



## Isolation, Modification and Characterization of Tiger-Nut, Maize, Cassava and Potato Starch

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**ABSTRACT:** Four different sources of starchy foods were used for the isolation of starch using commercially cheap and readily available chemical-hypo (3.5 % active Chlorine). The isolated starch was modified through NaIO<sub>4</sub> oxidation under mild reaction conditions. Carbonyl functional group test was employed for confirmation of the success of oxidation. FT-IR and Scanning Electron Microscopy (SEM) were used for functional group identification and morphological examination of both modified and native samples to further confirm the success of modification. The appearance of the carbonyl band at 1747-1746 cm<sup>-1</sup> and 1647 – 1637 cm<sup>-1</sup> indicated the successful synthesis of oxidized starch. Proximate results showed that the isolated starches were rich in mineral content: 0.25-2.13; crude fibre: 0.85-3.31; fat: 0.23-0.28 and energy: 1331-1410. The study showed that commercial hypo could be a useful replacement for metabisulphite for starch isolation without side effects on starch properties. SEM images showed that morphological architecture of granules was not destroyed during surface functionalization. Characteristic and nutritional features of the oxidized starch showed that it could find useful applications in food and pharmaceutical industries.

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Starch is a major carbohydrate storage product found in all chlorophyll-containing plants. It is formed in the presence of sunlight, CO<sub>2</sub> and H<sub>2</sub>O (Azeh *et al.*, 2014). It is a white, tasteless and odorless powder insoluble in cold water or alcohol. It is one of the most important flexible food ingredients valuable for useful industrial applications. Major sources are leaves, stems, tubers, seeds and roots of higher plants. Chemically, starch is a carbohydrate polymer consisting of anhydroglucose units linked by α1→4-glycosidic linkages. Research has shown that it contains 20-25 % amylose and 75-80 % amylopectin by weight (Brown and Poon, 2005). It is a biodegradable plastic material useful for the production of disposable items (Sun *et al.*, 2002). It is heavily used in food, textiles, cosmetics, plastics, adhesives, paper, and pharmaceuticals industries (Moorthy, 1996; Rowe, 2003). Common sources of food starch are corn, potato, wheat, cassava/tapioca, rice and maize are the most available and accessible sources of starch, but varieties of rice, including waxy rice, pea, sago, oat, barley, rye, amaranth and certain other source of starch indigenous to the areas in which they are produced can be used as localized commercial sources. Maize starch make-up about 80 % of the world market mostly produced in the US (Amani and Hopponen, 1996). Cassava is second to sweet potato

as the most important starchy root crop of the tropics (Grace, 1977). The advantages of cassava and potato for starch production over other grains or root crops includes: high purity, excellent thickening characteristics, neutral taste, desirable textural characteristics, relatively cheap with high starch content. Cassava and potato starch have many remarkable characteristics, including high paste viscosity, paste clarity and high freeze-thaw stability which are desirable for many industries. They are renewable, almost unlimited resources and one of the most abundant substances in nature. They are now grown widely as food crops and for industrial purposes. The properties required for a particular application, availability of the starch and economics play a role in selecting a particular native starch for subsequent chemical and/or physical modification.

In Nigeria, cassava and potato are staple foods for both rural and urban areas, which have been transformed from being subsistent crops to industrial cash crops. The use of starch now extends far beyond its original design as a source of energy. Practically, every industry in existence uses starch or its derivatives in one form or another. In food and pharmaceutical industries, starch is used to influence or control such

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characteristics as texture, moisture, consistency and shelf stability. It can be used to bind/disintegrate; to expand/densify; to clarify/opacify; to attract moisture/inhibit moisture; to produce smooth texture/pulpy texture, soft coatings or crisp coatings. It can also be used to stabilize emulsions or to form oil resistant films. It serves as a multifunctional ingredient in the food industry (Cock, 1982; Miyazaki *et al.*, 2006). As a functional carbohydrate, it may be modified physically, chemically or enzymatically to meet specific needs. Starch has been isolated from different sources, modified using different reagents for the production of valuable starch-based products useful for industrial applications.

The objective of the study was to isolate starch using commercial hypo (3.5 % active chlorine) as a replacement for the sodium metabisulphite solution, modify the isolated starch and study the morphological and functional changes.

## MATERIALS AND METHOD

**Reagents and Solvents:** The tiger-nut, maize, cassava and potato used were obtained in Lapai market, Niger State in Nigeria. All reagents used were of analytical grade. These include; ethanol, methanol, acetone, sodium chloride, sodium hydroxide, sodium periodate and Tollen's reagent. Distilled commercial vinegar was used for acetylation of samples while commercial hypo (3.5 % NaOCl) and sodium sulphate was used for starch extraction/isolation respectively.

**Removal of Gums/Waxy Substances:** Tiger-nut, maize powder, cassava and potato tubers cut to sizable pieces were soaked in solution of sodium hypochlorite (3.5 % NaOCl) separately and allowed to stand for 3 h to remove gums/waxes and discoloration of samples. Afterwards, it was washed and extensively rinsed with distilled water (Azeh *et al.*, 2014).

**Starch Isolation from Samples:** Pre-treated starch samples were each blended with a blender equipped with razor blades with the addition of solution of hypo at interval of 1 minute during blending to obtain slurries which were filtered using a double two-fold muslin cloth. The filtrate was washed extensively with cold tap water to separate the starch granules. The filtrate was allowed to stand to settle and was decanted after 24 h. Mucilage on the starch was continuously scraped until a pure white starch was obtained. Starch milk obtained was re-suspended in hypo solution for 1 h for further bleaching. Afterwards, it was washed with distilled water until odour-free of hypo, filtered and air dried overnight at room temperature to obtain white starch cake (Azeh *et al.*, 2014; Kenneth *et al.*, 2014).

**Mercerization:** 5 g each of oven dried isolated starch was mercerized using 20 cm<sup>3</sup> of 17 % sodium hydroxide in a beaker. The mixture was placed on a mechanical shaker and shake for 1 h (at 75 rpm). A very thick and colorless gel was obtained for tiger-nut starch samples while a pale-yellow solution was obtained for maize starch sample (Azeh *et al.*, 2014).

**Preparation of Dialdehyde Starch:** 9.5 g of sodium periodate (5.0 molar) was dissolved completely in 100 cm<sup>3</sup> of distilled water at room temperature followed by the addition of 40 cm<sup>3</sup> of prepared sodium periodate solution and 15 g of starch was added and stirred on a mechanically for 30 min with the pH adjusted to 7.0 and left overnight. The reaction temperature was raised to 55 °C. To confirm the success of the reaction, starch slurries obtained were subjected to Tollen's test where a silver mirror deposit on the wall of a test tube was an indication of the presence of aldehyde carbonyl functional group. It was then filtered and the product washed with warm distilled water continuously, until a pH of 7.0 was attained using a pH indicator paper. The slurry was filtered and dried for 24 h at 50 °C in an oven (Salisu *et al.*, 2013).

**Proximate Analysis of Starch Samples:** The proximate analysis of starch samples were carried out at National Cereals Research Institute, Badeggi, Bida, Niger state, Nigeria.

**Scanning Electron Microscopy and Infrared Spectroscopy:** Scanning electron microscopy and Infrared Spectroscopy of modified starch and control samples were done Ahmadu Bello University, Zaria, Nigeria.

## RESULTS AND DISCUSSION

**Proximate Analysis of Starch Samples:** The proximate analysis (%) of the modified/native starch samples was determined. The moisture content of the extracted starch were closely related and falls in the range 8.85-11.54 % Table 1. The order of increase in the amount of moisture was Potato>Cassava>Tiger-Nut>Maize starch. The amount of moisture in a food sample is important because it provides information on the storage shelf-life of a food. Potato starch had high moisture content than the others studied, which explains the inability of potato to resist microbial attack. Hence, it easily deteriorates when kept for a long period of time. The maximum allowable limit for moisture in starch flour is 14 % (Austin, 1984). The present results showed that all samples exhibited moisture content (%) within the maximum allowable limit. Cassava starch had the lowest crude protein (0.47 %) and fibre (0.82 %). The energy values of the

extracted starches showed close similarities with the exception of maize starch Table 1. Cassava starch had the highest ash content which was indicative of the amount of non-volatile inorganic matter in the sample. Carbohydrate contents obtained by difference for maize, cassava and potato starch were similar while tiger nut starch was an exception with its very low value (38.19 %) of carbohydrate. Proximate analysis (%) of tiger nut starch in the present study had closely related values in terms of ash-0.27 and moisture-9.36 while deviations were observed for fat-0.23; protein-2.65 and CHO-38.19 compared to the results obtained by (Kenneth *et al.*, 2014). The observed deviations may be due to differences in the method and / or sources of the sample used. The ash content (%),

cassava-2.13, was the highest, which implied that it had more of the non-volatile inorganic compounds than all other samples studied Table 1. The low ash content was an indication of clean processing (Alejandro *et al.*, 2008). In the isolated starch, the major component was carbohydrate, with high energy values obtained for all samples. All other proximate factors such as fat, protein, minerals and moisture were in minor amounts and varies from one starchy crop to the other (Taik *et al.*, 1999; Gonzalez *et al.*, 2002; Miyazaki *et al.*, 2006; Nandan *et al.*, 2006; Olawale *et al.*, 2007; Klanarong, 2009; Sangeethong *et al.*, 2010; Singh *et al.*, 2011; Azeh *et al.*, 2014; Kenneth *et al.*, 2014).

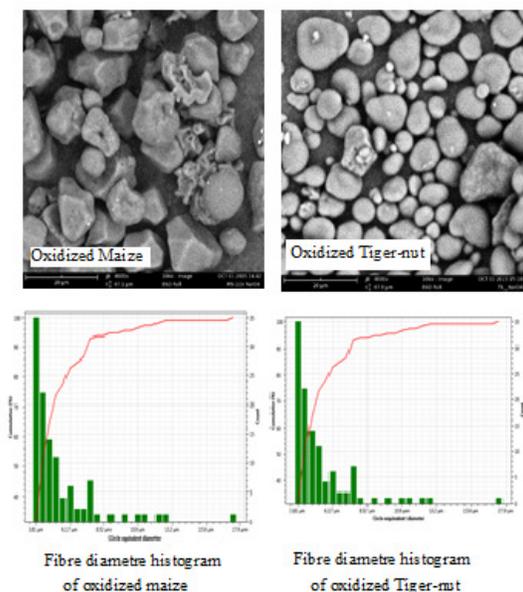
**Table 1. Proximate Composition of Isolated Tiger nut, Maize, Cassava and Potato Starch**

S/NO	Sample	Moisture (%)	Protein (%)	Fat (%)	Crude fiber (%)	Ash (%)	*CHO (%)	Energy (Kj)	Value (Kcal)
1	Tiger-Nut Starch	9.36	2.65	0.23	3.31	0.27	38.19	343.03	1372.12
2	Maize Starch	8.85	2.77	0.25	2.05	0.25	84.83	352.65	1410.60
3	Cassava Starch	10.48	1.73	0.39	2.47	2.13	81.69	332.97	1331.88
4	Potato Starch	11.54	0.47	0.28	0.85	0.26	82.54	337.66	1350.64

\*CHO was obtained by difference and energy values were by calculation. Minerals measured in mg/100 g.

*S. Morphological Properties of Modified and Unmodified Starch Samples:* Scanning Electron Micrographs of native and oxidized starch are shown in Figure 1. Native tiger-nut, maize, cassava and potato starch granules exhibited various morphologies ranging from spherical, round, grooved, and irregular polygonal shapes with truncated ends (Rutenberg and Solarek, 1984).

There were some visual changes on the external surface of modified samples such as maize, cassava and potato starches which have been attributed to chemical treatments. Modified tiger-nut starch had smoother surface after chemical treatment and this implied that periodate oxidation did not damage the granule's surface. Treated samples exhibited different granular morphologies and had smaller sized particles compared to untreated samples. The differences in the granular architecture and fragility of starch granules were due to differences in botanical sources (Rotenberg and Solarek, 1984).



**Fig. 1.** Morphology of Oxidized Starch Granules and Granule Diameter of Maize and Tiger –Nut

Surface erosion as revealed by SEM images showed that tiger-nut starch granules were more rigid and resistant to chemical attack than the others. The significance of such granular size and surface is that, they could easily be dispersed in aqueous medium with good stabilizing effect.

According to Rutenberg & Solarek (1984), periodate oxidation up to 6 % active ingredient left corn and rice starch surfaces unaffected. Kuakpetoon and Wang (2001), observed no changes on granule morphology of corn and rice starches modified with sodium periodate at the levels of 0.8 and 2 % active ingredient.

Similar observations were evidenced in the present study by SEM images of both treated and native starch samples. The changes observed are probably due to differences in the isolation methods.

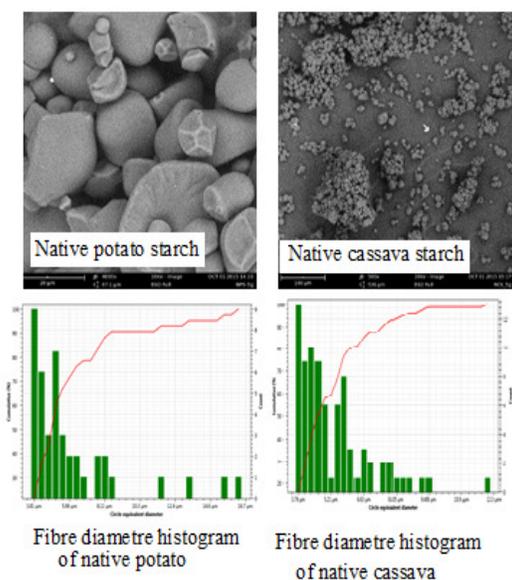


Fig. 2. Morphology of Oxidized Starch Granules and Granule Diameter of Potato and Cassava Starch

Starch granule diameter and frequency distribution shown by histogram (Figure 2) revealed granule diameters in the range 3.81 to 6.18  $\mu\text{m}$  for both oxidized tiger-nut and maize starch. The implication for the small sized particles is that, they would form good candidates for industrial and pharmaceutical applications due to their large surface area (Kong *et al.*, 2009).

**FT-IR Study:** This study revealed the formation of certain important functional groups due to oxidation of the  $-\text{OH}$  groups in starch molecules. The following important functionalities were revealed: The band at 3918 - 3360  $\text{cm}^{-1}$  was due to bonded  $-\text{OH}$  groups in starch (Salisu *et al.*, 2013; Azeh *et al.*, 2016). The band at 1747 - 1746  $\text{cm}^{-1}$  in tiger nut starch was due to carbonyl ( $\text{C}=\text{O}$ ) stretch, which confirmed the formation of oxidized starch. Other important absorption bands which confirmed the formation of carboxyl groups attributable to further oxidation of the carbonyl groups were observed around 1647 - 1637  $\text{cm}^{-1}$  (Azeh *et al.*, 2016). The presence of pectins and lignin were indicated by the appearance of the bands around 1559-1508  $\text{cm}^{-1}$  and 1458 - 1420  $\text{cm}^{-1}$  (Sunan *et al.*, 2011). The band at 1375 - 1339  $\text{cm}^{-1}$  has been attributed to  $-\text{CH}_2$  bending deformation vibrations in starch. Band peaks at 1243 - 1239  $\text{cm}^{-1}$  are assigned to vibrations of the methyl ester groups in starch. The peaks at 1144 - 850  $\text{cm}^{-1}$  are characteristic absorptions of  $\text{C}-\text{O}$  stretch in  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{H}$  of the glycosidic links in starch (Azeh *et al.*, 2016).

**Conclusion:** In conclusion, this study demonstrates that commercial hypo could be useful in the isolation of industrial/pharmaceutical grade starch. Proximate results of the starches isolated were within the range obtained with other standard methods. Granule morphology was intact as well as surface functionalities as revealed by SEM and FT-IR, which implied that the polymer structure was not destroyed. Hypo could be useful as a replacement for metabisulphite to prevent starch browning and for the isolation of anionic starch. Starch modification was successful as revealed by FT-IR results.

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