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Chapter

Cassava Biomaterial Innovations for Industry Applications

Kashub Steven Tumwesigye, Jorge C. Oliveira, Sheila Namuwaya and Maria Jose Sousa-Gallagher

Abstract

Breakthrough innovations can spur growth in the modern era industry to realise sustainability and high returns on investments. Nowadays, biobased innovations for application in diverse industry sectors are considered as future pillars to counter resource depletion and ensure positive environmental impacts. Cassava is a strong flagship biomaterial promoting solution for resource-efficient use and green environment. Innovative industrial application of cassava biomaterials enriches literature, presenting cassava as a versatile and unrivalled crop that is cardinal for more sustainable environment and biodegradable industrial products. Work on novel cassava biomaterials, which are low-cost, unexploited and with zero competition for food supply, are included. Using an integrated sustainable process, it shows how to indirectly reduce waste streams, through their effective use, guaranteeing zero carbon footprints and acting as a non-traditional strategy for equilibrium atmosphere and active packaging systems. Applications of Cassava biomaterial in food, as food supplements and in packaging systems are also covered in this chapter.

Keywords: Cassava biomaterial, waste, integrated process, biodegradable products, sustainable environment, packaging system

1. Introduction

"Breakthrough innovations" is a hot topic aimed at stimulating industry research towards realisation of bioeconomy, sustainability, and high returns on investments. Eco-friendly inequities exist due to rapid population explosion, continuous resource exhaustion, industry biomaterial supply concerns and linear model of produce-consume-dispose [1]. Ultimately, innovative research solutions have been sought to ensure sustainability along the entire food system [2] to address the above challenges. The research solutions have been mainly in biobased industries, notably renewable resources, a component of sustainable biobased industries. However, bio-industries are subjected to considerable technological innovations and sustainable alternative challenges. Thus, the trend is geared towards developing integrated biorefineries with the goal of achieving availability and flexibility of multiple feedstocks' low inputs and maximum outputs [3]. There are several waste resources that can be valorised to produce unmatched feedstocks for the sustainable biorefinery developments. Examples of current integrated biorefinery feedstocks and products include vegetable oils, high value-added bio-lubricants, cosmetics and bioplastics

obtained from low input and under-utilised oil crops, which are not in competition with food and feed supply [4]. Others include green, clean, post-use biodegradable, compostable and efficient alternative supplies.

Cassava resources are versatile biomass supply chains that are bio-transformed into industrial feedstocks to replace fossil oil product streams [5]. Their biopolymers' processing and products' development using traditional techniques is accompanied by significant wastes with negative environmental impacts [6]. Cassava is a higher producer of significant wastes (peel pulp, wastewater, and leaves) during postharvest processing. Nonetheless, a comprehensive impression of cassava biomaterials, covering a wide spectrum of novel processing technologies, and underutilised and low-cost biomass, is evident.

This chapter presents a thorough discussion of bitter cassava biomaterial innovations and novel processes for bio-transforming this low-cost underexploited crop. Use of an integrated sustainable process to indirectly reduce waste streams is demonstrated. A special focus is dedicated to production of biodegradable products from intact bitter cassava waste streams of nascent sector as promising feedstocks for application in food, supplement, and packaging systems. Ultimately, concretising the concept of innovative application of cassava biomaterials can be a useful resource for academia, industry, bioeconomy, and policy.

2. Bitter cassava

2.1 A versatile, unique, unrivalled, and resilient crop for biomaterials

Bitter cassava is an equivalent of sweet cassava. While sweet cassava is edible and safe for instant use in fresh and processed forms, bitter cassava is only safe for usage after intricate processing and is regarded as a staple food [6]. Bitter cassava roots contain high toxic hydrogen cyanide (HCN) levels above 100 mg/kg on fresh basis, even going beyond 900 mg/kg in tropical regions: with the minimum reference limit of 0.02 mg/kg on dry weight [7]. Increasing region-specific sweet cassava profiles as biomaterials for foods, feeds, pharmaceuticals, and confectionery industries have greatly augmented unparalleled investment into non-traditional underutilised crops [4, 8]. In East and Central Africa, bitter cassava varieties (such as Karangwa/Tongolo) have existed for decades. Anecdotal evidence points to the advantages of bitter cassava as a food and industrial crop with superior product (e.g., Flour and crude alcohol) qualities. Bitter cassava is highly preferred due to: i) its potential to be grown organically than sweet varieties because of their more toxicity levels deterring foraging rodents and pests from feasting on the crop; ii) imposing the need to process roots directly after they are harvested deters thieving from the field; and iii) as the processing adds value in terms of time invested, the social obligation of sharing cassava with neighbours is reduced [9].

2.2 Inherent challenges present unique opportunities for its exploitation

Due to high potential cyanide content in bitter cassava, the code of practice allows adequate postharvest processing [10]. The appropriate postharvest processing, in particular fermentation, is effective in reducing HCN to minimum concentrations. Conversely, inadequate, notably using rudimentary techniques, leads to high HCN residuals in the final products. The peel (cortex) contains more HCN than edible portion (parenchyma) (**Figure 1**). As such the peels are frequently detached from the edible portion and discarded. This underutilised waste, estimated at 30% represents a great loss of feedstock and energy resources as well as potential

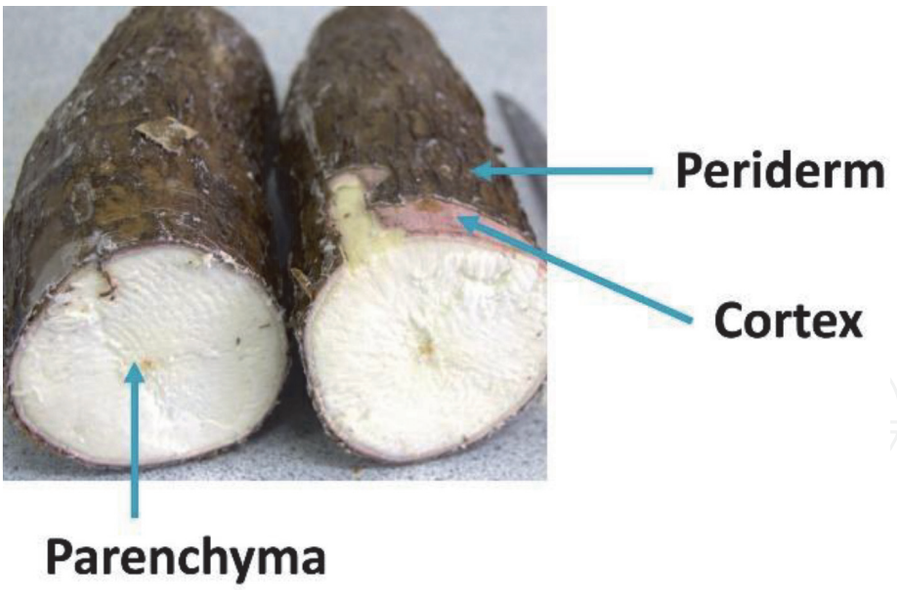


Figure 1.
Intact root showing different components.

source of eco-system contamination [4, 11, 12]. In major bitter cassava growing regions, it is transformed into primary, intermediary, and tertiary products using rudimentary fermentation processes. Traditionally, different detoxification processes, such as solid-state fermentation and retting in river ponds are used minimise HCN in bitter cassava [13]. This uncontrolled large-scale upstream and downstream process-fermentation into food and beverages contributes significantly to unsustainability, thus requiring valorisation [11, 14]. As the peel is disposed-off and its utilisation limited due to high HCN content, high fibre, and low protein; this presents exceptional opportunities to biotransformation into innovative biomaterials such as biodegradable plastics for diverse applications [4, 11, 15].

3. Bitter cassava biomaterial innovations

Cassava biomaterials are not restricted to only those produced with sweet cassava (such as food, pharmaceutical, beverage, coatings, civil works, textile industry), but emphasise biomaterials that are developed innovatively from bitter cassava wastes. Investments in bitter cassava biomaterial innovations are based on: i) the need to solve the increased environmental waste, which is caused by a linear and irreversible behavioural pattern that follows a produce-consume-dispose model; ii) innovations in biomaterial development, spurred by bitter cassava superior end-product qualities, that force nascent communities and processors to invest in the staple crop sustainably; iii) the need to reduce waste in environment and develop industrial products, in tandem, for a more competitive resource economy; and iv) solving issues of finite natural material sources and competition for food supply. Precisely, bitter cassava is a renewable resource with no competition for food supply, its valorisation minimises waste and environmental impact and is a cost-effective option.

To this end, a circular utilisation model is explored in tackling cassava biomaterial innovations. This strategy ensures that bitter cassava waste is transformed into value-added resources that later biodegrades into environment post-use, in a process of eco-designing of biomaterials for food and non-food applications.

3.1 A robust inventive process for sustainable cassava biomaterial production

Converting bitter cassava wastes into high premium resources demands an unusual approach, entailing departure from traditional cassava processing methods to robust processing methodologies. As such, a new systematic improved downstream processing methodology, known as "Simultaneous release recovery cyanogenesis (SRRC)" has been developed and piloted with success to ease downstream production of bitter cassava biomaterial as a template for diverse use [4]. The SRRC constitutes two main stages and unique procedures to produce a biopolymer derivatives biomaterial (**Figure 2**). The term "biopolymer derivatives" refers to the product recoveries from the intact root of bitter cassava, and these mainly consist of different proportions of starch, cellulose, hemicellulose, holocellulose and lignin [11, 16]. Waste derivatives are the product derivatives of waste solids and wastewaters.

3.1.1 Production of biopolymer derivatives biomaterial

Smart sourcing and preparation of starting materials is an indispensable step in the production of good quality, safe and adequate volumes of biomaterials. Bitter cassava is best sourced at maturity of 12–18 months after planting and should be designated as right harvesting time of adequate biopolymers. Using intact root (IR) is an indirect and logic approach of preventing wastes finding their way into the environment. The IR is a whole root of cassava that is composed of residues (peel, cambium, phloem, central xylem fibre) and edible parenchyma. The derivative wastes consist of the peel, internal root centre fibre (xylem bundles), unwanted trimmed solids and wastewaters. Using the SRRC methodology, intact roots are subjected to mechanical tissue rupture, biopolymer release and cyanide toxin loss. The processes typically involve feeding intact roots into automated grating machine

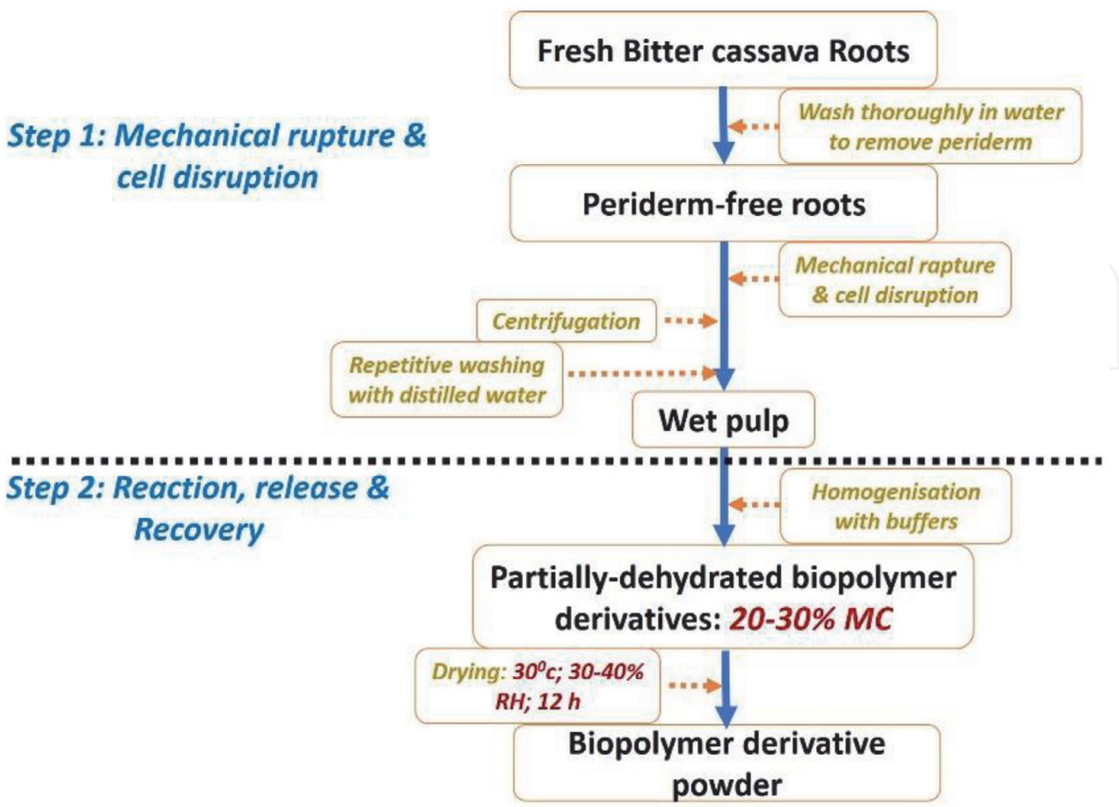


Figure 2.
Schematic flow of SRRC methodology for production of biomaterials.

and the resulting pulp mass obtained after mechanical tissue rupture and cell disruption (MTRCD). The MTRCD serves the twin role of actuating total cyanogens hydrolysis into release of volatile hydrogen cyanide and bringing together different biopolymer components for possible modification. In effect, the process involves crushing the intact root into finest pulp using high shear rate pulpers, which is also intended to improve the pulp texture and decrease the extraction time in the subsequent processes of release and recovery [16]. The biopolymer derivatives release is often achieved through homogenisation under the influence of extraction buffers (food grade NaCl and $NaHSO_3$), followed by filtration, centrifugation and washing in distilled water [4]. The derivatives recovery is realised by filtration, centrifugation, washing in distilled water, wastewater recycling and drying in a convectional laminar flow dryer. Resulting biomaterial powder is cooled and stored in airtight bags to prevent post-processing absorption of moisture as the derivatives powder is highly hygroscopic. Processing intact root using SRRC produces fibre-rich derivatives, which has been confirmed to offer better mechanical and barrier properties in the biomaterials [4]. Whether to use intact root or derived wastes depends on the envisioned final product; with edible bio-products, intact root is preferred while non-edible products (e.g., goods carrier bag, derived root residues) are the choice. During SRRC, an efficient mechanical pulping is crucial to achieve good quality (finer fibrous, 30–50 μm) and non-toxic (HCN threshold levels, near 0 ppm) biomaterials. Thus, a pulping efficiency (PE) of ≥90% was found to be sufficient when applied in pulping process using a time-dependent model (Eq. (1)) [16]. The PE of this magnitude is required because of the recalcitrant nature of most cellulosic fibre mass, which succumbs at higher shear rates. The achieved finer biomaterial powder (30–50 μm) is usually a result of softer cellulosic mass when compared to other woody plants.

$$S = 36144.36 + 33.11v - 875.74 \in + 0.01v^2 + 4.97 \in^2 \left(R^2 = 0.95\right) \quad (1)$$

S, pulping time; V, pulper velocity; Ɛ, pulping efficiency.

3.1.2 The SRRC unique outcomes

The SRRC concept restricts between 16 and 30% wastes disposed directly into the environment. This is achieved by processing fresh bitter cassava roots, and thus avoiding underlying costs, energy, time, intended and unintended disposal efforts, of additional alternative processes for waste management. The most economic SRRC design for sustainable valorisation of bitter cassava waste into value added biomaterials avoids the need to dispose indirectly wastes into environment leading to sustainability. The SRRC processing is a unique methodology concentrated at the early stage of the design (pulping, reaction, and release) to enhance biomaterial modifications, and therefore it can be applied in processes of sweet cassava waste and most crops' residues. The SRRC reduces the extraction time and improves biomaterial texture with nominal size of 30–50 μm (finer matrices) with potential for extensive application. The ≥90% PE confers total cells breakdown and disruption, ensuring that enzyme linamarase hydrolyses linamarin (precursor of cyanide related compounds) into HCN. Cyanogenesis process is proportional to PE, only achieved in SRRC and not common with traditional methods, ensuring the safety of biomaterials (HCN near zero) [11]. The total HCN loss can be attributed to the functionalised ionic buffers and bisulphite in solution (pH 5.0–5.5) during the reaction and release stage. The affinity of bisulphites for the ketones makes them unavailable. This creates the desired gradient leading to fast HCN loss and might explain the significant detoxification of biomaterials. Ketones are released together

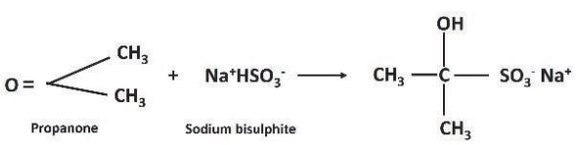
with HCN during linamarin hydrolysis. Concurrently, residual sulphur of the bisulphite forms complexes with HCN to form a non-toxic thiocyanate compound. This is a significant outcome of SRRC; in the absence of this process in traditional processing, there is partial detoxification with production of unsafe biomaterials that cannot be applied in industry. Strikingly, SRRC ensures better productivity of the biomaterials as illustrated by the optimised model [11]. The high yield (45.8% w/w) of biopolymer derivatives is attributed to ionic buffers converting nearly all root biomass into biomaterials.

3.1.3 Biomaterial (biopolymer derivative) properties

Biopolymer derivatives, a main biomaterial of SRRC and bitter cassava outcomes, can be used as a main ingredient in food, bioplastic, and packaging industries due to its compatible, biodegradable, polysaccharide-rich (starch, cellulosic fibrous, lignin), safety (0.4–2.5 ppm HCN), colourless (white) and particle size uniformity (30–50 μm and free-flowing) properties [4, 11, 15–17]. The biopolymer derivative is made available in powder form (**Figure 3**). The biomaterial colour is an impurity and often removed using rudimentary means in traditional processes. Nonetheless, the colourless characteristic of the biomaterial is achieved by reaction additives (sodium salts of bisulphites and ionic buffers) (Eqs. (2) and (3)), acting as bleaching agents. As indicated previously, compatibility was realised by combination and modification of different polysaccharides in the root during pulping and reaction processes. Biodegradable, polysaccharide-rich, toxin-free, and particle size uniformity are accomplished by using intact root and SRRC downstream processing. The amylose content of the biomaterial ranges between 18 and 24%, and higher corresponding amylopectin is attributed to inclusion of the peel waste and impact of SRRC on the peel structure [4].

The biomaterial powder is highly stable at moisture content of ≤5% but instability is often encountered when the powder is stored and handled under moisture content ≤10% because the powder is highly hygroscopic.

$$\text{Bisulphite } (HSO_3^-) \rightarrow HSO_4^- \tag{2}$$



(3)

The biomaterial has homogeneous particle sizes with round and polygonal shapes, and with slightly bigger round granule size [11].

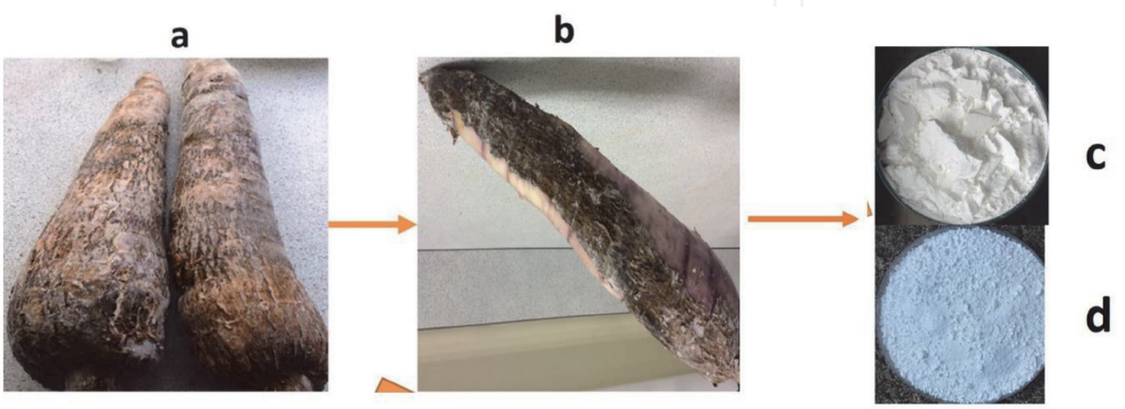


Figure 3.
Biomaterial route showing (a) intact bitter cassava root; (b) periderm-free intact root; (c & d) colourless biopolymer derivatives.

3.1.4 Production of polymeric film sheet biomaterial

Filmogenic solutions are prepared by using different proportions of the bitter cassava biomaterial powder, glycerol solution and distilled water (**Figure 4**). The resulting mixture is heated while agitated continuously until a gel is formed and turns clear. It is important that the gel is free from bubbles as they change the microstructure of the film sheet. Immediately, a known volume of the gel is cast onto glass plates and held shortly at ambient conditions to allow them to stabilise, concurrently bubble bleeding occurs. The stabilised gel casts are heated and maintained at known temperatures. The films are peeled off the plates and stabilised under environmental conditions of temperature and relative humidity.

3.1.5 Biomaterial (polymeric film sheet) properties

The physico-chemical characteristics of films (**Table 1**) perform a critical part in diverse end use systems, and knowledge of their properties is important in assessing package perform along the distribution chain. Intact bitter cassava-based films (BCFs) are transparent, with values as low as 3.6% than those obtained from starch of all botanical origin which posts 11.9% [4]. They are comparable to most commercial NatureFlex (4.6%) and Polylactide (3.9%), and much lower than polypropylene (13.6%). The low values tending to zero and higher values leaning to 100%, determined by spectrophotometric transmission and chroma lightness index respectively, indicate more transparency (**Figure 5a**). It can be confirmed that intrinsic modification of the intact bitter cassava root by SRRC produces more transparent films. Transparent films are important in many applications,

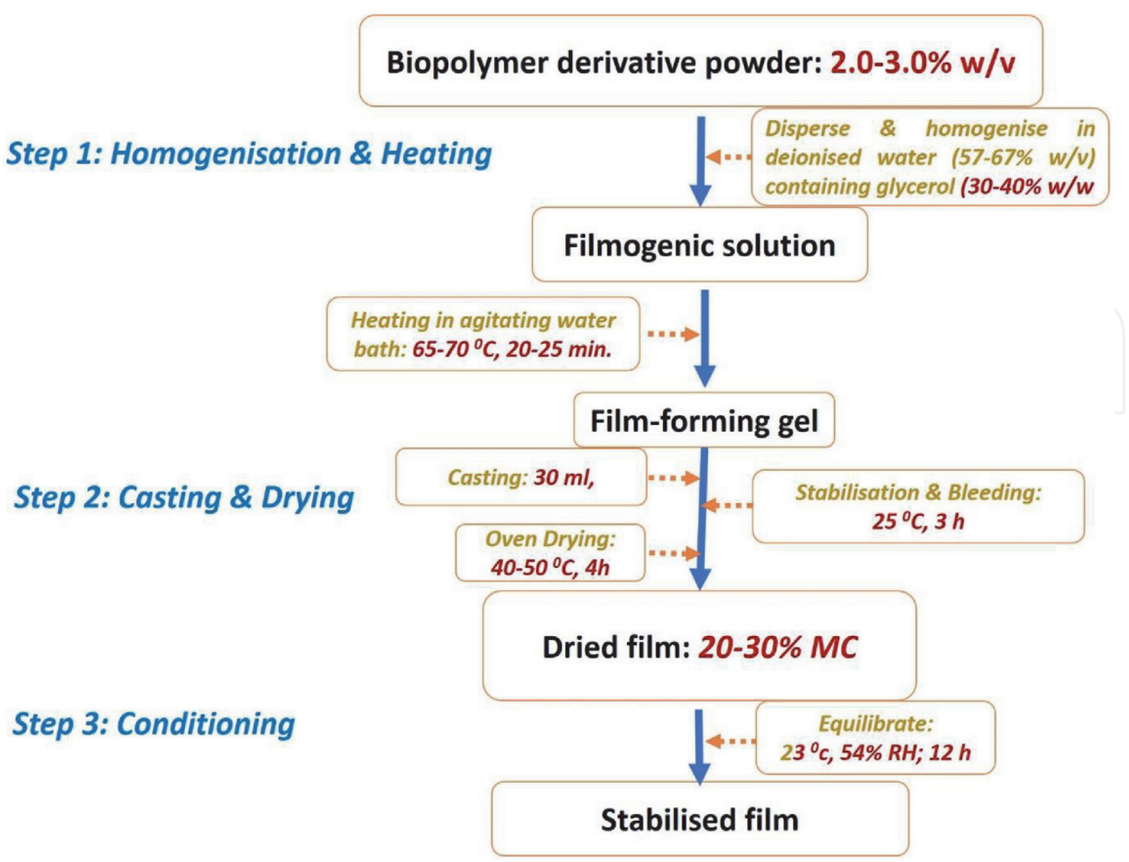


Figure 4.
Schematic flow of film fabrication process.

Property	Bitter cassava film	Commercial PLA film
Moisture (%)	0.19–0.45	0.10–0.20
Optical (%)	3.43–5.29	1.45–1.50
Solubility (%)	15.52–30.54	0.00
Water vapour permeability (gmm/(M^2.24h,kPa)	3.19–4.50	180.0–190.0
Glass transitional temperature (°C)	44.05–56.23	55.0–60.0
Melting temperature (°C)	193.57–213.63	130.0–180.0
Tensile strength (MPa)	3.71–48.44	40.1–49.5
Heat of fusion (J/g)	64.0–70.5	21.5–25.4
Degradation temperature (°C)	370.0–380.0	350.0–400.0
Glass transition temperature (°C)	50.0–60.0	60.0–65.0
Melting temperature (°C)	200.0–220.0	170.0–230.0
Crystallinity (%)	50.5–59.5	10.0–15.0
Elongation at break (%)	17.3–18.7	33.4–35.0
Elastic modulus (MPa)	0.11–15.95	2000–2300
Transparency (%)	3.0–5.0	3.0–5.0
Seal strength [N/25 mm]	305.0–325.5	25.5–30.5
Contact angle (^{0})	70–105 ^{0}	60.0–95.0
Biodegradability (days)	20–100	40–50

Table 1.
Characteristics of bitter cassava films in kin to commercial PLA bio-film.

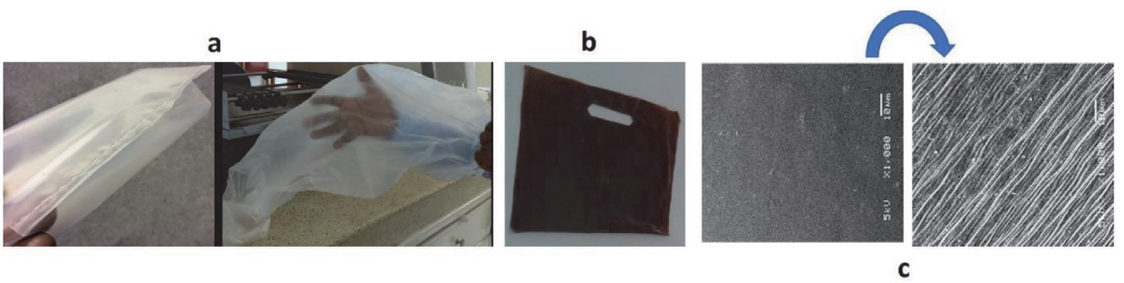


Figure 5.
Bitter cassava film depicting a) transparent nature; b) carrier bag; and c) scanning electron microscope revealed mesh structure.

particularly in packaging where products in the distribution chain are required to be viewed by buyers.

BCFs are fairly water resistant after 30 days, which is explained by the relatively stable network components in the film structure imparted by the root waste and SRRC [4, 15, 17]. Intact bitter cassava biopolymer derivatives is able to produce both water soluble and resistant films which can find application in packaging fresh foods and acting as a goods carrier bag used in an environment whereby high water resistance is high (**Figure 5b**).

BCFs possess homogeneous surfaces, which can be attributed to complete solubilisation of biopolymer derivatives in the polymer matrix, near zero solvent migration at the interface and strong and uniform adhesion of ingredients culminating into homogeneous mesh network structures in the film matrix (**Figure 5c**) [4].

BCFs are either hydrophilic or hydrophobic; those characterised with contact angles (CA) $700 \leq CA < 90^0$ contain polar functional groups that render them hydrophilic. The CA is the measure of wettability of solids and gives an indication of the extent liquids spread over solid surface [18]. The surface energy is essential in assurance of printability, adhesion, and transparency of flexible films. The BCFs have contact angles $<90^0$ (hydrophilic) and $> 90^0$ with printability features and can be used as goods carrier bags (**Figure 5b**) respectively. Nonetheless, BCFs are observed to swell differently at diverse RH; lower and higher swelling is clear at higher and lower RH respectively due to differences in plasticisation.

The fluid barrier properties of biomaterials are essential for prediction of the product-package shelf-life. The BCFs accurate performance veracity is a function of their flexibility in extremely demanding distribution situations, a role of their ability to respond timely and achieve fluid barrier appropriately. The BCFs have suitable permeability to water vapour (WVP) like commercial films polylactic acid (PLA) and Natureflex (NVS) currently applied in packaging fresh foods. This is fundamentally due to their widespread pore size distributions that contribute to fluid pathways, which are tortuous and exceedingly variable [19]. Depending on the nature of the films and their intended use, their equilibrium moisture contents (EMC) increase correspondingly with relative humidity (RH) at constant temperatures. This is caused by advanced amounts of moisture resulting into augmented mobility and dissociating. By contrast, the films EMC reduces when exposed to higher temperatures at constant RH due to film adsorption behaviour [19]. At high EMC, films moisture attraction is high with enhanced capacity adsorption and faster mobility of water causing a reduction in intermolecular attractive forces. The exponential increase of films WVP at higher temperatures is linked to higher activation energy for moisture permeation but also it is due to molecular initiation triggering film section crusade with creation of hollows that ease solvents motion through permeable films.

The permeability to oxygen (OP) of BCFs is higher than those of commercial NVS films. By contrast, permeability to carbon dioxide (CDP) by films is lower than the commercial ones. This is a good indication that the BCFs are adequate to be used in packaging fresh foods that are not highly respiring. When placed in distribution chain, BCFs under highly variable temperature and RH, the OP and CDP experience slight decreases due to antagonistic nature of RH on diffusion [19]. The interference of OP at higher RH and temperature is caused by increased molecular kinetics resulting into water molecules interfering with film voids but also on chain mobility. At higher RH and temperature, crystalline films are transformed into amorphous films (due to raised glass transition temperature and crystallinity) causing decreases in OP. The ability of these films to regulate barrier properties to gas and water, implies that they can be applied as breathable films, and is important for the choice of using them in commercial applications.

BCFs are permeable to organic and inorganic solvents differently [19] Toluene and paraffin, which are common organic solvents in the distribution chain, behave differently towards films. The higher interaction of paraffin is due to forming complexes with the film but also clinging to film surfaces. The information about the behaviour of solvents in contact with films is vital for their safe handling in the distribution chain. For example, toluene permeation makes film brittle and more crystalline with reduced molecular relaxation [19].

BCFs produce strong films that can have wide-ranging applications. Experiments have shown that BCFs tensile strength (TS) compares with commercial PLA and lies in the range of NVS and orientated polypropylene (OPP). BCFs flexibility is comparable to commercial PLA [4]. Similarly, it has also been shown that BCFs can be produced as weak films when the end use is targeted.

The seal integrity plays a vital role in packages and laminations in commercial setting. The BCFs have stand-alone self-sealing abilities compared to most commercial films that require an extra coating to enhance their sealing capacity. BCFs demonstrate comparable sealing strength with NVS, PLA and OPP that have supported sealing abilities [4]. BCFs exhibit last sealing strength for 12 h under environmental conditions (15–20°C and 50–60%RH), implying that films adhered firmly naturally [4].

BCFs are thermally stable under the influence of high temperatures. Their glass transition and melting temperatures, heat of fusion and crystallinity fall within the range of commercial PLA and LLDPE [4]. They are thermally stable than commercial films with the onset of total degradation occurring at 373°C, which is higher than most polymer networks degrading at 340–360°C [19].

BCFs are highly biodegradable in varying environmental conditions, decomposing in composite pits (within 21 days), open environment during wet conditions (maximum 45 days) and open environment during dry conditions (maximum 90 days). In all disposal environments, the bio-decomposition process uses naturally occurring bacterial/fungi to biodegrade the film into carbon dioxide, water, and compost. This is important for clean environment and sustainability, in contrast with fossil-based films that take more than 1000 years to decompose. When these biofilms are kept at room temperature and away from direct sunlight and humidity, they can biodegrade beyond 365 days. This is important when they are used as goods carrier bags and reused again.

3.2 Integrated sustainable system: a strategy to advance biodegradable products and ensuring green environment

A key part of sustainability is the minimisation of wastes during the biomaterial recovery from bitter cassava environmental waste. A sustainable system is an integrated and key strategy to realise green environment and value-added biodegradable products, and thus contributing to universal sustainability perception. The approach focuses on exploring individual process and model synergies and facilitating SRRC downstream process transition to advance cassava waste feedstocks for biodegradable product innovations. The approach emphasises developing and optimising an integrated process design based on optimising the structure of SRRC with efficient production of packaging materials and sustainable utilisation of cassava waste biomass feedstocks (waste solids and waste waters), meanwhile unlocking indirect and sustainable valorisation of cassava wastes. Apart from integrating individual processes, the strategy is intended to bring them, exclusively, into better efficient levels, through modelling and optimisations, and offer increased productivity of biodegradable packaging materials, thus creating a sustainable utilisation pull to reinforce the exploitation and competitiveness of bitter cassava crop. Standardisation, though process optimisation, of producing biomaterials eases the choice and cost of processes, by defining the design space, process parameters and biomaterial functional properties. In effect, robust production processes provide standard/optimal approaches for leveraging desired biomaterials with marginal costs and maximum functionality [20]. Besides, the effort is to bring the processing technology of small to medium enterprises (SMPs) to maturity through innovations in indirect waste disposal routes; and upgrading the development of simple, convenience and attractive substitute process designs that address cassava wastes accruing using SMPs rudimentary processing technologies.

Bitter cassava wastes that are generated by independent processes are being traditionally minimised in the environment by valorisation of bagasse into organic acids,

ethanol, aroma and biocomposites [20, 21]. Although the above processes are popular approaches, they have disadvantages of their fundamental high production costs, energy, and time. Optimal design models of individual processes are used as a solution, which gives best interface leverages in a sustainable cassava minimisation approach. In designing an integrated process, process modelling is used to ensure a holistic design for efficient utilisation of cassava wastes without compromising competition for food supply. Thus, to ensure efficient production of biomaterials, an integrated process design is used [16]. In this design, processes are well-defined and conceptualised before they are used in the integrated downstream processing model. In effect, only processes which add value in minimising waste at low cost, are energy efficient and time saving are selected and analysed in the integration design. Primarily, to increase the efficiency and functionality, the design is partitioned into unit operations whereby optimisations are focused. The source includes but not limited to recovering biomaterials from: i) the whole root of bitter cassava; ii) detached residue portions (peel, fibre, trimmings); and iii) wastewater streams.

The innovations to process design integration fall into three optimised and pooled processes to maximise recovery of safe biomaterials, i.e., efficient mechanical pulping; reaction and release; and recovery.

3.2.1 Maximise efficiency of intact root pulping

Efficiency of mechanical pulping is well explained in subsections 3.11–3.12. Precisely, the yield of biomaterials and loss of total cyanide certainly need to be augmented in optimising efficiency.

3.2.2 Modelling and optimisation for effective reaction and release of biomaterials

Reaction and release process is a key stage due to the need to free fully the biomaterials at minimum costs, taking into consideration protection of the environment due to released hydrogen cyanide. There are several variables to aid release, the processing conditions, and the desired biomaterial properties but their levels are highly variable. Resultantly, key buffers and bisulphates are preferred in order to infer release of biomaterials. Based on this approach, the research is done for purposes of not only releasing the biomaterials but also consider their yield, safety and customised for multiple functions.

Regarding reaction and release step, desirability function approach is used to optimise multiple response processes, which exploits optimal processing conditions and parameters and obtain the most desired yield, safety, and functionality of biomaterials. According to [16, 22], joint Pareto front and multi-objective desirability (MOD) approaches is used in the standardisation of the reaction and release process. In Pareto front/solutions, distribution to parameter choices is made in such a way that trade-offs ensure unequal distribution in which some factors are constrained in place of alternatives in order to find feasible choices that lie on the Pareto font [22]. In this case, choices are efficient and not dominated by any other choice. On the other hand, the MOD approach is used in target desirability optimisation due to its capacity predict desirables within anticipated ranges [16].

3.2.3 Optimisation for effective recovery of biomaterials

In the recovery step important processes take place, and they include: removing cyanogens and bisulphite residuals remaining in the wet biomaterials released; dehydrating released biomaterials in a safe and economic way through serial washing and recycling and optimal drying (**Figure 6**). In traditional washing and

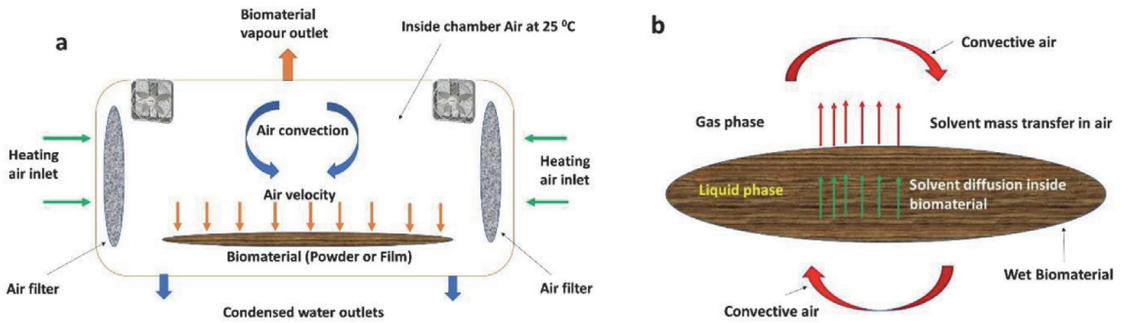


Figure 6.
Illustration of biomaterial drying process: (a) cross-sectional design of recirculating laminar flow chamber for studying optimisation and (b) mass and energy transfer.

clarification, a lot of purified water is deployed in serial washing with implications of energy costs in purification and biomaterials carried in wastewaters. In the current innovative designs, waste solvent is recycled thus reducing greatly on the costs of purification while ensuring zero contaminated biomaterials free from unwanted solvent and other clarifying-induced defects.

Conventional drying involves a lot of energy spent in the process, usually involving several hours (25°C, 12–16 h) of laminar flow drying without causing defects to the biomaterials in contrast to dying in ovens [16]. During the optimal recovery stage, energy is significantly minimised by optimised conditions in the designed recirculating laminar flow chamber (**Figure 6**). The purpose is to minimise the resident time of the biomaterial in the chamber while attaining the required residual solvent and drying process efficiency (productivity). As such operating conditions (air temperature, heat transfer coefficient, air flow rate, solvent partial pressure and velocity distributions) of the recirculating chamber are modelled and optimised to minimise significantly the polymer-solvent concentration and biomaterial resident time. Optimal conditions for drying polymer-solvent biomaterials is an outcome of a trade-off between minimising residual solvent dose producing gradients for fast dying without changing biomaterial quality. Thus, an adequate chamber with recirculating laminar flow is designed and deployed (**Figure 6**) for trial studies using computational fluid dynamics and mass and energy transport modelling [23]. In trying to attain optimal drying, interactions between biomaterial properties, dying conditions, biomaterial (polymer) solvent transport and mass/energy transport are managed. The fans enable to obtain uniform air flowing through the biomaterial. For a known uniform thickness (30 microns), temperature, time and polymer solvent amount profiles evolve as air (20–30°C, 30–40%RH) circulates through chamber containing biomaterials.

3.2.4 Characteristics of optimal drying process and dried biomaterials

Biomaterials from optimised recirculating laminar flow chamber processes are recovered and dried efficiently (high recovery, very low moisture, near zero contamination, low energy usage). The mechanism of drying biomaterial involves heat transfer from the convective air provided by external heat source and mass transfer in the biomaterial involving adsorption, diffusion, and desorption. At all stages of the drying process, drying rate is a function of solvent transport from the inside and surface of the biomaterial to the gas phase. Desorption (i.e., solvent transport from biomaterial surface) is characterised by mass transfer coefficients, gas temperature, velocity, and partial pressure, while diffusion (i.e., solvent transport within biomaterial) depends on temperature and solvent concentration [23]. Important scenarios above are modelled, optimised and outcomes presented (**Table 2**). The optimised

Parameters	Laminar flow	Recirculating airflow
Wet Biomaterial thickness, μm	30	30
Dry biomaterial thickness, μm	24	20
Initial air temperature, ^{0}C	25	25
Final air temperature, ^{0}C	30	30
Residence time, min.	360	240
Chamber partial pressure, kPa	102	102
Air Velocity, m/s	1.5	2.1
Initial solvent (moisture) content, mg	60	60
Final solvent content, mg at 240 min	32	5
Maximum weight loss, %	47	92
Heat transfer coefficient, cals^{-1} cm^{-2} °C^{-1}	0.0033	0.0024

Table 2.
Parameters at optimal drying of biomaterials in Laminar flow and recirculating laminar flow.

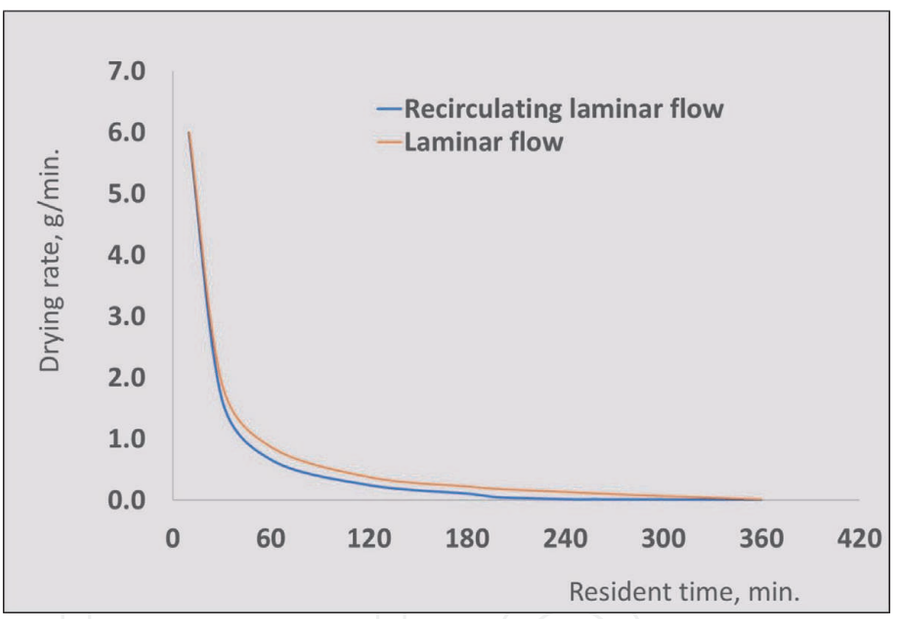


Figure 7.
Drying rates of biomaterials in recirculating laminar and laminar flows.

drying rate in recirculating laminar flow ensures short resident time compared to laminar flow (**Table 2**, **Figure 7**), implying reduced energy in drying.

The biomaterials' optimisation in recirculation laminar flow (RLF) chamber ensure that they are minimally degraded by heat and are more permeable to water vapour. Conversely, the RLF-based dying does not influence the structural and physico-chemical changes; this is also true for drying in laminar flow (LF) chamber [16]. By contrast, biomaterial thermal degradation increases in LF drying.

4. Cassava biomaterials as efficient matrices for key applications

4.1 Cassava waste powder in food supplements development

SRRC-produced biomaterials have benefits of a relatively low cost; particularly those from bitter cassava possess secondary metabolites with unrivalled properties

and varied uses, and thus have an edge over commercially available starch [4]. As a multifunctional, safe and dynamic matrix, bitter cassava biomaterials have potential application in pharmaceuticals, nutraceuticals and food supplements [15, 24]. SRRC-produced bitter cassava biomaterial is used as suitable matrix in the development of novel oral tablet excipient in iron and zinc supplements [11].

4.1.1 Fabrication of bitter cassava-based iron and zinc excipient tablets

In the production of iron and zinc tablets, the goal is to have a sustainable delivery system through chasing a carrier and delivery process that is inexpensive, green, and user-friendly. The manufacture follows a two-step process. Firstly, is to identify key bitter cassava biomaterial properties suitable for the development of self-sustaining excipient with important functionalities [11]. Next, based on the results from the first step, optimise the functionalities using granulation, formulate iron and zinc tablets and conduct dissolution tests.

In the preparation of biomaterial for excipient manufacture and dissolution tests, intact bitter cassava root biomass and SRRC methodology are explored [4]. In the conventional methods of producing biomaterials, peeled roots are the choice starting materials. For current innovation, tablets formation is done by exploring the capacity of biomaterial powder to produce strong tablets and is done by using both intact and peeled roots-derived biomaterials (**Figure 8**). Detailed procedure for tablets fabrication and dissolution tests can be found in the works of [11]. Iron and zinc are included prior to tablet formation and after granulation process. The quantities of iron and zinc included in the tablets are based on the dietary requirements of men (11 mg/day) and women (8 mg/day) while correcting for experimental loss [11, 25]. A suitable design is important if the minerals are to be distributed evenly in the tablets and an effective dissolution is needed. The design is defined based on three tablet sizes (100, 250, 500 mg), which corresponds with common pharmaceutical tablets in the market (**Table 2**) and the in vitro dissolution is accomplished using the US Pharmacopoeia (USP) method [11, 26]. For better

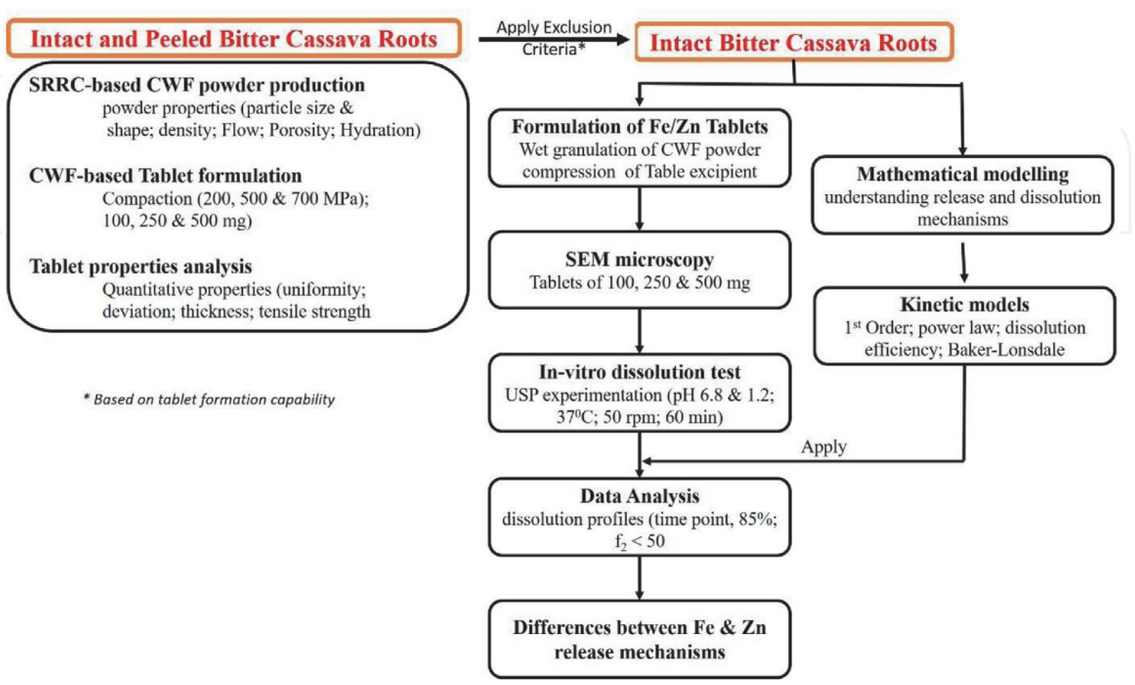


Figure 8.
Procedural investigation of excipient tablet production.

elucidation of the dissolution mechanisms (behaviour, release type, application angle of tablets), mathematical models are applied [11].

4.1.2 Physical properties of biomaterials for making iron-zinc excipient tablets

The physico-chemical properties of biomaterials play a vital role in tablet manufacture where flowability and compaction are the key properties. The biomaterials have uniform particle size and shape distribution of <3 mm, low bulk, and true densities, high tapped density and increased interparticle voids [11]. The uniform particle size is crucial in effective compaction/compression and regulated delivery matrices [11]. High tapped density is due to higher contract surface area, which is a benefit to tablet filling, higher solubility and dispersibility. Biomaterial flow properties and compressibility and solid excipient durability (desired strength, porosity and dissolution) are a function of bulk, tapped and true densities. The bulk and tapped density of the biomaterial are close to each other, which implies that it has better flow properties [11]. The biomaterial inter-particulate and intra-particulate interaction is low because of the low Carr's index (CI) and Hausner ratio (HR). The CI indicates compressibility or flowability of a powder, while HR is the number that relates to the flowability of a powder or granular materials. It has a low angle of repose and low porosity, an indication of particle uniformity and excellent flowability, which implies that the biomaterial powder cannot cake. The angle of repose of a powder or granular material is the sharpest angle of descent or dip relative to the horizontal plane to which a material can be heaped without dropping and is between 0 and 90^0. The biomaterials have low water retention capacity (WRC), water holding capacity (WHC) and swelling capacity (SC) although their WRC increases and WHC and SC decreases with time. The biomaterials have higher hydration capacity due to higher surface energy. The implication is the physical structural changes and hydration properties of the biomaterials fibres and their hydrophilic nature allows maximum moisture uptake offering a hint of better disintegrating of excipients [11].

4.1.3 Physical properties of iron-zinc excipient tablets

The novel Iron-Zinc excipient tablet (**Figure 9**) can be used extensively in developing food supplements, and as a pharmaceutical tablet with other active compounds due to its compatible, biodegradable, safe and fast dissolution

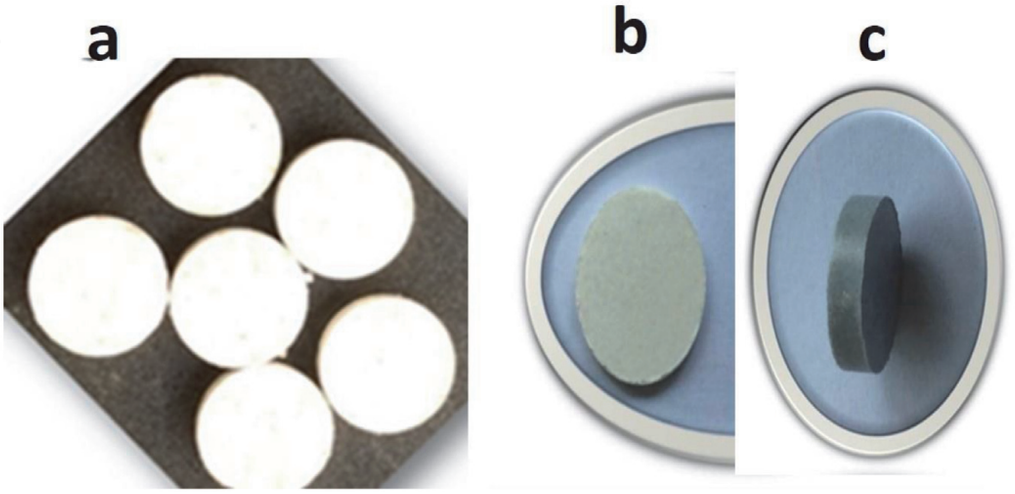


Figure 9.
The tablet prototypes containing biomaterial with: (a) no mineral; (b) iron; and (c) zinc.

Parameter	Biomaterial type		
	Derivatives powder	Tablet matrix	
Bulk density (g/cm^3)	0.38±0.0		
Tapped density (g/cm^3)	0.43±0.0		
True density (g/cm^3)	1.49±0.2		
Carr's Index (%)	9.38±0.0		
Hausner's ratio	1.13		
Flow rate (g/s^2)	20.91±0.8		
Angle of repose (^{0})	28.52±0.2		
Porosity (%)	68.87±0.9		
	CP200	**CP500**	**CP700**
Hardness (KG)	4.32±0.8	4.42±0.1	4.64±1.0
Diameter (mm)	13.09±0.0	13.08±0.0	13.07±0.0
Thickness (mm)	3.16±0.0	3.14±0.1	3.11±0.0
Weight (mg)	546.36±2.8	551.48±9.0	542.62 ±4.7
Tensile strength (MPa)	0.35±0.0	0.37±0.0	0.41±0.0
Disintegration time (s)	903±2.3	895±1.3	878±2.5
Friability	0.67±0.1	0.56±0.0	0.51±0.0

**Tablet size of 500 mg analysed at compaction pressures of 200, 500 and 700 MPa.*
CP, compression pressure.

Table 3.
Physical properties of bitter cassava biomaterial and excipient.*

properties [11]. Tablets have uniform weights (av. weight 484 ± 0.68 mg (**Table 3**), which is far lower than the recommended limit of 0.05. Uniformity and thickness of tablets are indication of good packing of tablets. The tablets exhibit reduced thickness corresponding to increases in compression force [11]. Tablets display adequate mechanical properties (hardness and tensile strength). The bitter cassava tablets are weak binders and strong disintegrants; these properties are crucial to the developments of fast release excipients where iron and zinc deliveries are fast demanded and in adequate amounts [24]. Tablet friability is compared to the USP standards implying that they can resist mechanical stress in the distribution chain. Tablet matrix porosity decreases as compression force is increased. Porosity is a function of particle size and shape; regular shaped particles become less and can fill up void spaces between large particles. In the low porosity tablets, small particle sizes allow flexibility for the tablets to pack more efficiently. However, the medium to high porosity biomaterials of bitter cassava does not permit flexibility in tablet packing suggesting a fast dissolution rate. Tablets exhibit higher disintegration time (DT) due to relatively medium to higher porosity, which facilitates rapid water penetration into the tablet resulting into bond rupture and disintegration [11]. The DT is the measure of time required for the tablet to disintegrate into particles under a given set of conditions.

The tablet matrix morphology and microstructure are considerably homogeneous, non-aggregated and uniformly blended with iron and zinc [11]. These patterns provide hope for tablets as inert excipients for oral dosage solid forms. Nutrient analysis has shown that zinc is released faster than iron in the tablet matrix, which seems to indicate that the matrix has minor resistance to zinc release than do for iron [11]. Tablet excipients release iron and zinc better in acidic

conditions than alkaline conditions within 45 minutes; this has implications for these tablets in the gastrointestinal movements and safe delivery in human body. This confirms that the nutrients have faster absorption in the stomach that in intestines. Furthermore, within 45 minutes of tablet disintegration suggests that they have one of the fastest release rates of iron and zinc nutrients and is attributed to easy tablet matrix erosion. Besides, high erosion rates of the tablet matrices are explained by high gelling, swelling and release of nutrients as fast as possible [11]. Noticeably, the low weight tablets release nutrient from the matrix faster because nutrients diffuse quicker from matrix surfaces.

4.2 Cassava waste film in equilibrium modified atmosphere packaging systems

Food industry packaging challenges created by the failure to maintain quality and safety of fresh and minimally processed foods in distribution have been mitigated mainly by modified atmosphere packaging (MAP). The MAP is a widely established system for the preservation of quality and managing shelf-life of fresh foods driven by the need and legislation to replace chemical preservatives. In the MAP system, the in-package environment is modified to match the requirements for storing fresh foods. While MAP is a popular packaging system, it has outstanding flaws such as design errors, which are corrected by active (gas flushing) and passive (equilibrium MAP) techniques [27]. Noticeably, Equilibrium MAP (EMAP) is universally used system for fresh respiring foods [15]. Notably, an EMAP is established inside the package when gas transmission rate matches product gas consumption rate [15]. Other current extenuation actions to the design errors include use low-cost biodegradable biomaterials for EMAP of fresh fruits and vegetables and cherry tomatoes [15, 28, 29] and joint plasma treatment and EMAP for cherry tomatoes [30]. A more robust package design was achieved using an ultimate EMAP across package distribution conditions [15]. This has an advantage of using the biomaterial film with heat sealing, heat resistance, relatively water resistance, good barrier, transparent and good mechanical properties in addition to their cost-effective, less competition with food supply biodegradability in all environments, ability to make pouches and bags, printing capacity, and non-perforation needs [4, 15, 16, 20].

4.2.1 Design of an EMAP system

When planning to design an EMAP for fresh foods, the fresh product respiration and transpiration behaviour and mass transfer of the package are important considerations and must be fully explored and understood [15]. The design trial includes defining the design requirements of bitter cassava biomaterial film EMAP that is stable in distribution chain characterised by low conditions (10°C, 75% RH). This is affected by knowing the impact of packaging parameters (perforation, RH, temperature) on gas (oxygen, carbon dioxide) composition, the optimal design parameters and gas composition and validated optimal EMAP [15]. The EMAP design follows the conceptual flow depicted in **Figure 10**. To design an integrated package, an active coated product is factored in the EMAP evaluation.

4.2.2 EMAP characteristics

The dynamics of an In-package headspace gas plays an important role in attainment of EMAP for food products. When cherry tomatoes are used in the EMAP trials and stored using BCFs, the headspace oxygen reached equilibrium (2–3%) after 180 h at 10°C for 75% RH (**Figure 11**). The recommended headspace oxygen is 3–5% for safe storage of tomatoes [30].

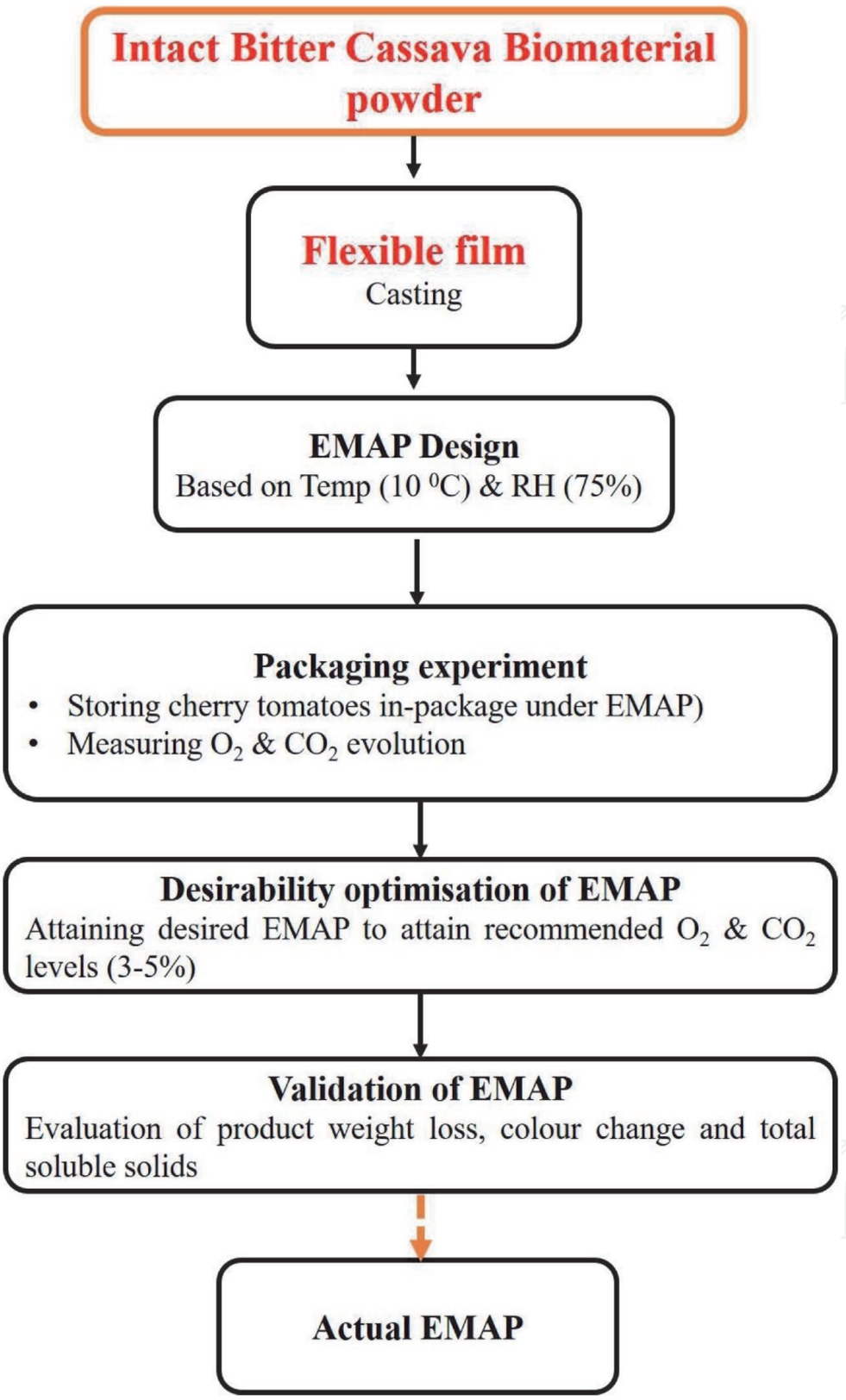


Figure 10.
Practical study of an EMAP design.

4.2.3 Properties of packed and stored product

Since the shelf-life of the products is associated mainly with microbiological quality, modifying the in-package atmosphere through EMAP is often intended to limit microbial contamination.

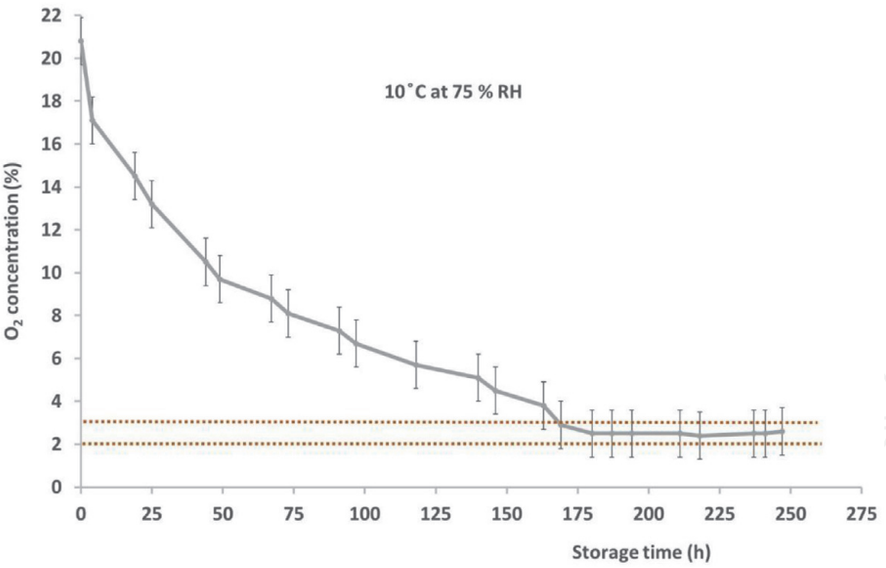


Figure 11.
Progress of headspace oxygen (%) of stored cherry tomatoes in EMAP.

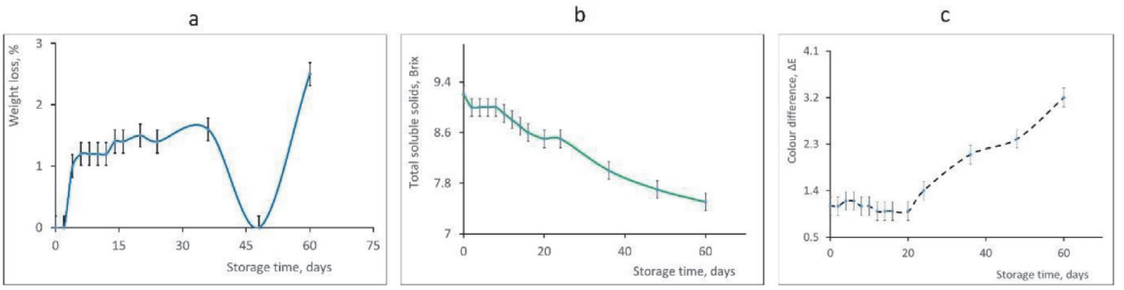


Figure 12.
Status of cherry tomato quality at different storage times: (a) weight loss; (b) TSS; (c) colour difference.

Cherry tomatoes stored in the EMAP show visible mould around 360 h at 10°C and 75% RH and demonstrated reduced weight loss. The loss in normal EMAP is attributed to the combined effect transpiration rate of cherry tomatoes and permeability of bitter cassava films [15].

Colour is a key indicator of market value of the product. An EMAP did not have significant effect on the colour of cherry tomatoes during the 21 days of storage; however insignificant changes are apparent due to the nature of biological materials. A colour index of 1.1 was observed with cherry tomatoes storage with EMAP.

Reduced total soluble solids (TSS) is often encountered when tomatoes are stored for a long time. Like any other storage medium, EMAP decreases cherry tomato TSS (**Figure 12**). In this case, there is a possibility of packaging contributing to the reduced hydrolysis of insoluble polysaccharides into simple sugar [31].

5. Other applications of cassava

According to [32], the global cassava processing market reached a volume of 298.8 Million Tons in 2020, implying that industrial application has grown correspondingly in food, ethanol, paper and cardboard, textiles, pharmaceutical, glues and adhesives. It is reported that food industry accounts for around a half of the total global cassava consumption followed by feed industry [32]. The use of cassava

in most industrial applications such as food, pharmaceuticals, beverages, civil works and textile industries is mainly done with sweet cassava starch and flour.

Food application of cassava. By improving properties of cassava flour using enzymatic and thermal modification, has been found to be acceptable in using modified flour as a key ingredient in the production of gluten-free baked products such as pasta and bread [33, 34].

Textile application of cassava. Because of starch qualities such as flexibility, resistance to abrasion and the ability to form a bond with the fibre, it is used in sizing, finishing, and printing in textile industry [35]. Of the total cassava starch used in textile, an estimated 80 percent go into sizing unit operation, which involves shaping and forming yarn fibres into warp. In this case, starch is used to coat the surfaces of the twisted warp that is then subjected to thermal treatment into a beam of warp ready for weaving. When the yarn is moisturised with cassava starch, the threads become smooth, greasy, slippery and hairless. In this case, starch behaves as a lubricant.

Pharmaceutical application of cassava. Tapioca starch, obtained from the roots of cassava by physical and chemical modifications (oxidisation, esterification, etherification, and treatment with enzyme) is applied in medicine and pharmaceuticals. Native and modified tapioca starch are used as diluents, binders and disintegrants in tablet and capsule formulations [36]. The excellent flowability and swelling power of native tapioca starch renders it useful as diluent for capsule and tablet formulations. Native tapioca starch produces tablets with higher tensile strength, less friability, least tendency to brittle fracture, longer disintegration time and slower drug dissolution rate, thus is preferred in paracetamol tablets when compared with cereal starches. Similarly, modified tapioca starch such carboxymethyl starch is generally used in medicine, pharmaceuticals, cosmetics and food due to their improved hydrophilicity, increased water absorption, reduced tendency of retrogradation, lowered gelatinization temperature, increased solubility in cold water with clear gel and higher storage stability [36, 37]. Acid-modified tapioca starch is an important filler or binder in direct compression with higher tensile strength, lower friability, faster dissolution than the native tapioca starch [38].

Application of cassava in civil works. Research has demonstrated that waste cassava is an ingredient in building materials [39]. It is demonstrated that when waste cassava, cement, charcoal and sand mixed in 2.5 kg composite and made into bricks, a denser texture of the bricks is obtained with perfect binding and compaction [39]. The relative strength is reported to be 711.5 kg/cm2 in addition to the brick being more environmentally responsive. Elsewhere, experimental trials of cassava starch modified concrete confirmed improved compressive, split tensile, flexural and elastic modulus of concrete at an optimum of 0.8% as well increased setting time and durability, with potential application in retarding admixtures [40, 41].

Application of cassava in beverages. Research trials confirm application of cassava into spirits and beers [42]. Using enzymes, cassava is liquefied and saccharified serially into, fermentable broth (circa 184 g/l of fermentable sugars), alcohol (circa10% ethanol) and spirits (40% ethanol by volume) with consumer acceptance [42].

Of recent, cassava coating is used in active packaging using both sweet and bitter varieties. Cassava-based edible coatings is used universally in preservation of foods. Trials have shown that edible cassava starch coating extended the shelf-life of Andean blackberries by 100% after 10 days in storage [43] and prevent decay and extend shelf life of black mulberries under refrigerated conditions [44].

6. Conclusion

Green environment, sustainability, resource renewability and efficiency, industry biomaterial supply, and circular produce-consume-dispose model could be spurred by exploiting innovative research solutions into cassava waste biomass. This chapter demonstrates that cassava varietal-specific waste can be transformed fully into sustainable and efficient feedstocks for bioplastics, packaging, and food supplement industries. Using innovative SRRC improved downstream processes and integrated sustainable process, up to 30% waste from bitter cassava can provide stand-alone feedstock requirements for food, medical, packaging industries. Valorisation of wastes reveals application in Iron-Zinc supplements and extending shelf life of tomatoes, which has advantage of improving nutrition status of vulnerable communities but also avoiding use of pesticides in fruit marketing. Either way, health is improved for the communities. Innovative SRRC improved processing methodology can be an alternative solution that eliminates the burden of drudgery and rudimentary process of small and medium enterprises (SMEs) to increase their market participation. As a supplementary bonus, valorisation of bitter cassava wastes into bioplastics would likely avert consequences of littering and burning of plastics (mainly carrier bags) that impact negatively on the environment and public health. Ultimately, committed used of SRRC in bitter cassava processing would help SMEs to have a sustainable non-food feedstock resource, contribute national environment programmes and improve community incomes.

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Conflict of interest

Author declare no conflict of interest for this work.

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Author details

Kashub Steven Tumwesigye[1,2], Jorge C. Oliveira[3], Sheila Namuwaya[2] and Maria Jose Sousa-Gallagher[3*]

1 Food Biosciences, National Agricultural Research Organisation, Kampala Uganda

2 Biological and Agricultural Sciences, Faculty of Science, Uganda Christian University Mukono, Uganda

3 Process and Chemical Engineering, School of Engineering, University College Cork, Cork Ireland

*Address all correspondence to: m.desousagallagher@ucc.ie

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