Chapter 4

EFFECT OF DRY HEAT PARBOILING TREATMENT VARYING IN TEMPERATURE AND TIME ON THE PROPERTIES OF RICE VARIETIES WITH DIFFERENT AMYLOSE CONTENT

4.1. Introduction

Rice is a major staple food crop. The physicochemical attributes of rice is determined by the status of the two basic fractions of the starch macromolecule, namely amylose and amylopectin. From the work of Juliano (1979), rice may be classified into high amylose (amylose content <25%), intermediate amylose (20–25%), low amylose (7–20%) and waxy or glutinous (1–2%) types. Parboiling is an age-old technique applied for quality enhancement of rice. Steam parboiling has been widely practiced and investigated. The rice variety, parboiling conditions and extent of gelatinization and retrogradation decides the properties of parboiled rice. Parboiled rice gives higher head rice yield because of the filling up of the naturally occurring fissures in the kernels by gelatinized starch. However, an inefficient drying step can cause severe moisture gradient within the kernel even after an efficient steaming step that may induce kernel fracture during milling. Drying involves lower temperature than steaming. At the molecular level, cooling causes rearrangement of the starch chains with release of water molecules. The crystallinity as determined by XRD is again developed due to retrogradation with formation of newer crystallites and permanent loss of the native ones. Formation of amylose lipid complexes has been reported. Thermal analysis of steam parboiled starch gives a peak for retrograded starch at temperature below the GT of raw rice and may give another peak at 90°C to 120°C for melting of amylose-lipid complexes. The phenomenon of gelatinization and
retrogradation is well understood when the pasting profile of starch is studied in a Rapid Visco Analyser (RVA). The viscosity profile however markedly changes in parboiled rice which may be attributed to varietal differences, amylose content, parboiling severity, granular damage and retrogradation, amylose-lipid complexes and protein network formation during processing.\(^{8-12}\) Parboiling increases the digestibility of rice starch.\(^{13}\) Englyst et al (1992) classified starch in foods into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS).\(^{14}\) While starch that gets digested under 20 min of incubation is considered as RDS, SDS is the starch that gets digested after another 100 min. RS comprises the residue remaining undigested after that. While RS has been considered suitable for incorporation in food for diabetics, a product with high RDS is suitable for person needing fast energy intake or non-residual digestion.\(^{15}\)

Dry heat parboiling is another important technique that involves rapid roasting of sufficiently soaked paddy with heated sand.\(^{16}\) It is comparatively a faster process than steam parboiling. The technique is generally applied for making speciality rice products, the popular being puffed rice.\(^{17,18}\) Although there are possibilities, dry heat parboiled rice has not been studied to understand its quality as staple parboiled rice (other than steam parboiled rice). In the present study, three rice varieties belonging to high amylose, low amylose and waxy types were dry heat parboiled at two different temperatures for three different time periods each.\(^{11}\) The changes in physical and physicochemical properties of the rice samples were analysed for determining desirable characteristics that can provide scope for possible food applications of the products.

4.2. Materials and methods

Pure line paddy samples of Ranjit, Kola chokua and Aghoni bora varieties with 27.2% (high amylose, HR), 12.6% (low amylose, LK) and 1.1% (waxy, WA) apparent amylose content respectively (as reported in the last chapter, section 3.2.2) from the harvest of 2012 were purchased from the Regional Rice Research Station of Assam Agricultural University at Titabor, Assam and local farmers of the region. The raw paddy samples were cooled at room temperature for 24 h and stored at 4°C for further processing. Enzymes, namely invertase from Baker's yeast (I4504), a-Amylase from porcine pancreas (A4268), amyloglucosidase from Aspergillus niger (A7095) and D-glucose standard (47829) were procured from Sigma-Aldrich (Missouri, USA).
4.2.1. Processing and coding of samples

Water (~2 L) was taken in an aluminium vessel and raised to 70°C over a burner. The flame was put off and 200 g paddy of each sample was immediately soaked in it. The temperature of water on addition of paddy immediately reduced to 60-62°C. The vessel was then covered with a gunny bag and kept for 18 h for hydration of the paddy. The excess water was then decanted and the soaked paddy was immediately roasted in a manually operated drum type roaster with sand (1:3 paddy to sand, 110-120 rpm). The sand particles (less than 3mm in diameter) were preheated to temperatures of 220°C and 270°C so that it came down to 140°C and 200°C, respectively after addition of the wet paddy. Temperature was maintained during processing by wrapping the drum of the roaster with a wet piece of gunny bag. The paddy samples were roasted under two conditions - low temperature for longer time (LTLT, 140°C for 11, 13 and 15 min) and high temperature for shorter time (HTST, 200°C for 3, 4 and 5 min). No popping of paddy occurred during processing. The roaster was tilted to take out the roasted paddy and sand. The hot sand was sieved out and the paddy was stored at room temperature (RT, 25±2°C) in a thin layer for 6 h allowing sufficient cooling down to RT. The samples were further stored at 4°C before milling in a dehusker and a polisher (Satake, Japan). The milled kernels (8-10% milling, w/w) were stored in polypropylene bags at 4°C for further analysis. For ease of identification, the rice varieties were coded as HR meaning high amylose Ranjit, LK meaning low amylose Kola chokua and WA meaning waxy Aghoni bora. HR, LK and WA suffixed with (N) indicated native raw rice. Processed sample code indicated variety code suffixed with roasting temperature and time of roasting. Thus, HR-140-11 indicates high amylose Ranjit paddy roasted at 140°C for 11 min.

4.2.2. Moisture content of raw, soaked and dry heat parboiled samples

Moisture content of raw paddy was estimated using a standard AOAC protocol (2000). The moisture content of soaked paddy was determined after surface moisture was carefully removed with a blotting paper. For dry heat parboiled samples, portions were immediately collected after roasting in a pre-weighed moisture cup and weighed for moisture estimation. Briefly, milled rice sample was taken in previously dried and
weighed covered dishes. The sample was allowed to dry in a vacuum oven at 100°C and vacuum pressure equivalent to 3 kPa till constant weight was attained. Weight of the dish containing sample was measured both before and after drying and moisture content was calculated (925.09, AOAC).

\[
\text{Moisture content (\% db) = \frac{\text{Initial weight} - \text{Final weight}}{\text{Final weight} - \text{Weight of empty dish}} \times 100}
\]  

Eq. 4.1

4.2.3. Head rice yield (HRY)

HRY (%) was determined as the weight average percentage of intact kernels obtained after milling to that of total milled rice containing both intact and broken kernels.

\[
\text{HRY (\%) = } \frac{\text{Weight of intact kernels}}{\text{Weight of total milled rice}} \times 100
\]

Eq. 4.2

4.2.4. Kernel hardness and physical dimensions

Milled whole rice kernels were tested for hardness (H) using a Texture Analyzer (TA.HD.plus, Stable Micro Systems, UK) with a 25 kg load cell using single compression. A single kernel was compressed with a 2 cm diameter stainless steel probe along the thickness at a speed of 0.5 mm/min and returned to its original position. The test was repeated for 25 kernels from each sample and the mean was calculated. The maximum force indicated by the force-time curve generated by the inbuilt software (Exponent Lite) was taken as the hardness. The length (L) and breadth (B) of ten milled kernels from each sample were determined using a Seed dial calliper (Baker, India) and L/B ratios were determined.

4.2.5. Colour measurement

The colour values (L, a, b) of all the samples were determined with a colour measurement spectrophotometer (Ultrascan Vis, Hunter Color-Lab). Raw rice was taken as the reference. The chroma value (C) of parboiled rice was then calculated.\(^{(20)}\)

\[
C = (a^2 + b^2)^{1/2}
\]

Eq. 4.3

4.2.6. Degree of gelatinization (DG)

DG (%) was calculated by the method of Wootton et al (1971).\(^{(21)}\) For this, 0.2g sample was dispersed in 100 mL distilled water with stirring for 5 min and centrifuged at
1500 rpm for 25 min. One milliliter supernatant was then diluted to 10 mL with distilled water and 0.1 mL iodine solution was added. The method was repeated using 100 mL of 10 M potassium hydroxide instead of water and absorbance of both solutions were read at 600 nm in a Spectrophotometer (Cecil Aquarius 7400, England).

\[
DG \, (\%) = \left( \frac{\text{Absorbance of fresh solution}}{\text{Absorbance of alkali solubilized solution}} \right) \times 100
\]

Eq. 4.4

4.2.7. Scanning electron microscopy (SEM)

Transverse sections of the milled raw kernels and samples roasted at 140°C and 200°C for 15 min and 5 min respectively were carefully cut using a sharp blade. The sections were then fixed using liquid nitrogen and sputter coated with gold before observing under a Scanning Electron Microscope (JEOL 6993V) operating at an acceleration voltage of 15 kV and magnifications of 30X and 2000X.

4.2.8. Equilibrium moisture content on soaking at room temperature (EMC-S)

The method of Indudhara Swamy et al (1971) was used to determine EMC-S(%) db of polished whole rice kernels. Whole-grain milled rice (about 3-5 g) with 11 to 13% moisture content (db) was put in 50 mL water in a covered 100 mL beaker and left aside. The rice was strained through a wire strainer after 20-24 h and dried between Whatman No.1 filter paper sheets. The moisture content of the rice was determined by a drying method (AOAC, 2000) and EMC-S calculated.

\[
EMC-S \, (\%, \, db) = \left( \frac{\text{Moisture evaporated (g)}}{\text{Dried weight of kernels (g)}} \right) \times 100
\]

Eq. 4.5

4.2.9. Sediment volume (SV)

The method of Bhattacharya and Ali (1976) was used to determine the SV of the raw and processed rice flour samples at ambient temperature. Briefly, 1 g each of desiccated flour samples was taken in a measuring cylinder and 15 mL of 0.05 N hydrochloric acid was added to it with agitation after each 5 min for 1 h. The level of the flour sediment was observed after 4 h and was reported as the SV of the sample.
4.2.10. Pasting properties

Twenty eight gram flour (with 12% moisture content) was mixed with 25 mL water to make slurry. A Rapid Viscosity Analyser (RVA Starchmaster2, Newport Scientific Instruments, Australia) was used to measure the pasting profile. The prepared slurry was held at 50°C for 1 min, heated from 50°C to 95°C at 12°C/min, held at 95°C for 2.40 min followed by cooling to 50°C at 11.25 °C/min, and finally holding at 50°C for 1 min. The pasting curves obtained were compared and the pasting parameters, namely peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown (BD), and total setback (SBt) were recorded using the inbuilt software. PV is the maximum viscosity during heating, HPV is the minimum viscosity at 95°C, CPV is the final viscosity at 50°C, BD is obtained after subtracting HPV from PV. SBt is obtained after subtracting PV from CPV.

4.2.11. Wide angle X-ray scattering (WAXS)

An X-ray diffractometer (Rigaku Miniflex, Japan) with a λ value of 1.54 Å and operating at an acceleration potential of 30 kV with 15 mA current and copper target was used to obtain wide angle X-ray diffraction spectra of the flour samples. The scanning range was 10-40° of 2θ values in steps of 0.05°. The total area under the curve and the area under each prominent peak were determined and the percentage crystallinity was calculated.

\[
\% \text{ crystallinity} = \frac{\text{area under peaks}}{\text{total area}} \times 100
\]

Eq. 4.6

4.2.12. Differential scanning calorimetry (DSC)

Flour slurries of raw rice and samples roasted at 140° and 200°C for 15 and 5 min respectively from each variety were analysed for thermal properties by a method modified from Liu et al (2009). Slurries were prepared in aluminium pans by weighing 4 mg flour and adding 8 mg deionized water to it. The pans were then saturated for 1 h at 4°C before hermetic sealing followed by heating in a Differential Scanning Calorimeter (model DSC-60; Shimadzu, Japan) against an empty reference pan from 30°-130°C at a heating rate of 5°C/min under nitrogen atmosphere. The instrument was periodically calibrated with pure indium for heat flow and temperature. The onset (To), peak (Tp), and conclusion (Tc) temperatures and enthalpy of gelatinization (ΔH, in J/g) were obtained from the thermograms using TA-60WS software.
4.2.13. Starch digestibility

Resistant starch (RS) present in the flour samples was measured by a method modified from Englyst et al (1992).(14) One hundred milligrams of flour was first added to 7 mL of acetate buffer (5.2 pH) at 37°C for 20 min and incubated in a shaking water bath. Then, 3 mL of an enzyme mixture composed of invertase (220 U/mL), pancreatic α-amylase (3000 U/mL) and amyloglucosidase (15 U/mL) were added and incubated further for 20 min. An aliquot was taken out and estimated for rapidly available glucose (G20) using a D-glucose oxidase-peroxidase assay kit (Robonik, India) and a standard curve was prepared in a similar manner with different concentrations of D-glucose. Another aliquot was similarly estimated for glucose after 120 min incubation (G120). Both these values were multiplied by a factor of 0.9 to measure the rapidly digestible starch (RDS) and slowly digestible starch (SDS) respectively and expressed as a percentage of dry matter. The difference between total starch (TS) measured by the standard AOAC method (2000) and the starch digested during the incubation period of 120 min was calculated as RS.(25)

\[
\begin{align*}
RDS &= G20 \times 0.9 \\
SDS &= (G120 - G20) \times 0.9 \\
RS &= TS - (RDS + SDS)
\end{align*}
\]

4.2.14. Statistical Analysis

All the experiments were carried out in multiple replicates and means are reported. Significant differences between means were determined by Duncan's multiple range test at a significance level of 0.05. The tests were performed using SPSS 11.5 (SPSS Inc., USA).

4.3. Results and discussion

4.3.1. Moisture content of raw, soaked and dry heat parboiled samples

The moisture content of raw Ranjit, Kola chokua and Aghoni bora was between 12.5 to 13.0 % (wb) that increased to 34.6%, 35.2% and 35.1% respectively on soaking, indicating sufficient hydration of the rice endosperms. Dry heat parboiling significantly reduced the moisture content of the paddy samples (Table 4.1). It was observed that temperature severity played the crucial role in moisture reduction than processing time.
4.3.2. Head rice yield (HRY)

LTLT dry heat parboiling significantly improved the head rice yield of all the three varieties (Table 4.1) with values nearing 100%. HTST processed samples however exhibited HRY values in between raw and LTLT samples. This might be attributed to the development of higher temperature and moisture gradient within the kernels during initiation of roasting and during sudden release of the roasted mass to room temperature that created internal fissures and cracks resulting in kernel breakage during milling. The pre and post-roasting temperature change hence needs to be controlled for getting a higher head rice yield out of the HTST samples.

4.3.3. Kernel hardness and physical dimensions

Dry heat parboiling increased kernel hardness of the three rice varieties (Table 4.1) and HTST processed samples were less hard than LTLT processed samples due to the development of internal fractures. All the three rice varieties were medium in size with L/B between 2.5 to 2.9. Reduction in kernel lengths with simultaneous increase in breadths of LK and WA samples resulted in marked reduction of L/B ratio making the dry heat parboiled rice bolder in shape. Possibly higher tension developed along the horizontal axis of the cylindrical kernels during starch gelatinization and drying. HR kernels however did not exhibit such notable changes indicating the effect of varietal differences.

4.3.4. Colour measurement

The reduction in L of the processed kernels was due to gelatinization of starch and inward migration of husk and bran pigments as was earlier observed in steam parboiled rice (Chapter 3, section 3.3.3). Similarly, the increased positive values of a and b were indicative of pigment migration and Maillard browning reactions (Table 4.1), as has been reported in steam parboiled rice. The high temperature used in dry heat parboiling probably increased the C value of the samples which were higher than those reported for steam parboiled rice.

4.3.5. Degree of gelatinization

LTLT processing resulted in rice kernels with some ungelatinized starch fractions in the kernels (Table 4.1). However, HTST processing resulted in complete gelatinisation of starch suggesting higher efficiency of the method in attaining gelatinization. High heat applied in HTST must have reached the centre of the rice
kernels extensively to result in sufficient gelatinization throughout the kernel, which the lower heat in LTLT samples could not. Precisely, HTST processing could overcome the temperature gradient occurring between the external layers and the centre of the paddy than LTLT. Effect of this was indicated by the observations made from the following electron microscopic study (section 4.3.6).

4.3.6. Scanning electron microscopy

Distinct morphological differences in the surface integrity of the sections of rice kernels were observed (Fig 4.1). The loss in starch granular structure and sealing of naturally occurring fissures in the raw endosperms after starch gelatinization on dry heat parboiling was seen from the SEM at 2000x (dii, eii, fii, gii, hii, iii). The effect of severity of gelatinisation was visible when HTST and LTLT samples were compared. Magnification at 30X however demonstrated development of a distinct cavity in radial direction of HTST kernels namely HR-200-5, LK-200-5 and WA-200-5 (gii, hii, iii). Probably, when suddenly subjected to very high temperature, the water in the soaked paddy simultaneously participated in starch gelatinization process as well as tried to migrate out of the gelatinized core of the endosperm. This releasing force pushed the softened kernel material in all directions creating a cavity in the middle of the kernel which because of instantaneous drying did not get sufficient scope to refill. The lower kernel hardness and head rice yield of the HTST samples may be attributed to this cavity formation. The characteristic splitting of dry heat parboiled rice kernel when subjected to alkali solution as reported elsewhere may also be related with this phenomenon.

4.3.7. Equilibrium moisture content on soaking at room temperature

EMC-S (% db) was higher for both raw and dry heat parboiled WA and LK samples than the HR samples clearly indicating the role of amylose content (Fig 4.2a). Dry heat parboiling increased the water absorption capacities of the three rice varieties due to extensive starch gelatinization. HTST treatment resulted in notably sharp increase in EMC-S than LTLT treated samples probably due to the accumulation of water in the cavity formed in the kernel.
Table 4.1. Moisture content, head rice yield, kernel hardness, L/B ratio, colour value and degree of gelatinization of raw and processed rice samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moisture (% wb)</th>
<th>HRY (%)</th>
<th>H (N)</th>
<th>L (mm)</th>
<th>B (mm)</th>
<th>L/B</th>
<th>L (%)</th>
<th>a (%)</th>
<th>b (%)</th>
<th>C (%)</th>
<th>DG (%)</th>
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<tbody>
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<tr>
<td>HR(N)</td>
<td>78.4±1.34</td>
<td>66.4±0.11</td>
<td>6.2±0.22</td>
<td>2.4±0.04</td>
<td>2.5±0.53</td>
<td>46.6±0.88</td>
<td>2.1±0.07</td>
<td>10.5±0.89</td>
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<tr>
<td>HR-140-11</td>
<td>93.9±0.91</td>
<td>87.4±0.68</td>
<td>6.2±0.13</td>
<td>2.4±0.07</td>
<td>2.6±0.24</td>
<td>37.3±0.27</td>
<td>2.6±0.35</td>
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<td>11.0±0.41</td>
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<td>HR-140-13</td>
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<td>6.3±0.12</td>
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<td>2.6±0.46</td>
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<td>98.6±0.19</td>
<td>87.6±0.33</td>
<td>6.2±0.12</td>
<td>2.5±0.03</td>
<td>2.5±0.41</td>
<td>26.3±0.19</td>
<td>3.1±0.06</td>
<td>11.8±0.22</td>
<td>11.8±0.12</td>
<td>95.3±0.08</td>
<td></td>
</tr>
<tr>
<td>WA-200-3</td>
<td>9.1±0.17</td>
<td>72.3±0.21</td>
<td>6.2±0.18</td>
<td>2.5±0.04</td>
<td>2.5±0.47</td>
<td>28.1±0.29</td>
<td>2.8±0.03</td>
<td>11.4±0.25</td>
<td>11.7±0.26</td>
<td>99.1±0.00</td>
<td></td>
</tr>
<tr>
<td>WA-200-4</td>
<td>8.7±0.24</td>
<td>70.4±0.19</td>
<td>6.2±0.11</td>
<td>2.6±0.05</td>
<td>2.4±0.20</td>
<td>23.8±0.17</td>
<td>2.9±0.04</td>
<td>11.7±0.19</td>
<td>12.1±0.26</td>
<td>100.0±0.00</td>
<td></td>
</tr>
<tr>
<td>WA-200-5</td>
<td>8.7±0.71</td>
<td>74.8±0.13</td>
<td>6.1±0.11</td>
<td>2.6±0.05</td>
<td>2.3±0.23</td>
<td>21.7±0.41</td>
<td>3.3±0.03</td>
<td>11.7±0.24</td>
<td>12.1±0.09</td>
<td>100.0±0.00</td>
<td></td>
</tr>
</tbody>
</table>

* Means with the same superscript in a column do not differ significantly from one another (p < 0.05)
4.3.8. Sediment volume

While EMC-S (%, db) was evaluated for whole kernels, sediment volume was determined for rice flour (Fig 4.2b). Although the pattern of increasing values was similar, the sharp rise in values observed for HTST treated samples in EMC-S test was not found in sediment volume test. This confirmed the role of the cavity in HTST treated rice kernel samples in accumulating water.
4.3.9. Pasting properties

RVA pasting curves of the raw and processed samples of the three varieties are given in Fig 4.3 (a, b and c). The effect of amylose content in pasting pattern of raw rice was evident. HR(N) required longer time to attain viscosity than LK(N) and WA(N). High amylose wheat starch was reported to be slower in swelling on pasting.\(^{(29)}\) Sang et al (2008) suggested it to be due to formation of amylose-lipid complex in the raw starch.\(^{(9)}\) These complexes were found in native rice in very low proportion with no significant quantitative difference amongst the varieties.\(^{(10)}\) Newer complexes are formed over process temperature above 50°C.\(^{(4)}\) Its formation and differential influence

![Fig. 4.3. RVA pasting curves of the raw and dry heat parboiled (a) HR, (b) LK and (c) WA samples.](image-url)
on the raw rice samples can hence be nullified. The higher PV in HR(N) also does not imply any such inhibitory effect of amylose on the extent of starch swelling. Amylopectin may however be attributed to the rapid absorption of water. This branched structure being more susceptible to damage by increased temperature during the heating phase of RVA resulted in lower PV.\(^{(31)}\) Probably, irreversible damage of the heat labile amylopectin structures and subsequent leaching out in processed LK and WA samples caused continuous rise of the pasting curves. The PV, HPV and CPV of the LTLT samples were even higher than the raw samples of LK and WA, indicating larger degraded fractions resulting in higher density of the heated slurry. The branched chains in waxy WA were probably longer than those of low amylose LK to explain for the highest value of CPV attained.\(^{(30)}\) HTST caused further breakdown, bringing the overall slurry viscosity to lower values. In addition, amylose-lipid complexes and a protein network formed during the hydrothermal treatment also may have restricted the swelling of the flour pastes to a minor extent.\(^{(11)}\) The low SB of all the processed samples indicated their scope for utilization in development of foods that particularly requires low cooked viscosity.

### 4.3.10. Wide angle X-ray scattering

The native A-type starch diffraction spectra of raw rice flours with major peaks at Bragg's angle \(2\theta\) positions near 15.2 (Peak 1), 17.4 (Peak 2), 18.1 (Peak 3) and 23.3 (Peak 4) were distinctly yet variably altered on dry heat parboiling (Fig 4.4. a, b, c). The crystallinity was highest in WA(N) followed by LK(N) and HR(N) that was related to the amylopectin content.\(^{(31)}\) Significant loss in crystallinity occurred on parboiling (Fig 4.4 d) owing to rapid amylopectin melting as was also observed in our work on steam parboiling of the same rice varieties (Chapter 3, section 3.3.8). This was also indicated by the DG values which were marginally higher for the HTST and LTLT treated WA and LK samples. Temperature severity results in breakdown of starch fractions.\(^{(24)}\) As the process temperature was lower in the LTLT process, starch breakdown occurred to a lesser extent allowing rapid recrystallization of the broken chains. HTST process formed even shorter chains due to thermal degradation which failed to recrystallize to the same extent as LTLT samples, thereby giving lower values of % crystallinity. The characteristic spectra obtained for LTLT and HTST treatments were also specifically different from each other for all the
three varieties owing to the moisture content of the end product. Formation and development of newer crystalline polymorphic structures in parboiled rice starch leading to B-type WAXS for retrograded amylose and V-type for amylose-lipid complexes have been reported.\(^{(5,32)}\) Lamberts et al (2009) reported presence of amylose crystallites in parboiled rice which also give B-type WAXS pattern.\(^{(7)}\) LTLT roasting of the three varieties resulted in distinct superimposition of B- and V-type spectra with minor A-type as suggested by major peaks at 2\(\theta\) positions of 17.5, 20.0 and minor peaks at 15.2, and 23.3. HTST roasting of HR also resulted in distinct superimposition of the three major types of spectra with peaks at 2\(\theta\) values of 18.1 (A-type), 20.02 (V-type) and 22.1 (B-type). However, roasted LK and WA samples of HTST gave strictly V-type spectra with a single peak at 2\(\theta\) positions near 20.02.

Fig. 4.4. (a), (b) and (c) Wide angle X-ray diffractinon patterns of raw and dry heat parboiled HR, LK and WA samples, respectively; (d) Changes in % crystallinity of different rice samples with processing.

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Bhattacharya and Ali (1985) opined that as dry heat parboiling involved rapid bringing down of the moisture content of paddy to below 18%, storing the rice below room temperature thereafter does not produce retrograded starch because there is no free moisture to be released. But in the present work, formation of partial B- and V-type spectra with traces of the native A-type was suggestive of occurrence of at least minor retrogradation or recrystallization and formation of amylose-lipid complexes. However, WA(N) with very low amylose content (1.1%, db) exhibiting V-type WAXS spectra upon HTST treatment was suggestive of the binding of lipid with either amyllopectin or long chains that are formed due to thermal degradation of amyllopectin during dry heat parboiling.

4.3.11. Differential scanning calorimetry

Raw rice starch shows a wide range of gelatinization temperature. Our study also supported the same (Table 4.2). The impact of amylose content on the gelatinization temperature has been strongly debated and impact of other factors like starch structures and nutritional composition of rice have been related to it. Two distinct peaks could be observed in most of the thermograms (Fig 4.5 a, b and c). While peak 1 was representative of gelatinization of raw rice starch and/or retrograded starch, peak 2 emerging after 90°C represented melting of amylose-lipid complexes. No peak for ungelatinized starch that as was earlier reported to be present from the test for DG was however observed in the DSC curves of the processed samples. This may be due the very low and undetectable amounts of these. Shi and Seib (1992) reported that this major peak shifted towards lower temperature after parboiling due to melting of retrograded amyllopectin formed during cooling of the starch gel. Retrogradation results in reordering of the amyllopectin branches but in less ordered manner, which explains the lower temperature of melting and lower melting enthalpy than gelatinization of the native starch. Peak 1 for HR-140-15 and HR-200-5 and LK-140-15 was hence for retrograded starch which melted at temperatures of 55.1°C, 54.1°C and 66.0°C respectively with melting enthalpies of 70.1, 68.8 and 33.3 J/g respectively. This is especially notable as it occurred even though there was excessive moisture reduction during dry heat parboiling. It also supports the observation from XRD patterns of LTLT treated HR samples that the gelatinized amylose in particular had a tendency toward recrystallization. Those fractions may have retrograded during the 1 h saturation time prior to DSC analysis. Some portion of the added water must
have been used by the starch chains to recoil into B-type polymorphic structures representative of retrograded starch that encompasses higher number of water molecules than native A-type, has a weaker coil structure and hence can be easily formed. Samples processed under HTST conditions however did not generate peak 1 in accordance with the WAXS results indicating formation of irreversibly gelatinized starch with no indication of retrogradation. Emergence of peak 2 with minor enthalpy (9.3 J/g) in thermogram of HR(N) may be considered to have emerged or developed under hydrothermal condition similar to cooking during the experiment in the DSC system. Peak 2 was not shown by the raw samples of the other two varieties which might be related to comparatively lower availability of free amyllose in them. The peak however emerged with much higher intensity for all the three HTST treated samples with LK-200-5 and WA-200-5 giving even higher values of melting enthalpy (39.1 J/g and 38.5 J/g, respectively) than HR-200-5 (37.8 J/g). Extensive thermal breakdown of amyllopectin during the high temperature roasting as observed in RVA profiles might have resulted in fractions that readily bind with the lipid bodies during cooling and storage after processing, which was also suggested by WAXS.

Fig 4.5. DSC thermographs of the flours of raw rice and samples dry heat parboiled at 140°C and 200°C for 5 and 15 min of (a) HR, (b) LK and (c) WA samples. 1 and 2 indicates DSC peaks emerging before and after 90°C that are representative of melting of the native and/or retrograded starch crystallites and of amyllose-lipid complexes respectively.
Different polymorphic forms of amylose-lipid complex exist and indirect evidence on existence of amylopectin-lipid complex has also been reported. Iturriaga et al (2004) suggested that amylopectin-lipid complex can originate in the very long amylopectin branches and extra granular complexing lipids. 

Table 4.2. DSC thermal parameter values of the flours of raw and rice samples processed for 5 and 15 min

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₀(°C)</td>
<td>Tₚ(°C)</td>
<td>Tc(°C)</td>
<td>ΔH(I/g)</td>
<td>T₀(°C)</td>
</tr>
<tr>
<td>HR(N)</td>
<td>44.8 ± 1.3</td>
<td>65.0 ± 0.9</td>
<td>78.2 ± 1.0</td>
<td>43.4 ± 1.2</td>
<td>112.0 ± 1.6</td>
</tr>
<tr>
<td>HR-140-15</td>
<td>40.7 ± 1.2</td>
<td>55.1 ± 0.2</td>
<td>70.1 ± 0.6</td>
<td>26.2 ± 0.8</td>
<td>100.8 ± 1.7</td>
</tr>
<tr>
<td>HR-200-5</td>
<td>38.7 ± 0.9</td>
<td>54.1 ± 0.3</td>
<td>67.8 ± 0.3</td>
<td>23.4 ± 0.2</td>
<td>100.4 ± 1.4</td>
</tr>
<tr>
<td>LK(N)</td>
<td>56.4 ± 0.8</td>
<td>79.2 ± 0.1</td>
<td>99.1 ± 0.7</td>
<td>48.9 ± 0.4</td>
<td>112.0 ± 0.8</td>
</tr>
<tr>
<td>LK-140-15</td>
<td>50.6 ± 0.6</td>
<td>66.0 ± 0.4</td>
<td>77.2 ± 1.0</td>
<td>33.3 ± 0.6</td>
<td>101.6 ± 0.4</td>
</tr>
<tr>
<td>LK-200-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>116.3 ± 0.3</td>
</tr>
<tr>
<td>WA(N)</td>
<td>51.4 ± 1.1</td>
<td>71.4 ± 0.7</td>
<td>87.9 ± 1.0</td>
<td>49.1 ± 0.3</td>
<td>95.8 ± 0.9</td>
</tr>
<tr>
<td>WA-140-15</td>
<td>62.2 ± 0.9</td>
<td>73.9 ± 0.4</td>
<td>87.6 ± 0.9</td>
<td>13.6 ± 0.1</td>
<td>107.2 ± 0.9</td>
</tr>
<tr>
<td>WA-200-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>116.8 ± 0.7</td>
</tr>
</tbody>
</table>

Means with the same superscript in a column do not differ significantly from one another (p > 0.05)

Peak 1 and peak 2 are the peaks emerging before and after 90°C in the thermograms respectively.

In dry heat parboiled samples, however, another hypothesis can be made drown. Gelatinization was accompanied with extensive cleavage in the amylopectin branched structures and formation of smaller branched fractions as suggested by RVA. Such short chains probably gets decoiled and possibly behaves like amylose chains which readily formed complexes with the available lipid molecules. Although present, the intensity of the representative peak for this complex in WAXS was not very sharp as is shown by the complex melting endotherm in DSC. Probably, additional formation of these complexes occurred in the aqueous environment used during DSC sample preparation. The free dehydrated starch fractions formed as a result of gelatinization and subsequent rapid drying were resposible for forming the newer structures. Dry heat parboiling followed by hydration can hence be further investigated as a tool for targeted formation of these complexes.

4.3.12. Starch digestibility

Quantified values of the different fractions of enzyme-hydrolysed starch are plotted in Fig 4.6. HR(N) samples exhibited lower in vitro digestibility indicated by lower RDS and higher RS than LK(N) and WA(N) implicating the effect of amylose. The RDS level significantly improved after parboiling for all varieties and was highest for
WA samples (66.6 to 94.8%). Extensive starch gelatinization along with molecular breakdown resulted in higher exposure of the starch fractions to the digestive enzymes as was also suggested by the DSC analysis.\(^{(44)}\) The dry heat parboiled rice samples were hence quickly digestible. HTST treated WA samples showed highest RDS along with higher levels of SDS. Severity of dry heat parboiling markedly reduced the RS content.\(^{(45)}\) RS reduced from 24.5% to 0.4% for HR, 21.2% to 1.9% for LK and 18.4% to 0.1% for WA making the samples almost devoid of RS. The findings indicate that the dry heat parboiled rice samples can have possible application in infant food formulae or may prove useful for post-operation recovery.

![Graphs showing RDS, SDS, and RS percentages in raw and dry heat parboiled rice flour samples.](image)

**Fig. 4.6.** (a) Rapidly digestible starch (RDS, % db), (b) slowly digestible starch (SDS, % db) and (c) resistant starch (RS%, db) in the raw and dry heat parboiled rice flour samples.

### 4.5. Conclusions

LT LT dry heat parboiling improved the HRY of rice near to 100%. The lower HRY in HTST was attributed to rapid development of temperature and moisture gradients within the kernel. Marked reduction of L/B ratio resulted in processed LK and WA kernels becoming bolder in shape than raw rice kernels. Varietal difference in
Adequate arrangement of kernel material after parboiling was hence suggested as L/B ratio of HR kernels were not as affected by the hydrothermal treatments. Biochemical analysis of DG suggested very limited occurrence of ungelatinized starch in the LT processed kernels, which however were not detected by DSC. The dry heat parboiled samples were highly hygroscopic as revealed by EMC-S and SV values. The extensive gelatinization and molecular breakdown led to the development of peculiar physicochemical characteristics. XRD and DSC curves suggested formation of additional B-type retrograded starch in the high amylose HR variety. Although peaks for amylose-lipid complex formation were feeble in the curves of HR, amyllopectin-lipid complex in processed LK and WA samples were clearly evident. This created scope for further research and application of the dry heat parboiling technique. The almost complete loss of resistant starch and increased cold paste viscosity may be exploited for targeted use of dry heat parboiled rice in food products specified for special population groups.

Bibliography


