". Four fractions of semolina with different particle size distributions were obtained  
101 by sieving the standard semolina over a column of 2 metallic sieves (0.315 and 0.25 mm).  
102 The fraction called "small semolina" was collected under the 0.25 mm sieve. The fraction  
103 called "low span semolina" was collected between the two sieves (0.25 and 0.315 mm). The  
104 fraction called "very coarse semolina" was collected over the 0.315 mm sieve. In addition,  
105 the fraction called "coarse semolina" was collected over the 0.25 mm sieve, after sieving the  
106 standard semolina over only one sieve at 0.25 mm. Three durum wheat semolina with  
107 different protein contents (called "very low protein semolina", "low protein semolina", and  
108 "high protein semolina") were also selected. These semolina were produced according to a  
109 standard milling process, using the durum mill pilot plant facility of the technological  
110 platform of the UMR IATE (Montpellier), from three different specific durum wheat grains  
111 (Miradoux, Dakter and Anvergur, respectively) produced in 2015 by the UMR AGIR  
112 (Toulouse) under the ANR Dur-Dur research project. **All the semolina were stored in  
113 hermetic containers at 4°C until experiments were carried out (less than 6 months to avoid  
114 significant changes).**

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

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

127

128

## 129 2.2. Wet agglomeration process

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

138 A sample of 780 g of semolina was introduced in the mixing tank and first mixed for 2 min at  
139 constant mixer arm speed (100 rpm) to equilibrate the temperature at 20°C. The wet  
140 agglomeration was conducted at 100 rpm. Water was directly sprayed over the semolina  
141 under mixing, using a single-fluid atomizing system (Spraying Systems Co., France, ref. TPU  
142 6501) to produce a flat spray of droplets. The flat spray nozzle was either connected to a  
143 regular water supply network with a stable pressure or to a peristaltic pump (520S/REM,  
144 Watson Marlow, France) in order to control the liquid flow rate. The water addition flow rate  
145 was  $2.10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$  and the diameter of droplets of water was estimated at 242  $\mu\text{m}$  according to  
146 Mandato et al. (2012). The calculated  $d_{50\text{semolina}}/d_{50\text{droplet}}$  ratio was found to range between 0.5  
147 when using the small semolina, and 1.6 when using the very coarse semolina. These process  
148 conditions induced a value of the dimensionless spray flux ( $\psi_a$ ) close to 0.1 (Litster et al.,  
149 2001). Taking into consideration the characteristics of the liquid and the native powders, the  
150 ratio of drop penetration time to granular circulation time was estimated close to 0.01,  
151 whatever the semolina tested. When depicting these values on the nucleation regime map  
152 (Hapgood et al., 2003), the nucleation regime could be located just near the drop controlled  
153 zone.

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

158

159

## 160 2.3. Agglomerates characterization

161 *Size distribution* - Size distribution of the wet agglomerates was measured immediately after  
162 completing the wet agglomeration process. Samples of 250 g were collected and sieved over

163 a column of eleven metallic sieves of decreasing mesh  $D_j \in (2, 1.25, 0.9, 0.8, 0.71, 0.63, 0.5,$   
164  $0.4, 0.315, 0.25,$  and  $0.160$  mm) to separate the different structures. The subscript  $j$  refers to  
165 the sieve number according to the mesh openings. The sieve column was manually shaken  
166 for 2 min. The size distribution was obtained by weighing the mass of the products collected  
167 on each sieve. The weight distribution according to size criteria was expressed as the percent  
168 of total weight. Measurements were conducted in triplicate. Immediately after sieving,  
169 products were sampled from the remaining on the sieves with 2, 1.25, 0.9, 0.8, 0.71 mm mesh  
170 openings, and are then characterized by their water content ( $w_j$ ) and compactness ( $\phi_j$ ).

171

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

176

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

181

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

185

#### 186 2.4. Statistical analysis

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

190

191

192



### 193 3. Results

194

#### 195 3.1. Agglomeration of standard semolina

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

202 The water content and compactness of the wet structure (with diameter up to 710  $\mu\text{m}$ ) were  
203 measured for each class as a function to their diameter (**Fig. 3**). The water content of the wet  
204 structures was positively linearly correlated with their diameter (**Fig. 3a**). The compactness of  
205 the wet agglomerates was negatively linearly correlated with their diameter (**Fig. 3b**).  
206 Previous works have already demonstrated that in almost comparable process conditions, the  
207 agglomeration growth of semolina to produce couscous grains leads to increasing water  
208 content and decreasing compactness, according to an increase in the median diameters of the  
209 structures ([Barkouti et al., 2014](#); [Bellocq et al., 2017](#); [Rondet et al., 2010](#); [Saad et al., 2011](#)).  
210 In the present study at unique process water content, we observe that the structures obtained  
211 on the different sieves are characterized by the same trend.

212 Taking into consideration the specific shape of the particle distribution curve (**Fig. 2**) and the  
213 hydrotextural characteristics (**Fig. 3**) of the wet agglomerates of standard semolina, it makes  
214 possible to distinguish different types of structures according to their diameter ([Benali et al.,  
215 2009](#); [Iveson et al., 2001](#); [Saad et al., 2011](#)). The small structures (diameter  $< 0.5$  mm) are the  
216 "native particles of semolina". Their water content is low and remains always smaller than  
217 the capillary condensation water content (0.21). The small structures can also contain slight  
218 amounts of fragments of the larger structures that could be generated by the mechanical  
219 erosion of larger structures due to the shear stresses during the wet-agglomeration. The  
220 structures called "fragments" (diameter close to 0.55 mm) are obtained by the breakage of the  
221 very large dough pieces due to the mechanical stress during process. The structures called  
222 "nuclei" (diameter between 0.63 and 0.9 mm) are structures obtained by primary association  
223 of the native semolina particles. The structures called "agglomerates" (diameter between 0.9  
224 and 2 mm) are obtained by the association of fragments and/or nuclei. Their water contents  
225 are located between the values of capillary condensation (0.21) and the plastic limit ( $w_p =$   
226 0.59) of durum wheat semolina. The very large structures (with diameter  $> 2.5$  mm) are

227 called "the dough pieces". Their water content is higher than the plastic limit ( $w_p$ ) of the  
228 semolina. The plastic limit is defined as the water content at which the sample maintains any  
229 applied deformation (Atterberg, 1911). The water content is then enough high to ensure their  
230 saturation (Rondet et al., 2013).

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

235

236

### 237 3.2. Influence of the diameter and the span of native particles

238 We investigated the impact of the size characteristics of the native particles, on the wet  
239 agglomeration mechanisms by testing the selected raw materials with different values of  
240 median diameter and/or span (Table 1). Experiments were conducted at similar mean water  
241 content. These selected semolina were characterized by almost constant values of protein  
242 contents (between 12.3 and 13.0%). The wet-agglomeration process generates different  
243 curves of size distribution of the wet agglomerates as depicted in Figure 4. **Whatever the  
244 characteristics of the raw materials, the curves of particle size distribution remain not  
245 unimodal. The unimodality reflects the formation of different types of wet structures, which  
246 are characterized by specific diameters (Saad et al., 2001).**

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

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

256 The present results demonstrated a significant effect of the span of the semolina on the  
257 weight fractions of the different structures (Table 2). The distributions of the hydrotextral  
258 properties (water content and compactness) as a function of the size are in the same range  
259 (Fig. 5). Besides, the homogenization of the population of native particles around the median  
260 diameter (*i.e.* lower span) seems to lead to a strong decrease of the population of the "small

261 particles" and of the "fragments" for the benefit of "nuclei" (Table 2). The high mass  
262 frequency observed for the population of nuclei suggests that the process of  
263 nucleation/growth is favoured. The conditions in which it takes place still lead to the  
264 formation of "dough pieces" and to lower contents of "agglomerates".

265 The impact of the median diameter of the semolina (at almost similar span) can be  
266 investigated at low values of span or at high values of span. The comparison of the small  
267 semolina ( $d_{50} = 129 \mu\text{m}$ ) and the standard semolina ( $d_{50} = 287 \mu\text{m}$ ) is done at similar high  
268 values of span (1.58 and 1.51) (Fig. 4a). The comparison of the results obtained with the low  
269 span semolina ( $d_{50} = 282 \mu\text{m}$ ), the coarse semolina ( $d_{50} = 339 \mu\text{m}$ ), and the very coarse  
270 semolina ( $d_{50} = 393 \mu\text{m}$ ) is done at similar low values of span (0.92, 1.02, and 0.77) (Fig. 4b).  
271 Using these semolina generates very different wet agglomeration conditions, according to  
272 values of the diameter ratio ( $d_{50\text{semolina}} / d_{50\text{droplet}}$ ) with values ranging from 0.5 to 1.6.

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

286 Experiments carried out using the semolina with the largest median diameter (low span  
287 semolina, coarse semolina, and very coarse semolina) were realized at high values of the ratio  
288  $d_{50\text{semolina}}/d_{50\text{droplet}}$  (up to 1). The increase of the diameter of semolina then generates a small  
289 increase in the weight fraction of the "dough pieces". The strongest trend comes from the  
290 increase of the weight fraction of the "fragment" in relation to the decrease of the weight  
291 fraction of the "nuclei". The increases of the weight fractions of "dough pieces" and  
292 "fragments", which have a pasty structure ("fragments" arising from the break of the "dough  
293 pieces"), induce lower compactness and higher water content than the other configurations

294 (Fig. 5). These results indicate that the process leads to a higher heterogeneity in the  
295 agglomerated structures, due to the increase in the median diameters of the native particles.

296

297

### 298 3.3. Influence of the protein content of semolina

299 We investigated the impact of the protein content (between 7.7 and 13.8%) of the native  
300 semolina on the wet agglomeration mechanisms by comparing three raw materials (Table 1).

301 The experiments were conducted at similar mean water content ( $\bar{w} = 0.44$ ) and at almost  
302 similar values of median diameter (227 to 262  $\mu\text{m}$ ) and span (1.25 to 1.13) of semolina. The  
303 wet agglomeration process generates different curves of the size distribution of the wet  
304 agglomerates as depicted in Figure 6. Whatever the protein content, the wet agglomerates are  
305 characterized by a large diversity in size, and the curve of particle size distribution remain not  
306 unimodal.

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

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

324

## 325 4. Discussion

326

### 327 4.1. Mechanisms of the wet-agglomeration of semolina

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

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

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

341 Previous works in semolina agglomeration highlighted that the follow-up of both the textural  
 342 and characteristic length (i.e. the diameter) of agglomerates allowed us identifying a fractal  
 343 morphogenesis process (Barkouti et al., 2014; Rondet et al., 2010). The suggested model

344 describing fractal growth of agglomerates can be written as:  $\phi = \phi_N \left(\frac{d_{50}}{d_N}\right)^{Df - 3}$ , where  $Df$  was

345 the fractal dimension of the generated agglomerates;  $d_{50}$  was the median diameter of the  
 346 agglomerate population,  $\phi_N$  and  $d_{50N}$  were respectively the solid volume fraction and the  
 347 median diameter of the nuclei (Rondet et al., 2010). Fractal structure of agglomerates  
 348 elaborated by a wet agglomeration process had ever been highlighted (Pashminehazar et al.,  
 349 2016; Turchiuli and Castillo-Castaneda, 2009). In the case of a fractal growth, this particular  
 350 process involves nuclei association by homothetic scale up, where nuclei constitute the  
 351 elementary structure of the generated agglomerates. Nuclei were identified after sieving and  
 352 optical microscopy observations. Their median diameter and solid volume fraction were  
 353 determined. This analyse is purposed to characterise the agglomerates.

354 Because small range of water contents has been explored, the present data are not completely  
 355 related to growing mechanisms. The fractal dimension had been calculated:  $Df \sim 3$ . This  
 356 value, which is an integer, is the fact of saturation. It indicates that agglomerate could be  
 357 assimilated to geometrical structures in which nuclei do not play the role of a base unit.

358 The agglomeration mechanism of nucleation/growth, which takes place here, occurs in three  
359 major stages. (i) The nucleation stage is both depending on wetting/mixing parameters with  
360 physicochemical properties of fluid and surface particle (Ax et al., 2008; Chouk et al., 2009;  
361 Iveson et al., 2001). (ii) The growing stage could be described as the formation of large  
362 grains by the association of several nuclei following a fractal morphogenesis (Rondet et al.,  
363 2010; Saad et al., 2011). (iii) The “pasting” stage occurs by adding water and leads to the  
364 transformation of the agglomerates in dough pieces through percolation (Rondet et al., 2013;  
365 Ruiz et al., 2011). The transformation of agglomerates in dough structures results in a  
366 considerable increase in grain size and biochemical changes with the formation of partial  
367 dough structures involving the proteins inside the grains. The percolation mechanisms could  
368 be described as the formation of very large structures by hydration and adhesion. It can be  
369 associated with a mechanical deformation of large agglomerates to generate some dough  
370 pieces, when the water content is close to the plastic limit. The compactness of the dough  
371 pieces is smaller than that of agglomerates and nuclei (Fig. 8). These structures could exhibit  
372 stronger strain, and when they are maintained in condition of agitation within a bed of more  
373 compact particles, is going to favour their disintegration. This situation takes place generally  
374 in high shear mixer conditions, where the shear stress field does not allow the stability of  
375 dough (Iveson et al., 2001). The breakage mechanisms generate small-sized fragments, which  
376 are strengthened as observed on the size distribution curve (Fig. 2). Besides their slightly  
377 lower size, the difference with nuclei comes because having been very hydrated, they have a  
378 dough texture, whereas nuclei is made by associations of semolina particles. Fragments have  
379 lower water content and higher compactness than dough pieces, due to the strengthening of  
380 their structure during the mechanical agitation. As explained by Wade et al. (Wade et al.,  
381 2015) and Rondet et al. (Rondet et al., 2016), the breakage mechanism of dough pieces is  
382 able to generate granules with high intragranular compactness, due to the complete filling of  
383 intra-particle pores by the binder liquid, but the addition of further powders can reduce the  
384 liquid saturation of the granules. So generated, fragments can interact with nuclei and  
385 contribute to build agglomerates with the same growing mechanism as ever described. This  
386 paste/fragmentation mechanism could be compared to a nucleation by downsizing, by  
387 difference with the "classic" nucleation, which is a bottom-up mechanism (Iveson et al.,  
388 2001). We can notice that this phenomenon could be totally developed in low shear mixer to  
389 generate agglomerates (Rondet et al., 2016). In the case of this study, the spray process  
390 conditions associated to mixing process conditions generate a very significant population of

391 dough pieces (Fig. 2). It occurs here a concomitant paste/fragmentation mechanism, which  
392 generates fragments, associated to nuclei in the growing process.

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

405

406

#### 407 4.2. Specification of durum wheat semolina for wet agglomeration

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

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

422

423

## 424 **5. Conclusion**

425

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

442

## 443 **ACKNOWLEDGEMENTS**

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447 DUR.

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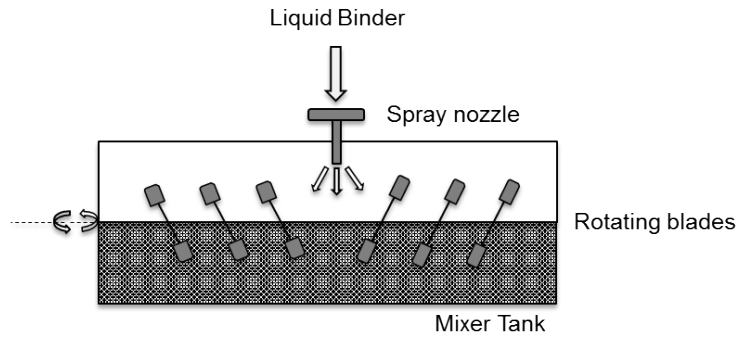
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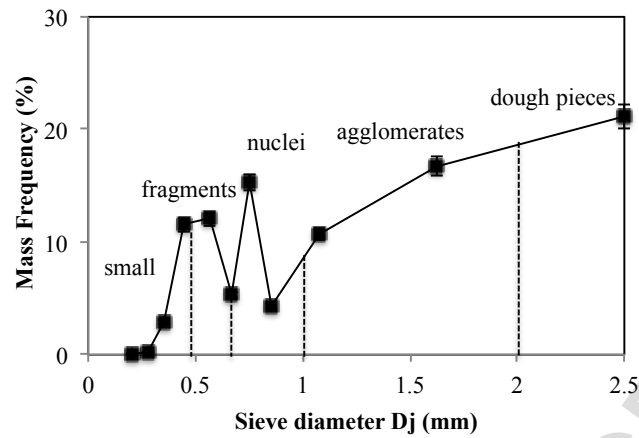
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Fig. 1. Sketch of the horizontal low shear mixer equipment.

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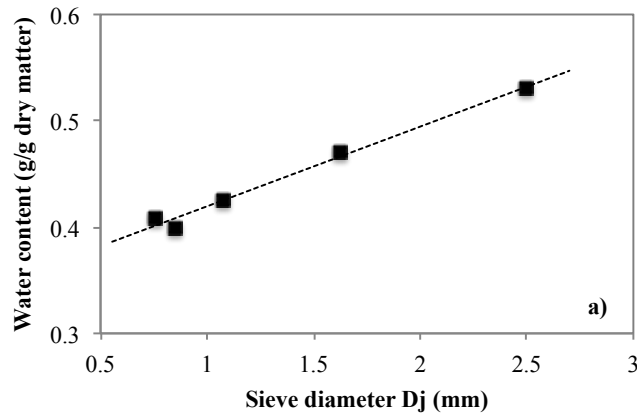
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**Fig. 2.** Distribution curve of the weight fractions as a function of the diameters of the wet agglomerates produced by the wet-agglomeration process of standard semolina.

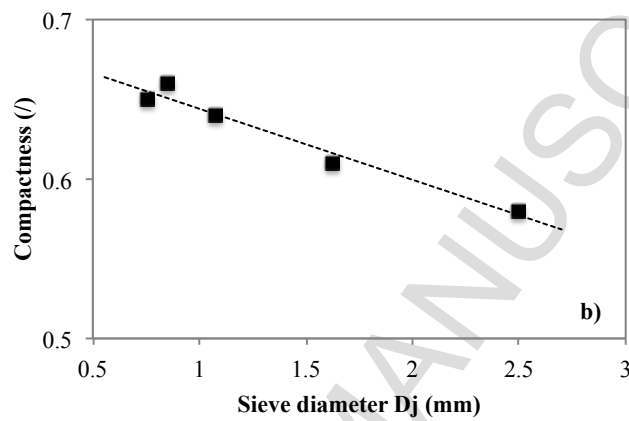
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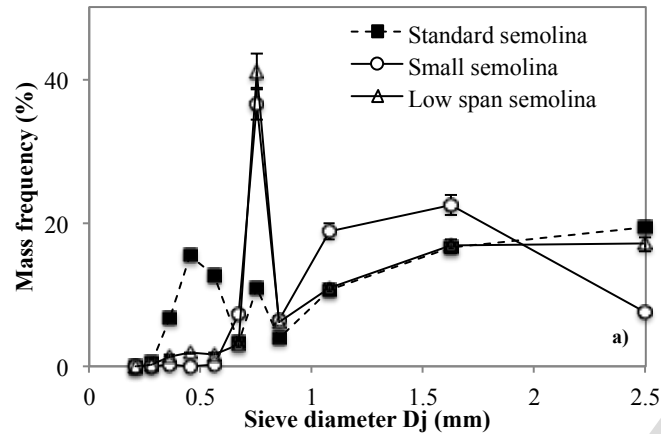


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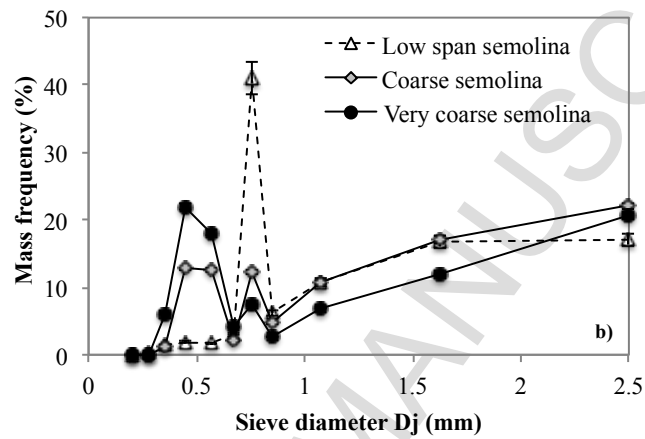
12 **Fig. 3.** Distribution curves of the measured values of water content (a) and compactness (b), as a function of the  
 13 diameter of the structures produced by the wet-agglomeration process of standard semolina.

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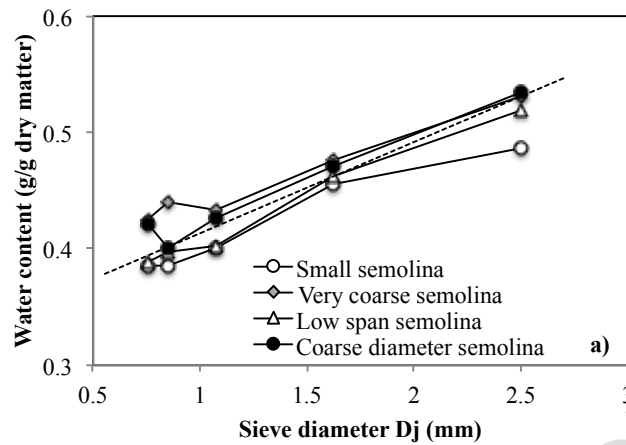


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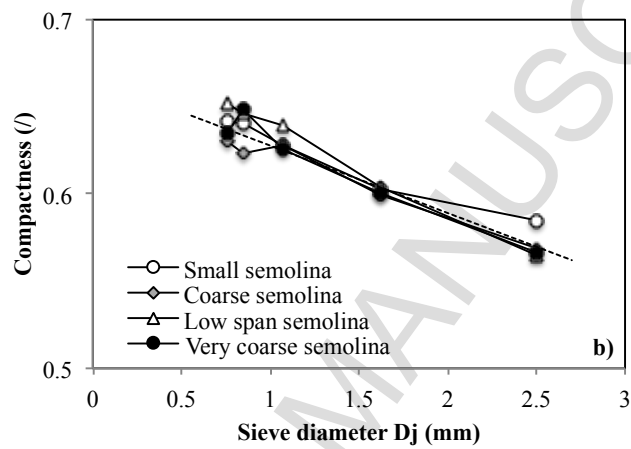
18 **Fig. 4.** Impact of the (a) median diameter at constant span (small semolina) and the span at constant median  
 19 diameter (low span semolina) and (b) of the median diameter (at constant span) of the native semolina, on the  
 20 distribution curves of the weight fractions as a function of the diameters of the wet agglomerates produced by  
 21 the wet-agglomeration process.

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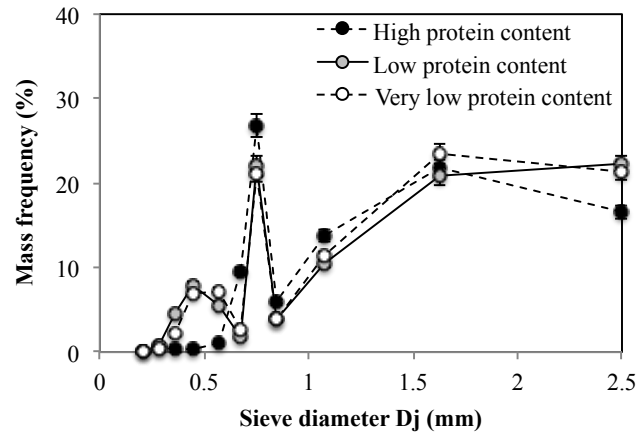
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26 **Fig. 5.** Impact of the median diameter or diameter span of the native semolina on the distribution curves of the  
 27 measured values of water content (a) and compactness (b), as a function of the diameter of the wet agglomerates  
 28 produced by the wet-agglomeration process of different semolina. The dotted line is the value of the standard  
 29 semolina.  
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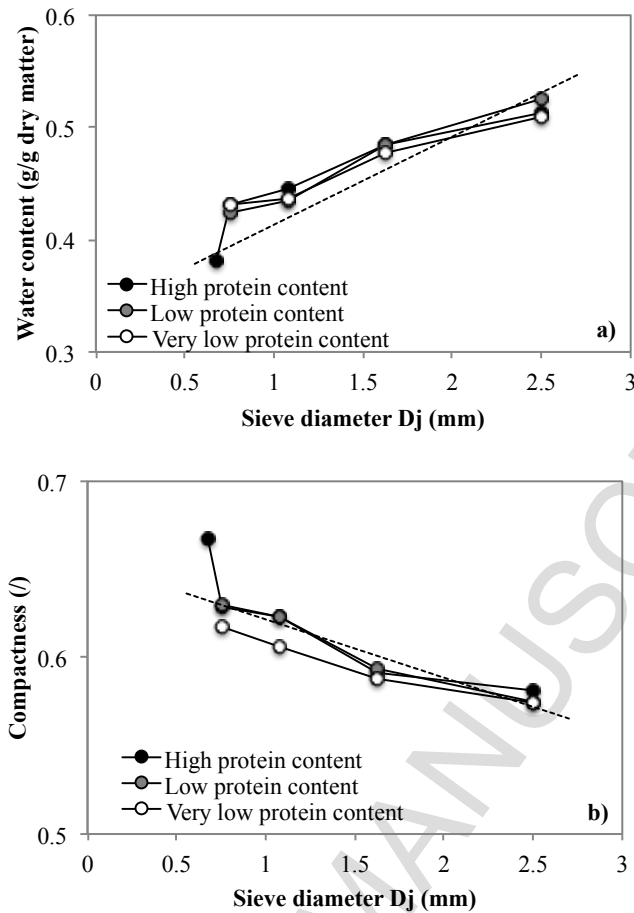




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32 **Fig. 6.** Impact of the protein content of the native semolina on the distribution curves of the weight fractions as a  
 33 function of the diameters of the wet agglomerates produced by the wet-agglomeration process.

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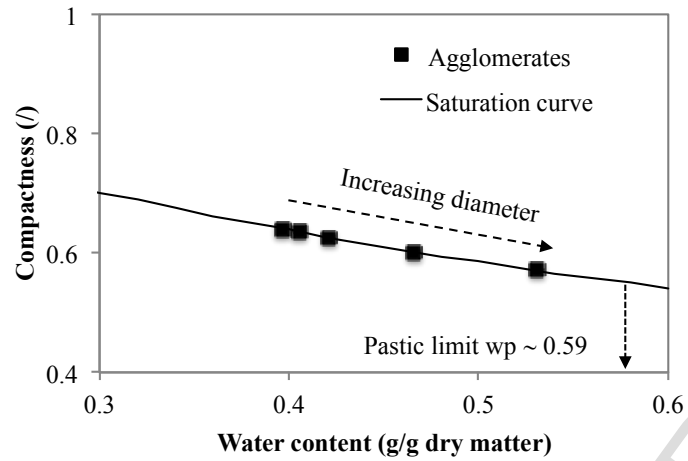


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37 **Fig. 7.** Impact of the protein content of the native semolina on the distribution curves of the measured values of  
 38 water content (a) and compactness (b), as a function of the diameter of the wet agglomerates produced by the  
 39 wet-agglomeration process of different semolina. The dotted line is the value of the standard semolina.

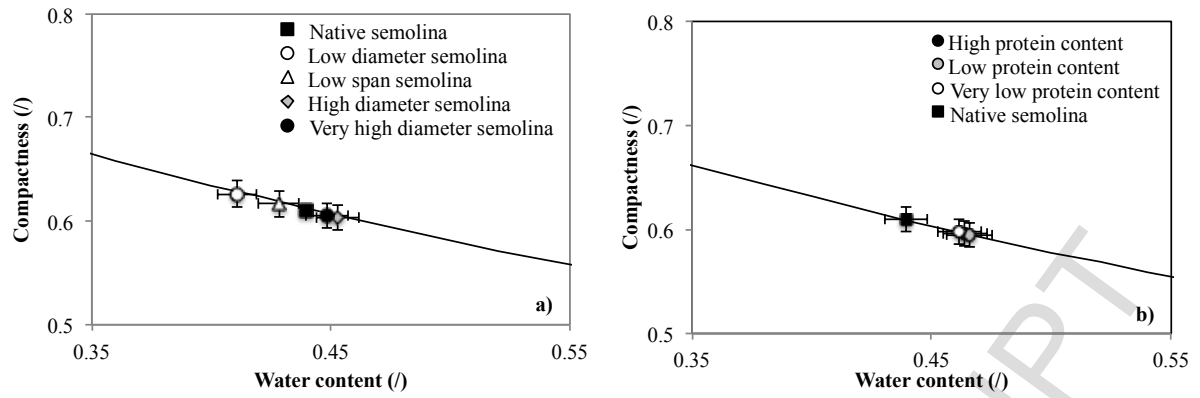
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42 **Fig. 8.** Hydrotextural diagram of the different structures collected on each sieve after the wet agglomeration of  
 43 standard semolina.  
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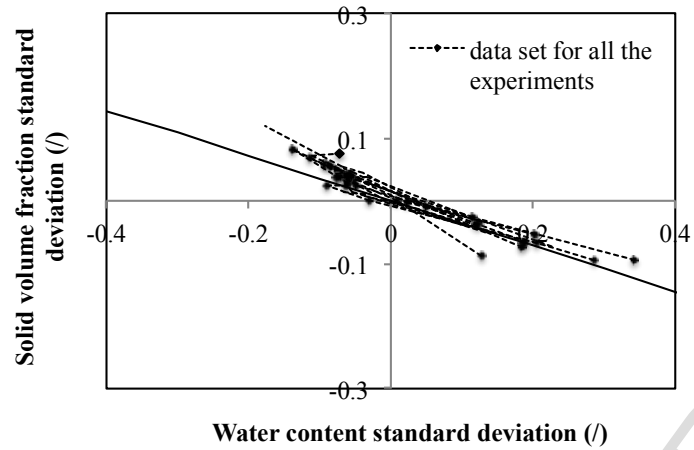
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**Fig. 9.** Hydrotextural diagram of the different structures collected on each sieve after the wet agglomeration of semolina with different size distributions (a) or with different protein contents (b).



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

1 **Table 1**

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

	$d_{50}$ ( $\mu\text{m}$ )	Span (/)	True density ( $\rho_s^*$ ) ( $\text{g}/\text{cm}^3$ )	Water content ( $\text{g}/\text{g}$ dry matter)	Proteins content ( $\text{g}/100$ g dry matter)
Standard semolina	287 ( $\pm 2$ ) <sup>f</sup>	1.51 (+/- 0.01) <sup>f</sup>	1.415 ( $\pm 0.003$ ) <sup>a</sup>	0.173 ( $\pm 0.001$ ) <sup>d</sup>	12.4 ( $\pm 0.1$ ) <sup>c</sup>
Low span semolina	282 ( $\pm 2$ ) <sup>e</sup>	0.92 (+/- 0.04) <sup>b</sup>	1.447 ( $\pm 0.004$ ) <sup>b</sup>	0.160 ( $\pm 0.004$ ) <sup>bc</sup>	12.7 ( $\pm 0.1$ ) <sup>d</sup>
Small semolina	129 ( $\pm 1$ ) <sup>a</sup>	1.58 (+/- 0.02) <sup>g</sup>	1.461 ( $\pm 0.003$ ) <sup>c</sup>	0.157 ( $\pm 0.001$ ) <sup>b</sup>	13.0 ( $\pm 0.1$ ) <sup>e</sup>
Coarse semolina	339 ( $\pm 2$ ) <sup>g</sup>	1.02 (+/- 0.01) <sup>c</sup>	1.451 ( $\pm 0.006$ ) <sup>b</sup>	0.139 ( $\pm 0.001$ ) <sup>a</sup>	12.4 ( $\pm 0.2$ ) <sup>cd</sup>
Very coarse semolina	393 ( $\pm 1$ ) <sup>h</sup>	0.77 (+/- 0.00) <sup>a</sup>	1.453 ( $\pm 0.002$ ) <sup>bc</sup>	0.161 ( $\pm 0.001$ ) <sup>c</sup>	12.3 ( $\pm 0.1$ ) <sup>c</sup>
Very low protein semolina	227 ( $\pm 3$ ) <sup>b</sup>	1.13 (+/- 0.02) <sup>d</sup>	1.462 ( $\pm 0.003$ ) <sup>c</sup>	0.178 ( $\pm 0.001$ ) <sup>ef</sup>	7.7 ( $\pm 0.1$ ) <sup>a</sup>
Low protein semolina	234 ( $\pm 3$ ) <sup>c</sup>	1.14 (+/- 0.02) <sup>d</sup>	1.448 ( $\pm 0.003$ ) <sup>b</sup>	0.177 ( $\pm 0.001$ ) <sup>e</sup>	9.4 ( $\pm 0.1$ ) <sup>b</sup>
High protein semolina	262 ( $\pm 3$ ) <sup>d</sup>	1.25 (+/- 0.02) <sup>e</sup>	1.458 ( $\pm 0.003$ ) <sup>c</sup>	0.180 ( $\pm 0.001$ ) <sup>f</sup>	13.8 ( $\pm 0.1$ ) <sup>f</sup>

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4 Values are means ( $\pm$  standard deviation).5 Values in column with the same letter were not significantly different ( $P < 0.05$ ).

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8 **Table 2**

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

	Weight fractions of the different structures after agglomeration				
	Small	Fragments	Nuclei	Agglomerates	Dough pieces
Standard semolina	22.7 ( $\pm$ 1.5) <sup>e</sup>	12.5 ( $\pm$ 2.0) <sup>d</sup>	10.9 ( $\pm$ 10.6) <sup>abc</sup>	27.2 ( $\pm$ 0.3) <sup>b</sup>	19.3 ( $\pm$ 2.2) <sup>bcd</sup>
Small semolina	0.3 ( $\pm$ 1.2) <sup>a</sup>	0.3 ( $\pm$ 2.6) <sup>a</sup>	36.5 ( $\pm$ 4.9) <sup>e</sup>	41.1 ( $\pm$ 3.6) <sup>c</sup>	7.6 ( $\pm$ 1.4) <sup>a</sup>
Low span semolina	3.7 ( $\pm$ 1.0) <sup>b</sup>	1.7 ( $\pm$ 0.8) <sup>a</sup>	41.0 ( $\pm$ 26.0) <sup>cde</sup>	27.6 ( $\pm$ 3.4) <sup>bc</sup>	17.0 ( $\pm$ 1.7) <sup>bc</sup>
Coarse semolina	13.9 ( $\pm$ 0.5) <sup>d</sup>	12.6 ( $\pm$ 6.5) <sup>cde</sup>	12.2 ( $\pm$ 1.0) <sup>b</sup>	27.9 ( $\pm$ 2.6) <sup>bc</sup>	22.1 ( $\pm$ 2.0) <sup>d</sup>
Very coarse semolina	28.0 ( $\pm$ 0.4) <sup>f</sup>	18.1 ( $\pm$ 0.0) <sup>e</sup>	7.4 ( $\pm$ 0.2) <sup>a</sup>	18.8 ( $\pm$ 0.3) <sup>a</sup>	20.6 ( $\pm$ 1.9) <sup>cd</sup>
Very low protein semolina	9.5 ( $\pm$ 0.1) <sup>c</sup>	7.3 ( $\pm$ 0.4) <sup>c</sup>	21.1 ( $\pm$ 1.1) <sup>c</sup>	34.8 ( $\pm$ 0.9) <sup>d</sup>	21.5 ( $\pm$ 1.1) <sup>d</sup>
Low protein semolina	13.2 ( $\pm$ 0.2) <sup>d</sup>	5.6 ( $\pm$ 0.3) <sup>b</sup>	22.1 ( $\pm$ 1.1) <sup>c</sup>	31.3 ( $\pm$ 0.8) <sup>c</sup>	22.2 ( $\pm$ 1.1) <sup>d</sup>
High protein semolina	1.3 ( $\pm$ 1.6) <sup>ab</sup>	1.1 ( $\pm$ 0.1) <sup>a</sup>	26.8 ( $\pm$ 1.3) <sup>d</sup>	35.4 ( $\pm$ 0.9) <sup>d</sup>	16.6 ( $\pm$ 0.8) <sup>b</sup>

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13 Values are means ( $\pm$  standard deviation).14 Values in column with the same letter were not significantly different ( $P < 0.05$ ).

15