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Research Article

LYE-Peeling of Cassava Roots

I. Process Optimization of Lye-digestion of Cassava Peel-specimens

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ABSTRACT

Significant dimensional changes resulted when swelling and ballooning induced by lye-treatment of strips of cassava-peel were compressed in a hollow-roller-cylindrical-compression-press (HRCCP-device). The dimensional changes were measured and applied to compute an index of cassava peel structural collapse (ICPSC) or deformation. 81 specimens (sample segments) of the peel of TME-419 cassava variety (12 months after harvest) were subjected to a factorially-designed-experimental protocol involving strip-immersion in 3 lye-concentrations at 5-temperatures over residence time-intervals between 2 and 60 minutes. Zero-order kinetic parameters (k_T, Q_{10} and Ea) values were generated from the data collected. The results clearly demonstrate a pattern of systematic correlation (within 99 % confidence limit) of ICPSC-values with sequential progression of the disintegrative breakdown of cassava peel from inception of immersion in lye to total collapse, resulting in a totally liquified-digest-sludge or pulp, such that when:

(a). ICPSC = 1.0: peel breakdown was just complete/adequate to ease total peel-removal from root;
(b). ICPSC < 1.0: peel breakdown was incomplete/inadequate for total peel-removal; and
(c). ICPSC > 1.0: peel breakdown was excessive leading to proportional loss of root starchy-flesh-tissue when peel is on the root during actual lye-peeling proper.

Compared to the relative complexity and high cost of sophisticated methodology of modern chemical analysis as applied in the study of cellulose chemistry and technology, the CPM-model and protocol as applied offer significant advantages in time and cost-savings to Food Engineering practice.

Keywords: Cassava root, peel-lignocellulose-complex, chemo-physico-mechanical (CPM) model-system, index of cassava peel structural collapse (ICPSC) or deformation, hollow-roller-cylindrical-compression-press (HRCCP), lye, starchy-flesh-tissue of peeled cassava root.

1. INTRODUCTION

1.1. Food, agro-economic importance of the cassava crop and its processing

Cassava (Manihot esculanta Crantz) is a very important root crop of the tropical and sub-tropical ecosystems of the world. It is only second to the cereal crops as a primary source of energy, industrial starch and livestock feed in countries where it is a food staple (Nweke *et al.*

2002; FAO 2010, 2012; Onabulu, 2001; and Benesi *et al.*, 2004). Nigeria is the world's largest producer of cassava with an estimated annual output of 26-million tonnes representing 25 % of the global and 60 % of the African crop. As a result of recurrent drought and associated food shortages in Africa, NEPAD (the new partnership for African development), an initiative of the European Union, identified cassava as one of its key mandate crops to reduce over-dependence on cereals and legumes (Fermont, 2009). Cassava root is the most perishable of the tropical root-and-tuber crops. It deteriorates within just two or three days after harvest as its useful starchy-flesh-tissue rapidly succumbs to attack by a variety of biological, chemical and biophysical agents of spoilage. Consequently strategic processing of the root immediately after harvest is necessary to transform it into more stable and palatable products that are easier and less-costly to transport and market. Cassava processing embraces a wide range of selective unit operations that include washing, peeling, size-reduction of a variety of types, separation methods involving extraction, dewatering, refining; fermentation; heat-treatment involving cooking, toasting, garifrying, drying, etc. depending on the end-product desired. Over the years, much progress has taken place in the mechanization of these unit operations. However, specific mechanization of cassava root-peeling, which is a preliminary-preparative step of the process and is fundamental for the achievement of any measurable degree of process-efficiency and defining product-quality and safety in every case, remains the greatest single worldwide technological challenge confronting cassava processing (Kolawole *et al.*, 2010; Oluwale and Adio, 2013; Egbeocha *et al.*, 2016; Kheiry et al, 2014).

1.2. R and D challenges and progress in mechanized cassava peeling

The fundamental reason for the unsatisfactory state of technical-progress in developing effective mechanization systems for cassava root-peeling is the extreme irregularity and non-uniformity of the root shape-and-size, its surface physiographical-contour and differences in peel thickness-and-tackiness. In consequence, despite all the mobilized R-and-D attention directed at mechanized cassava peeling over the last 40-years or so, hand or manual-peeling by rural women and their children estimated at the output rate of 25kg/h. only per capita remains not only the dominant but also arguably the most effective method of cassava-peeling for both domestic and industrial purposes (Odigboh, 1983; Anekwe, 1984; Nweke *et al.*, 2002; Egbeocha *et al.*, 2016). Much of the significant progress in mechanized cassava peeling has focused on the development of abrasive-type peelers. Without exception, abrasive-type peelers made locally and /or imported from China for small, medium and large-scale peeling of cassava roots in Sub-Saharan Africa and elsewhere, are both inefficient-and-ineffective because, by its very nature, the abrasive peeling mechanism cannot, *ipso facto*, navigate around the problem of irregularity and non-uniformity of shape, size and physiographical-contour of the root surface (Egbeocha *et al.*, 2016; Akoz et al, 2018). At their best, abrasive peeling machines can only achieve 70 % or less of peel-removal efficiency. Therefore, they demand significant hand-trimming of imperfectly peeled surface-fractions of the roots as they are discharged from the machine. In addition to its poor peel-removal efficiency, root irregularity predisposes cassava roots during peeling to unduly high levels of loss of the starchy-flesh-tissue. The combination of these two negative factors makes abrasive peelers generally inefficient-and-ineffective. These factors are exacerbated when abrasive peeling machines operate at high speeds and high rated-capacities (Odigboh, 1976a; Kolawole and Agbetoye, 2007; Oluwole and Adio, 2013; Savenkova et al, 2018). One response to these challenges which has received scant research attention by investigators is the lye-peeling of cassava roots.

1.3. The advantages of mechanized lye-peeling of cassava

Only a handful of disappointingly and largely dismissive studies have been reported in the literature on the lye-peeling of cassava roots (Wurdemann *et al.*, 1976; Igbeka,1985; Screenparayanan *et al.*, 1995; Deguchi *et al.*,

2006; Bakere *et al.,*2011) However, a recent exhaustive Master of Engineering (M.Eng.) degree thesis investigation by Tsekwi (2018) at the University of Uyo-Nigeria, has for the very first time ever, sought by experimental-empiricism, to explore and address the fundamental lignocellulosic nature of the peel of the cassava root. The lacuna created by the continuing absence of adequate insights into the composition and chemistry of the peel of the cassava root as a basic protective structural bio-material of every agricultural crop, has proved to be a serious neglect of past efforts to peel cassava, as indeed, decoat any other seed crop for that matter, by chemical treatment. Such understanding, needless to say, is a necessary pre-requisite for any attempt at the systematic optimization of lye-peeling proper in all relevant food crops. Mechanized lye-peeling of cassava roots has the following advantages over other methods. (i) As a liquid, lye invades the total surface of the cassava root when fully steeped in it uniformly and holistically, irrespective of size, shape, age, variety and whatever other differences or imperfections of root surface physiographical-contour or configuration including bends-and-crevices that may occur on the root. (ii) Three process variables (lye concentration, temperature, and residence-time-interval of immersion) can be readily manipulated using factorial-experimental-design methodology to optimize the lye-treatment process in order to achieve the highest possible process and product efficiencies as well as overall peel-removal effectiveness. (iii) Zero or near-zero loss of cassava root starchy-flesh-tissue can be achieved using previously optimized process parameters, followed by wet mechanical brushing-and-scrubbing.

1.4. Objectives of study in summary

The objectives of the study reported here are two-fold as serialized in two sequential papers (paper-1 and 2). The present report is focused on using a novel CPM-based kinetic model-system and protocol to monitor the hydrolytic digestion (or conformational-breakdown) process of strips of cassava-peel as distinct-entities (detached or removed from the whole root by careful hand-peeling), to determine optimal lye concentration(s), temperature(s), and residence time-intervals(s) of immersion to achieve measurable and progressive disintegration of the structural-conformation of the cassava peel-lignocellulose-complex, transforming it at collapse (or complete deformation), into a liquified-digest-sludge or pulp conducive to easy removal by scrub-brushing. Paper-2 will apply the findings of paper-1 on the whole cassava root with its peel *in-situ*, on the root to identify the optimal conditions for successful and total peel-removal, with zero or near-zero loss of root starchy-flesh-tissue and no heat ring.

2. Theoretical foundation of experimentation and analysis

2.1. Anatomy, Structure and Cell-wall Morphology of the Cassava Root

Figure-1 shows the profile of the cassava root (1a) and its transverse cross-section (1b). The root has a central fibrous core, the pith; surrounded by a white or cream starchy-flesh-tissue of parenchymatous cells that constitute the bulk of its main food storage organ, which is adjacent to and surrounded by a cambium layer of meristematic cells surrounding which is the peel of the root (Duckworth, 1966; Phirke, 2007). The peel has two distinct layers: an inner whitish cortex (1.2 to 4.15-mm thick) and an outside periderm composed of thin layers of brownish dead-corky-cells (less than one-tenth the thickness of the cortex) which protectively seals the root surface against water loss and possible invasion of predator biological agents (Dutta, 1981; Adetan *et al.,* 2003; Olomo and Ajibola, 2006).

As the root increases in size and diameter, the outermost portions of the periderm slough-off and are replaced by new cells; while the cortex becomes thicker and more rigid. It achieves this in an array of coaxial layers of cellulose-fibrils embedded in an amorphous matrix of hemicelluloses, lignin and pectic-substances (consisting of sols, gels and gums) mixed together to form a lignocellulose-fiber-complex. The fibres are first generated in the primary (or first) wall (designated P) which is very thin, followed coaxially by a sequence of secondary walls (designated S1, S2 and S3) around the

lymphatic channel (lumen) adjacent to the cambium layer (Soper, 1997).

2.2. Some helpful insights into the chemistry of cassava peel-lignocellulose-complex

According to Bogstrom (1969), the protective bio-structural tissues of plant food materials are lignocellulosic in nature. Therefore, the protective-covering of the cassava root is fundamentally a peel-lignocellulose-complex.

Figure-2 shows the chemical structures of lignocellulosic moieties which compose the complex, namely: (a) colloidal-emulsions chiefly of the oligosaccharide-moeity consisting of, but not limited to, sols, flocs, gels, gums and pectic-substances; (b) lignins; (c) hemicelluloses; (d) celluloses (Wills, 1989 and Wills et *al.,* 1996).

Sols , flocs, gels, gums and pectic-substances occur as extrudates, mucilages , essential oils and resins, which may exist as complex salts of organic acids transformable by heat and/or chemical treatment into liquid, semi-solid or solid phase with cementing properties of their own as entities and/or in combination with other bonding-substances.

Lignin forms a cementing matrix with sols, flocs, gels, gums, pectic-substances and hemicelluloses to bind cellulose fibrils in the fibre-structure. Lignin is a high alkyl-aromatic amorphous polymer with a high degree of polymerization (DP). It is easy to remove from the macroenvironment of the fibre-matrix of cellulose by aqueous alkali solvents, but not from the micro-environment of the macro-fibrils. When lignin reacts with solvent-chemicals, it produces dark-brownish soluble derivatives.

Hemicelluloses are polysaccharides associated with but less complex than cellulose in the protective structure of plant tissues. As amorphous copolymers of one or more sugars (e.g. xylose, mannose, arabinose or galactose) combined with uronic acids, their average molecular weight and therefore DP is low (about 100-200). They are hydrophobic, swell on water absorption and fairly soluble in aqueous alkaline or acid solvents which readily separate them from cellulose in their cellulose fibre-matrix, producing dark-brown coloured breakdown and/or derivative fragments.

Cellulose is the primary backbone of the protective bio-structure of plant tissues. It is a linear polysaccharide (C_6 H_{10} O_5) bio-polymer of glucose units formed by β-1, 4 linkages, quite different from the more easily hydrolysable α-1, 4 linkages of the starch molecule. Cellulose has a high DP (3,000-15,000 and above). It occurs in two forms, an amorphous paracrystalline-region composed of flexible mass of cellulose-chains which is more susceptible to chemical treatment; and the crystalline-region composed of tightly-packed bundles of cellulose-chains in rigid linear arrangement. Cellulose is insoluble in water and highly resistant to oxidative reduction (oxidation) and dissolution in aqueous alkaline or acid solvents. It exhibits no thermoplasticity or thermosetting properties and does not melt below its degradation temperature (Wang, 2008).

2.3. The chemo-physico-mechanical (CPM-model) system approach for monitoring cassava peel structural deformation to collapse

As the skin-covering of edible food crops, the peels (of fruits, vegetables, roots and tubers) and the seed-coats (of cereal and legume grains, nuts and oil-seeds) are examples of plant protective bio-structural tissues. As such, they are lignocellulosic in nature (Brogstrom, 1969).

It remains therefore something of a mystery that despite its long history that dates from the 1800s, when lye was first applied to de-coat corn hominy in the form of a solution of leachings from wood ashes, the technology and practice of lye-peeling failed to take cognizance of the basic cellulosic composition of seed coats and peels of edible food crops (Cruess, 1958; Watson and Ramstad, 1987).

For this and other reasons, research in lye-peeling, as its practice, appears to have developed more by the dictates of the specificities of trial-and-error. In the specific case of lye-peeling of cassava roots, much of the scanty research effort reported in the literature have been conducted by food and agricultural engineers dating from 1976 (Wurdemann *et al.*,1976; Igbeka, 1985;

Screenpparayanan *et al.*,1995; Bakare *et al.*, 2011). At best, the character of these studies have tended to be phenomenological rather than diagnostic and, often times, even dismissive of the practicability of the method until a recent M.Eng. (Master of Engineering degree) study by Tsekwi (2018) at the University of Uyo, Nigeria, which appears to be the first attempt ever to recognize the peel of the cassava root as a peel-lignocellulose-complex; and therefore, the systematic study of the complex must either engage the analytical tools of cellulose chemistry or find ways to navigate around the complex sophistry of modern methods used by polymer chemists via the exploration of methods such as what we now designate as the CPM-model system.

The chemo-physico-mechanical (CPM-model) system derives from empirical observations of the swelling which occurs when a strip of the peel of cassava root, after physical detachment from the root as an entity, is immersed in aqueous solution of NaOH (lye). The hollow-roller-cylindrical-compression-press [HRCCP-device] (Figure-3) was improvised as a tool that can be applied to systematically track and monitor the deformational effect of swelling, if allowed to progress to the collapse of the lignocellulosic structure of the peel.

Compression of swollen strips of the peel following immersion-and-withdrawal from lye of varying concentrations and temperatures for determinant time-intervals of immersion demonstrated clear reproducible patterns with progressive structural deformation of the peel-lignocellulose-matrix to eventual collapse of its fabric.

Linear dimensional-change measurements recorded from candidate sequences of:

[peel-immersion ⟶ peel-withdrawal ⟶ compression-to-collapse] were used by adapting the methods of Richard (2002) and Zhang (2012) to define and compute two factors as follows:

(a) Total deformation of cassava peel specimen at collapse (TDPSC), such that:

$$TDPSC = [t_{swps} - t_{swpsc}] \text{ (mm)} \quad (1)$$

(b) Index cassava of peel structural collapse (ICPSC), such that:

$$ICPSC = [TDPSC/t_{rcps}] = [(t_{swps} - t_{swpsc})/(t_{rcps})] \text{ (dimensionless)} \quad (2)$$

Where:

t_{swps} = thickness of the swollen peel-specimen after lye-treatment (mm);

t_{swpsc} = thickness of swollen peel-specimen after compression (mm);

t_{rcps} = thickness of raw cassava peel-specimen before lye-treatment (mm).

Plotting ICPSC-values against correspondent time-intervals of lye-treatment at designated concentrations and temperatures resulted in a system of reproducible linear zero-order kinetic plots. From the slope of each plot, the correspondent value of the kinetic rate constant (k_T) of hydrolytic digestion was computed.

Values of k_T so calculated were applied in accordance with equation-3 to compute correspondent values of the temperature quotient (Q_{10}) of the hydrolytic digestion, such that:

$$Q_{10} = [k_T/k_{T+10}] \quad (3)$$

Values of K_T and Q_{10} were thereafter applied to compute correspondent values of activation energy (E_a) of the hydrolytic breakdown process in accordance with equation-4 (Rao, 2005; Lee *et al.*, 2008; Tsekwi, 2018), such that:

$$E_a = [\log Q_{10} \times T(T + 10)/ 0.522] \quad (4)$$

3. MATERIALS AND METHODS

3.1. Materials

Materials used in the study were as follows: fresh raw cassava roots of the TME-419 variety harvested 12-months after planting at the University of Uyo farm, Nigeria. Chemical used was: sodium hydroxide pellets (NaOH), obtained at chemical supply stores in Uyo town. Water was used as tap and distilled water from the Food Engineering Laboratories, University of Uyo.

Laboratory equipment used include standard items and wares such as wooden spatulas, plastic bowls, conical flasks, pipettes and beakers, stop watch, hand fibre-brush, measuring cylinders (plastic), spectrophotometer (UV/Vis DO-83070-73 made in China), thermometers (mercury in glass type), protective hand-gloves (plastic), cooking pots assembled as

lye-immersion baths heated on gas, kerosene-stoves or electric heater, Mettler balance (electronic), measuring calipers (electronic),sharp stainless steel cutting knives; and an improvised hollow roller cylindrical compression press (HRCCP) described here-under.

Figure-3 is an improvised hollow roller cylindrical compression press (HRCCP) device developed from mild steel cylinder of mass 10-kg and dimensions [ID=15.3-cm, OD=19.1-cm, length=13.5-cm, and rolling force=7.26-N/cm] improvised as a quantifiable rolling force to be carefully rolled-over detached segments of cassava peel, one at a time, while mounted on a flat hard plastic cutting-board surface of dimensions [length=50-cm, width=30-cm and thickness=0.7-cm].

3.2. Methodology

A factorially designed work-plan was employed to generate 81-samples of lye-treated cassava peel-specimens.

To prepare the samples, cassava peel was detached carefully by hand-peeling from thoroughly washed wholesome fresh roots. The peel was cut into uniformly-sized sample-segments using a sharp knife. Each segment (in triplicate-samples) was subjected to lye-treatment by immersion in NaOH-solution embracing a compass of: 3-concentrations (25, 30 and 35 %), 5-temperatures (32, 50, 103, 105 and 108 ^{O}C) and 3 residence time-intervals of immersion ranging between 2 and 60-mintues.

Following withdrawal from lye-treatment, each swollen peel-specimen was compressed to collapse in the HRCCP-device (Figure-3). This was conducted by carefully rolling the steel hollow-cylinder over the full length of the specimen mounted flat on the hard plastic cutting-board. Careful measurement of specimen thickness using electronic calipers was taken on each specimen (in triplicate samples) before immersion in lye, following its withdrawal from lye and after compression in the HRCCP-device. Figure-4 is a simplified flow diagramme of the experimental protocol involved.

From recorded dimensional-change data collected on specimen thickness, two factors, namely: TDPSC and ICPSC were calculated respectively, using equations-1 and 2 (section-2.3). Values of ICPSC were plotted against correspondent residence time-intervals of lye-treatment to obtain k_T-values which were thereafter used to compute Q_{10}-values in accordance with equation-3. Values of k_T and Q_{10} were used to compute E_a-values in accordance with equation-4.

The model can lend itself readily for problem-solving in food engineering for exploring new opportunities that are opening up in cellulose science, engineering and technology as the potential of cellulose as the largest single renewable and exploitable bio-material of the plant kingdom becomes more apparent.

4. RESULTS

4.1 The effect of lye wetting and penetration into cassava root peel-specimens

Upon immersion of cassava peel-specimens in lye, the specimens absorbed the lye which simultaneously wetted and penetrated into the samples. One observed outcome of this process was a progressive change in colour of the hitherto colourless lye into an increasingly brownish liquid which became darker-brown with successive samples, their replications and withdrawals and with solution make-up using solid pellets of NaOH.

4.2 Swelling of cassava peel-specimens in lye (NaOH-water) aqueous solvent system

Figures-5, 6 and 7 show characteristic features of the peel-specimens following their withdrawal from lye-treatment at the respective temperatures of 32 and 50^{O}C; and at boiling point temperatures of 103, 105 and 108^{O}C corresponding to the 3 lye concentrations of 25, 30 and 35% employed in the study.

4.3 The effect of lye concentration, temperature and residence time-interval of immersion on the hydrolytic digestion of cassava peel as manifested in the index of cassava peel structural collapse (ICPSC)

Table-2 presents the averaged summary of recorded values of the ICPSC-parameter showing the effect of lye concentration, temperature and residence time-interval of immersion on specimens of the peel of cassava root during lye-treatment of peel samples

carefully removed by hand from the root prior to immersion in lye. The degree or extent of the associated hydrolytic digestion by lye is expressed as an index of cassava peel structural collapse (ICPSC).

4.4 Definition of lye-peeling effiency index (LPEI) and its relationship with ICPSC values

Using hand-peeling as the standard method for cassava root peeling operations, Wurdemann *et al.* (1976), Adetan *et al.* (2003), Olukunle (2007) and Bakere *et al.* (2011) defined a peeling efficiency index for any mechanized peeling method in competition with (or when compared to) hand-peeling on the basis of a universalized dimensionless ratio expressed as follows:

$$\left\{ \frac{\text{Root loss (\%) by Hand-peeling}}{\text{Root loss (\%) by Mechanized-peeling Method}} \right\} \quad \text{(dimensionless)}$$

Applying this formulation specifically to lye-peeling, led to the following expression:

LPEI = [(mphp/mrcr)] [(mpllp/mrcr)] = [(mphp/mpll)] (5).

Where:

mplhp = mass of peel-loss from hand-peeling [kg]

mrcr = mass of raw cassava root [kg]

mpllp = mass of peel-loss from lye-peeling [kg]

LPEI = lye-peeling efficiency index [dimensionless]

By definition therefore, the generic character of the LPEI factor was a numerical value which straddled the figure 1.0 such that when:

(a) LPEI= 1.0: lye-peeling was adequate (complete) because its peeling loss (%) was equal to the loss (%) of hand-peeling.

(b) LPEI< 1.0: lye-peeling was inadequate (incomplete) because its peeling loss (%) was less than the loss (%) of hand-peeling.

(c) LPEI>1.0: lye-peeling loss was excessive because the peeling loss (%) exceeded that of hand-peeling leading to proportional loss of the starchy-flesh-tissue of root below the peel.

Now recall the definition of ICPSC from equation-2 (section-2.3) which expressed the quantity as:

$$\text{ICPSC} = \left\{ \frac{\text{TDPSC (total deformation of cassava peel-spicemen at collpase) mm}}{\text{trcps (thickness of raw cassava peel-specimen) mm}} \right\} \quad \text{(dimensionless)}$$

Thus, ICPSC was a measure of the extent of hydrolytic digestion (or disintegration or degradation) of peel-specimens at collapse during lye-treatment.

As reported earlier, Table-2 recorded values of ICPSC that range from 0.62 to 1.55, which confered on it, a generic character straddling the figure 1.0 in such a way that when:

(a) ICPSC = 1.0: deformation at collapse was total (complete) so that lye-peeling loss (%) was equal to hand-peeling loss (%).

(b) ICPSC < 1.0: (between 0.62 to 1.0) deformation at collapse was incomplete translating to inadequate peel-removal so that lye-peeling loss (%) was less than hand-peeling loss (%).

(c) ICPSC >1.0: (between 1.55 to 1.0): deformation at collapse is excessive being greater than 1.0 suggesting that lye-peeling loss (%) exceeded hand-peeling loss (%) leading to proportional loss of the starchy-flesh-tissue of root below the peel.

In conclusion, ICPSC and LPEI were generically similar parameters with ICPSC being the precursor of LPEI.

4.5 Selection of optimal process variables or parameters for lye digestion of the peel of cassava roots using ICPSC-values as the choice criterion

As stated earlier, Table-2 provides recorded values of ICPSC in summary relating to all 3 process variable-combinations (81 of them) employed in the experiments.

ICPSC-values were plotted against the corresponding residence time-intervals of immersion used to generate Figures-8, 9 and 10.

Interpolating around ICPSC-values closest to 1.0 (not below it and not excessively greater than it) starting from Table-2 and navigating Figures-8, 9 and 10, furnished the following set of candidate-parameters tabulated in Table-3 as the optimal or near-optimal values for lye-digestion of cassava peel-lignocellulose-complex.

4.6 The kinetics of cassava peel structural collapse (CPSC)

Table-4 presents the averaged summary of values of the reaction rate constant (k_T); values of the temperature quotient (Q_{10}) and values of the activation energy (E_a) recorded from the study.

As stated earlier, k_T-values were calculated from the respective slopes of Figures-8, 9 and 10. The values so calculated were applied by interpolation and extrapolation to generate the values in the table. Q_{10}-values were calculated using equation-3 and Ea-values were calculated using equation-4.

5. DISCUSSION

5.1. Effect of Lye Wetting and Penetration into Cassava Root Specimen

Phenomena of lye wetting, penetration and absorption into the cassava peel specimens with the formation of brown clouration that resulted are in agreement with the findings of Lee *et al.* (2008) about the colour of alkali soluble and reactive moieties of lignocelluloses which are easily removed from the cellulose-matrix producing dark-brown colouration. The components which bind cellulose fibres in the matrix include colloidal emulsions (sols, flocs, gums, resins, pectic-substances, etc.), lignin and hemicellulose-associated oligosaccharides. According to Wang (2008), the dislodgement and removal of these substances from the environment of the macro-matrix of cellulose fibres allows more direct access of the solvent for attacking the cellulose fibres.

5.2. Efffect of swelling of Cassava Peel-specimens in Lye

Swelling of cassava peel-specimens in lye (NaOH-water) aqueous solvent system from ordinary visual observation of the photographs of the specimens suggested that at the lower temperature range of 32 and 50^{O}C and in-between, the peel-specimens swole, exhibiting a defined spiral shape irrespective of lye-concentration (see Figures-5 and 6). However, the mechanism of heterogeneous swelling of cellulose is complex as it involves so-called ballooning phenomena expatiated extensively by Zhang *et al.* (2013) for cotton cellulose fibres.

In that case, it is explained that structured shapes of collars, rings or spirals result from differential swelling-induced expansion of cellulose fibres in the secondary and primary walls. In the secondary wall, the microfibrils are aligned in a helical manner with respect to the long-axis of the fibre and swelling of the fibre is greater in the transverse (radial) direction than lengthwise. Therefore, the larger radial expansion of cellulose in the secondary wall causes the primary wall to burst, tearing its membranes. As expanding swollen cellulose pushes its way through the tears in the primary wall, it rolls up at the edges forming collars, rings and spirals. These structural shapes, by their very nature, impede further uniform expansion of the cellulose fibres and therefore generate balloons at selective sites of the cellulose-mass, which possibly exacerbate the shapes. Without the aid of optical microscopy, the ability to gain better direct insights from these observations was restrictive in the context of this study.

Figure-7 showed contrasting photographs at higher temperature lye-treatment of cassava peel-specimens following withdrawal from boiling lye at 25 % concentration (103 ^{O}C), 30 % concentration (105 ^{O}C) and 35 % concentration (108 ^{O}C). Visual inspection of the photographs of these specimens uniformly contrasted significantly from those of the

samples treated at lower temperatures as discussed earlier. No spiraling structured shapes (curls, rings or collars) were evident. However, a pattern of heterogeneous bumps (convexic protrusions) characterized the surface of the specimens, suggesting that ballooning occurred at selective sites of the samples. In general, expansion induced by swelling was much larger than observed at the lower temperature range, and obviously occurred more rapidly at boiling temperatures featuring much higher convective heat transfer coefficients induced by mixing turbulent bubbles of the solution.

Given the combined incidence of swelling with ballooning observed in all samples in the study, it made sense to try to explore the possible mechanism by which peel digestion (or disintegrative-degradation) of the cellulose-mass in cassava peel-lignocellulose-complex would have occurred with or without dissolution.

The process was described earlier as characterized by cassava peel structural collapse (CPSC) and calculated as an index of cassava peel structural collapse (ICPSC) associated with the process. Zhang *et al.* (2013), citing a wide range of foundational support for their findings, suggest five modes by which the hydrolytic breakdown process that can ultimately result in dissolution for wood and cotton fibres occurs in an alkali solvent system such as lye. The five modes are as shown in Table-1.

The 5-modes reflect the status of solvent quality which decreases from mode-1 to 5. Studies by Zhang *et al.* (2013) and others cited in their paper, suggest that the digestion mechanism proceeds in such a way that the solvent first wets and penetrates inside the fibres through the primary wall of the cellulose which acts as a semi-permeable membrane. The cellulose-chains of the secondary walls swell and break the primary wall exceeding its elastic limit.

Findings reported by Wang (2008) and Zhang *et al.* (2013), suggest that (NaOH-water) solvent system is, in relative terms, weak and may not always lend itself to swelling and ballooning leading to outright bursting of wall membranes. It may only swell and balloon the fibres to a certain level of maximum expansion smaller than indicated for mode-2 and stop without bursting and/or dissolving the fibres completely.

By mere visual observation using the naked eyes without the advantage of optical microcopy, only cautious conclusions were possible from the inspection of the photographs of lye-treated cassava peel-specimens. These were to the effect that at the comparatively high lye concentrations and temperatures (relative to the levels reported in the literature) at which the present study was conducted, only mode-3 of the scheme in Table-1 appeared to be relevant or to apply, with the important difference (a caveat), to the effect that the large levels of swelling and ballooning which were observed in all cassava peel-specimens, involved a systematic pattern of disintegration of the macro-structure of the gross-mass of the cellulose (not necessarily the fibres) possibly with minor dissolution resulting in a digest-sludge or pulp which, if it were to occur in the peel of cassava roots while (*in-situ*) on the roots, would be easy to scrub-off by wet brushing by hand and/or mechanically.

For purposes of effective cassava peel-removal only during lye-peeling, which was the goal of this study, these explanations seemed satisfactory even without significant levels of dissolution or derivatizatiion of the cellulose fibres. One seemingly important implication of this finding could be that the type of cellulose associated with the peel of the cassava variety and age employed in this study had a low degree of polymerization with (DP < 200), which had poor crystallinity, was paracrystalline and amorphous in character.

5.3. Effect of Lye-treatment on ICPSC at Varying Concentration, Temperature and Residence Time-interval of Immersion

Statistical analysis by ANOVA of the effect of lye concentration, temperature and residence time-interval of immersion on the hydrolytic digestion of cassava peel as manifested in the index of cassava peel structural collapse (ICPSC) (see Tsekwi, 2018), showed significant differences ($p<0.05$) in the residence time-intervals of immersion recorded among the 5 conditions of temperature (32, 50; and the corresponding lye boiling points of 103, 105 and

108^{O}C) investigated when peel-specimens were lye-treated at the 3 designated concentrations of 25, 30 and 35%, respectively. The residence time-intervals of immersion recorded were 20, 40 and 50 minutes at 32^{O}C; 5, 7.5 and 10-minutes at 50^{O}C; and 2, 4 and 6-minutes at corresponding lye boiling points of 103, 105 and 108^{O}C, respectively.

Process Optima-options	Process Variables		
	Lye concentration (%)	Temperature (^{o}C)	Residence Time-interval of immersion (Mins.)
1st optimum (a)	30	32	50
2nd optimum (b)	35	50	7.5

Figures-8, 9 and 10 were plotted on linear graph paper from the recorded values of ICPSC as a function of residence time-interval of immersion at 3 lye concentrations (25, 30 and 35%) and 5 temperatures (32, 50, 103, 105 and 108^{O}C), respectively. In and of themselves, the plots showed a consistent pattern of strong linear correlation between ICPSC-values and the residence time-intervals of deformation to collapse, which the CPM-model system defined as modeling the hydrolytic digestion (or disintegrative-breakdown) process of the peel-cellulose-complex to produce a liquidifed digest-pulp or sludge conducive for easy scrubbing using a brush.

The kinetics of cassava peel structural collapse (CPSC) presented in Figures-11, 12 and 13, respectively provided evidence of strong correlation between k_T-values, Q_{10}-values and E_a-values and temperature at all lye concentrations (25, 30 and 35%) investigated. Figure-11 showed that within the temperature range investigated, k_T-values increased rapidly with decreasing lye-concentration, peaking optimally for each concentration just below 60^{O}C ($\leq$ 60^{O}C) temperature, which instructively is the gelatinization temperature of cassava starch (Ezekiel *et al.,* 2007). This finding could be important for the lye-peeling of cassava roots because it suggested that, as much as possible, temperatures up to and higher than 60^{O}C should be avoided to avert the negative effect of gelatinization of the root starch in the environment of the peel due to excessive heat penetration into the root in the proximity of the cortex. In choosing from among the optimal parameters recorded in Table-3, this factor among others, must be taken into account; and indeed, it effectively disqualified Optima-option 3(c) which specified a temperature of 103^{O}C well above 60^{O}C (see entry at bottom of Table-3). Figure-12 showed that Q_{10}-values decreased with increasing lye concentration and temperature within the range of process variables investigated. On the contrary, Figure-13 showed that E_a-values increased with increasing concentration and temperature in the range of the variables investigated. These findings suggested that for cassava peel-lignocellulose-complex, hydrolytic digestion reactions with high activation energy are more temperature-sensitive, confirming earlier findings by Wang (2008) for cotton cellulose fibre dissolution in (NaOH + water) at low temperatures.

6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations can be drawn from the study.

1. A novel chemo-physico-mechanical (CPM-model) system for quantitatively tracking and monitoring the process of hydrolytic digestion (or disintegration) of cassava peel-lignocellulose-complex into a liquified-digest-sludge (or pulp) was developed, tested and successfully applied to .optimize 3-process variables [lye-concentration (%), temperature (^{O}C) and residence time-interval of immersion (minutes.)] involved in mechanized lye-peeling of cassava roots.

The protocol for achieving this involved the use of an improvised hollow-roller-cylindrical-compression-press (HRCCP-device) to generate and measure dimensional changes in swollen lye-treated cassava peel-specimens which were quantified to give an index of cassava-peel-structural-collapse (ICPSC-value). ICPSC-

values when plotted against residence time-intervals of lye-treatment, yielded zero-order kinetic parameter-values (k_T, Q_{10} and E_a) that provided a reliable basis of validation for the CPM-model system and its associated protocol as a viable approach for the manner of analysis which the study set out to explore.

2. The following tabulation presents 2-process optima-options (a and b) that resulted from the application of the protocol of the CPM-model system.

Further choice from among these options will be pursued in paper-2 of this series which, will report on their application for peel-removal proper from cassava peel (*in-situ*) while still on the roots, which constitutes the technique of mechanical lye-peeling.

3. In practical application, the ICPSC-values were used to signify and define 3-determinant levels of cassava peel hydrolytic digestion (or disintegration) that coincided with differential levels of peel-removal and their consequences as follows:

(a) ICPSC = 1.0: peel breakdown was complete or adequate leading to total peel-removal from root;

(b) ICPSC < 1.0: peel breakdown was incomplete/ inadequate because peel-removal from root is less than peel loss (%) in hand-peeling proper.

(c) ICPSC >1.0: peel breakdown was excessive leading to proportional loss of root starchy-flesh tissue during lye-peeling proper.

4. Because cellulose is the primary product of terrestrial bio-photosynthesis, it is the most abundant single renewable bio-polymer of the biosphere with an estimated yield of some 100-billion dry-tonnes per year of which less than 5-percent is currently exploited for fabric-material manufacture, energy, food and other uses. Food engineers, scientists, technologists and agricultural engineers have an important but, unfortunately so far hardly recognized role to play in the new and rapidly expanding frontier of cellulose resource exploitation. The CPM-model system as elucidated and elaborated in the paper, provides an alternative approach that could, down the line, complement the more complex and costly tools of modern polymer science, technology and engineering by which food, agricultural and bio-engineers can meaningfully make inroads into exploratory R-and-D in the study of multiple breakdown products of cellulose hydrolysis and derivatization to harness them for potential application in addressing challenges of the world food, hunger and poverty problem.

5. In particular, well over 100-million tonnes of lignocellulosic skin-covering of edible plant foods designated as peels (within the commodity group of fruits, vegetables, roots and tubers) and seed-coats (within the commodity groups of cereals, legumes, nuts and oil-seeds processing) are routinely wasted by industrial processing practice, which dumps them as discards with serious and compounding environmental consequences. Yet cellulosic biomass in this category can be a mine-field of opportunity for engineers if lye-peeling and lye-decoating can be more widely explored to generate exploitable lye-digested cellulosic by-products.

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