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Comparison of physical, chemical and functional properties of broken rice and breadfruit starches against cassava starch

(Perbandingan ciri-ciri fizikal, kimia dan fungsi kanji beras hancur dan buah sukun dengan kanji ubi kayu)

S.P. Koh* and K. Long*

Keywords: broken rice, breadfruit, starch, gelatinization temperature, amylose

Abstract

The physical, chemical and functional properties of starch differ with different starch sources. In general, breadfruit starch was closer to cassava starch characteristics compared to broken rice starch. Among the starch sources, cassava starch showed the highest paste clarity at all pH values. The broken rice starch had poor paste clarity even though it has the smallest starch granules. Compared to both broken rice and cassava starches, breadfruit starch was found to have the highest swelling power, water binding capability, water absorption index, bulk density, dispersibility capability and required the highest enthalpy energy during the gelatinization process.

Introduction

Starch is a basis of our food and plays a major role in industrial economy. It is one of the most abundant substances in nature. Starch is a renewable resource as this semi-crystalline carbohydrate is synthesized in many plant tissues including roots, tubers, rhizomes and seeds. Starch can be converted into many diverse products such as paper, beverages, pharmaceuticals, plastics, textiles and confectioneries either through chemical or biological process depending on the physical and chemical characteristics of the starch (Tester et al. 2004; Nand et al. 2008). The conversion of starch into biodegradable plastics can be achieved either by chemically modifying starch or by blending with other polymers as a substitute for petroleum-based plastics to reduce plastic wastes that cause serious impact to the environment (Demirgoz et al. 2000; Parra et al. 2004).

Breadfruit (*Artocarpus altilis*), typically consumed as a starchy staple when mature, is a nutritious and high-energy food with moderate glycemic index (Ragone 2009). It is also a good source of fibre, vitamins and minerals. Breadfruit is found throughout the tropics and cultivated on most pacific islands (Ragone 2009). Breadfruit flour can serve as a replacement for imported wheat flour in many baked products and snack foods which contain wheat allergens (e.g. wheat protein) that is associated with Baker's Asthma (Salcedo et al. 2011).

Rice is the second largest produced cereal in the world (Khoso and Raza 2008). Broken rice is the by-product of rice milling which is sold at a cheaper price. This lower grade rice, normally mixed with the local super/premium rice at 5%, is mostly sold in the rural areas and consumed by the lower-income earners. For the ruminant industry, broken rice is blended with

*Biotechnology Research Centre, MARDI Headquarters, Serdang, P.O. Box 12301, 50774 Kuala Lumpur, Malaysia
Authors' full names: Koh Soo Peng and Kamariah Long
E-mail: karenkoh@mardi.gov.my

some supplements and used as the locally available feedstuffs to reduce the cost of livestock production which depends heavily on imported feedstuffs.

In recent years, food technology has focused on providing high quality food products which are low in calories and cost. The pharmaceutical industry is more concerned with efficient delivery systems which are relatively inexpensive and easily accessible. So far, materials like maltodextrins that contain both simple sugars and polymers of saccharides have been widely used as ingredients in food products and pharmaceutical delivery systems (Fuisz 1997). Presently, cassava starch characteristics are well known to be suitable for production of high quality maltodextrin. Generally, the physico-chemical and functional properties of starch such as amylose content, swelling power, starch density, water binding capability and dispersibility are the principle factors that may affect the properties of maltodextrin (Akanbi et al. 2009). This is because maltodextrin with the same dextrose equivalent (DE) value might have very different physical properties like water holding, gelling, crystallization prevention and freezing point (Dokic-Baucal et al. 2004) which can have different properties in various applications that reflect differences in their molecular composition, linearity and branched structure. Therefore, it is very important to understand the physico-chemical properties of starch to determine the suitable process parameter for the production of high quality maltodextrin.

Presently, there is a lack of full spectrum study on the physico-chemical characteristics of the breadfruit and broken rice starches. Not much work has been reported on maltodextrin production from broken rice and breadfruit. Therefore, the objective of this work was to evaluate the physico-chemical and functional properties of broken rice and breadfruit starches so as to have a better understanding of the behaviour of these starches. This information is important to justify the use of breadfruit or broken rice starches as raw materials for production of high value-added maltodextrin using enzymatic processing technology. The differences in starch physico-chemical properties will influence the maltodextrin physico-chemical properties that eventually define its specific functional applications in food, textile, paper, pharmacy and plastic industries (Moore and Amante 2005; Debusk and Alleman 2006; Raida et al. 2007).

Materials and methods

Matured unriped breadfruit and broken rice (blends of local rice varieties, MR 219 and MR 220) were purchased from the local market. All the starches were prepared at laboratory scale (Akanbi et al. 2009). Cassava starch was used as reference as this starch was known to produce high quality maltodextrin.

Breadfruit starch was extracted from matured unripe breadfruit. Peeled fruits were washed, chopped and then pulverized in a high speed blender for 5 min. The breadfruit pulp was suspended in water 10 times its volume to allow the starch to come out from the pulp. The suspended starch slurry was sieved using a double fold muslin cloth to retain the fibres which were rewashed to remove any adhering starch. Sedimentation of the extracted starch was allowed overnight and the supernatant was decanted. The starch was washed a few times with distilled water to remove unwanted impurities and then allowed to settle at the bottom of the container overnight. The supernatant was then decanted. The resulting wet starch was spread in the chamber of the oven and dried at 50 °C for 2 days to obtain 10 – 11% moisture content.

The broken rice was washed a few times with distilled water before being pulverized in a high speed blender for 5 min. The starch slurry was suspended in water 10 times its volume and filtered through a double fold muslin cloth. The rice supernatant was allowed to sediment overnight and the starch was washed a few

times with distilled water to remove other impurities. The resulting wet starch was spread in the chamber of the oven and dried at 50 °C for 2 days to obtain 10 – 11% moisture content.

The dried starches were milled into powder with ultra centrifugal mill (Model: ZM 200, Retsch) using a mesh sieve of 0.5 mm and stored in glass bottles at 4 °C for further analysis. Starch yield was derived using the calculation described below:

Starch content (%) = (W_1/W_2) x 100 where W_1 is the weight of starch extracted from a known weight (W_2) of the edible portion of the raw materials.

The ash, fat and moisture content were determined by AOAC official methods and crude protein content was analyzed using Kjeldahl method (AOAC 1994). For the determination of pH, 5 g starch sample was added to 20 ml distilled water in a beaker and mixed for 5 min. The starch was then allowed to settle and the pH of the water phase was measured using calibrated pH meter.

Dried starch samples were viewed under a microscope at a magnification of 400X. The micrographs were used to compare the morphology of the starch granules.

Amylose content was determined using a spectrophotometer which involved the preparation of iodine solution and reagent (Williams et al. 1970). Pure potato amylose was used as a standard. The iodine stock solution was prepared by weighing 2 g iodine and 20 g potassium iodide and diluted to 100 ml in a volumetric flask. A total of 10 ml iodine solution was taken from the iodine stock solution and diluted to 100 ml to make an iodine reagent. About 0.5 g of starch sample was weighed in a beaker, exactly 10 ml of 0.5 N KOH solution was added and the starch was then dispersed with magnetic bar for 5 min. The dispersed samples were transferred to a 100 ml volumetric flask and diluted to the mark with distilled water. An aliquot of the test starch solution (10 ml) was pipetted into a 50 ml volumetric flask and 5 ml of 0.1 N HCl was added, followed by 0.5 ml iodine reagent. The volume was diluted to 50 ml and the absorbance of the blue colour was measured at 625 nm after 5 min. The amylose content of the sample can be calculated from the calibration curve equation based on the absorbance value obtained.

The test for water binding capability was carried out using Akanbi et al. (2009) method. A total of 37.5 ml distilled water was added into 2.5 g of starch sample and centrifuged for 10 min at 3,000 rpm. The weight of the centrifuge tube and contents was determined after decanting the water and allowed to drain for another 10 min. The bound water was determined by the change in the weight. The water binding capability was calculated as below:
Water binding capability (%) = (bound water/weight of sample) x 100

The starch swelling power was determined according to Takashi and Sieb (1988). One gram of starch sample was weighed into a 50 ml centrifuge tube, 50 ml of distilled water was added and mixed gently. The slurry was heated in a water bath at 60, 70, 80, 90 and 100 °C respectively for 5 min. During the heating, the slurry was stirred gently to prevent clumping of starch. After 15 min, the tubes containing the paste were centrifuged at 3,000 rpm for 10 min. The supernatant was decanted immediately after centrifuging. The weight of the sediment was recorded. The moisture content of the gel was thereafter determined to get the dry matter content of the gel. The starch swelling power was calculated as below:

Swelling power = (weight of wet mass of sediment/weight of dry matter of gel) x 100

Determination of water absorption index was carried out using the method of Akanbi et al. (2009). About 2.5 g of starch sample was suspended in 30 ml of distilled water in a centrifuge tube at 30 °C. The starch solution was stirred for 30 min

intermittently and then centrifuged for 3,000 rpm for 10 min. The supernatant was decanted and the weight of the gel formed was recorded. The water absorption index was calculated as below:

Water absorption index = (weight of bound water/weight of sample) x 100

The bulk density was determined according to the method described by Wong and Kinsella (1976). About 5 g of starch was weighed into a 50 ml graduated measuring cylinder. The sample was packed by gently tapping the cylinder on the bench top from a height of 5 cm. The volume of the sample was recorded and the bulk density was determined as below:

Bulk density (g/ml) = (weight of sample/volume of sample after tapping)

The dispersibility of starch was determined according to Kulkarni et al. (1991). About 10 g of starch sample was suspended in a 100 ml measuring cylinder and distilled water was added to reach a volume of 100 ml. The mixture was stirred vigorously and then allowed to settle for 3 h. The volume of the settled particles was recorded and subtracted from 100. The difference was reported as percentage dispersibility.

The gelatinization properties of starch were analysed using differential scanning calorimetry (DSC, Model: Diamond Pyris, Perkin Elmer) equipped with an intercooler (Tulyathan et al. 2006). The starch sample (3 mg) was weighed in an aluminium pan and 6 µl of distilled water was added. The pan was hermetically sealed using a sample sealing accessory. The sample was heated from 20 – 110 °C at a heating rate of 10 °C/min with an empty pan as the reference. The starch thermal transitions were defined in terms of T_0 (onset), T_p (peak) and T_e (end of gelatinization temperature). The enthalpy (ΔH, J/g) of the DSC endotherm was also calculated. All the samples were analysed in triplicate.

To determine the paste clarity the starch samples were suspended in distilled water to yield 1% (w/v) starch slurry in screw cap tubes. The pH of the starch slurries were adjusted to 2, 4, 6, 8, 10 and 12 by addition of 0.1 N HCl or 0.1 N NaOH as required. The tubes were then heated in a boiling water bath with occasional shaking for 30 min. The samples were cooled to ambient temperature and the percentage transmittance of the starch solution was determined using the spectrophotometer by reading the absorbance at 650 nm against water as the blank (Nand et al. 2008).

Statistical analysis

Data were statistically analysed by one-way analysis of variance using PAWS statistics (version 18). Significant differences ($p < 0.05$) between means were determined by Duncan multiple range test.

Results and discussion

Both rice and breadfruit starches produced in the laboratory contained a starch yield of 82.31% and 17.8% respectively. Rice is known to have high starch content, which is above 80% depending on rice cultivars (Srikaeo and Sopade 2010). The commercial breadfruit starch content falls in the range of 17.5 – 29.2% (Ragone 2009). The amount of starch in the breadfruit depends on the fruit maturity. In this case, we are using the matured unripe breadfruit and the low starch yield obtained might be due to the loss that may occur during the starch extraction process and varietal differences in starch content in the breadfruit. In this study, cassava starch was used as a reference as this starch was claimed to be the most suitable raw material for production of high grade maltodextrin with higher clarity appearance compared to other starchy sources (personal communication with maltodextrin industry).

In general, all three starches showed a low level of ash and fat content as summarized in *Table 1*. There was no protein found in both breadfruit and cassava starch but the rice starch still contained 5.91% of protein. According to Tanaka et al. (1980), the rice protein that exists in the

Table 1. Physico-chemical properties of cassava, broken rice and breadfruit starches

	Cassava	Broken rice	Breadfruit
Protein content (%)	0.00 ± 0.00a	5.91 ± 0.00b	0.00 ± 0.00a
Fat content (%)	0.02 ± 0.006a	0.09 ± 0.006b	0.03 ± 0.006a
Ash content (%)	0.16 ± 0.01b	0.07 ± 0.01a	0.09 ± 0.01a
pH	6.15 ± 0.00c	4.91 ± 0.01a	5.47 ± 0.05b
Amylose content (%)	52.80 ± 0.99b	22.75 ± 0.39a	52.73 ± 0.34b

Each value in the table represents mean ± standard deviation of triplicate analyses. Means within each row with different letters are significantly different (p <0.05)

endosperm is tightly bound on the surface of the starch granules and this makes it difficult to remove from the rice starch. Both rice (pH 4.91) and breadfruit starch (pH 5.47) were slightly acidic as compared to cassava starch (pH 6.15). The optical micrograph of the various starches showed that they were spherical in shape (*Figure 1*). The micrograph of the rice starch showed the smallest spherical-type particles, while the cassava starch had the biggest particle size with rounded borders and smooth surfaces.

The functional properties of the various starches studied showed that breadfruit starch had the highest water-binding capability as well as the water absorption index, indicating the lower intermolecular association and its high content of amylose as compared to the other starches (*Table 2*). The data obtained also indicated that the breadfruit starch had significantly (p <0.05) higher bulk density at 1.71 g/ml and 100% dispersibility capability within the first 3 h, compared to both rice and cassava starches. The highest bulk density in breadfruit starch indicated that the starch had maximum volume reduction due to close packing while cassava starch exhibited the lowest. Thus, it would appear that under the applied tapping pressure, the smaller particle size of the breadfruit starch with higher amylose content promote closer packing of particles than rice starch even though the latter exhibited the smallest particle size (Olayemi et al. 2008).

When starch is heated in the presence of excess water, the granules undergo an order-disorder phase transition, known as gelatinization over a temperature range characteristic of the starch source (Ratnayake et al. 2009). In general, the gelatinization temperature is defined as the temperature where 98% of the starch granules undergo birefringence loss when microscopically viewed with a Kofler hot stage microscope (French 1984). It is generally based on the physical changes of starch granules and suspensions during gradual heating to the full paste state. The thermal transitions of the different starches were defined in terms of T_o (onset temperature), T_p (peak temperature) and T_e (end of gelatinization temperature) using differential scanning calorimetry (DSC) technique.

In summary, the gelatinization temperatures of all starches were higher than 60 °C as shown in *Table 3*. The breadfruit starch showed the narrowest gelatinization temperature profile with the onset temperature at 71.38 °C and the end gelatinization temperature occurred at 77.61 °C, followed by the rice and cassava starches. Although the cassava starch had broader gelatinization temperature profile, the peak temperature was the lowest (71.02 °C) compared to the other starches. In general, rice starch required the highest gelatinization temperature with peak at 77.17 °C, indicating a greater degree of order in the crystalline structure.

The gelatinization temperature of starch is an important factor in the production of high quality maltodextrin

Breadfruit starch Rice starch Cassava starch

Figure 1. Micrograph of different starches, magnified 400X

Table 2. Functional properties of different cassava, broken rice and breadfruit starches

	Cassava	Broken rice	Breadfruit
Water binding capability (%)	25.46 ± 0.37a	36.17 ± 0.37b	48.52 ± 0.19c
Water absorption index (%)	26.30 ± 0.15a	38.97 ± 0.20b	48.70 ± 0.34c
Bulk density (g/ml)	1.27 ± 0.01a	1.34 ± 0.09a	1.71 ± 0.01b
Dispersibility (%)	87.00 ± 0.00b	76.80 ± 0.29a	100.00 ± 0.00c

Each value in the table represents mean ± standard deviation of triplicate analyses. Means within each row with different letters are significantly different (p <0.05)

Table 3. Differential scanning calorimetry (DSC) profile on starch gelatinization temperature

	Cassava	Broken rice	Breadfruit
Onset temperature (°C)	61.97 ± 0.36a	73.71 ± 0.03c	71.38 ± 0.24b
Peak Temperature (°C)	71.02 ± 0.18a	77.17 ± 0.08c	73.87 ± 0.09b
End Temperature (°C)	81.29 ± 0.26b	81.24 ± 0.02b	77.61 ± 0.12a
Delta H (J/g)	12.02 ± 0.05b	9.34 ± 0.32a	15.08 ± 0.11c

Each value in the table represents mean ± standard deviation of triplicate analyses. Means within each row with different letters are significantly different (p <0.05)

as it will affect the efficiency of starch hydrolysis either using enzyme or acid modification technique (Morehouse et al. 1972). At the starch gelatinization stage, the starch polymeric material is dispersed by swelling and gelatinization in water will result in significant hydrolytic cleavage of 1,4-glycosidic bonds in the starch (Moore and Amante 2005). The non-uniformity of gelatinization is particularly undesirable because a high proportion of very large molecules including some intact starch molecules will still be present and may contribute to haze formation in the maltodextrin as a result of starch retrogradation (Morehouse et al. 1972).

The swelling power of breadfruit, rice and cassava starches is shown in *Figure 2*. From the findings, the breadfruit starch showed the highest increment rate of swelling power significantly (p <0.05) with the interval temperature range from 60 – 100 °C. There was a rapid increased in the swelling power from 70 – 90 °C, similar to findings reported by Rincon and Padilla (2004). The starch swelling power has been related to the association of intermolecular binding within the starch granules. The high swelling power observed in breadfruit starch might be due to its lower degree of intermolecular association (Tian et al. 1991) and higher water absorption index as opposed to the other starches. The swelling power is also related to the associated binding within the starch granules. Apparently, the strength and character of the micellar network was related to the amylose content of the starch, whereby the

low amylose content was claimed to produce high swelling power (Wootton and Tumaalii 1984). However, the starch size distribution also determines its swelling functionality with granules being generally either larger and lenticular (lens-like, A-starch) or smaller and spherical (B-starch) with less swelling power.

The rice starch showed the lowest gradual increment of swelling power even though the temperature had been increased up to 100 °C, mainly due to the smaller size starch granules. The higher swelling power in breadfruit starch is important as it is favourable to enzyme penetration *via* amorphous regions that are known to be one of the factors that cassava starch was chosen in the maltodextrin production (Moore and Amante 2005). The highest swelling power in breadfruit starch also had the highest enthalpy energy in the DSC endotherm profile, which means that the breadfruit starch required the highest enthalpy energy during the gelatinization process, which was 15.08 J/g.

The paste clarity of various starches at different pH values is presented in *Figure 3* and was found to be pH dependent. The cassava starch showed the highest paste clarity compared to both rice and breadfruit starch at all pH values. The paste clarity of both cassava and breadfruit starches were high at pH 2 but significantly decreased up to pH 4 (p <0.05). In a very acidic solution, negatively charged phosphate groups are neutralized, and the ionization of hydroxyl groups is suppressed (Nand et al. 2008). Therefore, lysophospholipids complexed amylose chain contains only electropositive nitrogen and the coulombic repulsion between these positive nitrogens decreases the compactness of the amorphous region, thus increasing the light transmittance (Hoover and Vasanthan 1992).

Rice starch exhibited the lowest paste clarity at all pH values. The starch paste clarity is more closely related to the optical homogeneity within the swollen granules (Craig et al. 1989). At higher pH,

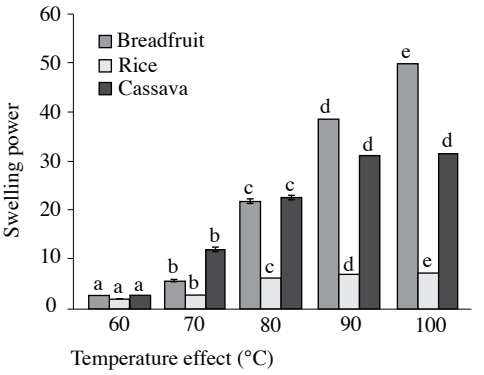

Figure 2. Effect of temperature on the swelling power of different starches [Each value in the graph represents mean ± standard deviation of triplicate analyses. Means within each bar with different letters are significantly different (p <0.05)]

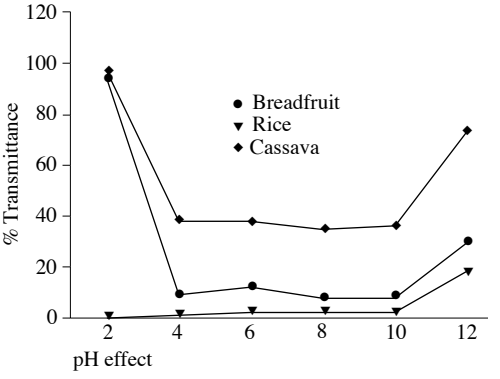

Figure 3. Effect of pH on the paste clarity of different starches (Each value in the graph represents mean ± standard deviation of triplicate analyses)

there were not much differences in the light transmittance especially between pH 4 and 10 and a significant (p <0.05) paste clarity was observed after pH 10. This can be explained in terms of granular swelling, resulting from repulsion between adjacent negative charges centred on the hydroxyl groups of the complexed lysophospholipid molecules (Hoover and Vasanthan 1992). Although both breadfruit and rice starch showed lower paste clarity compared to cassava starch, it did not mean that maltodextrin produced based on these starchy sources will exhibit low clarity as

their longer chain of glucose polymer or unreacted native starch will be removed during maltodextrin purification (Morehouse et al. 1972). However, lower paste clarity will affect the maltodextrin clarity quality and practical filtration procedures.

Conclusion

All the starches studied exhibited different physico-chemical and functional properties. Breadfruit starch had the highest swelling power at temperatures of 60 – 100 °C. The water binding capability, water absorption index, bulk density, dispersibility capability and the enthalpy energy required during the gelatinization of breadfruit starch was the highest among all starches. The paste clarity of all starches was pH dependent. Overall, cassava starch showed the highest paste clarity, followed by breadfruit starch. Rice starch had poor paste clarity at all pH values. Knowing the physico-chemical and functional properties of breadfruit and rice starch is important to determine the right protocol for producing high quality maltodextrin with desirable organoleptic properties. Future work will be conducted to develop optimized running parameter to produce high quality maltodextrin from breadfruit and broken rice starches.

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Abstrak

Kanji daripada sumber yang berlainan mempunyai ciri-ciri kimia-fizikal dan fungsi yang berbeza. Secara amnya, kanji buah sukun mempunyai ciri-ciri yang hampir sama dengan kanji ubi kayu berbanding dengan kanji beras hancur. Antara ketiga-tiga sumber ini, kanji ubi kayu menunjukkan kejernihan pes yang paling tinggi pada semua pH yang diuji. Kanji beras hancur menunjukkan kejernihan pes yang paling rendah walaupun mempunyai butir kanji yang terkecil. Berbanding dengan kedua-dua kanji beras dan kanji ubi kayu, kanji buah sukun mempunyai keupayaan mengembang paling tinggi, keupayaan mengikat air, indeks menyerap air, ketumpatan yang tinggi, keupayaan terlerai dan memerlukan tenaga entalpi yang tinggi semasa proses penggelatinan.

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