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Review

Cassava Starch for Sustainable Food Systems: Recent Advances in Processing Technologies and Structure–Function Relationships

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Abstract

Cassava (*Manihot esculenta* Crantz) starch is a promising renewable food ingredient for sustainable food systems because cassava combines high adaptability, climate resilience, and versatile starch functionality. However, its sustainability potential cannot be evaluated solely from crop productivity or starch recovery, as substantial water and energy requirements, postharvest physiological deterioration, processing losses, wastewater generation, and residue management remain important challenges. This review critically examines recent advances in cassava starch production and processing from a sustainability and structure–function perspective. Conventional wet extraction is compared with emerging green approaches, including ultrasound-, microwave-, and enzyme-assisted extraction, clean-label physical and enzymatic modification, fermentation, energy-efficient drying, water and wastewater management, and circular valorization of cassava processing residues. Genotype, environment, harvest and postharvest conditions, and processing technologies influence the hierarchical organization of starch, including amylose and amylopectin architecture, chain-length distribution, molecular size, crystalline order, lamellar organization, and granule characteristics. These structural attributes collectively determine pasting, gelatinization, rheological and gel behavior, retrogradation, freeze–thaw stability, and starch digestibility, thereby defining suitability for specific food applications. Building on these relationships, this review proposes a structure-directed sustainability framework in which starch is not simply produced with fewer resources but is deliberately designed to deliver target functionality with minimum processing and environmental burdens. This perspective supports application-specific design of cassava starch for conventional, gluten-free, health-oriented, and emerging food systems while enabling higher-value utilization and circular management of processing residues.

Keywords: cassava starch; structure–function relationship; structure-directed sustainability; sustainable processing; clean-label modification

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1. Introduction

Starch has emerged as one of the most important renewable biopolymers because of its abundance, biodegradability, affordability, and broad functional versatility across food and non-food sectors [1,2]. It is a plant-derived biopolymer and a major component of human diets, providing energy while remaining central to food formulations and global

nutritional systems [3]. In food manufacturing, native and modified starches act as thickeners, gelling agents, binders, stabilizers, emulsifying agents, texture modifiers, fat replacers, and shelf-life extenders, and they also serve as matrices for encapsulation and delivery of bioactive compounds [4–6]. Beyond food, starch and its derivatives are applied in pharmaceuticals, packaging, paper, textiles, adhesives, cosmetics, and other emerging bio-based materials [5,7,8].

Demand for starch-based products is increasing as industries seek renewable, biodegradable materials and functional ingredients aligned with circular bioeconomy goals [3,9]. Sustainable starch production therefore extends beyond maximizing yield and includes resource-efficient extraction, lower-emission processing, functional tailoring, and value creation within circular systems [10,11]. Current research also supports evaluating starch through a systems perspective that links source diversification, modification strategy, functional performance, digestibility, packaging performance, and end-use sustainability rather than treating these dimensions in isolation [3,12].

Rising global demand for starch has intensified vulnerabilities within traditional supply chains, with maize accounting for more than 70% of global starch production [13]. Because intensive cereal agriculture requires substantial fertilizer and irrigation inputs while suffering from climate-induced yield volatility and land-use competition [14], cassava (*Manihot esculenta* Crantz) starch may provide a potentially more sustainable alternative, characterized by high yield efficiency, stress tolerance, and a lower ecological footprint [15–18]. Strategic utilization of cassava starch may help mitigate regional raw-material deficits and reduce over-dependency on dominant cereal sources [15]. However, broader industrial adoption still requires overcoming sector-wide constraints, including native starch functional limitations, processing cost efficiency, and evolving market preferences for low-glycemic dietary alternatives [7,19].

In addition, realizing the full sustainability potential of cassava requires addressing several persistent challenges. Postharvest physiological deterioration (PPD) limits storage life [20], processing industries remain highly dependent on water and energy [21,22], and supply chains continue to experience quality variability and logistical inefficiencies [23]. PPD reduces starch content, resulting in poor functional properties [24]. These challenges highlight the need for integrated innovations spanning crop improvement, processing technologies, and sustainable value-chain management.

Cassava possesses a unique combination of agronomic, environmental, and industrial advantages that position it as a strategic crop for sustainable food systems [25]. Cassava is native to South America but is now cultivated extensively in more than 100 countries and fulfills the daily caloric needs of millions of people in tropical America, Africa, and Asia [26]. Cassava serves as a staple food for hundreds of millions of people while simultaneously supporting rapidly expanding starch-processing industries [7,15]. Its remarkable adaptability to diverse environmental conditions has made cassava one of the most resilient carbohydrate crops under changing climatic conditions [16,17].

Cassava thrives under conditions often unsuitable for intensive cereal cultivation, producing reasonable yields in poor soils with minimal inputs [26]. Deep rooting systems, high water-use efficiency, tolerance to intermittent drought, and the ability to grow in relatively poor soils enable stable production with comparatively lower agricultural inputs [27]. These characteristics provide important socioeconomic benefits for smallholder farmers while enhancing resilience against climate variability [17,18]. As extreme weather events become increasingly frequent, cassava is expected to play a progressively greater role in maintaining food and industrial starch supplies in many developing regions [25,26].

In addition to climate resilience, cassava demonstrates considerable flexibility within agricultural production systems. The crop can be integrated into mixed farming systems,

intercropping practices, conservation agriculture, and climate-smart production strategies that improve soil health and biodiversity while reducing production risks [28]. Continuous advances in breeding have further improved disease resistance, starch yield, and adaptation to changing environmental conditions [26,27]. These developments have strengthened the role of cassava not only as a food security crop but also as an important industrial raw material capable of supporting sustainable economic development [15,29].

Cassava's growing industrial importance is closely linked to the high starch content of its roots and to the functional properties of cassava starch that shape its end uses. Starch extraction yield, expressed on a fresh-weight basis using peeled cassava roots, was reported to range from 17.28 to 35.37% [30]. On dry weight, the starch yield from cassava root was estimated at 80% [31]. Cassava starch is often valued for its relatively low levels of non-starch components, with reported ranges of about 0.10–4.85% protein and 0.08–1.59% lipid [2], which contributes to its perceived purity in industrial applications. These properties have supported the use of cassava flour and starch in food applications including baking, soups, syrups, gluten-free products, and edible films [24]. Interest in cassava starch has also risen with growing demand for clean-label starch and environmentally friendly ingredients, particularly in gluten-free product development [32]. More broadly, rising demand for functional starches and expanding non-food interest in starch-based materials has increased attention to starch sources that combine useful functionality with renewability and biodegradability [33].

Advances in starch science have also expanded the application landscape of cassava starch into emerging technological fields. Modified cassava starches are increasingly incorporated into biodegradable films [34], edible coatings [35], pharmaceutical excipients [36], encapsulation systems [37], controlled-release matrices [38], hydrogels [39], and biomedical materials [40]. Additive manufacturing technologies have further highlighted the importance of controlling rheological behavior, gel formation, and structural stability through precise starch design [41]. Consequently, cassava starch is no longer regarded simply as a thickening agent but rather as a multifunctional biomaterial capable of supporting innovations across food, health, packaging, and advanced manufacturing industries.

Numerous reviews on cassava starch cover various aspects, such as biosynthesis, extraction methods, physicochemical properties, and industrial applications, contributing to the understanding in their fields [2,24,42–44]. Most previous cassava starch reviews have focused on biosynthesis, starch composition, extraction and processing, physicochemical and functional qualities, or industrial uses. Unresolved issues remain, including translation of traits into processing and end-use benefits, whether higher recovery improves total environmental performance, whether structural improvements produce measurable food-system benefits, trade-offs among functionality, energy, reagents, and scale-up, and attribution of environmental benefits to specific starch functionalities. This review creates a structure-directed sustainability framework that links genotype, environment, harvest, and postharvest conditions; starch extraction, modification, and drying technologies; molecular, supramolecular, and granular starch structure; techno-functional and nutritional performance; and environmental and economic sustainability outcomes to fill this gap. Sustainability should be assessed by reducing resource inputs during starch production and ensuring that the resulting starch structure provides the desired functionality with lower ingredient use, processing intensity, energy demand, product loss, and waste.

2. Methodology

A structured literature search was conducted using the Scopus and Web of Science databases. The search query applied Boolean and proximity operators (PRE/2, W/3) across title, abstract, and keyword fields (TITLE-ABS-KEY), combining four main con-

cept clusters: target starch sources (cassava, tapioca, manioc, *Manihot esculenta*), novel processing/modification technologies (ultrasound, microwave, high pressure, enzymatic, extrusion, heat–moisture, cold plasma), structural and functional properties (structure–function, physicochemical, rheological, digestibility, gelatinization, retrogradation), and sustainability terms (sustainable food systems, green technologies). The search was limited to peer-reviewed original research articles, reviews, and book chapters published in English within subject areas related to Agricultural and Biological Sciences, Chemistry, Chemical Engineering, and Biochemistry. Studies focused exclusively on non-food industrial applications (e.g., bioethanol production, textile manufacturing, wastewater heavy metal removal) were excluded to ensure alignment with sustainable food systems. The initial retrieved literature (more than 500 records) was screened for relevance to the scope and objectives of this review, with particular emphasis on studies providing evidence linking cassava genotype and production conditions, processing technologies, starch structural characteristics, techno-functional properties, and environmental or resource implications. Following this selection process, a total of 198 peer-reviewed publications were retained for critical review and synthesis. The selected literature was organized thematically to develop an integrated structure-directed sustainability framework connecting cassava production and postharvest factors with sustainable processing, starch multiscale structure, functional performance, and food-system applications.

3. Cassava as a Sustainable Starch Source

The transition toward sustainable food systems requires raw materials that can support food use, industrial functionality, and lower-impact material development. The sustainability of cassava starch production depends not only on the crop itself but also on how the starch value chain is managed from production through processing and downstream use [3]. Starch processing still faces limitations related to functionality, processing efficiency, and environmental impact, which has driven continued work on starch modification and greener processing approaches [1]. Current research therefore focuses on improving starch performance while aligning processing with green chemistry and sustainable development principles [2].

3.1. Global Production and Industrial Importance

Cassava is grown widely across tropical and subtropical regions and remains one of the major carbohydrate crops in developing countries [45]. According to FAO statistics, global cassava production reached 333.7 million tonnes in 2023. Africa accounted for 63.9% of the overall cassava production, making it the predominant region, trailed by Asia at 27.8%, the Americas at 8.2%, and Oceania at 0.1%. In terms of among countries, Nigeria emerged as the foremost producer internationally, accounting for 18.8% of total outputs, trailed by the DR Congo at 13.5%, Thailand at 9.2%, and Ghana at 8.0%. In the interim, Cambodia (4.2%), Vietnam (3.1%), and Laos (1.9%) have markedly increased their cassava production, with average annual growth rates of 9.6%, 1.3%, and 28.3%, respectively over the last 15 years (2009–2023). This expansion is attributable to investments from Thai and Chinese investors. Simultaneously, the overall worldwide export quantity of cassava products is recorded at 26.3 million tonnes, with Thailand identified as the preeminent exporter globally. Regarding export markets, the worldwide demand for cassava is predominantly bolstered by Asia, particularly China, which constitutes 40.8% of total global cassava imports [46]. Thailand is consistently identified as the leading exporter of cassava products, especially starch, flour, chips, and pellets. Thailand and Vietnam together account for over 90% of global cassava starch exports in the most recent trade analysis. China is the dominant importer and is a

major destination for Thai cassava, using imported chips for ethanol and imported starch for modified-starch applications in paper and textiles.

Cassava's industrial importance is well supported for starch, bioethanol, food processing, and several bio-based products [7,19,47]. In Asia, cassava is used predominantly as a processed industrial crop rather than as a direct staple food, especially in Thailand and neighboring countries [48]. The shift from small-scale starch making to larger industrial processing is explicitly documented in Thailand and China. Cassava roots are processed into starch, modified starch, sweeteners, ethanol, feed, and biopolymers [49]. Thai starch factories average about 200 tonnes of starch per day, reflecting large-scale industrialization. Cassava starch demand is linked to broader growth in bioplastics, edible films, plant-based foods, and other starch applications [49,50].

3.2. Sustainability Advantages

Cassava is consistently described as drought-tolerant and capable of producing under poor soils and marginal conditions [27,51]. That resilience is mechanistically linked to partial stomatal closure, leaf-canopy reduction, and extensive rooting, which reduce transpiration and help maintain water status under drought [27]. Cassava can also rely heavily on green water and has relatively low water requirements compared with many crops, although water remains a major production constraint under climate variability [52]. Cassava tolerates low-fertility soils better than many crops, but high yields still depend on better agronomy and improved varieties. It shows strong land-use efficiency because it can generate high carbohydrate yields per unit area and can remain productive on marginal land where other crops are not economically viable. Reported yields can reach 50–82 tonnes per hectare under favorable conditions, but African averages remain much lower [53]. In addition, cassava–legume intercropping improves biological efficiency, with a mean LER of 1.557 across 501 treatments. Benefits are larger in unfertilized rainfed systems than in fertilized irrigated systems. Legume intercrops can improve soil fertility, water retention, pest control, and total productivity [54].

Cassava supports food security and livelihoods for smallholder households across tropical regions [25]. Farmers value it because it tolerates dry weather and poor soils, and because roots can remain in the ground as a form of stored food until needed [55]. Cassava also supports income diversification, employment, and broader rural development when linked to functioning value chains and processing industries [52].

Cassava therefore has real sustainability advantages, especially in drought-prone, low-input, and smallholder systems. It is resilient and versatile, not input-free, and its sustainability gains depend on agronomy, intercropping design, and market access.

3.3. Challenges in Sustainable Starch Supply

Despite its strong industrial potential, cassava starch production still faces important sustainability constraints across the production-processing-marketing continuum [16]. These constraints arise from rapid postharvest deterioration, unstable root supply, pest and disease pressure, weak supply-chain coordination, and the resource demands of starch processing [56].

A major biological constraint is PPD, which sharply limits the economic and industrial value of fresh cassava roots. PPD begins rapidly after harvest, with visible symptoms reported within about 5 to 24 h, and the shelf life of fresh roots can be as short as 48 h. The deterioration process is associated with oxidative stress, including increased hydrogen peroxide, malondialdehyde, and antioxidant enzyme activity [57]. It also affects starch quality, because starch-synthesis genes are repressed and starch-degradation pathways are induced during PPD, reducing starch content during storage [58]. Visible vascular

streaking and discoloration make roots unmarketable, while rapid quality loss increases pressure for immediate transport and processing [16].

Climate and disease pressures add further instability to sustainable starch supply. Cassava remains more climate-resilient than many staples, but production is increasingly threatened by invasive pests, endemic diseases, and climate-sensitive stressors [59]. In Africa, cassava mosaic disease and cassava brown streak disease (CBSD) remain the dominant viral threats, and severe outbreaks still account for large harvest losses. CBSD also reduces industrial quality because diseased roots can show lower starch content and poorer suitability for high-quality flour and starch products [60]. Climate change further complicates management because changing environmental conditions are expected to shift the distribution of cassava, whitefly vectors, and CBSD risk across major African producing regions.

Sustainability of cassava starch production also depends on more reliable raw-material supply and stronger coordination between farmers, traders, and processors. Fresh-root supply is often seasonal and inconsistent, which disrupts factory operations and contributes to price volatility [56]. Limited governance, spot-market transactions, and weak grading and weighing systems reduce coordination and make quality standardization difficult [61]. Recent supply-chain studies similarly identify inconsistent quantity and quality, poor planting and delivery scheduling, and weak distribution efficiency as practical barriers to sustainable cassava starch processing [23].

Industrial starch processing itself remains a significant environmental challenge. Wet starch extraction uses large amounts of water, with one supply-chain analysis reporting 25,000 tonnes of freshwater per 1000 tonnes of starch, and extraction accounting for more than 60% of total freshwater use [23]. Water demand also varies markedly across technologies, from 10–62 m^3 per tonne of starch, depending largely on extraction design and water recycling practices [62]. Drying is the main energy hotspot in starch production, and electricity use is a major contributor to carbon footprint [63].

Wastewater management is another central sustainability issue. Cassava starch processing effluents contain high loads of organic matter, solids, nutrients, and cyanide, making them potentially highly polluting if untreated [64]. At the same time, these effluents are highly biodegradable, and anaerobic treatment can support biogas recovery and broader circular-use strategies. Process improvement studies therefore emphasize water recycling, starch-loss reduction, wastewater reuse, and conversion of residues into ethanol, electricity, heat, or other value-added products as realistic routes to lower environmental burdens [65].

4. Sustainable Processing of Cassava Starch

Conventional cassava starch manufacturing has long relied on wet extraction processes that successfully produce high-purity starch but consume considerable amounts of water and energy while generating large volumes of wastewater and solid residues [56]. As environmental regulations become more stringent and industries seek to reduce production costs and carbon emissions, there is growing interest in developing greener processing technologies that simultaneously improve resource efficiency and starch functionality.

4.1. Conventional Starch Extraction

Conventional wet extraction remains the standard industrial route for producing cassava starch across processing scales [66]. The basic sequence begins with washing fresh roots to remove impurities, followed by optional peeling and mechanical rasping to disintegrate root tissue into pulp [56]. Water is added during extraction and separates fibrous material from the starch-rich suspension (starch milk). Subsequent purification relies on sedimentation in basic setups or centrifuges and hydrocyclones in modern plants,

after which the purified slurry is dewatered and thermally dried, frequently via flash drying, to a target moisture content of 12–13% [67,68].

Process efficiency and starch recovery depend heavily on the performance of these individual unit operations rather than on extraction as a simple separation step [69,70]. Crucial stages like washing, peeling, grating, and straining govern processing speed, water demand, starch losses, and final product quality [71]. Postharvest processing delays degrade root starch quality [58], while extraction conditions directly influence starch composition, structure, and functional properties [72].

Despite its widespread industrial application, conventional wet extraction presents several resource-efficiency challenges. Reported water consumption and energy requirements vary considerably depending on factory configuration, root characteristics, extraction efficiency, water-recycling practices, and drying technology. For example, water consumption has been reported to reach approximately 62 m^3 per tonne of starch under specific processing conditions [23,62], while thermal drying has been identified as a major energy-consuming operation, accounting for more than 68% of total process energy in a reported production system [66]. These values should be interpreted in the context of the corresponding process configurations rather than as universal benchmarks for cassava starch manufacturing. In addition to resource consumption, conventional wet extraction generates solid residues, including peel, pulp, and bagasse, as well as wastewater containing organic matter, suspended solids, nutrients, and cyanogenic compounds [71,73]. Consequently, improvements in water circulation, starch recovery, dewatering, drying efficiency, and wastewater treatment should be evaluated collectively to determine their implications for resource use and environmental performance.

4.2. Modern Starch Extractions

Modern cassava starch extraction technologies, including ultrasound-assisted, microwave-assisted, enzyme-assisted, and hybrid approaches, have been investigated to improve starch liberation, extraction efficiency, and selected functional properties [74]. However, their reported advantages should be interpreted in relation to the experimental scale, raw-material characteristics, operating conditions, and process boundaries used in each study. Ultrasound-assisted extraction employs acoustic cavitation to disrupt the cellular matrix and facilitate starch granule release, potentially reducing extraction time under specific conditions [75]. Microwave-assisted extraction has also demonstrated promising extraction performance in comparative investigations involving different extraction media and cassava genotypes [76]. Microwave treatment improves gel strength and pasting characteristics while causing comparatively minor structural alterations in contrast to ultrasound in a study of dry bean starch [77]. The utilization of enzymatic biocatalysis, especially via pectinolytic and cellulolytic hydrolases, can specifically dismantle the parenchymatous matrix and facilitate the liberation of starch granules confined within cell walls [78]. Although these approaches may improve selected process parameters, their overall resource and environmental performance cannot be established solely from extraction yield, purity, or processing time. A comprehensive evaluation should also consider electricity consumption, thermal requirements, enzyme inputs, water use, starch recovery, and subsequent purification and drying operations. Table 1 compares key features among modern and conventional cassava starch extraction methods.

Table 1. Comparison of modern and conventional cassava starch extraction methods.

Methods	Yield/Recovery	Key Advantages	Starch Quality Effects and Functional Consequences	Limitations	References
Conventional wet milling	18–25 g/100 g tuber; purity up to 99.5%	High purity; simple equipment	Unmodified native granules	Time-consuming (~24 h); high water use; low yield	[10]
Ultrasound-assisted extraction (UAE)	~24.6% yield; purity 88.4%	Rapid extraction (~10 min); reduced solvent use; green technology	Lower viscosity; granule surface erosion; reduced crystallinity; increased hydration; altered viscosity; potentially reduced paste stability	Granule size alteration; requires equipment optimization	[75,79]
Microwave-assisted extraction (MAE)	Highest yield among tested methods	Fast; effective with water as solvent	Enhanced gel strength; limited structural changes; modified gel strength/pasting behavior	May reduce crystallinity	[76]
Enzyme-assisted	Up to 20% yield improvement; 93.9% purity	Preserves granule integrity; ~30% less energy; ~50% less wastewater	Intact granules; high swelling power; clear paste; higher recovery while retaining native swelling/pasting characteristics	Higher cost; longer processing time (~5 h)	[10,80]
Hybrid UAE + Enzyme	~87% recovery; synergistic cell-wall breakdown	Lower enzyme doses; enhanced recovery; tailored functionality	Surface pitting; reduced retrogradation; increased solubility and potentially altered retrogradation	Process complexity; dual equipment needs	[10,74,78]

Enzymes like pectinases and cellulases, sourced from microorganisms such as *Aspergillus aculeatus*, *Trichoderma reesei*, *Aspergillus niger*, and *Rhizopus* spp., have proven effective in hydrolyzing the structural elements of the plant cell wall, thus diminishing the necessity for rigorous mechanical processes and enhancing extraction efficacy [81]. Enzyme-assisted extraction employing polygalacturonase derived from *Wickerhanomyces anomalus* produced starch with preserved granules and functional characteristics akin to those of commercial starch [80]. Combined cellulase–pectinase treatment recovered up to 5.30 g of starch from 100 g of air-dried cassava peel material after 3 h of extraction, corresponding to a recovery of 5.30% (w/w) based on the initial air-dried sample mass. This treatment produced greater starch recovery than the individual cellulase, pectinase, and control treatments, demonstrating the potential synergistic effects of cellulolytic and pectinolytic enzymes in facilitating starch liberation from cassava peel [82]. However, because the moisture content of the initial air-dried material was not reported, the recovery value should not be interpreted as a dry-matter-based extraction yield [82]. Enzymatic techniques diminish

energy usage by around 30% and wastewater production by as much as 50% compared to traditional approaches [10].

Enzymatic extraction using cellulase and pectinase operates at mild conditions (40–50 °C, pH 4.5–5.5) and improves starch yield by up to 20% while reducing energy consumption by approximately 30% and wastewater production by up to 50% compared to conventional wet milling [10]. Combined cellulase–pectinase treatment recovered up to 5.30 g of starch from dry cassava peel, outperforming single-enzyme and control treatments [82]. Enzymatic methods also decrease harsh chemical use by over 30% and improve starch solubility and thermal properties, enhancing applicability across food and pharmaceutical products [10].

Microwave-assisted water extraction proved the most efficient method for recovering cassava stem starch, while ultrasound-assisted extraction showed strong potential for specific applications. A mechanical activation-assisted ternary deep eutectic solvent system achieved 82.52 wt% lignocellulose content from cassava residue, demonstrating that green solvent systems can effectively separate starch from lignocellulosic fractions [83]. Sustainable starch modification techniques can reduce the carbon footprint of starch production by up to 40% [10].

4.3. Clean-Label Modification

Clean-label starch manufacturing employs non-chemical methods, which represent an important sustainable processing strategy. Because native cassava starch often shows limited processing functionality, modification is used to create application-specific properties such as improved stability, altered viscosity, better digestibility, or targeted gel behavior [84]. Chemical modification remains the oldest and most widely deployed approach [43], but carries a triple burden: reagent manufacture and transport, reagent-laden effluent requiring treatment, and an ingredient-list declaration that an increasing share of consumers rejects [85]. Substituting physical and enzymatic methods therefore addresses environmental and commercial concerns simultaneously, which explains the rapid growth of this field. Table 2 shows the major cassava starch processing and modification technologies, their structural effects, and functional outcomes.

Table 2. Major cassava starch processing and modification technologies, their structural effects, and functional outcomes.

Methods	Structural Effects	Functional Outcomes	Typical Relevance	References
Chemical modifications	Functional-group substitution, altered granule behavior	Tailored pasting, stability, digestibility	Broad industrial use	[43]
Enzymatic modifications	Changes in branching and digestible fractions	Higher SDS/RS content, slow digestibility	Functional foods	[84]
Physical modifications	Modified crystallinity, hydration, granule order	Tuned viscosity and processability	Clean-label food systems	[70,84]
Extrusion	Granule disruption and depolymerization	Higher solubility, lower viscosity, less retrogradation	Snacks and instant foods	[86]
Fermentation/sour starch	Biochemical restructuring during wet storage	Bakery-specific expansion behavior	Breads, cakes, wafers	[70]

Note: The increased SDS/RS in enzymatic modifications depends strongly on enzyme specificity, starch substrate, degree of hydrolysis, reaction conditions, and subsequent recrystallization.

4.3.1. Physical and Non-Thermal Methods

Physical modification uses no chemical reagents and leaves no toxic residues, and physically modified starches are commonly positioned as clean-label ingredients [87,88]. Hydrothermal treatments remain central to this category. Heat–moisture treatment is generally conducted at moisture contents below 35% and temperatures above 90 °C, and it alters crystallinity, helix ordering, and granule architecture through heat and water alone [87]. More broadly, unconventional non-chemical technologies, including ozone treatment, ultrasound, high-pressure processing, high-pressure homogenization, pulsed electric fields, and cold plasma, have been investigated for their effects on starch granule structure and pasting behavior. A recent critical review combined an in-depth technical discussion with a bibliometric analysis based on 1679 unique publications, highlighting the growing research interest in unconventional starch modification technologies [89].

For cassava starch, ultrasound is well established as a physical modifier that acts through acoustic cavitation, producing grooves, notches, and other surface damage while operating over short treatment times with only modest bulk heating [79]. Cold plasma likewise modifies starch through plasma etching, cross-linking, depolymerization, and chemical functionalization driven by reactive species [90]. Recent work also shows growing interest in combined physical treatments, including ultrasound plus cold plasma, ultrasound plus annealing, annealing plus heat–moisture treatment, and thermal-ultrasound systems, because treatment combinations can produce structural and functional changes distinct from single-step processing [91,92].

A strong example in cassava is ultrasound or heat–moisture pretreatment followed by nanoprecipitation, which produced starch nanoparticles with distinct size distributions and improved suitability as Pickering emulsion stabilizers [87]. The sustainability caveat should be phrased more cautiously: the studies reviewed support concerns about energy consumption, scale-up, and cost for non-thermal technologies, but they do not directly establish that these methods are environmentally superior overall in starch modification [93]. So, the clean-label advantage is well supported, whereas the broader ecological advantage remains insufficient established.

Notably, the environmental impact of physical modification technologies depends on their operating circumstances and the resources needed to fulfill the desired function. Ultrasound, high-pressure processing, pulsed electric fields, and cold plasma may require additional electrical energy, specialist equipment, process optimization, and drying or conditioning. Thus, their processing speed, structural change, or product functioning benefits should not be associated with decreased environmental impacts. Comparative evaluation requires energy, water, treatment duration, equipment scale, downstream processing, and functional performance data. The cassava-specific literature shows promising structural and functional change, but quantitative evidence of their environmental advantage is lacking.

4.3.2. Enzymatic Methods

Enzymatic modification is presented as a green approach for starch applications because it enables the design of starches with new structures for improved industrial functionality. Enzymatic reactions can alter molecular mass, branch chain-length distribution, and the amylose/amylopectin ratio, creating a direct link between structural modification and functional performance. These structural changes affect properties including freeze–thaw stability of gels and the retardation of retrogradation during storage [85].

Enzymatic modification offers a strong sustainability case among alternatives to chemical derivatization because enzymes operate under genuinely mild conditions, pH 4–7 and 30–65 °C, with high regioselectivity and no reagent residue, with one comparative assessment reporting approximately 70% lower environmental toxicity than chemical modi-

fication [94]. However, the environmental performance of enzymatic modification depends on the specific enzyme, reaction conditions, enzyme dosage, processing time, and downstream operations. Relevant inputs may include enzyme production, fermentation, enzyme recovery and purification, transportation, incubation, thermal inactivation, and subsequent starch purification or drying.

Recent reviews of sustainable starch processing identify maltogenic amylase, cyclodextrin glycosyltransferase, branching enzymes, α-amylase, amylosucrase, and amylomaltase among the principal enzymes used for starch modification, while pullulanase and isoamylase provide selective debranching through cleavage of α-1,6 linkages [95].

Studies on cassava starch illustrate the degree of control achievable. Sequential maltogenic amylase and transglucosidase treatment produced a denser branched cassava starch with 12.76% branching density and 88.52% viscosity stability versus 64.92% for native starch, alongside better acid and freeze–thaw stability [96]. Amylomaltase treatment redistributed chain lengths by transferring hydrolyzed amylose segments onto amylopectin, extending shorter chains into longer fractions, and the long-to-short chain ratio was positively associated with long-term retrogradation [97]. More broadly, enzymatic debranching by pullulanase or isoamylase is valued because it offers specific control over starch modification, can improve water-holding and gel behavior, and is often discussed as milder and less environmentally impactful than traditional chemical processing [94].

Notably, enzymatic methods carry their own costs. Enzyme production has a footprint, thermal inactivation consumes energy, and reaction times can be long [85]. Accordingly, enzymatic modification should be considered a potentially resource-efficient strategy whose environmental advantages require evaluation within clearly defined process boundaries and against comparable functional performance.

4.4. Fermentation

Fermentation serves as a traditional low-input technology. Sour cassava starch deserves attention as a traditional clean-label process because spontaneous fermentation followed by sun-drying generates baking expansion in a gluten-free starch without chemical leavening [32,98]. The process is naturally driven rather than inoculated, and in the experimental workflow starch was fermented at ambient temperature for up to 30 days before either oven- or sun-drying [32]. Its functional gain comes from the combination of fermentation and sun exposure, not from fermentation alone: expansion increased from 3.37 mL g^{-1} in native tapioca starch to 3.71 mL g^{-1} after fermentation plus oven-drying and to 6.97 mL g^{-1} after fermentation plus sun-drying [98].

The mechanism is photochemical as fermentation generates organic acids and photosensitive compounds, and subsequent solar UV exposure depolymerizes the starch through a free-radical pathway, reducing crystallinity and molecular weight and increasing disordered regions [85]. Sun drying is therefore a reaction step, not merely dehydration, which is why oven drying cannot substitute for it. In cassava, fermentation reduced amylopectin molar mass and increased apparent molecular density and branching degree, with a more dramatic effect after sun-drying, and expansion increased as molar mass fell and branching rose [32].

The picture of sustainability is mixed in a way that is instructive. Since almost no energy is used and no chemicals are added, the process is more energy-efficient than many conventional industrial alternatives. However, several limitations remain, including high water consumption, long fermentation times, batch-to-batch variability, the risk of microbiological and dust contamination from fermentation and sun drying in the open air, and an organic-load fermentation effluent [85]. Due to these deficiencies, industrial adoption may favor chemically modified starches because of their greater process consistency and

economic practicality, despite their higher chemical and environmental burdens. Recent research suggests two promising strategies. The first approach uses selected starter cultures and controlled drying to shorten fermentation time, enhancing uniformity, and sustainable development [99]. The second approach is genetic control. Native amylose-free cassava starch had a specific expansion volume 3.5 times higher than wild-type starches (17.6 vs. 4.8 cm^3 g^{-1}) and was better in baked and expanded products than even fermented and sun-dried wild-type starch (8.4 vs. 16.4 cm^3 g^{-1} for native waxy) [32]. In summary, a defined starter culture may increase process inputs but could reduce fermentation time, variability and product losses.

4.5. Upstream Lever Strategies

Upstream levers including genotype, harvest and postharvest losses are also of concern. Processing sustainability is bound by what arrives at the factory gate, and three upstream variables deserve mention.

The principle can be generalized by selecting cultivars with intrinsically favorable amylopectin chain-length distributions or granule sizes that deliver the desired functionality without additional modification [100]. Breeding for processing traits is a sustainability intervention, rather than a purely agronomic one.

Harvest timing affects yield and functionality, and the two optima need not coincide, since molar mass and pasting behavior pass through a maximum at around nine months while starch yield continues to accumulate [101].

Postharvest physiological deterioration is the most severe and least tractable constraint, compressing the processing window, forcing factories to locate close to production, and generating losses that carry the full upstream environmental burden of cultivation with no product to show for it. Simple interventions such as improved storage bags have been evaluated in the field [102], but the underlying physiology remains the principal loss pathway in the chain.

4.6. Genetic Advancements in Cassava Growth and Starch Structure

Genetic improvement represents an important upstream strategy for enhancing cassava productivity, starch quality, and the sustainability of starch-based food systems. Conventional breeding, marker-assisted selection, genomic approaches, and emerging genome-editing technologies have expanded opportunities to develop cassava cultivars with improved agronomic performance and application-specific starch characteristics [103]. Recent advances in molecular markers, QTL mapping, and genomic selection have helped identify genetic areas linked to essential agronomic features. These methods are important because cassava has high genetic variability and genotype-by-environment interactions that affect root yield and starch quality [104].

Another sustainability goal is genetic control of PPD, which reduces starch quality and causes losses. Research has identified genetic variation in PPD susceptibility and investigated the regulation of oxidative stress, reactive oxygen species, and associated metabolic pathways [105]. Genomic and molecular approaches, including RNA interference and gene-expression manipulation, have demonstrated potential for delaying deterioration. However, the development of cultivars combining prolonged shelf life with high storage-root productivity and desirable starch characteristics remains challenging [20]. Moreover, genetic improvement of starch biosynthesis provides an opportunity to develop cassava cultivars with functionality tailored to specific food applications rather than relying exclusively on post-extraction modification [44]. The advances in CRISPR/Cas9-mediated genome editing allow cassava starch composition and structural modification. Amylose-free cassava starch was created by targeting the granule-bound starch synthase gene (GBSS), showing that

genetic alteration of a biosynthetic pathway can significantly affect starch functionality. Modifying protein targeting to starch 1 (PTST1), which is involved in GBSS localization, reduces amylose accumulation, but the starch phenotype varies from direct GBSS disruption [106]. Recent targeted editing of the soluble starch synthase gene MeSSIII-1 increased cassava storage root amylose, resistant starch, and total starch. The starch also changed amylopectin chain-length, granule-size, gelatinization, and pasting [107].

Genetic improvement offers several potential sustainability advantages throughout the cassava value chain. Nevertheless, these potential benefits should not be interpreted as established environmental improvements. The sustainability of genetically improved cassava depends on field performance, genotype-by-environment interactions, propagation systems, regulatory requirements, processing efficiency, and the functional performance of the resulting starch.

4.7. Cassava Harvest Residues as a Valorization Resource

4.7.1. Agricultural Residues Generated During Cassava Harvesting

Leaf, petiole, stem, fibrous root, and root crown remnants are harvested from cassava. Part of the stem biomass is used for planting, while the rest may be used for agriculture and industry. Protein and minerals are found in cassava leaves and structural carbohydrates and residual starch in the stems. A recent study of leaves and stems from two cassava clones showed their potential as food, animal feed, and bioenergy raw materials due to similar macronutrient compositions. Dehydrated leaf and stem material had 8.5% moisture, ~20.4% protein, 25% fiber, minimal pectin, and high lignin, indicating saccharification potential, especially in the stem. Leaves contain anti-nutritional and cyanogenic chemicals; thus, they must be treated before eating [108].

4.7.2. Industrial Residues from Starch Extraction

Cassava starch extraction generates bagasse (the fibrous fraction retained on extraction screens) and peel, both historically disposed of or fed to livestock at low value and both causing contamination when discarded untreated [109].

Bagasse retains a substantial starch fraction because mechanical rasping never achieves complete cell rupture, and residual starch granules in bagasse are morphologically similar to commercial cassava starch [110]. This makes bagasse simultaneously processing inefficiency and a resource. Its high moisture and poor handling characteristics have limited valorization, prompting studies of more efficient drying methods. It has been demonstrated that convective drying of cassava bagasse could be accelerated using ultrasound and pulsed electric field pretreatments, which generate micro-channels in the cellular structure and promote mass transfer [73].

Food-directed valorization is attractive because it retains material in the human food chain rather than downgrading it to fuel. Residual starch in cassava pulp can be converted to resistant starch type 3 by controlled retrogradation, yielding a high-fiber ingredient without chemical reagents [111]. This is genuinely circular as the retrogradation chemistry that limits shelf life in finished products becomes a functionalization route when applied deliberately to a by-product.

Peel is lignocellulosic, mineral-rich (potassium approximately 8570 mg kg^{-1}) and the anatomical fraction where cyanogenic glucosides concentrate [112]. Peel and bagasse have been characterized as matrices for biodegradable food packaging [110]. The cellulose, hemicellulose, and lignin fractions of cassava peel provide suitable substrates for the production of value-added products such as biochar, activated carbon, and biofuels [113]. It is important to emphasize that the cyanogen limitation is mandatory. Cassava peel contains high levels of cyanogenic glycosides that must be reduced before it is safe for feed or food [114].

Simple processing is insufficient; multistep methods are required to effectively remove these toxic compounds. Properly processed peels can achieve hydrogen cyanide levels below 50 mg/kg, which is considered safe for animal consumption. Sun drying, physical and enzymatic detoxification, chemical and fermentation methods, and combining these approaches provide the most robust detoxification [115].

In addition, starch recovery from cassava agro-industrial wastes offers a dual benefit of reducing disposal impacts and generating value-added products. Cassava peel starch yield reached 30 ± 2% by weight, with crystalline phases and morphology comparable to commercial cassava starch [116]. Cassava peel contains 42.12% starch, and drying at 50 °C preserves bioactive compounds including total phenolics (9.10 mg GAE/g) and antioxidant activity (80.00 µmol TE/g) [117]. Cassava husk waste yielded 3–4% starch, with the extracted starch demonstrating gelatinization suitable for adhesive applications [118]. Nano-starch synthesis from cassava peels via sulfuric acid hydrolysis achieved 97.01% yield under optimized conditions (25 °C, 2 M H_2SO_4, 9 h), valorizing peel waste for food, cosmetic, and textile applications [119]. Bioplastic films from cassava starch exhibited tensile strength up to 32.6 MPa and semi-crystalline morphology suitable for food packaging, offering a biodegradable alternative to conventional plastics [120].

Moreover, an integrated cassava biorefinery approach would connect agricultural residue management with industrial casava starch production and wastewater treatment, treating peel, bagasse, and wastewater as sequential recovery streams rather than independent wastes. This approach captures bagasse, wastewater and field residues in a single system yielding biogas, bioethanol, butanol and biohydrogen alongside non-energy products including succinic acid, lactic acid and glucose syrup [109]. A factory using both wastewater and cassava pulp for biogas achieved the highest net present value (6.14 million USD), shortest payback period (4.37 years), and lowest global warming potential (0.14 kg CO_2 eq per kg starch) [11]. Anaerobic digestion of processing residues reduced global warming potential by 26% and cumulative energy demand by 39% in industrial scenarios [121]. Cassava waste bioenergy generation can mitigate various environmental impacts by 42–99% and meet all energy demands of a starch plant [122]. A heat recovery system integrating economizers, biogas tanks, and boilers reduced freshwater demand by 66% and achieved annual greenhouse gas emission reductions of 123,564 kg CO_2 for a 20-tonne/day factory [122]. The integrated agro-industrial system combining cassava cultivation, livestock, and starch processing demonstrated potential for zero-emission goals through material and energy exchange networks [11].

4.8. Water Management and Wastewater Valorization

Conventional cassava starch processing is among the most water-intensive agro-industrial operations, with freshwater required at every stage from root washing through starch extraction, purification, and equipment cleaning. Producing one tonne of cassava starch can consume 9.8 to 62.1 m^3 of water, while generating 20 to 60 m^3 of wastewater laden with organic matter and cyanogenic compounds [123].

The recent literature shows that cassava starch processing can reduce water use and wastewater impacts through a mix of cleaner production, water recycling, and treatment technologies. Process upgrades such as raspers, centrifuges, and hydrocyclones reduced water consumption by 53.8%, wastewater generation by 49.0%, and improved starch recovery to 84.5% [67]. Water recycling and integrated waste-treatment systems that recover water for reuse reduced freshwater demand by 30–66% while also improving energy recovery through biogas production [124]. Anaerobic digestion appears especially suitable because cassava processing wastewater is highly biodegradable, full-scale systems are already used in several countries, and covered lagoons can make treatment more profitable while

recovering methane and process heat [125]. Biological polishing routes also show strong potential: microalgae cultivation reduced BOD by up to 92% while producing 2–4 g/L biomass, and algal–fungal co-culture removed 92.08% of COD, 83.56% of total nitrogen, and 96.58% of total phosphorus while generating higher-value biomass [126]. Emerging options such as microbial fuel cells and electroflocculation broaden the treatment portfolio: microbial fuel cells achieved 61.9% COD removal and 50–70% cyanide degradation while recovering electricity, whereas electroflocculation increased effluent pH and removed up to 86.78% of color [123]. For water conservation and reuse, sequential peroxide-oxidation plus adsorption using cassava-peel-derived carbon was proposed to recycle treated effluent for irrigation and groundwater recharge, with scenario estimates suggesting very large national water savings where adopted at scale [127]. Overall, the recent literature indicates that the most effective strategies combine process water reduction with resource-recovering treatment systems rather than relying on end-of-pipe treatment alone.

4.9. Energy-Efficient Drying Technologies

Drying represents one of the most energy-intensive stages in cassava starch production, accounting for a substantial proportion of total industrial energy consumption [128]. Energy-efficient drying technologies for cassava starch processing span pneumatic and flash drying systems, solar and biomass-fueled alternatives, and emerging hybrid and pretreatment-assisted methods. Drying performance should not be evaluated solely from specific energy consumption. Increasing drying temperature or reducing air flow may improve energy efficiency and throughput but can also alter starch thermal properties, whiteness, molecular structure, or functional performance. Conversely, solar or low-temperature drying can reduce fossil-energy demand but may increase residence time, land requirements, process variability, and contamination risk. Therefore, the appropriate drying strategy should be selected by jointly considering specific energy consumption, drying rate, throughput, final moisture, starch quality, product safety, and the energy source used.

4.9.1. Pneumatic and Flash Drying Systems

Pneumatic (flash) dryers are the most economical and widely used drying system for dewatered solids and are suited to cassava starch, high-quality cassava flour and powdered fufu, and they outperform fixed-bed dryers on energy performance because of better contact between grits and drying air [129]. Recent work targets energy performance through operating conditions and component design [68,128]. A pilot-scale flash dryer reduced mechanically dewatered cassava mash from 47.06% to 9.60% moisture (wet basis) at 298 kg wet cake/h and 186.34 kg dried product/h, giving 80.8% energy efficiency and specific energy consumption of 2570 kJ/kg product and 4560 kJ/kg water evaporated [68].

In a small-scale pneumatic dryer drying cassava starch, raising air temperature from 60 to 100 °C increased energy utilization from 0.34 to 0.76 J/s, with energy efficiencies of 30–40% [130]. Reducing air mass flow rate toward the calculated minimum cut the energy needed to evaporate 1 kg of water by 20% in Tanzania and 13% in Nigeria without jeopardizing evaporation rates or final moisture, and improved energy efficiency by 25% and 14% respectively; in Nigeria, however, the modification increased product color losses [131].

Numerical simulations indicate that air velocity and starch dilution should be minimized, and that residence time—set mainly by pipe length and air velocity—is the most influential factor and should be maximized, with pipes longer than 25 m allowing drying at limited air mass flow [128]. Experimental validation later showed particle size falls as air velocity rises, so higher velocity can raise capacity without harming drying efficiency [132].

4.9.2. Solar, Biomass, and Hybrid Drying

For cassava starch, a hybrid solar dryer combining solar with LPG auxiliary heating reached a maximum overall energetic efficiency of 20.82% at 60 °C, with exergetic efficiency ranging from 25.1% to 73.8%. Only the 60 °C run satisfied the maximum moisture limit for cassava starch, and higher temperature gave faster, more effective drying. The same group's LPG-assisted hybrid solar dryer for cassava starch required 240, 210, and 180 min at 40, 50, and 60 °C respectively to bring moisture below 14% wet basis [133].

Moreover, in modified casava flour, a TRIZ-designed hybrid dryer combining infrared heating, forced-air circulation, and LPG combustion dried 50 kg batches per six-hour cycle at 76 °C, 2.1 m^3/min airflow, and 413 g/h LPG, achieving a water removal rate of 315 g H_2O/h. Benchmarking against sun and cabinet dryers showed significantly reduced drying time with better structural and functional properties [134].

For cassava chips, a greenhouse-integrated hot air system at 60 °C with chips under 2.5 cm and a 2 cm bed cut drying time to 10 h, a 56.5% reduction, and lowered specific energy consumption from 9.30 to 4.41 MJ/kg versus sun drying. Maximum thermal efficiency was 71.60%, translating to 1.36 kWh/kg energy saving and 0.82 kg CO_2 reduction per kg water removed [135]. A rack-type hybrid dryer dried chips from 60% to 10–12% moisture in 12 h with combined solar and electrical energy, versus 18 h on solar alone [136], and a solar-assisted heat pump dryer reached 30.9% average thermal efficiency against 25.6% for a plain solar dryer [137].

4.9.3. Emerging Pretreatment and Hybrid Technologies

Future research directions emphasize integrating combined pre-drying and drying techniques to optimize resource utilization and processing efficiency. In general, hybrid drying methods, including microwave-assisted, infrared-assisted, and ultrasound-assisted techniques, can reduce non-renewable energy consumption by up to 80% [138].

In casava chips, far-infrared radiation (FIR) drying at 80 °C reduced cassava slice moisture to 12% within 50 min, accelerating the drying rate while maintaining higher lightness and reduced browning [139]. Convective hot air drying of 1.5 mm cassava slices resulted in the highest drying rate (0.24 $g \cdot g^{-1} \cdot min^{-1}$) and shortest drying time (180 min), while solar drying of thin slices best preserved starch content and whiteness [140].

Moreover, pretreatment with probe ultrasound at 26 kHz reduced drying time by 72% (3.83 h vs. 14.0 h) for cassava bagasse, while a pulsed electric field (PEF) at 7.5 kV/cm reduced drying time by 52.4% [73]. These technologies increased effective diffusivity and modified the molecular structure of the bagasse, improving drying process efficiency.

4.10. Sustainability Assessment and Future Directions

Life-cycle assessment (LCA) is used to evaluate the environmental performance of cassava starch production across defined stages, which may include cultivation, transport, starch extraction, drying, packaging, distribution, and waste management. The interpretation of reported greenhouse-gas (GHG) results depends on the selected system boundary, functional unit, treatment of biogenic carbon, and allocation of burdens and benefits among starch and co-products [109]. In an integrated cassava biorefinery, negative net GHG values (reported as −434 to −436 kg CO_2-eq per tonne of cassava roots) should not be described automatically as physical carbon storage. Such values may reflect a combination of emissions within the system, temporary or longer-term carbon retained in products, and avoided-emission credits for energy or materials displaced by co-products; the cited study's accounting assumptions must be consulted to determine their respective contributions [56]. For each tonne of starch produced, reported streams include approximately 2.5 tonnes of

bagasse, 100–300 kg of peel, and 17.4 m^3 of residual liquid, highlighting opportunities for recovery and valorization [141].

For clarity, physical carbon storage and avoided-emission credits are distinct accounting terms. Physical storage refers to carbon taken up from the atmosphere and retained in biomass or a product over the period specified by the assessment; it is reported only when uptake, storage duration, and release or end-of-life pathways fall within the study boundary. Avoided-emission credits are consequential or substitution-based benefits estimated when recovered energy or co-products displace a reference product or energy source; they are not a carbon physically stored by the cassava system. A cradle-to-gate assessment normally includes cultivation and processing up to the factory gate, whereas a gate-to-gate assessment covers only the defined plant operations. Credits for exported electricity, biogas, fertilizer, or other co-products should be reported separately and assigned using an explicit method (e.g., system expansion/substitution or allocation by mass, energy, or economic value). Because these choices can materially affect the sign and magnitude of net GHG results, comparisons should use harmonized boundaries, functional units, and allocation rules.

In addition, enzyme cost remains a barrier to industrial-scale adoption, though declining production costs through improved microbial fermentation and enzyme stabilization methods are narrowing the gap. Integrated bioprocessing transforms cassava peels and press cake into valuable co-products including citric acid (up to 1.42 g/L) and biofertilizer, advancing zero-waste management aligned with circular economy principles. The evidence indicates that green extraction technologies for cassava starch can simultaneously improve resource efficiency, reduce carbon emissions, and enhance starch functionality, though scaling requires continued optimization of enzyme economics and process integration [82].

5. From Sustainable Processing to Structure-Directed Functionality

The sustainability of cassava starch processing cannot be evaluated solely from extraction yield, water and energy consumption, or waste generation, because processing conditions also determine starch structure and thereby its techno-functional performance [43,70]. A sustainable process therefore needs to balance resource efficiency with structural integrity, functionality, and downstream value creation [116]. For instance, enzyme-assisted extraction and biocatalytic recovery routes have been associated with lower energy demand, effluent reduction or valorization, and preservation of starch purity or granule integrity alongside desirable functional properties [78]. By contrast, ultrasound- and microwave-based treatments are used precisely because they alter starch morphology, crystalline order, and rheological behavior, including pasting, gel, thermal, and retrogradation-related properties [142].

5.1. Processing as a Structural Design Tool

Processing should therefore be viewed not simply as a means of starch recovery but also as a structural design tool [12]. Physical, enzymatic, and fermentation-based processes alter molecular organization, chain-length distribution, crystalline order, and granule architecture [10], thereby generating starches with targeted pasting, gelation, stability, and digestibility characteristics [12]. Enzymatic modification is particularly relevant because its selectivity and mild reaction conditions enable controlled structural adjustment with fewer undesirable byproducts, offering an alternative to conventional chemical derivatization [10]. Accordingly, the preferred processing technology is not necessarily the one with the lowest immediate resource consumption, but the one that delivers the required functionality with the lowest overall processing and environmental burden [143].

5.2. Structure-Directed Sustainability

The integration of processing and structure–function relationships leads to the concept of structure-directed sustainability. Rather than optimizing starch production only for maximum recovery or minimum resource input, sustainable cassava starch systems should optimize the entire chain from genotype and raw-material quality to processing, structural characteristics, functionality, and final food performance. This is particularly important because functional performance can influence the amount of ingredient, processing intensity, energy input, shelf life, and waste generated during subsequent food manufacture. In this context, life-cycle assessment and techno-economic evaluation should be combined with structural and functional characterization to identify processing routes that provide genuine system-level benefits [109].

Thus, sustainable cassava starch is not simply starch produced with fewer resources; it is starch whose structure is deliberately aligned with its intended function while minimizing resource use and maximizing value creation. This integrated perspective provides the basis for the following section, which examines how the hierarchical structure of cassava starch determines its physicochemical, functional, and nutritional properties. The integrated relationships among upstream production factors, processing interventions, starch structural characteristics, functional properties, and sustainability outcomes are summarized in Table 3.

Table 3. Integrated sustainability–structure–function framework for cassava starch.

Levels	Sustainability Drivers	Processing/Management Levers	Structural Consequences	Functional Consequences	Sustainability Implications
Production	Climate resilience, resource efficiency	Genotype and agronomic selection	Amylose/amylopectin architecture; CLD	Gelatinization, pasting, digestibility	Reduced need for downstream modification
Postharvest	Reduced losses	Harvest timing; PPD management	Molecular integrity; starch content	Pasting and processing quality	Higher usable starch yield
Extraction	Water and energy efficiency	Enzyme-, ultrasound-, microwave-assisted extraction	Granule integrity, surface structure, crystallinity	Swelling, viscosity, paste clarity	Lower water/energy demand
Modification	Reduced chemical burden	Physical, enzymatic, fermentation processes	CLD, crystallinity, molecular organization	Stability, rheology, digestibility	Cleaner processing and targeted functionality
Formulation	Ingredient/resource efficiency	Protein/hydrocolloid co-structuring	Starch–biopolymer network	Gel strength, texture, stability	Potential reduction in formulation inputs
Application	Product performance and value	Structure-directed starch selection	Application-specific structural state	Targeted functionality	Higher-value utilization and reduced processing losses
Whole supply chain	Circularity and environmental performance	LCA, residue valorization, process integration	-	Overall process/product performance	Reduced waste, emissions and resource burden

A consistent baseline for mass throughput, techno-functional deliverables, and system restrictions is needed to evaluate cassava starch processing routes. A standard reference unit is 1 kg of dry starch (or 1 metric ton dry basis) with ≥99% purity and 13% moisture content [10]. The functional unit can be enlarged to offer equal mechanical or rheological performance in a formulated matrix, such as the mass of modified starch needed to achieve desired viscosity, gel firmness, or resistant starch content, for techno-functionality [86].

System boundaries are usually cradle-to-gate or gate-to-gate. Cradle-to-gate limits include agriculture, chemicals, root movement, and plant processing. Root reception, dry sieving, washing, peeling, cutting, rasping, slurry separation, dewatering, drying, and packaging are isolated by gate-to-gate boundaries [109].

Inventory measurements and impact category indicators are needed to quantify the environmental footprint. Power for rasping, pumping, and centrifugation and thermal fuel for starch drying are added to cumulative energy requirement. Wastewater generation counts organic effluent, while freshwater consumption evaluates total water extraction versus recycling loops. Fossil fuel burning, off-site energy generation, and wastewater degrading biogas are assessed for global warming potential. Eutrophication and acidification examine cassava whey's high chemical oxygen requirement and atmospheric acidification emissions [63]. Multi-Criteria Decision-Making (MCDM) tools like the Analytic Hierarchy Process (AHP) weight functional targets (viscosity, paste stability, cyanogenic detoxification), resource inventories, and life-cycle indicators to determine the best processing route [56].

The trade-offs between distinct processing routes depend heavily on whether modification and drying steps are integrated into a single operation or separated into chemical wet-milling lines. Comparative evaluation of conventional, thermomechanical extrusion, and circular biorefinery processing routes is illustrated in Table 4.

Table 4. Comparative evaluation of conventional, thermomechanical extrusion, and circular biorefinery processing routes.

Metric/Dimension	Conventional Wet Extraction	Extrusion Modification	Integrated Biorefinery
Functional unit	1000 kg dry native starch	1000 kg expanded starch	1000 kg starch + co-products
System boundary	Gate-to-gate factory boundary	Post-extraction thermomechanical	Integrated cradle-to-gate biorefinery
Resource inventory	4000 kg roots, 10–25 m^3 water	Dry flour feed, minimal water	Closed-loop water reuse & recovery
Energy & emission	Flash drying fuels; 407–468 kg CO_2eq	High electrical shear; no wastewater	Biogas offset; −434 kg CO_2eq net

Note: The values in this table are derived from individual studies with different functional units, processing configurations, and system boundaries [10,47,56,86]. Therefore, they are presented as illustrative examples of reported process characteristics rather than as a directly comparable ranking of environmental performance. In particular, the reported net greenhouse gas emissions for the integrated biorefinery depend on the assumptions regarding coproduct allocation, energy recovery, and avoided-product credits. Direct comparison requires harmonized functional units, system boundaries, and inventory assumptions.

6. Structure–Function Relationships

Explaining cassava starch's physicochemical behavior, processing performance, nutritional value, and industrial applications requires understanding its molecular architecture. Starch, unlike synthetic polymers, has a hierarchical structure where molecular organization at one level affects qualities at greater scales. Therefore, starch functioning cannot be fully

described by its chemical composition or granule form. Instead, molecular, crystalline, granular, and supramolecular structures must be integrated for complete characterization.

6.1. A Hierarchical Framework for Interpreting Functionality

Cassava starch is attractive to food formulators due to its low pasting temperature, high peak viscosity, bland flavor, exceptional paste clarity and comparatively weak retrogradation. This functionality emerges from a hierarchical structure organized across at least five length scales. At the molecular scale (10^{-1}–10^{2} nm), starch comprises two major glucan populations; amylose and amylopectin, defined by their branching architecture, chain-length distribution (CLD) and molar mass. At the helical scale (~1 nm) adjacent external amylopectin chains associate into left-handed double helices. At the lamellar scale (9–10 nm) these helices pack into alternating crystalline and amorphous lamellae. At the growth-ring scale (100–400 nm) semi-crystalline and amorphous shells alternate radially. Finally, at the granular scale (1–40 µm) the whole assembly is expressed as a discrete, birefringent, water-insoluble particle [2,42]. Figure 1 illustrates the multi-scale hierarchy, annotated with cassava-specific values and the technique that probes each level.

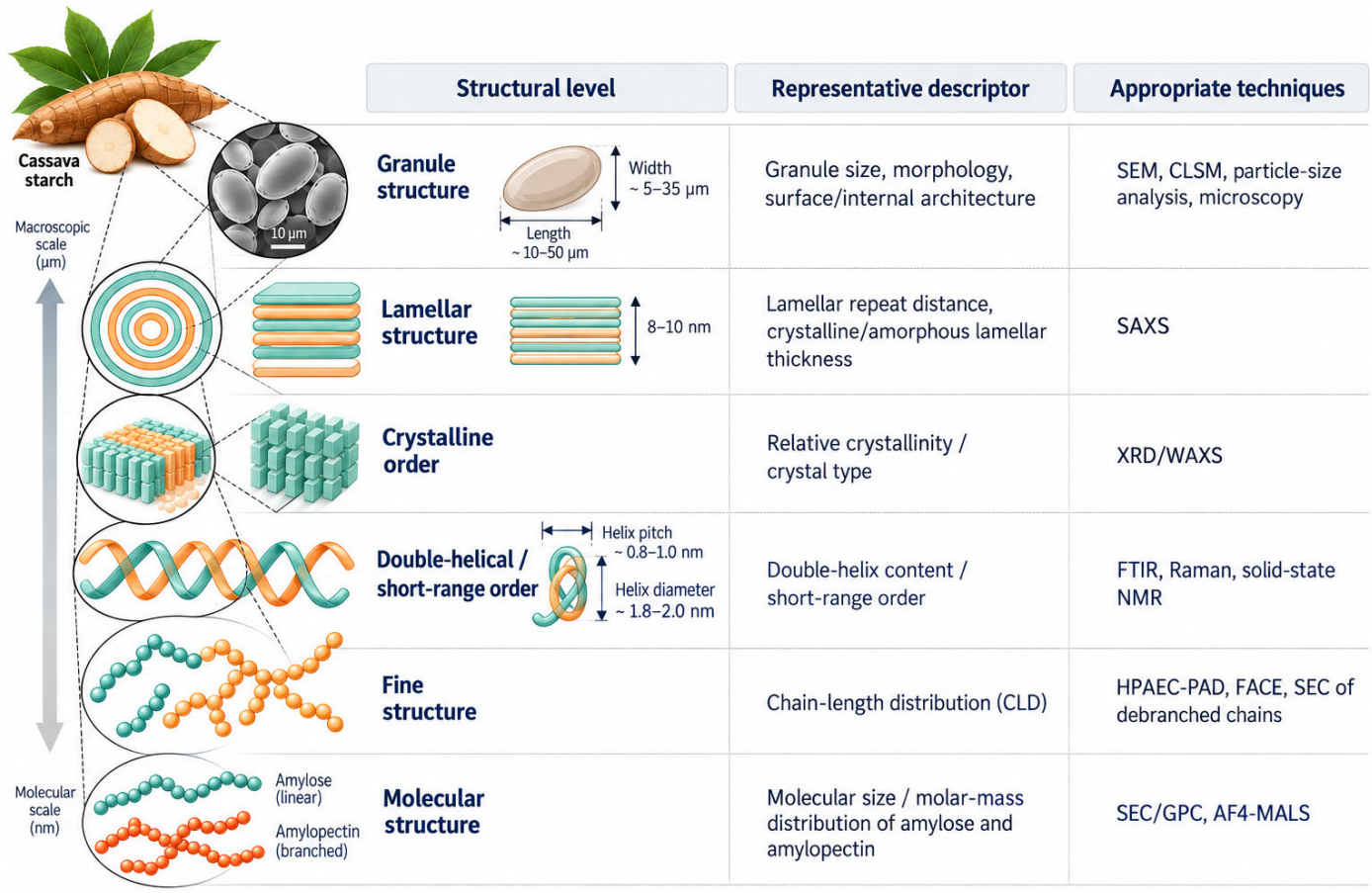

Figure 1. The multiscale structural organization of cassava starch, described in terms of its molecular, crystalline, granular, and higher-order structural characteristics, with cassava-specific structural parameters and representative analytical techniques incorporated where supported by the literature. (ChatGPT 5.5 (free version accessed on 12 August 2026, DALL-E 3 image generation engine; OpenAI, San Francisco, CA, USA; sourced via https://chatgpt.com) for the purposes of generating graphics (Figure 1). The prompt specified a multiscale structural hierarchy of cassava starch, while cassava-specific structural ranges and representative analytical techniques were edited for accuracy.).

As mentioned earlier, cassava starch functionality cannot be predicted from any single descriptor, least of all from apparent amylose content (AAC) alone, which remains the most reported and most commonly over-interpreted parameter in the cassava literature. Rather, function arises from the combination of molecular fine structure, supramolecular order, granule architecture and minor constituents, and the relative weight of each descriptor differs according to which functional property is being predicted. A study correlated pasting, thermal, and retrogradation parameters with fine-structural parameters derived from size-exclusion chromatography (SEC) across seven cassava cultivars, revealing a distinct division of roles: cool-paste viscosity and setback were primarily influenced by amylopectin fine structure; breakdown, peak time, and gelatinization peak temperature, along with retrogradation indices, were mainly dictated by amylose fine structure; and pasting temperature and gelatinization onset temperature were jointly reliant on both macromolecules [144]. Any model relating structure to function for cassava starch must be particular to its properties rather than universally applicable. Table 5 summarizes the structure–function matrix of cassava starch. In addition, Table 6 provides the principal mechanisms and key evidence for each structural descriptor on the functional and nutritional properties of cassava starch.

Table 5. Directional influence of structural descriptors on the functional and nutritional properties of cassava starch.

Structural Descriptor	SP	To/Tp	ΔH	PTe	PV	BD	SB	Gel Strength	Retro.	RS/SDS	Code
Apparent amylose content	↓	↑	↓	↑	↓	↓	↑	↑	↑	↑	C
Amylose molar mass/chain length	↓	↔	↔	↑	↓	↓	↑	↑	↑↓ [a]	↑	C/E
Amylopectin short A chains (fa, DP 6–12)	↑	↓	↓	↓	↑	↑	↑ [b]	↓	↓	↓	C
Amylopectin long B chains (fb2/fb3, DP ≥ 25)	↓	↑	↑	↑	↔	↓	↓ [b]	↑	↑ [c]	↑	C
Amylopectin molar mass/hydrodynamic radius	↑	↔	↔	↔	↑	↑	↔	↑	↔	↔	C
Macromolecular density/branching degree	↓	↔	↔	↔	↓	↓	↓	↓	↓	↔	C
Covalently bound phosphate monoester	↑	↓	↔	↓	↑	↑	↓	↓	↓	↔ [d]	C
Lipid/V-type complexed amylose	↓	↑	↔	↑	↓	↓	↓	↓	↓	↑	C [e]
Granule surface & channel protein	↓	↔	↔	↔	↔	↔	↔	↑	↔	↔	E
Relative crystallinity	↓	↑	↑	↑	↓	↓	↔	↔	↔	↑	E/M
B-type fraction within C-type polymorph	↔	↓	↓	↓	↔	↔	↔	↔	↔	↑	M
Crystalline lamellar thickness	↓	↑	↑	↑	↔	↔	↔	↔	↔	↑	E
Mean granule diameter	↔	↑ [f]	↔	↑	↑	↑	↔	↔	↔	↑	C/E
Surface pore & channel density	↑	↔	↔	↓	↔	↔	↔	↔	↔	↓	M

Note: Abbreviations: SP, swelling power; To/Tp, gelatinization onset/peak temperature (DSC); ΔH, gelatinization enthalpy; PTe, pasting temperature (RVA); PV, peak viscosity; BD, breakdown viscosity; SB, setback viscosity; Retro., retrogradation extent/rate on storage; RS/SDS, resistant and slowly digestible starch fractions; CLD, chain-length distribution; AAC, apparent amylose content; R_h, hydrodynamic radius. Arrows denote the direction of change in each functional property in response to an increase in the structural descriptor, with all other descriptors held nominally constant. Evidence provenance is coded to distinguish relationships demonstrated directly in cassava from those inferred from other botanical sources or from mechanism alone. Symbols: ↑ increases, ↓ decreases, ↔ little or no consistent effect, ↑↓ non-monotonic or context-dependent (see notes). Evidence code: C = direct cassava evidence, E = extrapolated evidence, M = mechanistic inference. [a] Retrogradation rate is non-monotonic in amylose chain length: intermediate degrees of polymerization (~DP 100) re-associate most rapidly, whereas very long chains are kinetically hindered. [b] The positive association of setback with fa, and the negative association with fb3, is as reported for cassava [144] and runs counter to the generalization derived from cereal starches. Setback is measured on cooling within the RVA cycle and is dominated by leached-glucan re-association, which is kinetically distinct from the long-term amylopectin recrystallisation captured in the "Retro." column. This divergence is a genuine

discrepancy in the literature and is flagged rather than reconciled. [c] Long-term retrogradation only. The long-to-short chain ratio in amylopectin was shown to govern long-term retrogradation directly in enzymatically remodeled cassava starch [145]. [d] Phosphate monoester substitution has little direct effect on RS. Phosphate cross-linking (STMP/STPP) has the opposite effect, generating RS4 by covalently tethering chains—the two must not be conflated. Phosphate monoester substitution and phosphate crosslinking are chemically distinct modifications. Monoester substitution introduces charged phosphate groups and generally has limited direct effects on RS, whereas crosslinking with reagents such as STMP or STPP forms covalent bridges between starch chains and can enhance RS4 formation. Their mechanisms and functional effects should therefore be considered separately [146]. [e] Cassava-specific evidence derives from induced complexation. Native cassava starch contains very low lipid (<0.2%), so this row describes a processing lever rather than a native compositional axis. [f] Larger granules generally show narrower gelatinization temperature range with a modestly higher onset; the effect on To is smaller in cassava than in potato because relative crystallinity is invariant across cassava granule-size fractions [147].

Table 6. The principal mechanisms and key evidence for each structural descriptor on the functional and nutritional properties of cassava starch.

Structural Descriptor	Principal Mechanism	Key Cassava Evidence	References
Apparent amylose content	Intragranular swelling restraint; forms continuous phase of paste; primary agent of short-term retrogradation	Waxy (*wx*/*wx*) mutants show elevated PV, elevated swelling index and dispersed-phase volume fraction, and outstanding freeze–thaw stability vs. wild type	[148–150]
Amylose molar mass/chain length	Longer chains traverse multiple amylopectin lamellae and bridge granule remnants; entanglement density governs network percolation	Tp, BD and retrogradation indices governed principally by amylose fine structure across 7 cultivars	[144]
Amylopectin short A chains	Chains too short to span the crystalline lamella generate defective crystallites; lower helix stability, greater enzyme accessibility	fa and fb1 differed significantly among cultivars and correlated with cool-paste viscosity and setback	[144]
Amylopectin long chains	Longer external chains form more thermostable double helices; entangle with amylose to build shear-resistant networks	High-To group (63.7 °C) vs. low-To group (57.3 °C) separated by proportion of long FI chains (DP 63–67); high group formed “true” gels with frequency independence	[151]
Amylopectin molar mass/Rh	Larger macromolecules occupy greater hydrodynamic volume, raising dispersed-phase viscosity at equal solids	Rh 53.35–58.45 nm across cultivars; amylose and amylopectin molecular sizes positively correlated	[144]
Macromolecular density/branching	Denser, more highly branched molecules occupy less volume per unit mass, lowering viscosity and re-association propensity	Fermentation reduced Mw and produced denser, more branched macromolecules; linked to high loaf volume in expanded products	[32]

Table 6. *Cont.*

Structural Descriptor	Principal Mechanism	Key Cassava Evidence	References
Phosphate monoester	Anionic groups produce inter-chain electrostatic repulsion, facilitating hydration and retarding re-association; acts in the amorphous phase	Phosphorylation to 0.160% altered pasting and digestibility with no detectable change in crystalline pattern	[152]
Lipid/V-type complex	Single-helix inclusion complexes are enzyme-resistant and restrain swelling; ligand chain length sets complex stability	Complex index 88.9% (lauric) and 80.9% (decanoic); V6/V7 conformations by NMR; lauric complex gave highest RS	[153]
Surface & channel protein	Physical barrier to amylose leaching; contributes to inter-granule aggregation in the set gel	Removal of channel and surface proteins raised amylose leaching and lowered G′, G″ and gel strength in rice and buckwheat (notably that this information is not from cassava starch)	[154]
Relative crystallinity	Quantity of ordered double-helical domains requiring thermal energy to melt	Reported 25–35% for cassava, method-dependent	[42,43]
B-type fraction (C-type polymorph)	Core-localized B-type allomorphs melt at lower temperature but resist α-amylase more than peripheral A-type	C-type assignment and shouldered DSC endotherm characteristic of cassava	[2]
Crystalline lamellar thickness	Thicker crystalline lamellae and semi-crystalline repeats retard amylolysis	Lamellar content lowest in small-granule fraction while crystallinity invariant across cassava size fractions	[147]
Mean granule diameter	Governs surface-area-to-volume ratio for enzyme adsorption and water uptake	Cassava (4.5–21 μm, AAC 28.4%) vs. yam (~1.7× larger, AAC 40.3%): cassava lower gelatinization temperature, lower RS, higher PV and SP	[155]
Surface pore & channel density	Pores and channels are the principal route for α-amylase access to the granule interior	Native cassava granules are smooth and pore-poor, limiting raw-state digestibility despite low gelatinization temperature	[156]

6.2. Molecular-Scale Determinants

6.2.1. Amylose Content, Molecular Size and Functional Consequences

Amylose in cassava starch is predominantly straight, with minimal branching, and is produced by GBSSI [101]. AAC generally ranges from approximately 15 to 30% of dry starch in germplasm collections, with an average near 20–21% across numerous genotypes; specific studies indicate narrower ranges based on their sampling. For example, 15.9–22.4% was reported for five Thai cultivars [151], 13.6–18.1% was reported for seven Ghanaian yellow-fleshed genotypes [156], and 24.8–27.6% was reported for the seven cultivars planted in Nakorn Ratchasima Province of Thailand [144]. A comprehensive Brazilian study on breeding populations revealed significant genetic variability in amylose and its systematic relationship with pasting behavior, advocating for the concurrent phenotyping of AAC and

paste characteristics in breeding processes instead of focusing solely on AAC [157]. Table 7 summarizes the germplasm variation in structure and function.

Table 7. Reported variation in structural descriptors and functional properties of cassava starch across germplasm, growth environment and harvest maturity.

Germplasm Set/Origin	Structural Descriptors	Key Structure–Function Findings	References
Thai cultivars $n = 5$	%AAC: 15.9–22.4 Granule size: 12.9–17.2 μm Fine structural: Trimodal AP: FIII DP 12; FII DP 24.3–24.7; FI DP 63–67 Thermal: To 57.3 °C (low group) vs. 63.7 °C (high group)	Proportion of long FI chains separated the two To groups; high group formed "true" gels with shear resistance, frequency independence and higher firmness	[151]
Cultivar panel (China) $n = 7$	%AAC: 24.8–27.6 Fine structural: Rh (whole starch) 53.35–58.45 nm; fa and fb1 significantly different Thermal: Differences in To, Tp Pasting: Differences in CPV, SB, BD, PTi, PTe	Property-specific control: CPV and SB by AP fine structure; BD, PTi, Tp and retrogradation by AM fine structure; PTe and To by both	[144]
Thai cultivars (2 locations) $n = 5 \times 2$	Fine structure: fa, fb2, fb3, average CLD genotype-controlled; fb1, AP2/AP1, Rh environment-controlled Thermal: To, Tp genotype-controlled Pasting: PV, BD environment-controlled Digestibility: RS not significantly affected by environment	Variance partitioning: G × E significant for BD, Rh, AP2/AP1 and fb2	[100]
Yellow-fleshed genotypes (Ghana) $n = 7$	%AAC: 13.6–18.1 Fine structure: Cultivar differences resolved by SEM, XRD and FTIR Pasting: PV 354–520 BU; BD 233–366 BU Digestibility: In vitro digestibility 11.4–18.5% (mean 15%)	Short-range order differences detectable by FTIR tracked with PV, BD and digestibility	[156]
Waxy (spontaneous) vs. commercial vs. high-amylose $n = 7$	%AAC: ~0 (waxy); 19.9 (commercial); 30.2 (high-amylose) Fine structure: GBSSI-null Pasting: Waxy: higher PV, lower pasting temperature	Waxy gels considerably clearer, with higher solubility and swelling power; excellent refrigerated, frozen and freeze–thaw stability	[149]
Original *wx*/*wx* mutant vs. wild type $n = 2$	%AAC: 3.4 (colorimetric); 0 (DSC); GBSS absent by SDS-PAGE Fine structure: GBSSI-null Pasting: Higher PV, BD and SB than normal cassava	Solubility considerably reduced; swelling index and dispersed-phase volume fraction increased	[148]

Table 7. *Cont.*

Germplasm Set/Origin	Structural Descriptors	Key Structure–Function Findings	References
Waxy vs. normal cassava (vs. waxy maize, rice, potato) $n = 6$	%AAC: 0 vs. normal Fine structure: λmax 535 nm (waxy) vs. 592 nm (normal)—loss of long linear helical segments Pasting: Waxy PV ~1119 cP	Waxy cassava positioned against established waxy starches under thermal, chemical and mechanical stress; paste clarity markedly improved	[150]
Amylose-free clone AM206-5 $n = 1$	%AAC: 0.54 ± 0.09 Granule size: 16.92 ± 0.20 Fine structure: Elliptical/spherical truncated, no aggregation Pasting: BD 698 ± 2 cP; final viscosity 731 ± 16 cP	Thermally less stable and lower final paste viscosity than commercial waxy maize starch	[148]
Cultivar SC5, harvest 7–11 months $n = 1 \times 5$ ages	%AAC: 20.93–22.61 Granule size: Slight change only Fine structure: Lamellar and crystalline structure changed slightly; molar weight peaked at 9 months Pasting: 9-month: PTe 64.6 °C (lowest), PV 2105 cP (highest) Digestibility: Changed slightly	Compositional descriptors near-constant while molar mass explained the pasting trajectory; 9 months identified as the physicochemical turning point	[101]
Commercial cassava vs. yam, and blends $n = 2 + 3$ blends	%AAC: 28.39 (cassava) vs. 40.32 (yam) Granule size: 4.5–21 (cassava); yam ~1.7× larger Thermal: Cassava lower gelatinization temperature Pasting: Cassava higher PV Digestibility: Cassava lower RS; RS rose monotonically with yam substitution	Granule size and amylose content jointly set the digestibility–viscosity trade-off, tunable by blending	[155]
Brazilian breeding population (large panel)	%AAC: Wide genotypic range Pasting: Correlated with AAC	Argues for simultaneous phenotyping of AAC and paste properties in breeding pipelines rather than selection on AAC alone	[157]
Amylose-free vs. wildtype across environments (multi-site)	%AAC: ~0 vs. wildtype Pasting: Waxy PV exceeds wildtype at low–intermediate altitude; effect diminishes with altitude	Environment and G × E significantly modulate swelling power and peak viscosity in both starch types	[158]

Note: Values are ranges across the genotypes examined within each study unless otherwise stated. Direct comparison of absolute values between studies should be made with caution, as amylose determination method (colorimetric, DSC, concanavalin A), viscometric instrument and units (RVA cP vs. Brabender BU), and crystallinity deconvolution protocol were not harmonized across sources.

Amylose functions in three separate capacities. Initially, within the unaltered granule, it functions as a swelling inhibitor: amylose chains are intermingled with amylopectin aggregates, creating temporary junction zones, and in certain plant sources, they complex with lipids, resulting in higher-amylose starches absorbing water less easily and necessitating elevated temperatures and shear for granule breakdown [159,160]. Secondly, after leaching, amylose transforms into the continuous phase of the starch paste, creating an entangled net-

work that incorporates swollen granule remnants as a filler phase; this composite structure governs the rheological properties of the paste and gel [161]. Thirdly, regarding cooling and storage, amylose serves as the principal factor in short-term retrogradation, re-forming into double helices and B-type crystallites within a matter of hours [2].

Cassava starch holds a peculiar status within this framework. Its amylose possesses a significant molar mass (about 10^5–10^6 Da) but is found in only moderate amounts, and its granules release amylose slowly compared to other tuber starches. A direct comparison during regulated gelatinization indicated that cassava granules generally retained their structure, with approximately 8.5% amylose leaching after 30 min at 60 °C, while potato granules expanded swiftly and compromised their integrity, resulting in about 51% leaching under the same conditions [161]. This limited initial leaching, along with a significant ultimate swelling capacity, is a primary factor for cassava pastes achieving exceptionally high peak viscosity while maintaining remarkable clarity, resulting in minimal dispersed-phase light scattering and a relatively sparse amylose network that does not obscure the system [24].

The functional significance of amylose is most clearly illustrated by the amylose-deficient (waxy) cassava mutants. The initial spontaneous *wx*/*wx* GBSSI mutant discovered at CIAT exhibited heightened peak viscosity, increased breakdown, and modified set-back compared to wild-type cassava, alongside significantly diminished solubility and augmented swelling index and dispersed-phase volume percentage [148]. The later identification of further spontaneous waxy sources validated the phenotype: waxy cassava gels exhibited significantly greater clarity, solubility, swelling power, and peak viscosity compared to conventional normal cassava starch, and demonstrated remarkable stability under refrigeration, freezing, and freeze–thaw conditions [149]. Comparative analysis of waxy cassava in relation to waxy maize, rice, and potato starches under thermal, chemical, and mechanical stress revealed that the peak wavelength of iodine absorption decreased from 592 nm in standard cassava starch to 535 nm in the waxy variant, indicating a direct optical signature of a reduction in long linear helical segments [150]. The molecular and supramolecular analysis of these waxy starches through asymmetrical flow field-flow fractionation and multi-angle light scattering demonstrated that the reduction in amylose correlates with significant alterations in amylopectin's macromolecular density and branching, rather than simply the removal of a single component [162]. The tangible benefits are now evident in actual matrices: native waxy cassava starch attained an average specific expansion volume 3.5 times greater than that of wild-type cassava starches (17.6 versus 4.8 $cm^3\ g^{-1}$) in gluten-free baked and expanded goods, surpassing even fermented, sun-dried wild-type starch [32].

6.2.2. Amylopectin Fine Structure

Amylopectin, constituting roughly 75–85% of cassava starch, is the structural scaffold of the granule and the direct determinant of crystallinity, gelatinization thermodynamics and much of paste stability. Its chains are conventionally partitioned by degree of polymerization (DP) into A chains (fa, DP 6–12), B1 chains (fb1, DP 13–24), B2 chains (fb2, DP 25–36) and B3+ chains (fb3, DP ≥ 37), or alternatively resolved by gel-permeation chromatography into trimodal fractions FIII (~DP 12), FII (~DP 24) and FI (~DP 63–67) [151].

Cassava amylopectin has a distinctive internal architecture. Systematic α-amylolytic dissection into domains and clusters showed that cassava amylopectin possesses clusters of comparatively uniform size, with β-limit dextrin clusters averaging DP 67–78; the bulk of clusters by weight fell in the DP 104–129 range and contained 13–16 chains, and adjacent clusters were interconnected by long B chains with an inter-cluster internal chain length of 10.5–12.3 residues, with no branching detected outside clusters [163]. This relatively homo-

geneous, tightly clustered internal organization, combined with a short average external chain length, helps explain why cassava starch gelatinizes at lower temperature than most cereal starches despite comparable relative crystallinity [151].

Differences in amylopectin chain-length distribution within cassava genotypes have clear functional effects on gelatinization, pasting, and gel properties [100]. In five cassava cultivars, starches separated into low- and high-gelatinization groups with average onset temperatures of about 57.3 °C and 63.7 °C, respectively, and these groups differed in swelling power, viscoelasticity, and gel firmness [151]. They found that the difference was due to the amount of long FI chains, which bind to amylose to make longer, more thermostable helical structures. The high-temperature group made true gels that were more resistant to shear, frequency independent, and gel firmness. Similar connections have been found in African germplasm, where the percentage of A chains ranged a lot (for example, from 42.3% to 46.6% in Ugandan varieties) and matched the profiles of pasting temperature and viscosity. Statistical analysis revealed significant differences among cultivars in the proportions of short fa (DP 6–12) and fb1 (DP 13–24) chains [144]. They also found that amylose and amylopectin molecular sizes were positively related. They also found that the position of the amylopectin SEC peak was positively related to cool-paste viscosity and setback while negatively related to fb3 and positively related to fa.

The mechanistic logic is consistent across botanical sources. A high proportion of very short A chains (DP $\leq$ 12) is destabilizing, because such chains are too short to form stable double helices spanning the crystalline lamella; they generate defective crystallites, lower gelatinization onset and enthalpy, and increase susceptibility to enzymatic attack. Conversely, an elevated proportion of intermediate and long chains (DP 25–36 and $\geq$37) raises gelatinization temperatures, increases thermal stability and reduces breakdown viscosity [164]. This gradient has been quantified in parallel systems: across ten waxy rice varieties, the cultivars with the highest proportions of intermediate and long chains showed the highest onset (60.2–66.4 °C), peak (~72 °C) and conclusion (79.4–80.8 °C) temperatures and the lowest breakdown viscosity, with relative crystallinity 19.3–22.8% and lamellar spacing 8.8–9.4 nm [165]. Enzymatic remodeling experiments confirm causality rather than mere correlation: amylomaltase treatment of cassava starch transferred hydrolyzed amylose segments onto amylopectin, elongating amylopectin chains and broadening their distribution, and the resulting long-to-short chain ratio directly governed long-term retrogradation behavior [145].

6.2.3. Macromolecular Size, Branching Density and Molar Mass Distribution

Cassava starch is characterized by unusually high molar mass in both fractions—amylose in the 10^5–10^6 Da range and amylopectin in the 10^7–10^8 Da range—which is one reason tapioca pastes reach such high peak viscosities at modest solids [43]. Hydrodynamic radius (Rh) of whole branched starch varied from 53.35 to 58.45 nm across seven cultivars, a narrow but functionally meaningful range [144]. Because SEC of high-molar-mass amylopectin is vulnerable to shear scission, field-flow fractionation coupled to multi-angle light scattering has become the preferred approach for cassava, and has revealed that molecular density (mass per unit hydrodynamic volume) and branching degree, not molar mass alone, discriminate functionally distinct starches. In the baking study, natural fermentation reduced weight-average molar mass and produced denser, more highly branched macromolecules, and these changes correlated with improved loaf volume independently of amylose content [32].

Molar mass is also developmentally dynamic. In cassava harvested at 7–11 months, granule size, lamellar structure, crystalline structure and digestibility varied only slightly and AAC remained within 20.93–22.61%, yet molar mass increased markedly to a maximum

at 9 months and then declined; pasting behavior tracked this trajectory closely, with the 9-month starch showing the lowest pasting temperature (64.6 °C), highest paste viscosity (2105 cP) and greatest retrogradation tendency [101]. This is an instructive case in which the conventional compositional descriptors were nearly constant while a molecular-architecture descriptor explained essentially all of the functional variation, a caution against structure–function models built exclusively on AAC and granule size.

6.3. Minor Constituents as Functional Modifiers

Cassava starch is compositionally clean relative to cereal starches, containing very low residual protein (typically < 0.3%), lipid (<0.2%) and ash. This purity contributes to its neutral flavor, high paste clarity, and white color, making cassava starch attractive for applications in which flavor and visual transparency are important [2,24]. It also means that cassava lacks the internal lipid-complexed amylose (V-type) that restrains swelling in cereal starches, which contributes to the very high swelling power and peak viscosity of tapioca pastes [153].

Covalently bound phosphorus, present largely as phosphate monoesters on C-6 and C-3 of amylopectin, is present at intermediate levels, well below potato starch (typically 400–1000 ppm) but above most cereals [166]. Because phosphate groups are anionic, they promote electrostatic repulsion between chains, facilitate hydration and swelling, retard retrogradation and increase paste clarity [30]. These effects are primarily associated with monoester substitution, in which phosphate groups are covalently attached to individual starch chains without forming interchain bridges. In contrast, phosphate crosslinking introduces covalent bridges between starch molecules, restricting chain mobility and limiting swelling. Therefore, the functional effects of phosphorylated starch depend on whether monoester substitution or crosslinking predominates. Genotypic screening has identified unmodified cassava accessions with unusually high native phosphorus, offering a clean-label route to properties conventionally achieved by chemical phosphorylation [167]. The functional leverage of phosphorus has been confirmed by the reverse experiment: response-surface optimization of cassava starch phosphorylation with sodium trimetaphosphate and sodium tripolyphosphate raised phosphorus content to 0.160% and altered pasting, physicochemical and in vitro digestibility profiles without any detectable change in the crystalline pattern, demonstrating that phosphate acts primarily through amorphous-phase hydration and chain repulsion rather than by remodeling crystallites [152]. This finding suggests that, under the reported conditions, phosphate monoester substitution primarily affects hydration and interchain electrostatic interactions in amorphous regions rather than substantially altering crystalline organization.

Surface- and channel-associated proteins are present at low levels in starch granules but can still be functionally important because they influence pore structure, diffusion, hydration, hydrolysis, and rheology [168]. In cereal starches, selective removal of granule channel proteins and surface-associated proteins increased amylose leaching and decreased storage and loss moduli and gel strength, with channel proteins exerting a greater effect than surface proteins [169]. Whether the same pattern holds in cassava remains unresolved, because the cassava evidence currently centers on protein–starch composite systems rather than selective removal of cassava's endogenous granule proteins; these composite studies still show that added proteins can strongly shift storage modulus, water retention, gel hardness, retrogradation, and network structure in cassava starch systems [170].

6.4. Supramolecular Order

Cassava starch is semi-crystalline, with relative crystallinity most commonly reported in the 25–35% range and a crystalline polymorph described as A-type or, more often, C-

type—a coexistence of A- and B-type unit cells within a single granule population [42,43]. Reported crystallinity values are, however, strongly method-dependent, with values as high as ~46% appearing in the literature depending on background subtraction and peak-fitting conventions; this heterogeneity is one of the least appreciated obstacles to cross-study structure–function synthesis in the cassava field [2].

The C-type polymorph has direct functional meaning. B-type allomorphs, which tend to be located in the granule core, melt at lower temperature and are more resistant to α-amylase than the peripheral A-type crystallites [171]. This spatial partitioning generates the characteristic broad or shouldered DSC endotherm of cassava starch, in which a main gelatinization peak is accompanied by a lower-temperature shoulder, and it also produces a two-stage hydrolysis profile in which the amorphous and A-type peripheral regions are digested before the B-type core [2,172].

Short-range molecular order—the population of double helices irrespective of their long-range packing—is conventionally probed by FTIR [173] (the absorbance ratio at 1047/1022 cm^{-1}) and by solid-state ^{13}C CP/MAS NMR [174]. This descriptor frequently predicts functional behavior better than X-ray relative crystallinity, because processing operations such as annealing, heat–moisture treatment and ultrasonication can perturb helical order and crystalline registry to different extents [175]. FTIR analysis of yellow cassava genotypes, alongside SEM and XRD, showed that structural differences among cultivars were detectable at the short-range level and tracked with peak and breakdown viscosity (354–520 BU and 233–366 BU respectively) and in vitro digestibility (11.4–18.5%) [156].

At the lamellar scale, small-angle X-ray scattering resolves the ~9–10 nm semi-crystalline repeat and, through one-dimensional correlation-function analysis, the individual thicknesses of crystalline and amorphous lamellae. These parameters are among the most direct determinants of enzymatic accessibility: thicker crystalline lamellae and thicker overall semi-crystalline repeats retard amylolysis, whereas lamellar disruption during digestion or hydrothermal processing accelerates it [176]. Fractionation of cassava granules by size showed that lamellar content was lowest in the small-granule fraction while relative crystallinity was essentially invariant across all cassava size fractions—in contrast to potato, where small granules were also less crystalline [147]. This dissociation of granule size from crystallinity in cassava is functionally important: it means that in cassava, unlike potato, size-based fractionation modulates lamellar organization and surface-to-volume ratio without substantially altering crystalline quality.

6.5. Granule Scale

Cassava starch granules are round to oval with a characteristic truncated or flattened face on one side, frequently accompanied by a central conical depression, and they present smooth, largely non-porous surfaces in the native state [156,177]. Individual granule diameters span roughly 5–40 μm, with cultivar means most often reported between 5 and 20 μm; representative examples include 12.9–17.2 μm across five Thai cultivars [151], and 4.5–21 μm for a commercial cassava starch compared with yam [155]. The mutation of the plastid-division gene *MeMinD* enlarges amyloplasts and broadens the casava starch granule size range, and this morphological change is accompanied by an increased apparent amylose content; separately, cassava mutants with extreme amylose contents (0% and 30–31%) have been characterized, with the waxy mutation leaving amylopectin structure unmodified [178,179].

Granule size influences function through surface-area-to-volume ratio [180]. Smaller granules present more surface per unit mass for enzyme adsorption and for water uptake, generally hydrate faster, gelatinize over a broader temperature range, and are digested more rapidly; larger granules typically show higher peak, trough and final viscosities [181]. The

relatively smooth, pore-poor surface of native cassava granules is one reason raw cassava starch, despite its low gelatinization temperature, shows only moderate native digestibility, surface pores and channels provide the principal route by which α-amylase gains access to the granule interior [182], and cassava offers relatively few. Nonetheless, in the gelatinized state cassava starch is highly digestible, with reported estimated glycemic index values around 78 [153], because the low-temperature, high-swelling gelatinization behavior that makes cassava attractive as a thickener also produces a fully hydrated, enzymatically accessible matrix [182].

In blending experiments, cassava and yam starches differ in granule size and amylose content, and blending them modulates functional, thermal and digestive properties, though the two factors interact rather than acting independently. Cassava starch, with small granules (4.5–21 μm) and low amylose content (28.39%), showed lower gelatinization temperature, lower resistant starch, higher peak viscosity and higher swelling power. Yam starch, with granules 1.7 times larger and high amylose content (40.32%), showed higher resistant starch and gelatinization temperature but lower viscosity. Progressive yam substitution significantly decreased rapidly digestible starch from 18.03% in cassava to 4.95% at the 25:75 cassava–yam blend, while resistant starch rose from 29.96% to 72.45% [155].

6.6. From Structure to Function

6.6.1. Hydration, Swelling and Solubility

Swelling power and solubility index integrate all structural levels. Swelling reflects the capacity of the amorphous growth rings and amorphous lamellae to imbibe water once inter-chain hydrogen bonding is disrupted, whereas solubility reflects the escape of soluble glucan, principally amylose, from the granule [2]. Cassava's combination of low amylose content, low lipid content, appreciable phosphate content and weakly ordered peripheral crystallites yields high swelling power at relatively low temperature [157]. Waxy cassava starches, lacking the amylose restraint entirely, exhibit still higher swelling power and dispersed-phase volume fraction; reports on solubility differ by genotype and test conditions, with one study finding reduced solubility and another higher solubility at 90 °C [183].

6.6.2. Gelatinization

Gelatinization onset and peak temperatures are set principally by the stability of the crystalline lamellae, which depends on amylopectin chain-length architecture and crystalline packing, whereas gelatinization enthalpy reflects loss of amylopectin crystalline order [184]. Cassava starches show substantial variation in gelatinization temperatures across samples, and initial gelatinization temperature rises as the proportion of short amylopectin chains falls [2]. Positive correlations of onset temperature with longer amylopectin chain classes also support a fine-structure basis for thermal stability [144]. In waxy cassava, gelatinization enthalpy can exceed that of 18–20% amylose cassava starches, consistent with a more organized double-helical structure [183].

6.6.3. Pasting

Rapid Visco Analyser profiles translate these same structural determinants into an industrially interpretable trace. In cassava genotypes with waxy functionality, pasting behavior varies with amylose status and amylopectin structure, and crystallinity correlates strongly with viscosity-related parameters [144]. Removal of amylose in cassava increased peak viscosity and breakdown in the original waxy mutant [148]. A later functional evaluation likewise reported higher maximum viscosity and breakdown for natural waxy cassava than normal cassava [2]. Genotypes selected for waxy-like functionality also showed low

final viscosity, consistent with improved freezing stability and reduced tendency toward reassociation during cooling [185].

6.6.4. Rheology and Gelation

Cassava pastes can be viewed as systems of swollen granule remnants dispersed in a continuous starch phase formed during gelatinization and pasting [2]. Retrogradation and gel setting reflect subsequent chain reassociation, with amylose contributing strongly to initial hardening and amylopectin contributing more slowly to network development [145]. Native cassava is widely described as having good gel formation capacity, stability, and comparatively low retrogradation tendency among common starches. Waxy cassava retains broadly similar thermomechanical behavior to waxy maize, supporting its use where soft, stable starch textures are desired [183].

6.6.5. Retrogradation, Syneresis and Freeze–Thaw Behavior

Retrogradation proceeds through polymer reassociation during cooling, altering viscosity, turbidity, gel-forming capacity, and crystallinity [185]. Amylose is a major driver of the fast retrogradation phase because it rapidly forms ordered matrices that nucleate slower amylopectin [186]. Starches with lower amylose therefore tend to retrograde less readily. In cassava specifically, normal root and tuber starch gels showed lower syneresis than cereal starches after refrigeration and freeze–thaw, while waxy cassava showed no syneresis after 5 weeks at 4 °C or −20 °C [150].

6.6.6. Digestibility and Glycemic Function

Digestibility is tightly linked to starch structure because crystalline order, double helices, and supramolecular packing reduce water accessibility and enzyme attack [2]. Cassava starch is usually 15–25% amylose, varies among cultivars and with plant development, and is generally valued for broad processing functionality rather than intrinsically high resistant starch [187]. Structural routes that lower digestibility work by adding or stabilizing ordered arrangements absent from the native hydrated state, especially helix-based crystalline structures [184].

6.7. Genotype, Environment and G × E as Levers on Structure

Because cassava starch quality is a breeding target controlled by starch-biosynthetic genes and mapped QTLs, structure–function relationships are reasonably framed as a breeding and agronomy problem [44]. Cassava breeding also faces substantial within-family variation and strong nonadditive effects for yield, which makes genotype-by-environment interpretation practically important [183]. More generally, cassava is cultivated across wide edaphoclimatic ranges and multiple varieties, so environmental plasticity is expected at the crop level as well [188].

Environmental effects on starch functional properties are also important. Molecular size was found to be strongly influenced by environmental conditions [100]. Cassava starch structure also varies with cultivar and growing conditions, including amylose content, further supporting the importance of genotype–environment interactions [188].

7. Functional Starch Design for Sustainable Food Applications

The structure–function relationships described above provide a basis for designing cassava starch according to specific food-processing and nutritional requirements rather than treating starch as a generic thickening ingredient [24]. Cassava starch and flour are already used in baking, soups, syrups, and edible films [24,189]. Cassava starch is also positioned as a high-value food ingredient whose applications depend on physicochemical

and pasting properties, including use as a thickener and stabilizer in food systems [190]. Variety-dependent functional and pasting differences further support broader, application-specific deployment rather than one-size-fits-all use [24].

A structure-directed approach can match structural characteristics with targeted functions because amylose/amylopectin proportion, molecular weight, and chain-length distribution fundamentally influence starch physicochemical behavior and starch-based food properties [10]. High swelling is directly tied to viscosifying behavior and food-processing functionality [191,192]. In cassava materials, higher swelling power has been linked to good thickening and stabilizing functionality [190,193]. Controlling swelling also shifts downstream properties: reducing swelling tends to increase gel strength and limit digestive-enzyme access, lowering digestibility [191]. Amylose generally restricts swelling, while waxy or lower-amylose systems are more swelling-sensitive [192].

Control of amylopectin architecture, crystalline order, and retrogradation can be used to improve gel stability, freeze–thaw behavior, and digestibility [24,194]. Amylose and amylopectin chain structures shape the ordered degree, gel strength, and digestibility of retrograded starches [194]. Cassava genotype screening for end use already uses amylose content plus swelling, gelatinization, pasting, and freeze–thaw stability traits [24]. Cassava starches also differ from other root starches in pasting breakdown and gel character, which affects culinary fit [10].

Structural modification can generate cassava starches with higher resistant starch and lower digestion rates for health-oriented foods [43]. Chemical modification strategies can raise RS4 yields by 40–60% while improving thermal stability and techno-functional properties. These modified cassava starches have already been applied in bakery products, breakfast cereals, and gluten-free breads with improved texture and reduced estimated glycemic index [146]. Physical and enzymatic routes also alter composition, structure, functionality, and digestibility, and can be selected to customize cassava starch for application [70]. Enzymatic treatment appears especially effective for increasing slowly digestible and resistant starch fractions [195].

Modification of rheological behavior also enables 3D food printing applications [154]. Starch printability depends closely on gel structure and sufficient gel strength to maintain printed shape [196]. Amylose content is one important lever: higher amylose can produce denser gels with stronger mechanics and better printing stability, whereas low amylose can weaken the network [197]. Multi-scale starch structure can therefore be designed for rapid gelation, print precision, and lower digestibility in health-focused printed foods [198].

It should be kept in mind that the sustainability benefit of structure-directed starch design should be evaluated at the food-product level rather than inferred from starch functionality alone. A starch with improved freeze–thaw stability, for example, provides a meaningful sustainability benefit only if the improved stability translates into lower syneresis, longer acceptable shelf life, reduced product rejection, or lower food waste. Similarly, a starch with higher viscosity is not inherently more sustainable unless the increased functionality allows a lower inclusion level, lower processing energy, or improved product yield. Thus, the relevant endpoint is not the structural modification itself but the net change in resource use and product performance at the food-system level.

8. Conclusions

Cassava starch has considerable potential to contribute to sustainable food systems because cassava combines climate resilience, broad geographical adaptability, and versatile starch functionality. However, sustainability cannot be attributed to the crop alone; it depends on how cassava is produced, harvested, processed, modified, and utilized across the value chain.

Recent advances in starch extraction, modification, drying, water management, and residue valorization demonstrate opportunities to improve resource efficiency while tailoring starch quality. Processing should therefore be viewed not merely as a means of starch recovery but also as a strategy for directing starch structure and functionality. Genotype, growing environment, postharvest management, and processing conditions collectively shape the molecular, supramolecular, and granular characteristics of cassava starch, which in turn influence its pasting, gelatinization, gelation, retrogradation, rheological, and nutritional properties.

Integrating these relationships provides a foundation for structure-directed sustainability, whereby starch is designed to achieve the required functionality while minimizing resource inputs and processing burdens. This perspective shifts the emphasis from maximizing starch recovery or pursuing extensive modification toward selecting suitable cassava genotypes, applying efficient processing technologies, and tailoring starch characteristics to specific food applications. Such strategies may support higher-value utilization, improved nutritional functionality, and more efficient resource use, while creating opportunities for circular valorization of cassava residues. Nevertheless, improvements in individual processing parameters do not necessarily translate into lower overall environmental impacts, which must be evaluated within clearly defined system boundaries.

Several limitations in the current evidence should be acknowledged. Much of the available research remains at the laboratory scale, and studies differ in cassava genotype, raw-material characteristics, processing conditions, functional performance criteria, and experimental design. Moreover, quantitative assessments of water and energy consumption, greenhouse gas emissions, and other environmental impacts are often based on different system boundaries and assumptions, limiting direct comparisons among technologies. The sustainability implications of emerging extraction and modification methods therefore remain insufficiently established in many cases, particularly when energy requirements, enzyme or chemical inputs, downstream processing, and residue management are considered together.

Future research should move beyond isolated measurements of starch composition or functionality toward an integrated framework of genotype × processing × structure × function × sustainability. Combining multiscale structural characterization with food-matrix studies, harmonized LCA, techno-economic analysis, and nutritional evaluation will be essential for translating laboratory-scale findings into scalable and commercially viable processes. Ultimately, the sustainable development of cassava starch will depend on optimizing the entire value chain to transform a resilient crop into high-performance, nutritionally relevant, and high-value food ingredients and products while minimizing resource consumption and environmental burdens.

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specified a multiscale structural hierarchy of cassava starch, while cassava-specific structural ranges and representative analytical techniques were edited for accuracy. The authors critically reviewed the generated image for scientific accuracy and consistency with the cited literature. The authors edited the final figure as required and took full responsibility for the content of this publication.

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Abbreviations

The following abbreviations are used in this manuscript:

PPD	Postharvest Physiological Deterioration
CBSD	Cassava Brown Streak Disease
SDS	Slowly Digestible Starch
RS	Resistant Starch
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
PEF	Pulsed Electric Field
FIR	Far-Infrared Radiation
LCA	Life-Cycle Assessment
CLD	Chain-Length Distribution
AAC	Apparent Amylose Content
SEC	Size-Exclusion Chromatography
RVA	Rapid Visco Analyser
DSC	Differential Scanning Calorimetry
ΔH	Gelatinization Enthalpy
QTL	Quantitative Trait Locus
GBSS	Granule-Bound Starch Synthase
GBSSI	Granule-Bound Starch Synthase I
PTST1	Protein Targeting to Starch 1
DP	Degree of Polymerization
SP	Swelling Power
To	Gelatinization Temperature (onset)
Tp	Gelatinization Temperature (peak)
PTi	Pasting Temperature (initial)
PTe	Pasting Temperature (end)
PV	Peak Viscosity
BD	Breakdown Viscosity
SB	Setback Viscosity
CPV	Cold Paste Viscosity
Rh	Hydrodynamic Radius

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