Effect of different extrusion treatments and particle size distribution on the physico-chemical properties of rice flour

Mario M. Martínez[1], Cristina M. Rosell[2], Manuel Gómez[1]*

[1] Food Technology Area, E.T.S. Ingenierías Agrarias. Valladolid University, Ed. La Yutera, Avd. Madrid 44, 34004 Palencia, Spain.

[2] Institute of Agrochemistry and Food Technology (IATA-CSIC). Avda Agustin Escardino, 7. Paterna-46980, Spain.

[*]Corresponding author e-mail: pallares@iaf.uva.es

Abstract

Rice flour is an interesting alternative for developing gluten free products, but its features do not meet the process requirements. The objective of this study was to modify the functional properties of rice flour by combining extrusion and size fractionation. Different extrusion conditions were applied to vary the severity of the treatment on the flour constituents. Extrusion and mechanical fractionation of the rice flours modified their behavior affecting hydration, thermal and pasting features, besides their susceptibility to enzymatic hydrolysis. Thermal properties (temperature and enthalpy) increased with the intensity of the extrusion and that effect was intensified with the greatest particle size of the flours. Fine flours with stronger extrusion showed the highest susceptibility to enzymatic hydrolysis and extrusion process increased that effect. Overall the combination of both physical treatment maybe an attractive alternative for obtaining clean label rice flours with modified features.

Keywords: extrusion, rice flour, particle size, thermal properties, hydration, enzymatic hydrolysis.

1. Introduction

Lately, there is an increasing interest for gluten free products that has prompted extensive research focused on improving the quality of gluten free products. The vast majority of studies have been centered in the substitution of wheat flour for different blends of gluten free flours, starches, protein isolates, hydrocolloids (Houben, Hochstotter, & Becker, 2012) and the enzymatic improvement of those formulations (Rosell, 2009). Nevertheless, the potential of the flours from gluten free cereals has been scarcely exploited. Physical treatments have the benefit over the chemical ones of changing starch functionalities keeping the Green label (Jacobs & Delcour, 1998).

Rice flour functional properties are fully dependent on genotype and environmental conditions (Yeh, 2004) and besides that, postharvest treatments could be an alternative for modulating flour functional features. It is well known that rice grinding significantly affects rice flour properties, like water binding capacity and swelling power (Perdon, Siebenmorgen, Mauromoustakos, Griffin, & Johnson, 2001). Recently (de la Hera, Gómez & Rosell, 2013a) showed that particle size fractionation of rice flour might be advisable for selecting specific physico-chemical properties like different hydration properties and enzymatic starch hydrolysis. Moreover, those fractionated flours showed different processing behaviour more suitable for bread or cake making depending on the particle size (de la Hera, Martínez & Gómez, 2013b; de la Hera, Martínez, Oliete & Gómez, In press).

Thermal treatments are highly attractive to modify the functional properties of the cereal flours. Extrusion cooking is considered high-temperature-short-time (HTST) during which flours are submitted to high temperatures and mechanical shearing at relatively low levels of moisture content (Camire, Camire, & Krumhar, 1990). This treatment allows starch pregelatinization,

denaturation of protein, enzyme (in)activation, and Maillard reactions, the extent of which are dependent on the severity of the extrusion. Those changes at the constituents' level modify the rheological behavior of flour (Hagenimana, Ding, & Fang, 2006). During extrusion, the starch properties are dependent on the temperature, initial moisture content and the screw speed (Wen, Rodis, & Wasserman, 1990). Raising the intensity of the treatment is possible to break down the amylopectin chains (Mercier & Feillet, 1975). In fact, (Colonna, Doublier, Melcion, Demonredon, & Mercier, 1984) described that extruded wheat starches have amylose and amylopectin chains of lower molecular weight than the ones obtained by drum drying due to the shear effect, and that gave low thickening ability at low temperature (Doublier, Colonna, & Mercier, 1986).

The extrusion also promotes important nutritional changes in the flours, like increase in the soluble fiber content and reduction in the lipid oxidation tendency, the content of antinutritional factors and the microbial population (Camire et al, 1990). Besides, it could be obtained an increase in the content of resistant starch in rice flours (Hagenimana et al, 2006), which is dependent on the treatment intensity, and it is always higher than the one obtained by other thermal treatments (Alsaffar, 2011). Extrusion cooking is responsible for gelatinization and degradation of starch and also for changing the extent of molecular associations between components, e.g. the amylose– lipid complex that can affect the *in vitro* starch digestibility of the flours (Hagenimana et al, 2006).

Despite the impact of the extrusion on the molecular level, little attention has been paid to the variation of the functional properties of the flours by hydrothermal treatments (Clerici, Arioldi, & El-Dash, 2009), even though physically modified flours are considered to be natural materials with high safety (Jacobs et al, 1998). In fact, Clerici et al (2009) included 10% of extruded acid-

modified rice flours for making gluten free breads. When using rice flours extruded in the presence of different amount of lactic acid, gluten free breads presented crust and crumb colour and texture values similar to those of wheat bread, although specific volume was rather low.

Considering the influence of the flour fractionation on the functional properties of the rice flours (de la Hera et al, 2013b), and the molecular changes induced by extrusion cooking, the combination of both physical treatments could modify rice flour functional properties keeping the green label. The aim of this study was to modify the functional properties of rice flour by combining extrusion and size fractionation. With that purpose, different extrusion conditions were applied to vary the severity of the treatment on the flour constituents. The impact of processing on the flours was also followed by assessing the susceptibility of the flours to enzymatic hydrolysis.

2. Materials and methods

2.1 Materials

Rice flours were provided by Harinera Los Pisones (Zamora, Spain) that carried out the extrusion treatment in a single screw extruder Bühler Basf (Bühler S.A., Uzwil, Switzerland). The length to diameter (L/D) ratio for the extruder was 20:1. Rice flour was subjected to different extrusion intensities (barrel temperature and moisture content of the mass feed) yielding three types of extruded flours (1-3). Rice flour 1 and 2 were extruded at a maximum barrel temperature of 110ºC with a feed rate of 700kg/h. For flours 1 and 2 feed moisture content and screw speed was 17% and 30%, and 453rpm and 397rpm, respectively. The diameter of the die hole used in those flours was 8mm. Rice flour 3 was extruded at a maximum barrel temperature of 140ºC with a feed-rate of 500kg/h and feed moisture content of 25%. The

screw speed was 340rpm and the diameter of the die hole was 6 mm. The same rice flour (rice flour 0) without any treatment was used as a control.

Extruded product was dried by convection air and then ground with a compression roller till particle size was lower than 200 microns. Ground extrudates were sifted in a Bühler MLI 300B (Bühler AG, Uzwil, Switzerland) with screens of 132 and 200 microns to obtain fine (f) – lower than 132µm- and coarse (c) – 132µm-200 µm- extruded flours.

Flours were stored in air-tight plastic containers and held at 4°C until analysis.

2.2 Methods

2.2.1. Flours characterization

Flours were analyzed following AACC method (AACC, 2012) for protein (AACC, 46-30.01) with a Leco TruSpec device (Leco, St. Joseph, MI, USA). The particle size distribution was measured using a particle size analyzer with laser diffraction Helos & Rodos (Sympatec, Clausthal-Zellerfeld, Germany) following AACC method (AACC, 55-40.01). Determinations were carried out in duplicate.

Free sugars

The glucose content was measured using a glucose oxidase-peroxidase (GOPOD) kit. The absorbance was measured using an Epoch microplate reader (BIOTEK EPOCH, Izasa, Barcelona, Spain) at 510 nm. In all cases four replicates were assayed for each experimental point.

Damage starch

The content of damaged starch was determined according to AACC 76-30A method (AACC, 2012). A fungal enzyme from *Aspergillus oryzae* (A6211, Sigma Chemical Co., St. Louis, MO,

USA) was used in that analysis. Three determinations were made for each sample. Damaged starch was expressed as percentage of flour weight on dry basis.

Hydration properties

Hydration properties included swelling and water binding capacity (WBC) (Nelson, 2001). Swelling volume or the volume occupied by a known weight of flour was evaluated by mixing 5g (±0.1mg) of flour with 100ml distilled water and allowing it to hydrate during 16h.

Water binding capacity defined as the amount of water retained by the flour after it has been subjected to centrifugation was measured as described the method 56.30 (AACC, 2012). Determinations were carried out in duplicate.

Emulsifying properties

Flour suspension (360 mL) of 0.5% (w/v) starch concentration was mixed with commercial sunflower oil (Langosta, F. Faiges S.L, Daimiel, Ciudad Real, Spain) (36 mL). The content was stirred for one min with a beater (Taurus Bapi 350 CP/CM, Taurus, Oliana, Lérida, Spain) to disperse the sample in the oil. The suspensions were then centrifuged at 800x*g* for 10 min. The emulsifying capacity (EC) was calculated as:

$$EC=(ev/tv)*100 \quad \text{(Eq. 2)}$$

where *ev* is the emulsion volume and *tv* is total volume.

Emulsion stability (ES) against high temperatures, were determined in the emulsions that were heated in a water bath at 80ºC for 30 min, and centrifuged at 800x*g* for 10 min. ES was calculated as:

$$ES=(fev/iev)*100 \quad \text{(Eq. 3)}$$

where *fev* is the final emulsion volume and *iev* is initial emulsion volume. Determinations were carried out in duplicate.

Foaming properties

Aliquots (150mL) of 4% w/v suspension were whipped at moderate speed for one min using a beater (Taurus Bapi 350 CP/CM, Taurus, Oliana, Lérida, Spain). Foam volumes were recorded after 30 s. The foam capacity (FC) was calculated as follows:

$$FC=(ifv/tsv)*100 \quad \text{(Eq. 4)}$$

where *ifv* is the initial foam volume and *tsv* is the total suspension volume.

The foam stability (FS) was calculated as the foam volume after 20 min.

$$FS=(ffv/tsv)*100 \quad \text{(Eq. 5)}$$

where *ffv* is the foam volume after 20 min and *tsv* is total suspension volume. Results were the average of two determinations.

Pasting characteristics

Pasting properties of flours were analyzed using the standard method (AACC, 2012), (AACC, 61-02.01) with a Rapid Visco Analyser (RVA-4) (Newport Scientific Pty Ltd., Warriewood, Australia) controlled by Thermocline software (Newport Scientific Pty. Limited, Warriewood, Australia) for Windows.

Thermal properties

Analyses were performed in a differential scanning calorimeter DSC-7 (Perkin–Elmer, Waltham, MA, USA), using aluminum pans (PE 0219-0062). The equipment was calibrated with Indium and an empty pan was used as a reference. Flour (3 mg) was loaded into the aluminum pan and distilled water (10µL) was added with the help of a Hamilton micro syringe. Samples were hermetically sealed and allowed to stand for 1 h at room temperature before

heating in the DSC. The calorimeter scan conditions were set as follows: samples were kept at 30°C for 2 min, heated from 30 to 110ºC at 5ºC/min. Onset temperature (T_o), peak temperature (T_p), gelatinization temperature range (T_p- T_o), peak height index (ΔH_g/ T_p- T_o) as well as the enthalpy of starch gelatinization (ΔH_g) (expressed as mJ/mg of sample) were determined. All samples were run in quadruplicate.

Colour of flours

Colour was measured using a Minolta CN-508i spectrophotometer (Minolta, Co.LTD, Tokyo, Japan) with the D65 standard illuminant and the 2° standard observer. Results were expressed in the CIE*Lab* colour space. Colour determinations were made 5×2 times on each sample of flour.

Enzymatic hydrolysis of starch

Starch hydrolysis was measured following the method described by Gularte and Rosell (2011) with minor modifications. Briefly, for free sugars removal, flour sample (100 mg) suspended in two milliliters of 80% ethanol was kept in a shaking water bath at 85ºC for five minutes, and then centrifuged for 10 min at 1000×*g*. The pellet was incubated with porcine pancreatic α-amylase (10 mg/ml) (Type VI-B, ≥10 units/mg solid, Sigma Chemical, St. Louis, MO, USA) and amyloglucosidase (3300 U/ml) (Sigma Chemical, St. Louis, MO, USA) in 10 ml of 0.1M sodium maleate buffer (pH 6.0) in a shaking water bath at 37 ºC (0.25–16 h). Aliquots of 200 µl were withdrawn during the incubation period. Aliquots were mixed with 200 µl of ethanol (96%) to stop the enzymatic reaction and the sample was centrifuged for 5 min at 10000×*g* and 4 ºC. The precipitate was washed twice with 50% ethanol (100 µl) and the supernatants were pooled together and kept at 4 ºC for further glucose determination.

The remnant starch after 16 h hydrolysis was solubilized with 2ml of 2M KOH using a Polytron ultraturrax homogenizer IKA-T18 (IKA works, Wilmington, NC, USA) during 1min at speed 3.

196 The homogenate was diluted with 8ml 1.2M sodium acetate pH 3.8 and incubated with 100µl
197 amyloglucosidase (3300 U) at 50 ºC for 30 min in a shaking water bath. After centrifuging at
198 2000×*g* for 10 min, supernatant was kept for glucose determination.
199 The glucose content was measured using a glucose oxidase-peroxidase (GOPOD) kit. The
200 absorbance was measured using an Epoch microplate reader (Biotek Instruments, Winooski, VT,
201 USA) at 510 nm. Starch was calculated as glucose (mg)×0.9. Replicates (n=2-4) were carried
202 out for each determination.
203 Experimental data were fitted to a first-order equation (Goñi et al., 1997):
204 $C_t = C_\infty (1\text{-}e^{-kt})$ Eq. 5
205 Where C_t is the concentration of product at time *t*, C_∞ is the concentration at the end point, and *k*
206 is the pseudo-first order rate constant. Although this equation requires the estimation of an
207 accurate C_∞, it was useful because long reaction times were applied to determine resistant starch
208 after complete enzymatic hydrolysis. The plot of ln $[(C_\infty - C_t)/ C_\infty] = -kt$ against *t* was used to
209 estimate the slope that corresponded to *–k.*
210 However, as recently suggested Butterworth, Warren, Grassby, Patel and Ellis (2012), the linear
211 plot of ln (d*C*/d*t*) against *t* was also represented to calculate the slope (-*k*), and the intercept on
212 the *y* axis was used for calculating the ln($k\ C_\infty$). This plot was used to demonstrate if the data
213 were of logarithmic form and the rate constant remained unchanged along the whole hydrolysis
214 reaction, as recommended Poulsen, Ruiter, Wisser, Jorgen and Iversen (2003).
215 **2.2.2. Statistical analysis**
216 Multiple analyses of variance were used to determine the individual effects of thermal treatment
217 and particle size of flours. Fisher's least significant differences test was used to calculate the
218 means with their 95% confidence intervals. Several correlations were also run. The statistical

analysis was performed with the Statgraphics Plus Centurion XVI software (Statpoint Technologies, Inc., Warrenton, VA, USA).

3. Results and Discussion

Rice flour was subjected to different extrusion treatments that differed on the maximum barrel temperature and feed moisture content in order to obtain different extrusion intensities. In addition, resulting extruded flours after grinding were separated in two fractions depending on their particle size obtaining coarse extruded flour (132µm-200µm) and fine extruded flour (<132µm). Overall eight samples were obtained from each batch, which differed on the level of extrusion (identified as 1-3) and the particle size (coarse, fine).

3.1 Damage starch and free sugars

To get a complete picture of the effect of extrusion and particle size a multiple analysis of variance was applied to the experimental results (Table 1). The extrusion intensity and particle size had a significant effect on the content of free sugars, which increased with the extrusion intensity and with the reduction of the particle size. Nevertheless, no significant differences were observed between the free sugars content of the control and the mild extrusion treatment (flour 1). Thus the hydrolysis responsible of the sugar release required a minimum barrel temperature and also sufficient feed moisture content, since flours 1 and 2 were extruded at the same temperature and with different moisture feeding. Extrusion induced a progressive increase of the damage starch content with the intensity raise, likely due to damage produced by the shears force and the heat during extrusion (Camire et al, 1990). Conversely, damage starch decreased with the particle size, showing coarser flours the greatest amount of damage starch, which

242 agrees with the trend observed by de la Hera et al. (2013a), when studying the features of
243 different particle size fractions of rice flours.
244
245 **3.2 Hydration, emulsifying and foaming properties**
246 Hydration, emulsifying and foaming properties were significantly affected by the extrusion
247 process and the particle size of the flours (Table 1). Hydrations properties (WBC and swelling)
248 increased with the extrusion intensity and also with the particle size of the flour. Those effects
249 were partially attributed to the increase in the amount of damage starch since it was found a
250 positive correlation between the amount of damage starch and WBC (r=0.88) and with the
251 swelling (r=0.88). Moreover, the cooking produced during extrusion led to gelatinized starch
252 that would have higher WBC and swelling, as occurred with the water absorption index
253 (Hagenimana et al, 2006). Camire et al. (1990) proposed that the breakage of the starch granule
254 integrity led to a poorly ordered molecular phase with hydroxyl groups prone to bind water
255 molecules.
256 The extrusion significantly reduced the emulsifying capacity of the flours, with the exception of
257 flour 3, compared to the control flour, and an increase of the EC was observed with the severity
258 of the extrusion (flour 3). That effect must result from the protein and starch changes during
259 extrusion process. Considering the proteins, extrusion forces the unfolding and aggregation due
260 to protein crosslinking involving SH/SS interchange, oxidation and hydrophobic interactions
261 (Rosell & Foegeding, 2007), which might result in a decrease of the EC of the flour. As the
262 extrusion intensity increase, starch modification might partially mask the consequence of protein
263 denaturation and EC increase due to gelatinized starch has greater number of hydroxyl groups
264 available to form hydrogen bonds with the proteins leading to better emulsion capacity.

Emulsion stabilities were higher in the flours obtained from lower extrusion intensities (flour 1 and 2), likely the denaturation of the rice proteins during extrusion increased the stability. The particle size of the rice flours did not affect significantly the EC, but the ES significantly increased with the particle size. A reduction in the particle size of the flour improves the emulsifying properties of the flours (Aluko, Mofolasayo, & Watts, 2009), but it seems that some time is needed for displaying that effect since only ES was affected by the particle size. In the present study, it was observed a significant positive relationship between the ES and the free sugars content (r=0.93, P<0.001), which could reduce the total charge of the proteins leading the formation of interfacial protein membranes that stabilize the emulsion (Aluko et al, 2009).

Extrusion improved the foaming capacity of the rice flours, but there was no trend with the extrusion severity. The foam stability could be only measured in flour 3 (50.00 for fine flour and 45.18 for coarse flour), because very unstable foams were obtained with the other flours. The FC has been attributed to its microstructure, size and distribution of the gas cells and the interfacial properties (Zhang, Bai, & Zhang, 2011). Hydrothermal treatments can improve the foaming properties, like it has been reported with corn kernels (Boladea, Usman, Rasheed, Benson, & Salifou, 2002). Nevertheless, the minor effect observed in the extruded rice flours could be attributed to the low protein content of the rice flour, since usually protein isolates show great foaming capacity that improves with the hydrothermal treatments (Wang & Johnson, 2001). The effect of extrusion on foam formation followed an opposite trend to the one observed on the emulsion formation, which suggests that different mechanisms are involved during interfacial membrane formation at the air-water and oil-water interfaces. Concerning the particle size, the major FC was observed in fine flours, which was explained by the greater availability of lowering interfacial components in those flour fractions, as proposed Aluko et al. (2009).

3.3. Colour

Luminosity (L^*) of the flours significantly decreased with the extrusion intensity (Table 1), and increased the a^* and b^*. Nevertheless, whereas the effect was steady with the extrusion severity in the case of the luminosity and b^*, no trend was observed in the case of a^*. The extrusion process could lead to Maillard reactions and a reduction of the lipids oxidation due to enzymes inactivation that induces the formation of melanoidins and the pigments protection, which in turn produces the modification of the flours color (Camire et al, 1990). Moreover, higher L^* and lower a^* y b^* were obtained in the fine flours. It has been proposed that fine flours had higher surface area that favors the contact of the constituents with the oxygen promoting the pigments oxidation (Atwell, 2001).

3.4. Pasting characteristics

Pasting plots of the extruded flours are displayed in Figure 1. When rice flours were suspended in water, the major viscosity (initial viscosity at 50ºC) was observed in the flour 3 at both particle sizes, due to the high amount of damage starch content and pregelatinized starch (Chao-Chi Chuang & Yeh, 2004). Concerning the extrusion treatment, the viscosity during heating and cooling decreased with the extrusion intensity, obtaining minimum viscosity in flour 3 (with the highest intensity). Nevertheless, when particle size was taken into account, a progressive decrease of viscosity was observed in the coarse flours, but fine flours from treatment 1 and 2 did not show any difference in the pasting profile (Figure 1 b). Since flour 1 and 2 were treated at maximum barrel temperature of 110ºC and the unique variation was the feed moisture

content, it seems that the effect on pasting profiles was independent on the feed moisture content during extrusion when small particle size were subjected to this treatment.

Peak viscosity was significantly dependent on the damage starch content (r=-0.79), which agree with previous studies connecting peak viscosity with gelatinized and damage starch that was related to the polymerization degree of the starch granules (Barres, Verges, Tayeb, & Della Valle, 1990). The reduction observed in the final viscosity and setback was displaying the extension of the effect on the amylose chains, which might lose the ability to retrograde during cooling due to their fragmentation during extrusion. This effect agrees with previous results of Doublier et al. (1986).

3.5. Differential Scanning Calorimetry (DSC)

The effect of extrusion treatment and particle size on the thermal properties of the starch is shown in Table 2. In the range of temperature tested, flours exhibited one endothermic peak corresponding to amylopectin gelatinization, with the exception of flour 3. The absence of an endothermic peak for flours 3 indicated total gelatinization of amylopectin. Indeed, these results agree with those previously discussed regarding the very small pasting curve observed in the extruded flours 3. The extrusion treatment significantly modified the gelatinization temperatures of the flours, and those temperatures were also dependent on the particle size of the flours. Gelatinization temperatures were sifted to higher values when flours were treated at increasing extrusion intensity, but the temperature range was not affected. Higher gelatinization temperature indicated that more energy is required to initiate gelatinization of the starch suggesting that extrusion is affecting the outer and more amorphous part of the granule and is

progressing to the core of the granule till no crystalline structure is left for gelatinization (flour 3).

When comparing extruded flours, the gelatinization enthalpy was significantly reduced due to the intensity of the extrusion, which was expected since extrusion induces starch gelatinization and an increase of the damage starch content (Chiu & Solarek, 2009), leading to a reduction of the native starch granules able to gelatinize (Biliaderis, Page, Maurice, & Juliano, 1986). Nevertheless, the mild extrusion treatment (flour 1) gave significantly higher gelatinization enthalpy compared to the untreated flour. Taking into account that treatment 1 was applied using lower feed moisture content (insufficient to complete gelatinization), the higher enthalpy of this sample could be attributed to a reorientation of the structure of the amorphous region to resemble that of the crystalline region (Camire et al, 1990). The extrusion process modifies the crystalline structure of the starch granule affecting the temperature at which swelling starts (Camire et al, 1990). Fine flours showed lower gelatinization temperatures than the corresponding coarse flours, but without affecting the peak high index and the gelatinization enthalpy (Table 2).

3.6. Starch hydrolysis

The susceptibility of the extruded flours to the enzymatic hydrolysis was analyzed. Figure 2 shows the kinetic plots of the extruded flours and the effect of the particle size. The enzymatic hydrolysis profiles were dependent on the particle size, and fine flours showed faster hydrolysis and reached higher asymptotic values than course flours. de la Hera et al. (2013) observed lower hydrolysis rate in the coarse flours when studied the effect of particle size distribution on the rice flour functionality. This result could be attributed to the high surface area of the fine flours

that increase the water diffusion and enzyme accessibility. The hydrolysis curves were fitted to a first order kinetics according to Goñi, García-Alonso and Saura-Calixto (1997) and also to Butterworth, Warren, Grassby, Patel & Ellis (2012) to obtain the kinetic parameters (Table 3). As it was observed in the plots, there was an increase in the equilibrium concentration (C_∞) parallel to the extrusion intensity (except flour 2f). Regarding the rate of the hydrolysis, *k*, there was no general trend with the extrusion intensity. There was great agreement with the equilibrium concentration estimated from both fitted methods, indicating that the kinetic parameters can be fitted to a logarithmic function and that the rate constant did not vary along the hydrolysis reaction (Poulsen, Ruiter, Visser, & Iversen, 2003).

Resistant starch was also quantified to determine the potential impact of the extrusion on the structural level of starch. Although there was no clear tendency about the resistant starch content, the highest extrusion intensity gave the flours with the lower level of RS (flour 3). This finding disagrees with previous observations of Hagenimana et al. (2006), who found an increase in RS content with the treatment severity. Those authors attributed the increase in RS to the formation of amylose-lipid complexes during the extrusion, which retarded the enzymatic digestion. Therefore, results divergence might be explained because of the lower content of amylose of the flours in the present study compared with the reported ones. In addition Chinnaswamy & Hannah (1990) reported a change in the percentage of amylose/amylopectin ratio in extruded corn flours that was ascribed to both chains fragmentation, being more intense in the former. That fact could affect the starch hydrolysis rate. Moreover, Hagenimana et al. (2006) stated that the susceptibility of the extruded starches to be enzymatically hydrolyzed was directly related to the intensity of the extrusion treatment.

The particle size did not significantly affect the hydrolysis rate, but fine flours showed higher values of C_∞ and lower amount in RS. Al-Rabadi, Torley, Williamsa, Brydena, & Gidley (2011) stated that fine extruded flours of barley and sorghum had major digestibility than the coarser ones. The most compact structure, besides the smaller surface area of coarser flours, could hinder the accessibility of the enzymes within the starch structure, since diffusion of the enzyme is the first stage in the enzymatic hydrolysis (Al-Rabadi et al. 2011; Ghaid, Al-Rabadi, Gilbert, & Gidley, 2009).

4. Conclusion

Extrusion and mechanical fractionation of the rice flours modified their behavior affecting hydration, thermal and pasting features, besides their susceptibility to enzymatic hydrolysis. The severity of the extrusion treatment was accompanied by an increase in the amount of damage starch and free sugars content, the former contributing to the Maillard reaction, which affected the luminosity of the flours. In parallel, hydration ability increased with the extrusion intensity, leading higher viscosity in cold solution, which might be very interesting for some food applications. Thermal properties (temperature and enthalpy) increased with the intensity of the extrusion and that effect was intensified with the greatest particle size of the flours. Fine flours with stronger extrusion showed the highest susceptibility to enzymatic hydrolysis and extrusion process increased that effect.

Acknowledgements

Authors acknowledge the financial support of Junta de Castilla y León (VA054A12-2), the Spanish Ministry of Economy and Sustainability (Project AGL2011-23802), and the European

Regional Development Fund (FEDER). Authors are also grateful to Harinera Los Pisones, (Zamora, Spain) for supplying the rice flours.

References

AACC. (2012). Approved methods of the American Association of Cereal Chemists, methods 46-30.01 (protein), 55-40.01 (particle size), 76-30a (damaged starch), 56-30 (WBC), 61-02.01 (RVA) (11th ed.). St. Paul, Minnesota: American Association of Cereal Chemists.

Al-Rabadi, G., Torley, P., Williamsa, B., Brydena, W., & Gidley, M. (2011). Effect of extrusion temperature and pre-extrusion particle size on starch digestion kinetics in barley and sorghum grain extrudates. Animal Feed Science and Technology, 168, 267-279.

Alsaffar, A. (2011). Effect of food processing on the resistant starch content of cereals and cereal products - A review. International Journal of Food Science and Technology, 46, 455-462.

Aluko, R., Mofolasayo, O., & Watts, B. (2009). Emulsifying and foaming properties of commercial yellow pea (Pisum sativum L.) seed flours. Journal of Agriculture and Food Chemistry, 57, 9793-9800.

Atwell, W. (2001). Composition of commercial flour. In W. Atwell (Ed.), Wheat Flour (pp. 27-42). St. Paul, Minnesota, USA: American Association of Cereal Chemists.

Barres, C., Verges, B., Tayeb, J., & Della Valle, G. (1990). Transformation of wheat flour by extrusion cooking. Influence of screw configuration and operating conditions. Cereal Chemistry, 67, 427-433.

Biliaderis, C., Page, C., Maurice, T., & Juliano, B. (1986). Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. Journal Agricultural of Food Chemistry, 34, 6-14.

Boladea, M., Usman, M., Rasheed, A., Benson, E., & Salifou, I. (2002). Influence of hydrothermal treatment of maize grains on the quality and acceptability of tuwon masara (traditional maize gel). Food Chemistry, 79, 479–483.

Butterworth, P.J., Warren, F.J., Grassby, T., Patel, H., & Ellis, P.R. (2012). Analysis of starch amylolysis using plots for first-order kinetics. Carbohydrate Polymers, 87, 2189-2197.

Camire, M., Camire, A., & Krumhar, K. (1990). Chemical and nutritional changes in foods during the extrusion. Food Science Nutrition 29, 35-57.

Chao-Chi Chuang, G., & Yeh, A. (2004). Effect of screw profile on residence time distribution and starch gelatinization of rice flour during single screw extrusion cooking. Journal of Food Engineering, 63, 21-31.

Chinnaswamy, R., & Hannah, M. (1990). Macromolecular and functional properties of native and extruded corn starch. Cereal Chemistry, 67, 490-499.

Chiu, C., & Solarek, D. (2009). Modification of starch. In J. BeMiller, & R. Whistler (Eds.), Starch. Chemistry and Technology (pp. 629-656). New York. USA: Academic Press.

Clerici, M., Arioldi, C., & El-Dash, A. (2009). Production of acidic extruder rice flour and its influence on the qualities of gluten free bread. Food Science and Technology, 42, 618-623.

Colonna, P., Doublier, J., Melcion, J., Demonredon, F., & Mercier, C. (1984). Extrusion cooking and drum drying of wheat-starch.1. Physical and macromolecular modifications. Cereal Chemistry, 61, 538-543.

de la Hera, E., Gómez, M., & Rosell, C. (2013a). Particle size distribution affecting the starch enzymatic digestion and hydration of rice flour carbohydrates. Carbohydrates Polymers.

de la Hera, E., Martínez, M., & Gómez, M. (2013b). Influence of flour particle size on quality of gluten-free rice bread. LWT-Food Science and Technology, DOI:10.1016/j.lwt.2013.04.019.

de la Hera, E., Martínez, M., Oliete, B., & Gómez, M. (In press). Influence of flour particle size on quality of gluten-free rice cakes. Food Bioprocess Technology.

Doublier, J., Colonna, P., & Mercier, C. (1986). Extrusion cooking and drum drying of wheat-starch. 2. Rheological characterization of starch pastes. Cereal Chemistry, 63, 240-246.

Ghaid, J., Al-Rabadi, G., Gilbert, R., & Gidley, M. (2009). Effect of particle size on kinetics of starch digestion in milled barley and sorghum grains by porcine alpha-amylase. Journal of Cereal Science, 50, 198-204.

Goñi, I., Garcia-Alonso, A. & Saura-Calixto, F. (1997). A starch hydrolysis procedure to estimate glycemic index. Nutrition Research, 17, 427–437.

Gularte, M.A., & Rosell, C.M. (2011). Physicochemical properties and enzymatic hydrolysis of different starches in the presence of hydrocolloids. Carbohydrate Polymers, 85, 237–244.

Hagenimana, A., Ding, X., & Fang, T. (2006). Evaluation of rice flour modified by extrusion cooking. Journal of Cereal Science, 43, 38-46.

Hasjim, J., Li, E., & Dhital, S. (2012). Milling of rice grains: The roles of starch structures in the solubility and swelling properties of rice flour. Starch/Starke, 64, 631–645.

Houben, A., Hochstotter, A., & Becker, T. (2012). Possibilities to increase the quality in gluten-free bread production: an overview. European Food Research and Technology, 235, 195-208.

Jacobs, H., & Delcour, J. (1998). Hydrothermal modifications of granular starch, with retention of the granular structure: a review. Journal of Agricultural and Food Chemistry, 46, 2895-2905.

Mercier, C., & Feillet, P. (1975). Modification of carbohydrate components by extrusion-cooking of cereal products. Cereal Chemistry, 63, 283-297.

Nelson, A. (2001). Properties of Hihg-fibre ingredientes. Cereal Foods World, 46, 93-97.

Perdon, A., Siebenmorgen, T., Mauromoustakos, A., Griffin, V., & Johnson, E. (2001). Degree of milling effects on rice pasting properties. Cereal Chemistry, 78, 205-209.

Poulsen, B., Ruiter, G., Visser, J., & Iversen, J. (2003). Determination of first order rate constants by natural logarithm of the slope plot exemplified by analysis of Aspergillus niger in batch culture. Biotechnology Letters, 25, 565-571.

Rosell, C. (2009). Enzymatic Manipulation of Gluten-Free Breads. In E. Gallagher (Ed.), Gluten-Free Food Science and Technology (pp. 83-98). Dublin, Ireland: Wiley-Blackwell.

Rosell, C.M., & Foegeding, A. (2007). Interaction of hydroxypropylmethylcellulose with gluten proteins: small deformation properties during thermal treatment. Food Hydrocolloids, 21, 1092-1100.

Wang, C., & Johnson, L. (2001). Functional properties of hydrothermally cooked soy protein products. Journal of the American Oil Chemists Society, 78, 189-195.

Wen, L., Rodis, P., & Wasserman, B. (1990). Starch fragmentation and protein insolubilization during twin-screw extrusion of corn meal. Cereal Chemistry, 67, 268-275.

Yeh, A. (2004). Preparation and applications of rice flour. In E. Champagne (Ed.), Rice: Chemistry and Tehnology (pp. 495-540). St. Paul, Minesota. U.S.A: American Association of Cereal Chemist.

Zhang, M., Bai, X., & Zhang, Z. (2011). Extrusion process improves the functionality of soluble dietary fiber in oat bran. Journal of Cereal Science, 54, 98-113.

Table 1: Significant individual effects of extrusion treatment (1-3) and particle size (coarse, fine) on free sugars, damaged starch, emulsifying, foaming and colorimetric properties of rice flours.

			Extrusion treatment				Particle size	
	Media	SE	3	2	1	0	c	f
Free Sugars (%)	21.47	4.57	49.91c	19.58b	9.49a	6.92a***	18.74a	24.21b**
Damaged Starch (%)	18.08	2.83	32.49d	23.33c	9.85b	6.66a***	19.98b	16.18a**
WBC (g water/g solid)	2.42	0.39	4.94d	2.13c	1.35b	1.26a***	2.46b	2.39a*
Swelling (mL/g)	3.50	0.79	8.60d	2.90c	1.55b	0.95a***	3.85b	3.15a**
EC	86.21	0.34	86.34bc	85.70ab	84.92a	87.58c**	86.60a	85.82a
ES	112.21	0.52	110.90a	113.23b	113.20b	111.49a***	110.80a	113.61b***
FC	24.85	1.61	30.04c	21.44b	29.97c	17.94a***	22.92a	26.77b***
*L**	91.0	0.67	88.62a	90.43b	90.55b	94.36c***	89.66a	92.31b***
*a**	0.19	0.08	0.55d	0.16b	0.23c	-0.17a***	0.23b	0.15a***
*b**	9.63	0.55	11.13c	10.37b	10.22b	6.82a***	10.83b	8.44a***

Particle size: coarse (c), fine (f). *P<0.05; **P<0.01; ***P<0.001.

WBC, water binding capacity; EC, emulsifying capacity; ES, emulsion stability; FC, foaming capacity.

Table 2. Significant individual effects (extrusion treatment and particle size) on thermal properties.

			Extrusion treatment				Particle Size	
	Media	SE	3	2	1	0	c	f
T_o (ºC)	68.0	1.2	n.d	71.1c	67.4b	65.5a***	70.3b	65.7a***
T_p (ºC)	74.0	1.0	n.d.	76.4c	74.4b	71.2a***	75.6b	72.4a***
T_c (ºC)	80.6	0.9	n.d.	82.5b	81.4b	77.9a**	81.8b	79.3a**
T_p-T_o (ºC)	6.0	0.4		5.3a	7.0a	5.8a	5.3a	6.7a
ΔH (J/g)	2.383	0.229	n.d.	1.550a	3.075c	2.525b***	2.483a	2.283a
PHI (J/g*ºC)	0.392	0.040	n.d.	0.275a	0.450b	0.450b*	0.433a	0.350a

Particle size: coarse (c), fine (f). *P<0.05; **P<0.01; ***P<0.001.

n.d.: Not detected.

T_o, gelatinization onset; T_p, peak temperature; T_c, conclusion temperature, T_p-T_o, gelatinization range, ΔH, enthalpy and PHI, peak high index.

Table 3. Kinetic parameters extracted from first-order and LOS plots of different flours.

	k (min^{-1}) by first order eq.	k (min^{-1}) by LOS	C_∞ (%)	C_∞ (%) by LOS	Resistant starch (%)
0f	0.043	0.044	137.48	150.63	5.52
0c	0.053	0.051	124.39	130.72	5.91
1f	0.074	0.071	358.42	388.85	3.29
2f	0.061	0.059	338.79	364.30	4.01
3f	0.145	0.143	387.35	727.46	2.23
1c	0.054	0.053	134.98	143.25	6.10
2c	0.076	0.073	143.38	156.65	5.75
3c	0.061	0.059	230.75	243.55	2.11

k, kinetic constant; C_∞, equilibrium concentration

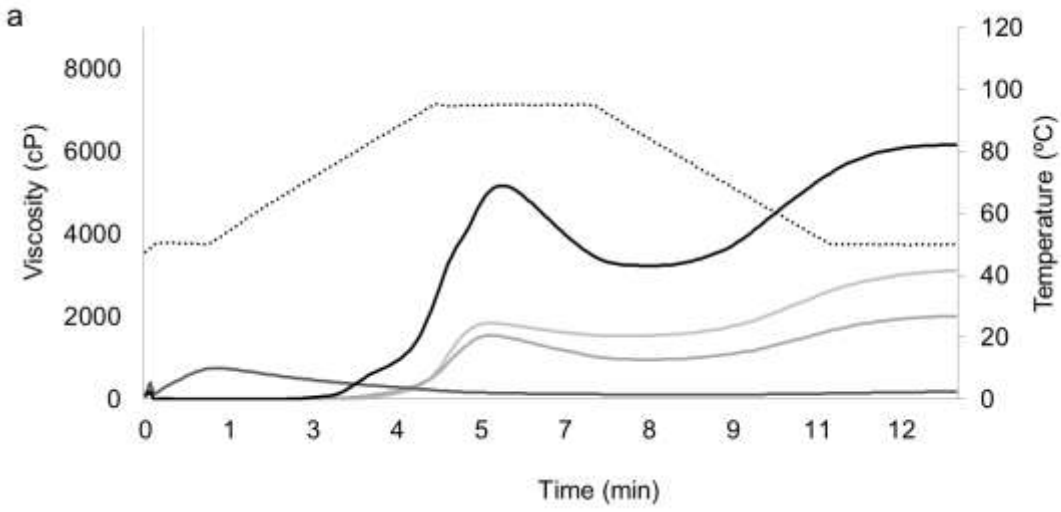
Numbers in sample codes are referred to extrusion intensity and letters are associated to coarse (c) or fine (f) flour.

FIGURE CAPTIONS

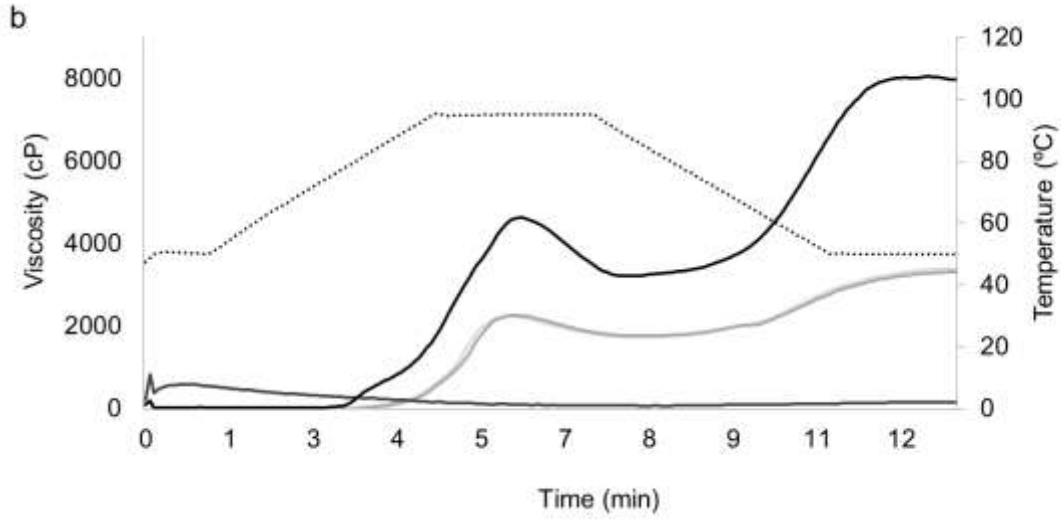
Figure 1. Effect of extrusion treatment on the pasting properties of rice flours with different particle size. Flour 0 (black line), flour 1 (clear grey line), flour 2 (intermediate tone grey line), flour 3 (dark grey line). Temperature profile (discontinuous line). Coarse flours (a), fine flours (b).

Figure 2. Effect of extrusion treatment on the enzymatic hydrolysis of rice flours with different particle size. Flour 0 (black line), flour 1 (clear grey line), flour 2 (intermediate tone grey line), flour 3 (dark grey line). Coarse flours (a), fine flours (b).

520 Figure 1



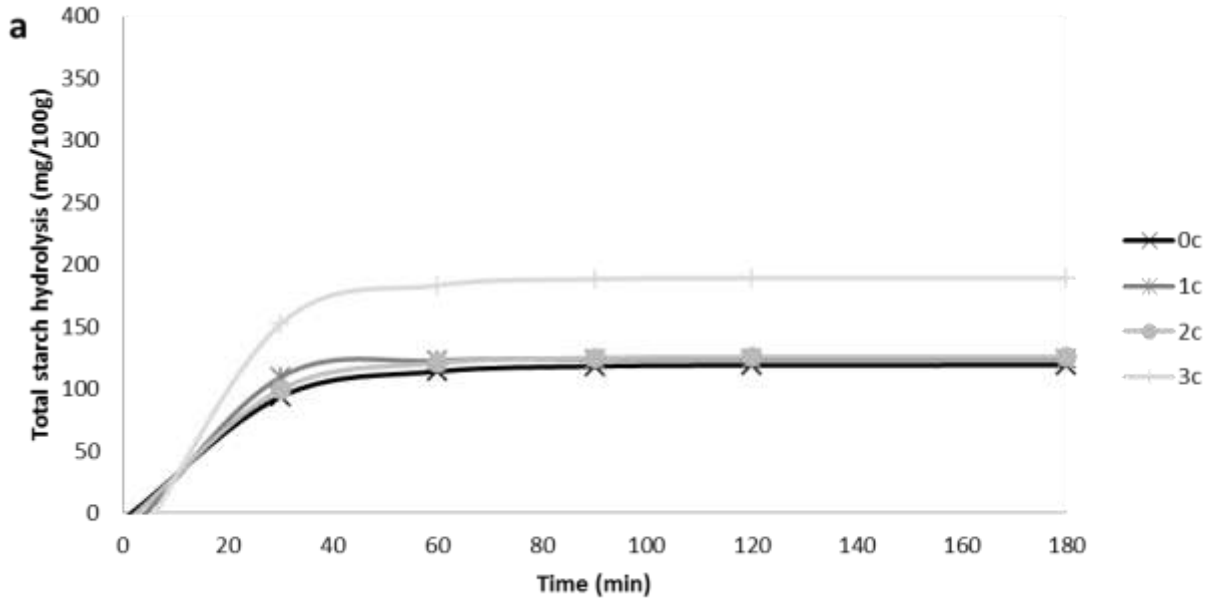
521



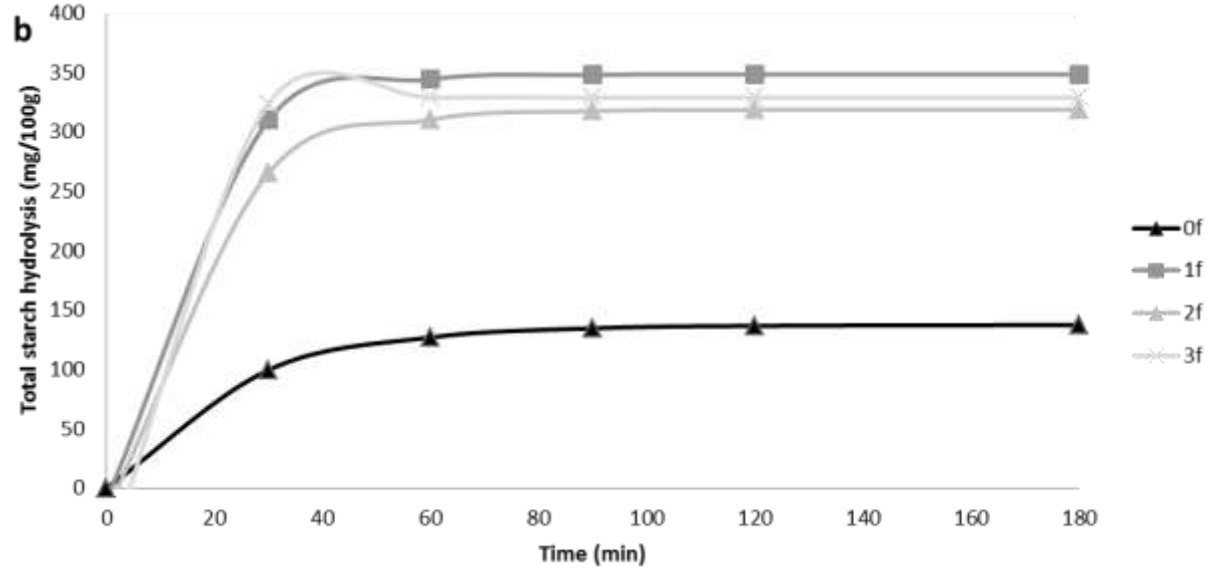
522

523

524 Figure 2



525



526