

PREPARATION AND PHYSIOCHEMICAL CHARACTERIZATION OF OXIDIZED KERSTING'S GROUNDNUT STARCH (*Kerstingiellageocarpa*)

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Abstract: Kersting's groundnut starch was isolated, chemically modified by oxidation using Sodium hypochlorite, NaOCl and subsequently characterized. The physicochemical properties of the oxidized starch were attributed to its granular size and shape and molecular structure. Oxidation occurred mainly in the amorphous region and oxidation level in terms of carbonyl group content which was largely dependent on the degree of crystallinity and the degree of polymerization. It was shown that the swelling power and solubility of the oxidized starch increased with increasing temperature. Water and oil absorption capacities revealed that hydrophilic tendency was greater than hydrophobic potentials. Gelation increased with increase in concentration of the oxidized starch and least gelation concentration was 6%. Comparing native and oxidized values, highest pasting temperature was obtained for native starch and highest peak viscosity value for oxidized starch (Pv) during heating, highest value of breakdown (Pv – Tv) was also recorded for oxidized starch. Gel clarity value for oxidized starch was 9.08% transmittance.

Keywords: Kersting's groundnut, starch, physicochemical properties, oxidation, hypochlorite

I. INTRODUCTION

Kersting's groundnut (*Kerstingiellageocarpa*) is an underutilized, indigenous, high protein, subterranean, herbaceous legume that is grown in the semi – arid and arid areas of West Africa by older farmers (Bampuori, 2007; Messiaen, 1994; Aremuet *al.*, 2008). It is predominantly cultivated in the semi – arid areas of all the coastal countries along the Gulf of Guinea from Senegal South to Guinea Bissau, Northern Nigeria and Cameroon (Bampuori, 2007; Mergeai, 2001). It is also cultivated in Burkina Faso, Niger and Mali.

The Kersting's groundnut has a high quality nutritional level, with 12.9% protein compared to 12.1 and 7.1% for Bambara groundnut and cowpea respectively (Aremuet *al.*, 2008). The nutritional value of Kersting's groundnut seeds was evaluated to further its use as food and feed. The seed contained 24.9% protein and 10.9% crude fibre. The major minerals content of the seed were 1.25g Potassium, 2.14g Calcium, 0.40g Magnesium, 3.32g Phosphorous and 0.87g Sodium per kilogramme. Some of the functional properties observed suggest that the seeds may be used as a meat additive, meat extender, binder formulation and in stabilizing colloidal food systems, hence greater use of the seed as a staple food is recommended. Feeding experiments with chicks showed normal growth with up to 15% whole seeds in the diet (Obasiet *al.*, 2002).

However, there is dearth of information on the preparation and characterization of its oxidized starch in literature. Native starch possesses many limitations which limit its use in the industry. Hence, modification (chemically or physically) is usually employed to improve its functional and physicochemical properties to meet the broad range of needs in pharmaceutical, ceramic, soap and detergents, paints and chemical processing industries.

II. MATERIALS AND METHODS

Collection of Samples

Kersting's groundnuts were purchased from Nasarawa market in Nasarawa State, Nigeria.

Preparation of Native Kersting's Groundnuts Starch

The seeds were screened to remove bad ones and stones after sun drying and kept in a sample bag prior to use.

Extraction of Starch from the Kersting's Groundnuts

Starch was extracted from the Kersting's groundnuts using the method of Scoch and Maywald (1968). A 2000g lot of dried seeds were steeped overnight at room temperature in 8 litres of 0.3% Sodium hydroxide solution. The pH of the final steep liquor dropped to 7-8 on various batches, presumably because of the consumption of alkali by the protein. The steeped Kersting's groundnuts were washed with water, then ground for 3min in the "Excella" blender in 0.2% Sodium hydroxide solution previously chilled to 5°C. The ground magma was screened through to mesh cloth and the pulp was again ground for 3min in the "Excella" blender with fresh 0.2% NaOH solution chilled and rescreened. The combined suspension was then screened through 220 – meshnylon bolting cloth. The suspension was allowed to settle overnight. Total contact time with alkali (including steeping) was about 40hr, the final alkaline deposit of starch was suspended in distilled water, neutralized to pH 6 with hydrochloric acid; decanted several times, washed with distilled water to remove the colour.

The starch was dried in a thin layer at room temperature and powdered to pass 80 meshes.

Preparation of Oxidized Kersting's Groundnuts Starch

The method of Forssle $et al$ (1995) was employed for the oxidation of the starch. A uniform slurry of starch was prepared by dispersing 40g of Kersting's groundnut starch in 200mL of distilled water. The pH was adjusted to 9.5 with 2M NaOH. 4g of Sodium hypochlorite (NaOCl) was added to the slurry over a period of 30min while maintaining a pH range 9 – 9.5 with constant stirring at $30 \pm 2^{\circ}\text{C}$. The reactions proceeded for 10min after addition of NaOCl. After the reaction, the pH was adjusted to 7 with 1M Sulphuric acid (H_2SO_4) and the oxidized starch was filtered, washed four times with distilled water and air dried at $30 \pm 2^{\circ}\text{C}$ for 48hr.

Determination of Swelling Power and Solubility at Different Temperatures

The method of Adebowale $et al$ (2002) was employed for the determination of the effect of temperature on the starch solubility and swelling.

Starch sample (1.0g) was accurately weighed and quantitatively transferred into a clear dried test tube and reweighed (w_1). The starch was then dispersed in 50cm^3 of distilled water using a blender. The resultant slurry was heated at the desired temperatures 55, 65, 75, 85, 95°C for 30min in a water bath. The mixture was cooled to $30 \pm 2^{\circ}\text{C}$ and centrifuged (5000rpm. 15min). Aliquot (5mL) of the supernatant was dried to a constant weight at 110°C . The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as g per 100g of starch in a dry weight basis. The residue obtained from the above experiment (After centrifugation) with the water it retained was quantitatively transferred to a clean dried test tube used earlier and weighed (w_2)

Swelling of starch was $w_2 - w_1$ weight of starch

Gelation Determination

Using the method of Coffman and Garcia (1977), samples of starch 2 -8% w/v were prepared in 5mL distilled water. The starch suspensions were mixed with Varl whirl mixer for 5min. The test tubes were heated in a water bath at 80°C for 30min, followed by rapid cooling under running cold tap water. The test tubes were further cooled for 2hr at 4°C . Least gelatinization concentration was determined as that concentration when the sample from inverted test tubes did not fall down or slip.

Determination of Water and Oil Absorption Capacity

Water and oil absorption properties were determined using the method of Sathe and Salunkhe(1981). 1.0g of sample was mixed with 10mL distilled water/oil (using a Varl Whirl mixer, fast) for 30s. The mixture was allowed to stand for 30min, and the volume of the supernatant, noted in a 10mL graduated cylinder. Density of distilled water was assumed to be 1g/mL and that of oil 0.689g/mL.

Starch Gel Clarity

This property was measured using the method of Bello – Perez *et al* (1999). The transmittance of a 1% starch paste at 650nm was measured using a spectrophotometer (Beckman Du – 650, CA, USA), with deionized water as the target. Starch suspensions (1%) in tubes with threaded caps were placed in a water bath at 100°C for 30min, agitated in a vortex every 5min, and left to cool to room temperature. From these, the percentage of transmittance was determined (%T).

Determination of Pasting Properties

The RVA paste viscosity was determined using the RVA -4 (Newport Scientific Pultry Ltd, Australia) as follows. Starch was added to 25M of distilled water to create a 4% suspension (dry weight basis, w/v). The suspension was kept at 50°C for 1min, heated to 95°C at 12 – 2% °C/min, and kept at 95°C for 2.5min, it was then cooled at 50°C at 11.8°C/min and kept at 50°C for 2min.

III. RESULTS AND DISCUSSION

The results of physiochemical characterizations of native and oxidized Kersting’s groundnut starches are presented below. Starch is composed of two fractions, amylose fraction, which constitutes the bulk of the amorphous region and amylopectin fraction, which constitutes the crystalline fraction. The yield in oxidized derivative might be attributed to degradative oxidation of glycosidic bonds in amylose, a development that probably results in loss of mass.

Effect of Temperature on Swelling Power

Effect of temperature on swelling power of both native and oxidized Kersting’s groundnut starch is presented in the figure 1. The results indicate that swelling power of the samples increased with increase in temperature. These results agree with the one observed for oxidized Bambara groundnut starch by Lawalet *al* (2004). Maximal swelling power was observed at 95°C. This suggests that increase in temperature enhanced penetration of water into the granules of the sample. Thermodynamic mobility of particles increased as temperature increased, thereby facilitating penetration of water into the granules. It is also reasonable that increasing temperature weakened the intragranular binding forces of oxidized Kersting’s groundnut starch, thereby facilitating less restricted swelling. Generally, hypochlorite oxidation is a highly effective means for weakening the internal structure of starch granules, thereby making starch more soluble, but with much reduced power to swell (Adebowale*et al.*, 2002).

Effect of Temperature on Solubility Pattern

Effect of temperature on solubility of native and oxidized Kersting’s groundnut starches is presented in figure 2. The results indicate that the solubility of the oxidized starch increased relative to its native starch with increase in temperature but with anomalous value at 55°C. The maximal solubility was observed at 95°C. These results are in tandem with the one observed by Lawalet *al* (2004). The anomalous value obtained at 55°C might due to the lower temperature. The increasing temperature weakened the intragranular binding forces of the oxidized starch, thereby enhanced the leaching of granular particles which led in increased solubility.

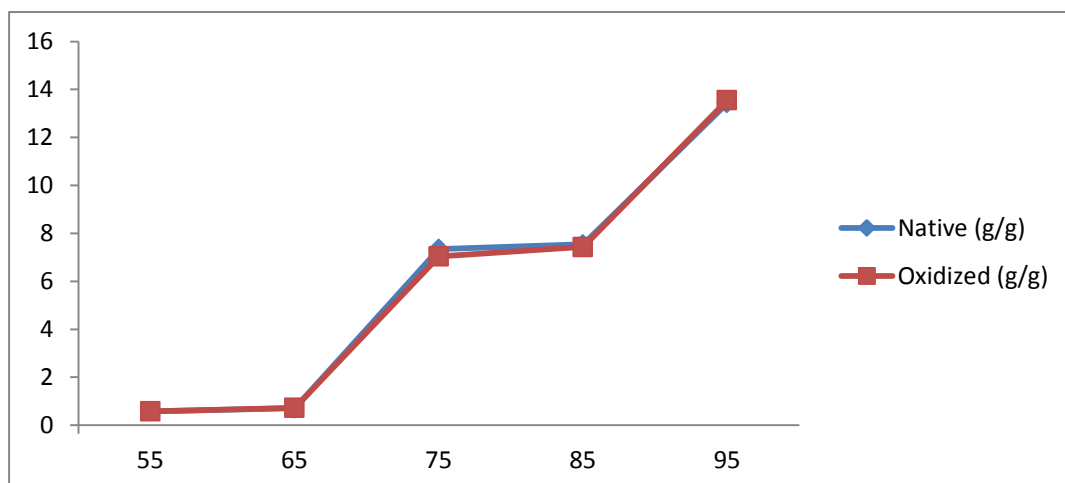


Figure 1: Effect of temperature on swelling power of native and oxidized starch

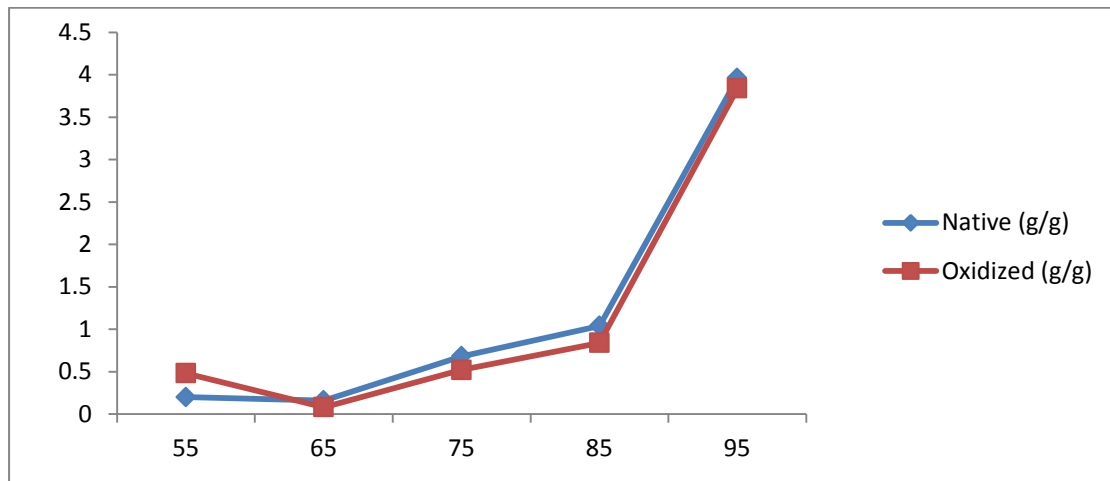


Figure 2: Effect of temperature on solubility

Gelation Properties

Gelation properties of native and oxidized Kersting's groundnut starches are presented in the table 1 below. The gelation properties increased with increase in concentration of both samples which are in accordance with the ones observed by Lawal et al (2004). Using the least gelation concentration (LGC) as the index of gelation, the results obtained for both native and oxidized starches was 6% respectively. This suggests that enhanced interaction occurred among the binding forces as the concentration increased. Probably, introduction of carbonyl and carboxyl groups caused intermolecular repulsion that increased interaction of oxidized starch molecules, which led to increase in gelation properties.

Table 1: Gelation capacity of oxidized Kersting's groundnut starch

Sample Concentration (%)	Native Description	Oxidized Description
2	- Liquid	- Liquid
4	- Viscous Gel	- Viscous Gel
6	+ Gel	+ Gel
8	+ Gel	+ Gel
10	+ Firm Gel	+ Firm Gel
12	+ Firm Gel	+ Firm Gel
14	+ Firm Gel	+ Firm Gel
16	+ Firm Gel	+ Firm Gel

Water Absorption Capacity

Water absorption capacities for both native and oxidized Kersting's groundnut starches were 120% and 140% respectively. These values were lower than those of Bambara groundnut, reported by Adebowale et al (2002). The value of oxidized starch was higher than that of native starch. Thus, oxidation of Kersting's starch favours water absorption capacity which is in contrast with the one observed by Lawal et al (2004).

Oil Absorption Capacity

Oil absorption capacities of both native and oxidized Kersting’s groundnut starches were 55% and 76% respectively. These values were lower than those of Bambara groundnut, reported by Adebowale *et al* (2002). The value of oxidized starch was higher than that of native starch. Thus, oxidation of Kersting’s starch favours oil absorption which is in contrast with the one observed by Lawal *et al* (2004).

Starch Gel Clarity

Starch gel clarity values for both native and oxidized Kersting’s groundnut starches are presented in the table 2 below. The %transmitted value obtained for the native starch was higher than the value obtained for the oxidized starch. The clarity of starch gel directly influences the shine and colour of products that contain it as a thickener.

Pasting Properties

The pasting properties of native and oxidized Kersting’s groundnut starches analysed with Rapid Visco Analyser are shown in the table 3 below. Oxidation reduced the gelatinization temperature of the starch due to weakening or scission of the D – glucosidic bonds during the processes of modification (Kruser and Rutenberg, 1976; Adebowale *et al.*, 2002).

The peak viscosity (Pv) at any concentration is an important distinguishing feature of a starch. The Kersting’s groundnut native starch shows a peak viscosity lower than that of the oxidized starch, attributed to unrestricted swelling of the starch, due to lack of substituent functional groups. The viscosity values obtained after the isothermal holding at 95°C (Tv) were generally lower than the peak viscosity value. The oxidized starch shows a lower final viscosity than that of the native starch because the hydroxyl group, which is the principal factor for this association, has been substituted. Oxidized Kersting’s groundnut starch shows the highest value of breakdown (Pv – Tv) and lowest set back (Fv – Pv) value, because the tendency toward setback or gel formation has been minimized in the substituted starch, due to the presence of functional groups which prevent the starch chains from associating. Another reason could be partial depolymerization that has occurred during the processes of modification.

Table 2: Pasting property

Parameters	Native	Oxidized
Peak viscosity (Pv)	548.38	552.80
Trough viscosity (Tv)	233.96	218.25
Breakdown (Pv – Tv)	314.42	334.54
Final viscosity (Fv)	361.88	340.80
Set back (Fv – Pv)	127.92	122.54
Peak time (min)	4.37	4.11
Pasting temperature (°C)	80.80	63.73

IV. CONCLUSION

The physiochemical properties of oxidized starch were attributed to its granular size and shape and molecular structure. Oxidation occurred mainly in the amorphous region and oxidation level in terms of carbonyl group content was largely dependent on the degree of polymerization of amylose. It is evident that oxidized Kersting’s groundnut starch can meet the needs of industries such as paper, leather and food processing industries based on its physiochemical properties studied.

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