Cocoa Pod Husks as Potential Sources of Renewable High-Value-Added Products: A Review of Current Valorizations and Future Prospects

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Cocoa is among the most cultivated and important tropical crops in the world, and it is economically viable in the agro-pastoral systems of tropical Africa. Further, the amount of cocoa residue is steadily increasing due to the strong worldwide demand for chocolate products. This review of cocoa residue found that an average of 18 publications per year were published in the last 10 years. The most common type of publication on cocoa pod husks (CPH) was newspaper articles, which comprised 50% of the publications. This review examines the use of CPH in sustainable development, agrochemical materials, and agro-materials through their potential valorizations into high value-added products. Indeed, CPH is an abundant, accessible, and renewable resource of bioproducts, dietary fibers, nutraceuticals, functional foods, pectin, antioxidant compounds, theobromine, and minerals. Potential food applications of CPH include the production of flavor compounds, gums, texturing agents, and others. The production of biomaterials for food and non-food use, biofuels, and organic acids, such as lactic acid (the polymerization of which produces the PLA used in bioplastic production), are several potential areas for the biotechnological development of CPH and its fractions.

Keywords: Cocoa pod husks; Pretreatment; Conversion; High value-added products; Biocomposite

INTRODUCTION

Environmental pollution is among the most serious problems facing humanity today (Cho et al. 2020). A fundamental problem linked to pollution is the elimination of the large quantities of organic waste that are continuously produced (Cho et al. 2020). Solving the problem of large quantities of organic waste or secondary raw materials is a necessity (Balentić et al. 2018). Consequently, specific applications are needed to use these raw materials in the most efficient way possible in the production process. The concepts of “wealth-generating waste” and “recyclable materials” are important for building a sustainable and healthy society through the efficient use of these waste resources (Daud et al. 2013). As global production of Theobroma cocoa beans (Malvaceae) has decreased, the
governments of several tropical countries (Vriesmann et al. 2011a) have strongly expressed their support for the expansion of the cocoa industry by encouraging cocoa farmers to plant additional trees. This initiative has led to an increase of more than 50% in the production of cocoa beans (Uy et al. 2019). However, the increase in production has also favored the proliferation of undesirable residues, such as cocoa pod husks, on cocoa farms and plantations. In addition, as petroleum resources continue to decrease and the environmental concerns caused by petroleum products grow, research (Vásquez et al. 2019) has focused on the capacity of cocoa pod husks to produce biofuels and other biopolymers. However, cocoa pod husk (CPH) remains under-exploited, as it is a renewable resource rich in dietary fiber, lignin, and bioactive antioxidants, such as polyphenols (Lu et al. 2018).

The recovery of lignocellulosic fractions and bioactive compounds from cocoa pod husks can lead to the development of profitable basic products. Consequently, these cocoa pod husks can generate income for farmers and promote economic development (Lu et al. 2018).

This review article first focuses on analyzing bibliometric data to determine the trends, research priorities, current topics, and important research areas of cocoa pod husks. Then, the stages in the development of CPH are presented to summarize the mineral and biochemical composition of CPH. The main pretreatment strategies and the different ways of converting cocoa pod husks are also reviewed. Finally, the current state of CPH valorization and future perspectives on CPH valorization are discussed.

**Dynamics of the Production of Beans and Cocoa Pod Husks**

Approximately 50 countries produce cocoa, and the Ivory Coast is the largest producer. Figure 1 (International Cocoa Organization (ICCO)) shows the evolution of cocoa production in west Africa. The African continent alone supplies approximately 74% of cocoa produced globally. Among various countries of Africa, Ivory Coast is the biggest producer of cocoa (42%), followed by Ghana (20%), Nigeria (6%), and Cameroon (5%). Figure 1 provides the statistics of cocoa production in cocoa-producing countries. However, Ivory Coast suffers many consequences due to its immense production.

![Fig. 1. Quantity of cocoa beans per y in the main producing countries of West Africa (International Cocoa Organization (ICCO) 2019)](image-url)
In fact, 10 tonnes of wet pods are generated for each tonne of dry cocoa beans (Campos-Vega et al. 2018). Therefore, a large area is necessary for disposal, and the wet pods represent a major challenge for waste management. Currently, in Ghana and Ivory Coast, approximately 1% of this biomass is used to make soap (Antwi et al. 2019).

Figure 2 shows the amounts of beans and cocoa pods husks produced in the main cocoa-bean producing countries during the 2018/2019 campaign. As Ivory Coast produced approximately 6,500,000 tonnes of CPH, it now must manage this waste, which is generally stored in fields, and its decomposition attracts flies and other insects harmful to cocoa. Furthermore, the decomposition of these residues is a potential source of pathogenic microorganisms, such as black pod disease (Mansur et al. 2014), which is caused by Phytophthora palmivora and P. megakarya fungi. The disease causes an estimated annual yield loss of 20% to 30% worldwide, whereas individual farms may experience an annual yield loss of 30% to 90% (Lu et al. 2018).

Cocoa pod husk is a lignocellulosic biomass that is rich in minerals (in particular, potassium), fibers (especially lignin, cellulose, hemicellulose, and pectin), and antioxidants (phenolic acids, etc.) (Kouakou et al. 2018). However, it is still largely under-exploited. Appropriate use of this lignocellulosic material could offer economic benefits and reduce its environmental impact (Adjin-Tetteh et al. 2018).

**Description of CPH**

The CPH is the outer part of the fruit (exocarp), which has an oval, rough, and relatively thick appearance (Fig. 3 and Fig. 4). Cocoa pod husk comes in different colors depending on the variety, and its roughness protects it against the elements, plagues, and damage that could be caused by impact (Vásquez et al. 2019). It is obtained after husking and removing the beans, and it represents 70% to 80% of the dry weight of the whole fruit. This natural, layered material comprises three distinct layers (Fig. 4), which are the epicarp, the mesocarp, and the endocarp, which constitute the outer, middle, and inner pericarp, respectively (Campos-Vega et al. 2018). The endocarp is the innermost part and occurs as a soft, whitish tissue that protects the cocoa beans in a well-lubricated inner chamber (Campos-Vega et al. 2018). The mesocarp has a hard composite structure capable of holding the cocoa beans in place even in severe conditions.
The relatively soft outermost layer is the yellow (or purplish red upon maturity) cover, and it is this part that is exposed to the sun. When it turns black, this indicates that the fruit is rotting and dry (Babatope 2005).

**Bibliometric Study on the Cocoa Pod Husk**

Bibliometric analysis is a useful tool for analyzing publications in several areas of research (Maassen 2016). It is a quantitative approach of studying the metadata of scientific publications (Maassen 2016). It is a useful method for detecting research trends in a given area (Maassen 2016). It concerns three elements of scientific activity, which are its inputs, its outputs, and its impacts. It allows an assessment of scientific activity and the place of actors in relation to a given theme. This new scientific approach has been increasingly used and considered before undertaking studies on a given theme.

In this study, several word combinations were searched to identify themes from 2005 to 2019, which included “cocoa pods,” “cocoa pod husks,” and “cocoa residues.” With this method, it was possible to overcome the weaknesses of individual keyword analysis and identify relevant points and current search trends in different countries (Maassen 2016) for a given theme. This bibliometry on CHP was produced on 05/07/2019 with the internet platform SCIFINDER that lists all forms of publication dealing with the topic to be addressed. This database allowed assessment of the scientific interest in the subject of CPH. A total of 268 publications met the selection criteria. The selected publications were then analyzed according to the characteristics of the articles (type of document, country of origin, and citations), publication models (main journals and journal category), the importance of research (number of publications per year), the number of publications per author, and the areas of valuation (Maassen 2016).

**Number of Publications per Year**

Interest in CPH began in 1905 with a single publication. However, an increased interest in CPH began in 2003 and has continued to grow (Fig. 5). Over the past 10 y, an average of 18 publications per year have been produced on CPH. Over the past 5 y, an average of 24.2 publications per year were produced. This growing interest in cocoa pod husks is probably due to the increasing amount of this residue in the fields, which is becoming an environmental problem. Further, the enormous losses caused to cocoa farmers due to cocoa diseases, such as brown and black pod rot, have likely driven this interest.
In addition, the demand for chocolate-based products has led cocoa-producing countries to increase their production, which has resulted in increased waste products, such as CPH, which constitutes approximately 76% of the weight of whole pods (Chun and Husseinsyah 2016). Several studies have shown that 10 tonnes of CPH are produced as waste for every tonne of cocoa beans (Mansur et al. 2014; Sanyang et al. 2017). Therefore, the theme related to this material was topical and relevant to the interest of researchers.

**Work Density by Publishing Type**

The most common type of publication on CPH was journal articles, which comprised 54% of the publications (Fig. 6). Therefore, CPH has great potential and requires further exploration based on the number of patents filed (12), which represented 15% of publications. A single bibliographic review article was produced on CPH, which looked at the biotechnological recovery of all residual biomass from the cocoa industry (Vásquez et al. 2019) and justified the present study. Figure 6 illustrates the distribution of publication types.
Areas of Valorization for Cocoa Pod Husks

The valorization of CPH has aroused interest in several fields, including radial electrochemical agrochemical bioregulators, thermal energy technology, soil fertilization, plant nutrition, food and animal chemistry, plastic treatment, and waste treatment and disposal (Fig. 7).

The large numbers of publications in the fields of soil fertilization, plant nutrition, food and feed chemistry, plastics manufacturing and processing, and waste treatment and disposal were justified by the rich mineral and fibre composition of this biomass. Several of these areas (soil fertilization, plant nutrition, and food and feed chemistry) have already been widely exploited and others (plastic manufacturing and processing) are still under study and deserve special attention.

The recovery of CPH begins with the harvest of the material, followed by drying. Indeed, the moisture content of the fresh pod is approximately 90% (Vriesmann et al. 2011a).

Therefore, quick drying is essential to avoid deterioration. Finally, the CPH residues are ground. A complete characterization (physico-chemical, biochemical, and thermal) and an appropriate delignification process are necessary to better explore the lignocellulosic components of CPH to identify the appropriate pathway for the residue.

![Fig. 7. Publications of the Index of Scientific quotes based on the areas of CPH valuation](image)

Cocoa Pod Husks Valorization Process

*Chemical, Physico-chemical, and Biochemical Characterization Process of Cocoa Pod Husks*

Figure 8 schematically illustrates the valorization process of CPH in value-added products. Several works have focused on the physico-chemical (Vásquez et al. 2019), thermochemical (Adjin-Tetteh et al. 2018), and biochemical (Giwa et al. 2020), characterization of CPH to identify the appropriate conversion pathways. Cocoa pod husks were found to be rich in raw energy, cellulose, hemicellulose, potassium, and many other minerals useful for soil improvement.
Table 1 summarizes the proximal composition of CPH obtained in several regions of the world after its characterization.

Table 1. Composition of Cocoa Pod Husks in Previous Studies

<table>
<thead>
<tr>
<th>Volatile Matter (%)</th>
<th>Ash (%)</th>
<th>Moisture (%)</th>
<th>( C_{\text{fixe}} ) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.73</td>
<td>16.24</td>
<td>11.07</td>
<td>10.96</td>
<td>Adjin-Tetteh et al. (2018)</td>
</tr>
<tr>
<td>68.47</td>
<td>10.81</td>
<td>10.29</td>
<td>10.43</td>
<td>Titiloye et al. (2013)</td>
</tr>
<tr>
<td>70.40</td>
<td>10.90</td>
<td>14.00</td>
<td>16.70</td>
<td>Kilama et al. (2019)</td>
</tr>
<tr>
<td>49.90</td>
<td>13.50</td>
<td>16.10</td>
<td>20.50</td>
<td>Syamsiro et al. (2012)</td>
</tr>
<tr>
<td>64.19</td>
<td>15.31</td>
<td>10.10</td>
<td>10.40</td>
<td>Asiedu et al. (2019)</td>
</tr>
<tr>
<td>58.75</td>
<td>06.99</td>
<td>14.43</td>
<td>19.83</td>
<td>Chan and Choo (2013)</td>
</tr>
<tr>
<td>92.60</td>
<td>07.39</td>
<td>-</td>
<td>-</td>
<td>Antwi et al. (2019)</td>
</tr>
<tr>
<td>-</td>
<td>07.40</td>
<td>11.04</td>
<td>-</td>
<td>Nazir et al. (2016)</td>
</tr>
</tbody>
</table>

Note: "-" = Not defined

Knowing of the moisture content of a biomass is crucial for the choice of the energy conversion method available for processing this biomass. According to Tsai et al. (2017), moisture content has a direct impact on the calorific value of a biofuel. The values obtained during various studies were all over 10%. Thus, the residue would be better suited for biochemical conversion than thermal conversion (Adjin-Tetteh et al. 2018). Further, moisture in the raw material can act as a binder (Adjin-Tetteh et al. 2018) and lubricant by improving the gelatinization of starch and facilitating the formation of van der Waals forces (Adjin-Tetteh et al. 2018) and the possible diffusion of water-soluble substances in the matrix of the raw material (Titiloye et al. 2013). The ash contents of the different samples were quite high, which reflected a higher level of inorganic substances that can act as catalysts for the whole thermal conversion process (Titiloye et al. 2013). Tables 2 and 3 present the lignocellulosic and mineralogical composition of CPH in different studies around the world.
An analysis of Table 1, Table 2, and Table 3 illustrates the rich lignocellulosic and chemical composition of CPH, which could lead to its use as a potential substrate for anaerobic digestion (Rastegari et al. 2019) to produce bioactive compounds.

These bioactive compounds have many applications, which include renewable energy, biopolymers, formulating plasticized composites, and acting as a fertilizer element (Djeke et al. 2011; Kouakou et al. 2018).

The disparities observed between the physico-chemical and biochemical compositions of the CPH could have been due to geographic factors, the location of the materials collected, the different methods of analysis, the variety of biomass, the differences in the solvents used, the different collection periods (Sandesh et al. 2020), and the different climatic and storage conditions (Titiloye et al. 2013), among other factors.

### Lignocellulosic Biomass Pretreatment

Lignocellulosic biomass is a renewable material that can be converted into fermentable sugars and then converted into ethanol (Rezania et al. 2017). However, this convention is hampered by the recalcitrant nature of this plant biomass (Woiciechowski et al. 2020) due to the presence of lignin and the consequent difficulty of obtaining complete...
enzymatic hydrolysis has led to the implementation of different pretreatment strategies (Beukes and Pletschke 2010). Pretreatment aims to modify the properties of raw materials, to remove or dissolve lignin and hemicellulose, and to reduce the crystallinity of cellulose (Thamsee et al. 2019). It is performed to increase the surface accessible to hydrolytic enzymes (Wang et al. 2015). The pretreatment process further alters the microstructure, macrostructure, and chemical composition of lignocellulose to improve the efficiency of the hydrolysis of sugars (Chandra et al. 2015) to make them accessible to microbial degradation (An et al. 2015). The pretreatment process improves the efficiency of and stimulates sugar hydrolysis (Chandra et al. 2015). As the separation of carbohydrates from lignocellulose is a key step in the process, the choice of pretreatment strategy is crucial to facilitate the transformation of lignocellulosic biomass into products with high added value (Arevalo-Gallegos et al. 2017). The four pretreatment strategies are physical, chemical, physico-chemical, and biological.

In general, chemical and physicochemical pretreatments give good results. However, excessive use of chemicals could lead to serious environmental problems (Chen et al. 2017). The biological method consumes less energy and is less polluting than other methods, but it is expensive and time consuming, and enzyme activity in the decomposition of lignocellulose is low (Chen et al. 2017).

The following section discusses the pretreatment technologies commonly used in the recovery of lignocellulosic biomass in general and those applied to valorize CPH in particular.

**Pretreatment with acid solution**

Acid pretreatment is a highly effective chemical technique used to break down the lignocellulosic matrix by cleavage of the glucosidic bonds (Woiciechowski et al. 2020). Acid pretreatment mainly solubilizes hemicelluloses and part of the lignin (Woiciechowski et al. 2020). Inorganic acids ((sulfuric acid (H₂SO₄), nitric acid (HNO₃), and phosphoric acid (H₃PO₄)) and organic ones (formic acetic and propionic acid) (Aslanzadeh et al. 2014) are generally used. However, most concentrated acids are highly toxic and corrosive, so the acid must be recovered, and the equipment used must be resistant to acid corrosion (Manzoor et al. 2013; Laurens et al. 2015; Chen et al. 2017). This results in high operational and maintenance costs, and the process destroys hemicellulosic sugars and transforms them into toxic compounds, such as acetic acid, furfural, and 5-hydroxymethylfurfural (5-HMF), which inhibits microbial growth (Woiciechowski et al. 2020). However, the conversion rate to sugar is higher than pretreatments that use hydrochloric acid, phosphoric acid, or nitric acid (Mosier et al. 2005; Sandesh et al. 2020). The optimization of biogas production by applying acid (H₂SO₄) pretreatments to CPH has been achieved (Ward-Doria et al. 2016). Likewise, cocoa pod husks have been used to release reducing sugars using autoclave-assisted hydrochloric acid hydrolysis to obtain reducing sugars (Shet et al. 2019). The concentration of hydrochloric acid (HCl) and the duration of the autoclave were used to optimize the hydrolysis process. Under optimized conditions 21.11 g/L of reducing sugar were released (Shet et al. 2019). Otherwise, a study by Dahunsi et al. (2019a) showed that cocoa pods husks could produce up to 71% biogas via the mono-fermentation of CPH pretreated with sulfuric acid (H₂SO₄) and alkaline hydrogen peroxide (H₂O₂). Additionally, xylitol has been produced from xylose from cocoa pod husks using sulfuric acid pretreatment, optimized by the response surface methodology (Santana et al. 2018). Xylitol was obtained at concentrations of 11.34 g.L⁻¹, corresponding to a yield (Y p/s) of 0.52 g.g⁻¹ with a fermentation efficiency of 56.6 %.
Alkaline pretreatment

Alkaline pretreatment is an economical process that is carried out by soaking a ground biomass in a basic solution at relatively low temperatures and pressures (Beukes and Pletschke 2010; Umagiliyage et al. 2015). It is an interesting technology, in which the formation of few fermentation inhibitors occurs (Beukes and Pletschke 2010). This pretreatment increases the surface area exposed to enzymatic hydrolysis and the accessibility of cellulose by removing the acetyl and uronic acid substituents associated with hemicelluloses (Umagiliyage et al. 2015). The alkaline solutions of sodium hydroxide \( (\text{NaOH}) \), potassium hydroxide \( (\text{KOH}) \), calcium hydroxide \( (\text{Ca(OH)}_2) \), and ammonium hydroxide \( (\text{NH}_4\text{OH}) \) are suitable for the pretreatment of lignocellulose (Mirmohamadsadeghi et al. 2016; Saratale et al. 2016). For example, \( \text{Ca(OH)}_2 \) can remove the acetyl group from hemicellulose to increase the digestibility of cellulose and reduce the steric hindrance of enzymes (Chen et al. 2017). Then, \( \text{Ca(OH)}_2 \) can increase the crystallinity index by eliminating amorphous substances (Chen et al. 2017). The optimal pretreatment conditions \( (\text{Ca(OH)}_2 \text{ and NaOH}) \) for sweet sorghum bagasse have been determined (Umagiliyage et al. 2015). Expected yields of 85.6% biomass to biofuel conversion and 35.5% lignin removal can be achieved.

Several upgrading processes that employ CPH as recoverable biomass have integrated alkaline pretreatment and led to the production of biogas from the anaerobic co-digestion of CPH and poultry manure after pretreatment with sulfuric acid and hydrogen peroxide (Dahunsi et al. 2019b). The use of alkaline hydrogen peroxide resulted in solubilization of up to 81% of the lignin from the CPH.

The optimization of biogas production by applying acid \( (\text{H}_2\text{SO}_4) \) and alkaline \( (\text{NaOH}) \) pretreatments to CPH has been achieved (Ward-Doria et al. 2016), and the alkaline pretreatment gave the best result of up to 43.8% delignification. The effect of reagent type \( (\text{NaOH}, \text{alkaline peroxide (H}_2\text{O}_2), \text{and sulfuric acid (H}_2\text{SO}_4)) \) was also evaluated on the delignification of CPH using response surface methodology (Nazir et al. 2016). The alkaline pretreatment still had the best results independent of reagent type.

Steam-explosion pretreatment

The steam-explosion process is among the most widely used physico-chemical pretreatment processes. This process occurs when water vapor is subjected to a high temperature for a few seconds to several minutes and then rapidly expelled from the reactor (Chen et al. 2017). The flow of vapor and liquid material cools rapidly due to the reduced pressure (Chen and Liu 2015). The main mechanism of the process is the high-pressure vapor in the fibers that causes the mechanical breakdown of the fiber. It is an inexpensive option for the pretreatment of agricultural residues, and it has a considerably reduced environmental impact (López-Linares et al. 2015). It has a lower environmental impact, lower requirements in terms of reaction conditions and cost, and fewer risks linked to chemical reagents and complete recovery of sugar than other methods. Further, this pretreatment leads to the formation of degradation products of sugars, such as acetic acid formed by the self-hydrolysis of acetyl groups at elevated temperatures or many phenolic compounds (Chen et al. 2017). This could justify why no valuation study of CPH has mentioned the application of steam-explosion pretreatment.

Explosion of ammonia-pretreated fibers

The explosion-of-ammonia-fiber (AFEX) pretreatment is a combination of steam-explosion pretreatment and alkaline pretreatment in anhydrous ammonia at high
temperature (90 °C to 100 °C) and high pressure (1 MPa to 5.2 MPa) (Chen et al. 2017). After a rapid release of pressure, the ammonia is vaporized, which leads to a sudden change in temperature. As a result, the structure of the biomass is severely damaged, thus exposing the cellulose surface to increased enzymatic hydrolysis (Chen et al. 2017). The main advantage of AFEX pretreatment is the absence of substances that inhibit microbial fermentation. This process also produces a residue of ammonium salt that can serve as a nutrient for microbial fermentation (Chen et al. 2017). Thus, the resulting hydrolyzate after pretreatment can be directly used without further specific treatment. Under these conditions, AFEX is therefore suitable for the pretreatment of agricultural waste and herbaceous plants that contain a high content of cellulose (Wyman et al. 2005). However, the ammonia used must be recycled due to its high cost and volatility (Taherzadeh and Karimi 2008). However, to our knowledge, no study in the literature has yet explored the use of pre-blast pretreatment of cocoa pods husks fibers with ammonia.

**CO₂-explosion pretreatment**

The CO₂-explosion pretreatment combines steam explosion and the addition of CO₂ to form carbonic acid, the presence of which greatly improves the efficiency of hemicellulosic hydrolysis (Chen et al. 2017). This process has enormous advantages, including the absence of inhibitors during subsequent fermentation; further, it is non-toxic, non-flammable, and cost-effective (Chen et al. 2017). In addition, the surface of the resulting substrate is easily accessible to subsequent enzymatic attack. A Box-Behnken design was applied to supercritical CO₂ extraction to develop an appropriate ecological process to obtain a soluble fraction rich in phenolic compounds from CPH (Alemawor et al. 2009).

**Microwave pretreatment**

Microwave technology makes cellulose more responsive and improves the accessibility and adaptability of the lignocellulosic feedstock to enzymes (Chen et al. 2017). It is an energy efficient technology that is applicable in chemical reactions (Chen et al. 2017). Several studies have focused on microwave pretreatment of fibrous raw materials (Manzoor et al. 2013; Lo et al. 2015). Microwave pretreatment allows a subsequent increase in enzyme activity (Chen et al. 2017), but it requires a high investment. Microwave-assisted pretreatment optimization of CPH using sulfuric acid (H₂SO₄) was also performed by comparing the efficiency of the response surface methodology to that of the network of artificial neurons to produce bioethanol (Shet et al. 2018b), and a maximum of 9.10 g/L of sugars was released.

**Biological method**

The degradation of lignin is facilitated by biological pretreatment, as it can generate enzymes that break down lignin during the process. Biological pretreatment usually uses wood-rotting fungi (Chen et al. 2017). Different lignocellulosic biomasses have been biologically pretreated using fungi, such as white rot, Ceriporiopsis subvermispora, Pleurotus ostreatus, Ceriporia lacerata, Cyathus stercoleus, Pycnoporus cinnbarinus, and Phanerochaete chrysosporium, on different lignocellulosic biomasses (Chen et al. 2017). Thus, the biological pretreatment of CPH has been carried out via the use of fungal species chrysosporium of the genus Phanerochaete (Laconi and Jayanegara 2015), and this species has shown its effectiveness in improving the nutritional value of CPH. Similarly, Pleurotus ostreatus (Alemawor et al. 2009) reduced cellulose, hemicellulose, and lignin.
content by 6 wt%, 3 wt%, and 6 wt%, respectively, with manganese ion supplementation (Mn^{2+}). These results show that the *Pleurotus* species has promising cellulytic and hemicellulytic activity on CPH (Alemawor et al. 2009). Table 4 summarizes past work on the pretreatment of CPH.

### Table 4. Main Pretreatment Strategies Applied to Cocoa Pod Husk in Previous Studies

<table>
<thead>
<tr>
<th>Pretreatment Method</th>
<th>Intended Use</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical (Na_2CO_3)</td>
<td>Optimization (reducing sugars)</td>
<td>0.94 g/L</td>
<td>Shet et al. (2016)</td>
</tr>
<tr>
<td>Chemical (H_2SO_4, NaOH)</td>
<td>Optimization (delignification)</td>
<td>74.48%</td>
<td>Nazir et al. (2016)</td>
</tr>
<tr>
<td>Chemical (H_2SO_4, NaOH)</td>
<td>Biomethane production</td>
<td>0.247 m^3 CH_4/kg VS</td>
<td>Ward-Doria et al. (2016)</td>
</tr>
<tr>
<td>Chemical (NaOH), sonification</td>
<td>Microcrystalline cellulose</td>
<td>286 nm</td>
<td>Jimat et al. (2016)</td>
</tr>
<tr>
<td>Chemical (H_2SO_4)</td>
<td>Bioethanol production</td>
<td>2 g/L</td>
<td>Shet et al. (2018a)</td>
</tr>
<tr>
<td>Chemical (H_2SO_4, H_2O_2)</td>
<td>Biogas production</td>
<td>243.3 ± 4.1 l(N)/kg VS</td>
<td>Dahunsi et al. (2019a)</td>
</tr>
<tr>
<td>Mechanical (grinding)</td>
<td>Methane production</td>
<td>22%</td>
<td>Dahunsi (2019)</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Biogas production</td>
<td>526.38 l(N)/kg VS</td>
<td>Antwi et al. (2019)</td>
</tr>
<tr>
<td>Biological (Phanerochaete chrysosporium)</td>
<td>Feed production for ruminants</td>
<td>Increased digestibility (28.5%)</td>
<td>Laconi and Jayanegara (2015)</td>
</tr>
<tr>
<td>Biological (Pleurotus ostreatus)</td>
<td>Improving nutritional status</td>
<td>17% Reduction (crude fiber and lignin)</td>
<td>Alemawor et al. (2009)</td>
</tr>
<tr>
<td>CO_2 explosion</td>
<td>Phenolic compounds</td>
<td>12.97 mg GAE/g</td>
<td>Valadez-Carmona et al. (2018)</td>
</tr>
</tbody>
</table>

Note: GAE = Gallic acid equivalent; Cumulative gas potential = (l(N)/kg VS)

### Cocoa Pod Husk Conversion Processes

Several conversion routes (physical, biochemical, and thermochemical) of biomass into products with high added value, such as biofuels and biochemicals, have been exploited (Tsai et al. 2017; Adjin-Tetteh et al. 2018). Volatile materials are suitable for combustion, gasification, and pyrolysis. As the volatility of a given material increases, the ignition speed of the resulting biofuel increases (Chan and Choo 2013). However, among thermochemical conversion technologies, pyrolysis has sizable advantages over other biomass and waste processing technologies (Adjin-Tetteh et al. 2018). Pyrolysis is the decomposition of matter under the influence of water vapor (Chen et al. 2017). During the pyrolysis process, cellulose decomposes rapidly when heated to above 300 °C, which results in the release of gaseous products and the production of coke-like residues (Chen et al. 2017). In addition, other polysaccharide degradation products, such as furfural and aldehydes, can form in the presence of acid and limit microbial fermentation (Laser et al. 2002). This treatment is applied only when the biomass has a solids content less than 20%, which results in high energy consumption and relatively low productivity (Laser et al. 2002). The high-value-added bio-oil it produces can compete with and potentially replace non-renewable fossil fuels (Adjin-Tetteh et al. 2018).

Cocoa pod husk has been shown to be an excellent raw material for pyrolysis reactions (Adjin-Tetteh et al. 2018). Moreover, CPH contains a mixture of cellulose,
hemicellulose, lignin, pectin, and crude fibers in large proportions. Therefore, it is a potential source of biomass substrates for biochemical production (Adjin-Tetteh et al. 2018). Indeed, a study on the technical-economic evaluation of five lignocellulosic biomass-treatment technologies (Maleka 2016) concluded that the two most effective treatment technologies for the recovery of cocoa pod husks are hydrothermal carbonization and anaerobic fermentation (Maleka 2016). Others studies have used CPH as a renewable energy source and analyzed its characteristics in a combustion chamber (Syamsiro et al. 2012). The crushed bales were charred at 400 °C for 2 h, which resulted in a higher calorific rate (17 M × Kg⁻¹) with a high ash content.

**Table 5. Main Conversion Processes Applied to Cocoa Pod Husk**

<table>
<thead>
<tr>
<th>Conversion Pathways</th>
<th>Applications</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Hydrothermal carbonization | - Phenolic compounds and sugars  
- Bio-oil production  
- Briquette production | Hernández-Hernández et al. (2019)  
Ogunjobi and Lajide (2015)  
Ofori and Akoto (2020) |
| Direct Combustion | - Heat energy production | Syamsiro et al. (2012) |
| Gasification | - Energy production | Martínez-Ángel et al. (2015) |
| Pyrolysis | - Biochar production | Tsai et al. (2017) |
| | - Amoxicillin and ibuprofen elimination | Tovar et al. (2018) |
| | - Bio-oil | Adjin-Tetteh et al. (2018) |
| | - Biofuel | Akinola et al. (2018) |
| | - Pyrolysis oil | Mansur et al. (2014) |
| Biochemical | Anaerobic Digestion | - Bio-oil and biogas | Chan and Choo (2013) |
| | | - Energy production | Acosta et al. (2018) |
| | | - Biogas production | Antwi et al. (2019) |
| | | - Biogas production | Mancini et al. (2016) |
| | | - Biogas production | Ward-Doria et al. (2016) |
| | | - Biobutanol production | Sandesh et al. (2020) |
| | | - Biogas | Dahunsi et al. (2019b) |

Ofori-Boateng and Lee (2013) evaluated CPH as a solid base catalyst for the transesterification of soy oil into biodiesel. According to their results, CPH potash could be a viable basic catalyst, generate high yields in biodiesel production, and offer engine
performance similar to that of petroleum diesel. Table 5 summarizes the routes for converting CPH into bioproducts for valorization.

Anaerobic digestion is a natural process that occurs in an oxygen-free environment (Morales et al. 2019). During this process, biodegradable materials are converted into biogas using microorganisms (Morales et al. 2019). Several studies have shown the application of this process to convert CPH to produce biogas (Ward-Doria et al. 2016) after alkaline and acid pretreatment. In addition, the use of response surface methodology to assess the effect of hydrothermal pretreatment on biogas yield and optimal pretreatment conditions was examined by Antwi et al. (2019). In addition, Acosta et al. (2018) demonstrated the potential of cocoa waste as a renewable energy source in rural areas via anaerobic digestion.

Artificial neural networks have also been used to predict biodigester production using CPH as biomass at the University of Piura pilot plant in Peru (Morales et al. 2019). Further, the co-digestion of biomass residues to produce fuel has also been presented in recent studies, in which biogas was produced from CPH and poultry manure (Dahunsi et al. 2019b).

Cocoa pod husks have also been explored commercially and industrially through patent research and development to take advantage of their rich chemical and biochemical compositions (Vásquez et al. 2019). Previous studies have shown the potential applications of CPH (Vásquez et al. 2019). Therefore, CPH is widely used because it allows the implementation of new products with high added value by using new processes that are applicable to the food, cosmetic, pharmaceutical, and biomaterial industries (Vásquez et al. 2019). Table 6 presents a brief list of product patents related to the use of CPH.

**Table 6. Patents Related to the Use of Cocoa Pod Husk**

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Use</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>US4206245A</td>
<td>Preparation of small animal feed from CPH</td>
<td>Drevici and Drevici (1980)</td>
</tr>
<tr>
<td>WO2014042517A2</td>
<td>Biofertilizer</td>
<td>Rahman et al. (2014)</td>
</tr>
<tr>
<td>ES2539845B1</td>
<td>Procedure and synthesis of activated carbon monoliths from cocoa pod husk</td>
<td>Monge (2016)</td>
</tr>
<tr>
<td>EP3613297A1</td>
<td>Procedure for extracting pectin from CPH and application in the food, pharmaceutical and personal care industries</td>
<td>Bernaert (2020)</td>
</tr>
<tr>
<td>WO2020038906A1</td>
<td>Cacao pod husk powder, method of its preparation and its use in food, pharmaceutical and cosmetic compositions</td>
<td>Bernaert and Kopp (2020a)</td>
</tr>
<tr>
<td>WO2020038905A1</td>
<td>Process to extract components of cacao pod husks and to utilize cacao fruit soluble extract obtained thereof and its applications</td>
<td>Bernaert and Kopp (2020b)</td>
</tr>
</tbody>
</table>

In the following sections, the current state of the valorization of CPH and its potential applications are described.

**Valorization of Cocoa Pod Husk Residues into High Value-added Products**

*Soap making*
Consumers are becoming more conscious of natural and organic personal care products, as certain synthetic chemicals have been shown to be harmful to humans (Gyedu-Akoto et al. 2015). Cocoa pods husks, which make up 60% to 75% of the cocoa fruit, contain a large amount of minerals, the most abundant of which is potassium (K); thus, this residue is an inexpensive source of caustic potash (Gyedu-Akoto et al. 2015). Cocoa pod husks could therefore be used for soap making in West African countries (Gyedu-Akoto et al. 2015). Indeed, each tonne of pods would produce approximately 6 kg of potash (Gyedu-Akoto et al. 2015). After filtering and concentration, this potash could be used for the saponification of oil to produce soap (Onyegbado et al. 2002). Some soaps derived from CPH have been successfully produced in a pilot plant in Ghana and in several African countries (Gyedu-Akoto et al. 2015). Potash-based soaps from CPH have higher solubility, consistency, cleaning power, and foaming capacity than chemical KOH-based soaps (Taiwo and Osinowo 2001). Appropriate use as a raw material for making commercial soap could also generate additional income for farmers in cocoa-producing countries.

**Extracting bioactive compounds**

The increasingly strong demand for crude oil reserves and the intensification of the effect of greenhouse gases are prompting researchers to implement chemical production processes based on biomass instead of petrochemical processes (Mansur et al. 2014). Lignocellulosic biomass is an accessible, renewable, and abundant resource. It is considered the only raw material for the sustainable production of platform chemicals (Mansur et al. 2014).

Lignocellulosic biomass has been increasingly used for the production of platform chemicals (Mansur et al. 2014). Among these chemicals with high added value, pectin, which is a natural food hydrocolloid, has use in the food industry for its gelling properties (Priyangini et al. 2018). Cocoa pod husks, which are a residual and abundant biomass, are part of the crop waste that can be used for this purpose (Vriesmann et al. 2011a; Mansur et al. 2014). The composition of CPH, the main waste product of cocoa production, and some of the characteristics of their hot-water-soluble pectins have been determined (Vriesmann et al. 2011a). The authors have shown that water, a natural extraction agent, could be used to obtain pectins more effectively than a conventional extraction based on mineral acids (Vriesmann et al. 2011a) because there was no pectin formation. This study demonstrates that cocoa pod husks have a high content of dietary fiber and phenolic compounds (Vriesmann et al. 2011a), which makes them a potential source of natural compounds with exceptional nutritional and functional qualities. The variables that influence the nitric acid extraction of pectins from cocoa pods husks were examined by Vriesmann et al. (2011b). The authors used a central-composite design based on the response surface methodology with three factors, which were hydrogen potential (pH), extraction temperature (T), and extraction time (t) (Vriesmann et al. 2011b). Cocoa pod husks were used by Priyangini et al. (2018) as a source for extracting pectin by treatment with sweet acid (ascorbic acid). A comprehensive factorial design was applied by these authors to examine the independent variables that affect yield and uronic acid content (Priyangini et al. 2018). A Box-Beihken design was used to optimize the supercritical CO2 (SC-CO2) extraction to develop an appropriate ecological process aimed to obtain an extract enriched in phenolic compounds from the pods of CPH (Valadez-Carmona et al. 2018). This process made it possible to reduce the extraction times (with low yield), to improve the quality of the extracts, and to reduce the loss of volatile compounds (Valadez-Carmona et al. 2018). In addition, it avoided the degradation of bio-compounds due to heat and reduced the high solvent.
consumption (Valadez-Carmona et al. 2018). The results of the study showed that supercritical fluid extraction could be used as a technique to obtain an extract enriched in phenolic compounds from CPH (Valadez-Carmona et al. 2018). Abdul Karim et al. (2014a) performed a study to determine the total phenolic and flavonoid content of CPH compared to cocoa bean shell. They determined that CPH and cocoa bean shell have antioxidant activity with promising amounts of total phenolic and flavonoid content (Abdul Karim et al. 2014b).

Therefore, CPH are agricultural residues of great importance and can be used as basic raw materials for the synthesis of useful products in cosmetics (Abdul Karim et al. 2016). The highly active and stable crosslinked enzyme aggregate (CLEA)-lipase from the pod husks has been tested for its hydrolytic activity and successfully characterized under optimal conditions (Khanahmadi et al. 2015). The core-composite design based on response surface methodology was used to achieve the optimal conditions for pectin extraction (Vriesmann and de Oliveira Petkowicz 2017). Pectin was extracted from cocoa pod husks using aqueous nitric acid as an extractant and boiling water (Vriesmann and de Oliveira Petkowicz 2017). This study showed that pectin from the CPH could form low pH gels with reduced water activity (Vriesmann and de Oliveira Petkowicz 2017). This discovery encourages further work on the application of pectins obtained in acidic products from CPH (Vriesmann and de Oliveira Petkowicz 2017). Mansur et al. (2014) treated CPH by pyrolysis to produce a pyrolysis oil that contained several chemical compounds, such as ketones, carboxylic acids, aldehydes, furans, heterocyclic aromatics, alkylbenzenes, phenols, and benzenediols (Vriesmann and de Oliveira Petkowicz 2017). The authors obtained an improved pyrolysis oil compared to that obtained from iron oxide catalysts.

Hernández-Hernández et al. (2019) have implemented industrial technologies, such as heat treatment between 50 °C and 200 °C, which are currently used for the use and recovery of other lignocellulosic by-products. This allowed the extraction of bioactive compounds from CPH of several Mexican genotypes (Hernández-Hernández et al. 2018). Hydrothermal treatments at 150 °C or higher increased the solubilization of bioactive compounds and the antioxidant activity of the liquid phase (Hernández-Hernández et al. 2018). Treatment at 170 °C with water for 30 min was the most effective temperature for extracting both phenolics and sugars (Hernández-Hernández et al. 2018). However, 200 °C for 5 min was the best temperature for extracting theobromine and catechin (Hernández-Hernández et al. 2018).

Cocoa pod husk oil was studied by Adewole et al. (2015) to reveal the various compounds that it contained. Essential fatty acids and other organic compounds were revealed via a mass spectrophotometer coupled with gas chromatography. Further, low molecular weight carboxylic acids with a high yield were obtained by Asiedu et al. (2019) via an oxidation method catalyzed by two catalysts supported by metals that used CPH as the renewable material. The profiles of the concentration-time curves enabled the authors to model the kinetics and use the results to develop a new industrial operating technique, namely the concept of accessible region (AR) (Asiedu et al. 2019). This technique made it possible to minimize the volume of the reactors (thereby of the mass of catalyst) and to maximize the yield using a geometric optimization approach. In addition, Uy et al. (2019) found that CPH could be effectively converted to furfural. The authors also noted that a relatively high furfural yield (460.7 ppm) was achieved using an experimental Box-Behnken model to obtain the optimal conditions for the extraction of crude furfural by acid catalysis (Uy et al. 2019).
The phytochemicals of CPH have been extracted (Rachmawaty et al. 2018). Their phenolic content and the bioactivity of a CPH extract against the pathogenic fungus *Fusarium oxysporum* were tested. Antifungal tests via the agar diffusion method revealed that an extract of CPH with acetone was capable of inhibiting the growth of *Fusarium oxysporum* (pathogen of the fungus on tomatoes) (Rachmawaty et al. 2018).

**Organic composts**

Depletion of fertile soils due to lack of nutrients is a concern in tropical regions (Fidelis and Rao 2017). Composting can potentially recycle waste to conserve natural resources. The high mineral content of cocoa pod husks (CPH) or cocoa pod biomass (CPB), mainly in potassium (K), calcium (Ca), and phosphorus (P), suggests a potential to partially replace conventional fertilizers. Cocoa pod husks have been used as an organic amendment to fertilize degraded and ferrallitic soils in the Oumé cocoa zone in Ivory Coast (Djeke et al. 2011). Cocoa pod husks are a source of organic matter that can improve the chemical parameters of soil and, under certain conditions, they could be used to fertilize degraded ferrallitic soils in the Oumé region. The sorption and desorption of phosphate-P, ammoniacal nitrogen, and nitrate-N in biochars from cocoa pods husks and maize cobs were studied by Hale et al. (2013). They showed that biochar can slowly add and release essential nutrients to the soil to improve soil properties.

Another study by Munongo et al. (2017) produced compost manure and biochar from cocoa pods husks. Similarly, Ibiremo and Akanbi (2015) evaluated the effect of using a biochar enriched with different formulations of NPK fertilizers (solids and liquids) on CPH on the absorption of nutrients by kola seedlings and soil properties. Biochar and compost have been found to be alkaline in nature, which makes them suitable as a soil amendment, especially in acidic tropical soils.

The compost potential of CPH was evaluated by Doungous et al. (2018) as a soil conditioner to reduce the severity of black pod rot and consequently promote plant growth. Their results showed that the compost application increased soil pH and majority of the essential elements but decreased Al content, which is toxic to cocoa growth in acidic soils (Doungous et al. 2018). Further, Fidelis and Rao (2017) examined the possibility of producing nutrient-enriched compost from CPH that was infested with parasites with chemical amendments. When composted with superphosphate and poultry manure, CPH have produced good quality composts (Fidelis and Rao 2017). Such environmentally friendly applications could potentially reduce the use of expensive NPK fertilizers (Lu et al. 2018).

**Activated carbon precursor**

In general, 10 tonnes of CPH are yielded in the production of 1 tonne of dry beans (Pua et al. 2013). Based on its lignocellulosic content (Tsai and Huang 2018) and its abundant quantity, CPH appears to be an excellent precursor of activated carbon (AC). In fact, CPH, which is abundantly produced in certain African and Asian countries, has been tested as a precursor of AC to give it added value and avoid serious environmental problems linked to its presence in production fields.

Several works have mentioned its use. According to Cruz et al. (2012) CPH contains three chemical activating agents (K$_2$CO$_3$, KOH, and ZnCl$_2$) that allow activated carbon to be obtained from them. The results obtained revealed that CPH can be used to produce AC by chemical activation (Cruz et al. 2012). In Nigeria, CPH have been used to adsorb heavy metals (Pb and Cu) from effluent water (Odubiyi et al. 2012). The resulting
products were tested to adsorb heavy metals in effluent water at variable pH levels, dosages, and contact times. The effects of physical activation by carbon dioxide (CO$_2$) on the porosity and surface functional groups of AC prepared from the cocoa pod husks were evaluated (Ahmad et al. 2013b). In addition, the effects of acid leaching from CPH have been reported (Ahmad et al. 2013a). The study focused on porosity and surface functional groups (Ahmad et al. 2013a). Cocoa pod husks have also been used as an adsorbent to remove methylene blue (MB) from aqueous solutions (Pua et al. 2013). Pereira et al. (2014) conducted a study on the recovery of two agricultural residues. Their work aimed to prepare AC from CPH and siriguela seeds and to assess the adsorption of whey proteins (Bovine Serum Albumin (BSA)) and α-bactalbumin) on the AC produced. Moreover, AC was synthesized and then characterized at low temperature from CPH that were modified with zinc chloride (ZnCl$_2$) to eliminate amoxicillin (Tejada et al. 2017). The biomass was characterized by elemental analysis, and the AC obtained was analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), followed by Brunauer-Emmett-Teller (BET) surface analysis (S$_{BET}$) to determine its chemical composition and its morphological and structural characteristics. The proximal analysis performed on the biomass (CPH) showed a high carbon content, which makes it a suitable raw material for AC synthesis. In addition, Tsai et al. (2017) focused on the thermochemical characterization of biochar on CPH prepared at low pyrolysis temperature.

The results obtained by Tsai et al. (2017) highlighted the thermochemical characteristics of CPH to provide basic information on the thermochemical properties of CPH-based biochars. The results of the thermochemical characterization, which included analyses of the calorific value and mineral components of CPH, showed the presence of a percentage of volatile matter and a calorific value greater than 17.8 MJ/kg, but there was a high K content in the ash (4.03 wt%) (Tsai et al. 2017). Cocoa residues were also used by Tovar et al. (2018) to produce AC at low pyrolysis temperature. The authors prepared and characterized the biochar by SEM analysis (Tovar et al. 2018). They determined the chemical composition of the CPH and evaluated its use as a precursor of AC to eliminate amoxicillin and ibuprofen (Tovar et al. 2018). Another study proposed a strategy to modify the chemical properties of CPH to provide additional value (Fiorese et al. 2017). The authors stated that the grafting of aryl diazonium salt on CPH is spontaneous (Fiorese et al. 2017). They also elucidated that lignin was mainly involved in the immobilization of the phenolic layer (Fiorese et al. 2017). A study by Tsai and Huang (2018) improved the adsorption capacity of AC from ground CPH, and the authors reused the solution as a liquid fertilizer after acid leaching. The effectiveness of pyrolysis techniques for the heat treatment of CPH has been demonstrated from the thermochemical conversion and characterization of CPH (Adjin-Tetteh et al. 2018; Tsai et al. 2020). The authors used rapid pyrolysis technologies that had notable advantages over other biomass- and wastetreatment technologies.

**Raw material for catalyst synthesis**

Biodiesel production is typically achieved through the process of transesterification (Abdullah et al. 2017). Indeed, this process is one of the simplest and most beneficial for producing biodiesel (Abdullah et al. 2017). It is catalyzed by a suitable heterogeneous or homogeneous catalyst (Abdullah et al. 2017). The use of lipases as a transesterification catalyst in reactions involving enzymes can be an excellent alternative to the production of environmentally friendly biodiesel (Khanahmadi et al. 2016). In this context, the transesterification of Jatropha curcas oil was enhanced using the enzyme aggregate-
crosslinked lipase (CLEA) that was extracted from CPH (Khanahmadi et al. 2016). Further, it has been shown that it is possible to produce heterogeneous green basic catalysts from CPH to sustainably produce biodiesel (Ofori-Boateng and Lee 2013).

This type of catalyst offers several advantages, in that it is renewable, non-toxic, and reusable (Abdullah et al. 2017). In addition, it has high catalytic activity, stability in acidic and basic conditions, and high tolerance to water (Abdullah et al. 2017). Abdullah et al. (2017) examined the development of a heterogeneous base and an acid catalyst derived from biomass to produce biodiesel. A biodiesel conversion rate of up to 85% was achieved, and the results of the study showed that the biodiesel produced complied with standard SNI 7182: 2015 (2017).

After the pretreatment of cooking oil to reduce free fatty acids, a comparison of the efficiency of catalysts based on chicken eggshells and CPH was carried out for the production of biodiesel by transesterification (Andherson et al. 2018). The authors obtained 81.4% conversion of biodiesel with the chicken eggshell catalyst (CaO) and obtained approximately 85% conversion of biodiesel with the reaction that used $\text{K}_2\text{CO}_3$ obtained from the cocoa pod husks (Andherson et al. 2018). Indeed, the use of heterogeneous catalysts from biomass to produce biodiesel seems to be a promising choice, as it eliminates the tedious tasks and problems of homogenous operations (Abdullah et al. 2017). However, more research on catalysts from cocoa residues is needed to improve the catalytic performance of biodiesel production and other chemical processes (Abdullah et al. 2017).

**Producing animal feed**

Recent studies have focused on the growth of pigs (Balentić et al. 2018). Magistrelli et al. (2016) showed that the use of CPH in pig feed can have a positive effect on the balance of the intestinal microbial ecosystem (Magistrelli et al. 2016). These studies were confirmed after analyzing the addition of 20% CPH to pig feed (Ogunsipe et al. 2017). The authors showed that this rate was the optimal biological level for the use of CPH as an energy substitute for maize in pig feed (Ogunsipe et al. 2017). All of these studies demonstrate that CPH have a high potential for use as livestock feed to replace expensive conventional food ingredients.

**Bioenergies and biofuels**

The problems related to the use of fossil fuels require a transition to renewable energy sources (Chan and Choo 2013). Currently, the replacement of fossil fuels with renewable energies is increasing worldwide (Morato et al. 2019). The use of renewable resources and clean technologies remains a challenge for developing countries (Morato et al. 2019). Given the growing demand for energy, the search for other sources of energy production that are cheap, ecological, renewable, and suitable to replace fossil fuels is underway. Chan and Choo (2013) focused on the pyrolytic conversion of CPH in an electric thermal reactor of the fixed-bed type. The average calorific values of biofuel and biogas were improved compared to those obtained with other fuels, such as coal and ethanol (Chan and Choo 2013). However, Titiloye et al. (2013) showed that, during the thermochemical characterization of agricultural waste from West Africa, CPH would be better suited for biochemical conversion (Titiloye et al. 2013). This was confirmed by Mancini et al. (2016), as they showed that CPH have good potential for biogas production with accumulated methane yields. Likewise, Acosta et al. (2018) used CPH to produce methane. Their work consisted of evaluating the bioenergetic potential of CPH by anaerobic digestion (Acosta et al. 2018). Anaerobic digestion can stabilize organic matter and help retain nutrients...
(Acosta et al. 2018). Further, it can increase the value of water for land applications and reduce potential negative impacts (Acosta et al. 2018). This study showed the potential of cocoa waste as a source of renewable energy in rural areas (Acosta et al. 2018). However, the structural and mechanical properties of cocoa waste hinder enzymatic and microbial degradation and impede the optimal production of biogas. To propose a solution to this difficulty, Ward-Doria et al. (2016) compared the effectiveness of acid (H₂SO₄) and alkaline (NaOH) pretreatments on CPH to increase the potential for biogas production by anaerobic digestion. Alkaline pretreatment had the best results in terms of reducing the lignin content. Shet et al. (2018a) performed hydrolysis with hydrochloric acid (HCl) to release reducing sugars from CPH (Shet et al. 2018a). These sugars were obtained under optimal conditions and subjected to alcoholic fermentation by Pichia stipitis to produce bioethanol (Shet et al. 2018a). Further, the thermal conversion of CPH was performed by Adjin-Tetteh et al. (2018) as a potential source of agricultural waste for the production of bio-oil via a rapid pyrolysis process. Thermogravimetric analysis indicated that CPH is an excellent raw material for pyrolysis (Adjin-Tetteh et al. 2018). To find an alternative to petroleum-based fuels and overcome the sharp fluctuation in market prices, Sandesh et al. (2020) conducted a comparative study of induction heating and liquefied petroleum gas (LPG) for acid hydrolysis from cocoa pod biomass (CPB). In their study (Sandesh et al. 2020), the optimization of the sulfuric acid pretreatment was preceded by a response surface methodology that studied the effect of the amount of acid used, the load of the biomass, and the time of stay in the reactor. Finally, an anaerobic acetone-butanol-ethanol (ABE) fermentation using Clostridium acetobutilicum MTCC11274 was carried out to produce biobutanol from optimized factors. The results showed that induction heating was more efficient than LPG heating.

**Incorporating into food systems**

The food industry has begun using more ingredients from natural sources, which is required by regulations and requested by consumers (Azila et al. 2014). Cocoa pods husks, which are used as a substrate to produce functional components in the food industry, offer the possibility of developing a new chain of products with high added value. Indeed, the rich composition in dietary fibers and antioxidants of CPH has been shown (Martínez-Ángel et al. 2015). Likewise, the nutritional quality of CPH was also evaluated by Kouakou et al. (2018) for plants and for humans. Analysis of the ash showed that CPH has a rich mineralogical composition (Kouakou et al. 2018). Cocoa pods husks could, therefore, contribute to the fight against hunger and malnutrition in cocoa-producing countries and be used as fertilizer for soils in rural areas. A study by Azila et al. (2014) demonstrated the utility of CPH as functional ingredients. In addition, CPH has great potential for use in body care products (Lu et al. 2018).

**Use in paper industry**

Much of global warming, soil erosion, and global climate change may be due to the large-scale deforestation of wood resources for the paper industry (Daud et al. 2013). Non-wood materials, such as CPH, are potential sources of fiber to produce pulp and paper (Daud et al. 2013). Daud et al. (2014) showed that the skin of CPH had a high lignocellulose content with linear fibrillar arrangements. This characteristic improves the resistance properties of the pulp and paper produced (Daud et al. 2014). In addition, chemical compositions and morphological surface studies indicated that CPH pulp is comparable to that of wood; thus, CPH would be a suitable pulp for use in paper
manufacturing industries (Daud et al. 2014). The authors conducted an additional study on the paper fibers of corn stalk and CPH (Daud et al. 2014). They showed an improved abundance of lignocellulosic substances from CPH and corn stalk, which could lead to improved fiber interfacial characteristics in papermaking.

**Use as natural filler in the formulation of biocomposites**

Recently, interest in the use of agricultural by-products as a natural filler in thermoplastic materials has arisen in research laboratories and industries (Chun et al. 2014b). Indeed, the use of natural fibers as reinforcement for composite materials can improve the properties or reduce the price of the final product. Efforts have been made by mixing and developing composites with other polymers and fillers (Helanto et al. 2019). In addition, composites based on natural fibers open up new outlets for agricultural products and promote the development of agro-materials and technologies that consider environmental impacts (Boudjema 2016). Natural fibers are valuable materials that have been produced and recycled naturally on earth for millions of years. They are biodegradable and renewable.

Cocoa pod husks are abundant in the Ivory Coast, as their annual production is estimated at over 50.25 billion pods (Kouakou et al. 2018). However, this biomass has no market value. In fact, CPH is typically thrown away as waste or composted to cultivate cocoa (Chun et al. 2014b). Using CPH as a reinforcing filler in biocomposites can generate economic benefits and reduce their ecological impact. However, the bonding strengths between agricultural waste reinforcements and polymer matrices are weak. Therefore, several strategies have been implemented to remedy this. Among them, the use of coupling agents to improve the charge-matrix interface and increase the thermo-mechanical properties of these biocomposites has been employed. In this context, the effect of the modification of the charge using methacrylic acid (MAA) on polypropylene composites (PP/CPH) was studied by Chun et al. (2013). These authors observed an increase in the stabilization torque, the crystallinity, and the thermal stability of PP/CPH composites. In addition, the strength and tensile modulus of the composites were improved (Koay et al. 2013). However, a reduction in elongation at break was observed. In another study, a biocomposite was developed by Chun et al. (2014b) from polypropylene and CPH to evaluate the effect of 3-aminopropyltriethoxysilane (3-APE) as a coupling agent in the treatment of CPH (Chun et al. 2014b). The treatment of CPH reduced the number of hydroxyl groups (–OH) on the surface, thus imparting hydrophobic properties to the filler and improving the charge-matrix interaction. The authors found a decrease in tensile strength and an increase in the tensile modulus with the addition of CPH and the treatment. This study also revealed that changes in filler content and processing have no influence on the melting temperature of biocomposites (Chun et al. 2014b).

Work has also focused on the use of CPH as a filler in PP biocomposites (Chun et al. 2015), and the thermal properties and morphologies of PP/CPH biocomposites were studied (Chun et al. 2015). The effect of different contents of palm oil-based coupling agent (POCA) on the tensile and morphological properties of polypropylene composites with different contents of CPH fillers was studied by Chun et al. (2014a). The results showed that 3% content of POCA gave the best tensile properties. Though the elongation at break decreased when the agent content was less than 3%, it began to increase beyond 3%. Further, SEM analysis showed better dispersion for the treated CPH and better adhesion with the PP matrix. Imoisili et al. (2013) studied the mechanical properties of CPH in a thermosetting polymer matrix (epoxy resin). The test results showed that the tensile and...
flexural strength of the composite decreases as the volume fraction of the load decreases, and the tensile modulus of the composite increases as the volume fraction of the load increases (Imoisili 2013).

A Taguchi method approach was used to optimize the processing parameters of thermoplastic polyurethane (TPU) composites reinforced with CPH fibers (El-Shekeil et al. 2014b). The parameters were temperature, speed, processing time, and fiber content (El-Shekeil et al. 2014b). The ANOVA analysis results showed that fiber content was the most important parameter for producing TPU/CPHU (El-Shekeil et al. 2014b). After this optimization study, El-Shekeil et al. (2014a) analyzed the effect of CPH loading on the mechanical and morphological properties of TPU/CPH composites using the optimal parameters.

Battegazzore et al. (2014) proposed a simple method to separate three fractions of hazelnuts and CPH to use them as plasticizers for PLA and as load enhancers for PLA and PP. Application of the solution casting method to PLA composite films filled with CPH showed that increasing the CPH load from 0% to 10% significantly increased the tensile strength of the PLA/CPH composite (Sanyang et al. 2017). However, the further increase of CPH load to 15% decreased this resistance. Bioactive compounds extracted from CPH may have health benefits; therefore, they may be an alternative source of important components. Figure 9 summarizes the potential uses, current applications, and potential upgrades of CPH.

**Fig. 9.** Potential uses and applications of CPH

**CONCLUSIONS**

1. The chemical, physico-chemical, and biochemical characterization of the cocoa pod husks (CPH) has been carried out in numerous works. This step of the recovery process for this residue is crucial in order to understand the conversion processes. Indeed, it makes it possible to identify the most suitable recovery route and therefore the best uses of the material.
2. Several studies have reported the use of cocoa pods husks in many fields, such as animal feed, cosmetics, and biodegradable composites. However, applications related to biotechnology and the use of CPH as feed are still under study. Many studies have given added value to CPH by using them as a natural filler in polymer composite materials. Their use offers good biodegradability to the final product.

3. However, due to the recalcitance of lignocellulose, optimal CPH pretreatment processes should be implemented to separate the main components at relatively low temperatures and (if possible) without the use of chemical agents. These processes are necessary to prevent the main components, namely lignocellulose components, pectin, and phenolic compounds, from losing their functionality. These components can have applications in food systems by offering improved nutritional value and can provide high yields of energy sources or chemicals for industry. Further, the present literature review on CPH residues has highlighted applications and products with a high commercial value.

4. However, no studies have been conducted using CPH as a natural filler in polylactic acid biopolymers to develop composite materials that have better thermomechanical and morphological properties, are green and fully biodegradable, and can replace conventional plastics from fossil resources. Consequently, the development of processes that are easy to implement, less expensive, sustainable, and green, is a necessity. This will transform cocoa waste into products with high added value and meet current and future challenges. The problems associated with poor cocoa waste management could be considerably reduced by the recovery and biotransformation of the molecular compounds available in CPH. Increased valorization of CPH will help to increase the overall sustainability of the cocoa agribusiness and open up a new source of income for cocoa farmers.

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CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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