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Physicochemical Properties Of Native And Acetylated Pigeon Pea Starches

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Abstract
Starch was extracted from pigeon pea, an underutilized legume, and acetylated (2.43%) using acetic anhydride. The starch yield increased from 28.24% (native) to 83.63% (acetylated). The pH was 6.8 and 6.9, respectively. Apparent amylose content decreased after acetylation (25.95% to 19.67%). Moisture, ash, fat, crude protein, and carbohydrate contents showed minimal variation between native and acetylated starches. Bulk density, water absorption, and oil absorption capacities increased with acetylation. Acetylated starch had higher dispersibility (98.50%) than native starch (87.50%), but a higher least gelation concentration (16% vs. 6%). Viscosity decreased with acetylation, while solubility index and swelling power increased. Acetylation improved pasting properties, particularly setback and breakdown. These findings suggest acetylation enhances the functional properties of pigeon pea starch for potential industrial applications.

Keywords: *Pigeon pea, starch, Acetylation, solubility, viscosity, physicochemical*

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I. Introduction

Legumes are the edible fruits or seeds of pod bearing plants belonging to the family leguminosae and are widely grown throughout the world (Singh et al., 2004). Food legumes are of prime importance in human diet and animal feed contributing the major source of vegetable protein. They are an economic source of not only protein but of carbohydrate, minerals and B-complex vitamins particularly in vegetarian diet. On an average, legumes contain 20-25% protein in their dry seeds, which is almost two to three times the value normally found in cereals. They are excellent sources of carbohydrates (50-60%), thus food legumes ensure nutritional security to the poor masses of the country. Legumes occupy an area of about 68.31 million hectare contributing 57.32 metric tons of production to the world food basket. India shared 35.2% of area and 27.65 percent of global legumes production. Thus India is the largest producer of legumes in the world occupying an area of about 23.81 million hectares with annual production of 15.11 million tonnes (Project Coordinators' report (2007-08), IPR, Kanpur). The commonly grown legumes in India are Chickpea, Pigeon pea, Cowpea, Field pea, Green gram, Urdbean, Lentil, Moth bean, and French bean. Besides being a source of protein legumes are also important for sustainable agriculture as they improve physical, chemical, and biological properties of the soil and function as mini- nitrogen factories. Legumes also have an inherent quality to trap moisture from the lower strata of the soil, therefore, they are considerably known to be drought tolerant and fit well in a rainfed environment. Legumes are equally important for maintaining soil health and sustainability of different cropping systems. By virtue of being a restorer of soil fertility, they have a unique position in cropping systems and dryland rainfed agriculture. The heavy leaf drop of pulses at maturity increases organic matter in the soil; various reports indicate that cultivation of pulses economizes nitrogen to the tune of 30-40 kg/ ha, for succeeding cereal crops and also improve soil health by ensuring environmental security. Pigeon pea (*Cajanus cajan*) is a locally available, affordable and under-utilized grain legume of the tropics and sub-tropics.

The legume can be utilized in several diverse ways, while the high genetic variability that exists within its cultivated and wild relatives remains to be explored for further uses. Attempts have been made to improve its utilization in the human diet due to the increasing need for cheaper and more readily available plant proteins to meet the growing demand of the Nigerian populace. Reduced cooking time and improved acceptability have been achieved for pigeon pea through the dehulling process (Fasoyiro et al., 2006). Apart from being hard to cook, pigeon pea seeds are also hard to dehull, making the labor-intensive dehulling process a limiting factor in their utilization for other products besides cooking the seeds (Fasoyiro et al., 2005). The isolation of starch from pigeon pea seeds using appropriate technology that improves the dehulling process will enhance the utilization of the seeds. Pigeon pea (Cajanus cajan), a member of the Leguminosae family, has been reported to contain 20-22% protein, 1.2% fat, 65% carbohydrates, and 3.8% ash (FAO, 1982).

Pigeon pea seeds can be processed into value added products like protein concentrate and food grade starch. Starch is a natural, cheap, available, renewable, and biodegradable polymer produced by many plants as a source of stored energy; it is the second most abundant biomass material in nature. Starch owes much of its functionality to the proportion of its two major constituents, Amylose (AM) and Amylopectin (AP), though the contribution of minor components (lipids and proteins) cannot be ruled out. It has been reported that starch is the most abundant polysaccharide in the legume seed (22-45%) (Hoover and Sosulski, 1991). Starch is of considerable commercial importance because of its numerous desirable functional properties, especially related to its ability to modify texture of products. An important property of starch in relation to its functionality is its ability to absorb water, resulting in gelatinization and loss of granular organization (Blazek and Copeland, 2008). Differences in starch physicochemical characteristics have significant impact on their functional and rheological behaviour, affecting their suitability for specific uses.

Starch is not completely digested and absorbed in the small intestine, as was previously thought before the early 1980s. Englyst, et al. (1992) first recognized the presence of starch fraction resistant to enzymic hydrolysis during their research on measurement of non-starch polysaccharides. Most starch products contain a portion that digests rapidly (rapidly digesting starch, RDS), a portion that digests slowly (slowly digesting starch, SDS) and, a fraction that is resistant to digestion (resistant starch, RS) (Englyst er al., 1992). RS has potential physiological benefits similar to dietary fibre and unique functional properties. Legumes have shown to contain significant amounts of RS which is especially beneficial for reducing the risk of several diseases.

The growing demand for starches for the modern food industry has created interest for new sources of the polysaccharides (Singh et al., 2004). The high carbohydrate content of pigeon pea therefore makes it a possible source of starch for the food industries. The commercial utilization of pigeon pea starch into numerous food products remains unpopular in food formulations. Therefore using starch to prepare food products such as noodles, bread, pastries etc. will serve the purpose of improving the utilization of this pea in the food industries.

Pigeon pea is primarily cultivated by rural communities but suffers from underutilization and neglect. Its hard seed coat makes cooking difficult and time-consuming, while its high oligosaccharide content often causes flatulence. This legume, associated with the poor, receives little research attention, raising concerns about its potential extinction. The commercial use of pigeon pea starch remains uncommon in food formulations, as legume starches are often viewed as inferior to cereal and root starches due to high retrogradation rates. Hoover and Sosulski (1991) noted that chemical modification can reduce these rates, making legume starches more competitive. Given their high thermal stability, modified pigeon pea starch could have advantages for food products like noodles, custards, binders, and stabilizers in yogurt. Chemical modification would enhance the commercial value and broaden the use of this underutilized legume starch. Hence, the aim of this study is to determine the physicochemical properties of native and acetylated Pigeon pea starches.

II. Materials And Methods

Material used for this study is pigeon pea (*Cajanus cajan*). It was sourced from lddo-market, oyingbo, Lagos State, Nigeria. All other reagents are of analytical grade.

Preparation of Pigeon pea

Pigeon pea were sorted, (to remove visual defects, insects or damaged seeds, extraneous materíals, stones, metals etc), soaked (in NaOH solution to ease the dehulling process and to solubilize the proteins), dehulled (to separate the coat from the seed), washed, blended, filtered, centrifuged, and oven-drying at 40°C for 24hrs.

Starch Extraction

200 grams of pigeon pea were steeped in a 0.2% sodium hydroxide solution for 24 hours with continuous stirring to enhance diffusion and break down the protein-starch matrix. Afterward, the seeds were dehulled, separating the seed coat from the seeds. The seeds were blended to form a starch slurry, which was filtered through 250 µm and 90 µm screens to remove large particles, primarily seed coat material. The filtrate was left to sediment, and the supernatant was discarded. The starch was recovered, dried at 40°C for 24 hours, ground with a mortar and pestle, and stored in airtight containers for analysis.

Pigeon Pea Starch Acetylation

Pigeon starch acetylation was carried out using the method of Wurzburg (1964) as modified by Golachowski (2003). Pigeon pea starch (200g) (db) were dispersed in 200ml of distilled water, and then made up to 560g with distilled water. The pH was adjusted to 8-9 using 38% NaOH. Predetermined volume of acetic acid anhydride was added at a constant rate of 1ml per minute while maintaining pH range 8-9 using 3% NaOH.

After all the acetic anhydride had been added, the pH was finally adjusted to 5.2-5.6 with 10% HCI. The modified starch slurry was centrifuged at 1000rpm, the residue obtained was washed with distilled water and dried in the air oven at 30°C. The dried modified starch were then pulverized, sieved and packaged in plastic containers and kept ina cool dry place for further analysis.

Pigeon Pea Starch

The degree of acetylation (expressed as percentage in dry basis) was determined according to the procedure of the procedure of Golachowski (2003). 10g of starch (db) and 65ml of distilled water was added and neutralized by adding few drops of 0.1M NaOH to obtain a faint pink colour using few drops of phenolphthalein indicator. 26ml of 0.5M NaOH was added and blended for 35minutes. The resultant mixture was titrated against 0.5M HCI until the pink colour disappeared. The percentage acetylation was calculated

Acetylation % = $\frac{(25 - x)0.043 \times 0.05 \times 100}{\alpha}$

Where x = amount of 0.5M HCl used for titration of a sample

α = weight of starch (db)

Determination of Proximate Composition

Proximate composition of the starches was determined. Moisture was determined using oven-dry method. Protein was determined by kjeldahl method, fat using Soxhlet apparatus, ash by charring in muffle furnace, crude fibre was also determined and carbohydrate by difference.

Determination of Moisture Content

The moisture content of the sample was determined using air oven method as described in AOAC (1990). The petri dishes were washed and dried in hot air oven. The hot, cleaned and dried petri dishes were then transferred to the desiccator and allowed to cool. The weights of the petri dishes were determined and 5.0g of the sample (W_1) was weighed into already weighed petri dish. The dishes and its content (W_2) were then transferred into the oven maintained at 105°C. The content was allowed to dry at this temperature for four hours. The petri dish and its content were removed from the oven and cooled in the desiccator and after cooling, the weight was determined. Then the dish and its content were later returned to the oven and process of drying and cooling continued. The subsequent weight was recorded after drying for few hours and cooling until a constant weight (W_3) was obtained.

% Moisture Content = $\frac{\text{Weight loss}}{\text{Weight of sample}} \times 100$

% Moisture Content = $\frac{(W2-W3)}{(W)} \times 100$

Determination of Ash

A crucible with its lid was washed, rinsed, dried in the oven and allowed to cool in a desiccator. The weight of empty crucible plus its lid, (W_1) was measured using an analytical balance. 2g of the sample was put into the crucible and covered with its lid. The new weight was taken and recorded as (W_2). The crucible with its content was then transferred in a muffle furnace maintained at 550°C and kept there for 6 hours for complete ashing. The ash obtained plus crucible was allowed to cool in the desiccator and weighed (W_3) (AOAC, 2005).

% Ash content = $\frac{\text{Weight of ash}}{\text{Weight of sample}} \times 100$

% Ash content = $\frac{(W_3 - W_1)}{(W_2 - W_1)} \times 100$

Determination of Crude Fat

The fat content was determined using Soxhlet apparatus as described in AOAC (1990). About 1.0g of the starch sample was accurately weighed into an already weighed filter paper (W_1). The filter paper and its content (W_2) was tied with thread and placed into a Soxhlet extractor. Hexane was used as the extraction solvent. The hexane was poured into a round bottom flask fitted and placed on the heating mantle. Extraction occurred as the solvent refluxed several times. The extraction continued for 4hours after which the flask was cooled and dismantled. The filter paper with the sample was removed and transferred to a hot air oven at 50°C. It was then allowed to cool in the desiccator and thereafter weighed (W_3) after untieing the filter paper.

The percentage fat content was then calculated as follows:

% Fat content (g/g) = $\frac{\text{Weight of extracted fat}}{\text{Weight of sample}} \times 100$

= $\frac{W_2 - W_3}{} \times 100$

W_1

Determination of Crude protein

Digestion: lg of the sample was weighed and transferred into the miero-kjeldahl flask. One tablet of catalyst and 10ml concentrated H_2SO_4 were added to the sample inside the flask. The flask with its content was heated on a heating mantle inside a fume cupboard for 3 hours until the black solution turned colourless. The clear solution was diluted with distilled water and made up to 50ml.

Organic Nitrogen + $H_2SO_{4(conc)}$ → $(NH_4)_2S0_{4(aq)}$

Distillation: 10ml of the resulting solution from the digest was measured and transferred into a distillation apparatus. Then, 25ml of 40% NaOH was added to the digested sample solution in order to make it alkaline. The cloudy nature of the sample solution after the addition of the 40% NaOH indicates that the NaOH was in excess. 25ml of 2% boric acid was pipette into a receiving conical flask; to which 2 drops of mixed indicator was added to produce a pink colour solution. The distillation was carried out with all joints tightened, making sure that the end of the delivery tube dipping below the boric acid solution. As the distillation proceeds, the pink colour solution of the receiver turned light green, indicating the presence of NH_3 Distillation was continued until the distillate was about 50 ml after which the delivery end of the condenser was rinsed with distilled water into the receiving flask. The chemical reaction during distillation is as follows:

$(NH_4)_2S0_{4(aq)} + 2NaOH_{(aq)}$ → $2NH_3 + Na_2SO_{4(aq)} + 2H_2O_{(l)}$

The received ammonia forms a complex with boric acid as follows:

$NH_3BO_{3(aq)} + NH_{3(g)}$ → $NH4^+ H_2BO_3^-{}_{(aq)}$

(Pink) (Light green)

Titration: The third step was the titration stage where the received ammonia in the boric acid was titrated against standard 0.01M HCl. A colour change of this solution from light green to pink due to the presence of the mixed indicator that was earlier introduced in the distillation stage indicated the end point. The titre value was noted and recorded

$NH_4H_2BO_3^-{}_{(aq)} + HCl_{(aq)}$ → $NH4Cl_{(aq)} + H_3BO3_{(aq)}$

(Light green) (Pink)

Calculations: The final step is to estimate the % Nitrogen in the sample and hence the Crude protein by multiplying that value by the general factor 6.25

$$\% \text{ Nitrogen} = \frac{\text{Titre value} \times M \times 0.0014 \times DF \times Cf \times 100}{\text{Weight of sample}}$$

Where; M = Molarity of HCl = 0.01 M; Cf = Correction factor = 10; Df = Dilution factor = 5; % Crude protein = % Nitrogen x 6.25

Determination of Total carbohydrate

Total carbohydrate estimation was determined by difference. The percentage total carbohydrate content is equal to the sum of the percentage Moisture, Crude protein, Ash, and Crude fat contents, subtracted from 100.

% Carbohydrate = 100 – (%Moisture + % Ash + % Crude protein + Crude fat)

Determination of Functional Properties

Determination of Yield

The yield of the starches was calculated based on the formula,

$$\text{Yield} = \frac{\text{Weight of starch after drying}}{\text{Weight of legume}} \times 100$$

Determination of pH

The method of Benesi (2005) was employed. 5g of the sample were weighed in triplicates into a beaker, mixed with 20ml of distilled water. The resulting suspension stirred for 5 mins and left to settle for 10 min. The pH of the water phase was measured using a calibrated pH meter.

Determination of Bulk density

Bulk density was determined by the method described by Oladele and Aina (2007). 50g of the sample was put into 100 ml measuring cylinder. The measuring cylinder was then tapped continuously on a laboratory table until a constant volume was obtained. Bulk density (g/cm^3) was calculated using the formula:

$$\text{Bulk density } (g/cm^3): \quad \frac{\text{Weight of sample}}{V_1 - V_2}$$

Where; V_1 = Initial volume
V_2 = final volume

Determination of Dispersibility

This was determined by the method described by Kulkarni et al. (1991). 10g of the sample was suspended in 100ml measuring cylinder and distilled water was added to make a volume of 100ml. The set up was stirred vigorously and allowed to stand for 3 hours. The volume of settled particles was recorded and subtracted from 100. The difference was reported as percentage dispersibility.

Determination of swelling power and solubility index

It was determined by using Takashi and Sieb (1988) method. 1g of sample was weighed into 50ml centrifuge tube. 50ml of distilled water was added and mixed gently. The slurry was heated in a water bath at 50, 60, 70, 80, and 90°C, respectively for 15 minutes. During heating the slurry was stirred gently to prevent clumping of the starch. After which the paste was centrifuged at 3000rpm for 10 minutes. The supernatant was decanted immediately after centrifuging. The weight of the sediment was taken and recorded. The moisture content of the gel was thereafter determined to get the dry matter content of the gel.

$$\text{Swelling power} = \frac{\text{Weight of mass sediment}}{\text{Weight of dry matter in gel}}$$

Determination of Water Absorption Capacity

Water Absorption Capacity is an index of the amount of the amount of water retained within a protein matrix under certain conditions. It usually refers to entrapped water but includes bound water and hydrodynamic water and depends upon the condition of determination. It was determined using the method of Sathe and Salunkhe (1981) as modified by Adebowale et al. (2005). 10ml of distilled water was added to lg of sample in a beaker. The suspension was stirred using magnetic stirrer for 3minutes. The suspension obtained was thereafter centrifuged at 3500rpm for 30minutes and the supernatant was measured into a 10ml graduated cylinder. The density of water was taken as 1.0g/ml. The water absorbed by the flour was calculated as the difference between the initial volume of the water and the volume of the supernatant

$$\text{Water absorption capacity (g/ml)} = \frac{\text{Weight of sample}}{\text{Volume of water used-Volume of water absorbed}} \times 100$$

Determination of Oil Absorption Capacity

Oil Absorption Capacity is an index of the amount of oil retained within a protein matrix under certain conditions. It was determined using the method of Sathe and Salunkhe (1981) as modified by Adebowale et al. (2005). 10ml of oil was added to lg of sample in a beaker. The suspension was stirred using magnetic stirrer for 30minutes. The suspension obtained was thereafter centrifuged at 3500rpm for 30 minutes and the supernatant was measured into a 10ml graduated cylinder. The oil absorbed by the starch was calculated as the difference between the initial volume of the oil and the volume of the supernatant.

$$\text{Oil Absorption Capacity(g/ml)} = \frac{\text{Weight of sample}}{\text{Volume of oil used-Volume of oil absorbed}}$$

Determination of Least Gelation Concentration (LGCc)

The method of Sathe and Salunkhe (1981) was employed for the determination of LGC. Sample suspensions of 2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, 18%, and 20% (w/v) were prepared in 5ml distilled water and the tubes were heated in a boiling water bath for 1 hour followed by rapid cooling under cold tap water. The test tubes were further cooled for 2 hours at 4°C. Least gelation concentration was determined as that concentration at which sample did not fall or slip on inversion of test tube.

Determination of Viscosity

Starch suspension of 2%, 5%, 7% was heated to 90°C for 30mins in a temperature controlled water bath with continuous stirring. The paste was transferred to a rotatory viscometer. Paste viscosity was then measured at 90°C to 30°C cooling phase

Determination of Pasting Properties

The pasting property was determined using a Rapid Visco Analyser (Newport Scientific Australia). 2.5g of the sample was weighed into a dried empty canister. 25ml of distilled water was dispensed into the canister containing the sample. The solution was thoroughly mixed and the canister was well fitted into the RVA, as recommended. The slurry was heated from 50°C to 95°C with a holding time of 2 minutes followed by cooling to 50°C with 2 minutes holding time. The rate of heating and cooling were at constant rate of

11.25°C/min. Peak viscosity, trough, breakdown, final viscosity, set back, peak time and pasting temperature were read from pasting profile with the aid of Thermocline for Windows Software connected to a computer.

Determination of Amylose

0.1g of starch was weighed into a test tube. 1ml of 95% ethanol and 9ml of 1M NaOH were added and the mouth of the test tube was covered with foil. The resulting solution was mixed together and heated for 10 minutes in boiling water to gelatinize starch. It was thereafter cooled to obtain 10ml extract, diluted to 10 folds. 1ml of extract was taken and made up to 10ml with 9ml of distilled water. An aliquot of 0.5ml of diluent was then used for analysis, 0.1ml Acetic acid solution, 0.2ml iodine solution and 9.2ml of distilled water was added to make up 10 ml. It was allowed to stand for 20minutes for colour development and absorbance reading taken at 620nm.

Calculation: % Amylose of sample = % amylose of standard x absorbence of sample x absorbence of standard

III. Result And Discussion

Physicochemical Composition of Pigeon Pea Starches

The yield, pH, amylose and amylopectin of native and acetylated pigeon pea starches are represented in Table 1. The yield of the native pigeon pea starch was 28.24% which is low compared to what was obtained for other legume starches such as black gram (45%), red bean (46%) (Hoover and Sosulski, 1991) but high compared to starches from beach pea (12.3%), grass pea (26%) (Chavan et al., 1999) and adzuki bean (21.2%) (Naivikul and D'Appolonia, 1979). The low yield of the extract could be as a result of the presence of highly hydrated fine fiber fraction (Vose, 1977) which is derived from the cell wall enclosing the starch granules which made starch isolation more arduous. It could also be due to the presence of some insoluble proteins compact association of pigeon pea starch granules with other biomolecules. The yield of acetylated starch was 83.63%. The yield obtained is within the range (82-88%) reported by Aiyeleye et al. (1993). The reduction in starch volume may be attributed to loss during repeated washing aimed at achieving a non-acidic starch.

pH is an important property in industrial application of starch as it is used generally to indicate the acidity or alkalinity of liquid medium. pH of the native and acetylated starch were 6.8 and 6.9 respectively which depicts that the starches are close to neutral attributable to repeated washing of the starch slurry prior to sedimentation and drying.

The amylose content was 2.5.95 and 19,67% while the amylopectin content was between 76.05 and 80.33% respectively. Legume starches have been characterised by a high amylose content of 24 – 65% (Hoover and Sosulski, 1991). Non mutant legume starches have been reported to be characterized by a higher amylose content than cereal starches, often in the range of 30-40%, for example 30% in chick pea, 31-32% in faba bean, 34% in pea and 38% in lentil (Hoover and Sosulski, 1986). Schoch and Maywald (1968) stated that as the amylose content increases, the swelling tend to be restricted and the hot paste viscosity stabilized, this implies that the native starch will have a reduced swelling capacity compared to the acetylated pigeon starch.

The amylose content of starches is important, as it affect pasting, gelatinization, swelling power and enzymatic vulnerability of starches (You and Izidorczyk, 2002). Higher amylose content is desired in starches that are to be used for the manufacture of noodles. Therefore pigeon pea native starch can be used for this purpose. The low amylose content of the acetylated starch may be as a result of introduction of the acetyl group. Both native and acetylated starches have high amylopectin content which implies that the can both produce a cohesive gel because they have the ability to bond large amount of water and swell to larger diameters (Pigott, 1986) whereas low amylopectin starches results in weak and brittle gels (Hermanson and Lucissano, 1982).

Proximate Composition of the Native and Acetylated Pigeon Pea Starch

The proximate composition of the starches is presented in Table 2. Isolation of starches from legumes is generally difficult owing to the presence of a highly hydrated fine fiber fraction, which is derived from the cell wall enclosing the starch granules (Hoover and Sosulski, 1985; Sohoch and Maywald, 1968). The moisture content is 7.52 and 9.01%. The low moisture content indicates potential for higher shelf life on dried products. The lower the initial moisture content of a product to be stored, the better the storage stability of the product (Akubo, 1997). The fat content of the starches are 0.42 and 0.47% respectively, generally pigeon pea is low in fat and the process of extraction could be responsible for the low values which ascertains starch purity.

The low fat content suggests that the starches and other products made from it are not susceptible to rancidity. The total ash content of the starches is 0.04 and 0.06% respectively this could be attributed to the removal of the other components of the pigeon pea seed. Crude fibre was not detected in the starches and this may be due to the fact that the seed coats and fibrous portion of the seeds were discarded in the process of extraction. The protein content is 1.76 and 1.76% respectively. The carbohydrate content is 90.26 and 88.70%

respectively; carbohydrates are inexpensive source of food energy. High percentage carbohydrate content in the native and acetylated starch depicts that the starches are good source of energy.

Functional Properties of the Native and Acetylated Pigeon pea Starch

The functional properties of the starches are presented in Table 3. The water absorption capacity, bulk density, oil absorption capacity, and dispersibility of the native and acetylated starch ranged between 1.13-1.96 g/ml, 0.84-0.92 g/ml, 1.21-1.61 g/ml, and 87.50-98.50%, respectively.

The bulk densities of the starches are 0.84 and 0.92 g/ml. Bulk density is essentially a measure of the degree of coarseness of the sample, implying that the particles of the acetylated starch are coarser than those of the native starch. The replacement of the hydroxyl group in the native starch with a bulkier acetyl group might have caused the increase in weight. Similar results were reported for acetylated winged bean flour (Narayana and Narasinga Rao, 1984) and cotton seed flour (Rahma and Narayana Rao, 1983).

Water absorption capacity is the ability of the flour to absorb water and swell, improving consistency in food. It is desirable in food systems to improve yield and consistency and give body to food (Osundahunsi et al., 2003). The water absorption capacities of the starches are 1.13 and 1.96 g/ml, respectively. The engagement of the hydroxyl group to form hydrogen and covalent bonds between starch chains in the native starch lowers the water binding capacity (Hoover and Sosulski, 1986). Low water binding capacity is attributed to a close association of starch polymers within the native starch granules, and legume starches are said to have lower water binding capacity than cereal starches (Halbrook and Kurtzman, 1975). A review of the literature reveals that acetylation improved the water absorption capacity of smooth pea, waxy maize starches, and glandless cotton seed flour (Halbrook and Kurtzman, 1975). However, pigeon pea starch can greatly contribute to the textural properties of many foods and industries as a thickening, gelling, and bulking agent, especially acetylated pigeon pea starch since it has a higher water absorption capacity than native starch.

The oil absorption capacity of the native and acetylated starch is 1.21 and 1.61 g/ml, respectively. Oil absorption increases more for acetylated starch than for native starch. The improvement in oil absorption capacity is a result of the introduction of functional groups into the starch molecules, facilitating a more enhanced oil binding capacity than the native starch.

The results of both water and oil absorption capacities indicate that acetylation altered the starch polarity (Rogols, 1986). Adebowale and Lawal (2003) reported that acetylation improved the water and oil absorption capacities of mucuna bean starch.

Dispersibility is a measure of the reconstitution of starch in water; the higher the dispersibility, the better its reconstitution in water (Kulkarni et al., 1991). The percentage dispersibility of the isolated starches is 87.50-98.50%, with the highest value for acetylated pigeon pea starch, while the lower value was for native starch. Since higher dispersibility implies better reconstitution, acetylated pigeon pea starch will reconstitute better than native starch. However, the value obtained for native pigeon pea starch is higher than the 40.67% obtained by Akanbi et al. (2009) for breadfruit starch.

Least Gelation Concentration of Native and Acetylated Starch

Gelation is a phenomenon associated with the disruption of the granular structure of starches. This phenomenon includes the disappearance of polarization cross linkages and irreversible swelling of the starch granule when heated in excess water to progressively higher temperatures (Ogungbenle, 2009). Gelation involves the formation of a continuous network, which exhibits certain degree of order. Sathe and Salunkhe (1981) associated the variation in gel formation of different leguminous flours and starch to the relative ratios of the different constituents (proteins, carbohydrates and lipids) that make up the legumes. Gels are characterized by relatively high viscosity, plasticity and elasticity.

The least gelation concentration of native and modified pigeon pea starches are shown in Table 4. The native starch has LGC at 6%w/v while acetylated pigeon pea starch is at 16%w/v. Gelling properties of five legume starches (gourd seed, white melon, yellow melon. benni seed and bulma cotton seed starches) were determined by Ogungbenle (2009). He reported that gourd starch (4 % w/v) had a better ability to form gel and therefore provides a structural matrix for holding water, flavour, and sugar of food products. Four of the starches (gourd seed, white melon, yellow melon and benni seed starches) set to the strongest gels while bulma cotton seed starch set to a soft weak gel.

The gelling effects on functional, sensory and cooking qualities of acid modified cocoyam starch were reported by Ojinnaka et al. (2009). The study revealed LGC at 10 % w/v for the three starches (native *Ede uhie* starch, native *Ede ocha* starch and 1ml glucoamylase treated *Ede ocha* starch). The starches had LGC of 14 % w/v for the acid modified starches. They concluded that the poor gelling ability of the native and acid modified starches could be due to the nature of the starch, protein and their interaction during processing.

Yusuf et al. (2007) also studied the effect of modification on the gelation of jack bean starches based on pH and temperature. Least gelation concentration (LGC) endpoints were observed at 6 % w/v for unmodified

jack beans starch while oxidized jack beans starch had LGC at 8% w/v and the acetylated jack beans starch 12 % w/v. The result obtained in this study indicated a higher LGC value for acetylated starch and a lower LGC value for unmodified starch.

Viscosity of native and acetylated pigeon pea starch at different concentrations

Viscosity of a substance refers to its resistance to flow which increases as temperature decreases or decreases as temperature increases (Coulson and Richardson, 2004). Starch paste viscosity can be increased or reduced by applying a suitable chemical modification (Agboola et al.. 1991). The viscosities of pigeon pea starches at different concentrations are presented in Figure 1 and 2. The viscosity of the starches at different concentration increases as the Temperature decreases. Viscosity of native starch was higher than acetylated starch; this implies that the introduction of acetylated starch in food systems will not have a much viscous product than native starch. Acetylation reduces viscosity and least gelation concentration this is due to the introduction of acetyl group.

Swelling power and solubility capacity of Native and Acetylated starch

Swelling power is a measure of the hydration capacity of starch. The solubility and swelling capacity are represented in Figure 3 and Figure 4. Acetylation increased the solubility and swelling power of the granules. The highest solubility and swelling capacity in both were observed at 90^{o}C this shows that penetrating power of water into the granules of the starches studied can be increased at high temperature. This trend has been observed for *Canavalia ensiformis* by Ancana et al. (1997) and bambara groundnut by Lawal et al. (2004).

The highest solubility and swelling capacities of acetylated sample starch may be due to the introduction of hydrophilic substituting groups that allow the retention of water molecules because of their ability to form hydrogen bonds. This ensures high retention of water that enters the granule, increasing the swelling capacity. This is a useful property in the manufacture of some confectionery products.

Pasting Properties of Native and Acetylated Pigeon pea Starch

Pasting is an episode following gelatinization in the solubilisation of starches. It involves granular swelling, exudation of the granular molecular component, and lastly completes disruption of the granules (Atwell et al., 1988). Legume starches have higher viscosity than cereal starches (Lineback and Ke, 1975) which indicate that these starches are more resistant to swelling and rupture towards shear. The factors which influence this property may include the shape and size of the starch granules, ionic charge on the starch, kind and degree of crystallinity within the granules, presence or absence of fat and protein, and perhaps, molecular size and degree of branching of the starch fractions (Schoch and Maywald, 1968). The pasting properties of the pigeon pea native and acetylated starch are represented in Table 5 The pasting temperature, peak viscosity, trough, breakdown, final viscosity, setback and peak time native and Acetylated starches are 84.95 and 87.40, 5887 and 408.5, 4348 and 293.92, 1539 and 114.58, 7944 and 576.75,359.6 and 282.83, 4.93 and 5.07 respectively.

Rapid Visco Analyzer (RVA) was used to determine the pasting behaviour of the native and acetylated starch from pigeon pea. The pasting curve were recorded and represented in Fig 5 and 6. Several changes may occur during heating a starch-water system, including enormous swelling, increased viscosity, translucency and solubility, and loss of anisotropy (birefringence). These changes are defined as gelatinization. The gelatinization temperature for native and acetylated starch is 84.95 and 87.40 respectively. The gelatinization temperature obtained was considerably higher than for wheat starch 55.6 to 63.0°C, chick pea 63.5 to 69.0°C and horse bean 61.0 to 70.0°C starches (Lineback and Ke 1975). Similarly, lower gelatinization temperature compared to the observed result was reported for kidney bean, black bean Lai and Varriano-Marston (1979). The high initial gelatinization temperature of pigeon pea starches indicated that the granules resisted swelling; Acetylated pigeon pea starch is more resistant to swelling than the native starch. The pasting temperature is one of the pasting properties which provide an indication of the minimum temperature required for sample cooking, energy cost involved and other component's stability.

The peak viscosity is the maximum viscosity developed during or soon after the heating portion of the pasting test and it correlate to the final product's quality, It also provides an indication of the viscous-load likely to be encountered during mixing (Maziya-Dixon et al., 2004), Higher swelling index is indicative of higher peak viscosity while higher solubility as a result of starch degradation results in reduced paste viscosity (Shittu et al., 2001).

Generally for starches, high viscosity is desirable for industrial uses, for which a high thickening power at high temperature is required (Kim et al., 1995), The peak viscosity of native pigeon pea starch is higher than the acetylated indicating that the starch can be incorporated into food that requires high thickening such as custard.

Peak time is a measure of the cooking time (Adebowale et al., 2005). Peak time is the duration taken for the sample to reach highest viscosity. The low peak time observed in the native starch is indicative of its ability to cook fast although, the difference in peak time between native and modified pigeon pea starch is not significant. Breakdown is regarded as a measure of the degree of disintegration of granules or paste stability (Newport scientific, 1988). Breakdown viscosity is the measure of the tendency of swollen starch granules to rupture when held at high temperatures and continuous shearing (Patindol et al., 2005) and it is indicative of the stability of the starch on heating. Breakdown viscosity was significantly higher in native starch which makes the starch very stable during heating. Aryee et al. (2006) reported that high paste stability is an i indication of very weak cross-linking within the starch granules which implies that such starch cannot be used for products where starch stability is required at very high temperature due to its tendency to breakdown. The final viscosity relates to the ability of the starch to form a viscous paste during cooling. The ability to form a viscous paste on cooling was higher native starch. The increase the final viscosity might be due to the aggregation of amylose molecules (Miles et al., 1985). A large increase in viscosity during the cooling stage is indicative of quick retrogradation (Lii et al., 1996)

The setback is a stage where retrogradation or reordering of starch molecules occurs. It is a tendency to become firmer with increasing resistance to enzymic attack (Ihekoronye and Ngoddy, 1985) and has a serious implication on the digestibility of dough when consumed. Higher setback values are synonymous to reduced dough digestibility (Shittu et al., 2001), while lower setback during the cooling of the paste indicates lower tendency for retrogradation (Sandhu et al., 2007). Setback measures ability of cooked starch to recrystallize, the acetylated starch is more susceptible to retrogradation because it has a lower setback compared to native pigeon pea starch this may be due to presence of acetyl group.

IV. Conclusion

The study revealed that starch can be isolated from pigeon pea which is an underutilized legume. Acetylation at 2.43% of pigeon pea has better functional properties in terms of increased water absorption capacity, oil absorption capacity, dispersibility, swelling power, solubility, bulk density and improved pasting properties, reduced viscosity and gelation than pigeon pea native starch which makes it a potential in industrial food application systems.

V. Recommendations

Further studies should be carried out on other functional properties of starch as applicable in food application and industries can adopt use of modified pigeon pea starch to food systems e.g. yoghurt, custard etc.

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Table 1: Physicochemical properties of Pigeon pea starch

Properties	PPNS	PPAS
Yield (%)	28.24	83.63
pH	6.8	6.9
Amylose	25.95	19.67
Amylopectin	76.05	80.33

PPNS: Pigeon pea native starch
PPAS: Pigeon pea acetylated starch

Table 2: Proximate composition of native and acetylation pigeon pea starch

Composition (%)	PPNS	PPAS
Moisture content	7.52 ± 0.01	9.01 ± 0.01
Ash	0.04 ± 0.01	0.06 ± 0.01
Fat	0.42 ± 0.00	0.47 ± 0.00
Crude protein	1.76 ± 0.00	1.76 ± 0.01
Crude fibre	Not detected	Not detected

Carbohydrate	90.26 ± 0.01	88.70 ± 0.01

Values are means ± standard deviation of three determinations.
PPNS: Pigeon pea native starch
PPAS: Pigeon pea acetylated starch
ND: not detected

Table 3: Functional properties of native and acetylated pigeon pea starch

Properties	PPNS	PPAS
BD (g/ml)	0.84 ± 0.01	0.92 ± 0.01
WAC (g/ml)	1.13 ± 0.01	1.96 ± 0.01
OAC (g/ml)	1.21 ± 0.01	1.61 ± 0.01
Dispersibility (%)	87.50 ± 0.71	98.50 ± 0.71

Values are means ± standard deviation of three determinations
BD: Bulk density
WAC: Water absorption capacity
OAC: Oil absorption capacity
PPNS: Pigeon pea native starch
PPAS: Pigeon pea acetylated starch

Table 4: Least gelation concentration of pigeon pea starches

Concentration (% w/v)	Unmodified gelation remark	Acetylated gelation remark
2	- Liquid	- Liquid
4	± Viscous	- Liquid
6	+ Gel (LCE)	- Liquid
8	+ Gel	- Liquid
10	+ Firm Gel	- Liquid
12	+ Firm Gel	- Liquid
14	+ Solid Gel	± Viscous
16	+ Solid Gel	+ Gel (LCE)
18	+ Solid Gel	+ Gel
20	+ Solid Gel	+ Firm Gel

(-): no gelation; (±): Viscous; (+): gelation, and LCE: Least concentration endpoint, which is the lowest starch concentration at which gel remained in the inverted tube.

Table 5: Pasting characteristics of native and acetylated pigeon pea starch

Samples	P_{temp}	P_{time}	PV	TV	FV	BD	SB
PPNS	84.95	4.93	5587	4348	7944	1539	3596
PPAS	87.40	5.07	408.5	293.92	576.75	114.8	282.83

PPNS: Pigeon pea native starch
PPAS: Pasting temperature (°C)
P_{temp} : Pating temperature (°C)
$P_{time:}$ Pasting time (mins)
PV: Paste viscosity
TV: Trough viscosity
FV: Final viscosity
BD: Breakdown
SB: Set Back

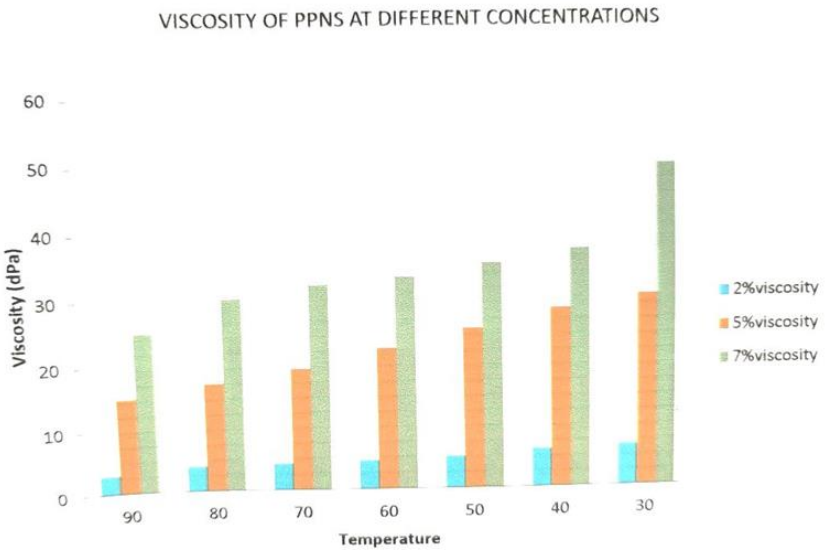

Figure 1: Viscosity of Pigeon pea native starch at different concentrations and temperatures

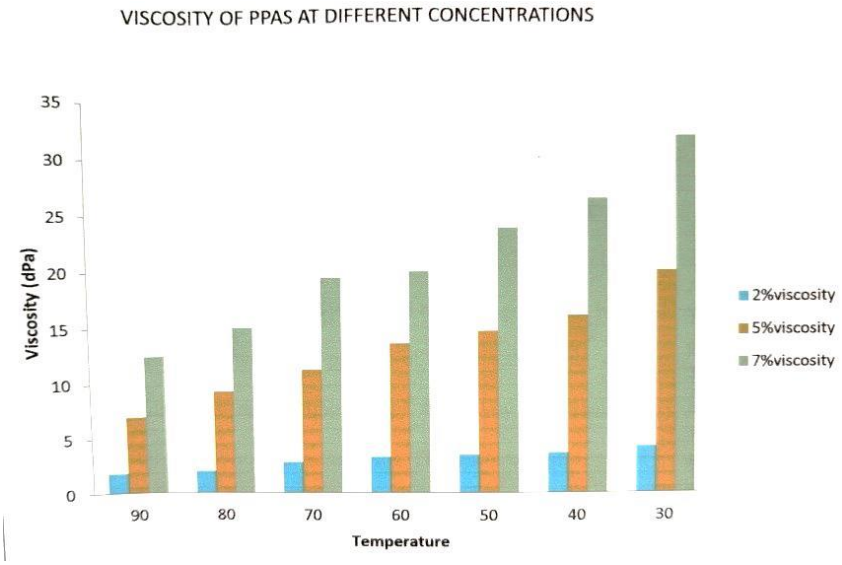

Figure 2: Viscosity of Pigeon pea acetylated starch at different concentrations and temperatures

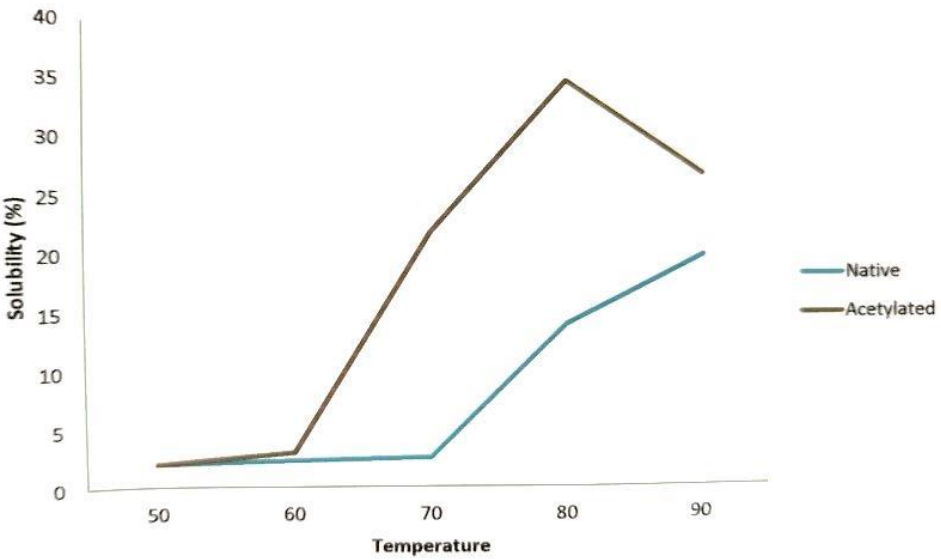

Figure 3: Solubility comparison of native and acetylated starch at various temperatures

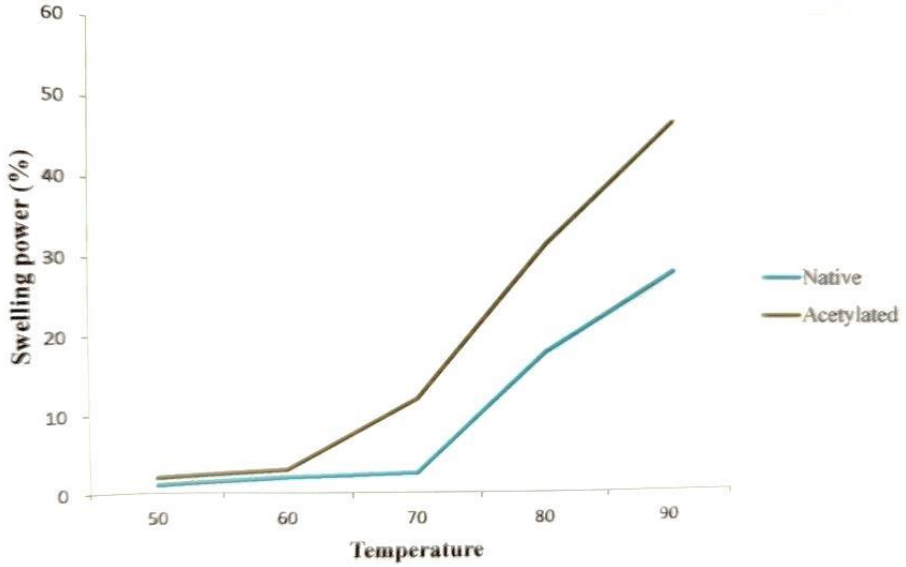

Figure 4: Swelling power comparison of native and acetylated starch at various temperatures

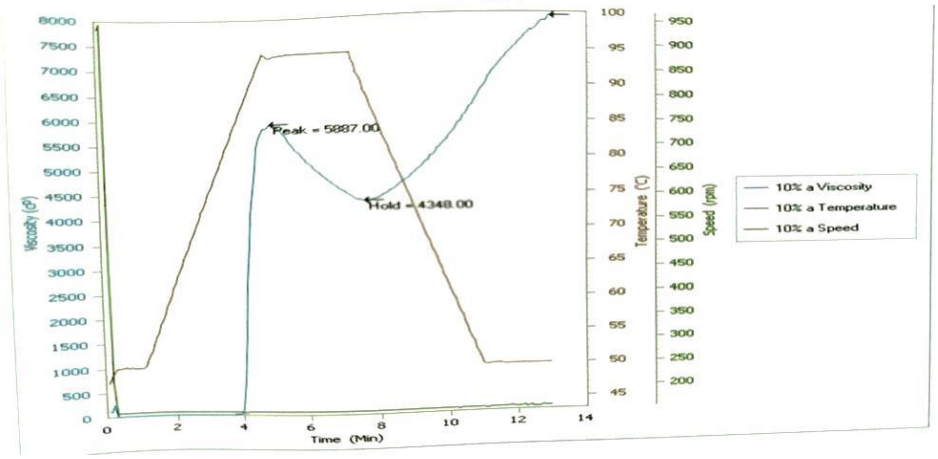

Figure 5: Pasting curve analysis of native pigeon pea starch

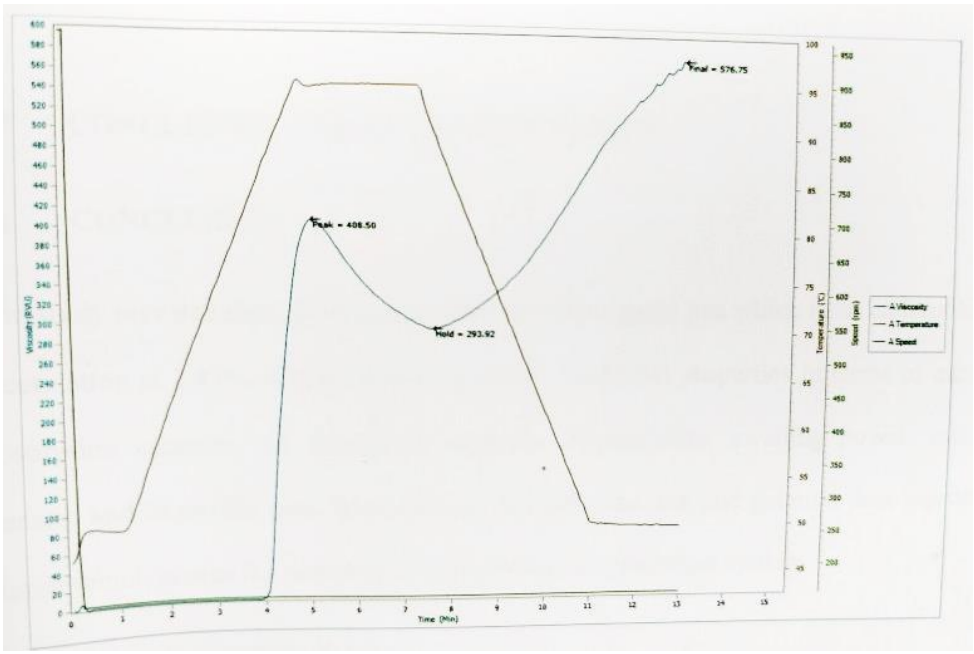

Figure 6: Pasting curve analysis of acetylated pigeon pea starch