

# Cocoa processing residues in a circular bioeconomy: integrated valorization pathways, applications, and future perspectives

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**Abstract:** Cocoa (*Theobroma cacao* L.) is a major tropical cash crop that generates large volumes of underutilized residues, including cocoa pod husks (CPH), cocoa bean shells (CBS), mucilage, and placenta tissues. These residues are generally dumped in the open field where they constitute environmental challenges, especially in the West African region, where cocoa production is dominant, with an annual estimated yield of 40–50 million tonnes CPH and nearly one million tonnes CBS. However, these residues can be integrated into the bioeconomy through valorization. This review synthesizes current knowledge on cocoa residue generation, composition, and its possible applications in different sectors. Analyses showed that cocoa residues are rich in phytochemicals such as polyphenols, flavonoids, methylxanthines, high in dietary fibres, and essential minerals, making them good antioxidants and antimicrobial agents. These components confer techno-functional properties suitable for food, nutraceutical, cosmetic, and pharmaceutical applications. Emerging valorization pathways include bioenergy production (biochar, biogas, briquettes, and bioethanol), functional food ingredients, cosmetics, renewable packaging materials, and agricultural inputs (organic fertilizers, mulches, animal feed after detoxification). Innovative approaches for effective valorization and sustainability, such as extraction, fermentation, and thermochemical processing, were explored. However, the presence of toxic theobromine, mycotoxins, heavy metals, high moisture content (perishability), and inadequate infrastructure for cocoa waste handling remain serious challenges, especially in West Africa. Pretreatment technologies, regulatory frameworks, and integrated biorefinery approaches manage these challenges for effective valorization. Overall, cocoa residue valorization into high-value products supports sustainable agriculture, rural income diversification, waste reduction, and the realization of a circular bioeconomy, which contributes to all SDGs, and is most impactful for SDGs 8, 12, and 13.

*Keywords: Cocoa residues, Valorization pathways, Biomass circularity, Sustainable agriculture, Bioenergy, Nutraceuticals*

## Introduction

The cocoa plant (*Theobroma cacao* L.) is a small perennial tropical tree extensively cultivated for its seeds, which are used in making chocolates. The cocoa tree crop is native to the Amazon Basin but is now cultivated extensively across tropical regions of West Africa, Latin America, and Southeast Asia (Swamy, 2023). The tree is relatively small in height, reaching about 4-8 meters, and grows better in the shade of other trees, in warm and humid conditions typical of rainforest climates. The shade of other trees provides moderated microclimates, facilitating good adaptation by reducing evapotranspiration stress. Solar radiation, temperature, and vapour pressure significantly influence cocoa tree transpiration and growth (Omotayo, Oguntunde, & Olufayo, 2019). The annual temperature and rainfall requirements are between 21-32°C and 1,500-2,000 mm, respectively. It is characterized by clusters of small flowers that grow directly from the trunk, branches, and lanceolate leaves. The cocoa fruit, the pod, is 15–30 cm long, with approximately 10 distinct vertical ridges running from the stem to the tip, and is typically oval to oblong in shape. A pod contains 20-50 seeds surrounded by a sweet, white pulp (Agronoblog, 2024; Omotayo et al., 2019). Because of the unique climate requirements for cocoa production, Bunn et al. (2018) emphasized the need for adaptive cultivation practices to avert the threat posed by prevailing climate change, including higher temperatures and more severe dry-season conditions in key producing regions (Bunn, Castro, Lundy, & Läderach, 2018).

This review adopts a circular bioeconomy framework to systematically evaluate cocoa processing residues as renewable resources for value-added applications. Unlike conventional reviews that focus primarily on compositional analysis or isolated applications, this study integrates feedstock characterization, conversion technologies, and end-use applications within a sustainability-oriented framework. The scope encompasses: (i) identification and quantification of cocoa processing residues, (ii) evaluation of their physicochemical and bioactive composition, (iii) critical analysis of valorization pathways across bioenergy, agriculture, food, pharmaceuticals, and materials science, and (iv) assessment of technical, environmental, and economic challenges limiting large-scale implementation.

The novelty of this review lies in its integrated, cross-sectoral analysis and emphasis on recent advances (2020–2025), particularly in biorefinery approaches, green extraction technologies, and high-value applications such as bioplastics and cosmeceuticals. Several recent reviews have examined cocoa by-products and their applications. For instance, a study published in *Biofuels, Bioproducts and Biorefining* focused primarily on biomass conversion technologies for cocoa residues, with emphasis on energy recovery pathways, with limited attention to non-energy applications or cross-sector integration (Morales, Moreno, Contieri, Rostagno, & Forster-Carneiro, 2025). Similarly, a recent article in *Heliyon* provided a broad overview of cocoa waste management and emerging applications, but with limited critical comparison of technological efficiencies and scalability (Anoraga, Shamsudin, Hamzah, Sharif, & Saputro, 2024). In contrast, the present review addresses these gaps by offering a holistic, systems-level framework grounded in the circular bioeconomy, explicitly linking feedstock composition, processing technologies, and diversified end-use applications across sectors such as bioenergy, agriculture, food, pharmaceuticals, and materials science. Furthermore, the review introduced a context-specific perspective focused on developing

economies, particularly West Africa, where infrastructure, policy, and socio-economic factors significantly influence implementation.

### **Annual Global Production and Residue Generation**

According to the International Cocoa Organization (ICCO, 2024), global cocoa production is dominated by West Africa, with the annual production fluctuating between 4.8 and 5.2 million metric tonnes. Côte d'Ivoire and Ghana jointly accounted for about 60–70% of total output (International Cocoa Organization, 2024). Other West African countries with reasonable production are Nigeria and Cameroon. Indonesia and Ecuador also do large-scale production. The annual production fluctuation is mainly due to seasonal and climatic factors, such as rainfall patterns and temperature variations, as well as disease outbreaks like black pod and swollen shoot virus.

At various stages, cocoa processing yields a significant quantity of biomass residues. Such residues include cocoa pod husks (CPH), cocoa bean shells (CBS), mucilage, and other minor residues. Cocoa pod husks (Figure 1a) are the outer shells of cocoa fruit, separated from the cocoa beans during processing. It represents 70-75% of the fresh cocoa fruit weight (International Institute of Tropical Agriculture, 2024; Mariatti et al., 2021). Afedzi et al. (2023) reported that for every 1 tonne of cocoa beans harvested, about 8–10 tonnes of fresh pod husks are generated (Afedzi et al., 2023). This agrees with Lu et al. (2018), who also reported 10 tonnes of fresh pod husks (Jayeola et al., 2018; Lu et al., 2018).

Cocoa bean shells (Figure 1b) are by-products of bean roasting and sifting; they are rich in fibre and polyphenols (Fetriyuna et al., 2025). This constitutes 10–17% of the bean dry weight (Rojo-Poveda et al., 2020), and the annual residue generation is estimated at 500,000–850,000 tonnes (Barišić et al., 2020; Botella-Martínez et al., 2021). Another cocoa residue that represents 2-3% of the wet cocoa bean mass is the Mucilage (Figure 1c), a sticky, sugary liquid drained during fermentation in cocoa processing (Jayeola et al., 2018). A mass-balance study by Vergara-Mendoza et al. (2022) reported that cacao mucilage exudate or sweating accounts for up to  $4.13 \pm 0.80$  wt % of the cacao fruit's total biomass (Vergara-Mendoza et al., 2022). Other minor residues are placenta (Figure 1d), which comprises the central tissue of the pod, damaged beans, and some fermentation waste (Jayeola et al., 2018). Studies have shown that in Ghana alone, cocoa processing generates approximately 858,720 tons of cocoa pod husks and 180,000 tons of cocoa bean shells yearly (Afedzi et al., 2023). A detailed summary of global cocoa production and cocoa residue generation in 2023 is provided in “Supplementary Table S1”. These residues contribute to environmental concerns if not well managed, yet they present a significant opportunity for valorization.



Figure 1. Cocoa bean residues in pictures

### Economic Importance of Cocoa

In many tropical countries, cocoa is a major source of foreign exchange earnings, generating significant foreign exchange that supports national budgets and trade balances. Countries like Côte d'Ivoire and Ghana are notable examples in West Africa (Adomako, 1983; Kongor et al., 2024). Cocoa farming is a serious source of employment for millions of smallholder farmers, often contributing over 50% of household income in rural communities. Typical examples of where cocoa farming has played a significant role in boosting the economy are presented in Table 1.

Table 1. Recent examples of how cocoa farming has boosted employment and rural livelihoods

COUNTRY/REGION	HOW COCOA FARMING BOOSTED EMPLOYMENT & LIVELIHOODS
Ghana	Adoption of sustainable farming methods (e.g., agroforestry, improved cultivation techniques) increased yields, incomes, and created more jobs in farming and post-harvest handling (Binam, Gockowski, & Nkamleu, 2008).
Indonesia (Sulawesi)	Growth of small-scale cocoa processing units and local cocoa-based businesses provided direct jobs in farming and indirect jobs in processing, transport, and marketing (Neilson & McKenzie, 2016; Zulfiandri & Rasjidin, 2022).
East Java, Indonesia	Cocoa farming contributed over 50% of household income for rural farmers, providing economic security and sustaining their livelihoods (Franzen & Borgerhoff Mulder, 2007; Indah, 2015).
Nigeria	Cocoa production supported the livelihoods of thousands of smallholder farmers through income generation and local market participation (Afolayan, 2020; Akeem, May 29, 2025).
Cameroon	The expansion of the cocoa sector increased smallholder incomes and improved access to education and healthcare in farming communities (Mukete, Li, Beckline, & Patricia, 2018).

## **Phytochemicals of Cocoa Bean Seeds**

Cocoa beans are rich in bioactive phytochemicals. These phytochemicals include polyphenols, catechins, anthocyanins, and procyanidins, with polyphenols as the largest constituent. The antioxidants, anti-inflammatory, and cardioprotective properties of cocoa are basically due to these phytochemicals (Kim, Lee, & Lee, 2011). Cocoa bean also has methylxanthine alkaloids known as Theobromine, and other various minerals, which further enhance their nutritional and therapeutic value (Pezzani, 2021). These compounds are not only concentrated in the cocoa bean but are also in by-products (the residues), making them valuable targets for recovery during residue valorization. Comprehensive phytochemicals and mineral components of the cocoa bean and its by-products, as well as their importance, are presented in “Supplementary Table S2 and S3”.

## **Valorization Pathways — Bioenergy Production from Cocoa Residues**

Cocoa-processing residues that are suitable for bioenergy purposes are cocoa pod husk (CPH), cocoa pulp/mucilage, and cocoa bean shell (CBS). Recent studies have highlighted three principal pathways: (1) anaerobic digestion for biogas production, (2) fermentation of sugars for bioethanol, and (3) thermochemical conversion to solid fuel (briquettes/biochar) and value-added by-products through pyrolysis and densification.

### *Biogas via Anaerobic Digestion*

Though CPH and pulp are abundant, their lignocellulosic structure and composition make them low in biodegradability. Due to this, digesting them alone (mono-digestion) usually yields limited biogas. It involves long lag phases, i.e., it takes the microbial community a longer time to adjust, start metabolizing the feedstock and produce a significant amount of methane gas. Recent work underscores pretreatments (e.g., mechanical, thermal, or enzymatic breakdown of the husks) or co-digestion with other substrates (e.g., animal manure or food waste) to shorten lag times and enhance methane yield. Co-digestion balances the C: N ratio and improves buffering. For example, the study of Arthur et al. (2025) and Dutra (2023) reported biogas yield improvement of 30–80 % over untreated CPH, as well as reduced inhibition and greater process stability (Arthur et al., 2025; Dutra et al., 2023). Empirical results by Arthur et al. (2025) indicate that the potential for several cubic metres of methane per tonne of dry CPH under optimized pretreatment and co-digestion can yield between 200–300 m<sup>3</sup> of methane per tonne of dry CPH. Aggregated, centralized systems (e.g., cooperatives or small industrial facilities near wet-processing sites) are seen as most feasible (Arthur et al., 2025).

While anaerobic digestion of CPH can achieve methane yields of 200–300 m<sup>3</sup> per tonne under optimized conditions, its reliance on pretreatment and co-digestion substrates introduces operational complexity and increases costs. In decentralized cocoa-producing regions, where access to controlled digestion systems and co-substrates is limited, this may reduce scalability. Compared to anaerobic digestion, thermochemical routes such as pyrolysis offer greater robustness to feedstock variability and lower dependence on biological stability, suggesting that they may be more suitable for rural or low-infrastructure settings (Sikarwar et al., 2021).

### *Bioethanol from Mucilage Fermentation*

The cocoa pulp (mucilage) surrounding the cocoa bean is rich in fermentable sugars—glucose, fructose, and sucrose, making it highly suitable for the production of ethanol using the

conventional fermentation yeast known as *Saccharomyces* spp. Laboratory-scale studies by Delgado, J. et. al. (2025) demonstrates that cocoa mucilage, can be sustainably valorized for bioethanol production by optimizing fermentation with *Saccharomyces cerevisiae* at 35 °C, pH 4, and 8 g/L yeast, achieving high yields (28.3 g/L), productivity (1.35 g/L·h), and validated kinetics ( $R^2 = 0.95$ ), thereby adding economic value while reducing environmental impacts (Delgado et al., 2025). Yet another empirical study is bioethanol production by the modified Gompertz model, and the Andrews–Levenspiel model, at optimal conditions of 35 °C, pH 4, and 3 g/L yeast, bioethanol concentration reached 25.41 g/L, with models showing strong fits ( $R^2 > 0.9$ ). This model demonstrated yields comparable to other fruit-based substrates (Delgado-Noboa et al., 2021). A two-stage valorization scheme involving fermentation of mucilage followed by aerobic digestion or composting of residual solids has been shown to increase overall energy/resource recovery (Villarroel-Bastidas et al., 2025). However, the challenge of mucilage's perishability within hours or days remains, requiring viable preservation techniques.

Although bioethanol production from cocoa mucilage demonstrates high yields under controlled fermentation conditions, its practical implementation is constrained by the rapid perishability of mucilage and the need for immediate processing infrastructure. In contrast to solid residues such as CPH, which can be stored after drying, mucilage-based systems require tightly integrated processing chains. Consequently, while bioethanol production is attractive in centralized facilities, it may be less feasible than biogas or biochar production in dispersed farming systems.

### *Biochar and Briquettes from Thermochemical Conversion*

Thermochemical valorization involves the pyrolysis or gasification of CPH and CBS to yield biochar, bio-oil, and syngas, depending on temperature, heating rate, and feedstock moisture. Two recent research works in Ecuador and India typically illustrated thermochemical valorization of cocoa wastes. Annually, Ecuador generates about 2 million tons of cocoa waste, and its valorization through low-cost pyrolysis and catalytic upgrading of cocoa pod husks shows strong potential for producing bio-oils, biochar, and gases, thereby supporting sustainable development, the bioeconomy, and broader environmental, economic, and societal benefits (Villasana et al., 2023). On the other hand, Indian cocoa farmers struggle with disposing of 15–17 tonnes/ha of pod husk waste; they therefore adopted pyrolysis as a recycling option, yielding biochar rich in 10–11% readily available potassium. This has helped to address potassium deficiency in organic agriculture (Gopal et al., 2025). Mechanical densification (briquetting/pelletizing) of dried CPH and CBS offers a low-technology method for producing transportable solid fuel with compact bulk energy density (Akam et al., 2024). Recent experimental studies and energetic/physicochemical assessments between 2021 and 2024 reported acceptable calorific values and combustion behaviour for CPH briquettes when properly dried and bound (often with small shares of starch or charcoal fines) (Akam et al., 2024; Thompson & Rough, 2021). Briquette production is appealing where markets for charcoal/wood fuel exist and where small enterprises and rural homes largely depend on it for energy supply. According to Gopal et al. (2025), biochar from cocoa husk waste offers agronomic advantages, such as being rich in potassium (K-rich), pH-balancing, water-retentive, and significant potential as activated carbon for pollutant adsorption (Gopal et al., 2025). A flow diagram of the Valorization Pathways from the cocoa pod to the products is shown in Figure 2.

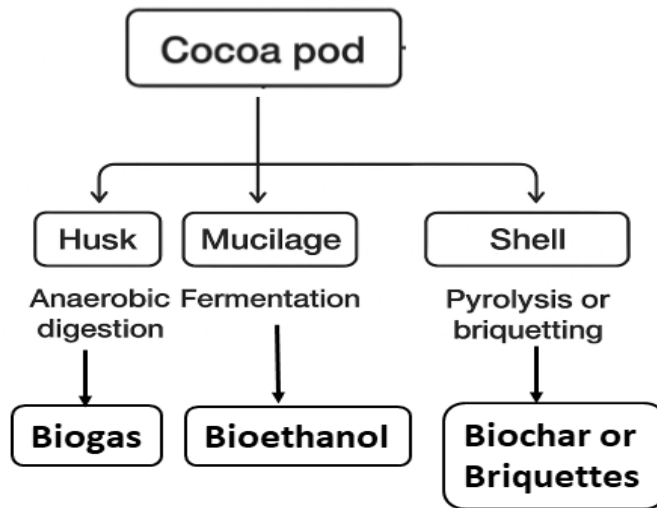


Figure 2. Valorization Pathways from cocoa pod to the bioenergy products

Despite promising results, many of the reported studies are conducted at laboratory scale, with limited pilot or industrial-scale validation. Variability in feedstock composition, lack of standardized pretreatment protocols, and insufficient techno-economic analyses limit the comparability of findings. Furthermore, reported yields (e.g., methane or bioethanol) often depend heavily on controlled experimental conditions, which may not be replicable in decentralized rural settings. Future research should prioritize scale-up studies, lifecycle assessment (LCA), and cost-benefit analysis to establish feasibility.

A comparative assessment of bioenergy pathways indicates that no single technology is universally optimal; rather, suitability depends on local conditions (Alcocer-García et al., 2025). Anaerobic digestion offers high energy recovery but requires process stability and co-substrates. Bioethanol production is efficient but constrained by the perishability of feedstock and the demands of infrastructure. Thermochemical conversion, while sometimes less energy-efficient on a per-unit basis, provides superior scalability and robustness, particularly in decentralized systems. Therefore, integrated approaches combining multiple technologies may offer the most sustainable solution.

### **Valorization Pathways: Agricultural Uses of Cocoa Residues**

Cocoa residues, traditionally considered waste, have emerged as valuable resources for sustainable agricultural practices. Valorization strategies focus on their application in organic fertilizers, mulching, and animal feeding. Through valorization, cocoa residues are cleared from the environment, reducing pollution while enhancing soil health, crop productivity, and livestock nutrition.

#### *Organic Fertilizer or Compost from CPH and CBS*

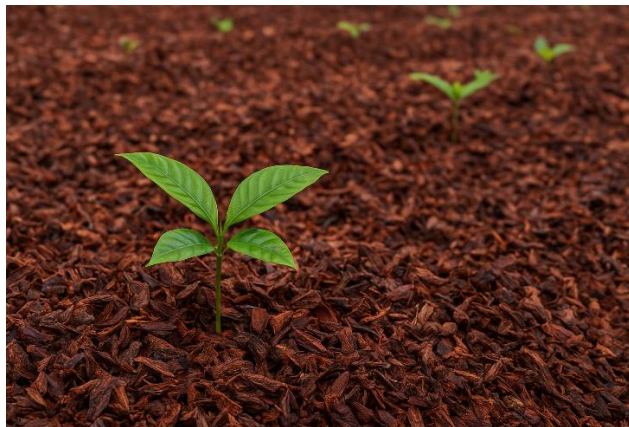
Analysis of cocoa pod husks has revealed that it is rich in macro- and micronutrients, particularly potassium (K), calcium (Ca), and phosphorus (P), making them ideal for composting and soil amendment (Mwafulirwa et al., 2024). They reported a substantial increase in soil pH from 4.8 up to 8.6 when soil was amended with CPH products, especially

in acidic Ferralsols, and an increase in soil electrical conductivity. Studies have shown that CPH improves soil organic matter, enhances microbial activity, and boosts crop yields when composted with other agricultural wastes such as poultry manure (Anoraga et al., 2024). Cocoa bean shells, likewise, contain nitrogen and lignin, which contribute to soil conditioning (FeedTables, 2025). Recent studies emphasize that compost derived from CPH can replace part of synthetic fertilizers, promoting environmentally friendly nutrient cycling (Ogunlade & Orisajo, 2020). In Ghana and Côte d'Ivoire, known for large-scale cocoa planting, farmers have adopted CPH composting practices to reduce fertilizer costs and improve soil fertility (Amponsah-Doku et al., 2022). This valorization pathway aligns with the goal of the circular economy, transforming residues into nutrient-rich soil amendments that sustain cocoa production.

Although composting cocoa residues improves soil fertility and reduces reliance on synthetic fertilizers, its economic advantage depends on labor availability and composting time (Morales et al., 2025). Compared to direct valorization into higher-value products such as bioenergy or nutraceuticals, composting yields lower economic returns but offers greater accessibility for smallholder farmers. Thus, composting remains the most feasible low-technology option, though with limited value addition.

#### *Mulch for Soil Moisture Retention and Weed Control*

Dried and shredded cocoa pod husks serve as effective mulching material (Figure 3), which eventually decomposes into organic manure. CPH mulch, as illustrated in Figure 3, provides surface cover, which regulates soil temperature, conserves moisture, and suppresses weed growth (Arentoft et al., 2013; Demo & Asefa Bogale, 2024). Mulching with CPH significantly reduces the need for herbicides and irrigation requirements in humid tropical regions, where waterlogging and weed infestation affect cocoa productivity (Mwafulirwa et al., 2024). Mulching also enhances soil biological activity by providing organic matter that slowly decomposes, thereby contributing to long-term soil fertility. A field experiment in Ghana was that of Akpalu et al. (2020), where they evaluated the combined effects of cocoa pod husk (CPH) mulching and irrigation on cocoa seedling establishment. Using a  $2 \times 2 \times 3$  factorial design involving daily irrigation, CPH mulch application at 5.6 t/ha, and three growing media, they reported a marked improvement in survival rates of 94.5% when mulching was combined with irrigation, compared to only 47.1% without either treatment (Akpalu et al., 2020). This agricultural use thus adds value to CPH as an affordable and eco-friendly alternative to synthetic weed control practices.



*Figure 3. Cocoa pod husk mulch around young cocoa seedlings, highlighting moisture retention and weed suppression.*

### *Animal Feed after Detoxification*

Cocoa by-products, particularly CBS and CPH, are used as livestock feed ingredients. These residues are rich in fibre, proteins, and carbohydrates, though they contain a toxic alkaloid called theobromine, which is harmful to animals if consumed in large quantities (Sánchez et al., 2023). Its harmful effects stem from its pharmacological action as a methylxanthine, structurally related to caffeine, leading to restlessness, tremors, seizures, and hyperexcitability, reducing feeding efficiency and welfare (Adamafio, 2013). However, various detoxification methods such as microbial fermentation, alkali treatment, or ensiling have been used to reduce theobromine content, making the residues safe for feed formulation (Adamafio, 2013). Fermented CPH and CBS have been incorporated into the diets of ruminants, pigs, and poultry with encouraging results. Studies (see Table 2) indicate that inclusion of detoxified cocoa residues can improve weight gain, feed efficiency, and milk production without adverse effects on animal health. Moreover, using cocoa residues as feed addresses the dual challenge of waste management and the rising cost of conventional feed ingredients like maize and soybean, which are staple foods.

While the use of cocoa by-products as animal feed provides a cost-effective solution to rising feed prices, the need for detoxification processes introduces additional processing steps and costs. Compared to applications in bioenergy or materials, feed utilization may offer lower economic returns but higher immediate applicability at the farm level (Tabiri & Antwi, 2024). Therefore, its adoption is likely to be driven more by accessibility than by profitability.

Table 2. Effects of Detoxified Cocoa By-products in Livestock Feeding

ANIMAL SPECIES	TREATMENT / INCLUSION LEVEL	POSITIVE OUTCOMES
Sheep (Ruminants)	20–40 % fermented CPH replacing concentrate	↑ Protein & fiber digestibility; ↑ weight gain (65.8 → 85 g/day); improved FCR (14.0 → 8.4) (Rakhmani & Puastuti, 2022).
Broilers (Poultry)	10–20 % fermented or enzyme-treated CPH	Safe inclusion without adverse effect on growth/carcass traits (Alemawor, Oddoye, Dzogbefia, Oldham, & Donkoh, 2010).
Rabbits	30 % fermented CPH vs. unfermented	↑ Feed intake, weight gain, and FCR; fermented form superior (Alemawor et al., 2010).
Dairy Goats	200 g concentrate replaced with pelleted CBS	Milk yield unaffected; ↓ milk urea; ↑ branched-chain fatty acids (improved nutritional profile) (Renna et al., 2022).
Dairy Ewes	11.7 % CBS in concentrate (Comisana breed)	Milk yield & fat/protein content unchanged; ↓ milk urea; ↑ cheese fat content; altered milk FA profile (Campione et al., 2021).
Dairy Cows	5 % CBS in former food product-based concentrate	Energy-corrected milk yield unchanged; ↑ milk fat percentage (Reiche, Tretola, Eggerschwiler, Pinotti, & Dohme-Meier, 2025).

Key: ↑ denotes increase, ↓ denotes decrease

### Valorization Pathways — Food and Nutraceuticals from Cocoa By-products

Food and nutraceuticals are closely related concepts. While all nutraceuticals are food-derived, not all food is a nutraceutical. Nutraceuticals are bioactive compounds, foods, or their parts that provide health and medicinal benefits beyond basic nutrition. They are often used to treat or prevent diseases (Hardy, 2000).

#### Dietary Fibre from Cocoa Bean Shells

Cocoa bean shells are rich in fibre, with a substantial amount of some insoluble fractions of cellulose, hemicellulose, and lignin. They also contain pectic substances and bound phenolics that confer techno-functional benefits that make them useful in processing, product development, and stability, as well as physiological benefits that give them nutritional or therapeutic advantages beyond basic sustenance. Recent compositional and extraction studies by Younes et al., 2023a confirm total dietary fibre in multiple CBS lots at approximately 50–64% and describe protocols to isolate cell-wall material suitable for food incorporation (flours, fibre concentrates) without harsh solvents (Younes et al., 2023). Beyond proximate composition, research has begun to probe *in vitro* colonic fermentation of CBS flour and extracts, to track phenolic biotransformation (microbial or enzymatic modification of phenolic compounds into structurally different metabolites) and to assess their modulatory effects on gut microbial metabolism, which is an important step in providing evidence for the prebiotic potential of CBS (Cañas et al., 2024). The safety and functionality assessment of CBS by Gil-Ramirez et al. 2024, argues that CBS can be formulated as a safe bioactive ingredient if theobromine/caffeine levels and contaminants are well controlled (Gil-Ramírez et al., 2024).

Despite the high fibre content and promising prebiotic potential of cocoa bean shells, their commercialization is constrained by issues related to sensory properties, regulatory approval, and the presence of residual alkaloids. Compared to conventional fibre sources, additional processing is often required to ensure safety and consumer acceptability, which may increase production costs.

### *Antioxidant extracts (polyphenols, flavonoids) from shells and husks*

CBS and CPH contain extractable polyphenols with strong antioxidant capacity (See Supplementary Table S2). Recent process-focused studies emphasized the role of optimizing solvent systems and operational parameters in enhancing the recovery of bioactive compounds from cocoa by-products. For example, Sánchez et al. (2025) demonstrated that autohydrolysis treatment of cocoa bean shells (CBS) can yield phenolic-rich and prebiotic oligosaccharide fractions. They achieved up to 2.8 g/L total phenolics and substantial antioxidant activity, without the use of toxic chemicals (Sánchez, Ferreira-Santos, Gomes-Dias, Laca, & Rocha, 2025). Complementing this, Disca et al. (2024) compared combined microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) at 90 °C with conventional stirring and Soxhlet extraction approach, and found that the former resulted in higher polyphenol recovery with better antiradical activity (Disca et al., 2024). These processing advances and bioactivity evidences underscores the significance and expanding opportunities of these by-products in foods, nutraceuticals, and cosmeceuticals.

Although advanced extraction techniques such as microwave- and ultrasound-assisted methods enhance polyphenol recovery, their large-scale implementation remains uncertain due to limited industrial validation and concerns regarding cost-effectiveness (Disca et al., 2024). Conventional extraction methods, while less efficient, may be more economically viable for large-scale operations. Thus, the selection of extraction technology involves a trade-off between yield optimization and industrial feasibility.

### *Functional Ingredients for Beverages, Cereals, or Supplements*

In beverages, two main applications are (i) aqueous CBS extracts/hydrolysates as antioxidant bases for functional drinks. Post-fermentation has been reported to increase the antioxidant activity of aqueous CBS extracts/hydrolysates to above 80%, and (ii) addition of CBS-derived fibres as flavour-modulating and stabilizing components. Recent product-oriented case study was that of Sánchez et al., (2024), where cocoa bean shell (CBS) was successfully utilized as a substrate to formulate a fermented functional beverage through hydrothermal hydrolysis, with and without whey supplementation, followed by fermentation using *Lactiplanctibacillus plantarum*. Fermentation significantly improved the bioactive profile, yielding high antioxidant activity (83.5 µmol TE/L), total phenolic content (1.4 g/L), and methylxanthines (0.4 g/L theobromine and 0.05 g/L caffeine) after 48 hours. However, sensory evaluation revealed preference for unfermented samples, underscoring the challenge of balancing functional enhancement with consumer acceptability (Sánchez et al. 2024).

Another application angle is in Cereals/bakery, where CBS flours/fibre concentrates are used to enhance total dietary fibre, water absorption, and antioxidant capacity of cereal products. Formulation success is highly dependent on particle size, roasting history, which affects flavour, and managing bitterness due to theobromine presence. A recent ingredient-safety review guides the incorporation levels of CBS and the quality control (Gil-Ramírez et al., 2024).

Standardized polyphenol-rich extracts from CBS or CPH and pectin from CPH are often used as supplements for capsules/gummies or as carriers for probiotic delivery (Santiago-Gómez et al., 2025).

While numerous studies demonstrate the bioactive potential of cocoa by-products, there remains a lack of clinical validation and long-term safety assessments. Many findings are based on in vitro assays, which may not translate directly to in vivo efficacy. Additionally, issues

such as bioavailability, dosage standardization, and regulatory approval remain insufficiently addressed.

### **Valorization Pathways: Cosmetics and Pharmaceuticals from Cocoa By-products**

In modern circular bioeconomy strategies, cocoa bean shells (CBS) and cocoa pod husks (CPH) are sources of affordable bioactive ingredients for dermato-cosmetic and pharmaceutical applications. This is possible because they are rich in polyphenols (catechin, epicatechin), phenolic acids, flavonols, methylxanthines, polysaccharides, and lipids, which are relevant to skin care because of their antioxidant, anti-inflammatory, barrier-supporting, and pigment-modulating effects.

*Bioactive Compounds for Skincare and Anti-inflammatory Products (See Supplementary Table S2)*

When the phenolics and flavonoids bioactive agents are extracted using advanced, skin-friendly methods like polyol-based microwave-assisted extraction, they can effectively suppress melanin overproduction, reduce oxidative stress, and calm inflammation in skin cells. This makes them good natural ingredients for cosmetic products aimed at brightening skin and improving overall skin health (Pattanakitjaroenchai et al., 2025). Draelos et al. (2024), study revealed how cocoa-derived flavanols (specifically catechin and epicatechin) behave when applied to the skin. Catechin and epicatechin actually penetrate into the stratum corneum of skin, which was proven using tape-stripping analysis. This is important evidence that cocoa antioxidants can be effectively delivered into the skin, supporting their potential use for skin protection and anti-aging in dermatology and cosmeceuticals (Draelos et al., 2024). Beyond CBS, standardized CPH extracts are now characterized for phenols/polyphenols and tested in small clinical settings. Research has shown that 1% w/w CPH extract improved skin hydration by approximately 52.5%, reduced transepidermal water loss by approximately 7.7%, with a decreased in melanin index by approximately 9.1% after 4 weeks. These outcomes are consistent with moisturization and gentle lightening claims (non-strict cosmetic clinical) (Anatachodwanit et al., 2025; Elbouzidi et al., 2025).

#### *Theobromine and other methylxanthines*

Cocoa by-products are rich in theobromine (cocoa-derived methylxanthine), which is structurally related to caffeine. Theobromine exhibits antioxidant, anti-inflammatory, and vasodilatory effects (See Supplementary Table S2). A study by Sitarek et al. (2024) linked these benefits to its ability to modulate NF- $\kappa$ B and cytokine signaling pathways, establishing a scientific rationale for its use in skincare formulations with claims of anti-redness, barrier-protective, soothing, and anti-ageing benefits.

#### *Polysaccharides and film-forming hydrators*

Polysaccharides derived from CPH exhibit hygroscopic and film-forming properties (Adi-Dako et al., 2016). In cosmetics production, this enhances water retention, thereby reducing transepidermal water loss (TEWL). Industrial-materials study reported hydration efficacy of CPH polysaccharide fractions and their suitability as moisturizing actives, aligning with current

“skin minimalism” trends favoring multifunctional humectants, i.e., not only functioning as moisturizer but as film-forming protection, soothing effects, or barrier repair (Tantapakul et al., 2024).

Compared to other valorization pathways, cosmetic and pharmaceutical applications offer significantly higher value addition but require stringent quality control, regulatory approval, and advanced processing technologies. This makes them less accessible in low-resource settings but highly attractive for industrial-scale operations. Consequently, these applications are likely to be driven by private-sector investment rather than smallholder-level initiatives.

### **Valorization Pathways: Bioplastics and Packaging from Cocoa By-products**

Global packaging demand and plastic wastes generated from conventional plastics, which are generally nondegradable, create an urgent need for a biodegradable, sustainable alternative. Cocoa processing generates very large volumes of CPH and CBS (CPH  $\approx$  60–70% of pod fresh weight), which are rich in cellulose, hemicellulose, lignin, pectin, and minor extractives; these constituents make them viable feedstock or composite for biodegradable polymer packaging materials (Anoraga et al., 2024).

#### *Feedstock chemistry and implications for polymer routes*

Cocoa pod husk (CPH) and cocoa bean shell (CBS) are lignocellulosic in nature. They are primarily made up of cellulose, hemicellulose, and lignin, which collectively determine their physico-chemical and structural characteristics, enabling their tailored valorization in biorefinery applications. CPH has an appreciable amount of pectin in their outer tissues, making it particularly suitable for the development of edible coatings and biodegradable films, while CBS retains residual lipids, phenolic compounds, and methylxanthines, which enable its compatibility with polymer matrices and provide antioxidant functionalities which are mostly needed in the formulation of active packaging systems (Sánchez et al., 2024). Hence, a comprehensive understanding of the compositional variability between CPH and CBS is essential for optimum utilization strategies that aid the bioeconomy.

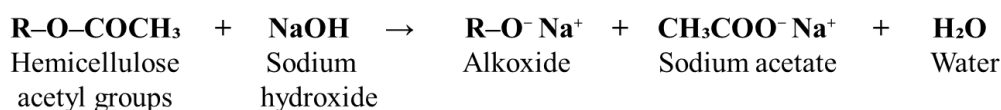
#### *Routes to biopolymers and packaging materials*

##### *Cellulose-based films and composites*

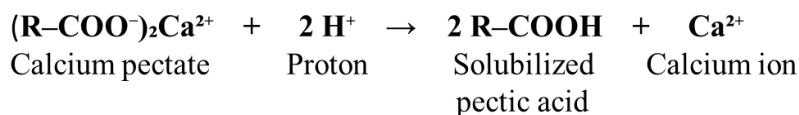
Through alkali pre-treatment, bleaching, and mechanical fibrillation cellulose can be isolated from CPH and processed into films or used as reinforcement in either thermoplastic starch (TPS), polylactic acid (PLA) or polyhydroxyalkanoate (PHA) matrices. Studies have successfully demonstrated blending of bioplastic films from CPH cellulose with natural binders like  $\kappa$ -carrageenan, starch or with PLA to form biocomposites with better barrier properties and tensile strength (Meza-Sepulveda et al., 2025; Posso et al., 2024).

Key chemical steps commonly involved in cellulose isolation and modification:

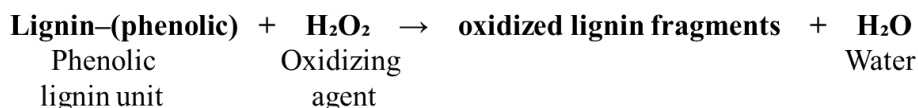
Saponification of hemicellulose acetyl groups (during alkaline pulping):



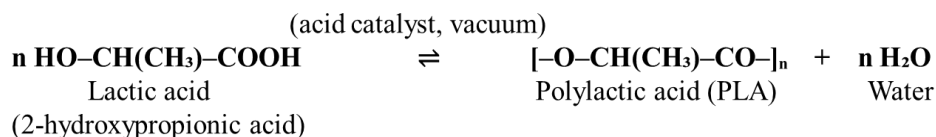
Demetallation of pectates (liberation of Ca<sup>2+</sup> crosslinks in the middle lamella):



Oxidative lignin removal (illustrative peroxide stage; lignin fragments, L-Ar-OH):



PLA matrix formation (Direct polycondensation of lactic acid):



### *Pectin and edible films/coatings*

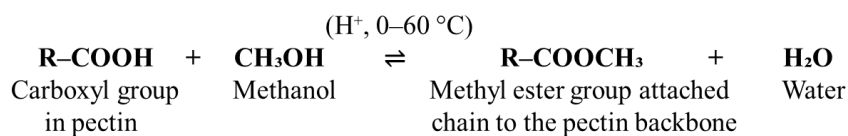
CPH pectin (extracted by mild acid hydrolysis) is a promising raw material for edible films and coatings: pectin-based coatings can extend shelf life, act as carriers for antioxidants, and be cast into thin films for light food packaging. Reviews and process studies (2024–2025) provide protocols for citric-acid and enzymatic recovery and discuss degree-of-esterification (DE) control for gelling/film properties (Anoraga et al., 2024; Santiago-Gómez et al., 2025).

Key chemical steps commonly involved in Pectin and edible films/coatings:

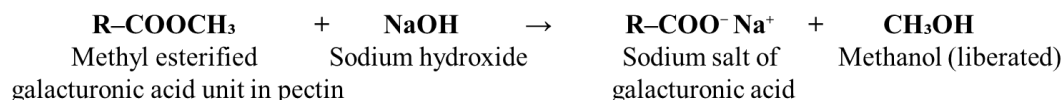
Protopectin solubilization (acid extraction):

Insoluble protopectin  $\xrightarrow{(\text{H}^+, 70\text{--}90\text{ }^\circ\text{C})}$  soluble pectin (poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid, partially methyl-esterified)

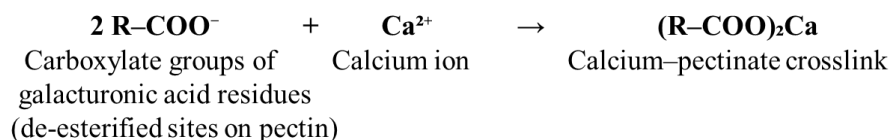
Pectin esterification (controls DE; acid-catalyzed):



Pectin de-esterification (alkaline saponification or PME-enzymatic):



Calcium-induced gel (egg-box crosslinking characteristic of low-methoxyl pectin):



### *Whole-fiber reinforcement and paper-like packaging*

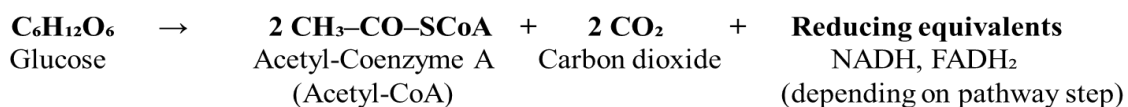
CBS has been trialled as a fibre source for paper or paperboard-like substrates and as filler/reinforcement in PLA/other biopolymer matrices. Studies (and pilot projects) show CBS can form paper sheets or be milled into powders that improve mechanical stiffness and introduce antioxidant properties (active packaging) when retained in a matrix (Süfer, Özkan Karabacak, & Pandiselvam, 2024).

### *Microbial biopolymers (PHAs, PHB) via substrate conversion*

CBS (after hydrolysis or as a carbon source following pre-treatment) can be fermented by PHA-producing microbes to produce polyhydroxybutyrate (PHB) or mixed PHAs. Laboratory reports indicate CBS hydrolysates can support PHA biosynthesis, although yields depend on effective saccharification and nitrogen management. This process utilizes the carbon in agricultural residues to create fully biodegradable thermoplastics (Shah & Kumar, 2021).

Representative biochemical pathway (to PHB)

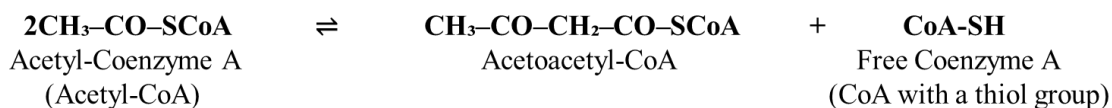
Sugar catabolism to acetyl-CoA (simplified from glucose):



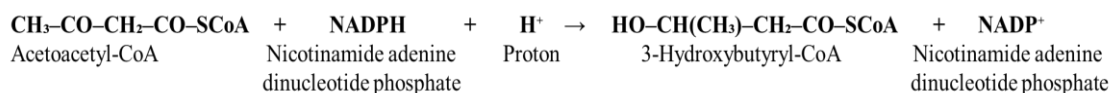
(Pathway: Glycolysis → Pyruvate → Pyruvate dehydrogenase complex → Acetyl-CoA)

PHB monomer precursor formation (three enzymatic steps):

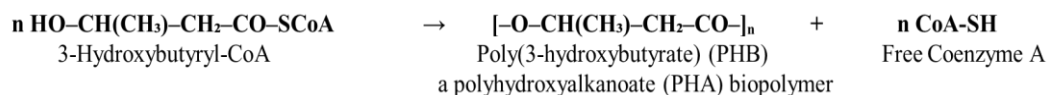
a) **β-ketothiolase (PhaA):**



b) **Acetoacetyl-CoA reductase (PhaB):**



c) **PHB synthase (PhaC) — polymerization:**



This showed the fact that cocoa bean shell (CBS) hydrolysates can be converted via microbial metabolism into PHB bioplastics.

Although cocoa residues show potential as biopolymer feedstocks, current research is largely limited to experimental formulations. Challenges such as mechanical performance, moisture sensitivity, scalability, and cost competitiveness with petroleum-based plastics must be addressed before commercialization. However, their biodegradability and alignment with circular economy principles provide a strong incentive for continued research and development.

## Challenges in Cocoa Residue Valorization

The key challenges of cocoa-residue valorization are mostly linked to their high moisture content and perishability, presence of toxic compounds such as theobromine, and lack of infrastructure for waste collection and processing in cocoa-producing countries.

Across all valorization pathways, a clear trade-off emerges between economic value, scalability, and technological complexity. Low-technology applications such as composting and animal feed are highly accessible but generate limited economic returns. In contrast, high-value applications such as nutraceuticals, cosmetics, and bioplastics offer greater profitability but require advanced infrastructure and regulatory compliance. Bioenergy pathways occupy an intermediate position, balancing scalability and value creation. Therefore, the optimal utilization of cocoa residues lies in integrated biorefinery systems that strategically combine multiple pathways to maximize both economic and environmental benefits.

### *High Moisture Content and Perishability*

Cocoa residues, particularly mucilage (pulp) and cocoa pod husk (CPH), usually have very high moisture content. This severely limits storage time and negatively affects downstream valorization. For example, the average percentage moisture of cacao mucilage is about 86%, therefore, immediate processing is needed to avoid spoilage (Sotelo-Coronado, Oviedo-Argumedo & Alvis-Bermúdez, 2025). Also, the storage of CPH poses a major challenge of quick spoilage even at ambient room temperature, because they tend to brown and grow mould within a few days, while cooling to 5 °C delays spoilage by just a week (Anoraga et al., 2024). These moisture and perishability characteristics cause logistic and technical problems, necessitating urgent collection and aggregation, especially during the cocoa harvest season (May to October), demanding rapid handling and processing (Anoraga et al., 2024). A robust transportation and drying system must be engaged to reduce spoilage and freight volume; otherwise, there will be a risk of microbial degradation, odour generation, and loss of valuable components (Anoraga et al., 2024).

### *Presence of Toxic Compounds (e.g., Theobromine, Mycotoxins, Heavy Metals)*

Studies have shown that cocoa bean shell (CBS) and cocoa pod husk (CPH) contain compounds that can cause serious safety hazards if not properly managed. Table 3 discusses these compounds, including the cocoa by-products in which they are found, their safety and health implications, and management strategies for effective valorization. Thus, proper management such as monitoring, decontamination, and regulation of these residues are essential before any valorization into food, cosmetics, or packaging.

*Table 3. Toxic or Hazardous Compounds Found in Cocoa Residue and Management Strategies for Effective Valorization*

COMPOUND	COCOA BY-PRODUCTS	SAFETY / HEALTH IMPLICATIONS	MANAGEMENT APPROACH FOR EFFECTIVE VALORIZATION / UTILIZATION
Theobromine	Cocoa pod husk (CPH), Cocoa bean shell (CBS)	Methylxanthine has stimulant effects; potentially toxic to humans and animals. CPH contains up to ~6.79 mg/100 g dry weight; CBS is also significant as a secondary source (Nguyen & Nguyen, 2017; Panak Balentić et al., 2018).	Implement ingredient specifications and regulatory limits; apply detoxification (e.g., water/solvent extraction, microbial “detheobromination”) (Oduro-Mensah et al., 2018); use only in applications where theobromine is acceptable or desired (e.g., pharmaceuticals, controlled nutraceutical formulations).
Mycotoxins (Ochratoxin A, Aflatoxins)	CBS (and occasionally CPH) through fermentation, drying, storage	Potent nephrotoxic, immunosuppressive, and possibly carcinogenic (OTA is IARC Group 2B) (Rojo-Poveda et al., 2020).	Enforce Good Postharvest Practices (drying, storage humidity control); screen products via mycotoxin assays; use biocontrol agents (e.g., lactic acid bacteria) to limit fungal contamination (de Melo Nazareth, Pérez, Luz, Meca, & Quiles, 2024).
Polycyclic Aromatic Hydrocarbons (PAHs)	CBS during roasting or smoke drying	Genotoxic, carcinogenic compounds formed under high-temperature/smoke-exposed drying or roasting methods (Barišić et al., 2020; Liu et al., 2024).	Avoid open-fire or smoke-based drying; switch to indirect or clean-energy drying; apply post-processing purification (e.g., activated carbon, supercritical CO <sub>2</sub> ) when needed.
Heavy Metals (Cd, Pb, etc.)	CBS (absorbs metals from soil or environment)	Chronic toxicity: Cd and Pb can cause kidney damage, neurotoxicity, carcinogenicity; CBS levels often exceed bean levels (e.g., Cd 0.629 mg/kg in shell vs. 0.072 in bean) (Anyimah-Ackah, Ofosu, Lutterodt, & Darko, 2019; Rojo-Poveda et al., 2020).	Implement soil management and selective breeding to reduce uptake; specify and test residue raw materials; use extraction or leaching detox before food/cosmetic use; redirect contaminated materials to non-food uses like bioenergy or packaging.

### *Lack of Infrastructure for Waste Collection and Processing*

Infrastructure gaps severely constrain the practical valorization of cocoa residues, especially in the poorly developed cocoa-producing regions like Sub-Saharan Africa and parts of Latin America. The majority of cocoa producers are smallholder farmers with limited financial resources, technical skills, and cannot access modern processing facilities. As a result, cocoa by-products are commonly disposed of in fields, used as compost, or fed to animals, with little or no integrated valorization systems (Anoraga et al., 2024). Because the farmers are mostly subsistence farmers, there is no centralized collection system, and governance is hindered by a lack of funding, insufficient staff competency, and policy ambiguity, making residue valorization very ineffective (Anoraga et al., 2024). In many African countries, food and agricultural waste (including cocoa residues) are not segregated. There are no structured waste collection systems; hence, waste is mixed with municipal solid waste and emptied in landfills, reflecting broader systemic deficiencies in waste management infrastructure (Mmereki et al., 2024). Lack of transport infrastructure, such as accessible roads, absence of aggregation centers, and limited or no cold storage for preservation, further discourages collection. For example, in Ghana and Nigeria, perishable residues may be abandoned or burned due to

deteriorated rural roads, which severely hinder the movement of farm produce (Food and Agriculture Organization of the United Nations, 2003).

Overall, the feasibility and scalability of cocoa residue valorization pathways (sections 6-9) vary significantly depending on technological requirements, economic considerations, and local context. A comparative assessment of cocoa residue valorization pathways indicates that composting and animal feed applications rank highest in feasibility due to their low technological demands and immediate applicability. Bioenergy production represents moderate feasibility, offering scalable potential where infrastructure exists. In contrast, high-value applications, including nutraceuticals and biopolymers, are constrained by technological complexity and economic barriers, limiting their widespread implementation.

### **Future Research Directions**

Despite the significant progress made in the valorization of cocoa processing residues, several critical gaps remain that must be addressed to facilitate large-scale implementation and industrial adoption. Future research should therefore focus on the following key areas.

#### *Scale-Up and Industrial Implementation Challenges*

Most existing studies on cocoa residue valorization are conducted at laboratory or pilot scale, with limited transition to full industrial application. This presents challenges related to process optimization, consistency of feedstock quality, and operational efficiency. Variability in the composition of cocoa residues due to geographic, seasonal, and processing differences further complicates scale-up efforts. Future work should prioritize pilot-scale demonstrations, process standardization, and techno-economic analysis (TEA) to evaluate commercial feasibility. Additionally, life cycle assessment (LCA) studies are necessary to ensure that proposed technologies deliver genuine environmental benefits.

#### *11.2 Policy, Regulatory, and Economic Considerations*

The successful valorization of cocoa processing residues is strongly influenced by policy and regulatory frameworks, particularly in major cocoa-producing regions. Currently, there is a lack of coordinated policies that incentivize waste-to-value initiatives, as well as limited access to funding and infrastructure required for implementation. Governments and stakeholders should develop supportive policies, including tax incentives, subsidies, and clear regulatory guidelines for the use of biomass-derived products in food, pharmaceuticals, and materials applications. Furthermore, the establishment of public-private partnerships and regional biorefinery hubs could significantly enhance resource utilization and economic viability.

#### *Integration of AI and Advanced Biorefinery Approaches*

Emerging technologies such as artificial intelligence (AI) and machine learning offer significant opportunities to optimize the valorization of cocoa residues. AI-driven models can be applied to process optimization, predictive modeling of product yields, and design of efficient biorefinery systems. In addition, the development of integrated biorefinery platforms capable of simultaneously producing biofuels, biochemicals, and biomaterials from cocoa residues represents a promising direction for maximizing resource efficiency. Future research

should explore the integration of data-driven approaches, process intensification strategies, and green extraction technologies to enhance both sustainability and economic performance.

### *Standardization and Quality Control*

Another critical area requiring attention is the lack of standardized methods for the characterization and processing of cocoa residues. Differences in analytical techniques and reporting metrics make it difficult to compare results across studies. Establishing standard protocols for compositional analysis, processing conditions, and performance evaluation will improve reproducibility and facilitate the translation of research findings into industrial practice.

### *Socio-Economic and Regional Considerations*

Given that a significant proportion of global cocoa production occurs in developing regions, particularly in West Africa, future research should also consider context-specific challenges such as infrastructure limitations, technology accessibility, and local capacity building. Community-based valorization models and decentralized processing systems may offer practical solutions for enhancing sustainability while creating economic opportunities for local populations.

High-value applications, including nutraceuticals and biopolymers, while economically attractive due to their strong market potential, are currently constrained by technological complexity, high capital investment requirements, and regulatory barriers, which limit their immediate large-scale deployment. In contrast, lower-complexity pathways such as composting, animal feed production, and decentralized bioenergy systems demonstrate greater short- to medium-term feasibility, particularly in resource-constrained cocoa-producing regions. These distinctions provide a clear framework for prioritizing future research and development efforts, whereby immediate emphasis should be placed on scalable, low-cost valorization strategies, while advanced biorefinery-based applications should be pursued as long-term innovation targets supported by policy development, infrastructure expansion, and technological maturation.

## **Conclusions**

This review presents a holistic and systems-level evaluation of cocoa processing residues within a circular bioeconomy framework, demonstrating that cocoa pod husks, cocoa bean shells, and mucilage are not merely agro-industrial wastes but strategic renewable resources with substantial potential for value creation. Diverse valorization pathways across bioenergy, agriculture, food and nutraceuticals, cosmetics, pharmaceuticals, and sustainable materials, are made possible because cocoa wastes are rich in bioactive compounds, lignocellulosic materials, and fermentable sugars.

A critical insight from this analysis is that no single valorization pathway is universally optimal; rather, each presents context-dependent trade-offs between scalability, technological complexity, and economic return. Low-technology applications such as composting and animal feed are highly accessible and immediately beneficial at the farm level, while high-value applications (nutraceuticals, cosmeceuticals, and bioplastics) offer better economic returns but require advanced infrastructure and regulatory compliance, making them more capital-intensive. Bioenergy pathways offer a practical middle-ground solution, especially when

designed to work in small, local systems within cocoa-producing communities, where they can efficiently convert waste into useful energy.

Importantly, the valorization of cocoa residues directly advances key global sustainability priorities. By creating new value chains, generating employment opportunities, and supporting income diversification for smallholder farmers and rural communities, these strategies contribute significantly to SDG 8. The transformation of cocoa waste into high-value products promotes resource efficiency, waste minimization, and sustainable production systems, aligning strongly with SDG 12, and the utilization of cocoa residues for bioenergy production and carbon-sequestering materials such as biochar contributes to greenhouse gas mitigation and climate resilience, thereby supporting SDG 13.

Despite these promising opportunities, the transition from laboratory-scale innovation to industrial implementation remains constrained by several challenges, including feedstock variability, high moisture content and perishability, the presence of toxic compounds such as theobromine and mycotoxins, and inadequate infrastructure for residue collection and processing, particularly in West Africa. Moreover, the lack of standardized methodologies, techno-economic analyses, and life cycle assessments limits the comparability and scalability of current research.

To fully realize the potential of cocoa residue valorization, there is a need for integrated biorefinery approaches that strategically combine multiple conversion pathways to maximize both economic and environmental benefits. Emerging technologies, including green extraction methods, process intensification, and artificial intelligence-driven optimization, offer transformative opportunities to enhance efficiency and scalability. Equally critical are supportive policy frameworks, investment in infrastructure, and the establishment of public–private partnerships to enable technology deployment and capacity building in cocoa-producing regions.

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## Supplementary Materials

**Table S1.** Top 30 countries in cocoa bean production and estimated cocoa residue generation in 2023 (Ramos et al., 2023; Sánchez, Laca, Laca, & Díaz, 2023).

COUNTRY	PRODUCTION 2023 (T)	EST CPH WET (T)	EST CBS LOW (T)	EST CBS HIGH (T)
Côte d'Ivoire	2377442	23774420	285293	475488
Ghana	653700	6537000	78444	130740
Indonesia	641741	6417410	77009	128348
Ecuador	375719	3757190	45086	75144
Brazil	296145	2961450	35537	59229
Cameroon	295819	2958190	35498	59164
Nigeria	284232	2842320	34108	56846
Peru	166709	1667090	20005	33342
Dominican Republic	65930	659300	7912	13186
Colombia	59831	598310	7180	11966
Papua New Guinea	43200	432000	5184	8640
DR Congo	35000	350000	4200	7000
Uganda	35000	350000	4200	7000
India	30000	300000	3600	6000
Venezuela	29359	293590	3523	5872
Mexico	29047	290470	3486	5809
Guinea	23164	231640	2780	4633
Madagascar	20000	200000	2400	4000
Liberia	20000	200000	2400	4000
Sierra Leone	18000	180000	2160	3600
Togo	15000	150000	1800	3000
Tanzania	12000	120000	1440	2400
Guatemala	11652	116520	1398	2330
Philippines	10759	107590	1291	2152
Nicaragua	9317	93170	1118	1863
Bolivia	5971	59710	717	1194
Solomon Islands	4000	40000	480	800
São Tomé and Príncipe	4000	40000	480	800
Haiti	2500	25000	300	500

*Key:*

*Units: Production = tonnes (t, dry beans). CPH = wet mass (t). CBS = dry mass (t).*

*Calculations: CPH = 10×Production; CBS(low) = 0.12×Production; CBS(high) = 0.20×Production.*

*Est: Estimated.*

**Table S2. Bioactive Phytochemicals in Cocoa Bean and By-Products**

CLASS → REPRESENTATIVE COMPOUNDS	MATRIX WHERE COMMONLY FOUND	IMPORTANCE / FUNCTIONAL NOTES	SOURCES
Flavan-3-ols (flavanols) → (-)-epicatechin, (+)- catechin; procyanidins (dimers–oligomers)	Beans (nibs), cocoa powder; present in CBS	Potent antioxidants; support endothelial nitric oxide and vascular function; contribute to cocoa’s cardiometabolic effects	2025 metabolomics & quant methods confirm flavanols are dominant phenolics in beans(Lima et al., 2025); 2024 metabolomics review highlights flavanols/procyanidins as primary polyphenols(de Sousa Dias et al., 2024); functional health review 2025 (Metabolic Syndrome)(Dimeji et al., 2025). Named anthocyanins and decline during fermentation (2024– 2025)(Chóez-Guaranda et al., 2024; Dehghani, Taheri, & Asgary, 2024; Lima et al., 2025). CBS phenolic profile including gallic/ellagic; catechin/epicatechin major, 2025/2025 data(Umali et al., 2025); broader cocoa phenolics overview, 2024(Tušek et al., 2024).
Anthocyanins → cyanidin-3-arabinoside, cyanidin-3-galactoside	Fresh/unfermented beans (decline during fermentation)	Color precursors in purple beans; antioxidant activity; fermentation index tracks anthocyanin loss	
Phenolic acids → gallic, caffeic, ferulic, ellagic acids	Beans, cocoa powder; enriched in CBS	Antioxidant and anti- inflammatory actions; contribute to radical scavenging and metal chelation	
Flavonols / flavones → quercetin, rutin (reported at trace–low levels)	Beans, CBS	Antioxidant; potential anti- inflammatory signaling	CBS rutin/myricetin quantified (2025)(Umali et al., 2025); cocoa polyphenol classes (2024)(de Sousa Dias et al., 2024). Contemporary reviews (2024– 2025) on theobromine roles and typical predominance over caffeine in cocoa(Hermund et al., 2025; Zhang et al., 2024).
Methylxanthines → theobromine (major), caffeine (minor)	Beans, cocoa powder, CBS	Mild CNS/cardiac stimulant, mood and alertness; diuretic; theobromine shows cardiometabolic/anti- inflammatory effects	
Tocopherols (vitamin E) → $\alpha$ -, $\beta$ -, $\gamma$ -tocopherol	Cocoa butter (minor fraction)	Lipid-phase antioxidants; oxidative stability of fat matrices (chocolate, cosmetics)	Cocoa butter tocopherols reported in 2024 pharma/food review(Loke et al., 2024).
Phytosterols → $\beta$ - sitosterol, campesterol, stigmasterol (minor)	Cocoa butter (trace– minor); chocolate matrices	Competes with cholesterol absorption; may aid LDL- C lowering when enriched	Cocoa bioactives include phytosterols (2024)(Tušek et al., 2024); chocolate phytosterol enrichment work (context of functionality)(Botelho et al., 2014; Topka, Rudzińska, Poliński, Szydłowska-Czerniak, & Tańska, 2024).
Fatty acids / TAGs (bioactive lipid context) → stearic (C18:0), oleic (C18:1), palmitic (C16:0); TAGs POP/POS/SOS	Cocoa butter	Stearic acid is considered neutral on LDL-C relative to other SFAs; FA profile drives melting/crystallization behavior and sensory properties	2025/2024 syntheses on cocoa butter composition and major FAs/TAGs(Alotaibi, AlTilasi, Al-Mutairi, & Alharbi, 2024; de Souza Silveira et al., 2025; Loke et al., 2024)

CBS-specific oligo/polysaccharide–phenolic conjugates → feruloylated oligo-/polysaccharides (FOs)	Cocoa bean shell	Emerging prebiotic, antioxidant, antimicrobial potential; techno-functional fiber with phenolic linkages	2023 CBS chemical/bioactive review (FOs)(Younes, Li, & Karboune, 2023).
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**Table S3. Minerals in Cocoa Bean and By-Products**

MINERAL (MACRO/MICRO)	MATRIX WHERE COMMONLY FOUND	IMPORTANCE / FUNCTIONAL NOTES	RECENT SOURCES
Potassium (K)	Beans/powder; very high in CBS; high in CPH; present in mucilage	Electrolyte & blood pressure regulation; tech-functional in extracts	CBS K often 2,382-3,114 mg/100 g (2024); K dominant in shell extracts (2024); cocoa powder K often several g/kg (2023)(Alda, Lazar, Bordean Despina Maria, & Nistor Eleonora, 2023; Ampomah et al., 2024; Gil-Ramírez et al., 2024).
Magnesium (Mg)	Beans/powder; mucilage	Cofactor for >300 enzymes; neuromuscular and cardiometabolic health	Cocoa discussed as Mg source (2023); mucilage reported Mg ≈ 213 mg L <sup>-1</sup> (2025)(Palma-Morales, Melgar-Locatelli, Castilla-Ortega, & Rodríguez-Pérez, 2023; Rocha et al., 2025).
Calcium (Ca)	CPH (structural biomass); CBS; powder	Bone/teeth; signaling; gelling (with pectin)	CPH/CBS mineral richness (2024); cocoa powder Ca 567-1,027 mg/kg (2023)(Alda et al., 2023; Anoraga et al., 2024).
Phosphorus (P / phosphate)	CBS, CPH; beans/powder	Energy metabolism (ATP); bone/mineral homeostasis	CBS P second-most abundant mineral (2024); husk phosphates quantified in biovalorization (2025)(Ampomah et al., 2024; Barros Tiburcio, de Carvalho Neto, Soccol, & Medeiros, 2025).
Sodium (Na)	CBS/CPH (lower levels)	Electrolyte balance	Relative abundances in cocoa by-products tables (2023-2024)(Soares & Oliveira, 2022).
Iron (Fe)	Beans/powder; CBS/CPH	Oxygen transport; enzymatic cofactor; some loss during fermentation	Fermentation dynamics of trace minerals in beans (2021 high-quality study)(Calvo et al., 2021).
Zinc (Zn)	Beans/powder	Catalytic/structural cofactor for many enzymes; immunity	Fermentation study shows Zn dynamics in beans (2021)(Calvo et al., 2021).
Copper (Cu), Manganese (Mn), Boron (B)	Beans/powder; agricultural biomasses (CPH)	Antioxidant enzyme cofactor (Cu, Mn); cell wall/plant metabolism (B)	Fermentation dynamics in beans (2021)(Calvo et al., 2021).
Magnesium, Calcium, Iron, Potassium, Phosphorus in CPH pectin	CPH (pectin fraction)	Nutritional minerals co-extracted with pectin; relevant to food-grade pectin streams	Comprehensive CPH/by-product review (2024)(Anoraga et al., 2024).
“Cocoa honey” (mucilage) minerals → Mg, K	Mucilage	Useful nutrient profile for beverages/fermentation media	Food Chem 2025 shows K (~157 mg L <sup>-1</sup> ) & Mg (~213 mg L <sup>-1</sup> ) in cocoa honey(Rocha et al., 2025).

Cadmium (Cd), Lead (Pb) ( <i>undesirable contaminants</i> )	Beans/powder (Cd uptaken from soil; Pb often post-harvest surface contamination); also detected in finished chocolates	Risk: nephrotoxicity, neurotoxicity; regulatory limits apply—mitigation via agronomy, blending, and process controls	2025 update on Cd/metal contaminants and mitigation; 2024 multi-brand dark chocolate metal survey (US)(Letort, Chavez, Cesaroni, Castillo-Michel, & Sarret, 2025).
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**Additional Notes**

The tables included here provide extended datasets supporting the discussions in Sections 2 and 4 of the main manuscript.

These data are presented as supplementary material to improve readability and conciseness of the main text.