

**PHYSICOCHEMICAL , MORPHOLOGICAL, PASTING AND SOFETENING KINETIC PROPERTIES OF
SELECTED RICE VARIETIES FROM WEST-AFRICA**

by

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Suggested Short Title

Characterization of rice varieties from West Africa

FOREWORD

This thesis is reported in the form of original papers expected to be published in journals. The first two sections of this study comprises of a general introduction presenting a brief review of the literature on the topics in addition to the rationale and objectives behind the study. The next two sections make up the body of the thesis with each chapter representing a complete manuscript, while the last chapter is a summary of the major conclusions. This format has been approved by the Faculty of Graduate Studies and Research, McGill University in accordance with the conditions provided in the Guidelines for Thesis Preparation, Thesis Specification, section 3 entitled "Traditional and manuscript-based theses" which as follows:

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Additional material must be provide where appropriate (for example in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. Supervisors must attest to the accuracy of such statements. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all authors of the co-author of any component of such a thesis serve as an examiner for that thesis".

While the study reported in this thesis is the responsibility of the candidate, it was supervised by Dr. Benjamin Simpson, Department of Food Science and Agricultural Chemistry and Dr. Michael Ngadi, Department of Bioresource engineering, both from McGill University.

ABSTRACT

The physicochemical, morphological, pasting and softening kinetics of rice varieties selected from West-African countries were investigated. The studies conducted were aimed at enhancing the adoption and use of these local varieties in improving food security in Africa through the development of acceptable new rice-based products. The varietal, morphological and physiochemical impacts on appearance, pasting, textural properties and softening kinetics were also analyzed. To unravel structural properties of the respective isolated rice starch from the selected rice varieties, scanning electron microscopic analysis was also carried out.

The varieties studied were Faro 61, Faro 60, Faro 44, Tox 3145 and Nerica 3. Microscopic studies carried out on the isolated starch indicated that the starch granules were 4.43 - 5.62 μm . The structural variations observed did not clearly provide an explanation for the pasting and textural properties of the studied rice varieties. Morphological studies also revealed that the rice granules were polyhedral, irregular in shape and tightly packed. Proximate studies indicated that the rice varieties were composed of 0.35 - 0.52% fat, 0.32 - 0.57% ash, 8.97 - 10.35% protein, 88.63 - 90.08% carbohydrate and 22.4 - 28.50% amylose. The proximate results indicate that these varieties are high protein containing waxy rice varieties.

Color parameters (L^* and b^*) studies of uncooked rice flour samples indicated high values of L^* and low values of b^* for all the rice varieties. The order of increasing whiteness was found to be Faro 61 > Faro 44 > Faro 60 > Nerica 3 > Tox 3145 while the b^* values ranged from 5.09 - 7.26. The high degree of whiteness and low values of yellowness of these rice varieties indicate that their flours would be highly acceptable by most consumers.

Results of the pasting properties studies indicated significant differences in the peak viscosity, trough viscosity, final viscosity and set back viscosity of the rice flours. Faro 44 showed a higher peak viscosity value (3984.5 cP) while Nerica 3 indicated the lowest peak viscosity value (2850.5 cP). Faro 44 and Tox 3145 had the highest and lowest trough viscosities, respectively. Break down viscosities were within the 546.5 and 1164 cP range for the rice varieties. Faro 44 had significantly higher breakdown viscosities than other varieties. The result indicated that Faro 44 flour is suitable for the production of value added products such as noodles, due to the ability of its paste to swell sufficiently while remaining intact and stable during sheering. Setback

viscosity varied from 865.5 to 2138.5 cP. Faro 44 showed the highest setback viscosity (2138.5 cP) while Faro 61 showed the least (865.5 cP). The pasting temperature of Faro 44 was higher than the other rice varieties and found to be 85.5⁰C.

Textural studies indicated hardness decreased with increase in cooking time. When cooked from 5 minutes to 25 minutes, there was gross disintegration of the rice granular structure . These structural changes provide an explanation for the corresponding changes in the tissue strength and elasticity of the studied rice varieties. In addition, the rate of textural changes related with the cooking temperature utilized in this study was found to confirm with two pseudo first-order kinetic mechanisms. The kinetic model utilized indicated that the apparent rate constants K_a^1 varied from 0.03776 to 0.4468 min⁻¹ while K_b^1 varied from 0.008475 to 0.013665 min⁻¹ . Over all, variations were observed in the morphological, physicochemical, pasting and softening kinetic properties of all the studied rice varieties. These studies are vital in ensuring an improving quality of rice by thermal processing.

RÉSUMÉ

La cinétique physico-chimique, morphologique, ainsi que les propriétés gélifiantes et adoucissantes des différentes variétés de riz ouest-africains ont été étudiées. Cette recherche avant buta renforcer l'adoption et l'utilisation de ces variétés locales afin d'ansurer la sécurité alimentaire africaine en développant de nouveaux produits acceptables à base de riz. Les effets variétaux, physico-chimiques et morphologiques sur l'apparence, les caractéristiques de la gélatinisation, de la texture, ainsi que la cinétique de l'adoucissement ont également été analysés. Pour éclaircir les propriétés structurales de l'amidon isolé des variétés de riz sélectionne, la technique de la microscopie électronique à balayage a dû être utiliser.

Les variétés de riz étudie étaient Faro 61, 60 Faro, Faro 44, Tox 3145 et Nerica 3. Les observations microscopiques réalisées sur l'amidon isolé ont indique que les granules d'amidon variaient eutre 4.43 et 5.62 μm . Ces variations structurelles n'expliquait pas clairement les propriétés texturales et collantes des variétés de riz étudie. Des études morphologiques ont aussi révélé que les granules d'amidon de riz étaient polyédriques, serre et de forme irrégulière. L'analyse immédiate des macronutriments a révélé que les variétés de riz sont composées de 0.35 à 0.52% de matières grasses, de 0.32 à 0.57% de cendres, 8.97 à 10.35% de protéines, de 88.63 à 90.08% de glucides et, enfin, 22.4 à 28.50% d'amylose. Ces résultats indiquent que ces variétés sont les variétés de riz sont riches en protéines.

L'étude sur les paramètres de couleur (L^* et b^*) des échantillons de farine de riz non cuite indique de valeurs élevées de L^* et de faibles valeurs de b^* pour toutes les variétés de riz. L'ordre croissant de blancheur a été jugée être Faro 61 > Faro 44 > Faro 60 > Nerica 3 > Tox 3145, tandis que les valeurs de b^* variaient entre 5,09 et 7,26. Un haut degré de blancheur combine a un faible de jaunissement de ces variétés de riz indiquent que ces farines seraient bien acceptées par la plupart des consommateurs.

Les résultats des études des propriétés collantes ont dénoté des différences significatives pour la viscosité maximale, minimale, finale et la viscosité de rechute des farines de riz. Faro 44 a montré une valeur de viscosité maximale élevée (3984,5 cP), tandis que le Nerica 3 indique la valeur du sommet de la viscosité moins grande (2850,5 cP). Faro 44 et Tox 3145 avaient respectivement les plus hautes et les plus basses viscosités minimales. Les viscosités de

dégradation se rangeaient entre 546,5 et 1164 cps pour toutes les variétés de riz. Faro 44 avait une viscosité de dégradation nettement plus élevés que les autres variétés. Ce résultat indique que la farine de riz Faro 44 est appropriée pour la production des produits à valeur enrichie, tels que les nouilles, en raison de la capacité de la pâte de gonfler suffisamment tout en restant intacte et stable pendant le cisailage. La viscosité de rechute varie de 865,5 à 2138,5 cP. Faro 44 a montré la viscosité de rechute la plus élevée (2138,5 cP), alors que Faro 61 a montré la moindre (865,5 cP). La température de gélatinisation de Faro 44 était plus élevée que les autres variétés de riz et établie à 85.5°C.

Les études texturales ont indiqué que la dureté diminue avec la hausse du temps de cuisson. À la fin du cuisson de 5 minutes à 25 minutes, il y a eu une désintégration brute de la structure granulaire de riz. Ces changements structurels fournissent une explication pour les changements correspondants dans la solidité du tissu et l'élasticité des variétés de riz étudiées. En outre, le taux de changements de texture en rapport avec la température de cuisson utilisée dans cette étude correspond à deux mécanismes cinétiques de pseudo premier ordre. Le modèle cinétique utilisé a indiqué que les constantes de vitesse apparentes K_a^1 ont varié de 0,03776 à 0,4468 min^{-1} , tandis que K_b^1 se rangeaient entre 0,008475 et 0,013665 min^{-1} . Ces études sont essentielles afin d'assurer et améliorer la qualité du riz par traitement thermique.

Dans l'ensemble, les variations des variétés du riz étudiées ont été observées en tant que leur caractéristiques morphologiques, physico-chimiques, les propriétés de gélatinisation, ramollissement ainsi que les propriétés cinétiques.

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CONTRIBUTION TO KNOWLEDGE

1. The morphological, physicochemical and softening kinetic properties of selected West-African rice varieties had been evaluated and the rice varieties shown to have varying properties. This is the first study illustrating the morphological, physicochemical and softening kinetic properties of selected West-African rice varieties.
2. Microscopic scanning electron studies of the isolated starch from the various rice varieties was indicated. This results can be applied in defining the appropriate food applications of the studied rice starches. So far, no study has been carried on the morphological characterization of the starches from these rice varieties.
3. Physicochemical results such as proximate composition and appearance of flour was shown to vary among the studied rice varieties. No definitive study on the physicochemical properties of selected West-African rice varieties has been reported.
4. Pasting properties of rice flour as a result of defined temperature regimen has been shown to be applicable for the production of specific food products. To our knowledge this is the first study that aims at defining a clear influence of the proximate composition of these rice varieties on it's pasting attributes. This is the first study demonstrating the pasting properties of these selected West-African rice varieties.
5. Kinetic models capable of predicting softening of rice with cooking time were developed based on selected cooking times and temperature. To our knowledge, this is the first thermal softening study carried out on rice.

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CHAPTER I

INTRODUCTION

Rice (*Oryza sativa* L.) is one of the world's most important staple food sources consumed by more than half of the world's population (FAO 2000). It is indeed one of the most essential cereals in the world with more than two thousand varieties of rice being cultivated commercially around the world (FAO 1996). Rice is the one of the several cereal crops prepared and eaten typically as a whole grain, therefore quality concerns of this type of grain is important. Rice can also be milled into gluten free flour. This flour is utilized in making of several types of foods such as noodles, rice milk etc. (Hossain et al 2009).

Rice is a great source of energy. The major reserve of rice polysaccharide is starch, which is composed of two components, amylopectin and amylose, both composed of anhydroglucose units. Starch is a widely recognized ingredient used globally in several food and non-food applications. For example, in the food industry starch is utilized as a gelling, stabilizing, thickening and coating agents whereas in the nutraceutical industries, starch is utilized as encapsulating agents for the production of pharmaceutical products (Manisha and Zakiuddi 2011). Apart from being a great source of dietary energy source, rice is also a uniquely great raw material used for the production of extruded food products due to the fact that this cereal is non-allergic, gluten-free, has low amounts of sodium, easily digestible carbohydrates, high-quality protein with little or no amounts of fat and also possesses a starch with a bland taste. These unique properties mean rice starch can be used for the production of specialty products, such as infant foods which require low allergenicity ingredients (Dziezak 1991).

Rice has also been observed to contain protein. Although this cereal is deficient in lysine, its protein is considered to be of high quality and occurs in well balanced proportions primarily because rice possesses all the eight essential amino acids in adequate quantities. Several studies have been carried out on the proximate composition of rice (Oyenuga, 1968; Temple and Bassa, 1991; Adeyeye and Ajewole 1992; Bishnoi and Khotarpaul 2003; Adeyemi et al 1986; Abulude 2004). Recently a study was carried out on the chemical nutrient composition of 15 selected indigenous and five of the newly introduced hybrid rice varieties in Ebonyi State, Nigeria. The results showed that the "Faro" varieties possessed good proximate and mineral composition values. "Faro14 (I)" contained the least fat (0.5 %) and least crude fibre value of (1.0 %). "E4197", one of the newly introduced hybrid rice varieties, had a very high moisture content of

9.6 % as against “E4212” (also another new introduced hybrid rice variety) which had the least moisture content of 5.0 %. “One of the newly introduced hybrid varieties “E4212” had relatively higher protein and mineral contents, but less fat content” (Oko et al 2012).

In 2001- 2003, the production of milled rice in Africa averaged about 11.80 million tons per annum (equivalent to 17.59 million tons paddy), while the average rice consumption per year was 15.27 million tons. In 2006, the production of paddy rice in West Africa was estimated to be about 6 million tons, a great improvement from the 4.2 million tons produced in 1986 (FAO 2009). Rice is cultivated in almost every ecological zone in West Africa. There have been reported to be about 100 promising varieties from West and Central Africa, in addition to the improved rice varieties promoted by INGER-Africa, which have eventually been released for widespread cultivation (WARDA 2002). Between 1961 and 1992, rice consumption in West Africa increased by 5.6% per annum, more than twice the population growth rate, with consumption and production spreading well beyond the traditional regions of West Africa and Madagascar (FAO 1996). FAO 2000 projects that the annual increase in consumption of rice in West Africa will stay as high as 4.5% from the year 2000 and beyond. This increase in rice consumption has led to an upsurge in importation of rice into West Africa. USDA 2012, projects West Africa’s rice consumption for 2012 and 2013 to be about 7,022 and 7300 million tons respectively. Processing technologies such as milling, parboiling has been observed to affect the nutritional and quality properties of rice. A good example of the effects of polishing on the nutritional composition of rice can be seen in brown rice which undergoes minimal processing and therefore retains most of its initial nutrients within the grain, while white rice or polished rice loses a large portion of its nutrients as the rice grain are pushed into the husk of the grain during processing which is then detached during polishing (Srisawas and Jindal 2007).

Rheological properties, such as particle size distribution of flour have been observed to play an essential role on the functional properties and the quality of finished food products. These properties such as swelling capabilities, pasting properties, water absorbing capabilities etc., not only affect consumer’s acceptance of rice and rice products (such as baby foods, puffed grain, soup, candy, noodles, snack foods, breakfast cereals etc.), but also define the domestic and industrial application of rice flour. For instance, the gelatinization and pasting properties of rice flour is an index of the ease or difficulty of cooking starch, while rheological profiling gives a clear picture on its viscoelastic tendencies (Hse et al 2000; Lapasin et al 1992; Lii et al 1996). It

is very essential to determine the rheological properties of rice flour as these properties are important in controlling production conditions, designing flow systems and in the production of rice flour-based products with desirable textures (Lopez et al 2004).

Despite the pertinence of information pertaining to the rheological and pasting properties of rice flour needed to harness the industrial application of several indigenous rice starches from West Africa, there is still a paucity of research and data in respect to these rice flours. The pasting property of rice flour is the underlying property which defines its use in rice-based product development. The pasting property of rice flour is the underlying property which defines its use in rice-based product development. Pasting properties are essential in categorizing the end-product application of flour. For instance, the peak viscosity of rice flour indicates their water binding capacity of their respective starches. A relatively high peak viscosity is indication that its starch may not be suitable in the production of products requiring high gel strength and elasticity.

Several studies have shown a relationship between increase in protein content and increase in pasting properties of rice flour (Zhu et al 2010; Zhu and Liao 2008).

Amylose and Amylopectin contents in rice endosperm have been suggested to have impact on rice and rice based product quality (Zhu et al 2010). Singh et al 2006 reported a positive correlation between peak, final and setback viscosity with amylose contents. Amylopectin and amylose structure has also been observed to influence gelatinization, texture, retrogradation and the pasting properties of rice (Okadome et al 2000; Tan et al 1999; Zhu et al 2012). Zhu et al 2012 reported that rice flours with longer average chain lengths and longer exterior chain lengths had higher gelatinization, pasting and retrogradation properties. In addition to amylose and amylopectin, several conflicting correlations have been suggested between protein and pasting properties of rice. Several studies have shown a relationship between increase in protein content and increase in pasting properties of rice flour (Zhu et al 2010; Zhu and Liao 2008).

Several studies have been carried out on the characterization of food products from rice flour. The results of these studies have shown a relationship between the starch material utilized and the final products derived (Guha et al 1997; Hanwu-Lei et al 2005; Ohtsubo et al 2005; Hagenimana et al 2005; Phoungchandang et al 2006; Clerici et al 2009; Dileep et al 2010;

Sompong et al 2011). Lai et al (2001), studied the effects of rice properties on the quality of rice pasta, and observed a significant relationship between the physical properties of rice e.g texture, pasting properties and the final product derived from the rice flour. Little et al (1958); Webb (1991); Juliano (1985); Unnevehr et al (1992) and Tan et al (1999) also observed a direct relationship between the cooking quality of rice and the physical and chemical characteristic of its starch. Starch is not only responsible for supplying the major source of energy in cereals, but also plays a crucial role in defining the physicochemical and functional properties of many foods through phenomenon such as gelatinization and retrogradation (Ibanez et al 2007). Therefore, cooking and processing behavior of rice is greatly dependent on the behavior of its starch, thus highlighting the importance to understand the behaviour of rice starch.

Several studies have also been carried out on the characterization of rice starch from different cultivars around the world. For instance, Sodhi & Singh 2003 studied the characterization of rice starch from rice varieties cultivated in India, while Noosuk et al 2005 and Frei 2003 carried out the same characterization on rice starch from rice cultivars from Thailand and Philippines respectively.

Few studies have been carried on rice varieties from West Africa. Otegbayo et al (2001) studied the effect of parboiling treatments on physicochemical qualities of local rice cultivars in Nigeria, Adeyemi et al (1986) also observed the physicochemical and cooking qualities of Nigerian rice varieties. Oko and Ugwu (2011) also studied the proximate and mineral composition of five major rice varieties in Abakaliki, South-Eastern Nigeria. Recently, Olayide et al (2011) studied the rheological and functional properties of starches isolated from five improved rice varieties from West Africa. The results of these studies have showed that cultivars influence the morphological and rheological properties of rice starch

Despite the great numbers of rice varieties emanating from West Africa, West Africans still prefer to eat foreign rice brands instead of local rice varieties produced in their immediate country. The acceptability of these rice varieties can be related to quality and rheological issues associated with milling and parboiling of rice. This lack of recognition of West African rice varieties, in addition to several other factors have led to rice production being undertaken in these west African countries by small farmers who are without any aid or subsidy from their respective governments. Therefore, in order to put West African rice varieties on the top front of local and global rice production, market competitiveness, industrialization and acceptance, there

is a need for research to be carried out on the functionality and rheological properties of West African rice cultivars.

In conclusion, it can be seen that rice quality and the development of rice based products is a multi-faceted dimension defined by several elements such as the physical appearance, cooking and eating qualities, and nutritional value. Therefore, by studying the relationship between the processing techniques utilized in the production of these rice varieties and the morphological and the rheological properties of these cultivars, the findings of this experiment can help increase the practical application and acceptability of rice flour from West African countries.

1.1.Statement of problem.

This study aims at studying the morphological and rheological properties of rice flour from local West-African rice varieties since not much work has been out in this area of research work.

1.2. Objectives of study

The main objective of this study is to examine the morphological and rheological properties of rice flour derived from local West African rice varieties.

The specific Objectives are:

- (a) To study the starch structure and composition of the various flours.
- (b) Characterization of the proximate composition , in particular amylose and color properties of the rice varieties.
- (c) To study the rheological properties of the rice flour, in particular the pasting properties.
- (d) To investigate the kinetics of softening of different rice cultivars during cooking.

CHAPTER II

LITERATURE REVIEW

2.0. Rice Milling

Harvested rice, *Oryza sativa* L is made up of outer hull, bran layer and an inner white starchy endosperm (Figure 2.0). The removal of the hull from rough rice (i.e., intact rice with its hull) produces what is referred to as brown rice. The de-hulling process of rice results in scratches to the inside layer of the bran which in turn sets the stage for the release of lipases, that can cause hydrolysis and oxidization of the lipids present in the rice. These reactions lead to rancidity and off-flavors such as soapy taste, bitter taste and off taste in rice. Once rice is de-hulled, it could be sold as brown rice or milled. Milling basically involves the removal of the bran from rice and then polishing the rice grains. After the outer bran layer is removed by abrasive milling and the rice bran polished via heat or non-heat treatment to inactivate the activities of lipase, the residual milled rice is sorted into fractions based on their sizes.

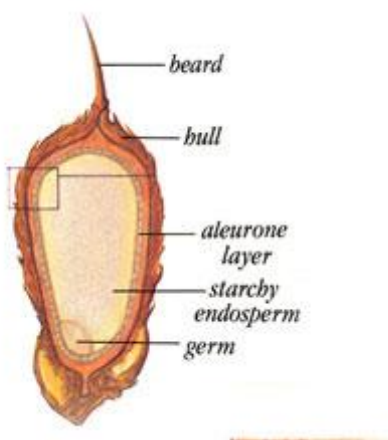


Figure 2.0. Diagram of a rice kernel (Juliano, 1985)

Industrial flours with various functionalities and granulations are produced from waxy broken rice with low to high amylose contents. Broken rice is a by-product derived from the milling of

rice. Although it is usually cost intensive, whole grains can also be milled to produce rice flour with closely related functional properties to that of milled broken rice.

2.1. Chemical composition of rice and their influence on rice functionality

2.1.1. Protein

Kennedy and Burlingame (2003) reported that the protein contents of milled rice ranges from 4.5 to 15.9%. Rice protein is made up of four fractions; albumin (water soluble), globulin (salt soluble), glutelin (alkali-soluble) and prolamin (alcohol-soluble). Protein in rice is generally less than 0.5%. (Singh et al 2000). On the contrary Oko and Ugwu 2011 reported high protein contents(1.58- 6.22%) in five West-African rice varieties namely Sipi , Faro 14, Faro 15 , Awilo and Canada. In addition Osaretin and Abosede 2008 showed that an indigenous rice variety cultivated in southeastern Nigeria "Ofada" , contained more protein (7.30%) than "Aroso", rice (6.95%), a foreign and imported rice produced in Thailand. Generally, the protein in rice is soluble in alkaline systems, therefore alkaline steeping techniques are utilized routinely in the production of rice starch to result in good recovery and low residual protein composition (Hogan 1967; Lumduwong and Seib 2000).

Fitzgerald et al (2003), studied the viscosity of rice flour and observed that proteins contributed to the peak height, offset thixotropy and final viscosity of rice flour. Protein is also involved in defining the textural characteristics of rice. Lyon et al (2000), observed that protein negatively affected the adhesiveness of cooked rice. A study carried out by Baxter et al (2004), observed that the three-dimensional network of rice flour gel was weakened as a result of the presence of prolamin in the rice flour matrix. The weakness in the three-dimensional network of rice flour gel was suggested to be due to the fact that during cooking, prolamin and partially broken down starch interact to form a reversible adsorption complex which affects the stickiness of cooked rice. Based on this, Zan-Hui et al (2007), suggested that a decrease in the protein content of fermented rice flour would benefit the three-dimensional structure of fermented rice flour gel. A reduction of the protein contents in rice can be achieved by the denaturing effect of temperature during cooking of rice.

2.1.2. Starch

2.1.2.1. Amylose

Structurally, amylose is a linear polymer made up of glucose units linked together by α -1, 4 glycosidic bonds. Amylose content has been utilized as the basis for differentiating between rice varieties. Basically, there are two types of rice namely, common and waxy rice (also referred to as 'glutinous' rice). Waxy rice has been reported to have an amylose content of 0-2%, while the amylose content of common rice cultivars could vary from low (9-20%), medium (20- 25%) or high (greater than 25%) (Majzoobi and Farahnaky 2008).

The interaction and affinity between iodine and rice flour (most especially the amylose fraction) whether in its native or defatted form has been the basis of determining the concentration of amylose in rice for several years (Jane et al 1999). The fraction determined by this affinity assay is referred to as apparent amylose content (AAC) or amylose equivalent (AE). As a rule of thumb, the amount of AAC in the rice starch is usually higher than the total amylose concentration. This total amylose concentration (TAC) is usually determined by the interaction and affinity of iodine to the fractionated and purified amylopectin. The total amylose concentration is also equivalent to the soluble apparent amylose content. The soluble apparent amylose content is equivalent to the true amylose content in rice while the insoluble apparent amylose content represents the amylopectin content with iodine affinity.

Ashogbon and Akintayo (2012); Adu-Kwarteng et al (2003) investigated the physicochemical properties of some West-African rice varieties namely, IGR, EAR, ILR, N2R, ITA 318, GRUG 7, ITA 92, TOX 3052, TOX 3108, ITA 312, TOX 3118, TOX 3142, TOX 3027 and WAR 100 and reported that their apparent amylose content varied from 21.88% to 30.78%. The amylose content of rice is an important parameter that defines its cooking and pasting characteristics (Adu-Kwarteng et al 2003).

The amounts of AAC have been observed to differ with respect to the type of rice cultivars. The difference in AAC among various rice cultivars has been suggested to be as a result of environmental factors like climate and soil conditions during grain maturity. For instance, it is a well-known fact that certain rice which flowers and develops at relatively low temperatures

generally contains greater amounts of AAC. Chen et al (2003) observed no amounts of AAC in waxy rice cultivars and reported amylose ranges close to 30% in non-waxy rice cultivars.

2.1.2.2. Amylopectin

This is a soluble polysaccharide with highly branched polymers of glucose molecules. The amylopectin molecule has both α -(1-4) and α -(1-6) glycosidic linkages with the branch points at the α -(1-6) bonds. The degree of polymerization of amylopectin in rice has been reported to be in ranges of 2,700 – 12,000 glucose units and the chain number (NC) in the ranges of 128-586 (Lu et al 2009).

Amylopectin structure and distribution in rice starch have been reported to be influenced by factors such as genetics as well as the growing and harvesting environment (Umemoto et al 1999; Suzuki et al 2003). For instance, storing grains at low temperatures was observed to increase the proportion of short chains and decrease the proportion of long chains (Umemoto et al 1999).

2.1.3. Other constituents

Apart from proteins and glucides, rice starch contains other minor compounds such as lipids and trace elements. Trace elements such as phosphorous play a vital role in providing starch certain functional properties such as viscosity consistency, paste clarity and paste stability. The phosphorous in rice is commonly evident in two forms, phosphate-monoesters and phospholipids. Phospholipid (0.013%) is the concentrated form of phosphorous in non-waxy rice, while phosphate-monoesters (0.003%) are the main form of phosphorous in waxy rice (Lim et al 1994; Jane et al 1999). Phosphorous contents of 0.50-0.55% were observed in fifteen different rice cultivars grown in Ebonyi state, Nigeria (Oko et al 2012).

Magnesium (Mg), calcium (Ca) and potassium (K) have also been reported as the most abundant of all the minerals in rice (Rivero-Huguet et al 2006). Horino and Okamoto (1992), reported that Ca and K have a negative correlation to the overall palatability of cooked rice. Adu-Kwarteng et al (2003), also reported high potassium and calcium concentrations in Tox 3108(west-African rice variety). While these minerals are generally beneficial to human's nutrition, they adversely affect the palatability of rice (Mi-Young et al 2010). Ibukun et al (2008) reported Ca levels of

1.40 - 1.66 mg/100g and K ranges of 7.20 -7.31 mg/100g in selected rice varieties collected at Ondo state, Nigeria.

2.2 . Rice starch structure.

Starch granules are basically composed of starch molecules fractionated into highly branched amylopectin and less branched amylose. Rice starch can be classified into 3 types depending on its resistance to amylolytic enzymes. These fractions are namely: rapidly digestible starch (RDS), which is hydrolyzed within 20 minutes, slowly digestible starch (SDS), which is hydrolyzed between 20 and 120 minutes, and resistant starch (RS), which is not hydrolyzed within 120 minutes (Jumaane et al 2011; Englyst et al 2002).

Rice endosperms are made up of starch granules which grow as single components in the cellular amyloplasts organelle (Ibanez et al 2007).The granules found in rice starch are basically compound granules which grow within each amyloplast (Martin and Fitzgerald 2002). These amyloplasts apart from being responsible for the synthesis and storage of starch granules are also responsible for chalkiness in rice (Ibanez et al 2007; Martin and Fitzgerald 2002). Chalkiness occurs as a result of loosely packaging of amyloplasts in rice. The irregular development of these amyloplasts can be observed through the aid of scanning electron microscopy. These compound granules form clusters containing 20 to 60 individual granules which make up the principal space of rice endosperm(Ibanez et al 2007). The endosperm of waxy rice is opaque primarily because of the air slots that exist between accumulated starch granules.

Of all the cereals, rice starch is reported to contain the smallest granules (3 - 8 μ m). The sizes of these rice starches are similar in size to homogenized fat globules. Depending on the type of rice genotype, several differences in the granular size of starch have been observed (Ibanez et al 2007; Martin and Fitzgerald 2002). In a study by Sodhi and Singh (2003) on the morphological, thermal and rheological properties of starches separated from rice cultivars grown in India, the size of the starch granules were within the ranges of 2.4-5.4 μ m. Qi et al (2003), reported size ranges of 4.9- 5.7 μ m for starches isolated from waxy rice.

Starch rice granules have a fine texture. Rice starch differs in size and shape. For example in a study carried out by Wong et al (2003), on the structures and properties of amylopectin phytyglycogen in the endosperm of sugary-1 mutant of rice, the starch granule of the sugar

mutant rice was observed as rough and more asymmetrical in comparison to wild rice. Rice starch granules are loosely packed clusters with/without holes and cracks.

Generally, rice starches have the A-type X-ray diffraction sequence (Wong et al 2003). Wong et al (2003) observed the same A-type X-ray diffraction sequence in sugary rice starches. On the other hand, rice mutant starches with high amylose contents have the B-type X-ray sequence which is similar to the same pattern observed in maize amylose-extender mutants and potato starches. Studies by Vandeputte et al (2003a), on the crystallinity and gelatinization behavior of granular starch concluded that rice starches have a low degree of crystallinity.

Several investigations have been made to estimate the crystallinity levels of rice starch. Wong et al 2003 reported crystallinities levels of 22.9% and 18.3% in two sugary rice starches. Several investigations have suggested that rice crystallinities are influenced by amylose amounts and amylopectin arrangement. Vandeputte et al (2003a) observed much more crystallinity in waxy rice starch in comparison to non-waxy rice starch.

2.3. Functionality of rice

2.3.1. Swelling ability and solubility

Heating of starch in the presence of excess water causes starch granules to swell and gelatinize. The heat applied to starch causes the disruption of the crystalline matrix which is followed by water molecules linking up of hydrogen bonds with the exposed hydroxyl regions of amylopectin and amylose. The sum effect of the above phenomenon is an increase in granule swelling and solubility.

The swelling ability of starch provides proof to the extent of affinity between the several starch chains within the amorphous and crystalline region. The degree to which starch chains interact is suggested to be influenced by the amount of amylose, structure of amylose and amylopectin, extent of granulations etc. Solubility of starch has been linked with the degree of polymerization. For instance, Vandeputte et al (2003b), observed that short amylopectin chains with degree of polymerization in the ranges of 6-9 had a higher swelling ability while longer amylopectin chains with degree of polymerization in the ranges of 12-22 had a lesser swelling ability.

Singh et al (2000), studied the swelling abilities of three rice flours and observed the highest swelling ability in the waxy rice flour thus supporting the notion that the less rigid the granular structure is, the higher it's swelling abilities. An inverse relationship has been suggested between the amylose content of rice starches and its swelling ability. For instance a study by Sodhi and Singh (2003), on starches from rice cultivars grown in India reported that the rice starch with the lowest amylose contents (7.8%) had the greatest swelling abilities, while those rice starches with the highest amount of amylose had the lowest swelling ability (Table 2.0). Solubility was also observed to have a linear relationship with respect to the amylose content.

Table 2.0. Amylose content, swelling ability and solubility of rice starches from different cultivars (Sodhi and Singh, 2003)

Cultivar	Amylose content (%)	Swelling ability (g/g)	Solubility (%)
PR-106	16.1 _{bc}	28.8 _{bc}	0.319 _b
PR-114	16.1 _c	28.6 _b	0.360 _d
IR-8	15.6	30.1 _c	0.307 _b
PR-103	7.8	33.2 _d	0.287 _a
PR-113	18.9	26.1 _a	0.346 _c

Values with similar letter in column do not differ significantly ($p < 0.05$)

Differences have been observed in the starch solubility and swelling ability within the same waxy rice cultivars (Wang and Wang 2002).

2.3.2. Gelatinization

When starches are heated in the presence of water, an irreversible disruptive phenomenon referred to as gelatinization occurs on the molecular arrangement of the starch granule (Sivak and Preiss, 1998). Typically, the amorphous regions of starch need to melt first or go through the glass transition phase (i.e., a reversible change from a hard or brittle state to a molten or rubber-like state) for gelatinization to occur in the starches.

GT (gelatinization temperatures) is usually determined by differential scanning calorimetry (DSC). This DSC provides the transition temperature ranges needed to bring about gelatinization in starch materials. The DSC system reports the thermal properties of the material as gelatinization start time/onset (T_0), gelatinization peak/optimum (T_p), gelatinization conclusion/end time (T_c) and enthalpy (ΔH).

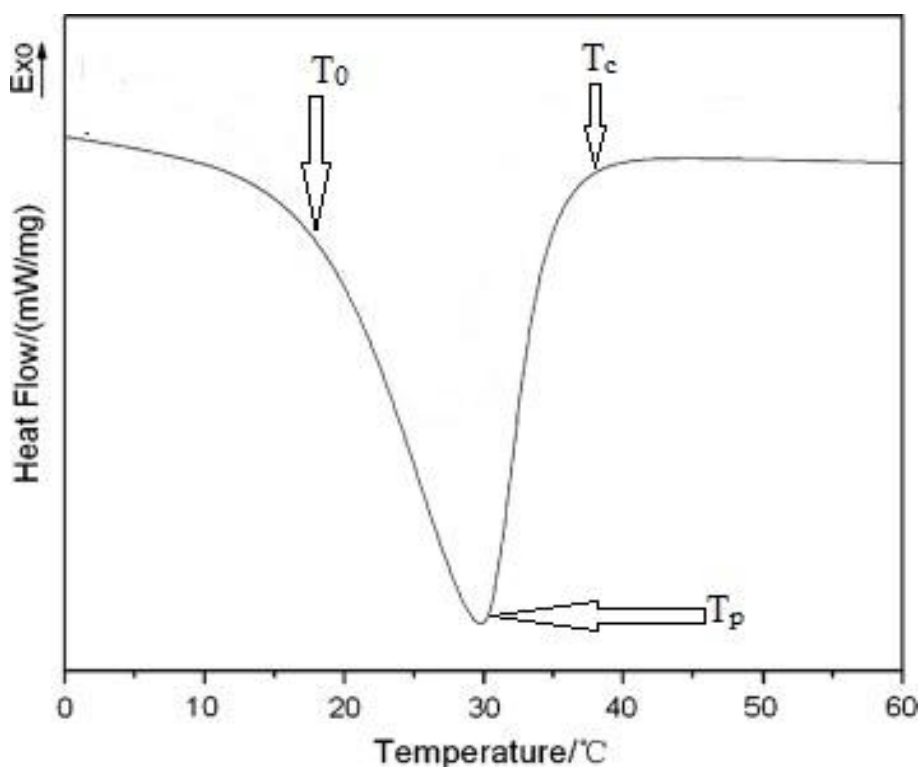


Figure 2.1. A diagram showing the thermal parameters of rice starch as determined by differential scanning calorimetry (Noda et al 2003)

Several studies have suggested that the DSC thermal properties are dependent upon the molecular arrangement of the crystalline part of starch (Cooke and Gidley, 1992 and Tester, 1997). These crystalline part of starch are mainly the amylopectin short chain regions with degrees of polymerization of 6-11 and not the amylose portion. In addition to the loss of the double helical arrangement (Tester, 1997), relationships have been suggested between the ΔH values of gelatinization and the quality and amount of starch crystallinity (Cooke and Gidley, 1992). Another relationship has been suggested between the degree of crystallinity of rice flours and its gelatinization temperatures (Tester, 1997). The molecular framework of amylopectin,

composition of starch and granular framework have an impact on the extent of crystalline perfection.

Several studies have shown that the thermal values derived by DSC are influenced by the way the samples are prepared and the mode of operation of the DSC instrument (Chiang and Yeng 2002; Teo et al 2000; Wang et al 2002). The frequency of temperature variation, soaking time, particle size of the rice flour and enthalpy changes, have made it difficult, and in some cases impossible to compare DSC data obtained from several DSC studies. Moisture content of the sample also affects the degree of gelatinization of rice starch (Jumaane et al 2011).

The temperature required for gelatinization does not depend on the amylose content of rice. Although, several studies have suggested a correlation between these two parameters and reported negative, positive and null relationships (Tetens et al 1997; Bhattacharya et al 1999; Nakamura et al 2002; Noda et al 2003). Several studies have also suggested that the distribution, degree of polymerization and branch chain lengths all influence the changes in enthalpy, pasting characteristics and the temperature required for gelatinization to occur (Jan et al 1999; Nakamura et al 2002; Noda et al 2003; Umemoto et al 2002). Nakamura et al (2002), investigated the endosperm structure of Asian rice cultivars and reported that amylose entities with low DP, i.e., a DP of 10, exhibited a negative correlation with T_0 while amylose entities with high DP, i.e., > 10 , exhibited a positive correlation with T_0 . It can thus be concluded that the differences observed in starch gelatinization temperatures from one cultivar to another is as a result of the differences in amylopectin molecules, i.e., the number of short chains in respect to the number of long chains.

Decades of scientific investigations have shown that the gelatinization temperature of rice flour is dependent upon both environmental and post-harvest conditions. For example Suzuki et al (2003), observed a positive correlation between gelatinization and growing temperature conditions. Fan et al (1999), also reported a significant influence on the enthalpies and gelatinization characteristics of rice flour as a result of conditions such as pre-drying, drying, storage treatment and duration. Storage of rice permits starch retrogradation, thus making the starch more resistant to enzymatic breakdown (Eerlingen et al 1994; Fredriksson et al 1998; Frei et al 2005).

2.4. Rheological properties of rice

Food rheology is the study of deformation and flow of food under well-defined conditions. The data obtained from rheological studies are relevant in quality control, plant design, research and development of new food products (Patindol et al 2008). Thermal processing of rice starch results in several types of rheological properties in rice.

2.4.1. Pasting Properties

This property of rice flour is as a result of gelatinization which involves heat and mass transfer. These phenomena result in loss of crystallinity and intake of water into the granular framework, with the later resulting in an increase in the size of the rice granule.

Viscometers such as Barbender Visco Amylograph (BVA), Rapid Visco Analyzer and rotational rheometers are utilized in determining the pasting properties or more specifically, the pasting viscosity of rice flour swelling and gelatinization. The underlining principle with this technique is to determine the viscosity of the rice flour as the temperature is varied with. A typical viscosity profile of rice flour usually begins with a rapid increase in viscosity with respect to an increase in temperature. This first phase of the viscosity profile is normally characterized by rice granules swelling. The second phase of the viscosity profile of rice flour involves the viscosity profile reaching a peak, also known as Peak viscosity(PV). This second phase of the viscosity profile is as a result of the equality between the swollen granules and broken granules brought about by stirring. Generally, stirring continuously leads to more break-down of rice granules and its fragments, thus leading to a decline in viscosity. Retrogradation is usually the final step of a viscosity profile and is as a result of cooling which partially brings together the starch molecules to create gels or precipitates that are surrounded by a network of amylose fragments. Typically, the paste form appears when the gel network disappears.

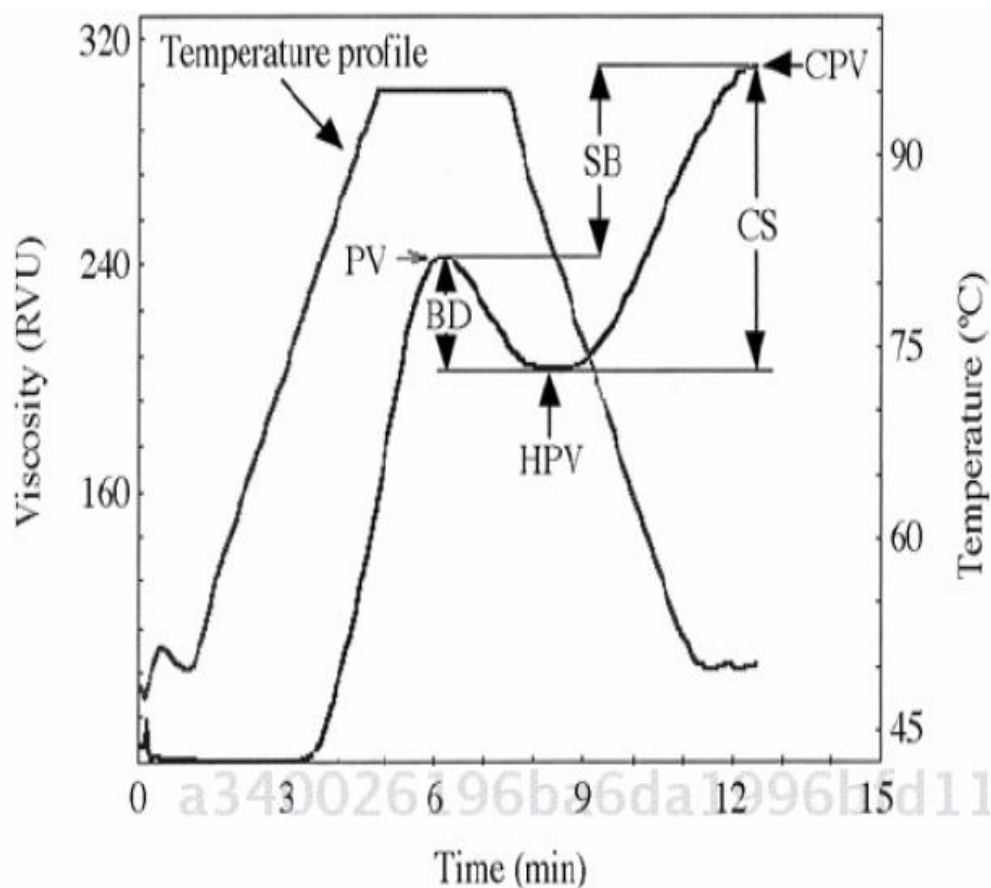


Figure 2.2. A typical viscosity profile indicating the temperature profile, PV: peak viscosity; BD: breakdown viscosity (PV – HPV); HPV: hot paste viscosity; SB: set back viscosity; CPV: cold paste viscosity; and CS: consistency (CPV- HPV) (Ibanez et al 2007)

Typically, a high PV is an indication of maximum swelling of starch granules which is related to the amylose content (Ikegwu et al 2010). Also, rice samples with high BD value reflect the fragile nature of the swollen starch granules under shear and temperature. In contrast, low values for PV and BD are a typically the result of high protein and lipid contents (Carolina et al 2011). Generally, the peak viscosity of rice flour occurs as a result of a balance between swelling of starch granules and shear, which is due to the leaching of amylose, formation of complexes between some amylose and lipids, and denaturation of protein (Fitzgerald et al 2003). Therefore, proteins impact the height of peak viscosity due to its ability to bind water (Baxter et al 2004). Also, the intact disulfide bond in proteins means that the swollen granules are less prone to breakdown.

Several correlations have been suggested between the pasting properties of rice flour and its amylose content (Bao et al 1999; Noda et al 2003; Vandeputte et al 2003b) while some have not been observed (Bhattacharya et al 1999). The SB value in a typical viscosity profile is an indication of retrogradation of rice paste, and it is well known that rice cultivars with high amylose contents have higher SB and FV values (Carolina et al 2011).

Also, it has been observed that differences between the amylopectin structures, i.e., long chains against short chain amylopectin can negatively or positively influence the pasting properties of a rice cultivar (Han and Hamaker, 2001). Vandeputte et al (2003b), however observed no significant relationship between the differences in amylopectin structures and pasting.

Studies have shown that apart from rice starch, proteins and lipids affect the pasting viscosity of rice flour (Fitzgerald et al 2003; Martin and Fitzgerald, 2002; Singh et al 2000). Alterations in the protein structure of rice flour during rice storage have been observed to reduce the peak viscosity of rice flour (Martin and Fitzgerald, 2002; Teo et al 2000; Zhou et al 2003). The strength of rice starch granule and its grain also influence the pasting properties of rice flour (Lai 2001; Wang et al 2002).

2.5. Thermal processing of rice.

Thermal processing basically involves the application of heat energy in order to transform food materials into desirable safe and stable forms. Industrially the application of heat to food depends on conditions such as the product's heating rate properties, surface heat area transfer coefficient, initial temperature of the food, cooking vessel temperature, and heating medium (steam or hot water).

Heat treatment of rice grains results in significant quality degradation particularly to its thermal nutrients and organoleptic components (Balsa-Canto et al 2007). Transformations in the mechanical properties and softening of the rice tissues are the major limiting factors defining the use of heat treatment on rice. These transformations are pertinent because they are linked to the textural and sensorial nature of rice, and subsequently, quality and consumer's acceptance of rice (Mayor et al 2007).

Rice softening is basically characterized by the loss of turgor pressure, intake or adsorption of water during heat processing. In addition to the chemical, enzymatic and non-enzymatic transformations that occur during thermal processing, thermal treatment reduces the cohesiveness of the matrix and softens the cell wall of rice (Vu et al 2004).

While thermal processing of rice results in the formation of a desirable texture or colour, it can also result in a lot of chemical reactions which in turn cause quality degradation. Therefore such undesirable side reactions need to be minimized. As a result of the intricate chemical makeup of rice, it is impossible to quantify all the transformations that can take place in rice during heating and thus correlate quantitatively the chemical changes to physical transformations like softening.

Mathematical models have been designed to maintain or optimize food quality during thermal processing and thus provide better information required in designing food production processes. The success of these predictive kinetic mathematical models is dependent upon factors such as temperature, pH, and moisture content.

2.5.1. Reaction Kinetics

Reaction kinetics define the rate of reaction in a system. Reaction kinetics is dependent on factors or components that determine the reaction velocity in the system. Such factors or components include the physicochemical components of the food and thermal temperature utilized.

Typically, the first-order reaction model is used to define the texture softening kinetics for rice grains. First-order reaction is a reaction where the rate depends on the physicochemical components of the food and thermal conditions. The general first order reaction is:

$$-dC/dt = k.C \quad (1)$$

Where C is the concentration of the reactant at time t , and k is the rate constant. Integrating the equation:

$$\ln C = \ln C_0 - k.t \quad (2)$$

C_0 is the concentration of the reactant at zero time. Plotting $\ln C$ versus time gives a linear relationship and the negative slope of the line gives the rate constant k . The intercept of the ordinate at time zero gives $\ln C_0$.

Typically, the slope of the logarithm of the concentration ($\log C$) against time (in this case minutes) is referred to as the apparent first order rate constant. The term "apparent" is used to indicate that the chemical process in chemical reality isn't really first order, but that the experimental results provide a good fit to the first order kinetic model.

From studies on kinetic softening of cereals and legumes, two apparent first order mechanism have been assumed and the texture of these food products has been proposed to be composed of two substrates, "a" and "b". The model proposes that the substrate "a" softens rapidly whereas substrate "b" softens slowly. The softening mechanism of both substrates are completely different.

The chemical reaction model for these two simultaneous first order mechanism can be expressed as

$$-da/dt = k_1.a \text{ and } -db/dt = k_2.b \quad (3)$$

Where "a" is the texture as a result of the first mechanism and "b" the texture as a result of the second mechanism.; t is time, k_1 and k_2 are the apparent rate constants for softening processes 1 and 2 respectively.

Integrating and transposing Eq. (3) yields:

$$\log H = \log H_0 - K_a^1 t \text{ and } \log H = \log H_1 - K_b^1 t \quad (4)$$

Where H is the hardness at time t , H_0 is the hardness at zero cooking time, H_1 is the intercept of the straight line plot asymptotic to the curve for the slow softening period and is referred to as "thermal firmness" (Bourne 1987). K_a^1 and K_b^1 are the apparent rate constants for the rapid and softening mechanisms, respectively.

2.5.2. Textural properties of rice

The texture of cooked rice represents one of the defining properties influencing consumer acceptance of the various rice cultivars. Despite the fact that the texture of rice is multi-faceted, hardness and stickiness in particular are critical parameters that define the palatability and consumption of cooked rice.

Rice quality is impacted by the methods of parboiling and cooking time. Traditional parboiling primarily involves three stages namely, soaking of the whole brown rice in water at room temperature, thermal treatment and finally drying the rice to the required moisture content. Steam under pressure is being utilized as the source of heat for parboiling in the United States and Europe (Patindol et al 2008) . This source of heat proffers advantages such as: relatively shorter processing time and an increase in yield. The application of high temperatures above the gelatinization temperature of rice have been observed to impact negatively on the textural and cooking properties of parboiled rice. Therefore, hydrothermal methodologies have been suggested as an alternative technology to pressurized steam (Bello et al 2006; Patindol et al 2008). Hydrothermal processing simply involves soaking of the brown rice, tempering of the soaked grain, heating of the tempered rice kernel with hot water so as to parboil the rice kernel, and lastly drying the parboiled rice(Bello et al 2006).

Bello et al (2006) conducted a study on the effect of hydrothermal conditions on the quality of rice reported greater intermediate values of textural properties between raw and traditional parboiled rice. The study observed that cooking time of rice had a great impact on the texture responses studied with the exemption of cohesiveness and resilience, which are only affected by tempering (Bello et al 2006). Naprinder et al., (2005), observed a negative correlation between the textural parameters of cooked rice and cooking time (Fig 2.3 and Fig 2.4)

Parboiled rice products offer certain merits over non-parboiled rice such as an increase in the milling recovery and strength of the rice kernel. This positive impact is due to the pre-gelatinization effects that occur during parboiling. These partial gelatinization causes closure in the fissures and granular spacing in the rice kernel thus also reducing cooking losses during cooking. Parboiling also imparts firmer and less sticky characteristics on rice, attributes appreciated by consumers in western societies (Bello et al 2006) Differences observed in the

textural properties of rice varieties have also been suggested to be as result of the differences in amylose content, water intake (at higher p value, i.e., $p \leq 0.05$), ratio of short versus long pectin chains and the granular structure. Singh et al., (2003), reported the highest hardness value in Basmati-370 rice which had the smallest size starch granules.

Positive correlations exist between amylose content and cooked rice firmness (Narprinder et al 2005) (Fig 2.3). Bhattachararya et al (1999), suggested that rice with high amylose content and long chain amylopectin exhibited a hard texture, whereas rice varieties with low amylose content and shorter chain amylopectin exhibited softer texture. Rice varieties with long amylopectin chains and high amylose content have been suggested to provide a conducive environment for inter and/or intra molecular interactions of starch with other rice components like lipids or proteins (Ong and Blanshard, 1995). A positive correlation has been established between the protein content of rice and its texture.

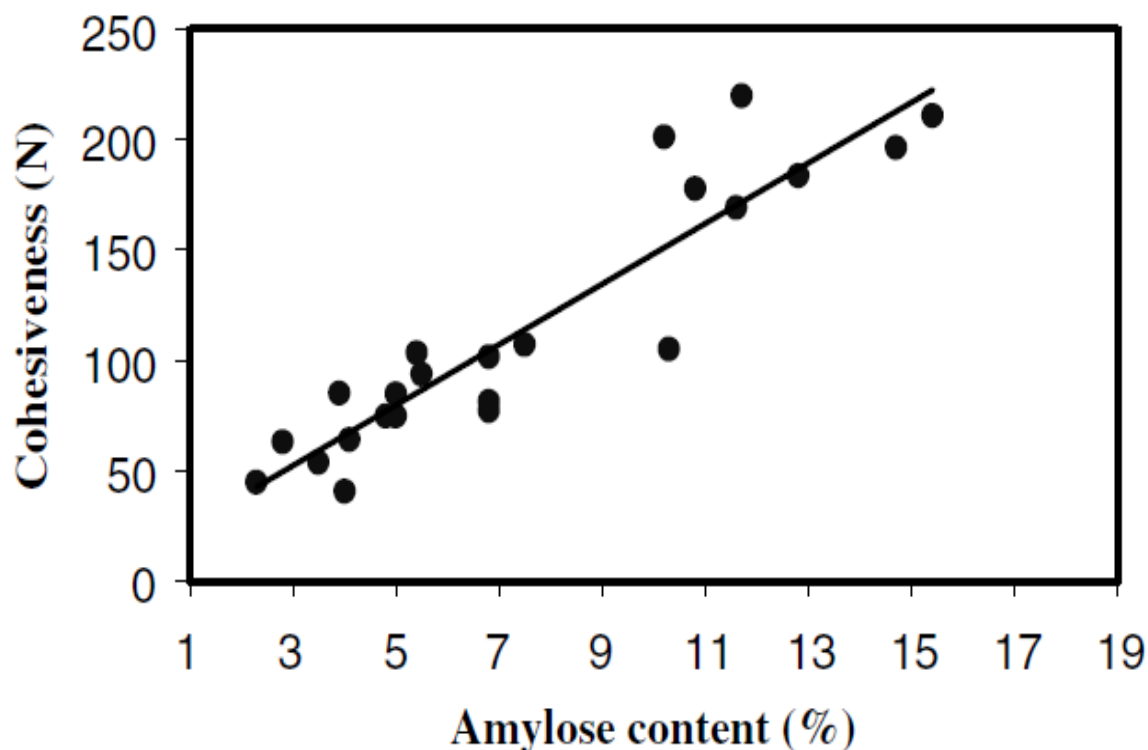


Figure 2.3. Relationship between amylose content of rice and cohesiveness of cooked rice (Narprinder et al 2005).

Textural parameters such as hardness showed a significant negative correlation with the cooking time (Narprinder et al 2005) (Fig 2.4) The cultivars with high amylose content were observed to have a hard texture and less cooking time.

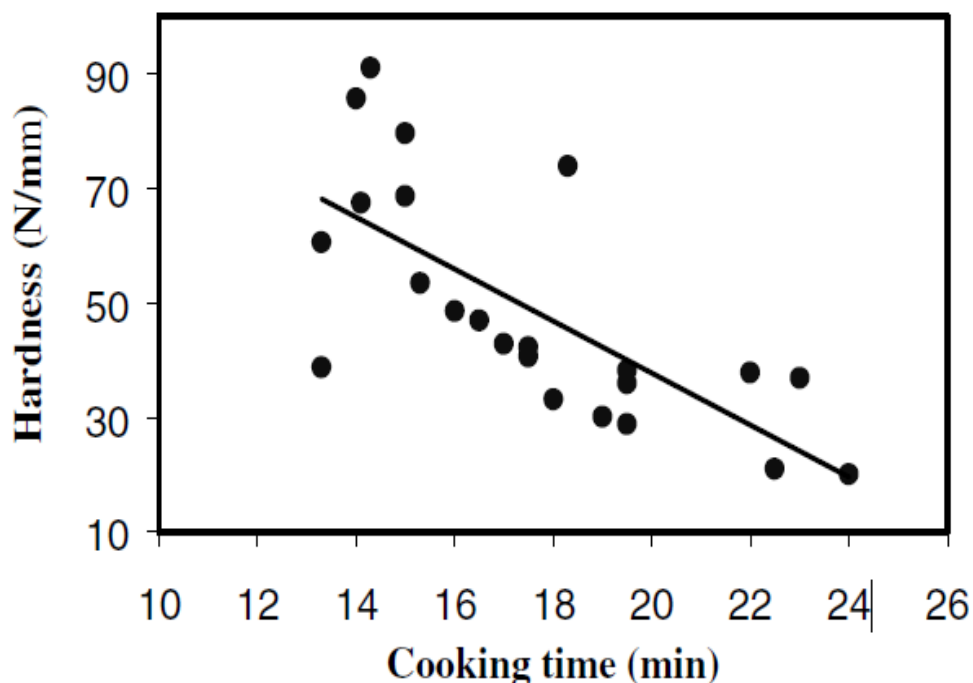


Figure 2.4. Relationship between hardness of rice and cooking time (Narprinder et al 2005).

2.6. Utilization of Milled Rice and its By-products

2.6.1. Milled Rice

Milled rice is made up of head rice, i.e., whole unbroken rice kernels and kernels that are at least three-fourths of an unbroken kernel; second heads, i.e., largest of the broken kernels, typically between one-half and three-fourth of an unbroken rice kernel; and brewer's rice, i.e., broken rice kernel that are about one-fourth of an unbroken kernel.

2.6.2. Rice flour

Rice flour is utilized in so many food applications and systems. Worldwide, several rice varieties with certain amylose- amylopectin are being used in the production of so many on-demand rice-flour based food products such as crackers, breakfast cereals, noodles, baby foods,

bread, candy, snacks, etc. Rice flour can hamper syneresis in stored, frozen and thawed food products (Wang and Wang 2002). Rice flour is generally utilized as a separating powder for baked products such as pizza and refrigerated-performed- unbaked biscuits, and as coating agents in the production of French fries (Islam et al 2012). In instances where rice flour is incorporated in deep fat frying of batters, rice flour provides functionalities such as coated crispiness, reduction in oil absorption capacity, retardation of moisture movement and an increase in shelf life (Islam et al 2012).

To so many homes across the world, rice flour can be prepared in a multitude of ways. In India, rice flour and coconut are steamed together in bamboo to make *puttu* (Vijayan and Sumathi 1997). *Appam* (a cake) is made from the fermentation of the same rice flour and coconut milk batter (Wang and Wang 2002). In China, rice stick noodles are made from rice flour which could be fried or not (Bhattacharya 2012). Rice flour is also utilized in the making of a Vietnamese delicacy produced from salad rolls and deep fried spring roll stocked with a collection and combination of several meats and vegetables (Wang and Wang 2002). *Horchata*, a rice flour based beverage of Mexican origin, is now growing popularity in the United States (Wang and Wang 2002). West African rice can be utilized for all the same reasons as listed above. In West Africa, the Susu people use rice flour and honey in making bread, while the Nigerian people produce a special rice beer called *Buza or Betso* also made from fermented rice flour and honey (NRC 1996).

Flour color is essential in determining the appropriateness and acceptability of the final product made from rice flour. The flour color of rice flour varies from white to yellow where the yellowness depends on the degree of pigmentation (i.e. build up of carotenoids like xanthophylls) (Lamberts et al 2007). Flour color is determined by the degree of L* (brightness/whiteness) and b* (yellowness) value (Lamberts et al 2007).

2.9.3. Rice starch

Starch and its derivatives are of significant importance to both food and non-food applications. In contrast to rice flour, there are few food applications that utilize rice starch. A good example of rich starch utilization can be seen in the production of non-dairy ice cream. This fat replacing application in products like salad dressings, ice cream and yoghurt is made

possible as a result of the small granule size and soft gel made from rice starch(Wang and Wang 2002). The production of smooth textures and fat-less fillings has made rice starch a notable ingredient in the manufacture of pastry cream products (Bao et al 1999). Rice starch is also utilized in the production of maltodextrins which is used as texture modifiers, sweetness reducers, fillers and flavor carriers(Nakorn et al 2009). Industrially, native rice starch is also used in the production of cosmetic dusting powder, laundry stiffening agent, paper and photographic paper powder, sugar coating for confectionary applications (Majzoobi and Farahnaky 2008) . Pure rice starch is utilized in pharmaceutical industries as a filling agent (Puchongkavarin et al 2005). Rice starch in conjunction with the enzymes secreted by *Aspergillus oryzae*, the fungus in Koji, is used in the production of the Japanese traditional beverage referred to as *Sake* (Okuda et al 2004).

In conclusion, if rice starch is to be used for more value added food applications, a thorough understanding and analysis of the rheological, morphological and textural properties of rice starch is required.

2.9.4. Rice hull

This non-digestible, fibrous, abrasive and high ash content fraction of paddy rice can be utilized as animal feed, chicken liter and as bio fuels.

2.9.5. Rice bran

Typically due to the bitter flavour produced by lipolytic enzymes on the oil in rice, the use of rice bran as animal feed and food materials suitable for human food products is limited. Although recently the development of thermal methods to inactivate these enzymes has contributed to the production of stable rice bran with good oil, fiber, carbohydrate and protein quality. These modified rice bran are used in the production of baked food products and energy bars.

CHAPTER III

Morphological, physicochemical and pasting characterization of selected non-parboiled rice varieties from West-Africa

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Abstract

This study was carried out to evaluate the morphology, physicochemical and rheological properties of five West-African rice varieties. The varieties studied were Faro 61, Faro 60, Faro 44, Tox 3145 and Nerica 3. The starch granule sizes in the rice samples as obtained with the aid of a Variable Pressure Scanning Electron Microscope (VP-SEM) were from 4.43 -5.62 μm . The rice granules were polyhedral, irregular in shape and tightly packed. The rice varieties were composed of 0.35 - 0.52% fat, 0.32 - 0.57% ash , 8.97 - 10.35% protein, 88.63 - 90.08% carbohydrate and 22.4 - 28.50% amylose. All the color parameters (L^* and b^*) of uncooked rice flour samples exhibited high values of L^* and low values of b^* for all the rice varieties. The order of increasing whiteness was found to be Faro 61 > Faro 44 > Faro 60 > Nerica 3 > Tox 3145 while the b^* values ranged from 5.09 - 7.26 . Results of the pasting properties shows significant differences in the peak viscosity , trough viscosity, final viscosity and set back viscosity of the rice flours. Over all, variations were observed in the morphological, physical, chemical and pasting properties of all the rice varieties.

Practical Application

The utilization of rice as a possible food commodity for house hold and industrial applications would depend largely on its physical, chemical and functional properties . The work reported in this chapter addresses the physical, chemical and rheological attributes of rice with the sole aim of reporting a basis for the subsequent applications of these rice varieties in several food and non-food applications.

INTRODUCTION

Rice (*Oryza sativa* L.) is cultivated in tropical West-Africa (Emmambux and Taylor 2013). Presently, rice production in West-African states has immensely increased with countries like Nigeria joining the world's top 20 leading rice producers (FAO 2011). Unfortunately, increase in demand for local rice varieties has not been affected by the increase in production of local varieties. This lack of interest in local rice varieties can be linked to several issues including poor physical and cooking quality of rice grains and poor post-harvesting practices (e.g. storage and parboiling methods) which can affect consumer preference and finished product quality. AfricaRice in collaboration with the Canadian International Development Agency (CIDA) are pursuing programs aimed at introducing better-quality rice varieties to local farmers and consumers in order to enhance competitiveness and patronage of locally grown rice.

One may be forced to ask why is color of rice flour an important attribute? Color is a vital sensory attribute that is known to influence acceptability of food products and thus it is necessary that this property conforms to consumer requirements. Consumer preference and demand can be influenced by the degree of whiteness or yellowness of rice and its rice based product (e.g. Flour). This physical property of rice flour is an important quality parameter that defines end-use products and is determined by the buildup of carotenoids in the endosperm. For instance in manufacturing processes such as extrusion and baking, the color of the rice flour can impact the color of the final products (Lamberts et al 2007; Nishita and Bean 1959; Mares and Campbell 2001). It can thus be concluded that color characterization is essential in determining rice flour conformance to final product specification.

Starch is a major component of rice grains (Patindol et al 2009). There are few studies describing and comparing the morphological characteristics of starch from some West-African rice varieties (Lawal et al 2011). This is perhaps surprising since starch morphology is a striking property of rice that affects its performance in terms of pasting properties, textural and product development. For instance, the smooth taste feeling derived from small rice granule size of starch offers new and improved potentials in the production of several food products such non-dairy ice-cream , infant baby food, thickeners, emulsifiers, gravies and sauces etc. Several other viscoelastic properties such as water uptake rate, swelling power are dependent upon the granule size and strength. A general rule of thumb is that smaller granules absorb lesser water than larger granules (Noosuk et al 2005). Literature review shows that little or virtually no studies have been carried out on the size and shape of starch derived from local rice varieties in West-Africa. The existing studies on rice have been on rice processing and marketing e.g. effect of parboiling treatments on physicochemical qualities of local varieties (Otegbayo et al 2001). In view of this paucity of data , it is necessary to extract starch from local varieties of West-Africa and study their morphology so as to encourage the manufacture of functional food products from these West-African rice varieties which could stand world market competitiveness.

Pasting property of rice flour is the underlying property which defines its use in rice-based product development. Singh et al 2006 reported a positive correlation between peak, final and setback viscosity with amylose contents. Amylopectin and amylose structure has also been observed to influence gelatinization, texture, retrogradation and the pasting properties of rice (Okadome et al 2000; Tan et al 1999; Zhu et al 2012). Zhu et al 2012 reported that rice flours with longer average chain lengths and longer exterior chain lengths had higher gelatinization, pasting and retrogradation properties. In addition to amylose and amylopectin, several correlations have been suggested between protein and pasting properties of rice. Several studies have shown a relationship between increase in protein content and increase in pasting properties of rice flour (Zhu et al 2010; Zhu and Liao 2008). Amylose and Amylopectin contents in rice endosperm have been suggested to have impact on rice and rice based product quality (Zhu et al 2012).

Therefore, in-order to increase industrial and consumer acceptability of West-African rice varieties, this study aims at exploiting the functionality of rice through properly defining the morphological, physicochemical and pasting properties of its flour .

Materials and Methods

Materials

A total of five improved rice varieties were used in this study; three varieties (Faro 44, Faro 60 and Faro 61) from Nigeria and two cultivars (Tox 3145 and Nerica 3) from Cameroun. These varieties were selected based on their popularity among rice cultivating communities in their respective countries. All the samples were harvested in 2010. The Nigerian rice varieties were supplied by the Breeding Unit of Rice Research Program, National Cereal Research Institute (NCRI), Badeggi, Nigeria while the Cameroonian samples were obtained from a rice farmer in Ndop, in the northwestern Region of Cameroun. The moisture content of the panicle picked grains was brought to 12% by solar drying and stored at room temperature until the samples were manually threshed and cleaned. The amount of 300 g cleaned paddy of each variety (moisture content $\leq 12\%$) were dehusked by using (THU 35A, Satake Corporation, Tokyo, Japan). The rice recovered from the dehulling process was further polished to remove the bran and therefore yielded white rice. Polished grains were later milled with a coffee grinder (SUMEET Multi Grind, India) and sieved with a 0.5mm sieve mesh to obtain particle size uniformity.

Proximate composition determination

Amylose content (%) of the rice flour was determined by AACC approved method (2000) with the aid of the continuous flow analyser (SEAL AutoAnalyzer 3HR, Model AA3 HR, U.S.A). The moisture, ash, protein, lipid and carbohydrate content of the rice flour were determined using the Association of the Official Analytical Chemists (AOAC) method. The moisture content was determined by oven drying the flour at 105°C until constant weight was achieved while the ash was determined by combustion of the flour samples at 550°C in muffle furnace. The Nitrogen content of rice flour was determined with the aid of the Leco Nitrogen analyzer and the nitrogen value multiplied by a factor of 6.25 to determine the total protein content. Lipid content was determined by Soxhlet extraction using petroleum ether as solvent. The total

carbohydrate content was estimated by difference using the following formula: 100 - (weight in grams [protein + fat + water + ash] in 100 g sample).

Starch extraction

Isolation of rice starch from rice flour was obtained by slightly modifying Lim et al 1999 alkaline deproteination method. The quantity of 100 g of sieved 0.55 mm rice flour was mixed with 300 ml of 0.5% NaOH. The mixture was constantly stirred for 4 hrs and left to stand for 24 hrs at 10 °C. The supernatant was decanted and the solid phase washed several times with distilled water several times until the pH of the filtrate was between 6.0 and 6.5. The isolated starch was oven-dried at 40°C for 48 hrs and later ground in a mortar to pass through a 0.55 mm mesh sieve.

Morphological characterization of rice flour

The morphology of rice starch granules was determined using a Variable-Pressure Scanning Electron Microscope (VP-SEM) (JOEL JSM - 6460LV). The isolated rice starch was mounted on a circular aluminum specimen stub with double sided sticky tape. The evenly distributed starch samples were then gold-coated in a vacuum using a sputter coated and examined at an accelerating intensity of 10 kV. Images were taken at magnifications of x 1500 and x3000.

Color measurements studies

A color meter (CR-400, Minolta Co., Ltd., Tokyo, Japan) was used to measure color value of the raw material rice flour utilizing the L, a, b uniform color space procedure. The instrument was calibrated with a standard white reference plate having Y, x, and y values of 88.7, 0.31 and 0.33, respectively. The obtained results were expressed in terms of L*(lightness) and b* (yellowness) values.

Pasting properties studies

Pasting properties of flour was determined using a Rapid Visco Analyzer (RVA) Model 3D (Newport Scientific, Warriewood, Australia) and Thermocline for Windows v.2.3 software. The general pasting method (162, ICC 2004) for flour samples was used, employing 3 g of rice flour in 25 ml of distilled water (corrected to compensate for 14% moisture basis correction of

sample). The method profile used an initial 50°C temperature setting and a paddle speed of 960 rpm. After 10 sec, the speed was reduced to 160 rpm and after 1 min, the temperature was ramped to 95°C over 4.42 min then ramped down to 50°C starting at 11 min and ending at 13 min. Data was taken every 2 sec. The data was plotted as time versus centipoise (cP). The following parameters were determined from the RVA pasting profile: Peak Viscosity i.e. maximum viscosity during heating, Trough /Hot paste viscosity, Break down viscosity (difference between the peak and trough viscosities), Final/cold paste viscosity i.e. viscosity obtained at the end of the cooling period and Setback viscosity (difference between the final viscosity and the peak viscosity)

Statistical analysis

Experimental data were determined in triplicate and data reported are averages of effectively three overlapping traces. Statistical analysis was conducted using SAS version 9.2 (SAS Institute Inc., 2010, Cary, NC, USA). Results were subjected to a one way analysis of variance at a 95% confidence levels to determine significance of difference.

RESULTS AND DISCUSSION

Physiochemical properties

Physiochemical properties of rice are evaluated to provide vital facts in defining their appropriate uses (Majzoobi et al 2008).

Proximate composition

The variations in the proximate compositions of the studied rice varieties are depicted in Table 3.0. The rice variety Tox 3145 indicated the highest ash content (0.57%) while Faro 60 indicated the lowest ash content (0.32%). Typically, the ash content of a food sample is an indication of the levels of essential minerals (Bhat and Sridhar 2008). Protein content for all the rice varieties evaluated ranged between 8.97% to 10.35%, while fat content ranged between 0.35% up to 0.52%. Overall, Faro 44 indicated the lowest fat content (0.35%). The carbohydrate content was high in all varieties (> 88%) and therefore these varieties can be considered as a good source of carbohydrate.

Amylose content

The amylose content of rice plays a vital role in determining its cooking, texture and pasting properties (Adu-Kwarteng et al 2003, Asghar et al 2012). Apart from the amylose content, proteins, lipids or amylopectin also influence the cooking quality of rice (Cai et al 2011). In this present study, no correlation was observed between the amylose content and its pasting properties. The amylose results of this study were within the intermediate amylose ranges (20-28%) (IRRI, 1985). The results of this investigation indicated that among the studied rice varieties, Nerica 3 had the lowest amylose content of 22.4% while Faro 44 showed the highest amylose content (28.55%). Rice varieties with high amylose content have been known and proven to exhibit hard textures on cooling after cooking. This textural attributes have been associated to the retrogradation of the amylose molecules (AduKwarteng et al 2003)

Table 3.0 Proximate composition of non-parboiled rice varieties (% dry matter)

Rice cultivars	Fat (%)	Ash (%)	Protein (%)	Total carbohydrate (%)	Amylose (%)
FARO 61	0.39±0.01 _{bc}	0.47±0.01 _b	10.02±0.00 _a	89.12±0.08 _b	24.9±0.00 _c
FARO 60	0.35±0.04 _c	0.32±0.03 _c	9.92±0.02 _a	89.41±0.08 _{ba}	27.8±0.00 _b
FARO 44	0.52±0.01 _{ba}	0.45±0.08 _{ba}	9.59±0.23 _{ba}	89.44±0.14 _{ba}	28.5±0.00 _a
TOX 3145	0.39±0.06 _{bc}	0.57±0.04 _a	8.97±0.08 _b	90.08±0.01 _a	24.15±0.35 _d
NERICA 3	0.51±0.15 _a	0.52±0.00 _{ba}	10.35±0.7 _a	88.63±0.86 _c	22.4±0.14 _e

Mean ± SD values with the same superscript letters in a column are not significant different(p>0.05)

Morphological properties of isolated starch granules

The scanning electron micrographs of the rice starch from the various rice varieties are shown in Figures 3.1 - 3.3. Starch granules size were within the 4.43- 5.62 µm range. The SEM micrographs revealed relatively similar morphology for all the samples. The starch granules of all the rice samples were polyhedral, irregular in shape and tightly packed. Similar morphology were observed in the morphology of rice varieties from Asia (Ibanez *et al* 2007; Singh *et al*

2003). High level of crystallization was also observed in all the rice varieties. That is to say the shapes of the characterized isolated rice starches were similar where as the granule sizes differed. Obviously, the tightly packed arrangement can be attributed to the presence of residual protein (Cardoso et al 2006). Residual proteins cause the granules to adhere together thus forming aggregates (Newman et al 2007). In addition, apart for Nerica 3, the surfaces of the starch granules of the other rice samples were smooth with little or no surface depressions probably as a result of residual lipids left over during starch extraction (Ibanez et al 2007). The effect of the milling on the flour particles was evident with the presence of central cavities within and spaces between starch granules of all the studied starch samples.

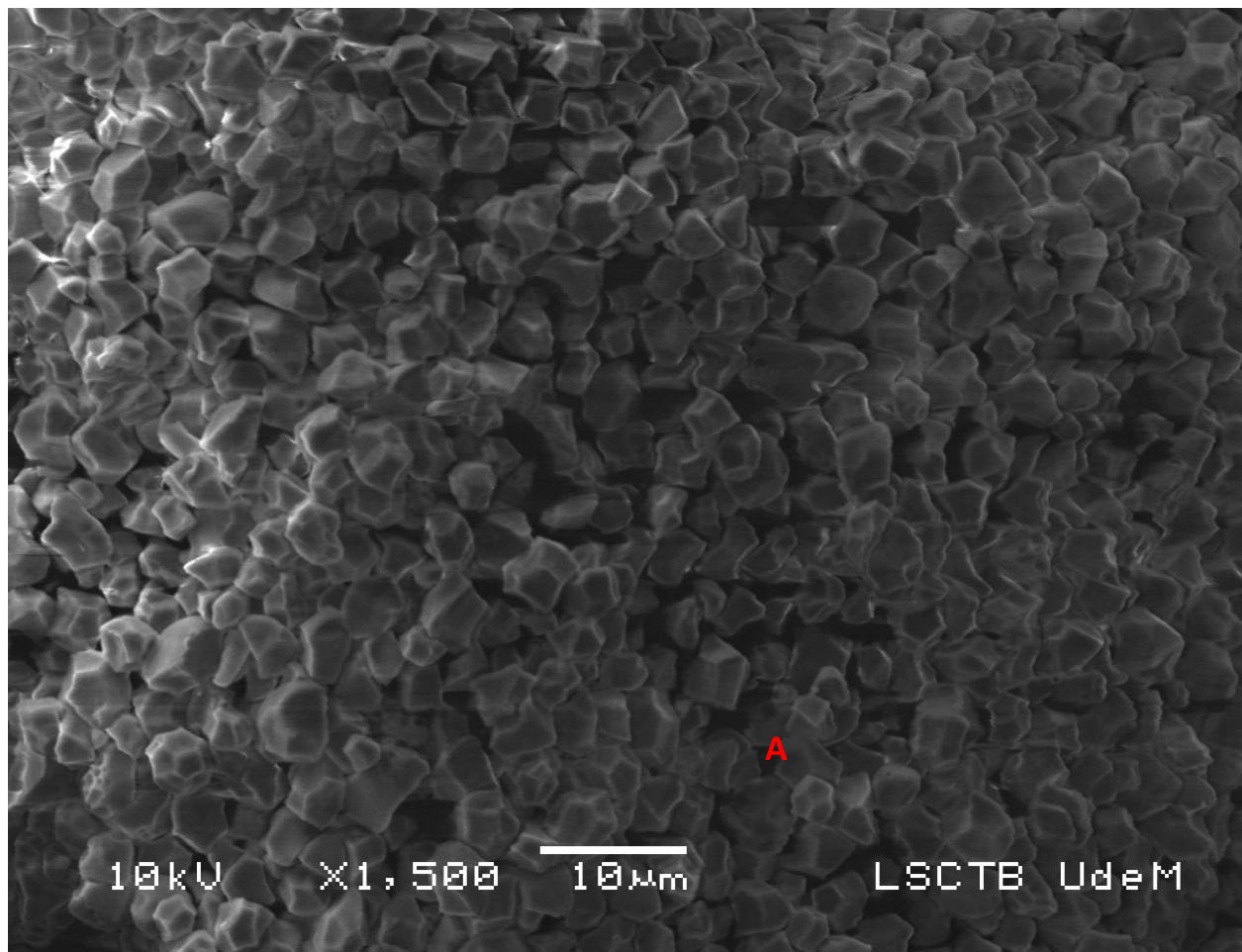


Figure 3.1. Scanning electron micrograph of (A) NERICA 3 rice starch

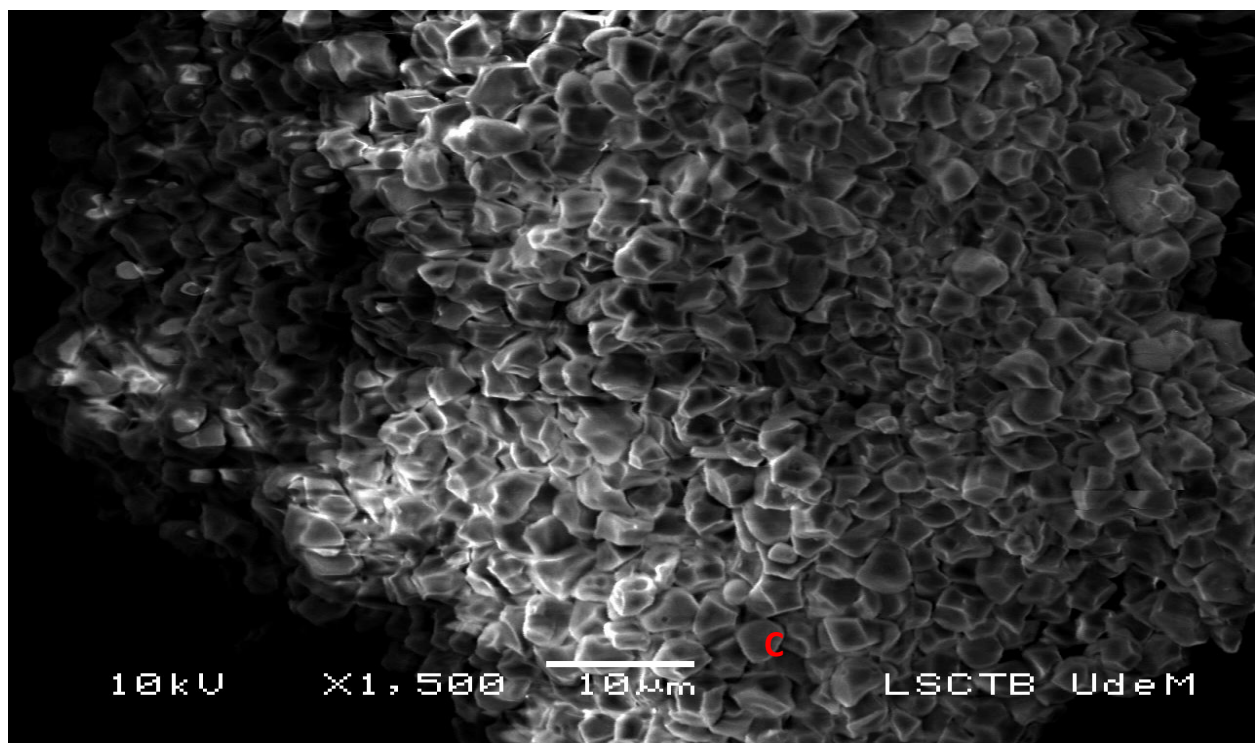
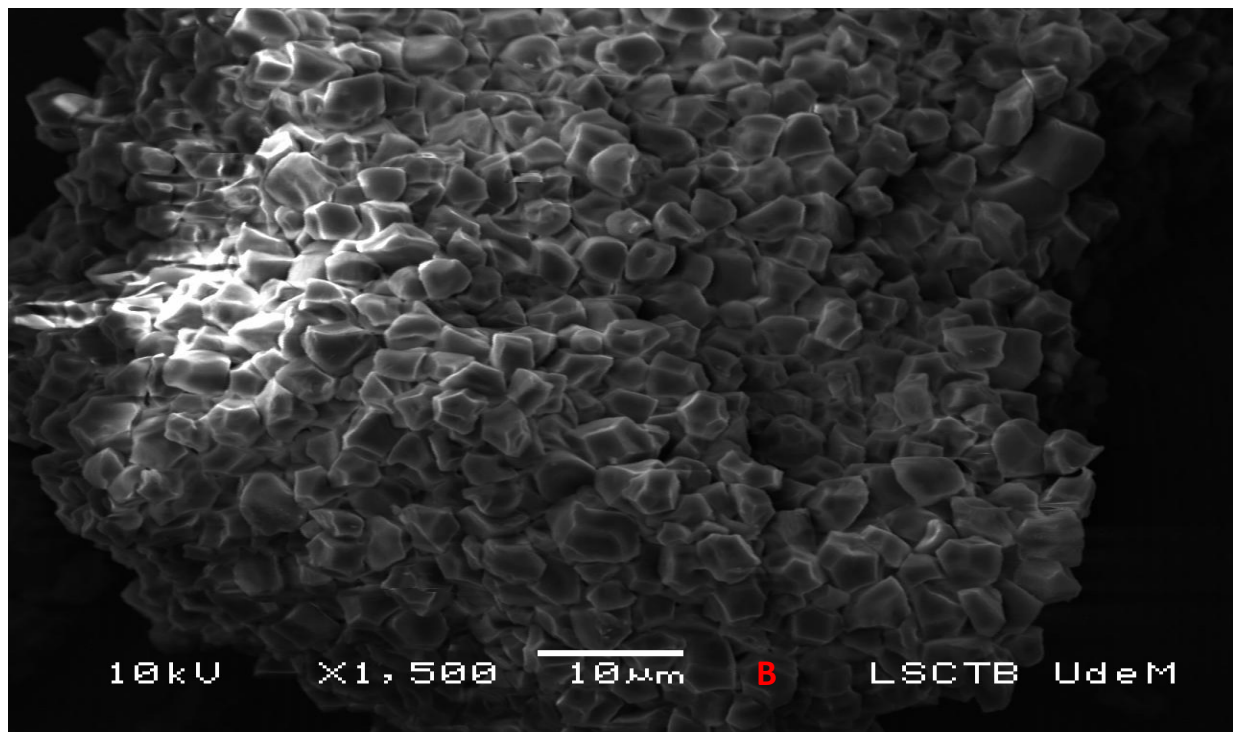


Figure 3.2. Scanning electron micrographs of (B) TOX 3145 and (C) FARO 44 rice starches

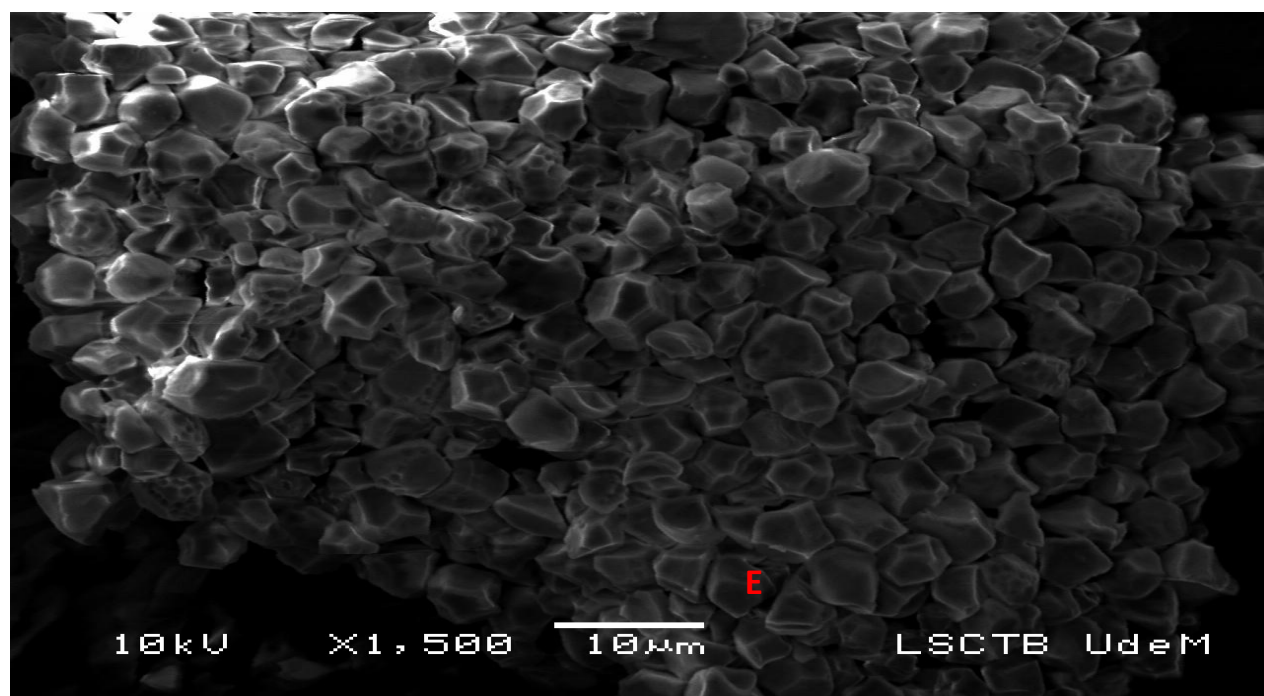
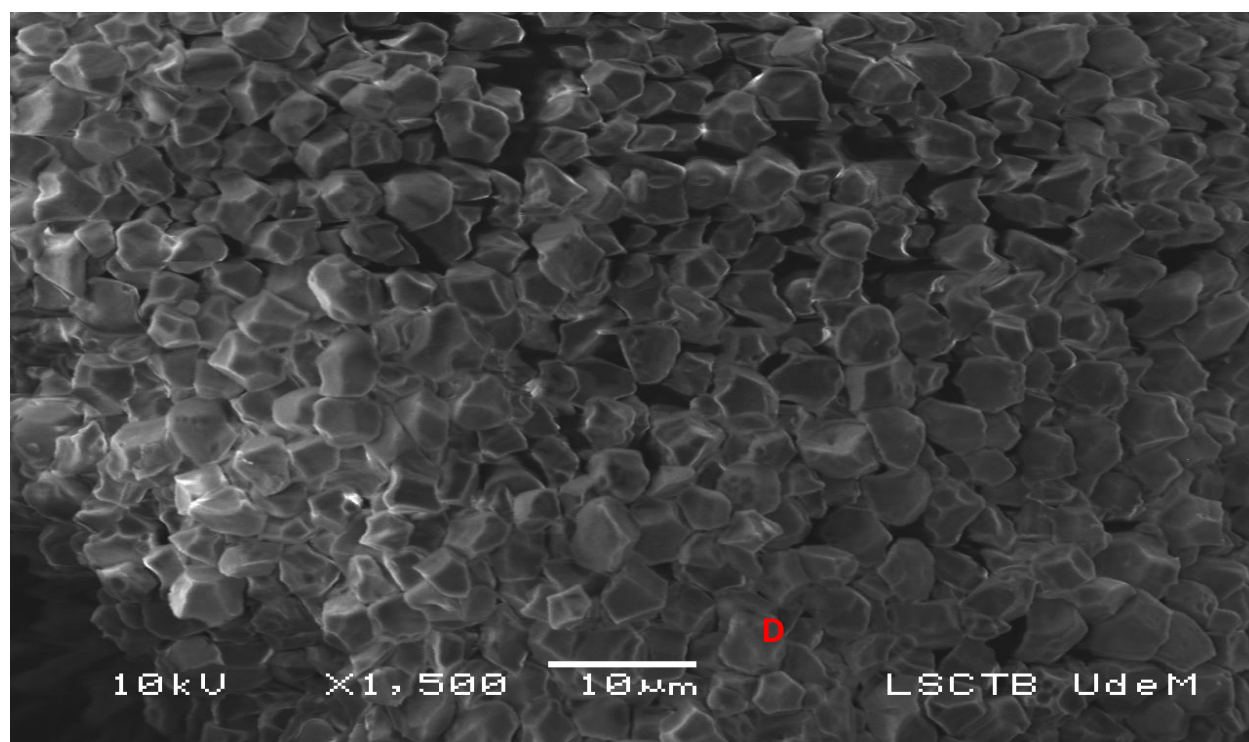


Figure 3.3. Scanning electron micrographs of (D) FARO 61 and (E) FARO 60 rice starch

Flour Color measurements

There was significant differences in the L^* and b^* ($p < 0.05$) of the rice varieties studied. Flour color is critical in determining consumer preference and acceptability because of high visual appeal of white flour (Adu-Kwarteng et al 2003). A high value of L^* and a low value of b^* is important for the flour to positively meet the consumer's preference and acceptability. Figure 3.4. and 3.5 indicated that all the flour samples displayed excellent color properties. The degree of yellowness (b^*) ranged from 5.09 - 7.26 for the rice varieties (Figure 3.5). The order of increasing whiteness was found to be Faro 61 > Faro 44 > Faro 60 > Nerica 3 > Tox 3145.

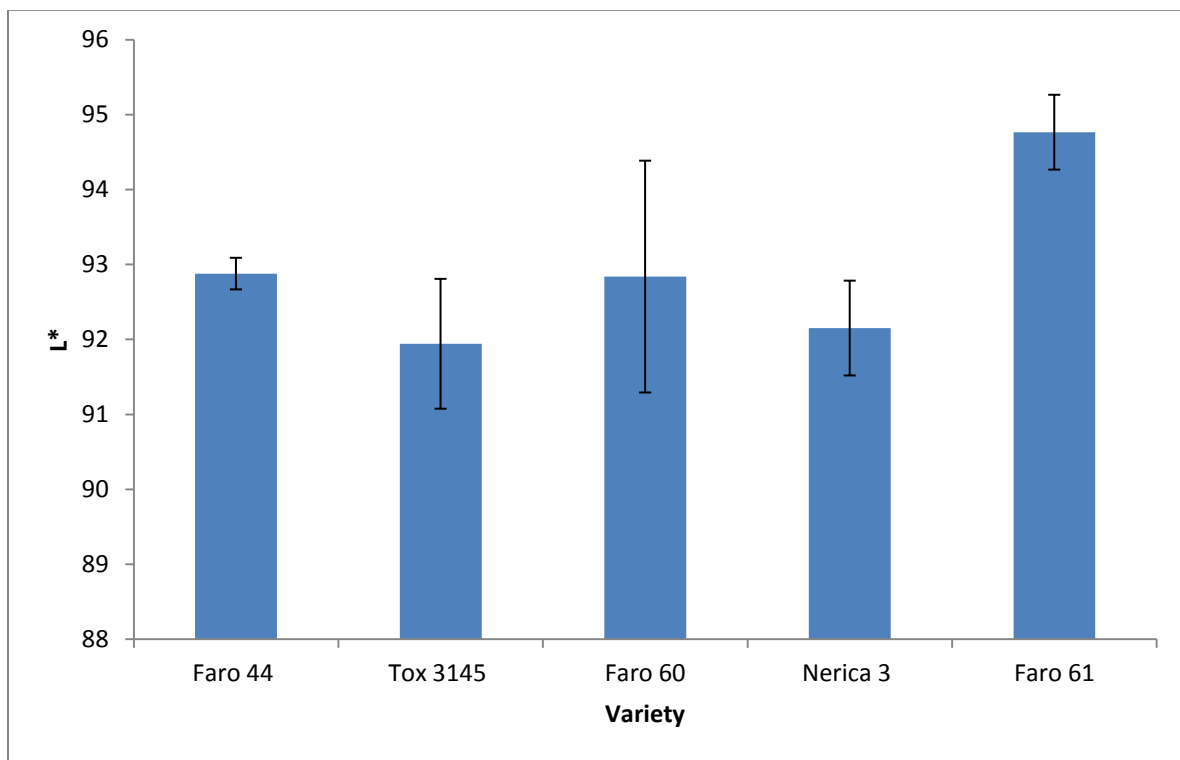


Figure 3.4 Whiteness(L^*) of the rice flours . Means \pm standard deviations from 3 replicates

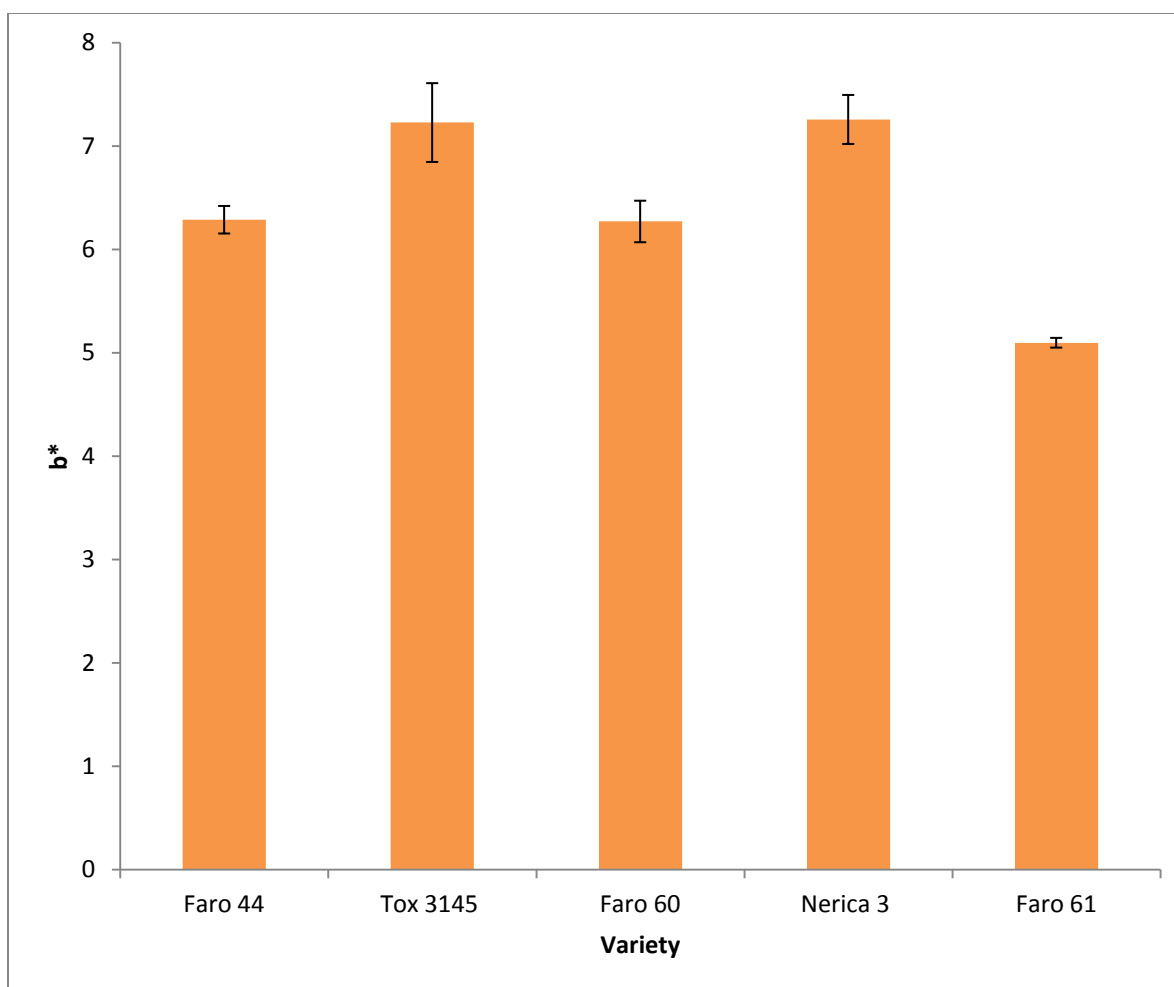


Figure 3.5. Yellowness (b*) of the rice flours . Means \pm standard deviations from 3 replicates

The L* and b* values observed in this study were better than L* value (85.6) and b* value (12.4) of the dehulled brown rice (*Oryza sativa* L.) from the long grain variety Puntal harvested in Spain (Lieve *et al* 2006). The superb L* and b* values observed in this study are related to low pigment accumulation (for e.g. carotenoids such as xanthophylls) in the rice varieties (Ikegwu *et al* 2010; Adu-Kwarteng *et al* 2003; Lamberts *et al* 2007).. In most West-African countries like Ghana and Nigeria, consumers would view these rice flours as excellently acceptable.

Pasting properties

Pasting properties is essential in categorizing the end-product application of flour. Figure 3.6 and Table 3.1 summarizes the pasting properties of the various rice flours. This functionality is said to be dependent upon factors such as granule size, amylose/amylopectin ratio and starch property (Simi and Abraham 2008).

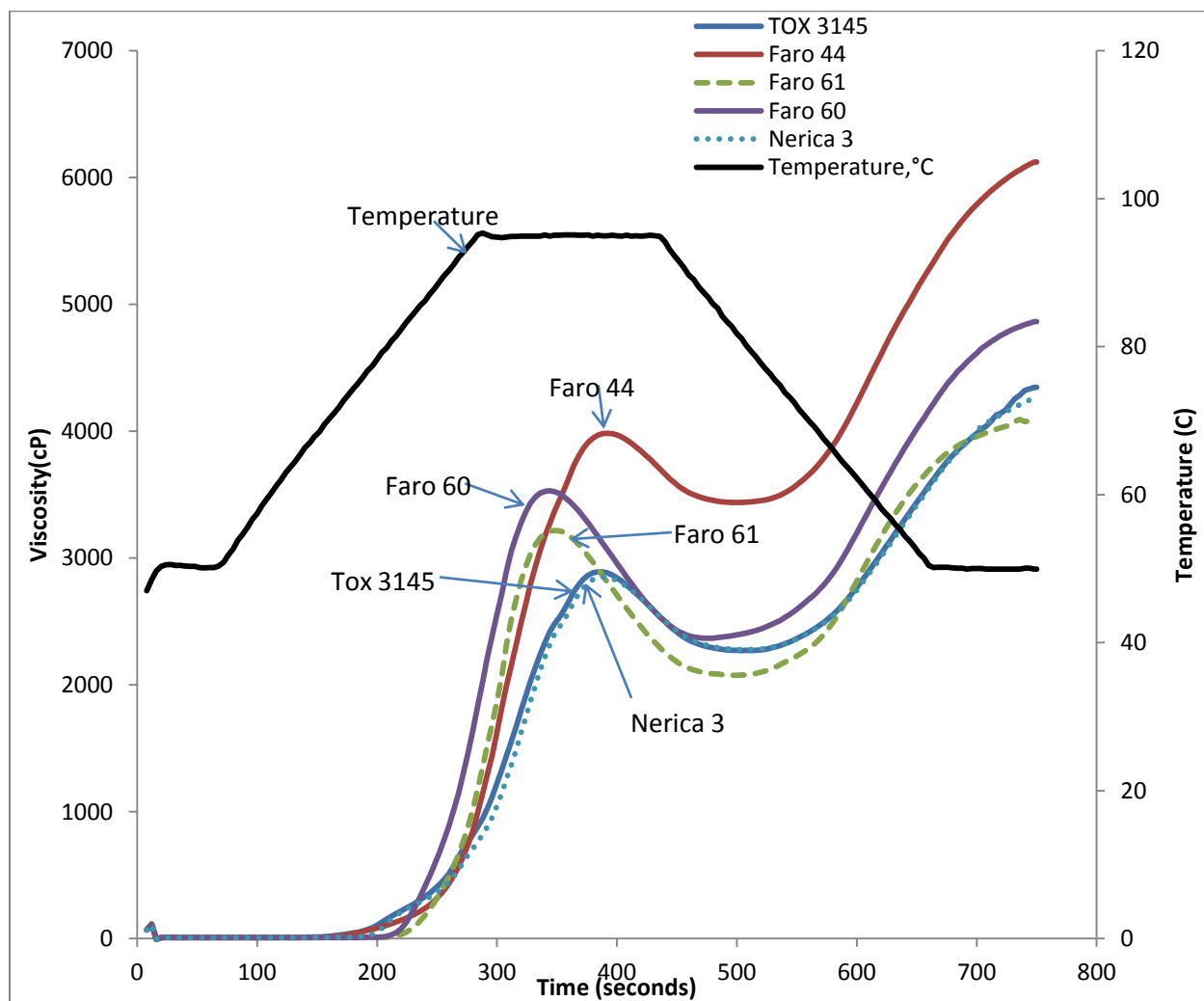


Figure 3.6. Rapid Visco-Analyzer profile curves of flour of the rice varieties

The peak viscosities of the respective rice varieties indicate their water binding capacity of their respective starches. FARO 44 showed a higher peak viscosity value (3984.5 cP) than the other rice varieties probably due to its higher amylose content which in turn increases the swelling capacity of flour. Amylose molecules interactions produce matrixes that increase the

viscosity of the rice flour (Ibanez et al 2007). On the other hand, the low peak viscosity of Nerica 3 (2850.5 cP) can be attributed to its low granule size (4.54 μm). It is generally believed that flour particles with smaller granule size absorb less water thus producing lower viscosities. The low peak viscosity of Nerica 3 implies that the flour can be utilized in the production of foods that need thickening e.g. porridges.

Accordingly, the trough viscosities values obtained for the different rice varieties in this study were different. Faro 44 and Tox 3145 had the highest and lowest trough viscosities respectively. The break down viscosity on the hand is a measure of the ability of the flour's paste to withstand heating and shear stress during cooking. Starch breakdown is typically characterized by the disruption of the flour's granule and the leaching of amylose into the solution. Break down viscosities were within the 546.5 and 1164 cP range for the rice varieties. Typically, the higher the breakdown viscosity of the flour paste, the lower its capacity to withstand heating and shear stress during cooking. The low breakdown viscosity of Faro 44 means that this variety can be used in the production of dishes that do not need to stick together and retains its firmness, whereas the high breakdown viscosity of Faro 60 makes it suitable for applications that require a sticky texture e.g. mashed paste-like rice balls and dumplings (Diako et al 2010; Gayin et al 2009; Park et al 2007)

Table 3.1 showed that Faro 44 had significantly higher breakdown viscosities than the rest varieties. This result indicated that Faro 44 flour is suitable for the production of value added products such as noodles, due to the ability of the paste to swell sufficiently while remaining intact and stable during sheering. The high amylopectin content in Nerica 3 can be suggested as the reason for its weak gel strength thus final viscosity. The final viscosity results observed are similar to those observed in other rice flour studies (Park et al 2007)

Setback viscosity varied from 865.5 to 2138.5 cP. Setback viscosity is a measure of retrogradation. During setback, there is viscosity increase as a result of the rearrangement of leached out amylose molecules from the starch molecules during cooling. FARO 44 showed the highest setback viscosity (2138.5 cP) while FARO 61 showed the least (865.5 cP). The general rule of thumb is the higher the setback viscosity value of the flour, the lower the rate of retrogradation during cooling.

The pasting temperature of FARO 44 was higher than the other rice varieties and found to be 85.5⁰C. This could be due to its high amylose content. Studies have shown that flours with high amylose contents require more energy to disintegrate its inter- and intra- molecular bonds (Rungarun and Athapol 2007; Nakorn *et al* 2009). In addition, Faro 44 exhibited the highest peak time, i.e. the time required to attain peak viscosity. This high peak time may be a result of the packaging of the starch molecules inside the flour as well as the starch molecular structure. For instance, Majzoobi and Farahnaky 2008 reported that flours with high degree of crystallinity exhibited high peak times while those with low degree of crystallinity exhibited short peak times (Zhong *et al* 2009)

Several other factors such as structure of starch, degree of branching of amylose/amylopectin, degree of interactions between starch and other compounds like fat or protein can contribute to the varietal differences observed in the pasting properties in this study (Ibanez *et al* 2007; Zhu *et al* 2012). For instance, Baxter *et al* 2004 showed that the peak viscosity of rice flour decreased as a result of the binding effect of the disulfide linkages in protein with the molecules. This indicated that the amylose and amylopectin molecules were less susceptible to swelling and eventually breakdown (Derycke *et al* 2005). This protein- starch interaction could also be another reason for the low peak viscosity of Nerica 3 due to its high protein content (10.35%). In addition, it has been proven that lipid interaction with amylose and amylopectin can limit hydration of flour therefore reducing its peak viscosity (Murillo *et al* 2011; Newton *et al* 2011).

Table 3.1 Pasting properties of rice flours as affected by variety

Rice variety	Peak viscosity (cP)	Trough viscosity (cP)	Breakdown viscosity (cP)	Final viscosity (cP)	Setback viscosity (cP)	Peak Time(min)	Pasting Temp (⁰C)
TOX 3145	2892 ± 35.36 _d	2270.5 ± 7.78 _c	621.5 ± 27.58 _b	4346 ± 35.36 _c	1454 ± 70.71 _b	6.40 ± 0.00 _b	81.20 ± 4.95 _{ba}
FARO 44	3984.5 ± 14.85 _a	3438 ± 46.67 _a	546.5 ± 31.82 _b	6123 ± 4.24 _a	2138.5 ± 19.09 _a	6.50 ± 0.05 _a	85.55 ± 0.00 _a
FARO 61	3218 ± 84.85 _c	2076 ± 24.46 _d	1142 ± 59.40 _a	4083.5 ± 0.71 _e	865.5 ± 84.15 _c	5.80 ± 0.00 _c	83.18 ± 0.04 _{ba}
FARO 60	3531 ± 67.88 _b	2367 ± 24.04 _b	1164 ± 43.84 _a	4863.5 ± 26.16 _b	1332.5 ± 41.72 _b	5.70 ± 0.00 _d	80.75 ± 0.00 _{ba}
NERICA 3	2850.5 ± 13.45 _d	2279 ± 9.90 _c	571.5 ± 354 _b	4260.5 ± 50.20 _d	1410 ± 36.77 _b	6.47 ± 0.00 _a	77.58 ± 0.04 _b

Mean ± SD values with the same superscript letters in a column are not significantly different (P>0.05)

Conclusion

The proximate, morphological, color and pasting properties of rice cultivars from Nigeria and Cameroun were studied and differences were observed. Faro 44 indicated the highest fat content and Faro 60 the lowest. The amylose content of the rice varieties varied significantly. Faro 44 rice showed the highest amylose content in contrast to Nerica 3 which indicated the lowest amylose content. Tox 3145 exhibited the highest carbohydrate content while Nerica 3 had the lowest. The proximate composition of the rice varieties varies significantly. Rice varieties studied also exhibited good morphology characteristics especially starch granule shape and size. The shapes of the characterized isolated rice starches were similar where as the granule sizes differed. Although all the rice varieties exhibited similar morphology, the most remarkable observation was the Nerica 3 rice variety and its starch granules demonstrated rough surfaces with little depressions. The highest L* values for Faro 61 might be due to low pigment accumulation in the rice varieties. Variations in the proximate composition resulting from varietal differences did not clearly result in variations in the pasting attributes of the studied rice varieties. Pasting properties indicated that the varieties that demonstrated variations had higher peak viscosity, break down viscosity and set back viscosity. Faro 44 demonstrated the highest values of peak viscosity, trough viscosity, final viscosity, setback viscosity, peak time and pasting temperature when compared to the other rice varieties. Due to the high peak viscosity/water absorption capacity of Faro 44, this rice variety can be widely and specifically used in the production of thermally stable products like noodles.

In conclusion, the excellent proximate, morphological, color and pasting results of the rice varieties in this study clearly show that the flours or starches derived from these rice varieties are suitable for domestic and industrial applications such as non-dairy ice cream production.

CHAPTER IV

Thermal softening of improved non-parboiled rice varieties from West-Africa

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Abstract: This study was carried out to evaluate the kinetics of texture softening of five West-African rice varieties with the aim of defining their specific food applications while improving the industrial and local acceptability of the various varieties . The varieties utilized were Faro 61, Faro 60, Faro 44, Tox 3145 an Nerica 3. The various rice varieties were cooked in a temperature controlled bath a 100° C at 5 selected cooking times. The cooked samples were cooled immediately after cooking and subjected to a two-cycle compression test with the aid of a texture analyzing machine (Instron Universal Testing Machine). Three textural attributes (Hardness, Stickiness and Gumminess) were obtained from the resulting force - deformation curves. The textural attributes of the various cooked rice varieties decreased with increase in cooking time. In addition, the rate of textural changes related with the cooking temperature utilized in this study was found to confirm with two pseudo first-order kinetic mechanisms. The apparent rate constants were determined and observed K_a^1 varied from 0.03776 to 0.4468 min⁻¹ while K_b^1 varied from 0.008475 to 0.013665 min⁻¹. Overall, the results of this investigation is vital in ensuring and improving quality of rice by thermal processing.

Connecting Statement

In precedent chapter three, the morphological, physicochemical and pasting properties were evaluated. This study will be published in due course, thus providing the basic theories of chemical kinetics to the rate of thermal softening of rice tissues and ultimately reveal if the physicochemical components of the various rice varieties contributed to softening during the cooking process.

INTRODUCTION

Rice (*Oryza sativa* L) constitute an important category in the diet of sub-Saharan Africans (Tomlins et al 2007). In Ghana, the *per capita* consumption of rice comes second after maize while rice consumption in Benin has been reported to have the highest annual growth rate 21% in sub-Saharan Africa (Rutsert et al 2012) (Quaye et al. 2000). Typically, thermal processing techniques such as cooking is required to soften these dried un-cooked west-African rice varieties and render them edible and acceptable.

Softening of rice is associated with loss of turgor pressure, adsorption or uptake of water during thermal processing which cause pertinent chemical and physical changes in the matrix that consequently result in softer textures (Anzaldua-Morales et al 1996; Vu et al 2004). During cooking, several chemical changes occur which cause cell wall softening and disruption. These changes in texture during thermal treatment processes are usually the result of changes in the chemistry of the starch content and structure of rice during gelatinization. Due to the high starch content of rice(> 75%) during cooking, physical and structural alterations take place in the starch matrix which result in significant impacts on the cooking quality of the rice grains. As a result of the complex chemical composition of rice, it has been impossible to clearly quantify the changes that take place in rice as a result of thermal processing and therefore come up with a quantitative approach of converting the chemical alterations to physical data (Taherian and Rawaswamy 2012). However, reaction order and apparent reaction rate constants(K_{values}) can be used as useful analytical parameters for estimating softening kinetics and maximizing quality and minimizing losses during thermal processing (Wen-Ching et al 2007).

Texture is an important quality property that determines the acceptability of cooked rice grains. Changes in texture is vital because they are associated to the textural and sensorial

properties of rice, and eventually, with the quality and consumer acceptability (Mayor et al 2007). During cooking, the nutritional value, texture and color are usually also altered. Texture is an essential quality attribute in rice and uncontrolled or excessive softening during cooking can render the grain un-saleable and unacceptable.

Thermal processing causes tissue softening at different rates, most of which is governed by different physicochemical mechanism (Taherian and Rawaswamy 2012). A striking example of this influence is the study of Bhattacharya 2009 which reported that high amylose contents in rice resulted in strong cooked rice texture, while low amylose contents led to weaker and fragile textures (Derycke et al 2005). Derycke et al 2005; Onate et al 1964 also suggested that cooked rice with high protein contents are softer but less sticky than otherwise. Therefore it is important to look at the psychochemical make up of rice to better understand its effect on texture attributes during cooking.

For optimal quality to be achieved during thermal processing of rice, thermal design processes depend on important and precise kinetic data. Rice softening induced by cooking depends on the temperature reached at the thermal center of the rice in the heating medium, and on the heating rate achieved. Therefore it is important to establish softening kinetics and develop kinetic parameters related to the softening that takes place in rice during thermal processing.

Like most studies that quantify loss of firmness in food during cooking, softening behavior of rice can be explained by two pseudo first-order kinetic. This two simultaneous first order reactions that take place when rice is subjected to thermal processing involves a fast rate of turn over followed by a second rate. These mechanisms are due to two substrates, one more sensitive to heat than the other (Alvarez and Canet (2001) ; Alvarez et al (2001); Huang and Bourne (1983) and Nourian and Ramaswamy 2003). Several studies have been carried out on the effect of thermal processing on food products like beans, turnips, cassava, potatoes, e.t.c (Alvarez et al 2001; Nourian and Ramaswamy 2003; Sajeev et al 2010; Taherian and Ramaswamy 2009) but no study has been conducted on the kinetics of softening on rice during cooking.

Apparently this paper is inspired by the fact that, the knowledge of the textural properties of rice at different cooking times is important in analyzing rice performance under mechanical

forces, which in turn can aid in the design of suitable post harvest equipments for processing rice. Among the numerous units of post-harvest processes used in rice processing, mechanization is primarily utilized in cooking rice grains. For instance, the design and development of rice cookers depends on the impact of cooking time and temperature on the textural properties of rice, for which several studies have been carried out on. Therefore, the objective of this study was to study thermal softening for five improved West-African rice varieties during cooking at 100°C, for times ranging from 5- 25 minutes.

Materials and Methods

Materials

A total of five improved rice varieties were utilized in this study; three varieties (Faro 44, Faro 60 and Faro 61) from Nigeria and two cultivars (Tox 3145 and Nerica 3) from Cameroun. These varieties were selected based on their popularity among rice cultivating communities in their respective countries. All the samples were harvested in 2010. The Nigerian rice varieties were supplied by Breeding Unit of Rice Research Program, National Cereal Research Institute (NCRI), Badeggi, Nigeria while the Cameroonian samples were obtained from a rice farmer in Ndop, in the northwestern Region of Cameroun. The moisture content of the panicle picked grains was brought to 12% by solar drying and stored at room temperature until the samples were manually threshed and cleaned. 300 g of cleaned paddy of each variety (moisture content \leq 14%) were dehusked (THU 35A, Satake Corporation, Tokyo, Japan). The rice recovered from the dehulling process was further polished to remove the bran and therefore yield white rice. Polished grains were later milled with a coffee grinder (SUMEET Multi Grind, India) and sieved with a 0.5mm sieve mesh to obtain particle size uniformity.

Proximate composition studies

Amylose content (%) of the rice flour was determined by AACC approved (2000) with the aid of the continuous flow analyser (SEAL AutoAnalyzer 3HR, Model AA3 HR, U.S.A). The moisture, ash, protein, lipid and carbohydrate content of the rice flour were determined using the Association of the Official Analytical Chemists (AOAC) method. The moisture content was determined by oven drying the flour at 105 °C until constant weight was achieved while the ash

was determined by combustion of the flour samples at 550 °C in muffle furnace. The nitrogen content of rice flour was determined with the aid of the Leco Nitrogen analyzer and the nitrogen value multiplied by a factor of 6.25 to determine the total protein content. Lipid content was determined by Soxhlet extraction using petroleum ether as solvent. The total carbohydrate content was estimated by difference using the following formula: 100 - (weight in grams [protein + fat + water + ash] in 100 g sample).

Textural analysis

The Instron Universal testing machine (Model 4500, Instron, Buckinghamshire, England) was used to measure the texture (i.e., hardness, adhesiveness/stickiness and cohesiveness) of rice kernels. 10 grams of washed whole grains (milled) were selected and washed with 10 ml water three times and drained. After draining, rice kernels were placed in the glass beaker containing 20 ml water. The glass beaker (containing water and rice kernels) was placed in a boiling water bath for 4, 8, 12, 16, 20 and 24 min. Water was drained from the glass beaker and the 5 grains of the drained cooked rice kernels were transferred to the platform's grid of the Instron instrument. The test was carried out with a 50 N load cell and a cylindrical probe with a diameter of 25 mm was used to compress the kernels to 50 % deformation at a crosshead speed of 1.25 mm/min. The resulting force-deformation data were analyzed and the average values of hardness, stickiness and gumminess were calculated. The operation was duplicated. A force-distance curve as obtained for the two-bite cycle compression test and the following texture parameter were determined:

Hardness- Maximum force of the first compression (N/mm) (1)

Adhesiveness(stickiness)- Negative area of the first compression (J). (2)

Gumminess - Hardness x Cohesiveness (Area of the first compression divided by the Area of the second compression) (J) (3)

Kinetic analysis

The kinetic model of softening utilized in this study was assumed to be first order. The first order reaction is characterized by the rate of the chemical reaction at any time being directly proportional to the concentration of the reactant. This model is described by equation :

$$-dC/dt = k.C \quad (4)$$

Given that C is the concentration of the reactant, t is the time and k, the rate constant. Integrating and transposing Eq. (4) gives:

$$\ln C = \ln C_0 - k.t \quad (5)$$

where C_0 is the concentration of the rice at the beginning of the reaction or time zero. Plotting $\ln C$ against time yields a linear graph for a first order reaction. The slope of this linear plot is the rate constant k, while the intercept on the y axis at time zero yields $\ln C_0$.

Typically, the slope of the logarithm of the concentration ($\log C$) against time (in this case minutes) is referred to as the apparent first order rate constant. The term "apparent" is used to indicate that the chemical process in chemical reality isn't really first order, but that the experimental results provide a good fit to the first order kinetic model.

From studies on kinetic softening of cereals and legumes, two apparent first order mechanism have been assumed and the texture of these food products has been proposed to be composed of two substrates, "a" and "b". The model proposes that the substrate "a" softens rapidly whereas substrate "b" softens slowly. The softening mechanism of both substrates are completely different.

The chemical reaction model for these two simultaneous first order mechanism can be expressed as

$$-da/dt = k_1.a \text{ and } -db/dt = k_2.b \quad (6)$$

Where "a" is the texture as a result of the first mechanism and "b" the texture as a result of the second mechanism.; t is time, k_1 and k_2 are the apparent rate constants for softening processes 1 and 2 respectively.

Integrating and transposing Eq. (6) yields:

$$\text{Log } H = \text{Log } H_0 - K_a^1 t \text{ and } \text{Log } H = \text{Log } H_1 - K_b^1 t \quad (7)$$

Where H is the hardness at time t, H_0 is the hardness at cooking time zero, H_1 is the intercept of the straight line plot asymptotic to the curve for the slow softening period and is referred to as "thermal firmness" (Bourne 1987). K_a^1 and K_b^1 are the apparent rate constants for the rapid and softening mechanisms, respectively.

RESULTS AND DISCUSSION

Kinetic studies

A typical softening reduction curve of the log mean of hardness against different cooking time at 100 °C for all the rice varieties is shown in Figure 4.0. The curve depicts two pseudo first order reaction, one more sensitive to heat than the other and is characterized by an initial rapid decreases in hardness. The plots indicate a rapid softening at the start of cooking after which there was a reduction in the rate of softening. The reduction in hardness associated with cooking time and thermal processing can be anticipated for all food products. The results of this study typically support the first order process for softening processes as indicated by their associated relatively high R^2 (0.8727 - 0.9623) (Nourian and Ramaswamy 2003).

Irrespective of the rice varieties studied in this work, hardness reduced at faster rate at the initial stages of cooking time i.e. up to 15 minutes as indicated from the steep slope of the hardness reduction-cooking time plot (Figure 4.0). Thereafter the rate of decrease was not significant thus indicating the optimum time of cooking to be 15 minutes for all the varieties.

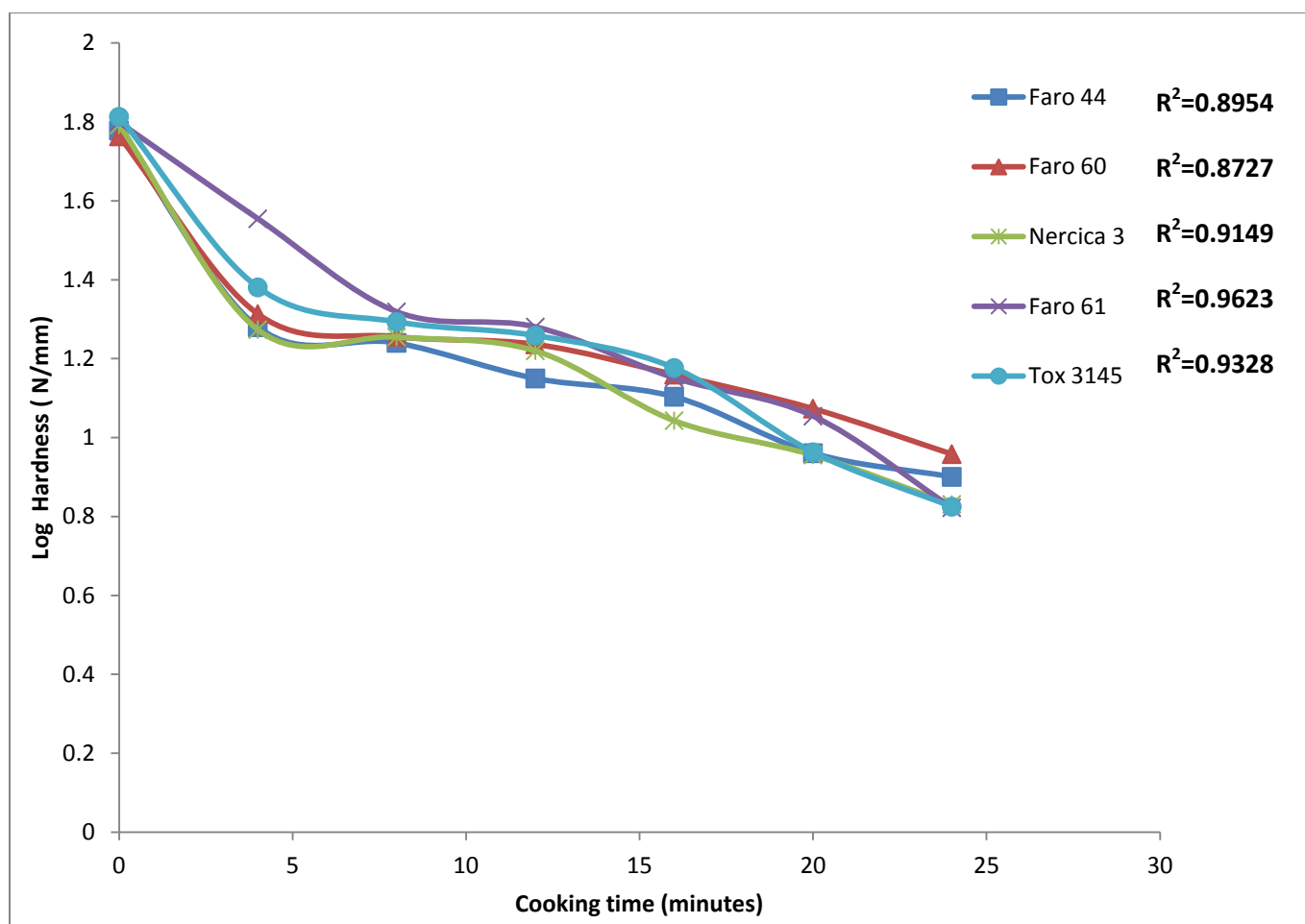


Figure 4. Typical softening behavior for the different rice varieties at 100 °C.

The results of the reaction rate constants (k) revealed similar trends with higher values linked with the rapid softening process than the slower mechanism (Table 4.1). The rate constant K^1_a varied from 0.03776 to 0.4468 min^{-1} while K^1_b varied from 0.008475 to 0.013665 min^{-1} . The results of this study in all cases showed that the softening by rapid mechanism 1 is approximately 3.7, 4.5, 3.3, 3.7 and 3.2 times faster than the mechanism 2 for Faro 44, Faro 60, Nercica 3, Faro 61 and Tox 3145 respectively. The changes in the texture of the cooked rice varieties during mechanism 1 is probably due to alterations in the starch structure during cooking. In conclusion, the varieties can be grouped based on their K^1_b ranges for their ease of cooking as follows: Nercica 3, Tox 3145, Faro 44, Faro 61 and Faro 60.

Table 4.1. Apparent rate constant and intercepts (thermal firmness) for thermal softening of rice varieties during cooking at 100°C

Variety	$K^1_{a \text{ min-1}}$	$K^1_{b \text{ min-1}}$	Thermal firmness (N/mm)
Faro 44	0.04262	0.01158	1.77815125
Far60	0.03776	0.008475	1.763427994
Nerica 3	0.04468	0.013665	1.792391689
Faro 61	0.04106	0.0111	1.799340549
Tox 3145	0.04357	0.013587	1.812913357

Changes in textural properties during cooking

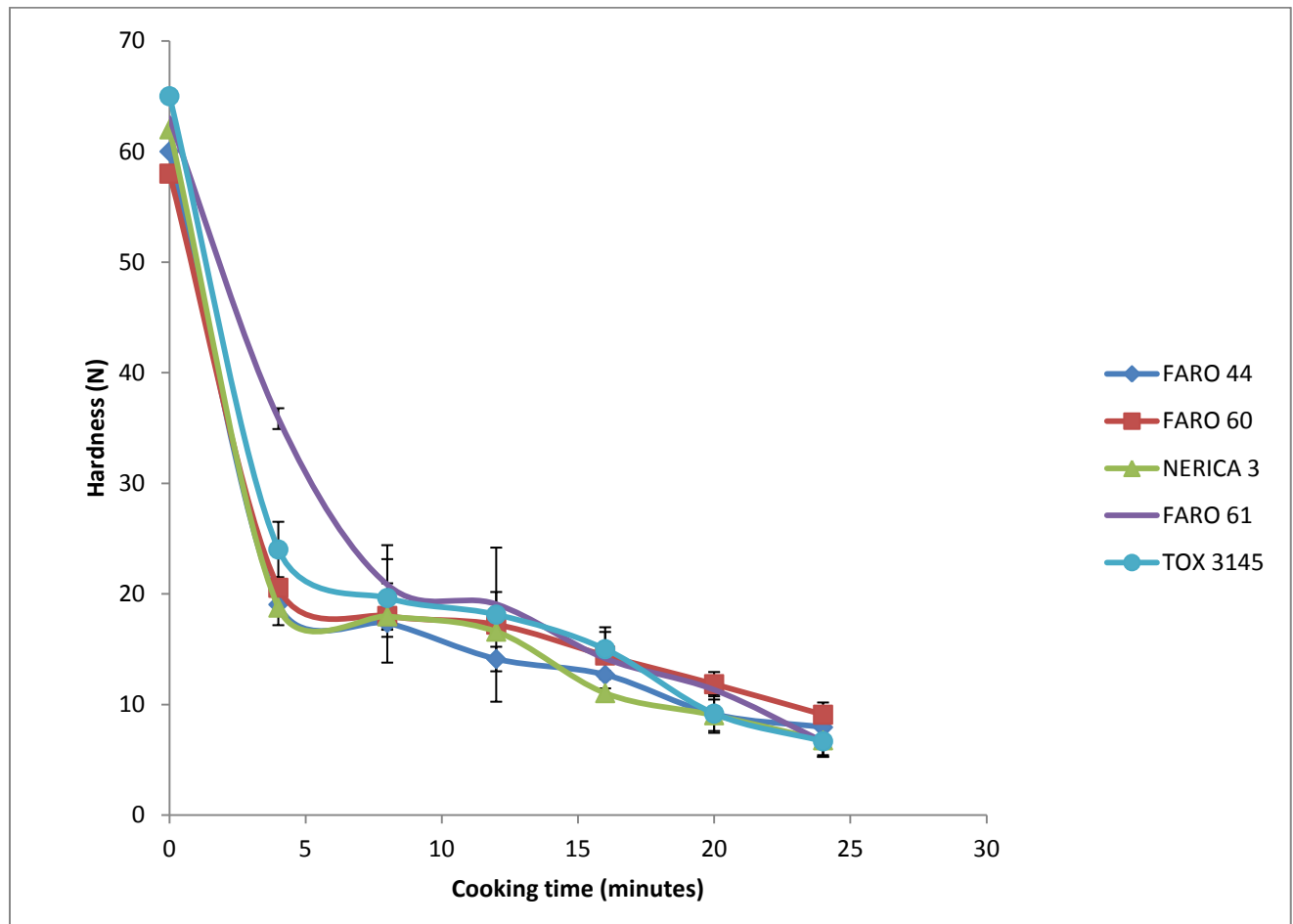
The textural properties of cooked rice is an important characteristic of rice that determines the appropriate cooking time - temperature condition and consumer acceptability. Textural properties depends greatly on the degree of starch degradation, physical characteristics (fissures in the grain), gelatinization and re-association of gelatinized starch etc. (Islam *et al* 2002; Murillo *et al* 2011).

Based on the Texture Profile Analysis , all the rice samples exhibited different texture properties at different cooking times (Table 4.3). Hardness apparently reduced with cooking time for all the samples (Figure 4.3). The apparent amylose contents of the rice samples ranged from 22.4 - 28.15% (Table 4.2). The protein contents were 8.97 - 10.35% (Table 4.2). However, this study didn't show any clear relationship between hardness of the cooked rice grains and its amylose-amylopectin and protein content. This could be as a result of the degree of amylose -lipid complexes inherent in the starch or formed during the cooking (Derycke *et al* 2005). These complex form a barrier which inhibits the breakdown of granule structure and reduces the water absorption and solubility index during cooking (Nakorn et al 2009).

Table 4.2 Proximate composition of non-parboiled rice varieties (% dry matter)

Rice cultivars	Fat (%)	Ash (%)	Protein (%)	Total carbohydrate (%)	Amylose (%)
FARO 61	0.39±0.01 _{bc}	0.47±0.01 _b	10.02±0.00 _a	89.12±0.08 _b	24.9±0.00 _c
FARO 60	0.35±0.04 _c	0.32±0.03 _c	9.92±0.02 _a	89.41±0.08 _{ba}	27.8±0.00 _b
FARO 44	0.52±0.01 _{ba}	0.45±0.08 _{ba}	9.59±0.23 _{ba}	89.44±0.14 _{ba}	28.5±0.00 _a
TOX 3145	0.39±0.06 _{bc}	0.57±0.04 _a	8.97±0.08 _b	90.08±0.01 _a	24.15±0.35 _d
NERICA 3	0.51±0.15 _a	0.52±0.00 _{ba}	10.35±0.7 _a	88.63±0.86 _c	22.4±0.14 _e

Mean ± SD values with the same superscript letters in a column are not significant different(p>0.05)

**Figure 4.3 Effect of cooking time on hardness of the rice varieties.**

The results of the relationship between cooking time of rice grains and hardness shows that the amylose-amylopectin and protein content is not the most influencing factor as reported in several other studies like that of Singh et al., 2005. However, the ratio of crystallinity of amylopectin chains- amylose contents could be another reason for the variations observed in the hardness of the cooked rice varieties (Shifeng et al 2012). Studies have suggested that rice with higher amylose content and long amylopectin chains produced harder textures, where as rice varieties with low amylose content and short chain amylopectin produced softer textures (Juliano et al 1987; Singh et al 2005). The former creates a favorable medium for inter and intra molecular association of starch with protein and lipid thereby inhibiting starch disintegration and eventual gelatinization, while the latter prevents the interactions of starch with protein and lipids, thus encouraging amylose absorption of water. (Bhattacharya 2009; Singh et al 2005; Zhu et al 2012).

Stickiness and gumminess differed significantly for the various rice varieties. Although the trend between these textural parameters and cooking time was unclear, differences were observed in the stickiness and gumminess of all the rice varieties (Figure 4.4 and 4.5). The amount of leached starch chains during cooking at different cooking times and the rate of retrogradation during cooling contributed to the variations in gumminess and stickiness values (Chung et al 2007; Derycke et al 2005; Han and Lim 2009).

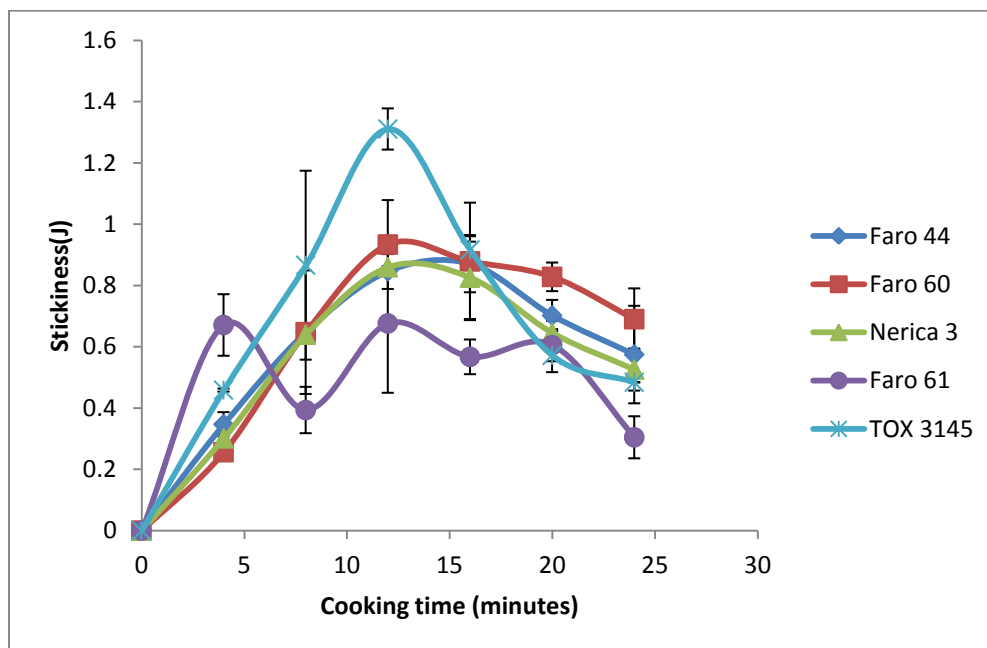


Figure 4.4. Effect of cooking time on the stickiness. Stickiness values are negative

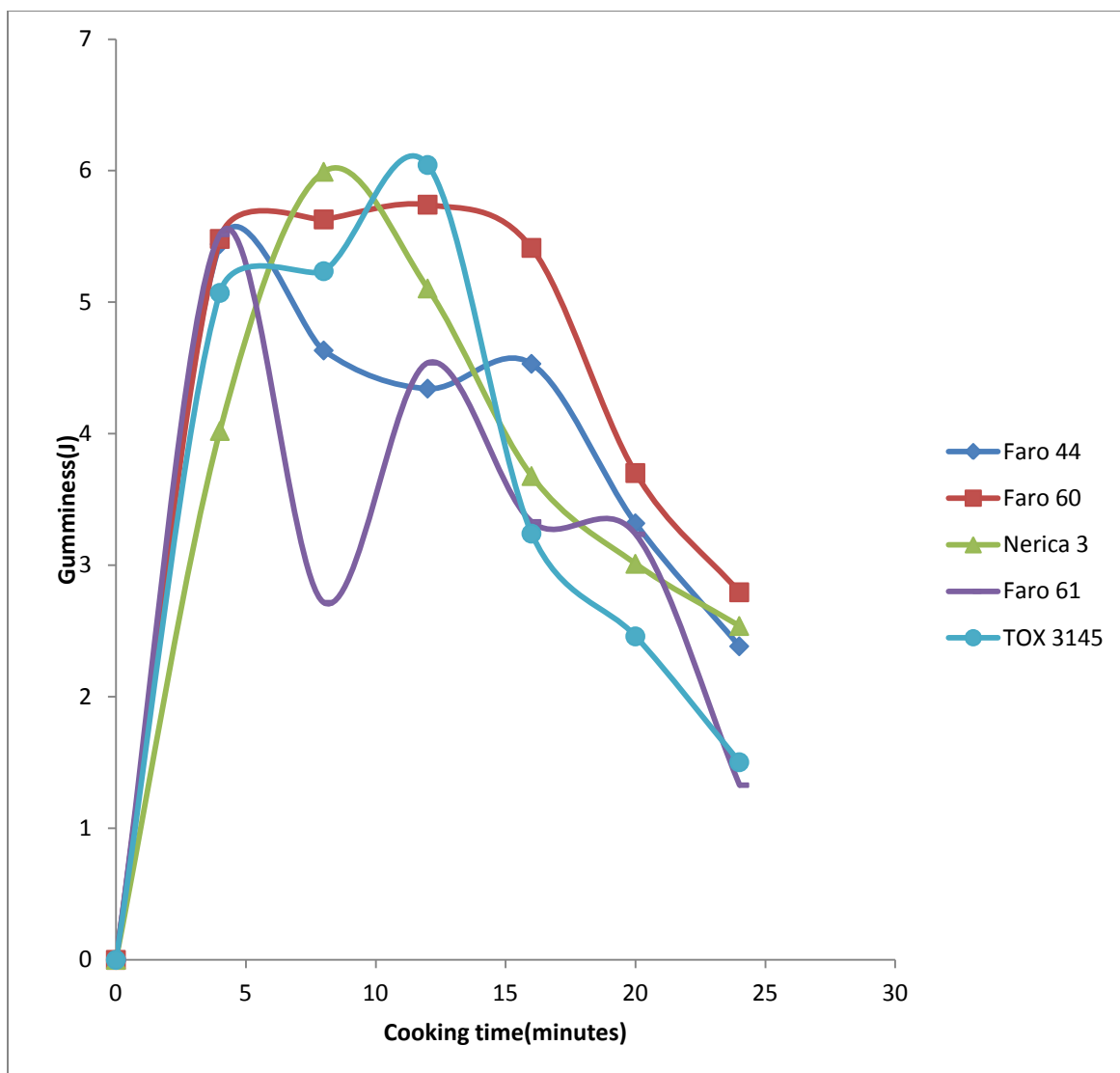


Figure 4.5. Effect of cooking time on the gumminess

The overall textural attributes of rice was probably due to the gelatinization of starch and break down of cell wall structure of the rice varieties. Gelatinization involves loss of crystallinity of granules as a result of heating. The initial cooking time range in combination with temperature effect cause texture changes and gelatinization all together, while the second cooking time range is characterized by the full completion of the gelatinization process. In conclusion, the variations observed in the studied textural properties of the different rice varieties could be the result of the difference in the amount of starch, amylose-amylopectin composition, interaction between

various physicochemical components, inter cellular spacing and turgor pressure(Charonenkul et 2006; Kilcast 2004; Sajeew et al. 2008).

Conclusion

The results of this study show the kinetic parameters for the loss of textural attributes in rice varieties during cooking at a selected cooking times and temperature. The softening mechanism follows two steps, one faster than the other. Therefore confirming the studies and findings of Huang and Bourne (1983). The study showed a rapid loss in hardness during a short cooking time and thermal exposure to 100°C.

This study also indicated that all three textural attributes (hardness, stickiness and gumminess) changed similarly as function of cooking time. All the rice varieties softened over the first 5 minutes of cooking , but their texture improved with an increase in cooking time.

The practical worth of this study is the fact that cooking at a certain time yielded further deterioration in the texture properties of the various rice varieties

CHAPTER V

GENERAL CONCLUSIONS

Rice from West-Africa was characterized with respect to morphology, colour, proximate composition, pasting properties and softening kinetics. The shapes of the characterized isolated rice starches were similar where as the granule sizes differed. Although all the rice varieties exhibited similar morphology, the most remarkable observation was the Nerica 3 rice variety and the starch granules demonstrated rough surfaces with little depressions.

The color of the rice varieties differed among rice varieties. The high value of whiteness(L^*) and low degree of yellowness (b^*) indicates that the flour of these rice varieties would command great consumer acceptability. Also variations observed in the proximate composition of these studied rice varieties suggest exceptional nutritional quality. The findings of this study also depicted that the pasting attributes of the selected rice varieties showed high peak viscosity, trough viscosity, break down viscosity, pasting temperatures and set back values. Varietal differences in pasting properties were not totally as a result of its respective proximate compositions. These good pasting, color and nutritional attributes are essential in categorizing and defining the end-product application of these rice varieties.

This study also indicated the thermal kinetics of texture softening of the selected rice varieties. The findings of this result depict two pseudo first order reaction. Irrespective of the rice varieties studied in this work, hardness reduced at faster rate at the initial stages of cooking time i.e. up to 15 minutes. Hardness apparently reduced with cooking time for all the rice varieties. However, this study didn't show any clear relationship between hardness of the cooked rice grains and its amylose-amylopectin and protein content. The rate constant K_a^1 and K_b^1 varied among varieties and the rice varieties can be grouped based on their K_b^1 ranges for their ease of cooking as follows: Nerica 3, Tox 3145, Faro 44, Faro 61 and Faro 60. Although stickiness and gumminess exhibited an unclear trend with cooking time, differences were observed in these textural parameters for all the studied rice varieties. Textural properties of cooked rice is a vital attribute of rice that determines the appropriate cooking time - temperature condition and consumer acceptability.

The various analytical characterization carried out in this study holds a pivotal position in the adoption and utilization of these local varieties, and could therefore enhance food security in Africa through the development of acceptable new rice-based products. This study has laid the foundation and provided necessary information on some fundamental attributes of these rice varieties which could increase industrial interest and consumer acceptability of these West-African rice varieties.

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