PROCEEDINGS

Starch Update 2015

The 8th International Conference on Starch Technology

3 – 4 December 2015

The Sukosol Bangkok Hotel, Thailand

Organized by

In collaboration with

National Science and Technology development Agency

Ministry of Science and Technology

111 Thailand Science Park, Phahonyothin Road, Khlong Nueng,

Khlong Luang, Pathum Thani 12120 THAILAND

Tel. +662-564-7000, Fax. +662-564-7002-5

Published by:

National Center for Genetic Engineering and Biotechnology (BIOTEC)

113 Thailand Science Park, Phahonyothin Road, Khlong Nueng,

Khlong Luang, Pathum Thani 12120 THAILAND

Tel. +662-564-6700, Fax. +662-564-6701-5

http://www.biotec.or.th

O-STARCH-2

Contribution of thermo-hydric conditions to the prediction of the in vitro digestibility of cooked plantain flour

Olivier Gibert[1,*], A. Giraldo-Toro[1,2], J. Ricci[1], D. Dufour[1,3], C. Mestres[1] and P. Bohuon[2]

[1] Centre de coopération internationale en recherche agronomique pour le développement (CIRAD), UMR Quali Sud, Montpellier, France
[2] Montpellier Sup Agro, UMR Quali Sud, Montpellier, France
[3]CIAT, International Center for Tropical Agriculture, AA6713, Cali, Colombia
* Corresponding author: Tel +33-467616597; E-mail: olivier.gibert@cirad.fr

Abstract

Cooking bananas are staple food for million inhabitants worldwide. Starch is the main component of cooking bananas and plantains at green stage of maturity. The cooking process needed for the consumption of cooking banana is often applied in excess water, leading to an irreversible order-disorder transition of starch, namely gelatinization. Both water and thermal conditions applied are known to affect the functional quality of starch and of the final product, including its nutritional quality.

Thus, various thermo-hydric conditions were applied to investigate the thermal transitions linked to starch gelatinization, with temperature and water content ranging 55-120°C and 1.4-2.0 $kg.kg^{-1}$ of dry starch. A banana flour-water mixture was characterized using DSC while taking into account the effective glass transition temperature, and using a hermetically sealed test cell to get an equivalent extent of starch gelatinization. The corresponding digestibility was evaluated using an *in vitro* technique.

A powerful predictive mathematical tool was developed for monitoring the starch digestibility during process while optimizing its nutritional quality. The degree of plantain starch gelatinization was revealed being mainly dependent on temperature in non-limiting water conditions (> 70% moisture content, wet weight basis). Different thermo-hydric conditions resulted in the same digestibility values, i.e. higher temperatures compensated lower moisture contents, and vice-versa, to reach similar digestibility properties.

Keywords: Plantain, cooking banana, starch, DSC, digestibility

1. Introduction and objectives

Common in Africa and Latin America (Lescot, 2013), plantain banana (Musa spp. AAB) classified into the cooking banana group (Gibert et al. 2009) requires a cooking process before its can be eaten. As a major source of macro-elements, and containing dietary fibre, native banana starch is known for its resistant starch fraction, higher at the green ripe stage of maturity (Tribess et al., 2009). Banana resistant starch fraction could remain unhydrolyzed after 120 min *in vitro* amylolytic enzyme attack using a similar procedure to the *in vivo* digestion one, as earlier mentioned by Giraldo et al. 2015. With a 67% about fraction of starch resisting to α-amylase activity (Englyst and Cummings 1986), no massive rise in the postprandial glycaemic response is observed (Miao, Zhang, Mu, & Jiang,2010), which in turn could be beneficial for nutritional quality and health.

In addition, starch functional properties are known to be affected by processing, and in particular with starch thermo-hydric history. The physical state of the starch ingested has a major impact on its digestibility, which is closely linked to the processing techniques (Singh, Dartois, & Kaur, 2010). A fraction of starch can remain ungelatinized using an insufficient

heating temperature (Parada & Aguilera, 2009) or a limited water content (Briffaz et al., 2013), which, in turn will lead to significant changes in the starch's nutritional quality (Holm, Lundquist, Björck, Eliasson, & Asp, 1988). As earlier mentioned (Wang & Copeland, 2013), the extent of disruption caused by heat and moisture will directly impact the ease and extent of enzymatic hydrolysis of cooked starch.

In this study we propose to use Differential Scanning Calorimetry (DSC) and an *in vitro* technique to monitor the potential health benefits of cooked banana, while carrying out investigations in the 1.4-2.0 kg kg^{-1} db flour range (water/flour), corresponding to a non-limiting water content range in plantain pulp (Gibert et al. 2010). We propose to establish a quantitative relationship between the degree of plantain starch gelatinization linked to thermo-hydric conditions applied, and *in vitro* digestibility, while constructing a state diagram of plantain flour. Such powerful tool could help to predict the degree of starch gelatinization for developing food processing methods with a specific functional quality.

2. Materials and methods

2.1 Raw material and starch extraction

One Dominico Harton plantain bunch harvested at optimal green stage of maturity was collected in Colombia. The pulp of the second hand of the bunch was cut into thin slices, oven-drying at 40◦C overnight, prior to fine grinding. Starch extraction process was carried out using freshly cut pieces of pulp being suspended in distilled water and crushed in a Waring blender. After slurry filtration, washing and decantation, the dark top layer removed, the starch was centrifuged prior to oven-drying at 40°C for 48h and grinding in a mortar. Both flour isolated starch were stored at 4°C in airtight plastic bags.

2.2 Total starch content and free glucose

Total starch content (TS) was estimated after hydrolysis by heat-thermostable α-amylase enzyme and then with amylo-glucosidase. The total released glucose was measured by colorimetry after reaction with glucose oxidase and peroxidase (GOD-POD) enzymes as per Holm et al. 1986. Free glucose was estimated separately after the sulphuric acid extraction of plantain flour and the GOD-POD system.

2.3 Thermal properties and effective glass temperature

The measurements of thermal transitions associated with starch gelatinization were determined by the variation of enthalpy (ΔH kJ kg^{-1}db starch) at a water content (noted X_1) adjusted to 1.4 and 2.0 kg kg−1db by DSC, corresponding to the raw plantain water content and to the maximum cooked plantain water content, respectively (Gibert et al., 2009; Gibert et al., 2010).

2.4 Degree of starch gelatinization in both DSC and test cell

Plantain-water mixtures were introduced in sealed stainless steel pans, heated for 10 min at various temperatures T and X_1, cooled down, held for at ambient temperature, prior to reheating to measure the specific residual variations of enthalpy (ΔH_r) in DSC. Thermal transitions and respective degrees of gelatinization α (in the 0 to 1 range, namely α_0 and α_1) were calculated taking into account both whole enthalpy (ΔH_e) and (ΔH_r) as described earlier (Giraldo et al. 2015).

In parallel with DSC thermal treatment, plantain flour/water samples were prepared by mixing plantain flour with deionized water to reach targeted water contents X_1, in the 1.4–2.0 kg kg−1db range and kept for equilibrium under partial vacuum conditions. Flour/water mixture samples were heated in a hermetically sealed custom-designed test cell as described earlier (Jiménez et al., 2010). The cooking conditions applied in the test cell were defined in order to obtain an equivalent extent of starch gelatinization as per DSC, and later having sufficient amount of flour paste for starch digestibility measurements. After each thermal treatment, the flour paste was then removed from the test cell and weighed into stainless steel capsules prior to the DSC measurement.

2.5 Starch digestibility

The remaining amount of flour paste from test cell was the used to measure the starch *in vitro* digestibility as per Englyst, Veenstra, and Hudson (1996) with slight modifications. After each thermal treatment, 500 mg of starch db was introduced in a centrifuge tube, prior to the addition of guar gum and pepsin solution as described by Giraldo et al. (2015). After dispersion homogenization, a pancreatin-invertase-amyloglucosidase mixture was added prior to water bath mixing at 37◦C for 20 min. An aliquot of the dispersion was collected at 20 min and 120 min to obtain the both rapidly digestible (RDS) and slowly digestible (SDS) fractions, respectively. The total glucose content was later estimated by spectrophotometry after the reaction with glucose oxidase and peroxidase. The data were computed in g/100 g starch db excluding free glucose. Both rapidly digestible and resistant starch fraction estimates were later non-dimensionalize (RDS^* and RS^*) as per Giraldo et al. (2015), which in turn can be helpful as it makes it possible to run multiple transformations with different absolute amounts of RDS within the $[\alpha_0\ \alpha_1]$ range, that can be compared on the same plot.

3. Results and discussion

3.1 Starch thermal transition

After baseline subtraction, DSC thermograms were normalize for Dominico Harton flour-water mixtures with different water contents, as illustrated in Figure 1. Temperatures were independent of water content with the absence of shift on onset, peak and end temperatures for the gelatinization transition at 69.7 ± 0.3 °C, 73.7 ± 0.4 °C and 79.7 ± 0.8 °C, respectively. A slight increase in the whole enthalpy change (ΔH_e) was observed between 1.4 and 2.0 2.0 kg kg^{-1} db, with 19.0 ± 1.1 kJ kg^{-1} db and 20.5 ± 0.9 kJ kg^{-1} db, respectively. As earlier described by Donovan (1979), a biphasic endothermic transition was observed with a first endotherm labelled as "G endotherm" followed by a small shoulder corresponding to the starch fusion peak labelled as "M1" as per Donovan & Mapes (1980).
The intensity of the G endotherm increased whereas its temperature was stable with increasing water content. In the meantime, the M1 endotherm intensity and transition temperature gradually decreased with an increase in X_1. This progressive shift was successively described as the variation of the melting point of starch crystallites, the melting temperature, the cooperative processes that occur during crystallite melting and starch swelling at high water content (Donovan, 1979; Biliaderis et al., 1980; Colonna & Mercier, 1985.

Complementary DSC thermogram for a native flour-water mixture at 1.4 kg of water per kg of dried plantain flour was compared to endotherm after reheating at 65, 75, and 90 °C (Giraldo et al. 2015). An increase in the onset temperature, the peak temperature and the end temperature and decreases the intensity of the G and M1 endotherms was observed, as earlier reported (Donovan, 1979, Biliaderis et al., 1980, Briffaz et al., 2013).

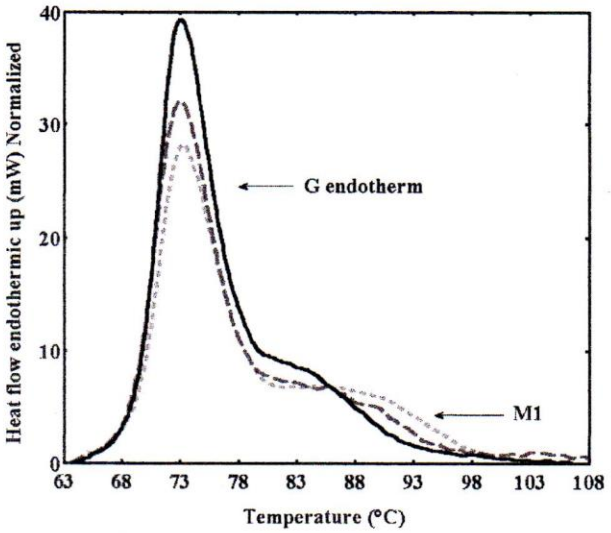

Figure 1. Endotherms recorded for Dominico Harton plantain flour mixture with different water contents: 1.4 kg kg^{-1} dry basis (⋯⋯), 1.5 kg kg^{-1} dry basis (– –), 2.0 kg kg^{-1} dry basis (——).

A small shift of the baseline was observed at the beginning of the thermal transition. It could correspond to the glass transition (T_g) and induce an overestimation of ΔH_e Thus, the location of the temperature of the effective T_g was used for computing corresponding ΔH_e, after both intermediate heating and complete heating scans as per Slade and Levine (1988). T_g was identified below the onset of gelatinization in the 56 - 60 °C range. However, one could expect a decrease in T_g while increasing water content of the starch mixture (Slade & Levine, 1991). The lack of variation of T_g could be hypothesized being due to the narrow water content range used here. ΔH_e was thus calculated considering the thermal event dedicated to the plantain starch non-equilibrium melting transition. The computation of the degree of starch gelatinization α at various water contents and temperatures led us to consider variations of enthalpies for gelatinization while taking into account the sum of all thermal transitions G and M1.

3.2 Modelling phase diagram of plantain flour-water mixtures

A 3-parameter Weibull cumulative model was successfully used to describe the starch gelatinization. The empirical model fitted the experimental α values on the whole X_1 domain as illustrated in Figure 2A. As earlier suggested by (Van Boekel, 2002), the 3 parameters β, θ and γ correspond to the shape parameter, the scale parameter, and location parameter, respectively. The 3 parameters were identified using non-linear regression. The β and θ values did not significantly differ from one another between 1.4 and 2.0 kg.kg^{-1} db. θ corresponds to the "start transition temperature". It is independent of X_1 according to some previous research. However, the γ-parameter is strongly dependent on the water content (a_α / X_1). The parameter values identified by non-linear regression were $\beta = 1.3 \pm 0.1$, $\theta = 59.6 \pm 0.5$ °C and $a_\alpha = 19.1 \pm 1.0$. In the 55 – 120 °C range and 1.4 and 2.0 kg.kg^{-1} db range. The determination coefficient values (R^2 = 0.99) showed that the Weibull model provided quite an accurate reflection of the state diagram for plantain flour. Moreover, with the degree of starch gelatinization α determined for the 3 parameters a close fit between the experimental and simulated degree of starch gelatinization was obtained with a root-mean-

square error of starch gelatinization equal to 3 %. θ value was located close to the upper limit of the T_g range (56 °C $\leq T_g \leq$ 60 °C).

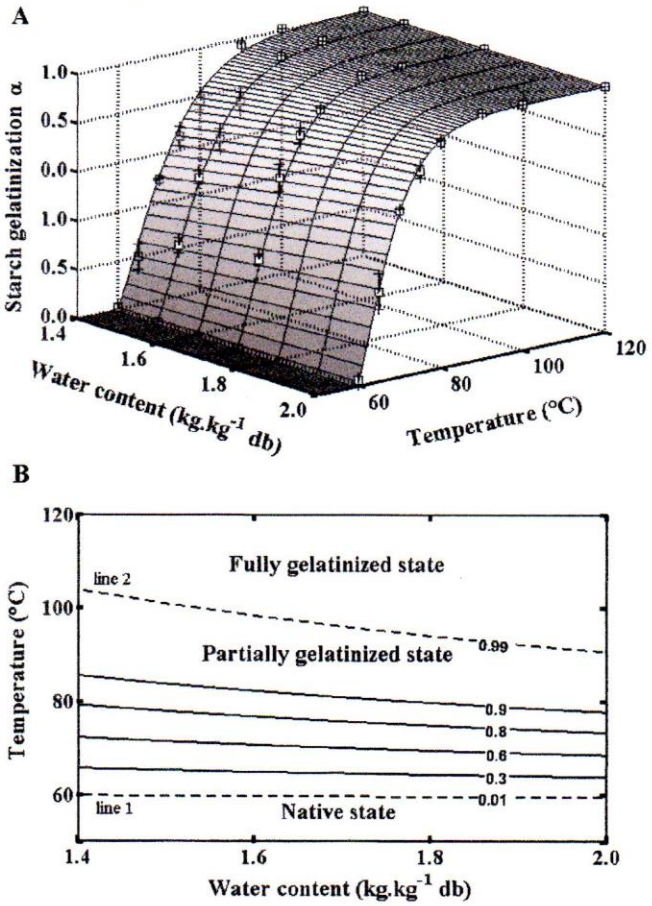

Figure 2 Modelling phase diagram of plantain flour-water mixtures (starch conversion α *vs.* treatment temperature and water content db).

The corresponding phase diagram was constructed to monitor the extent of plantain starch gelatinization over temperature and water content (Figure 2B). Below 70 °C as the lowest temperatures of the model, an almost horizontal iso-response in terms of α of the plantain starch over water content was observed. As expected, below the θ-temperature, whatever X_1, no gelatinization occurred. As soon as the temperature rised, the iso-responses for the extent of starch gelatinization became more vertical, and there was a potential reduction in the contribution of water to the phenomenon. It suggests that the extent of starch gelatinization is very dependent on temperature in such non-limiting water conditions. The result was confirmed by a strong correlation between the temperature and extent of starch gelatinization on experimental data (data not shown). The phase diagram could then be used to predict α according to the processing conditions, *i.e.* water content and temperature. Three states were distinguished: native state (below iso-response line 1 for $T < 59.6 \pm 0.5$ °C), partially gelatinized state (area between iso-responses $0 \leq \alpha \leq 1$) and fully gelatinized state (above line 2, $\alpha = 0.99$).

3.3 Relation between the degree of starch gelatinization and digestibility in vitro

As expected, the *RDS* increased and the *RS* decreased when the extent of thermal gelatinization increased. *RDS* values for native flour (11.0 ± 0.7 %) were consistent with previous works (Zhang & Hamaker, 2012). A plantain flour-water mixture cooked at 100°C

or above also exhibited slightly higher *RDS* values (90.5 ± 3.7 % at 1.4 kg kg^{-1} db) than those reported by previous authors (72.8 ± 4.2 %). The difference could be partially attributed to the use of different varieties. As far as the resistant starch fraction is concerned, the investigation carried out by Zhang & Hamaker (2012) reported 83.4 % db in raw banana flour. However, in the present study no significant difference was observed for native starch, irrespective of the water content (with 84.3 ± 3.8 % and 81.2 ± 1.0 % db), although for full-gelatinized samples, a slight remaining *RS* fraction was observed at 1.4 kg kg^{-1} db whereas no remaining *RS* fraction was observed at 2.0 kg kg^{-1} db (0.0 ± 0.1 % db). The corresponding normalized *RDS** and *RS** over the extent of starch gelatinization are illustrated in Figure 3. The model obtained for both *RDS** and *RS** fitted experimental data well for both water conditions.

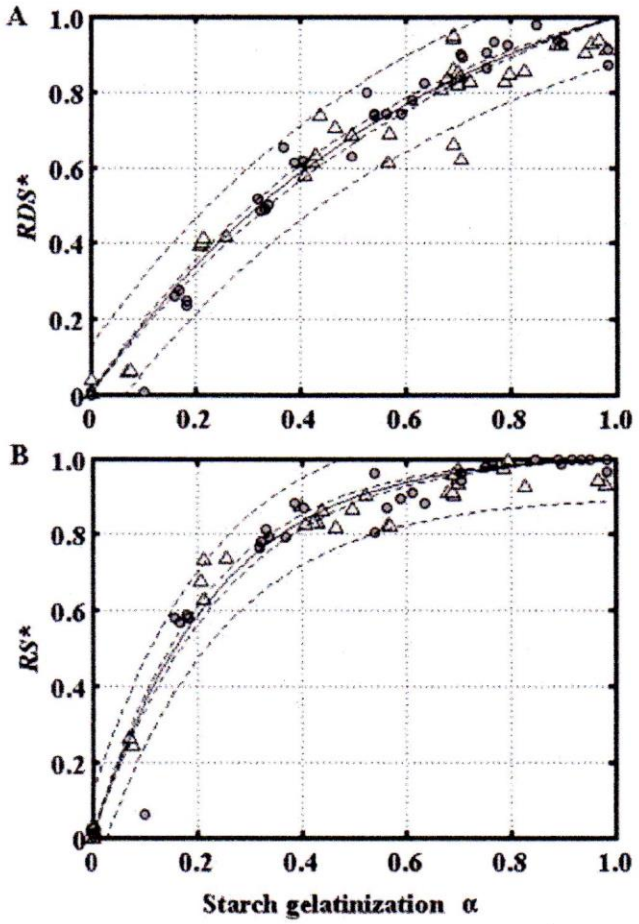

Figure 3 Dimensionless rapidly digestible starch fraction (RDS^*) and resistant starch fraction (RS^*) of plantain flour as a function of the degree of plantain starch gelatinization (α). Experimental data at different water contents 1.4 kg.kg^{-1} db (△) and 2.0 kg.kg^{-1} db (○) and predicted curves: dashed (-.-) line represent the confidence interval and (--) the predicted interval ($P = 0.05$).

In addition, the a_Y parameters were identified for both dimensionless fittings of *RDS** and *RS**, with a reliable RMSE and an indicative R^2, around 6 % and above 0.96, respectively. No significant differences between experimental *RDS* over water were observed at either $\alpha = 0$ or $\alpha = 1$, with approximately 11 % db and 87 % to 90 % db, respectively.

A continuous increase of the normalized RDS^* fraction was observed along the starch gelatinization rate (Figure 3A). While starch gelatinization explained 95 % of the variation of *RDS**, temperature accounted for 69 % of the variation of *RDS**. The same results were observed for *RS**, however *RS* content decreased with extent of starch gelatinization, but as far as *RS** concerned, an increase of *RS** was observed on Figure 3B with starch gelatinization. The *RS** values seemed very dependent on starch gelatinization in the 0.0 – 0.4 α range. The 0.0 – 0.4 α range corresponded to the highest rate of production of *SDS* (data not shown). Thus, cooked plantain starch seems a promising starch ingredient with relatively balanced energy release, and a good proportion of SDS, and RS fractions. A slight variation of the RS^* was observed for a more advanced rate of starch gelatinization, corresponding to the minimal production of *SDS* and *RS*. The dependence of starch gelatinization on temperature illustrated by the phase diagram (Figure 2) was confirmed by a strong correlation observed between α and T for RDS^* and RS^*.

4. Conclusion

As a first stage, starch thermal transitions have been modelled using plantain flour-water mixture. An empirical Weibull model was fitted with DSC data for any water content (X_1).The combined effects of temperature and water content on the *in vitro* digestibility properties can be summarized by starch conversion (α) irrespective of the heat-treatment history. So, two empirical models were proposed to predict *RDS* and *RS* as a function of starch gelatinization. In the water content range of banana plantain (raw to water-cooked), the temperature seems the main factor that influences starch conversion and digestibility. An investigation is expected to be later conducted between plantain flour and pieces of pulp soon after cooking aiming at comparing their respective degree of starch gelatinization (α) and *in vitro* digestibility, which in turn, could be used to predict the gelatinization and digestibility behaviour of plantain starch in whole pieces of pulp. Moreover, the state diagram, *RDS* and *RS* response models will be later integrated in a heat and mass transfer model with the aim of optimizing the plantain cooking process.

Acknowledgements

The authors gratefully acknowledge the help of Dr Agnès Rolland-Sabaté and Bruno Pontoire, and the financial support of COLFUTURO (Colombian Organization) and Bourse EIFFEL (French Ministry for International Relations) institutions for funding this work.

References

Biliaderis, C. G., Maurice, T. J., & Vose, J. R. (1980). Starch gelatinization phenomena studied by differential scanning calorimetry. Journal of Food Science, 45(6), 1669–1674.

Briffaz, A., Mestres, C., Matencio, F., Pons, B., & Dornier, M. (2013). Modelling starch phase transitions and water uptake of rice kernels during cooking. Journal of Cereal Science, 58(3), 387–392.

Colonna, P., & Mercier, C. (1985). Gelatinization and melting of maize and pea starches with normal and high-amylose genotypes. Phytochemistry, 24(8), 1667–1674.

Donovan, J. W., & Mapes, C. J. (1980). Multiple phase transitions of starches and nägeli amylodextrins. Starch – Stärke, 32(6), 190–193.

Donovan, J. W. (1979). Phase transitions of the starch–water system. Biopolymers, 18(2), 263–275.

Englyst, H. N., Veenstra, J., & Hudson, G. J. (1996). Measurement of rapidly available glucose (RAG) in plant foods: A potential *in vitro* predictor of the glycaemic response. British Journal of Nutrition, 75(3), 327–337.

Englyst, H. N., & Cummings, J. H. (1986). Digestion of the carbohydrates of banana (Musa paradisiaca sapientum) in the human small intestine. American Journal of Clinical Nutrition, 44(1), 42–50.

Gibert, O., Dufour, D., Giraldo, A., Sánchez, T., Reynes, M., Pain, J. P., Fernandez, A., & Diaz, A. (2009). Differentiation between cooking bananas and dessert bananas. 1. Morphological and compositional characterization of cultivated Colombian musaceae (Musa sp.) in relation to consumer preferences. Journal of Agricultural and Food Chemistry, 57(17), 7857–7869, Err. 58(16) 9090.

Gibert, O., Giraldo, A., Uclés-Santos, J.-R., Sánchez, T., Fernández, A., Bohuon, P., Reynes, M., Gonzalez, A., Pain, J. P., & Dufour, D. (2010). A kinetic approach to textural changes of different banana genotypes (Musa sp.) cooked in boiling water in relation to starch gelatinization. Journal of Food Engineering, 98(4), 471–479.

Giraldo Toro, A., Gibert, O., Ricci, J., Dufour, D., Mestres, C., Bohuon, P. (2015) Digestibility prediction of cooked plantain flour as a function of water content and temperature. Carbohydrate Polymers, 118, 257-265.

Holm, J., Lundquist, I., Björck, I., Eliasson, A. C., & Asp, N. G. (1988). Degree of starch gelatinization, digestion rate of starch *in vitro*, and metabolic response in rats. American Journal of Clinical Nutrition, 47(6), 1010–1016.

Holm, J., Björck, I., Drews, A., & Asp, N. G. (1986). A rapid method for the analysis of starch. Starch – Stärke, 38(7), 224–226.

Jiménez, N., Bohuon, P., Lima, J., Dornier, M., Vaillant, F., & Pérez, A. M. (2010). Kinetics of anthocyanin degradation and browning in reconstituted blackberry juice treated at high temperatures (100–180 degrees C). Journal of Agricultural and Food Chemistry, 58(4), 2314–2322.

Lescot, T. (2013). World plantain and banana production systems. In A. L. Borges, & L. Lichtemberg (Eds.), Proceedings of the 20th international meeting ACORBAT: 40 years sharing science and technology, Reunion international ACORBAT 2013 Fortaleza, Brazil, 9–13 September, 2013, (pp. 27–34), 2013-09-09/2013-09-13.

Miao, M., Zhang, T., Mu, W., & Jiang, B. (2010). Effect of controlled gelatinization in excess water on digestibility of waxy maize starch. Food Chemistry, 119(1), 41–48.

Parada, J., & Aguilera, J. M. (2009). In vitro digestibility and glycemic response of potato starch is related to granule size and degree of gelatinization. Journal of Food Science, 74(1), E34–E38.

Singh, J., Dartois, A., & Kaur, L. (2010). Starch digestibility in food matrix: A review. Trends in Food Science & Technology, 21(4), 168–180.

Slade, L., & Levine, H. (1991). A food polymer science approach to structure-property relationships in aqueous food systems: non-equilibrium behavior of carbohydrate–water systems. Advances in Experimental Medicine and Biology, 302, 29–101.

Slade, L., & Levine, H. (1988). Non-equilibrium melting of native granular starch: Part I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. Carbohydrate Polymers, 8(3), 183–208.

Tribess, T. B., Hernández-Uribe, J. P., Méndez-Montealvo, M. G. C., Menezes, E.W., Bello-Perez, L. A., & Tadini, C. C. (2009). Thermal properties and resistant starch content of green banana flour (Musa cavendishii) produced at different drying conditions. LWT – Food Science and Technology, 42(5), 1022–1025

Van Boekel, M. A. J. S. (2002). On the use of the Weibull model to describe thermal inactivation of microbial vegetative cells. International Journal of Food Microbiology, 74(1–2), 139–159.

Wang, S., & Copeland, L. (2013). Molecular disassembly of starch granules during gelatinization and its effect on starch digestibility: A review. Food & Function, 4(11), 1564–1580.

Zhang, P., & Hamaker, B. R. (2012). Banana starch structure and digestibility. Carbohydrate Polymers, 87(2), 1552–1558.