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Valorization of Ghanaian cocoa processing residues as extractives for value-added functional food and animal feed additives – A review

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ABSTRACT

Cocoa farming and processing are the main preoccupations of Ghana's cocoa-based pillar industry, generating annual quantities of 858,720 tons of cocoa pod husk (CPH) and 180,000 tons of cocoa bean shell (CBS) as cocoa processing residues (CPRs) and solid waste in Ghana. Numerous nonstructural extractable compounds with bioactivity are being intensively explored for their potential applications in plant-based functional food and animal feed additives. This review presents the potential applications of extractives from CPH and CBS in Ghana and summarizes and discusses the recent advanced technologies for their extraction. The findings of this review demonstrate that CPR extractives vary based on the type of cocoa, geographical location, and extraction method. Phenolic compounds, pectin, and alkaloids are the primary extractives found in CPRs, and their applications in functional food and animal feed additives hold promise. Microwave-assisted extraction, ultrasonic-assisted extraction, subcritical water extraction, supercritical fluid extraction, and the optimization of solvent extraction are the most recently developed and advanced technologies due to their improved extraction efficiency. However, they still require further improvements to fully realize their efficiency potential. Key factors for improving these technologies include reducing extraction time, lowering temperatures to prevent compound degradation, enhancing extraction selectivity, simplifying the extraction system's complex configuration for improved operation and energy efficiency, and minimizing chemical usage. The development and commercialization of residue-extractive technology offer promising new approaches for valorizing the cocoa processing residues, as well as the related food and animal feed sectors, not only in Ghana but also in cocoa-producing countries worldwide.

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1. Introduction

Cacao (*Theobroma cacao* L.), commonly called cocoa, is mostly grown for its edible seeds and processed into products such as cocoa butter and chocolate. Cocoa is one of the most known and valuable crops in Africa, cultivated on a large scale, and Ghana is the second-largest producer after Côte d'Ivoire. Ghana contributes 16.3% (771,000 metric tons) of the global cocoa bean production (ICCO, 2022a). In Ghana, the cocoa tree is also called "the golden tree". Cocoa beans are one of the largest exported commodities in Ghana, generating huge economic value. About 2.7 million hectares of land, corresponding to 11.3% of Ghana's land, represent the total cocoa plantation area (Abu et al., 2021). The agricultural sector of Ghana provides one-fifth of the country's gross domestic product (GDP) (World Bank, 2018), of which cocoa accounts for 1.9% (MOFA and A, 2021). This serves as not only the main livelihood for rural communities but also for all the key players in the cocoa industry. According to the Ghana Commercial Bank (GCB), in 2021, cocoa contributed about 533 million USD to the country's GDP. The cocoa industry in Ghana is experiencing rapid growth due to increasing competitiveness in the global market. As of December 2022, there was a 76% increase, amounting to 350,000 tons of graded and sealed cocoa beans, compared to the previous season's 199,000 tons (ICCO, 2022b). In 2022, the global demand for cocoa was expected to grow by 2%, going from 4.981 million tons to 5.081 million tons.

Recently, there have been international concerns about socio-economic and environmental challenges in cocoa production and processing, and this is attracting the interest of various key players in the cocoa production and supply chain, especially the utilization of cocoa processing residues (CPRs). This has given rise to the exportation and importation of cocoa residues, accounting for the world's 4416th traded product. In 2021, the top exporters of cocoa shells, husks, skins, and waste were Nigeria ($8.56M), Germany ($5.72M), France ($5.61M), Ghana ($4.76M), and Netherlands ($4.43M). Whiles the top importers of Cocoa shells, husks, skins, and waste were Netherlands ($10.7M), Germany ($7.59M), Malaysia ($3.01M), Belgium ($2.99M), and France ($2.6M) (OEC, 2021). The Netherlands, Brazil, and China are the highest importers of cocoa residue from Ghana as of 2021. It could be observed from Fig. 1 that about 12.2% of the world's total exportation of CPRs comes from Ghana, and this suggests a significant abundance of CPRs.

Cocoa processing residues (CPRs) refer to the by-products obtained during the processing of cocoa into various cocoa products, such as chocolate and cocoa powder. The main parts of cocoa and their residues are shown in Fig. 2. These residues contain abundant polyphenols, methylxanthine, dietary fibers, and phytosterols, all of which have the potential to be extracted and employed in a range of food and health products (Belwal et al., 2022). In Ghana, CPRs are often discarded as waste and burned, and they can pose environmental and health risks if not properly managed. Meanwhile, these residues could serve as inexpensive, available, and renewable sources of energy, chemicals, and other value-added products (Haq et al., 2021). For example, in Ghana, fermented pulp is a rich source of organic matter and is often used as fertilizer or soil conditioner to improve soil fertility (Amponsah-Doku et al., 2022). There

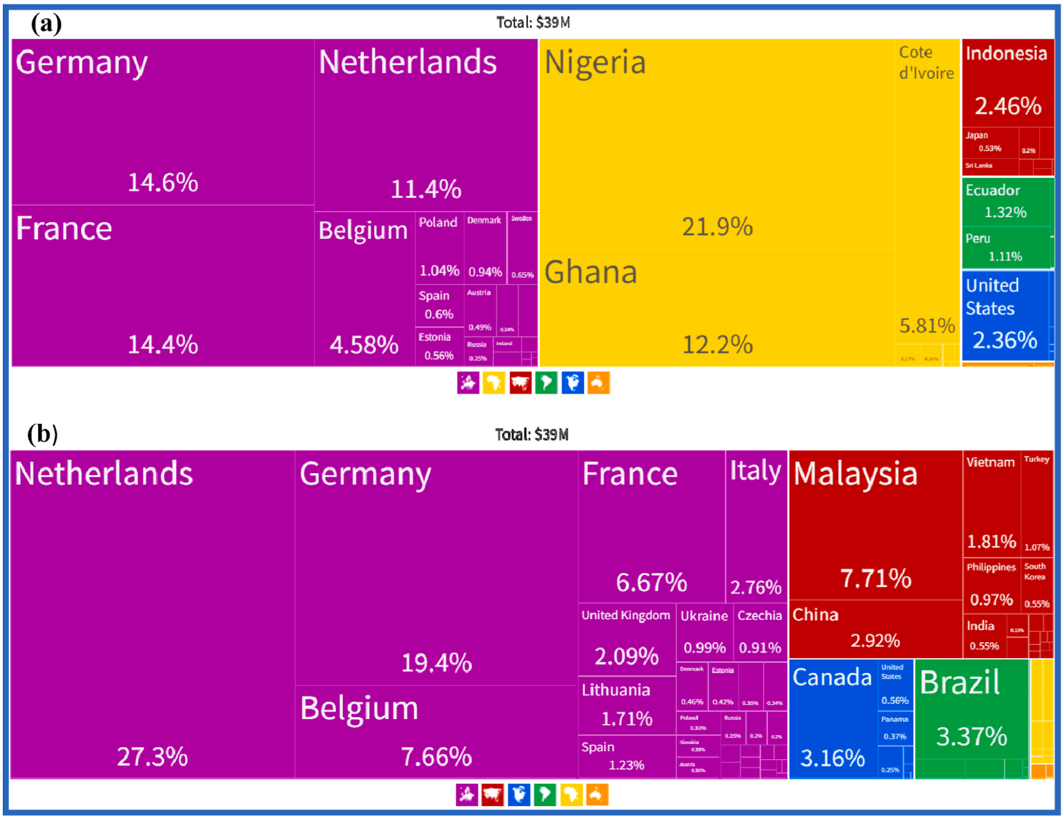

Fig. 1. Traders of cocoa residues; (a) exporters and (b) importers of cocoa shells, husks, skins, and waste in 2021 (OEC, 2021).

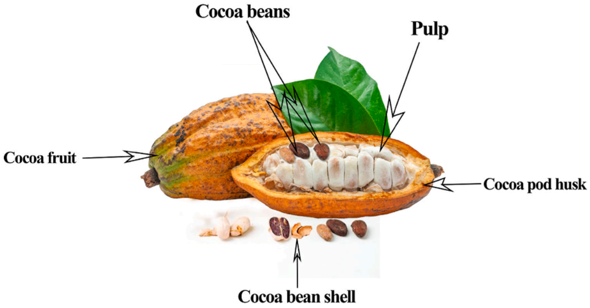

Fig. 2. The parts of cocoa fruit and their residues.

are various initiatives underway to reduce waste and increase the utilization of cocoa processing residues in Ghana. For instance, examples include using cocoa bean shells as fuel in the boilers of cocoa processing factories, employing fermented pulp as a feed ingredient for livestock, and harnessing its potential to generate biogas for energy production. However, new emerging applications of CPRs valorization include extractives. Ghana is a subscriber to all seventeen of the United Nations Sustainable Development Goals (UN SDGs). The efficient and sustainable utilization of CPRs could contribute to some Sustainable Development Goals (SDGs), including SDG 2, SDG 7 and SDG 9. Despite the various chemical components of CPRs, this paper will focus on the extractives (extractable compounds), as there is insubstantial attention given to them because of their minor proportion (14.42–23.66 % wt. on a dry ash-free basis) (Garcia-Brand et al., 2021; Mumbach et al., 2022; Titiloye et al., 2013). The valorization of CPRs into extractives could contribute to the achievement of SDG number two, which is focused on ending hunger, achieving food security and improved nutrition, and promoting sustainable agriculture. Depending on the type of plant or crop, residues contain a measurable amount of extractives. West African countries are increasingly investing in various renewable energy projects. Consequently, research on agricultural processing residues is of significant interest, as these residues contain exploitable high energy content and are abundantly available (Titiloye et al., 2013). Nevertheless, little attention is given to other components of CPRs, such as extractives, that can be valorized into value-added products with beneficial bioactivity.

Extractives are components of plant biomass that can be extracted using organic solvents like ethanol, acetone, benzene, and hexane. In recent times, advancements in technology have led to the development of alternative approaches for effectively extracting components from plant biomass (Santos et al., 2022). In the pulp and paper industry, which heavily utilizes wood and crop fibers, certain extractives such as rosin and fatty acids are extracted from black liquor (a by-product from pulp digestion through the kraft process) and further processed into crude tall oil (Bajpai, 2018a). The conversion of these resources into valuable products generates additional revenue and addresses environmental needs. However, in the preparation of certain materials like composites, the presence of extractives can have a detrimental effect on mechanical properties by hindering the interaction between the matrix and reinforcement. A recent report demonstrated the feasibility of using cocoa residues for composite production, utilizing a recycled low-density polyethylene matrix while avoiding the presence of extractives (de Araújo Veloso et al., 2021). Extractives thus pose a challenge in polymer composite production, particularly when employing cocoa residues. The definition of biomass extractives varies based on the extractable compounds present in a specific biomass, given that the composition differs between different species. For example, fats, waxes, proteins, terpenes, gums, resins, essential oils, fatty acids, sterols, and phenolics, including flavonoids, are considered wood extractives (Kallioinen et al., 2003; Nisula, 2018), while proteins, polyphenols, starch, pectin, and other exudates are considered extractives in some agricultural crop residues (Romaní et al., 2020). In this paper, extractives will be defined as the primary extractable compounds. These extracted compounds are safe for consumption and, when utilized, can be added to functional foods and animal feed as additives.

Recently, new technologies have emerged in the biorefinery sector for producing value-added products from agricultural residues and food processing by-products. (Tang et al., 2022a, 2023). The suitability of a particular technology is reliant on the availability of feedstock, including type, quality, and quantity, and the end-use application (Adams et al., 2018). Generally, in the valorization of CPRs into value-added products, various technologies are employed, including biochemical, physical, physicochemical, and thermochemical processes. In this review, extractives will be considered the main fraction of CPRs. While extractives are a component of the biorefinery concept, specific processes or technologies are necessary for their extraction due to the diverse nature and quantities of extractives present in biomass.

This review centers on the valorization of the main CPRs generated from Ghana's cocoa-based industry, including cocoa pod husk (CPH) and cocoa bean shells (CBS). The chemical and biological properties of the various extractive compounds present will be described. The application of these extractive compounds in functional food and animal feed additives will also be discussed. The complex and rigid three-dimensional nature of these biomasses demands that they undergo specific pretreatment for conversion into the desired extractives. The review therefore outlines the current extraction technologies used for the valorization of cocoa residues into extractives, termed cocoa residue extractives (CREs). Finally, the prospects of the various extraction technologies have been outlined. Overall, the proper utilization of cocoa processing residues can have positive environmental, economic, and social impacts.

2. Overview of Ghana's cocoa-based industry

The cultivation of cocoa takes place in the forest regions such as the Eastern, Ashanti, Brong Ahafo, Volta, Central, and Western North and South Regions. It's estimated that approximately 850,000 farming families across these cocoa-rich areas of Ghana are engaged in cocoa farming and its associated activities (COCOBOD, 2022). The annual cocoa harvest in Ghana varies from year to year, but on average, it is around 800,000 to 1 million metric tons. In 2021, the cocoa industry employed about 800,000 cocoa farming families. The crop generates approximately $2 billion in foreign exchange annually, making it a substantial contributor to government revenue and the GDP (GCB, 2022). Ghana's cocoa-based industry plays a significant role in the country's economy, offering manifold advantages to both the government and its citizens. Moreover, the industry creates employment opportunities for hundreds of thousands of individuals in Ghana, including farmers, traders, stakeholders, as well as workers in the processing and export sectors.

Cocoa processing industries in Ghana play a crucial role in transforming raw cocoa beans into refined products, including cocoa butter, liquor, cocoa powder, and chocolate. This value addition to the raw cocoa beans enhances their economic viability and increases export revenue (van Huellen and Abubakar, 2021). Nonetheless, the industry faces challenges such as low farmer productivity, inadequate income, and environmental degradation resulting from inappropriate farming practices. The Ghanaian government, alongside international organizations, is actively working to tackle these issues and enhance the industry's sustainability. In Ghana, the primary cocoa processing residues (CPRs) produced in large quantities are cocoa pod husk (CPH) and cocoa bean shell (CBS) (refer to Fig. 3). A key strategy involves utilizing cocoa processing residues to generate additional income and mitigate environmental pollution. In Ghana, the cocoa industry involves various stakeholders, including farmers, researchers, buyers, transporters, public officials, consumers, and policymakers (Essegbey and Ofori-Gyamfi, 2012). These participants collectively form a network to collabora-

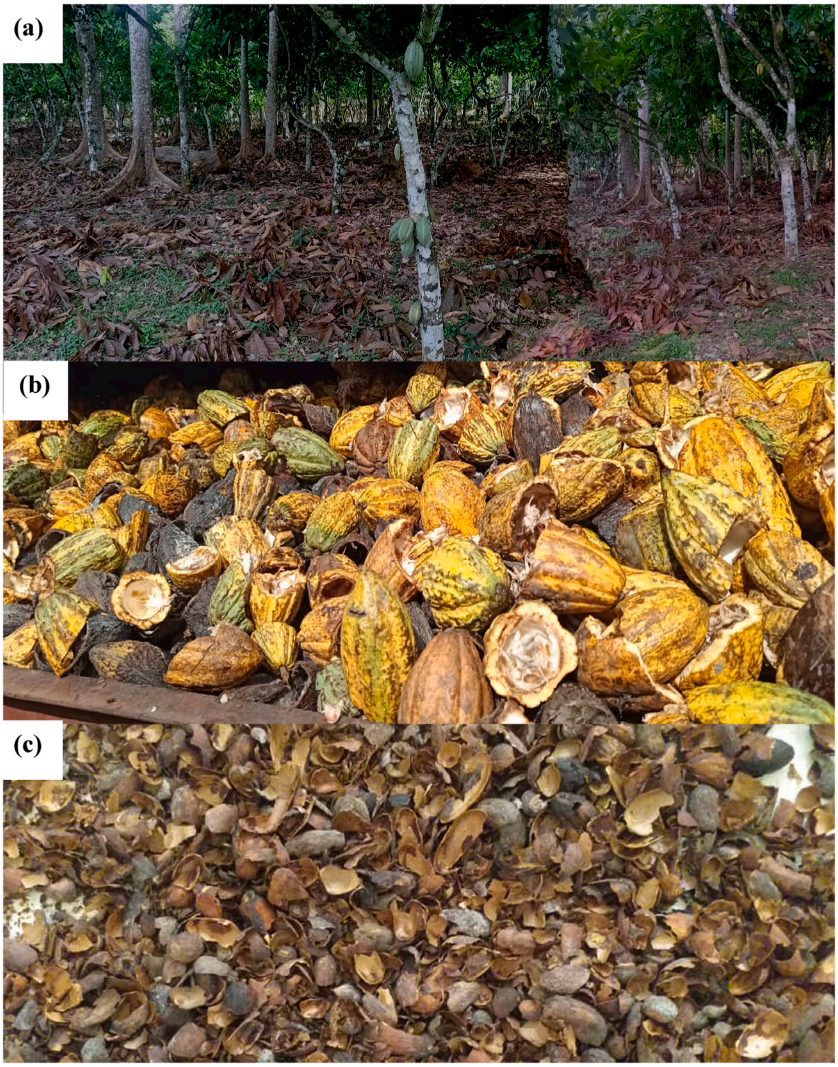

Fig. 3. A picture showing: (a) An experimental cocoa farm, (b) a heap of cocoa pod husks and (c) cocoa bean shells, at the Fermentary Unit of Cocoa Research Institute of Ghana (CRIG), New Tafo.

tively address socio-economic challenges within the cocoa industry. These include critical drivers such as cocoa farmers, the Ghana Cocoa Board (COCOBOD), processing companies, and research institutions.

In summary of their roles: (i) cocoa farmers play a critical role in the cocoa industry as they are the primary producers of the raw material used for cocoa-based products. Their main activities include growing cocoa trees and harvesting cocoa pods to extract the beans, which they ferment and dry before selling to maintain quality standards. They also adopt sustainable practices to increase production and engage in fair trade of the cocoa beans. Therefore, cocoa farmers form the backbone of the supply chain in the Ghanaian cocoa industry (Ahoa et al., 2020); (ii) COCOBOD is the main regulatory body responsible for overseeing the cocoa industry in Ghana. Its primary role is to ensure the sustainable production, processing, and marketing of cocoa beans by establishing and enforcing quality standards for cocoa beans, managing marketing and export, stabilizing prices, and conducting research and development; (iii) processing companies play a crucial role in transforming raw cocoa beans into finished cocoa products. The companies are responsible for sourcing raw cocoa beans, processing and refining, quality control, packaging and labeling, and marketing and distribution. Examples of these companies include Barry Callebaut, Olam Ghana Ltd., CHOCOMAC Ghana Ltd., AFROTROPIC Cocoa Processing Company Ltd., Cargill Ghana Ltd., and many more; and (iv) research institutions conduct research and development activities aimed at improving the quality, yield, and sustainability of cocoa production. They carry out breeding programs, agronomic research, pest and disease management, and climate change adaptation, thereby providing technical support and developing new technologies that improve the efficiency and sustainability of cocoa production. Some of the research institutions are the Cocoa Research Institute of Ghana (CRIG), the International Cocoa Organization (ICCO), the Council for Scientific and Industrial Research (CSIR), the Cocoa Health and Extension Division (CHED) of COCOBOD, and the Kuapa Kokoo Farmers and Fair-trade Association.

From the four primary key players in the Ghanaian cocoa industry, it's evident that the generation of CPRs primarily comes from farmers and processing companies. The collection and proper storage of these residues are prerequisites for effectively preparing the material before extracting the valuable compounds. Proper collection and storage not only save costs and time but also streamline the sorting and cleaning processes.

3. Valorization of cocoa residues into extractives

Extractives are nonstructural components, usually with a low molecular weight capable of undergoing solubilization in organic solvents such as water, benzene, ethanol, toluene, hexane, and acetone. Several compounds are found in the extractives of a single biomass feedstock, and the content and amount vary in each biomass, and even in different parts of the plant. Examples of compounds found in extractives include rosin, fats, proteins, waxes, phenolics, sterols, starches, glycosides, saponins, and essential oils. Although these extractives are present in minute quantities (0–15%), they provide the plants with color, odor, taste, and sometimes endurance (Bajpai, 2018b). Annually, tons of agricultural biomass are produced from agricultural crops and their residues, processing residues, forest residues, food processing waste, and municipal solid waste. Plant biomass is the most abundant and renewable, and it has been used for various value-added products, including the generation of power, heat, steam, and transportation fuels. Other applications are evident in the food processing, animal feed, and wood processing industries. Biomass resource utilization in Ghana has mainly focused on biofuel production (Nelson et al., 2021). A comprehensive review of the utilization of these biomasses for biofuels has been conducted (Duku et al., 2011). However, the utilization of some of these biomasses for extractable compounds with biological activities would be of valuable importance. There has been immense interest in and use of cocoa residues for valuable products, leading to extensive research and patents exploiting their composition. Table 1 presents the chemical composition of cocoa pod husk and cocoa bean shells.

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Table 1
Chemical composition of the main lignocellulosic-based cocoa residues.

Cellulose (%, w/w)	Hemicellulose (%, w/w)	Lignin (%, w/w)	Ash (%, w/w)	Extractives (%, w/w)	Protein (%, w/w)	Reference
Cocoa pod husk (CPH)						
–	–	–	7.9	7.0	9.0	Yapo et al. (2013)
35.4	37.0	14.7	12.3	17.6	–	Hatta (2013)
31.7	27.0	21.7	3.7	16.8	–	Dahunsi et al. (2019)
35.0	11.0	14.6	9.1	6.1	5.9	Campos-Vega et al. (2018)
15.45	11.47	30.18	8.35	33.46	–	Valladares-Diestra et al. (2022)
–	–	21.4	6.7	4.6	8.6	Vriesmann et al. (2011)
–	–	–	9.3	8.8	9.4	Ozung et al. (2016)
–	–	–	7.6	7.62	8.6	Valadez-Carmona et al. (2018)
Cocoa bean shell (CBS)						
–	–	–	5.9–11.4	7.6–15.5	10.3–27.4	Rojo-Poveda et al. (2020)
–	–	–	11.4	5.8	16.7	Lecumberri et al. (2007)
–	–	–	5.9	4.6	16.9	Nsor-Atindana et al. (2012)
–	–	–	11.4	37.1	16.0	Öztürk and Ova (2018)
–	–	7.7	9.0	38.7	–	Nsor-Atindana et al. (2012)

(–) Not applicable.

3.1. Cocoa pod husk

After the removal of the cocoa beans, the non-edible outer part of the cocoa is called the cocoa pod husk (CPH), which comprises 67–76% of the total cocoa pod. The CPH is usually left in the field to decompose as manure or burned. Due to the long period of decomposition, CPH can introduce plant pathogenic diseases such as black pod rot, as it serves as a host for the development of Phytophthora spp. Additionally, when CPH is burned in the field, it contributes to global warming by increasing particulate matter, causing health hazards to the environment, and deteriorating soil fertility. In Ghana, CPH is mostly used as a source of potash for soap making, compost, and animal feed. For each ton of cocoa beans, about 10 tons of wet CPH are produced, with a moisture content of about 80% (Campos-Vega et al., 2018). Efficient utilization of this large volume is necessary, as it contains a significant amount of chemicals and energy. The chemical composition of CPH attracts innovative technology that utilizes it to produce value-added products such as activated carbon, animal feed, fertilizer, biofuels, paper, and nutraceuticals. These products contribute to a sustainable society and a circular economy. CPH consists of 19–35% cellulose, 8–13% hemicellulose, 14–23% lignin, and 6–13% pectin (Bruna et al., 2009; Soares and Oliveira, 2022; Titiloye et al., 2013). The characteristics of cocoa pod husks and their impact on the global market have already been reported (Porto de Souza Vandenberghe et al., 2022).

The chemical components of CPH present different biochemicals with great biotechnological potential and high added value. Nevertheless, extractives, the smallest component of CPH, contain essential chemicals that can be applied in the food, feed, pharmaceutical, and cosmetic industries. The chemical composition and energy density of CPH vary depending on the cultivation method, soil type, and environmental factors (Adjin-Tetteh et al., 2018). As a result, the properties of CPH after extraction will differ at different locations. Phenolic compounds are a significant component of CPH extractives and are rich in antioxidant properties. Phenolic compounds possess epidemiological activities with potential anti-carcinogenic, anti-inflammatory, and antimicrobial effects.

Pectin is another essential component of CPH extractives, as indicated in the literature. Pectin mainly constitutes galacturonic acid units linked by α-(1 → 4) linkages, which find vast applications as thickening, emulsifying, and stabilizing agents in the food, cosmetic, and pharmaceutical industries (Li et al., 2023). The primary sources of commercial pectin are by-products from the food industry, such as citrus peel, watermelon rinds, sugar beet pulp, tomato waste, banana peels, and mango peels (Guo et al., 2016; Liew et al., 2016; Maran et al., 2017; Wang et al., 2016; Wikiera et al., 2016). The type of biomass and the extraction method significantly influence the physicochemical properties of pectin and its application.

3.2. Cocoa bean shell

In the production of cocoa products, specifically chocolate, the cocoa bean shell (CBS) is removed. Thus, the shell on the bean is removed together with the germ before or after roasting. The nibs (crushed fragments of the cocoa bean free of the shell) are used in chocolate production. The CBS is regarded as an industrial cocoa by-product, generally used as waste for the fuel generation for boilers (Fontes et al., 2019), and for animal feed and fertilizer preparation (Karim et al., 2014). The chemical composition of CBS is quite variable, as it depends mainly on its origin and the processing it undergoes. Cocoa bean shells are also known as hulls. Ghana is estimated to produce about 180,000 tons of CBS out of the 900,000 tons produced globally.

Fresh cocoa beans contain high amounts of polyphenols, which give them a very bitter taste. This bitterness is mostly reduced during processing such as fermentation, alkalizing, and roasting. The phenolic compounds are majorly stored in the cotyledons of the seed (Hernández-Hernández et al., 2018), and these compounds diffuse outside of the cotyledons (Jokić et al., 2018). Consequently, the cocoa shell can absorb these compounds, making it an enriched material for phenolic compounds. The main phenolic compound identified in CBS is epicatechin, the most abundant flavonoid (6.93–17.70 mg/g), followed by catechin (1.02–6.16 mg/g) (Hernández-Hernández et al., 2018). A similar observation was made during optimization by using response surface methodology and artificial neural networks for phenolics extraction in cocoa shell, where protocatechuic acid and mono- and dimeric flavanols were the main components (Rebollo-Hernanz et al., 2021). A recent study of Ghanaian cocoa bean shells has revealed seven compounds with a polyphenolic profile, including epicatechin and catechin (values ranged 4.56 to 6.33 and 2.11 to 4.56 mg/g, respectively) as the most abundant (Botella-Martínez et al., 2021). However, when CBS were sampled from different origins, including Madagascar, Ghana, Venezuela, Ecuador, and Trinidad, the polyphenol content and their antioxidant activities differed, with Ghana being third on the list (Bruna et al., 2009). This suggests that CBS constitutes a valuable coproduct for the food industry due to its high content of valuable bioactive compounds.

4. Application of cocoa residue extractives

The extractive compounds of CPH and CBS discussed in the previous sections can be viable for various industrial applications. Despite the minimal content of extractives in plants, their characteristics become evident through the color, taste, smell, and durability of the plants (Yang and Lü, 2021). These characteristics can find application in food and animal feeds based on the compounds responsible for such activities. The primary extractives identified in both CPH and CBS are phenolic compounds (epicatechin, catechin, and tannins) and pectin (uronic acid). The application of these compounds in functional foods and animal feeds has been discussed below.

4.1. Cocoa residue extractives for functional foods

Functional food is any modified food or food ingredient that may provide health benefits beyond the traditional nutrients it contains, among other potential healthful products. A functional food must have a component that positively influences one or more targeted bodily functions. At times, the high cost of functional food items and food supplements makes it challenging for people to afford them, especially in sub-Saharan Africa. As a result, more individuals in that region opt for lower-nutrient foods, contributing to the rise in malnutrition in Africa. Many believe that these inappropriate dietary behaviors contribute to poor health and the high expense of related medical care. However, bioactive molecules contained in extractives can be extracted from agricultural processing residues, which are often considered waste and contribute to environmental pollution. These molecules can be harnessed using both traditional and cutting-edge extraction techniques.

Cocoa processing residues are suitable and affordable ingredients for incorporation in the manufacture of functional foods due to the extraction of valuable components such as flavonoids, proteins, and antioxidants. Opportunities exist to establish a novel value chain by utilizing functional components produced from cocoa residues in food applications (Belwal et al., 2022). Cocoa processing residues, such as cocoa husk powder or extract, which is a rich source of bioactive chemicals, have been investigated and utilized as ingredients in various food products to enhance their physical, chemical, and biological qualities (Campos-Vega et al., 2018). The utility of cocoa pod husk as a functional component has been established (Karim et al., 2014). However, it's important to note that cocoa pod husk is not commonly consumed directly as a food source. Instead, it is often repurposed for purposes such as animal feed or compost due to its nutraceutical nature and high fiber and polyphenol contents. Cocoa bean shell (CBS) has been primarily recommended as a clean label component and/or additive among its many applications (Rojo-Poveda et al., 2020). Cocoa bean shell extract has undergone testing in several food products to enhance product functionality owing to its polyphenols and methylxanthine content. To enhance the functionality and consumer acceptance of a flavored beverage, cocoa bean shell extract containing polyphenols and methylxanthine was added to the beverage after in vitro digestion. Interestingly, it was observed that polyphenols (B procyanidins and epicatechin) had 50% bioaccessibility compared to 100% for methylxanthine. The beverage also exhibited increased α-glucosidase inhibitory activity and was well-received by customers (Cantele et al., 2020). Polymeric polyphenols (procyanidins) were recovered from the cocoa bean shell using a methanolic extraction technique (Arlorio et al., 2005). Subsequent reports indicated that, when applied in functional food applications, procyanidins demonstrated protective activity against ischemia damage.

Cocoa residue extractives can be utilized in the oil industry to enhance the quality of cooking oil and improve consumer health with affordability. One application involves enhancing the stability of soya cooking oil by incorporating a polyphenolic extract from CBS, resulting in oils with lower free fatty acid and peroxide generation indices after repeated uses (Manzano et al., 2017). A similar approach involves adding encapsulated CBS polyphenol extract to olive oil jam, preventing it from becoming rancid (Hernández-Hernández et al., 2019). The potential use of CBS as a fat substitute in pound cakes made with ingredients like wheat flour, sugar, sunflower oil, eggs, salt, whole milk, and baking powder was examined. The result indicated higher bioactive components in the pound cakes due to the high phenolic content and total antioxidant activities of CBS. This study demonstrated that replacing 50% of the vegetable oil with raw CBS led to a significant enhancement in the chemical, physical, and sensory properties of the cakes (Öztürk and Ova, 2018). CPH-pectin exhibits potential pharmaceutical applications, such as serving as a carrier for the chrono-delivery of hydrocortisone intended for adrenal insufficiency (Adi-Dako et al., 2017).

The rheological property is an important factor considered in functional foods. CPH-extracted pectin exhibited shear-thinning behavior, characterized by a high consistency factor (k) and flow behavior index, which could serve as a natural food additive and a fat substitute in food products (Priyangini et al., 2018). The gelling property of pectin enables its application in functional foods with health benefits, including appetite regulation and coronary disease prevention (Li and Nie, 2016). This gelling capacity is a typical behaviour of high-methoxyl pectins at low pH (Hennessey-Ramos et al., 2021). Surprisingly, despite the high acetyl content, rheological analysis showed that low-methoxyl pectin extracted from CPH could form gels at low pH under reduced water activity (Vriesmann and de Oliveira Petkowicz, 2017). Stronger polymer chain interaction was reflected in gel textural properties (Luo et al., 2019), suggesting a potential application of CPH extractives in acidic food products. The antioxidant activity of phenolic compounds makes them valuable components in the food industry. CBS contains a substantial amount of phenolic compounds and organic pigments, providing a good and cost-effective source. These antioxidant activities and pigments could be utilized as colorants and bioactive compounds with functional properties. The colour of CBS was reported to be similar to cocoa bean powder (Delgado-Ospina et al., 2021). The brown colour is a result of the complex interaction of polyphenols and anthocyanins during the fermentation, drying, and roasting processes. High molecular weight melanoidins are also produced during roasting through oxidation, polyphenol polymerization, protein degradation, and the Maillard reaction (Sacchetti et al., 2016). With the global aim of reducing the use of artificial colorants, extracted pigments from CBS can serve as a natural replacement and a potential colorant in food. Tannins, including procyanidins, are also found in CBS (Pérez et al., 2015), with biological properties (Miller et al., 2006).

Thus, extractives from CBS can be used as food additives or flavor enhancers. This was evident when CBS extract was compared to a synthetic antioxidant for lipid oxidation in cooked beef (Ismail and Yee, 2006). The study showed that beef treated with CBS extract had significantly lower lipid oxidation than beef treated with the synthetic antioxidant. This suggests the promising oxidative stability potential of CBS extracts. Many food companies are capitalizing on CBS, with some obtaining patents for its application in recent years (Okiyama et al., 2017). Notably, Kraft Foods patented a theobromine and phenolic compound extraction process from the CBS. Extractives containing bioactive ingredients play an essential role in technological applications. A recent study showcased the use of CBS in a functional beverage. The beverage had a total phenolic content of 1803.83 mg GAE/L, a high antioxidant capacity of 7.29 mmol TE/L, and antidiabetic properties with 52.0% α-glucosidase inhibition (Rojo-Poveda et al., 2019). These values were generally higher than those reported for drinking chocolate (600 mg GAE/L) or hot cocoa (300 mg GAE/L) (Zujko and Witkowska, 2014). In some cases, the total phenolic content values were also higher than those of various tea types, including white tea (1040 mg GAE/L), green tea (850 mg GAE/L), black tea (720 mg GAE/L), and red tea (380 mg GAE/L). Additionally, the reported TPC values for red wine (2410 mg GAE/L) and white wine (260 mg GAE/L) (Zujko and Witkowska, 2014) fell within the range of the values obtained for CBS beverages. The primary compounds responsible for the total phenolic content were flavonoids, constituting 20.8%–34.7% of the TPC. The highest recorded value for flavonoids was 566.42 mg CE/L. When CBS was added to corn extruded snacks, an increase in dietary fiber and phenolic contents was observed, albeit with an increase in hardness and breakage (Jozinović et al., 2019). Specifically, the addition of 15% CBS resulted in a doubling effect on the polyphenol content, yielding a value of 109.91 mg GAE/100 g d.m. for the non-extruded sample with 15% CBS, compared to 55.17 mg GAE/100 g d.m. for the non-extruded corn grits. Considering these findings, extrudates containing 15% cocoa husks constitute a valuable source of cocoa flavanols. Despite the extrusion process leading to a reduction in polyphenol content, the extruded sample retained a substantial amount of these compounds, measuring 105.68 mg GAE/100 g d.m. It's worth noting that polyphenols from CBS exhibit low stability against oxidation and thermal degradation in practical applications.

One approach to mitigating this challenge is to microencapsulate CBS phenolic extracts through spray-drying (Papillo et al., 2019). The addition of CBS heightened the antioxidant activity, primarily due to the augmented polyphenol content. After the extrusion process, there was a further increase in antioxidant activity, potentially stemming from the formation of Maillard products, particularly hydroxymethylfurfural (HMF). These Maillard products are known for their dark brown coloration. These observations suggest that CBS could serve as an intriguing ingredient for new functional foods with potential health benefits. The various studies presented in this review have demonstrated that the development of new technologies for extracting extractives from biomass will contribute to the reduction of malnutrition and various health issues resulting from the intake of inadequate functional foods, both in Africa and Ghana. This reduction is particularly relevant due to the abundance of these biomass residues produced annually in the country.

4.2. Cocoa residue extractives for animal feed additives

The most notable increases in meat production have been attributed to advancements in animal nutrition, particularly the increased utilization of feed additives. Feed additives can generally be defined as minerals, vitamins, or any other chemicals added by farmers to natural feedstuffs, either for nutritional purposes or as medicine for subclinical diseases (Pandey et al., 2019). An important consideration when selecting animal feed additives is the promotion of animal health alongside excellent growth performance. Farmers use additives in animal feed for various objectives, including nutrient enrichment, enhanced growth performance, increased feed intake, and other critical factors. Given the growing concern among consumers in many countries, the use of feed additives, such as antibiotics and B-agonists, is being restricted due to their potential adverse health effects. Therefore, the feed sector is actively seeking viable alternatives that align with customer preferences.

Animal feed additives made from high-fiber agricultural by-products have long been used to improve animal health and performance. However, the use of lignocellulosic-based residues in animal feeding is limited by their poor nutritional value, often characterized by low and imbalanced protein content. Furthermore, issues such as antinutritional factors like phytates, oxalates, or hydrocyanic acid, as well as mycotoxins contamination, must be addressed with caution (Ajila et al., 2007). Bioactive compounds like theobromine and tannins, found in substantial quantities in CBS, may function as anti-nutrients in certain animals, hindering the absorption of essential nutrients and diminishing their bioavailability. Theobromine can also lead to adverse effects such as liver and thyroid dysfunction in horses and even death in dogs when consumed in large quantities (Rojo-Poveda et al., 2020). Efforts to enhance the quality of meat, eggs, and milk should extend beyond animal feed composed solely of proteins and carbohydrates. Incorporating other nutritional aspects, such as antioxidant compounds, is equally vital. The utilization of whole cocoa pod husk in animal feed presents challenges, particularly when the proportion of CPH exceeds 20%, especially in monogastric animals, due to its high fiber content, substantial water holding capacity, and swelling potential (Delgado-Ospina et al., 2021). The incorporation of extractives from CBS and CPH into animal feeds has shown potential to enhance meat and egg quality, as demonstrated with other co-products like grape pomace flour (Reis et al., 2019). However, the realization of these benefits may depend on extraction technologies that enhance antioxidant activities and nutritional qualities. Further studies should be undertaken to evaluate the impact of incorporating extractive compounds into animal feeds on the quality of animal products.

Cocoa residues, including cocoa pod husk, pulp, and cocoa bean shells, are among the agricultural processing wastes often utilized as feed additives. This practice is commonplace for by-products within the food processing industry, and the use of cocoa bean shells (CBS) as a feedstock has been advocated for an extended period of time. CBS, owing to its substantial protein, mineral, and vitamin content, serves as a unique and cost-effective feed ingredient. Its inclusion in animal feed is widespread, particularly in pig, poultry, rabbit, and fish diets, aimed at replacing traditional feed components like maize and bran. Extensive research on this approach has been conducted in West Africa (Lu et al., 2018). The utilization of cocoa pod husk in pig feed has demonstrated positive effects on the balance of the intestinal microbial community. Notably, studies following the addition of 20% CPH to pig diets have substantiated these findings (Magistrelli et al., 2016). This rate was found to be the biologically optimal level for utilizing CPH as an energy substitute for maize in pig diets. Evaluations of employing cocoa shells as a supplementary food source for rabbits have been carried out. Optimal growth results and the best cost-benefit ratio were observed when cocoa shells heated in hot water were added to rabbit feed at up to 200 g/kg, in contrast to the untreated usage of 100 g/kg (Ayinde et al., 2010). However, some researchers have suggested that poultry growth might be adversely affected by feeds containing over 10% CPH, possibly due to CPH's high fiber content, which could decrease digestibility and increase intestinal viscosity in monogastric animals (Lateef et al., 2008). This, in turn, could negatively impact animal body mass gain. Yet, recent research has demonstrated that pre-treating CPH with various enzymes, such as Viscozyme, Pectinex, and the fungus *Phanerochaete chrysosporium*, can enhance CPH digestibility by around 30%, rendering it suitable for both poultry and steers (Lu et al., 2018).

In 2022, a team of researchers explored the use of cocoa husk as a natural biological feed additive for broiler chickens. Substituting 5% of wheat with alkali-treated extruded cocoa husk was found to enhance nutrient digestibility (Grechkina et al., 2022). Their findings revealed that introducing cocoa husk to the starting feed of experimental group II broiler chickens, which had been subjected to prior chemical treatment with NaOH (45 g/kg), led to a 4.3% increase in the digestibility of raw fat, 7.8% for protein, and 4.4% for fiber. This was coupled with a reduction in the utilization of nitrogen-free extractives compared to the poultry consuming the basic diet. In terms of feeding tilapia with additives, a study indicated that incorporating cocoa husks and other agricultural processing wastes like banana peel and cassava peel had no detrimental effects on the condition of tilapia (Yossa et al., 2022). The report suggested that additional processing, such as fermentation, could enhance the nutritive value and digestibility of these raw components, necessitating further research in this domain. Prior to this study, fish fed feed containing 20% cocoa husk exhibited greater weight gain than those fed a diet comprising 40% maize (at the expense of 50% of the latter) (Ashade and Osineye, 2010). Hence, the extraction of cocoa processing by-products holds significant economic value and can contribute to reducing feed costs. This is due to its status as an economical raw material for extracting various components capable of serving as dietary supplements to replace more costly maize flour, wheat bran, and rice bran in tilapia diets.

5. Current technologies for valorizing cocoa residues into extractives

There exist various technologies for extracting extractive compounds from diverse residues or biomasses. A clear understanding of the chemical composition of these biomasses aids in identifying the appropriate technologies for extracting extractive compounds. In the valorization of different lignocellulosic biomass for value-added products like biofuels and chemicals, pretreatment stands as a crucial prerequisite (Afedzi et al., 2022; Tang et al., 2022b; Tareen et al., 2021). For the extraction of phenolic compounds from various biomasses, conventional or traditional methods like Soxhlet extraction, cold pressing, reflux, and maceration have traditionally been used. The terms “traditional” or “conventional” have generally been used to encompass commonly accepted practices. However, when these techniques are adapted or optimized by altering one or more parameters to enhance efficiency and yield, reduce costs and process stages, and enhance environmental sustainability, they are termed “advanced” or “current” technologies. This does not imply that conventional technologies are obsolete; rather, they remain foundational.

In this review, we focus on the current or advanced technologies employed for valorizing extractives from the two major cocoa residues, cocoa pod husk (CPH) and cocoa bean shells (CBS). While these technologies offer advantages, they also come with drawbacks such as prolonged extraction times, reduced quality and yield, and the loss of essential volatile compounds. As such, the need for novel extraction technologies for agricultural processing residues, particularly cocoa residues, is evident. Diverse techniques exist for extracting extractives from various biomasses. Thanks to innovative green extraction technologies, a more sustainable and environmentally friendly method for processing and extracting compounds from cocoa pod husks and cocoa bean shells has recently emerged. These ecologically friendly extraction techniques bolster productivity while harnessing natural resources without posing harm to the environment. The subsequent section delves into the recent technologies for cocoa residue extractives (CRE), as depicted in Fig. 4.

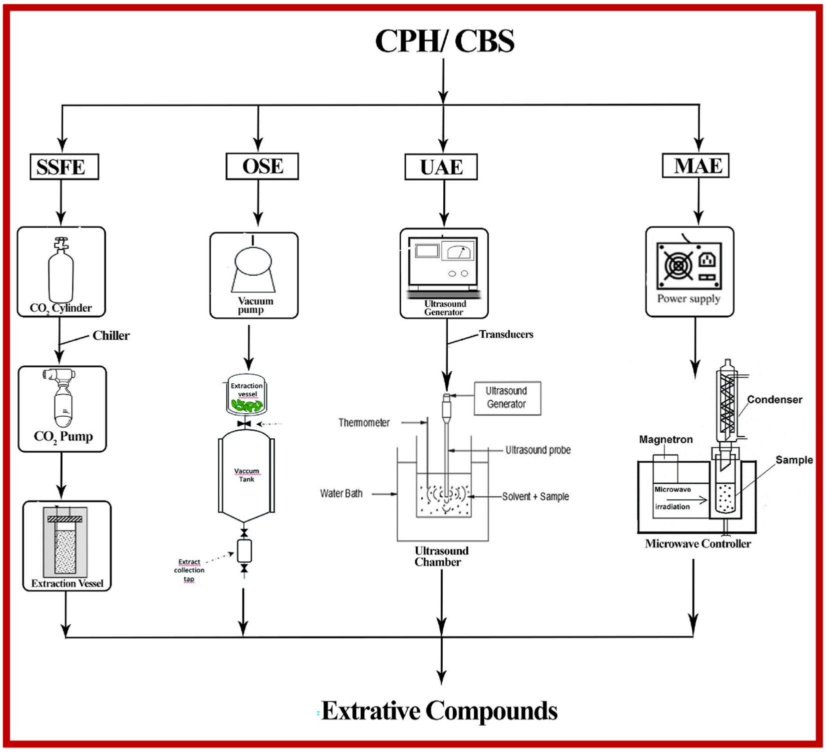

Fig. 4. Scheme of the various technologies used for the valorization of cocoa processing residues into extractives. CPH: cocoa pod husk, CBS; cocoa bean shell, SSFE; super and subcritical fluid extraction, OSP; optimized solvent extraction, UAE; ultrasound-assisted extraction, MAE; microwave-assisted extraction.

5.1. Super and subcritical fluid extraction

The term "supercritical fluid" refers to a fluid that has been heated and compressed beyond its critical points, at which point it exhibits both gaseous and liquid characteristics. This state is achieved through precise adjustments in pressure and temperature. The gas is heated and pressurized several times to reach a supercritical condition before being sent to the extractor, where it permeates the matrix. When the fluid reaches the separator, it is swiftly decompressed, changed back into a gas, and then recycled (Montalbán and Víllora, 2022). In addition, the attributes of supercritical fluids can be tailored by regulating temperature or pressure, enabling modifications in density that subsequently impact solubility performance in alignment with specific requirements (da Silva et al., 2016). Common supercritical fluids include CO_2, methanol, ethane, and ethene, with supercritical CO_2 being the commonest due to its critical values (31 °C, 7.38 MPa). The relatively low critical temperature minimizes thermal degradation of the desired compounds, and the absence of air contact eliminates undesirable oxidation reactions (Chemat et al., 2017; Essien et al., 2020).

Supercritical fluid extraction (SFE) is employed in laboratories and on a large scale in industries to extract specific molecules or recover large amounts. It stands as a green, non-conventional technique for extracting polyphenols. SFE has been utilized for extracting extractives, such as phenolic compounds from CPH, owing to its merits, including rapid extraction time, eco-friendly process, minimal organic solvent usage, improved extractive yield, and recovery of oxidizable bioactive compounds. This method comprises subcritical water extraction, supercritical water extraction, and supercritical CO_2 extraction.

Supercritical CO_2 (SCC) extraction utilizes CO_2 in lieu of organic solvents for extraction. However, for efficient extraction of highly polar compounds, co-solvents are utilized. The successful extraction of phenolic compounds from CBS involved SCC in conjunction with pressurized liquid (ethanol as a co-solvent). This combined approach, executed using a cost-effective multifunctional unit, raised total phenolic content from 35 to 51 mg GAE/g and antioxidant activity (EC50) from 115 to 177 μg mL^{-1} (Mazzutti et al., 2018). This combined approach, executed using a cost-effective multifunctional unit, raised total phenolic content from 35 to 51 mg GAE/g and antioxidant activity (EC50) from 115 to 177 μg mL^{-1} (Mazzutti et al., 2018). This combination presents an effective means to selectively retrieve extractives from cocoa bean shells, serving as an environmentally friendly and cost-effective solution for the food industry. SCC is equally adept at extracting phenolic compounds from CPH, with improved yield when co-solvents are employed. Under optimal conditions (60 °C, 299 bar, and 13.7% ethanol), the extracted phenolics resulted in a yield of 0.52%, totaling 12.97 mg GAE/g extract (Valadez-Carmona et al., 2018).

Subcritical water (SCW) extraction utilizes water as the sole extractant, maintaining its liquid state within the range of 100 °C–374 °C through optimization of water's critical temperature (374 °C) and pressure (22.1 MPa). SCW can be optimized through variations such as compressed hot water extraction, pressurized hot water extraction, supercritical extraction, or hydrothermal extraction (150–230 °C and 4.9–20 bars). The properties of water, including its non-flammability, non-toxicity, affordability, and environmental safety, render it promising for mitigating the limitations of chemical methods. Increased temperatures lead to significant changes in various physicochemical properties; decreased surface tension and viscosity, along with increased diffusivity, foster improved mass transfer and enhanced wetting of the sample, facilitating better penetration of water into the matrix (Plaza and Turner, 2015). While enhanced solubility and mass transfer can inadvertently lower selectivity during solid-liquid extraction, careful optimization of extraction parameters, particularly time and temperature, can counteract these challenges. The impact of pressure is negligible if water remains in its liquid state (Plaza and Marina, 2019; Plaza and Turner, 2015).

The use of SCW extraction improved the yield of pectin to 10.9% with a molecular weight of 750 kDa, surpassing the yield of 8% obtained through citric acid extraction (Muñoz-Almagro et al., 2019). SCW extraction also proves effective for extracting phenolic compounds from cocoa shells. Under optimal conditions (220 °C, 75 min, 20 mL/g), a total phenolic content of 130.33 mg GAE/g was achieved in CBS (Jokić et al., 2018). The technology even yields up to 100% of total phenolics from CBS in a single extraction stage involving pressurized hot water, minimizing the need for organic solvents due to the dual use of about 50–80% ethanol for precipitation (Jensch et al., 2022). Microencapsulation of SCW extract of CBS through spray-drying technology has been successful, enhancing the stability of bioactive compounds and yielding favorable outcomes in terms of total phenolic (37.68 mg GAE/g) and total flavonoid (66 mg CE/g) contents while retaining quality (Jokić et al., 2020).

In hydrothermal extraction (HTE), pectin is produced as a by-product. The typical operating conditions for HTE include temperatures within the range of 150–230 °C and pressures ranging from 4.9 to 20 bars. HTE shares similar features with dilute acid hydrolysis, as it induces the formation of acetate from xylan and facilitates the hydrolysis of glycosidic bonds (Zhuang et al., 2017).

5.2. Optimized solvent extraction

Solvent extraction is the main technology employed in the isolation and purification of pectin from cocoa pod husks. Commonly used inorganic acids for this purpose include hydrochloric acid and nitric acid. Although effective, these acids generate effluents that pose environmental challenges and offer limited economic value. Alternatively, water and citric acid have been employed in pectin extraction from CPH, taking into account factors such as temperature, pH, extraction time, and substrate-solvent ratio to optimize their effectiveness (Vriesmann et al., 2011, 2012).

In some cases, the extraction solvent, such as water, is heated to increase the extractable compounds. For example, hot aqueous extractions conducted at 100 °C for 90 min resulted in a 12.6% yield of pectin (Vriesmann et al., 2011). To further improve extraction yield, catalysts, often organic acids, are introduced. Strong inorganic acids like hydrochloric and sulfuric acids, while efficient, are not recommended due to their production of toxic by-products. Instead, recent studies employ food-grade organic acids such as acetic acid, citric acid, and ascorbic acid. For instance, an effective pectin extraction condition involves ascorbic acid at pH 2.5 at a temperature of 95 °C for 45 min, yielding 74.5% methoxy pectin (uronic acid) with an 8.1% degree of esterification (Priyangini et al., 2018).

Pectin extracted from CPH using citric acid demonstrated better suppression of drug release in aqueous medium compared to hot-water extraction (Adi-Dako et al., 2017).

Deep eutectic solvent (DES) is a solvent mixture formed by combining a halide salt or hydrogen bond acceptor with a hydrogen bond donor. DES offers several advantages, including low cost, minimal toxicity, simplicity, rapid processing, and biodegradability. It finds application in extraction processes for isolating or fractionating compounds. DES has been successfully employed to enhance the accessibility of acetic acid hydrolyzed wheat bran, increasing glucose yield to 72.8% (Ying et al., 2022). Furthermore, DES has demonstrated effectiveness in extracting compounds from cocoa residues. The use of a 1:2 ratio of choline chloride and lactic acid resulted in the enhanced extraction capacity of phenolic compounds, specifically chlorogenic acid and caffeine from CPH (Ruesgas-Ramón et al., 2020). DES stands as a sustainable and high-yielding technology for extractive valorization.

5.3. Ultrasound-assisted extraction

Ultrasound-assisted extraction (UAE) employs low-frequency, high-intensity ultrasound to induce fragmentation and pore formation in cell walls, facilitating the extraction of target compounds. Ultrasound encompasses sound waves ranging from 20 kHz to 10 MHz. As ultrasonic waves traverse a liquid medium, they trigger acoustic cavitation, a phenomenon involving alternating compressions (positive pressure) and expansions (negative pressure) due to the wave propagation. This process transforms sonic energy into mechanical energy, generating shock waves with pressures equivalent to several thousand atmospheres (Mussatto, 2015). This technique is typically carried out using ultrasonic baths or probes. UAE offers several advantages, including reduced time and energy consumption, extraction at lower temperatures, and a high-quality yield of the extract (Kumar et al., 2021). Hydrodynamic cavitation (HC) is a related technology also based on cavitation formation. Various HC systems fall into categories based on reactor design, such as rotational and non-rotational reactors. These systems are cost-effective, user-friendly, and capable of continuous fluid processing, making HC a potential alternative to acoustic cavitation (Gevari et al., 2020).

The optimization of UAE parameters for CBS, including extraction times and solvents, was carried out to enhance extraction yields using a titanium ultrasonic horn (15 min, 150 W, 19.9 kHz). Results revealed that a phenolic content of 125.0 mg/g extract was achieved using a mixture of hexane, ethanol, and water in the ratio of 30:49:21, respectively, for 15 min (Grillo et al., 2019). Upon scaling up the optimized protocol using an HC reactor, the total phenolic content increased from 125.0 to 197.4 mg/g extract. A study aimed at maximizing flavonoid content from CBS directly from fresh fruit involved optimizing three key variables: ethanol concentration (70–90%), temperature (45–65 °C), and ultrasound irradiation time (30–60 min) (Md Yusof et al., 2019). This extraction occurred in a 40 kHz, 296 W ultrasonic bath. The optimized conditions of 80% ethanol, 55 °C temperature, and 45 min of ultrasound irradiation yielded a total flavonoid content of 7.47 mg/g. A synergistic effect was observed when UAE was combined with deep eutectic solvent (DES) (Ruesgas-Ramón et al., 2020). The authors noted that specific temperature and pressure conditions led to a decrease in the intrinsic viscosity of the DES, enhancing mass transfer.

Biological methods, such as enzymatic extraction, are regarded as essential biotechnological methods with high industrial potential. Enzymatic extraction is environmentally friendly, usually performed under mild conditions, and generates little to no toxic inhibitors. When enzyme extraction was assisted by sonication, a pectin yield of 8.28 g/100 g feedstock and a galacturonic acid content of 42.77 g/100 g pectin were obtained (Hennessey-Ramos et al., 2021).

5.4. Microwave-assisted extraction

Microwave-assisted extraction (MAE) is an automated green extraction technique that employs microwave radiation to accelerate the extraction process by promoting heat transfer and improving mass transfer kinetics within the sample. Traditional extraction methods, such as solid-liquid extraction or Soxhlet extraction, can be time-consuming and require substantial solvent volumes. In contrast, MAE offers several advantages, including reduced extraction time, lower solvent consumption, and enhanced extraction efficiency (Llompart et al., 2019). Over the past two decades, microwave technology has been studied for its commercial application and advancements in extracting bioactive components from cocoa residues. Two distinct types of microwave extraction exist: solvent-free procedures (typically focusing on volatile components like oils) and solvent methods (usually targeting non-volatile compounds such as polyphenols and pectin). MAE provides better yields in less time than conventional extractions due to the heat and mass gradient that occurs from the bulk to the walls of the extracting vessel. This technology aligns with process intensification strategies for the recovery of valuable compounds.

Polysaccharide-pectin-based films were generated from cocoa bean shells using MAE, and a biofilm was created from pectin-cocoa bean shell extract. To enhance thermal, barrier, structural, morphological, and optical properties, ZnO/Zn nanoparticles were incorporated into the biofilm after its formation. The resulting biofilm exhibited improved UV and oxygen barrier qualities, making it suitable as active packaging to extend the shelf life of food products (Mellinas et al., 2020a). Additionally, the total phenolic content and total catechin content of cocoa pod husk were extracted and analyzed using the microwave-assisted extraction method, employing 100% ethanol, a temperature of 70 °C, and 3:100 g/mL sample to solvent ratio, resulting in 8.65 mg GAE/mL and 51.03 μg/mL, respectively (Rosyidi et al., 2019). In a recent study, MAE conditions were optimized for the effects of pH, time, temperature, and the solid-liquid ratio of CBS. The optimal conditions yielded a 34.2% yield, 115.2 mg GlcA/g of uronic acid, 35.9 ± 0.9 mg GAE/g DW total phenolic, and 35.5 ± 0.4 mg TE/g DW antioxidant activity, with values of 5 min, pH 12, 97 °C, and a solid-liquid ratio of 0.04 g/mL (Mellinas et al., 2020b). Antioxidant activity increased from 11.75% to 55.44% when MAE was combined with DES, with extraction conditions optimized for temperature, time, and water content in DES (Pavlović et al., 2020). A summary of the technologies is presented in Table 2.

The particle size has a significant impact on MAE. Smaller particles expose a larger surface area to the solvent, facilitating the diffusion of solutes from the matrix. The choice of solvent depends on its ability to absorb microwaves. Solvents with high dielectric con-

Table 2
Advanced technologies for the extraction of lignocellulosic-based cocoa residue extractives.

Cocoa residue	Technology	Conditions	Extractives	Outcomes	Reference
CPH	Supercritical fluid extraction	60 °C, 299 bar and 13.7% of Ethanol	Phenolic compound	0.52% yield	Valadez-Carmona et al. (2018)
CPH	Supercritical fluid extraction	121 °C, 103.4 bar and 30 min	Pectin	10.9%	Muñoz-Almagro et al. (2019)
CPH	Thermo physical	2% citric acid with hydrothermal, 120 °C and 10 min	Pectin	19.3%	Valladares-Diestra et al. (2022)
CPH	Optimized solvent extraction		Pectin	4.2%	Priyangini et al. (2018)
	Ultrasound-assisted extraction	6.0% feedstock, 40 μL g^{-1} of enzyme, 18.54 h	Pectin, phenolic compound	10.20 g/100 g, 988.09 ± 75.47 (mg GAE/100 g)	Hennessey-Ramos et al. (2021)
CPH	Supercritical CO_2 extraction	60 °C, 299 bar and 13.7% ethanol	Phenolic compound	12.97 mg GAE/g	Valadez-Carmona et al. (2018)
CPH	Enzymatic inactivation by thermal treatments	Boiling water for 10 min, freeze (−23 C for 24 h)	Phenolic compound	16.6 mg GAE/g	Delgado-Ospina et al. (2021)
CPH	Optimized solvent extraction	Ethanol (70%), 90 min, 80 °C,	Alkaloid	6.79 mg/100 g	Nguyen and Nguyen (2017)
CPH	Microwave-assisted extraction	10 min	Phenolic compound	8.65 mg GAE/mL	Rosyidi et al. (2019)
CBS	Heat-assisted extraction	100 °C, 90 min, 0% citric acid, and 0.02 g cocoa shell mL−1 water	Phenolic compound	7.99 mg/g	Rebollo-Hernanz et al. (2021)
CBS	Supercritical CO_2 Extraction with pressurized liquid extraction	20 MPa/40 °C, 10 MPa and 70 °C	Phenolic compound	51 mg GAE/g	Mazzutti et al. (2018)
CBS	Ultrasound-assisted extraction	Fractions with the 30:49:21 Hex/EtOH/H_2O, 15 min,	Phenolic compound	197.4 mg GAE/g	Grillo et al. (2019)
CBS	Subcritical water extraction	220 °C, 75 min, 20 mL/g substrate	Phenolic compound	130.33 mg GAE/g	Jokić et al. (2018)
CBS	Microwave assisted extraction combined with deep eutectic solvents	11.41 min, 35.12 °C, 49.39% water	Alkaloid	5.004 mg/g	Pavlović et al. (2020)
CBS	Ultrasound-assisted extraction	Ethanol (80%), 55 °C, for 45 min	Flavonoid	7.47 mg RE/g dw	Md Yusof et al. (2019)
CBS	Microwave assisted extraction	10 min and microwave power (450 W)	Flavonoid	1.435 mM	Rahmawati et al. (2021)

stants and dielectric losses, such as water, methanol, and ethanol, heat up rapidly. The solvent's affinity for the solute also affects compound recovery, and using combinations of solvents can enhance selectivity. While increasing temperature can boost extraction yields, caution is needed to prevent excessive heating that might lead to thermal degradation of delicate compounds (Chemat and Cravotto, 2012).

6. Conclusions and future prospects

The increasing awareness of environmental concerns underscores the importance of embracing circular economy principles and unlocking the value of underutilized by-products. Agricultural and food by-products are often viewed as significant challenges for the bioindustry due to their disposal costs and negative environmental impacts. In the Republic of Ghana, cocoa processing residue (CPR) has seen limited utilization, primarily for emerging bioenergy applications that are still in their infancy. The waste generated during cocoa production, including cocoa pod husk and cocoa bean shells, accounts for approximately 80% of the fruit and is typically discarded as residual biomass. However, these seemingly waste materials, which pollute the environment, harbor bioactive molecules that can be extracted using both traditional and cutting-edge extraction technologies. The resulting cocoa residue extractives (CREs) have demonstrated considerable potential for enhancing human and animal health and promoting growth and development.

In this review, we have delved into the valorization of Ghanaian agricultural processing residues, specifically cocoa residues, into CREs for use as functional foods and animal feed additives. While conventional technologies have been employed for extracting valuable compounds from cocoa processing residues, some of these methods often require substantial time, energy, and solvents. Thus, there is a pressing need for innovative technologies that can efficiently extract these compounds without causing environmental harm. Among these advanced techniques are supercritical fluid extraction, pressurized liquid extraction, subcritical water extraction, microwave-assisted extraction, ultrasound-assisted extraction, and optimized solvent extraction. It is evident that the chemical composition of CREs is influenced by factors such as cocoa cultivar, geographical origin, and extraction methodology. While agricultural processing residues have historically found use in various applications, including animal additives and functional foods, their efficacy can be limited by poor nutritional value stemming from imbalanced protein content, particularly in animal feeds.

In the context of the biorefinery concept, the discussed technologies hold promise as initial steps in overcoming biomass resistance. Successfully implementing these methods will yield valuable extractives such as phenolics and pectin, which can be incorporated into animal feed additives and functional foods without adverse effects, thereby enhancing health and functionality.

The growing research interest in CPR valorization foreshadows a bright future for the bioeconomy, particularly in extraction technologies for these valuable compounds. Therefore, the abundant cocoa processing residue in Ghana should be targeted for commercial utilization in the production of functional foods and feed additives. To facilitate the manufacture of bioactive compounds from CPR, a combination of extraction techniques or a hybrid approach involving multiple technologies could expedite the extraction process. While many extraction techniques are relatively straightforward to perform, their widespread adoption by industries remains limited. This presents an opportunity for future development, as proper implementation can contribute to addressing environmental waste concerns. With a focus on zero waste or full utilization of cocoa residues for food and feed purposes, the extraction processes employed should not only mitigate the environmental release of hazardous chemicals but also lead to more cost-effective, labor-efficient, and productive product outcomes. However, further research is essential to fully comprehend the applicability of these greener extraction technologies in the cocoa industry. Moreover, it is crucial to transition from laboratory-scale applications to commercial-scale production to unlock the full potential of these technologies across various industries.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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