COMPARATIVE EVALUATION OF NATIVE AND MODIFIED STARCHES PRODUCED FROM RICE, COCOYAM AND CASSAVA

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ABSTRACT

The study focused on comparative evaluation of native and modified starches produced from rice, cocoyam and cassava. Starch was respectively extracted from rice, cocoyam and cassava. The starch from each of the food material was divided into two parts. One part was modified while the other served as the raw counterpart giving a total of six samples. The functional, pasting and physical properties of the samples were analyzed. The results obtained for functional properties of the starches ranges from 1.21% to 3.82% (water absorption capacity), 0.26% to 0.85% (Bulk density), 0.84% to 2.49% (oil absorption capacity), 1.12% to 3.61% (swelling capacity), 1.61 to 7.63±0.04% (foaming capacity) and 6.34±0.05 to 6.56±0.02% (pH). Significant (p<0.05) differences were observed from the functional properties of the starches due to modification. The pasting properties analyzed were, peak, trough, breakdown, final and setback viscosities as well as pasting temperature and peak time with their values ranging from 96.40 to 216.16RVU, 32.32 to 163.94RVU, 17.89 to 64.51RVU, 59.33 to 276.3RVU, 25.24 to 111.39RVU, 60.78 to 83.26 ⁰C and 3.80 to 6.00 minutes respectively. All the parameters analyzed for pasting properties as well as physical properties (solubility, pH, etc.) differed significantly (p<0.05) from each other. The study generally proved that modification enhanced the functional, pasting and physical properties of the respective starch samples. The modified starches are therefore recommended for inclusion in food formulation where their qualities can be harnessed.

Key words: Starch, native, modification, functional, pasting properties

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INTRODUCTION

The polymeric carbohydrate known as starch is made up of multiple glucose units connected by a glycosidic bond. It is a major reserve polysaccharide that is produced by most green plants for energy storage (Dolas et al., 2020). Across the globe, pure (or native) starch is a white, tasteless, and odorless powder that is insoluble in cold water or alcohol. It is stored and cyclically mobilized during seed germination, fruit maturation, and tuber sprouting. Starch can be processed into a variety of sugars in an industrial setting, but half of the starch that is separated globally is turned into glucose. Due to its abundance, starch is widely used as a raw material in many industries, including oil fields, construction, adhesives, bookbinding, corrugated board, plastics, textiles, paints and varnishes, chemicals, and others (Fan & Picchioni, 2020; Maniglia et al., 2021). Furthermore, it's a common thickening, stabilizer, and processing component in cuisine, such as ice creams, soups, curries, gravies, and batters, as well as dairy and bread goods and meat-based products (Coria-Hernández et al., 2018). It's expanded applicability as an ingredient and additive controls and manages the consistency, textural variation, and stability of liquid foods; additionally, it prolongs the shelf life of products by preventing gels from disintegrating during processing (Santana & Meireles, 2014). Additionally, alcohol-containing fuels, thin-films, biodegradable packaging, and thermoplastics with increased mechanical and thermal activity all include starch (Kaur et al., 2012; Shweta & Ajay, 2023). Native starch varies extremely unfavorably in stability at various pH levels and temperatures. For example, natural starch granules are highly resistant to enzymatic degradation and insoluble in water at ambient temperature. Furthermore, native starches are rarely ingested in their intact state, and the majority of starches have limited direct applications due to their inertness and instability to changes in pH and temperature as well as shear pressures (Berski et al., 2011). According to Berski et al. (2011), they exhibit a considerable propensity for retrogradation and breakdown, and for this, native starches are not as functional as they could be in the industrial world.

Numerous techniques have been devised to generate altered starches possessing an array of attributes and uses. According to Lopez et al. (2010), all of these methods modify the starch polymer, increasing its flexibility and altering its structural and functional characteristics. This increases the polymer's value for the food and nonfood industries. The field of starch modification is continuously developing new ways to modify starch by enzymatic, chemical, and physical means (Yadav et al*.*, 2013). Physical methods include the addition of functional groups to the starch molecule through breakdown reactions such as hydrolysis and oxidation, or through derivatization reactions (e.g., etherification, esterification, cross-linking) (Singh et al., 2012). These processes can modify starches from cereal and tubers such as rice, maize, yam, cassava, etc., making them more useful for industry by improving their solubility, texture, viscosity, retrogradation tendency, and thermal stability; properties that are essential for the desired product or function in the industry. Modification procedures have the potential to significantly enhance the features of native starch by augmenting its physicochemical and structural attributes, while also augmenting its technological value. The exploration of additional non-conventional starch sources (such cocoyam) for potential industrial usage is another reason why this research is important. This will undoubtedly increase the food materials' economic significance and industrial uses, particularly for the underutilized cocoyam starch.

MATERIALS AND METHODS

Sources of Materials

Raw (unpolished) rice was bought from Relief Market in Owerri, Imo State while cassava tubers and cocoyam corms were obtained from Agricultural Development Program (ADP), Owerri.

Starch Extraction

The Benesi et al. (2004) wet milling process was utilized to extract starch. The cassava and cocoyam were peeled and thoroughly cleaned, and the rice grains were sifted to remove any extraneous objects. After three rounds of rinsing, the materials soaked in water for an entire night. An attrition mill that was locally built was then used to grind the materials into pulp. Using a magnetic stirrer, each sample's pulp was suspended in ten times its volume of water and agitated for five minutes. The mixture was sieved using a muslin clothe. The filtrate was allowed to stand for two hours for the starch to settle at the bottom of the container while the supernatant (liquid) was decanted into a stainless bowl. Water was added to the sediment and again for five minutes. After filtration and decantation, the sediment was put in a stainless tray placed at five feet (5ft) above the ground and sundried for 24 hours. It was later milled to flour and then stored in air tight bags.

Modification of Starch Samples

The method of thin-boiling or acid treatment was used to modify the starch extracted from rice, cassava, and cocoyam, as stated by Shogbon et al. (2014). A beaker containing fifty grams (50 g) of starch sample and fifty milliliters (50 ml) of water was filled, and the combination was constantly agitated. The beaker was placed in a water bath with a temperature range of 40 to 50°C (Techmel and Techmel 1045). A small amount of 0.5N hydrogen chloride was added to the mixtures, and they were constantly stirred. Boiling the mixture to 100 degrees Celsius was necessary to turn the starch solution translucent and dark brown. Dilute sodium hydroxide was used to neutralize the final slurry, bringing its pH down to 7.0 or 7.1. After being dried, the altered starches were ground into flour.

Determination of Functional and Pasting Properties of Starch Samples

The procedures described by Onwuka (2018) were adopted for the evaluation of functional properties of the starch samples while the pasting and physical properties were determined according to AOAC (2018). Data obtained from the analyses was subjected to statistical analysis which includes standard deviation and analyses of variance (ANOVA). Tukey's test was used to separate the means using SPSS 20.0 Software Inc. USA.

RESULTS AND DISCUSSION

Functional Properties of Starch Samples

Bulk density of the starch samples

The results show that the bulk density of the samples ranged from $0.26g/ml$ to $0.85g/ml$. It was observed that the bulk density of all the raw starches decreased significantly ($p < 0.05$) after the modification. The results obtained in this study correspond with the findings of Funmilayo et al. (2020) which reported a decrease in the bulk densities of cocoyam and white yam starches after the two starches were modified with acetic anhydride and phthalic anhydride. The values obtained from this present study were also found to be closely related to 0.28 to 0.81g/ml reported by Ariwaodo et al*.* (2017) for cassava, sweet potato and cocoyam starches. Bulk density is an important parameter that determines the ease of packaging and transportation of powdery or particulate foods. It is a measure of the degree of coarseness of the starch samples (Nwabueze et al.*,* 2009). A crucial functional characteristic in a lot of food applications is bulk density. It has been observed, for example, to have an impact on the sensory acceptability of starch noodles, handling and packaging specifications, and transportation expenses. According to Onimawo and Egbekun (1998), high bulk density restricts the amount of calories and nutrients that may be consumed, which causes growth to stall.

Water absorption capacity (WAC) of the starch samples

The water absorption capacity of the starch samples ranges from 1.21% to 3.82% and were all found to be significantly ($p \le 0.05$) different from one another. From the results obtained, it was also observed that the water absorption capacity of the modified samples were lower than their native counterpart except for the modified rice starch that was significantly higher than the native rice starch. Raphael et al. (2022) reported higher water absorption capacities of 38.6% and 40.4% for starch obtained from two new cassava accessions. The structural composition of the starch molecules accounts for the differences; thus, high-water absorption could be due to the looser structure in the starch polymer, while lower water absorption is due to a more compact starch polymer structure (Adebowale et al*.,* 2008). Other factors including varietal difference, harvesting time, and botanical source or geographical location are also known to affect water absorption capacity (Falade & Okafor, 2015). One benefit of highwater absorption is that it contributes to simple softening and easier digestion. The drawback is that it also makes food more susceptible to deterioration due to an increase in water activity (Raphael et al., 2022). It is possible to conclude that cassava starch is more easily absorbed than that of rice or cocoyam starch, in that order. High water absorption capacity is detrimental to supplementary feeding because it restricts the absorption of nutrients, according to Afam-Anene and Ahiarakwem (2014). Therefore, it could also be said that any food formulated from starches with the least water absorption capacity may provide a more nutrient-dense food product that could be readily assimilated.

Oil absorption capacity (OAC) of the starch samples

The oil absorption capacity of the starch samples varied from 0.84% to 2.49% with samples E (native cassava starch) and F (modified cassava starch) recording the highest and least oil absorption capacity respectively. From the results presented in Table 1, it was observed that modification significantly reduced the ability of starch obtained from tubers (cocoyam and cassava) to absorb fat while that of the cereal (rice) increased. The high oil absorption capacity recorded in the modified rice starch could mean that the modification process used decreased the hydrophilic component of the rice starch because Raphael et al. (2022) reported that the higher the hydrophilic components (carbohydrate and protein), the lower the oil absorption capacity and

vice versa. Oil absorption components maximize the absorbance of fat-soluble vitamins (A, D, E, and K) in most lipid-based fortified food products (Eleazu et al., 2014). It also enhances flavour retention.

Swelling capacity of the starch samples

The swelling capacity of the starch samples varies from 1.12% to 3.61%. All the modified starch samples recorded a lower swelling capacity than their native counterparts which is an indication that the modification reduced the swelling capacity of the starch. Peroni et al. (2006) proposed that the high phosphorous content, large granule size and high number of hydrogen bonds formed between the very long-branch chains of amylopectin and water would contribute to the swelling power of starch.

Foaming capacity of the starch samples

The foaming capacity of the starch samples varied from 1.61% to 7.63%. The LSD showed that the starch samples differed significantly ($p < 0.05$). From the results presented in Table 1, a decrease of 31%, 71.3% and 43.3% were observed in the modified rice, cocoyam and cassava starch samples. Ayele and Nip (1994) reported that foaming capacity of starches can be rated as low since they do not contain high amount of proteins, a good foaming agent. According to Rachel et al. (2021), the foaming capacity of different types of rice starch ranges from 0.97 to 3.96%, which is quite similar to the figure found for native rice starch in the current investigation. Foaming capacity is defined as a liquid's ability to produce foam following aeration (Khuwijitjaru et al., 2007).

Pasting Properties of the starch samples

The results obtained from the evaluation of pasting properties of native and modified starch from rice, cocoyam and cassava were shown in Table 2. Pasting property measures the ability of starch to form a paste. According to Adebowale et al*.* (2008) it is a parameter that cannot be sidelined in the measurement of the quality of starch since it dictates the textural integrity of products.

Peak viscosity of the samples

The peak viscosity of the starch samples ranged from 96.40 to 216.16RVU and values obtained showed significant ($p < 0.05$) differences from one another. It was observed that the modification treatment reduced the peak viscosity of cocoyam and cassava starches but increased that of rice starch by 33.1%. The increase recorded in the modified rice starch could be attributed to the source because Schirmer et al. (2015) reported that the main factors affecting the rheological properties of starches are their source and the presence of other polymers. The peak viscosity in this present study were found lower when compared to 379.29RVU and 376.29RVU reported by Adebowale et al. (2011) for cassava starch and sweet potato starch respectively. Raphael et al. (2022) also reported a higher peak viscosity (3134.5 and 3960.5RVU) for two new cassava accessions. Peak viscosity is a measure of the highest viscosity a starch granule can attain before

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collapsing. Peak viscosity occurs at the equilibrium point between swelling that causes an increase in viscosity and rupture and alignment that cause its decrease (Adebowale et al*.,* 2011).

Trough Viscosity

Trough viscosity obtained for the starch samples ranges from 32.32 to 163.94 RVU. The values obtained were significantly ($p < 0.05$) different from each other. The trough viscosity from this present study was found to be low when compared to 201.83 RVU and 203.42 RVU reported by Adebowale et al*.* (2011) for cassava and sweet potato starches. However, this low trough viscosity could be an indication that the starch samples can withstand break down during cooling since Iwe et al. (2001) reported that high trough viscosity indicates the tendency of breakdown in viscosity during cooling.

Breakdown Viscosity

The breakdown viscosity of the starch samples presented in Table 2 above ranges from 17.89 to 64.51RVU and the breakdown viscosity of all the starches differed significantly ($p < 0.05$) from one another. It was observed that the modification treatment reduced the break down viscosity of the cocoyam starch, but increased that of rice and cassava significantly. The lower breakdown in viscosity recorded in cocoyam starch could be the reason while cocoyam is a good soup thickener and it could also be said that cocoyam starch samples (samples C and D) are thermally stable and could be useful in products that require sterilization, as in baby food and food for the elderly (Novelo-Cen & Betancur-Ancona, 2005). Adeleke (2014) reported a breakdown viscosity of 52.90RVU for wheat starch and the value closely relates to the value of the native cassava starch. They also reported a higher breakdown of 266.15RVU for cocoyam starch. Breakdown Viscosity is the measure of the degree of susceptibility of the starch granules to shear stress and thermal agitation (Adeleke, 2014).

Final Viscosity

The starch samples recorded final viscosity in the range of 49.1 to 276.3RVU. It was also observed that the modification treatment reduced the final viscosity of cocoyam and cassava starch by 34.1% and 75.4% respectively. Based on Moorthy's (2002) report, it is possible to draw the conclusion that modified rice starch, like native cocoyam starch, may be helpful in food products such as soups and sauces because of its high ultimate viscosity. Final viscosity, which shows the flour's capacity to form a viscous paste after cooking and cooling, is frequently used to assess the quality of specific starch-based flour (Iwe et al., 2001). Additionally, it provides a measurement of the paste's resistance to shear force under stirring (Adebowale et al., 2008).

Setback Viscosity

The setback viscosity of the starch samples ranges from 6.57 to 111.39RVU. The values obtained revealed that native cassava starch (sample E) had the highest setback viscosity than other starch samples and there were significant differences ($p < 0.05$) amidst all the starches. Adebowale et al. (2011) reported a setback viscosity of 72.67RVU for cassava starch, lower than

111.39RVUbut higher than 18.03RVU obtained from this present study for native and modified cassava starches respectively. The texture of different goods has been linked to setback, and excessive setback has also been linked to syneresis or weeping during freeze/thaw cycles (Maziya-Dixon, et al., 2007). Higher setback values result in less retrogradation during cooling and decreased staling rate for starch-based products (Adeyemi & Idowu, 1990).

Pasting Temperature

The native rice, modified rice, native cocoyam, modified cocoyam, native cassava and modified cassava starches gelatinized at temperature 77.17, 60.78, 83.2, 75.96, 79.00 and 62.19 $^{\circ}$ C respectively. The pasting temperature of the starch samples showed significant differences ($p \leq 0.05$) from each other. Native cocoyam exhibited the highest pasting temperature (83.26^oC) while the least pasting temperature was seen in modified starch sample obtained from rice (60.78^oC) . It was observed that the modification treatment reduced the pasting temperature of the starches. Higher pasting temperatures of 81.68° C and 82.55° C for cassava and sweet potato starches and 81.45° C and 88.20° C for cocoyam and wheat starches, respectively, were reported by Adebowale et al. (2011) and Adeleke (2014). The native cocoyam starch temperature (83.26^oC) found in this study, however, is closely related to the pasting temperatures mentioned above. In addition to being crucial for controlling energy expenses and the stability of other food ingredients in a product, the pasting temperature indicates the lowest temperature needed to cook or gelatinize starch (Kaur & Singh, 2005).

Peak Time

The peak time required to attain the peak viscosity for the starch samples ranged from 3.80 to 6.00 minutes. The peak time of all the samples showed significant differences ($p < 0.05$) from each other. It took the modified rice starch (sample B) 6.00 minutes to attain peak viscosity while the modified cassava starch (sample F) attained a peak viscosity at a lesser peak time (3.80min.). The least peak time value of the modified cassava starch indicates that it began to form paste earlier than the other starch samples. Two novel cassava accessions' starch showed a greater peak time of 6.9 and 6.7 minutes, according to Raphael et al. (2022). Certain food companies favor lower peak time value starches due to their lower manufacturing energy costs (Adeleke, 2014).

Some Physical Properties of the Starch Samples

Solubility

The result of solubility of the starch samples presented in Table (3) shows 1.64, 1.71, 1.77, 2.13, 1.89 and 2.38% for native rice, modified rice, native cocoyam, modified cocoyam, native cassava and modified cassava starches respectively. Modified cassava starch (sample F) recorded the highest solubility (2.38%) while native rice starch (sample A) had the lowest (1.64%). There were significant differences ($p < 0.05$) in the solubility of all starch samples analyzed. The results obtained revealed that the modification treatment increased the solubility of the rice,

cocoyam and cassava starches by 4.3, 20.3 and 25.9% respectively. The increase in the solubility of the modified starch samples is in total agreement with Bremiller (1993), which suggested that altering starches could make them more soluble. The solubility increase for cocoyam starch reported by Ojinnaka et al. (2009) was stated to be 26.67%, which is higher than the results achieved in this investigation. Dolas et al. (2020) examined the impact of starch modification on the physico-chemical, functional, and structural characterisation of cassava starch (Manihot esculenta Crantz) and reported a similar trend of increasing starch solubility.

Gelation Temperature

The gelation temperature of the starch samples ranges from 80.20 to 88.00° C without any significant differences ($p > 0.05$) amidst them. The results obtained revealed that modification treatment reduced the gelation temperature of the starches. Lower gelation temperatures (67.15– 72.50 $^{\circ}$ C for cassava starches and 83.25–85.05 $^{\circ}$ C for cocoyam starches) were reported by Ariwaodoet al. (2017), and these values are consistent with the findings of the current investigation. Higher associative force results in a lower gelation temperature, as the gelation temperature indicates the strength of associative force within the starch granules (Ariwaodo et al., 2017).

Amylose Content

The amylose content of the starch samples as presented in Table (3) ranged from 18.10 to 23.38% There were significant ($p < 0.05$) differences amongst all the samples with exception to native cassava and modified cassava starch samples that did not have any significant differences $(p > 0.05)$. Again, modification treatment also increased the amylose content of the starch samples. Adeleke (2014) reported amylose content within the range of 22.60 to 44.00% for starch samples of cocoyam, wheat and their blends. He also reported that starches that are high in amylose are desired in the production of noodles. Amylose is the most important fraction in starch granules. Typically, the starch granule is composed of 25% amylose and 75% amylopectin (Alcázar-alay & Meireles, 2015). According to Alcázar-alay and Meireles (2015), edible films require starches with high amylose content and the high percentage amylose content of both modified cocoyam and cassava could imply that these starches can be used alongside cellulose, gums and chitosan in food industry for the manufacturing of edible films. The amylose content of starches is important, as it affects pasting, gelatinization, retrogradation, swelling power and enzymatic vulnerability of starches to digestion (Gerard et al., 2001).

Amylopectin Content

Amongst the starch samples, native cassava starch contained the highest amylopectin (84.50%), followed by modified cassava starch (77.45%), native cocoyam starch (76.48%), modified cocoyam starch (73.15%), native rice starch (69.60%) and modified rice starch (68.10%) and these samples differed significantly ($p < 0.05$) from each other. From the results obtained it was observed that modification caused significant ($p > 0.05$) decrease in amylopectin content of starch samples by 8.70, 4.5 and 2.2% in rice, cocoyam and cassava starches respectively. The amylopectin content of cocoyam and cassava starch in the present study were found to be higher *Journal of Agriculture and Food Sciences Volume 22, Number 1, April 2024, pp .* 211 - 226

than 75% reported by Alcázar-alay and Meireles (2015) with exception to modified cocoyam starch. Aprianita (2010) reported an amylopectin content ranging from 58.40 to 71.22% for roots and tuber starches and these values are lower than values reported for cassava and cocoyam in this study respectively.

CONCLUSION AND RECOMMENDATION

The study proved that the modification process greatly improved the characteristics of native starch by altering its functional, pasting and physical properties thereby increasing their industrial potentials. The improved solubility, gelation temperature, amylose and amylopectin of the food samples could be adopted in food formulations where the properties are of interest. Thus it is recommended that modified rice, cocoyam and cassava starch should be applied in food industry especially modified rice starch. Furthermore, studies should be carried out on the modification of composite starches to also determine their functional, pasting and physical properties. This will help to ascertain the potentials of modified composite flour blends.

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APPENDICES

Fig. 1: Extraction of starch from rice, cassava or cocoyam

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Fig.2: Modification of starch from rice, cassava and cocoyam

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Table 1: Functional Properties of Native and Modified Rice, Cocoyam and Cassava Starch

Mean values having different superscript along the same column are significantly different (p≤0.05) from each other.

 $A =$ Native Rice Starch, B = Modified Rice Starch, C = Native Cocoyam Starch, D = Modified Cocoyam Starch, $E =$ Native Cassava Starch, $F =$ Modified Cassava Starch, Abs. = Absorption.

Table 2: Pasting properties of native and modified rice, cocoyam and cassava starch

Peak			Parameter Peak	Trough	Break Down	Final Time	Set Back Viscosity	Pasting Temp. Viscosity
	Viscosity		(^0C) Viscosity	(min)				
(RVU) Samples								
A		$123.79^{\circ} \pm 0.04$		$82.64^d \pm 0.03$ $25.36^d \pm 0.01$	$99.99^{\text{d}} \pm 0.05$ 6.57 ^f ± 0.03		$77.19^{\circ} \pm 0.03$	5.49° ±0.09
B			$164.80^{\circ} \pm 0.03$ $155.24^{\circ} \pm 0.04$ $41.26^{\circ} \pm 0.04$ $183.00^{\circ} \pm 0.07$ $45.29^{\circ} \pm 0.01$ $60.78^{\circ} \pm 0.04$					$6.00^a \pm 0.03$
\mathcal{C}		$116.36^{\text{d}}\pm0.03$	$93.27^{\circ} \pm 0.01$	$21.87^{\circ} \pm 0.03$	$120.74^{\circ} \pm 0.03$		$33.31^{\circ} \pm 0.02$ $83.26^{\circ} \pm 0.01$	$5.80^b \pm 0.01$
D		$96.40^{\text{f}} \pm 0.02$	$73.16^{\circ} \pm 0.05$	$17.89^{f} \pm 0.05$	$59.33^{\circ} \pm 0.03$		$25.24^d \pm 0.02$ $75.96^d \pm 0.04$ $4.29^e \pm 0.02$	
E		$216.16^{\circ}+0.05$	163.94° ± 0.06	$53.26^b \pm 0.01$	276.3° ± 0.02	$111.39^a \pm 0.03$		$79.00^{\rm b} + 0.05$ 5.21 ^d + 0.01
\mathbf{F}		$101.58^{\rm e}$ ±0.06	$32.32^{f} \pm 0.09$	$64.51^a \pm 0.04$	$49.41^{f} \pm 0.08$	18.03° ± 0.05	$62.19^{\circ} \pm 0.03$	$3.80^{f} \pm 0.07$
LSD	0.08		0.15	0.07	0.15	0.06	0.09	0.14

Mean values having different superscript along the same column are significantly ($p \le 0.05$) different from each other.

A = Native Rice Starch, B = Modified Rice Starch, C = Native Cocoyam Starch, D = Modified Cocoyam Starch, $E =$ Native Cassava Starch, $F =$ Modified Cassava Starch

Mean values having different superscript along the same column are significantly (p≤0.05) different from each other.

A = Native Rice Starch, B = Modified Rice Starch, C = Native Cocoyam Starch, D = Modified Cocoyam Starch, E = Native Cassava Starch, F = Modified Cassava Starch